Electronic Excitation in Molecular Collisions

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In Memory of
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Abstract

This thesis concerns the study of electronic excitation in ion/atom-molecule collisions. An extensive review of the subject is given first. At high energies, the quasidiatomic correlation diagram, that is so useful in the interpretation of atomic inelastic collisions, can also be applied in the case of molecular collisions. The model breaks down at small impact parameters where orientation of the molecule begins to play a role, and diabatic potential energy surfaces must be calculated instead. Recent developments in this area are reviewed. At lower energies, a host of new theoretical techniques can now be used, notably the infinite order sudden approximation, and time-dependent semiclassical methods. With these recent theoretical developments, it is concluded that the experimentalist must increasingly turn to the coincidence technique, to probe the orientation of molecules during collisions, and to supply state-specific data.

Such an experiment on the K + CH$_3$I collision system is described next. In these collisions, CH$_3$I is excited to Rydberg levels and subsequently ionises and fragments. The process is known to onset at low scattering angles (500 eV$^\circ$), and the aim here was to observe these fragment ions in coincidence with the scattered atoms. No coincidence signal was observed, from which an upper estimate of the cross section ratio $\sigma_i(\theta)/\sigma_{tot}$ could be set. Previous workers have interpreted the excitation mechanism as involving excited ionic intermediate surfaces, and a discussion here using a correlation diagram confirms this view. A comparison with the analogous atomic systems suggests an alternative interpretation, in which the collision is viewed as a scattering of the potassium valence electron off the molecule.

In the final part of the thesis, work on an apparatus designed specifically for photon-ion coincidence measurements is described. The apparatus features a multi-angle particle detector, that will allow 45 angular measurements to be made simultaneously. Here, the performance of the apparatus is critically assessed, and suggestions are made for improvement. Two pulsing devices are described. The first generates bunching fields for pulsing the ion beam, and will allow us to perform time-of-flight measurements. The second is positioned after the collision zone, and is designed to deflect away the elastically scattered ions that would otherwise contribute to noise in the coincidence experiment.
Declaration

This thesis has been composed by myself and it has not been submitted in any previous application for a degree. The work reported within was executed by myself, unless otherwise stated.

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1

Guide to the Thesis

Intermolecular collisions are fundamental to chemistry. Chemical and thermal equilibria are maintained by collisions, and rates of reaction and energy transfer are governed by the rate and dynamics of collisions. A central theme in physical chemistry has been to relate observable bulk properties to the basic laws of physics via collision theories.

The subject of this thesis is electronic excitation in molecular collisions. In high temperature gas samples (> 10eV), such as plasmas, a wide range of collision processes involving the excitation of electrons become important. Excitation may occur in one or both collision partners, ionisation may occur, and the molecule may even fragment, creating highly reactive free radicals. The transfer of an electron from one partner to another is a particularly efficient process, occurring in some cases at very low energies (< 1eV).

At first sight, the theoretical treatment of electronically inelastic collision processes is daunting. The collision involves the interaction of many electrons and nuclei, and in the case of molecules the quantised nuclear motion considerably complicates the problem. Nevertheless, the problem can be simplified by first separating the electronic motion from the nuclear motion, and the aim then is to determine how states of the ‘quasimolecule’ formed during the collision evolve and couple. Today, the field of atomic collision theory can be considered mature, and very recently advances have been made in treating inelastic collisions involving a molecule. A comprehensive review of the theoretical techniques now available is given in chapters 2 and 3.

Experimentally, the study of inelastic molecular collisions is equally challenging. Molecular beam scattering experiments, in which streams of particles are collided inside a vacuum, have proven to be most useful. The advantages over gas cell experiments are that the initial energy and quantal states can be selected, and that the angular and energy dependence of the scattering can be investigated over a very large range. The review is completed in chapter 4 with a survey of different techniques that can be used in a scattering experiment.

The main theme running throughout this thesis is that the difficult coincidence technique is increasingly being called upon to supply state-specific and orientational information on a collision process. In the coincidence technique, both scattered particles (or a particle and a photon or electron) are detected, and the signals correlated to give information on specific processes.

In chapter 5, a coincidence experiment on the K + CH₃I collision system is described. Up to 12 different electronically inelastic processes have been observed in these collisions through scattered atom time-of-flight measurements by previous workers. In addition,
an abundance of positive molecular fragment ions have been observed recently from the same collisions. A coincidence experiment was attempted to correlate these signals, with the aim of establishing the dynamics by which the molecule excites to a Rydberg state and fragments.

Results from this experiment are discussed in chapter 6. Despite the fact that an experiment was run for 35 hours, no correlated signal was seen. The implications of this result are discussed, and new thoughts on the possible excitation mechanism are given. The K + CH₃I collision system is important, as it is provides an example of a new class of excitation mechanism in which highly excited molecular states are populated by mechanism involving 'harpooning' to excited ionic intermediate surfaces.

In the rest of the thesis, work on a new crossed molecular beam apparatus is described. The apparatus was designed specifically for performing scattered ion-photon coincidence experiments, and features an ion detector that monitors 45 different scattering angles simultaneously. Data rich in scientific information can be obtained, as initial and final states are specified and a wide range of scattering angles (0° to 7°) and collision energies (100–1000eV) can be explored. It is possible also to measure the polarisation of the photon emitted, and thus the orientation of the molecule during the collision can be established.

So far work on this apparatus remains in the development stage. In chapter 7, the apparatus is described and its performance is critically assessed. The main problem at the moment is with the generation of a stable ion beam, and a number of suggestions are made for improvements. A new data collection system is also reported. In chapter 8, a device is described that will allow time-of-flight measurements on the scattered ion signal to be made. The lens simply generates a bunching field to pulse the beam, allowing experiments to be run with maximum possible duty cycles.

The main problem in a scattered ion-photon coincidence experiment is the large contribution to the noise rate from elastically scattered ions. In chapter 9, a 'coincidence blanker' is described, consisting simply of a pair of deflection plates positioned after the collision zone. By deflecting away the interfering elastic noise, the coincidence signal is cleaned, and the required experimental run time is significantly shortened. Finally, a summary is given of the work that must be done before a coincidence experiment can be run on the apparatus.
2

Excitation Mechanisms

2.1 Introduction to the Review

Much progress has been made over the last 20 years in understanding the physical nature of processes which occur when 2 atomic species collide. During a collision, different electronic states of the ‘quasimolecule’ couple when they become degenerate (or nearly degenerate) at some internuclear distance, and non-adiabatic transitions can occur. These potential energy curve crossings arise as atomic orbitals interact and electrons are promoted when going to the united atom limit.

The development of the molecular orbital (MO) promotion model [10], which describes how one electron H\textsuperscript+(\textsuperscript{+})-like orbitals of the separated atoms correlate with those of the united atom, has proved successful in understanding excitation mechanisms that involve both inner and outer shell electrons. These mechanisms could be investigated quantitatively owing to the rapid progress in computing technology in the 70’s, and curve crossing theory has progressed far since the first descriptions by Landau [94], Zener [162] and Stuekelberg [150]. Now, semiclassical and even fully quantal calculations can adequately model phenomena such as partial wave interference seen as oscillations in recorded cross sections. Recently, the measurement of polarised photon emission in coincidence with energy analysed scattered particles has taken both theory and experiment closer to a complete description of state-to-state scattering processes.

In contrast, the understanding of inelastic collisions involving molecules is much less advanced, as the situation is much more complex. Motion is now controlled by 3 dimensional potential energy surfaces, and a much greater manifold of electronic states may interact. Perhaps worst of all, the molecule has a constantly changing internal coordinate to which electronic motion can couple during a collision, creating a very complex situation. In fact, it was only recently that theorists began to understand and treat the dynamics of molecular collisions satisfactorily.

Broadly speaking, there have been two approaches to the problem. The first recognises that under certain collision conditions the molecule may be considered as atom like. For instance, at high enough velocities the bond can be considered frozen during the collision, and thus vibration plays no role (the Franck-Condon approximation). Also, if only large distances of closest approach are probed, then the effect of the molecule’s shape and symmetry will not be felt. Quasimolecular models developed for atomic collisions can then be used as a starting point, and then adapted to account for the molecular behaviour that manifests itself as conditions change. In the second approach, a fresh
look at ways Schrödinger's equation can be approximately solved is taken, so that the interaction of vibrational and electronic motion that characterises molecular collisions (especially at low energies) is fully accounted for. Some very promising new techniques have now emerged, and are being applied to increasingly more complex molecular systems, bridging the gap between these high and low energy approaches.

The aim of the review is to describe our current understanding of molecular collision processes, and the tools used to study them. The rest of this chapter, after briefly outlining some basic collision theory, will discuss the use of the quasimolecular promotion model in understanding quite complex electron dynamics in high energy collision processes. Chapter 3 focuses on low and medium energy collisions where vibration of the molecular bond has an important influence on the electron dynamics, and the assortment of theoretical techniques used in this energy regime are described.

Experimentally, the study of molecular collision processes is challenging. High energy resolution is required to resolve ro-vibrational structure in energy loss experiments, and clever experimental setups are required for obtaining data on specific processes. The review is completed in chapter 4 with a discussion of the different ways experiments can probe collision processes.

2.2 An Overview of Collision Theory

In this section we introduce some of the basic ideas used in atomic and molecular collision theory. We begin by giving a quantum mechanical description of an atomic collision system, with a discussion of the origins of inelastic scattering. Theoretical methods for treating inelastic scattering are then introduced, and the results of some simple two-state models given. Finally, we turn our attention to molecular collisions, and see how our basic picture of a collision must be modified.

2.2.1 Adiabatic and Diabatic Basis Sets

Consider a diatomic system composed of two atoms A and B (reduced mass μ) and N electrons (mass m), as illustrated in Figure 2.1. The internuclear coordinate is denoted R, and the electronic coordinates by \{ρ_i\} = ρ_1, ρ_2, ..., ρ_N. The time-independent Schrödinger equation for such a system is

\[
[T_n + H_{el}] \Psi(R, \{ρ_i\}) = E \Psi(R, \{ρ_i\}) ,
\]

\[
H_{el} = T_e + V
\]

where \(T_n\) and \(T_e\) are the kinetic operators for the nuclei and electrons,

\[
T_n = \frac{\hbar^2}{2μ} \nabla_R^2
\]
2.2. AN OVERVIEW OF COLLISION THEORY

Figure 2.1. Coordinates used in the discussion of a diatomic system. Here, the frame of reference is spaced-fixed. The origin is positioned at the centre-of-mass of the system.

\[ T_e = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_{\rho_i}^2 \right) \]

and \( V \) is the total potential energy of the system. This consists of a sum over all electron-electron, electron-nuclei and nuclei-nuclei coulomb interactions.

If we choose an orthonormal set of electronic eigenstates \( \phi_i(\mathbf{R}, \{\rho_i\}) \), then the total wavefunction may be expanded as

\[ \Psi(\mathbf{R}, \{\rho_i\}) = \sum_i F_i(\mathbf{R}) \phi_i(\mathbf{R}, \{\rho_i\}) \]  

(2.3)

Here, \( F_i(\mathbf{R}) \) are wavefunctions representing the nuclear motion when the electronic system is in state \( i \). Substituting this into the Schrödinger equation we get

\[ [T_n(\mathbf{R}) + H_{el}(\mathbf{R}, \{\rho_i\})] \sum_i F_i(\mathbf{R}) \phi_i(\mathbf{R}, \{\rho_i\}) = E \sum_i F_i(\mathbf{R}) \phi_i(\mathbf{R}, \{\rho_i\}) \]  

(2.4)

Multiplying both sides by \( \phi_j^* \) and manipulating the equation so that all diagonal terms are on the left, we arrive at the set of coupled equations

\[ \langle \phi_j | T_n | F_j \phi_j \rangle + \{ \langle \phi_j | H_{el} | \phi_j \rangle - E \} F_j = \sum_{i \neq j} \{ \langle \phi_j | T_n | F_i \phi_i \rangle + \langle \phi_j | H_{el} | \phi_i \rangle F_i \} \]  

(2.5)

When the right-hand side of eqn (2.5) is zero, we have a situation in which the electronic motion is completely decoupled from the nuclear motion – a dramatic simplification of the problem. One way of achieving this is to choose an *adiabatic* electronic basis set...
2.2. AN OVERVIEW OF COLLISION THEORY

Figure 2.2. Adiabatic and diabatic (dashed lines) potential energy curves in the curve crossing situation.

that diagonalises the electronic Hamiltonian:

$$\langle \phi_i^A | H_{el} | \phi_j^A \rangle = \delta_{ij} \varepsilon_{ij}^A(R) \quad (2.6)$$

A consequence of choosing this basis is the Wigner-Von Neumann [111] rule which states that if adiabatic states are of the same symmetry then the potential curves will not cross. If in addition we assume that the nuclei are clamped, the first term on the RHS of eqn (2.5) is also zero. This is known as the Born-Oppenheimer approximation, and is valid whenever Massey’s adiabaticity criterion for nuclear velocities \( v \) is satisfied:

$$v \ll \left[ \varepsilon_{ij}^A(R) - \varepsilon_{ii}^A(R) \right] \delta R / \hbar \quad (2.7)$$

where \( \delta R \) defines some characteristic length. Because of the enormous mass difference between the light and very mobile electrons and the heavy slow nuclei, the Born-Oppenheimer approximation works well for describing many stationary molecular phenomena. Indeed, it is the basis of our understanding of molecular spectroscopy.

For scattering systems even at low velocities, however, the dynamical coupling term \( \langle \phi_j|T_n|\phi_i \rangle \) is often non-zero, and so nuclear motion can induce changes in electronic state. This is the origin of an inelastic collision process. Usually, strong coupling between different states occurs at highly localised collision regions where at some internuclear distance \( R \), the states \( \phi_i^A \) and \( \phi_j^A \) are nearly degenerate (see Figure 2.2). We see for each adiabatic state a drastic change in electronic character around this region. During a collision, the electrons cannot relax in this way fast enough, and a non-adiabatic transition occurs instead to preserve the electronic character.

In such situations, it is often more convenient to describe the system using a different electronic basis that involves fewer coupling terms. Any basis that deviates from the adiabatic basis is termed diabatic. The simplest choice is one that diagonalises the
nuclear kinetic energy operator [144]:

\[ \langle \phi_i^D | T_n | \phi_j^D \rangle = \delta_{ij} \varepsilon_{ij}^D \]  

(2.8)

The diabatic states \( \phi_i^D \) now preserve their character as they pass through the crossing region. As Figure 2.2 shows, diabatic and adiabatic curves are largely similar, except in regions of strong coupling. Transitions between diabatic states are induced by the non-zero terms \( \langle \phi_i^D | H_d | \phi_j^D \rangle \).

We shall see during the course of the review examples of collision systems that behave mainly diabatically at high energies and adiabatically at lower energies, and in any theoretical treatment of the collision the choice of the basis set should reflect this behaviour. Potential energy curves and coupling terms are of course of great use to a theorist, as they will determine exactly how the particles will interact. Adiabatic curves and couplings can for simple systems be calculated very accurately, using many of the methods and approximations developed by spectroscopists. In principle a transformation can be made between the basis sets defined in eqns (2.6) and (2.8). However the diabatic basis defined above has been criticised as it incorporates no \( R \) dependence. Various approximate prescriptions in which some weak \( R \) dependence is incorporated have been developed, but the calculation of useful accurate diabatic states still remains a problem.

A full discussion of potential energy surface calculations is beyond the scope of this review. In the next section, however we indicate how an \textit{ab initio} calculation is set up using molecular orbital theory. For more details on such calculations, the reader should consult the various review papers that are cited in the review.

\textit{2.2.2 Molecular Orbital Theory}

The molecular orbital (MO) theory of the electronic structure of molecules is a natural extension of atomic orbital theory, and was first used by Hund, Mulliken and Lennard-Jones in the late 1920's. It is assumed that the electrons in molecules occupy orbitals which extend around all the nuclei in the molecule. The adiabatic state is then defined by allocating electrons to molecular orbitals, subject to the Pauli exclusion principle. Usually, one-electron MO's are built from linear combinations of atomic orbitals (the LCAO approximation). The rationale for this is that near a nucleus, the molecular orbital must look like an atomic orbital, and so the assumption that it can be described as a linear combination of AO's is reasonable. For example, in the case of \( \text{H}_2^+ \), the ground state electronic wavefunction may be built from H(1s) orbitals

\[ \phi_g(R; \{ \rho_1 \}) = \frac{1}{\sqrt{2}} [\psi_{1s}(\rho_A) + \psi_{1s}(\rho_B)] \]

\[ \phi_u(R; \{ \rho_1 \}) = \frac{1}{\sqrt{2}} [\psi_{1s}(\rho_A) - \psi_{1s}(\rho_B)] \]
where \( \phi_g \) and \( \phi_a \) are bonding and antibonding orbitals. In fact, in this case these are fairly close to the true wavefunctions. More generally, for any diatomic molecule, the MO's may be written in the form:

\[
\phi_i = \sum_k c_{ik} \chi_k
\]  

(2.9)

(Note that for this section only, we have switched notation for convenience – \( \Psi \) is now the many-electron adiabatic wavefunction; \( \phi \) denotes a molecular orbital; \( \chi \) denotes an atomic orbital).

The nature of MO's, and their behaviour as the internuclear distance varies is usefully illustrated in a correlation diagram (an example of which may be found on page 20). These diagrams show how the relative MO energies vary from the separated atom (SA) limit \( R \to \infty \) to the united atom (UA) limit \( R \to 0 \). In section 2.2, we shall see how correlation diagrams have also proved very useful in interpreting many complex collision phenomena in terms of transitions where molecular orbitals cross.

Molecular orbitals, then, are a useful concept in describing the electronic structure of a molecule, and provide a starting point for \textit{ab initio} calculations. In these calculations we use spin orbitals which are simply molecular orbitals multiplied by a spin wavefunction (\( \alpha \) or \( \beta \)), representing the orientation of the electron in the orbital. A matrix is constructed containing the spin-orbitals that define a particular state, and the total wavefunction of the molecule in that state is then given by the determinant of that matrix. This ensures that the wavefunction is antisymmetric with respect to the exchange of electrons. As an example, the wavefunction for the ground state \( ^1\Sigma_g^+ \) of hydrogen would be written as

\[
\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix}
\phi_g(A)\alpha(A) & \phi_g(A)\beta(A) \\
\phi_g(B)\alpha(B) & \phi_g(B)\beta(B)
\end{vmatrix}
\]

To obtain the MO's that most accurately describe the wavefunction of the molecule iterative calculations using the variational principle of quantum mechanics are performed. Here, the coefficients \( c_{ik} \) of eqn (2.9) are varied until the energy of the state, \( \langle \Psi | H_{\text{tot}} | \Psi \rangle \), is minimised. This is known as the self-consistent field (SCF) method, and results in reasonably accurate wavefunctions and potential energies. Finally, to calculate the best \textit{ab initio} wavefunctions, we must relax our assumption that the state of a molecule is defined as a single configuration of MO's, and allow mixing with other configurations of the same symmetry, termed \textit{configuration interaction}:

\[
\Psi = a\Psi_0 + b\Psi_1 + ...
\]

Again, the coefficients \( a, b, ... \) are obtained using an iterative process to minimise the
2.2. AN OVERVIEW OF COLLISION THEORY

total energy. In some calculations, both iterative processes are performed simultaneously, resulting in very accurate wavefunctions, but requiring great computer power.

2.2.3 Types of Coupling Between States

We shall now take a closer look at the dynamical coupling term \( \langle \phi_j | T_n | F_i \phi_i \rangle \), in eqn (2.5). Expanding the operator \( \nabla_R^2 \) given in the definition of \( T_n \) (eqn (2.2)), the coupling term may be written

\[
\langle \phi_j | T_n | F_i \phi_i \rangle = -\frac{\hbar^2}{2\mu} \left[ \langle \phi_j | \nabla_R | \phi_i \rangle \nabla_R + \langle \phi_j | \nabla_R^2 | \phi_i \rangle \right] F_i
\] (2.10)

The terms on the RHS of the equation are concerned with the velocity and acceleration of the system. Usually the second term is dropped, as it is much smaller than the velocity term. If we choose a body-fixed angular coordinate system in which \( \{\rho_i\} \) are defined instead with respect to a rotating internuclear line, then we can readily interpret the first term

\[
\langle \phi_j^A | T_n | \phi_i^A \rangle \nabla_R F_i = -\frac{\hbar^2}{2\mu} v \left[ \langle \phi_j^A | \dot{R} | \phi_i^A \rangle + \langle \phi_j^A | \frac{i}{\hbar} \dot{\mathbf{L}} | \phi_i^A \rangle \right]
\] (2.11)

(where \( \mathbf{L} \) is the angular momentum operator, and \( \nabla_R F_i \) is recognised as relative velocity \( v \)). The two main types of coupling that are most commonly met in collision studies are now shown. The first is a radial coupling term which only operates on states of the same symmetry \( \Sigma \leftrightarrow \Sigma, \Pi \leftrightarrow \Pi \) (i.e. \( \Delta M_L = 0 \)). The other term, which leads to rotational coupling, has the selection rule \( \Delta M_L = 1 \). Transitions induced by rotational coupling occur with the highest probability near the distance of closest approach, where angular velocity \( \dot{\theta} \) is the highest. For symmetric collisions, the additional rules \( g \not\leftrightarrow u \) and \( \Sigma^+ \not\leftrightarrow \Sigma^- \) also apply in both cases.

The only other type of coupling that is sometimes met in slow collisions between light particles is spin-orbit coupling. This can be incorporated by including the spin-orbit operator \( H_{so} \) alongside \( H_{el} \) in eqn (2.1).

2.2.4 Atomic Inelastic Scattering Theory

Many atomic collision processes can be quite complex, especially at high energies where many transitions between different potential curves can occur, often involving the innermost shell electrons. Here, qualitative models have been used in which the diatomic one-electron orbitals or states are calculated over a large range of \( R \) and correlated with the separate atom states (see section 2.3).

For simpler processes at lower energies however, involving say only one or two curve crossings, we can go one step further and obtain a quantitative understanding. A number of theoretical approaches have been developed to calculate experimental observables,
such as total and differential cross sections and transition probabilities. The problem amounts to solving the potential and coupling terms (defined usually in the diabatic basis), and using them to solve the coupled equations (2.5).

Partial Wave Analysis

In the fully quantal treatment, the Schrödinger equation is usually recast into the form

\[ [\nabla_R^2 + k_i^2] F_i(R) = \sum_j U_{ij}(R) F_j(R) \]

(2.12)

\[ k_i^2 = \frac{2\mu(E - U_{ii})}{\hbar^2} \]

\[ U_{ij} = \frac{(2\mu/\hbar^2) \langle \phi_i^P | V(R, \{\rho_i\}) | \phi_j^P \rangle}{\langle \phi_i^P | \phi_j^P \rangle} \]

where \( V(R, \{\rho_i\}) \) is the interaction potential, which vanishes at \( R \to \infty \). We require the wavefunctions to have the asymptotic form

\[ F_i(R) \quad R \to \infty \quad \tilde{F}_i(R) + \sum_j f_{ij}(\theta, \phi) e^{ik_i R/R} \]

(2.13)

\( \tilde{F}_i(R) \) represents the state of the system in the absence of a scattering potential. This takes the form of a plane wave \( e^{ikz} \), which includes all impact parameters of momentum \( k_i \hbar \) in direction \( z \). The other terms represent flux scattered to channels \( j \), and take the form of spherical outgoing waves. The factors \( f_{ij}(\theta, \phi) \) will determine the angular distribution of the scattering, and are related very simply to the total and differential cross sections by

\[ d\sigma_{ij}/d\Omega = (k_f/k_i) |f_{ij}(\theta, \phi)|^2 \]

(2.14)

\[ \sigma_{ij} = (k_f/k_i) \int_0^{2\pi} \int_0^\pi |f_{ij}(\theta, \phi)|^2 \sin \theta \, d\theta \, d\phi \]

(2.15)

To solve eqn (2.12), we begin by expanding the nuclear wavefunction \( F_i(R) \) over the orthonormal set of Legendre Polynomials \( Y_{lm}(\theta, \phi) \)

\[ F_i(R) = \frac{1}{R} \sum_{l,m} A_{l,m} F_j^l(R) Y_{lm}(\theta, \phi) \]

(2.16)

Note that angular momentum is conserved during the collision, and so \( l \) is a constant of the motion. \( F_j^l(R) \) are partial waves that determine the scattering to channel \( j \). The problem is now reduced to solving the one dimensional set of coupled radial equations

\[ \frac{d}{dR^2} + k_j^2 - \frac{l(l+1)}{R^2} \] \[ F_j^l(R) = \sum_j U_{ij}(R) F_j^l(R) \]

(2.17)
It can be shown that $F^l(R)$ behave asymptotically as

$$F^l(R) \sim \sin(kr + \eta_l)$$

where $\eta_l$ is the shift in phase caused by the scattering potential. Thus, partial waves of different phaseshift will interfere, leading to the many quantal effects that have been observed experimentally. Effects such as oscillations in cross sections are particularly important at low energies where only a few partial waves contribute to the scattering pattern. Eqns (2.17) are relatively easy to solve in the case of elastic scattering of atoms, where $U_{ij}(R)$ is zero. The factors $f_{ij}(\theta, \phi)$ can then be determined from the calculated phase shifts, and differential cross sections have proved very accurate.

For inelastic collisions, however, the calculation is much more difficult, especially at energies where a large number of partial waves are important. A number of approximations have therefore been developed to reduce the number of degrees of freedom. Perhaps the greatest simplification is to treat the nuclear motion classically, and this is considered next.

**Time-Dependent Semiclassical Methods**

There is a strong correlation between a partial wave $F^l(R)$ that shows most of its probability of being found at $R$, and the trajectory of a particle that has impact parameter $R$ and classical angular momentum $\mathcal{L} = [l(l + 1)]^{1/2}. The approximation that nuclear motion can instead be treated classically is valid when changes in momentum are small relative to the average values:

$$\Delta p(R) \ll \bar{p}(R)$$

$$\Delta l \ll l$$

For inelastic scattering, there are additional requirements that the kinetic energy is large in comparison to internal energy changes. These conditions are met in many heavy particle collision studies, and lead to a great simplification in the theory, in which internal motion is treated quantally and relative motion classically. Of course, no such method can be expected to reproduce any quantal effects, but we shall see in the course of this review that it does give a good account of the non-adiabatic behaviour.

As a consequence of these approximations, the kinetic energy operator $\nabla_{\mathcal{R}}$ may be omitted from eqn (2.1), and we are left with the first order time-dependent Schrödinger equation

$$H_{el}(R(t), \{\rho_i\})\Phi(\{\rho_i\}, t) = \frac{i\hbar}{\partial t}\Phi(\{\rho_i\}, t)$$

(2.18)
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where $H_{el}$ is now a time-dependent operator and $\Phi(\{\rho_i\}, t)$ defines a wavefunction describing internal motion. This may be expanded in terms of the orthonormal (adiabatic or diabatic) set of electronic wavefunctions $\phi$:

$$\Phi(\{\rho_i\}, t) = \sum_j a_j(t) \phi_j(R(t), \{\rho_i\}) \exp[-\frac{i}{\hbar} \int^t H_{jj}(R) dt]$$

$$H_{ij}(R(t)) = \langle \phi_i | H_{el} | \phi_j \rangle$$

Substituting this into eqn (2.18) and multiplying both sides by $\phi^*_k$, we arrive at the basic set of coupled equations

$$i\hbar \dot{a}_k = \sum_{j \neq k} a_j(H_{jk} - i\hbar \nabla_R (\phi_k | \nabla_R | \phi_j)) \exp[-\frac{i}{\hbar} \int^t (H_{jj} - H_{kk}) dt] \quad (2.19)$$

Solving these coupled equations for some assumed trajectory $R(t)$ will yield the transition probabilities

$$P_{jk} = |a_k(\infty)|^2$$

from which differential and total cross sections can be obtained.

2.2.5 Some Simple Two State Models

Two situations that lead to non-adiabatic transitions frequently arise in collision studies. The first results from an intersection between two potential surfaces, as typified by the systems $M + X$, $M + X_2$ ($X = F, Cl, Br, I$). These crossings are characterised by the small range of $R$'s over which non-adiabatic coupling is strong, and often occur at relatively large $R$'s, where they are well separated from other crossings. Such crossings play an important role, for example in reactive scattering, where a transition to an intermediate ionic surface can lead to a large cross section for chemical reaction (the 'harpoon' model).

The second situation occurs (again at large $R$'s) when two potential curves lie close to each other over a large range of $R$, for example in the systems $F + Xe$, $Ar^+ + CO$, $N_2$. This often arises when spin-orbit coupling becomes quenched by the onset of electron-neutron and electron-electron interactions. Non-adiabatic coupling is now strong over a large range of $R$, and can have striking consequences when the energy defect is small.

Often in these situations, the assumption that only two electronic states interact is valid, and so the coupled equations (2.17) and (2.19) can be solved relatively easily. The resultant formulae giving the transition probability are particularly useful, and are given here.
Landau-Zener Model

Landau [94] and Zener [162] originally tackled the curve crossing problem in 1932, by assuming in addition to the two-state approximation that the diabatic coupling potential is essentially constant over the crossing region

\[ H_{12}(R) = H_{21}(R) = \text{constant} \]

and that the energy difference varies linearly with \( R \)

\[
\frac{\epsilon_{22} - \epsilon_{11}}{\hbar} = B(R - R_c) = \alpha t
\]

(2.20)

\[
\alpha = \frac{v_R}{\hbar} \frac{d}{dR}(\epsilon_{22} - \epsilon_{11})|_{R=R_c}
\]

With this model, assuming only radial coupling, they integrated the coupled eqns (2.19) and obtained the probability \( P_{12}^D \) that a transition occurs between diabatic curves 1 and 2

\[
P_{12}^D = 1 - e^{-2\pi \gamma}
\]

(2.21)

\[
\gamma = \frac{|H_{12}|^2}{\hbar \frac{d}{dt}(\epsilon_{22} - \epsilon_{11})|_{t=0}}
\]

where \( H_{12} \) is the diabatic coupling potential evaluated at the crossing. Here, a diabatic basis was used, as the adiabatic curves avoid in the case of radial coupling due to the non-crossing rule for symmetric states.

For the case of rotational coupling, adiabatic curves do cross, and the analogous equations for either basis are

\[
P_{12}^D = 1 - e^{-2\pi \gamma} = 1 - P_{12}^A
\]

(2.22)

\[
\gamma = \frac{\omega^2 |H_{12}|^2}{\hbar \frac{d}{dt}(\epsilon_{22} - \epsilon_{11})|_{t=0}}
\]

where \( \omega \) is the angular velocity.

Assuming a straight line trajectory, the terms \( \gamma \) may be rewritten in terms of the relative velocity \( v \) and impact parameter \( b \):

radial coupling \[
\gamma = \frac{|H_{12}|^2}{v \hbar \frac{d}{dR}(\epsilon_{22} - \epsilon_{11})|_{R=R_c}} \cdot \frac{1}{(1 - b^2/R_c^2)^{1/2}}
\]

(2.23)

rotational coupling \[
\gamma = \frac{v |H_{12}|^2}{\hbar \frac{d}{dR}(\epsilon_{22} - \epsilon_{11})|_{R=R_c}} \cdot \frac{b^2}{R_c^2(R_c^2 - b^2)^{1/2}}
\]

(2.24)

Note also that as a crossing region is passed twice during a collision, the final probability
Figure 2.3. The evolution of rotational excitation as a function of internuclear orientation $\Theta$. $\Theta$ is negative for the incoming part of the trajectory, zero at the distance of closest approach, and positive for the outgoing part. Level crossing points $R_c$ are marked by the vertical arrows. The vertical axis on the right gives the transition amplitude squared as this trajectory evolves, and is equivalent to the final transition probability at the largest value of $\Theta$. Curves are shown for several incident velocities, but with identical $b$ and $R_c$. (Taken from [130]).

for exciting the system to the upper diabatic state is

$$ P = 2P_{12}^D(1 - P_{12}^D) $$

It can be shown that for radial coupling, the interval over which the transition takes place is

$$ \Delta R = \left( \frac{\pi \hbar v R_s}{B} \right)^{1/2} $$

where $s$ is a number of the order of but greater than unity, and $B$ is defined in eqn (2.20). Thus, if the turning point is outside this region, each traversal of the crossing during the collision can be considered as independent, and the Landau-Zener model gives quite accurate probabilities.

The equations for rotational coupling, however, are less satisfactory. By numerically solving the time-dependent coupled eqns (2.19), Russek [130] showed that in fact the main change in probability occurs inside the region between the two points when $R = R_c$, and so the two crossings cannot be considered as independent. This is seen in Figure 2.3, which shows no indication of rapid variation in probability centered about each crossing, with rather constant probability elsewhere. Russek found also that impact parameters greater than $b = R_c$ contribute significantly to the total cross section. The variation of transition probability with $b$ is shown in Figure 2.4 for a high velocity.

The Landau-Zener model, then, can give insights into the important curve-crossing problem. The most important difference between radial and rotational coupling is in the velocity dependence: as velocity increases, the probability of a transition between diabatic curves decreases for the case of radial coupling, and increases for rotational
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Figure 2.4. Rotational excitation probability $P$ versus impact parameter, for a velocity of $v/B = 0.6$ (atomic units). The arrow indicates the position of the level crossing. (Taken from [130]).

coupling. We have seen also the different behaviour of the transition probability as a function of internuclear distance. Finally, we note that in both cases a large diabatic coupling potential is an important factor that leads to a transition.

**Demkov Model**

Various authors have given expressions for the transition probability when potential curves are parallel and nearly resonant. One of the more useful expressions was derived by Demkov [49] who assumed that the diabatic coupling potential had an exponential form

$$H_{12}(R) = A \exp(-\alpha R)$$

and $H_{22} - H_{11} = \Delta E = \text{constant}$

Integrating the coupled equations (2.19) in the two-state approximation gives

$$P_{12}^D = \frac{1}{2} \text{sech}^2 \left( \frac{\pi \Delta E}{2av} \right)$$

This has a bell shaped form, with a maximum when $\Delta E = 0$ and a full-width-half-maximum proportional to the velocity $v$.

**2.2.6 Extension to Molecular Scattering**

So far we have talked about collisions between atoms, and seen some of the ways in which we can obtain a quantitative understanding of an inelastic event. As soon as a molecule is involved, the situation becomes vastly more complex - not only is there a denser manifold of states but the molecule has shape and there is a changing internal nuclear degree of freedom. Also, motion is governed by a three dimensional surface, rather than a two dimensional curve.
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Figure 2.5. Spaced-fixed coordinates \((X,Y,Z)\) are used to describe the nuclear motion. Electronic motion, however, is more conveniently described in the body-fixed frame \((x,y,z)\). The Euler angles \((\phi, \theta, \delta)\) are used to effect the transformation from SF to BF frames. The origin of both frames is at the centre-of-mass of the system.

To illustrate these problems, consider the triatomic system illustrated in Figure 2.5. Following Sidis [141], \(r\) and \(R\) are the internal molecular (B-C) and relative particle (A-BC) coordinates defined in the space-fixed frame \((X,Y,Z)\). \(\{\rho_i\}\), the electronic positions, are given more conveniently in the body-fixed frame \((x,y,z)\). This frame accompanies the overall rotation of the three nuclei about the centre-of-mass of the system (the origin). The Euler angles \((\phi, \theta, \delta)\) are used to effect the transformation between the two frames, and relevant equations are summarised by Sidis [141].

The Schrödinger equation is now written

\[
(-\frac{\hbar^2}{2\mu} \nabla^2_R - \frac{\hbar^2}{2M} \nabla^2_r + H_{el})\Psi(\{\rho_i\}, R, r) = E\Psi(\{\rho_i\}, R, r)
\]  

(2.26)

where \(M\) is the diatomic reduced mass. The wavefunction may be expanded over both electronic \(\phi_n\) and ro-vibrational \(G_{n\nu}\) basis sets.

\[
\Phi(\{\rho_i\}, R, r) = \sum \sum N_n(R, r)\phi_n(\{\rho_i\}; R, r, \gamma)
\]  

(2.27)

\[
N_n(R, r) = \sum \sum F_{n\nu}(R)G_{n\nu}(r; ...)
\]  

(2.28)

Here, \(\nu\) is a collective index spanning vibrational and rotational quantum numbers. Performing a partial wave expansion as in eqn (2.16) (choosing a diabatic basis for both
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\[ \phi_n \text{ and } G_{\nu \nu}, \]

and comparing the radial equation

\[
\left[ \frac{d^2}{dR^2} + k_{n\nu j}^2 - \frac{l(l+1)}{R^2} - \frac{\mu j_n(j_n+1)}{Mr_n^2} \right] F_{n\nu j} = \left( 2\mu/\hbar^2 \right) \sum_{l', n', j'_{n'}} \Omega_{n\nu j, n'\nu j'}^l \left( R \right) F_{n'\nu j'}^l k_{n\nu j} = 2\mu (E - U_{n\nu j})/\hbar^2
\]

with that for atomic scattering (eqn (2.17)), we readily see the increased complexity caused by the diatomic bond! (The term involving \( j_n \) has appeared due to rotational angular momentum of the molecule).

Normally, the ro-vibrational wavefunctions \( G_{\nu \nu} \) are written as

\[
G_{\nu \nu}(r; ...) = g_{\nu \nu}(r; ...) | j_n m_{j_n} \rangle
\]

where \( | j_n m_{j_n} \rangle \) and represents a rotational wavefunction of the isolated BC molecule. The functions \( g_{\nu \nu} \) can also be chosen as the diabatic vibrational eigenfunctions of the isolated molecule, and satisfy the equation

\[
\left[ -\frac{1}{2M} \frac{d^2}{dr^2} + W_n(r) \right] g_{\nu \nu}(r) = \varepsilon_{\nu \nu} g_{\nu \nu}(r) \quad W_n(r) = \lim_{R \to \infty} \langle \phi_n | H_{el} | \phi_n \rangle
\]

If a diabatic basis is also chosen for the electronic wavefunction \( \phi_n \), then the potential surfaces and couplings are defined by

\[
H_{\nu n \nu' n'}(R, \tau, \gamma) = \langle g_{\nu \nu} | \frac{D}{D \phi_n} | H_{el} | \frac{D}{D \phi_n} \rangle - W_n(r) \delta_{n n'} | g_{\nu' \nu'} \rangle
\]

This effectively generates a grid of vibronic potential surfaces \( W_n + \varepsilon_{\nu \nu} \), as illustrated in Figure 2.6 for the curve-crossing and near-resonant situations. The coupling term will cause purely electronic transitions when \( \nu = \nu' \) and vibrational transitions when \( n = n' \). The other elements will couple both electronic and vibrational motion simultaneously.

As seen in Figure 2.6, the two idealised cases commonly met in atomic collisions that could be modelled simply and accurately are now replaced by a complex situation involving many close potential surfaces and crossings. Experimentally, quite striking behaviour has been seen in the final state populations of collision systems governed by these surfaces.

How can we understand such dynamics quantitatively? No fully quantal calculation can be made even for the simplest of triatomic systems because of the huge number of coupled equations involved (eqn (2.19)). Also, a classical treatment of all the nuclear degrees of freedom seems perilous, as the vibrational motion of the molecule is
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Figure 2.6. Diabatic vibronic networks for (a) surface crossing, and (b) Demkov models.

highly quantised. In fact, it was only recently that adequate theoretical methods were
developed. This is reviewed in chapter 3.

At high velocities, however, the assumption that the molecular bond is frozen during
the collision is often made. This allows us to forget about the internal motion of the
molecule and concentrate only on the electronic motion. For example, in the often in-
voked Franck-Condon approximation, the electron jump between two crossing potential
surfaces is considered sudden, and the initial vibrational wave packet simply projected
onto the final one. Thus, the final vibrational population can determined by multiplying
a Landau-Zener transition probability by a Franck-Condon factor:

\[ P_{1v \rightarrow 2v'} = P_{LZ} | \langle g_{2v'} | g_{1v} \rangle |^2 \]

In calculating the Landau-Zener probability, no r-dependence in the coupling potential
is assumed, and the grid of vibronic surfaces for each electronic state is replaced by a
Franck-Condon weighted curve.

At the energies at which the Franck-Condon approximation may be valid (discussed
in chapter 3), the collision processes observed experimentally are usually very complex.
Distances at which the electron clouds of the colliding particles overlap are often probed,
and many surface crossing regions may be passed. For such processes it is not feasible
to perform quantitative calculations, and the best we can hope for is a good qualitative
understanding of the dynamics. Remarkably, much understanding of these collisions
has been obtained by considering the molecule as a shapeless atom-like particle. The
theoretical approach at high energies, therefore, has been to use and adapt the qualitative
models developed for atomic collisions. This is reviewed in the rest of this chapter.
Barat and Lichten Correlation Rules

The total number of nodal surfaces of diabatic (H$_2^+$-like) wavefunctions are conserved going from the UA limit ($R = 0$) to the SA limit ($R = \infty$). This leads to the following rules which connect UA wavefunction quantum numbers ($n_r^{ua}$, $l^{ua}$, $m^{ua}$) to SA quantum numbers ($n_r^{sa}$, $l^{sa}$, $m^{sa}$) of one of the atoms $a$ or $b$. Note that the principal quantum numbers in the UA and SA limits are given by $n^{ua} = n_r^{ua} + l^{ua} + 1$, $n^{sa} = n_r^{sa} + l^{sa} + m^{sa} + 1$.

\[
\begin{align*}
n_r^{ua} &= n_r^{sa} \quad (2.33) \\
l^{ua} - m^{ua} &= l^{sa}(a) + l^{sa}(b) \quad \text{gerade} \quad (2.34) \\
&= l^{sa}(a) + l^{sa}(b) + 1 \quad \text{ungerade} \\
m^{ua} &= m^{sa} \quad (2.35)
\end{align*}
\]

Swapping of correlations takes place when two SA energy levels with the same values of $m^{SA}$ and $l^{SA} - l^{SA}$ change their relative order on an energy level diagram. This often occurs in the case of asymmetric many-electron systems.

Table 2.1.

2.3 Development of the Promotion Model for Atomic Systems

When atomic projectiles suffer hard collisions with other atoms, electron shells deeply interpenetrate. Large discrete energy losses occur at characteristic internuclear distances, and electrons are thrown out at velocities far different from those of the electrons in the original projectile. To explain these non-classical phenomena, the promotion model was developed which considers states of the 'quasimolecule' formed during the collision. These states correlate separated atom (SA) states to united atom (UA) states, and inner shell excitations are interpreted in terms of transitions in regions where potential curves cross (as described in the previous section). Often, electrons are promoted to a higher energy shell as the united atom limit is approached, generating many crossings with other curves. This can lead to inner shell vacancy production and ionisation even at relatively low collision energies (a few keV).

Because accurate ab initio calculations of quasimolecular potential curves are difficult for all but the simplest systems, a simpler qualitative model was developed by Barat and Lichten [10]. They devised rules used to generate schematic correlation diagrams (see Table 2.1), an example of which is shown in Figure 2.7. They defined the quasimolecular diabatic states simply in terms of the nodal structure of H$_2^+$-like orbitals, ensuring that the number of radial nodes in the wavefunctions of diabatically connected UA and SA orbitals are identical. Such a definition suffers the drawback that the effect


2.3. DEVELOPMENT OF THE PROMOTION MODEL FOR ATOMIC SYSTEMS


Figure 2.7. Schematic MO correlation diagram for a slightly asymmetric quasimolecular system. (Taken from [10]).

of subshell splitting and screening is not accounted for properly. Nevertheless, their correlation diagrams have proved very powerful in interpreting high energy processes that predominantly involve Rydberg and inner shell electrons. This success is largely due to the H$_2^+$-like nature of these shells, and the model was expected to break down when the subshell splitting of the separated atoms becomes comparable to the promotion energy.

Efforts to extend the model to account for processes involving outer shell electrons has led to the introduction of two new rules. Using new *ab initio* techniques, Eichler et al. [60] calculated accurate adiabatic correlation diagrams for a number of atomic systems, and discovered a series of avoided crossings not predicted by the Barat and Lichten rules. These all appeared between MO energy curves that correlate to the same SA principal shell, and occurred whenever the SA subshell splitting ($W$) is small in comparison to the linear Stark splitting ($\Delta E$) (see Figure 2.8). This effect was incorporated into a 'maximum promotion' rule which replaces Barat and Lichten's radial node conservation rule (eqn (2.33)) whenever $W$ is small:

$$n_{r}^{ua} = I^{sa} - m^{sa}$$  \hspace{1cm} (2.36)

The effect of this is seen in Figure 2.9, which shows clusters of crossings on the SA side of the diagram not apparent previously (Figure 2.7).

Another new rule was suggested by Brenot et al. [31] in their study of the He,He$^+$ + Ar systems at low keV energies. The correlation diagram for this system is shown in Figure 2.10. As the He 1s orbital (labelled 3d$\sigma$) is promoted (dot-dashed curve), one
Figure 2.8. Schematic diagram for the adiabatic MO correlations to the separated atom L shell in a slightly asymmetric quasimolecular system in the case of weak (a) and strong (b) subshell splitting. Dashed curves show the energy levels for a coulombic one-electron system. Solid curves illustrate the situation for a screened system. (Taken from [60]).

Figure 2.9. Schematic diabatic MO correlation diagram drawn according to the ‘maximum promotion’ rule for a slightly asymmetric quasimolecular system. Solid lines denote σ states while the dashed lines indicate π states. Orbitals with \( m \geq 2 \) have been omitted. (Taken from [60]).
2.3. DEVELOPMENT OF THE PROMOTION MODEL FOR ATOMIC SYSTEMS

Figure 2.10. MO correlation diagram for the He + Ar system. The question mark indicates doubt whether the crossing predicted by Barat and Lichtens' rules (dot-dashed curves) truly exists. The full lines give the corrected diagram using the new rule. (Taken from [31]).

would expect helium to be preferentially excited through 1 and 2 electron transitions at crossings with empty orbitals. However, this is contrary to their experimental findings which showed almost exclusive excitation of Ar. In addition, in the case of collisions with He+, almost no charge exchange (at the questioned 3pσ/3dσ crossing) was observed. Brenot et al. concluded that such a crossing is unrealistic and suggested that whenever there is a large interaction between an inner and outer orbital, the outer orbital is always preferentially excited. Validity of this new rule was further born out in their later studies of open shell atom collision systems [53, 151].

Thus, we conclude that MO correlation diagrams can give a useful description of even low keV energy collisions (the subject of this thesis), where outer shell electrons are active. As we have seen, they can readily explain the broad features of a collision system. However, experiments record changes in state of a collision process, and so for a more complete description of a collision process we must consider state correlation diagrams.

As we have seen in section 2.2.1, there are many different ways of defining the (diabatic) state of the system. One way is to describe them as a single configuration of diabatic MO's. A state correlation diagram may then be simply constructed by filling each MO according to the Pauli exclusion principle, and using the MO diagram as a guideline, correlate each state of the SA with that of the UA. State correlation diagrams constructed in this way were used by Brenot et al. [11, 29, 30, 31, 138] in their extensive investigation of rare-gas collisions. As an example, the state correlation diagram for the He+ + Ar system is shown in Figure 2.11. In general, when an outer MO is promoted (such as 3dσ in Figure 2.10) it will correlate to a UA orbital of Rydberg character. In
2.3. DEVELOPMENT OF THE PROMOTION MODEL FOR ATOMIC SYSTEMS

2.3.1 Ar

\[ \text{Ar}(3p^5) \]

\[ \text{Ar}(\text{Rydberg series}) \]

\[ \text{Ar}^{13p} \text{(1D4s)} \]

\[ \text{Ar}^{3s3p^6} \]

\[ \text{Ca} \]

Figure 2.11. Diabatic state correlation diagram for the He$^+$ + Ar system. (Taken from [138]).

In the state diagram, the corresponding state must therefore pass through a set of crossings corresponding to one or more Rydberg series. This is seen in Figure 2.11, where the initial state $B^2\Sigma^+$ crosses the series labelled C,D,E and F. In the MO diagram, we see that one or two electrons may be excited at the $3\sigma/4\sigma$ crossing. In the state diagram, this appears as a triple crossing (indicated by the circle). Before this region is reached, we see that state B passes through the Rydberg series C. These crossings don't correspond at all to a crossing in the MO diagram, and arise through a correlated two-electron rearrangement to the core-relaxed series C (see later). We also note that the initial state passes through the continuum, and so ionisation processes can occur.

We discuss the evolution of a collision and the various excitation mechanisms involved in the next subsection. We end, however, by noting that a calculation of the potential energy curves will of course give the most complete information required to interpret collision processes. We have seen in outline how \textit{ab initio} adiabatic potential energy curves may be calculated (section 2.2.2) and many computer packages are available for this, but the calculation of diabatic curves poses more of a problem. There is no agreement in the literature over best definition of a diabatic state, and no detailed method and computer software has been developed for their computation. One way of overcoming this was devised by Sidis and Lefebvre-Brion [136]. By calculating potential energy curves from
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Various excitation mechanisms have been identified in low keV atomic collisions: -

Diabatic I

This class of crossings occurs whenever a filled, promoted MO crosses an empty MO. One or two electron transitions can occur, resulting in complicated multistate crossing regions. The circled crossing in Figure 2.11 is a good example of this. If the system is symmetric, or 'quasisymmetric', then only 2 electron transitions can occur between...
Figure 2.13. Illustration of the diabatic II process. In (a), a double vacancy in molecular orbital B can be filled by a correlated two electron jump from the core C and outer orbitals A. This appears as a series of crossings in the state correlation diagram, (b).

u and g orbitals. In addition, the Wigner Von Neumann spin conservation law holds well, except in collisions where there is significant spin/orbit interaction, for example with heavy targets. States couple both radially and rotationally, with the selection rules given in section 2.2.3. The crossings tend to occur at small internuclear distances (compared to the following mechanisms), and can lead to a variety of secondary mechanisms, especially if an inner vacancy is created. Radially coupled Diabatic I (DI) processes are characterised by sharp onsets in the differential cross section (DCS), which increases as collision energy increases, possibly exhibiting Landau-Zener-Stuekelberg oscillations. Rotationally coupled crossings are usually less localised, resulting in a DCS that onsets less sharply, peaking at large $\tau$, and not exhibiting oscillatory behaviour.

Theoretically, DI processes are difficult to treat as a three-state approximation is needed, and the calculation of the $d/dR$ matrix is difficult. All excitations in symmetric rare-gas collisions were explained by this mechanism [30]. Also, excitation of He in collisions with He$^+$ by rotational $2p\sigma - 2p\pi$ coupling has been confirmed as a dominant mechanism [29].

Diabatic II

In contrast, diabatic II (DII) do not relate to any MO crossing. They arise whenever there is a double vacancy in an MO: that is less promoted than an outer filled one. A correlated 2 electron jump from the core (C) and outer (A) orbitals filling the vacancy (B) occurs at internuclear distances for which $2\epsilon_B - (\epsilon_A + \epsilon_C) = 0$, where $\epsilon$ is the MO energy (see Figure 2.13(a)). This results in the population of a core excited repulsive state (correlating to a Rydberg UA state) which must cross an infinite series of singly excited Rydberg states having a lower core excitation (Figure 2.13(b)). Thus, this
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primary mechanism again leads to a range of secondary transitions, as the quasimolecule dissociates. An example of a diabatic II crossing is again seen in Figure 2.11, indicated by the full circle (see also the MO diagram, Figure 2.10). In this case, the reverse of the mechanism discussed above occurs. The initial state contains a single vacancy in the core \((3p\sigma)\), and so is highly repulsive, correlating to an autoionising \([iA\) state. At the crossing, a correlated two electron jump occurs, \((3p\sigma)^{(3d\sigma)^2} \rightarrow (3p\sigma)^{(4s\sigma)}\), resulting in a state of lower core excitation.

In a quasidiabatic basis the \(d/dR\) operator between the two states is zero, (rotational coupling between states differing in more than one orbital is not favoured) and couplings are due to interelectronic repulsion. Because the core-excited initial state is highly promoted, crossings occur, at larger internuclear distances than DI crossings, and in fact are responsible for inelastic processes seen at energies as low as 10eV (see \cite{30} and references therein). Processes involving a primary DII excitation are characterised by a sharp onset in Theoretically, diabatic II processes are easier to treat because the first crossing of the series is well separated from the others, allowing the use of a two-state approximation (such as discussed in section 2.1). The requirement of an initial vacancy results in a dramatic difference in neutral and ionic rare-gas collisions. These processes are also important in collisions of open shell atoms \cite{25, 26, 53}.

Diabatic III

Barat et al. \cite{11} suggested this new class of crossings to account for population of \(Ne^*\) and \(He^*\) in \(He^+ + Ne\) collisions. They appear at larger internuclear distances as secondary crossings of two Rydberg series, involving a one or two electron core rearrangement (a long range interaction, induced by core relaxation). They have been shown to involve large couplings resulting sometimes in strong avoidance of the crossings, and so influence the final dissociation of states. In Figure 2.11, DIII crossings occur between the \(C\) and \((D,E)\) series, and so allow the population of charge exchange states as the core dissociates.

Demkov Processes

As we saw in the previous section, strong radial couplings between two curves of low energy defect can also result in a transition. This mechanism, known as the Demkov model has been investigated by numerous authors \cite{44, 49, 113}. These couplings occur at large internuclear distances, and theoretically is well understood using a two-state approximation. They form an efficient mechanism for population of near resonant charge exchange channels, resulting in a DCS that onsets at very small \(\tau\), perhaps exhibiting oscillations (through the interference of different partial waves). Demkov processes become more important as the energy increases.

To summarise, the collision evolves in 3 stages :-
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Figure 2.14. Results for the C⁺ + Ne system. (a) shows a typical energy loss spectra of C⁺. The peaks labelled X, A, B, C, D, E represent the elastic (X) and inelastic scattering with C⁺ excitation. (b) shows the reduced differential cross sections for these peaks as a function of reduced scattering angle $\tau$. Also seen is the cross section for formation of C²⁺. (Taken from [53]).

- Primary excitation mechanism occurs at small internuclear distances - either the promotion of a molecular orbital (DI) or, if an inner shell vacancy is present, a correlated two-electron rearrangement (DII). This initial process characterises the shape of the differential cross section.

- Core dissociation then follows, perhaps involving further (weakly coupled) DII crossings, or strongly coupled DIII crossings due to core relaxation.

- Finally, Rydberg electrons are shared (possibly involving Demkov type transitions between near resonant states). Note that if the Rydberg series associated with two different core-dissociation channels are well separated, the one lying closest to the incoming channel is strongly favoured.

The C⁺ + Ne System

To illustrate the above scheme, we now consider the C⁺ + Ne collision system. This was studied by Dowek et al. [53] to see if the above mechanisms developed from studies of rare-gas collisions in the energy range 0.1–4keV would apply more generally to open shell systems, with only a few electrons in the outer shell. Here, we have one outermost 2p_e electron, which is expected to be active.

Their experiments show that in the energy range 500–2000eV, excitation is almost entirely of C⁺. A typical energy loss spectrum is given in Figure 2.14(a). Five peaks
2.4. EXCITATION MECHANISMS

Figure 2.15. Qualitative MO correlation diagram for the C$^+$ + Ne system, showing the promotion of the 4f$\sigma$ orbital and the subsequent MO crossing. Also shown is the possibility of a DII crossing at $R_1$. (Taken from [53]).

(A-E) are identified and assigned to C$^+$ excited states. Evidence that Ne is excited is also just seen at this angle. In the charge exchange channel, excitation is mainly to the ground state. They also saw some evidence for the formation of doubly charged C, and suggested these were formed when highly excited C$^{++}$ autoionises. Reduced differential cross sections for processes A to E are compared in Figure 2.14(b). Important features are that the elastic cross section does not suffer any strong absorption over a wide range of $\tau$. Also, the inelastic processes have a common threshold in the range 0.5–1k eV$^\circ$.

To interpret these results, we must look at the MO and state correlation diagrams, given in Figures 2.15 and 2.16. To begin with, we note that the population of incident states is shared as 1/3 for the $[(3p\sigma)^24f\sigma]^2\Sigma^+$ state and 2/3 for the $[(3p\sigma)^23d\pi]^2\Pi$ state. Since inelastic processes can be induced only via the X state, only 1/3 of the elastic DCS can suffer absorption which is consistent with the experimental results. With the 2$p_\sigma$ electron in the 4f$\sigma$ orbital, we can identify two types of primary excitation mechanisms from the MO diagram. Firstly, DI processes can occur at crossings with the promoted 4f$\sigma$ orbital. Also, DII transitions may occur to fill the 3d$\pi$ double vacancy: $(3p\sigma)^2(4f\sigma) \rightarrow (3p\sigma)(3d\pi)^2$. This is confirmed by the state diagram which shows a DII-type crossing with the A state followed by DI crossings with states C,D,E.

The shape of the differential cross section (DCS) for each process will reflect the type of primary mechanism involved. Thus, a transition at the first X-A crossing would be a strong candidate for the population of C$^+(2s2p^2)^2D$ (process A). The DCS for
process A (Figure 2.14(b)) shows a decrease as energy increases - a characteristic of DII mechanisms. Similarly, a transition at the second crossing should populate $\text{C}^+(2s^23s)^2S$ (process C). As this is of DI type, we expect the DCS to increase as energy increase - confirmed by Figure 2.14(b). The fact that the DCS for processes A and C maximise at around the same $\tau$ value tells us also that the X-A and X-C crossings probably lie very close. Finally, transitions at X-D and X-E crossings are thought to be responsible for the population of channels $\text{D(C}^+(2s^23p)^2P)$ and $\text{E (C}^+(2s^23d)^2D)$. These crossings must occur at smaller $R$ as the DCS maximise at larger values.

As the collision evolves, the core dissociates and Rydberg electrons are shared between the two atoms. This is seen in the state correlation diagram as a series of secondary DII and DIII crossings, which determine the final distribution amongst channels. We see for example that at large $R$, state A interacts (through the long range configuration interaction process) and mixes with state B, before finally dissociating into channels A and B. Channel B may also be populated through a secondary DII crossing between states C and B. However, this was expected to be weak, due to the very different configurations involved.

The charge exchange and Ne* channels may also be populated through secondary crossings with the F and G states. This involves a DIII-type core rearrangement ($\text{C}^+ + \text{Ne}^+$)$_\text{core} \rightarrow (\text{C}^2+ + \text{Ne})_{\text{core}}$ which is known to be quite strong. Thus, the population
of state C will be diminished at the C-F crossing, and in fact the DCS for the charge exchange and C channels are of similar shape and magnitude. A similar mechanism would also exist for the less populated D and E channels. Finally, at large internuclear distances Demkov coupling between curves of low energy defect can become important. Dowek et al. predicted using a simple two-state formula (eg. section 2.1) that population transfer from states A and B to F may amount to about 10%.

To summarise, we see that most of the features of C⁺⁺ Ne collisions can be explained fairly convincingly using MO and state correlation diagrams. The predominant excitation of C⁺ is readily understood from the relative energies of the states in Figure 2.16. Inelastic processes are interpreted in terms of a primary DI or DII transition followed by population sharing and secondary DII, DIII or Demkov transitions as the core dissociates and Rydberg electrons are shared. The recorded differential cross sections are shown to give a good indication of the primary mechanism.

2.5 Extension of the Model to Triatomic Systems

We have seen so far how simple quasimolecular models have proved successful in explaining the underlying excitation mechanisms in atomic collisions. Can excitations in molecular collisions be explained in a similar way? (A recent review by Pollack and Hahn [125] on studies of the charge exchange channel is useful here).

Of course the differences between atomic and molecular collision systems are great. The molecule has shape, and so interactions will involve different symmetries and be dependent on orientation. Also, there is the complication of a changing internal degree of freedom. However, at high enough collision energies the bond can be considered frozen during the collision, and if only large distances of closest approach are probed, then the molecule may well behave as atom-like. In such circumstances, an interpretation of a collision using the simple quasimolecular approach discussed for atoms so far may well be valid.

The first evidence that this is true was given in a series of papers by Dowek et al. [54, 55, 56]. They studied the collision spectroscopy of He⁺ + H₂, N₂, O₂, CO and NO systems at energies of 0.2-4keV in the angular range 0° to 3°. In these ranges, the Franck-Condon principle was shown to be valid. Charge exchange was found to be the most important process, with endothermic channels appearing in more violent collisions and exothermic channels remaining weak. Similarities were drawn with the electronically similar He⁺ + rare-gas atom collision systems, which show a similar pattern of results. Constructing a correlation diagram with the molecule replaced by its united atom, Dowek et al. could tentatively account for their results. Figure 2.17 shows such a diagram for the He⁺ + N₂, O₂ systems. (Note the similarity with Figure 2.11 which shows the He⁺ + Ar diagram). Agreement with the spin conservation rule was seen. Endothermic channels were thought to occur through the familiar primary DII
2.5. EXTENSION OF THE MODEL TO TRIATOMIC SYSTEMS

Figure 2.17. (a) The relative positions of the molecular orbitals and the atomic orbital He(1s) are displayed together with an empty Rydberg orbital. (b) Qualitative state correlation diagram for the He$^+$ + N$_2$, O$_2$ systems. This was constructed by taking Ar as the united atom for N$_2$ and O$_2$. The arrow indicates the possibility of a direct Demkov transition, at large internuclear distances. (Taken from [54]).
transitions (only possible due to the He\textsuperscript{+}(1s) vacancy, followed by secondary population sharing. Exothermic channels can also be populated by Demkov-type transitions (indicated by the arrow in Figure 2.17). A calculation using the simple two-state Demkov model showed agreement in the velocity dependence, although results were overestimated by a factor of 5 to 10 (thought to be because the model didn’t take anisotropy of the molecule into account). In a separate study of He\textsuperscript{+} + H\textsubscript{2} collisions at low (extrathermal) energies, Hopper et al. [79, 80] also suggested DII processes to explain excitations and even processes leading to chemical bond formation.

The important role of the He(1s) vacancy in these collisions was finally confirmed by Dowek et al. [55] in a comparative study of He,He\textsuperscript{+} + H\textsubscript{2} collisions, one of the simplest and most studied systems. In violent collisions ($\tau \geq 3k$ eV) both systems show very similar excitation processes, whereas in softer collisions only the He\textsuperscript{+} + H\textsubscript{2} system showed a nonselective excitation of various overlapping Rydberg series. In addition, total cross sections for He\textsuperscript{+} + H\textsubscript{2} processes are characterised by two maxima, indicating the existence of two different excitation mechanisms. This is strong evidence that DII primary processes also occur in molecular systems when there is a vacancy in an inner shell. This process is illustrated in Figure 2.18, which shows the quasidiatomic MO correlation diagram. The diagram predicts also that excitation to n=2 levels will occur at small internuclear distances through rotational (DI) coupling, which is consistent with results.

Can such a quasidiatomic correlation diagram give an adequate representation of processes that occur at small internuclear distances? Symmetry in the triatomic case will be lower at such distances, and the 2p degeneracy will be lifted in the He\textsuperscript{+},He + H\textsubscript{2} system. Also, rotation may occur both in and out of the plane, possibly explaining the excitation of both 2p$\sigma_u$ and 2p$\pi_u$ orbitals of H\textsubscript{2}. The quasidiatomic rotational (DI)

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**Figure 2.18.** Schematic quasidiatomic MO correlation diagram for the He\textsuperscript{+},He + H\textsubscript{2} systems. Rotational coupling can occur small internuclear distances leading to the population of n=2 levels. The possibility of DII processes for the ionic system is also illustrated. (Taken from [55]).
coupling mechanism is clearly more complicated in triatomic systems, and for a realistic analysis a triatomic model must be used.

This was recognised by Dowek et al. [55], who attempted to extend the MO promotion model to the triatomic case by the introduction of correlation cubes – see Figure 2.19. These were built by fixing the H\(_2\)/He angle \(\gamma\) at \(\pi/2\) and 0 radians, corresponding to \(C_{2v}\) and \(C_{oov}\) geometries. Faces 1 and 2 correspond to He-He and H-H correlation diagrams, and face 3 is the free atom limit. The remaining face (4) is triatomic, and is constructed by correlating linear combinations of atomic orbitals of specific symmetry and nodal structure to the Be united atom limit. Energy surfaces are then drawn between these faces, ensuring continuity of symmetry.

In both geometries, promotion of the (dotted) surface correlating to the \(1s\sigma\_g\) \(\text{H}_2\) orbital is seen, implying that DII processes occur in both geometries: one of the \(2a\_1^2\) (\(2\sigma^2\)) electrons fills the initial vacancy in the (lowest) \(1a\_1\) (\(1\sigma\)) surface, with the other electron excited into a Rydberg MO. More surprisingly, an intersection between \(2a\_1\) and \(1b\_2\) surfaces is seen in \(C_{2v}\) (allowing excitation of \(\text{H}^\ast\) (\(1s\sigma\_g2p\sigma_u\)) and \(\text{H}_2^\ast\) (\(2p\sigma^2\))). This crossing only appears in a triatomic view, and becomes avoided moving to \(C_{oov}\) geometry.

This is demonstrated more clearly in Figure 2.20, which shows a correlation cylinder, constructed by fixing the \(\text{H}_2\) bond length at its equilibrium value. Transitions then at the crossing \(C\) will lead to the excitation of \(\text{H}_2^\ast\) (\(1s\sigma\_g2p\sigma_u\)) whereas rotational coupling at \(R\) gives \(\text{H}_2^\ast\) (\(1s\sigma\_g2p\pi_u\)) and \(\text{He}^\ast\) (\(1s2p\)), which is consistent with their experimental results. They also noted that \(R\) could only be reached after diabatically passing through the intersection seam \(C\), for which there was some experimental evidence. To summarise, then, in violent collisions (\(\tau \geq 3\text{keVdeg}\)) two highly selective DI mechanisms govern the...
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Figure 2.20. Triatomic correlation cylinder showing the $C_s$ conformation, with $r = r_s$. The arrows represent examples of elastic scattering (1), electronic excitation following a transition at crossing $C$ (2), electronic excitation due to rotational coupling at $R$ (3). (Taken from [55]).

The arrows represent examples of elastic scattering (1), electronic excitation following a transition at crossing $C$ (2), electronic excitation due to rotational coupling at $R$ (3).

population of excited states, whereas in softer collisions where there is an He(1s) vacancy DII processes are efficient.

The applicability of this MO correlation picture was confirmed experimentally by Jaecks et al. [84], in their study of the process $H_2^+ + He \rightarrow H^+ + H(2p) + He$. When detected in coincidence, the direction of detected $H^+$ gives information about the final orientation of the $H_2^+$ axis, while $L_\alpha$ polarisation provides information about the alignment of $H(2p)$ orbital relative to that axis. They found that rotational coupling leads to two dominant excitation channels. For $H_2^+$ orientations perpendicular to the beam direction the $2p\pi_u$ state is excited, whereas for a parallel orientation (leading to $C_{2v}$ geometry at the distance of closest approach) the $2p\sigma_u$ dominates – in accord with the triatomic correlation diagram.

Jaecks et al. went on to study the systems $H_2^+ + Ne$ and $H_3^+ + He$ using the same coincidence technique [156, 157] (see also page 79). As we have seen, multi-dimensional correlation surfaces become highly complicated even for simple molecules, and so their aims were to investigate further the use of the quasidiatomic diagram. In the case of $H_3^+ + He$, polarisation analysis allowed them to identify the main $H_3^+$ state contributing to the Lyman-$\alpha$ emission, and the orientation of the molecule during that collision. They constructed a correlation diagram by examining the nodal structure of different $H_3^+$ orbitals and defining a set of replacement ‘atom-like’ orbitals. The Barat and Lichten rules could then be applied in the usual way. Their diagram gave a reasonable account of the excitation mechanism. In the case of $H_2^+ + Ne$, a similar diagram was also successful.
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Their overall conclusion was that despite its simplicity, a quasidiatomic model can give a reasonable description of the changing nodal structure of the wavefunctions during a collision.

A more quantitative study of these excitation mechanisms requires the calculation of diabatic potential surfaces. Kubach et al. [91] calculated 'quasidiabatic' potential energy surfaces that are involved in the DII curve-crossing pattern in the $(\text{He} + \text{H}_2)^+$ ion – see Figure 2.21. They found that the energy surfaces were more repulsive in the $C_{\text{coo}}$ than $C_{2v}$ (due to the greater He-H interaction in the linear geometry), and in both cases the series of curve crossings occurred at larger distances than the isoelectronic He$^+$ + He system. These locations agreed with the experimental results of Hopper et al. [79, 80]. Also seen was the change in shape of the state correlating to $^2\Sigma'$ in going from 0 to $\pi/2$, consistent with the MO diagram.

Russek and Furlan [131] also computed diabatic states for the $(\text{He} - \text{H}_2)^+$ ion, but this time from a different approach. They defined a diabatic Hamiltonian in terms of topologically defined projection operators. These are constructed from linear combinations of Gaussian orbitals, and allow diabatic states to be characterised by their nodal structure. Their approach is essentially an extension of the ideas of Barat and Lichten [10], who defined diabatic states in terms of the number of nodes on an internuclear line. In this case, although the number of nodal surfaces may change as the collision proceeds, their odd or even quality with respect to the He-H$_2$ line remains constant.

Their potential curves are shown in Figure 2.22. In addition to DII processes leading...
2.6. IONISATION MECHANISMS

Diabatic Energies

Figure 2.22. Diabatic potential energy curves computed by Russek and Furlan [131] for the H$_2^+$ + He system. Diabatic states are defined through pseudosymmetry considerations, and at $R \to \infty$ they are identified as follows: $(1g^+)^2(1u^+) = H_2^+(1s\sigma_p) + He(1^1S)$; $(1g^+)(1u^+)^2 = H_2(b^3\Sigma^+_u) + He^+(1^2S)$; $(1g^+)^2(1^1-^1) = H_2^+(2p\sigma_u) + He(1^1S)$; $(1g^+)(2g^+)(1u^+) = H_2^+(1s\sigma_g) + He^+(1snl)$. Their adiabatic counterparts are shown as the dashed curves. The circle identifies the newly discovered crossing. (Taken from [131]).

to excitation of H$_2^+(1\sigma u)$ and then charge exchange, they discovered a new crossing not predicted by Kubach et al. that produces a Rydberg excited He. This in turn crosses the charge exchange channel, suggesting that this channel could exhibit oscillations. Their prediction of Rydberg excitation of He has been confirmed experimentally by Quintana et al. [128].

To summarise, then, the simple quasidiatomic MO correlation diagram is useful for understanding excitations in molecular collisions when the distance of closest approach is greater than the diatomic internuclear distance. The diabatic II mechanism is particularly efficient at energies 10–100's eV, operating at internuclear distances of 2–6 Å. DI processes arise at much smaller distances of approach ($R=1\text{Å}$) and are efficient at higher energies. Quasiresonant charge exchange by Demkov coupling is also efficient, occurring with a probability of 0.5 in many systems. To fully understand more violent collisions, a triatomic picture is essential. There have been few quantitative studies of processes other than quasiresonant charge exchange. However, recent studies by Kubach et al. and Russek et al. have described successful methods for the calculation of diabatic potential surfaces.

2.6 Ionisation Mechanisms

We end this chapter with a brief discussion of ionisation processes. In addition to electronic excitation, ionisation and dissociation are important by-products of many collisions, and these processes can again be understood within the framework of the quasimolecular model. Ionisation involves the coupling of a state to the continuum, which can be
described easily using quantum mechanics, and there are various mechanisms by which this situation arises. If the final ionic state is repulsive, then ionisation may be accompanied by dissociation. Ionisation processes are most commonly studied using electron spectroscopy, each identified by a characteristic shape in the spectra. The mechanisms leading to ionisation that are frequently met are:-

Autoionisation
The population of discrete (autoionising) states that lie above the ionisation limit is well understood within the quasimolecular model in terms of the usual diabatic I and II couplings between states. These states can then decay by making a radiationless transition to the continuum. Autoionisation is fast, taking typically $10^{-15} - 10^{-16}$ sec., and will occur in preference to other decay channels, such as radiative transitions to lower states.

The importance of the process varies from system to system depending on the relative position of the first ionisation limit. For example, in many open shell atoms and ions only the lowest members of a Rydberg series lie below the first ionisation limit. In their collisions with rare-gas atoms and molecules population of autoionising states has been shown recently to contribute significantly to the total electron detachment cross section, producing characteristic peaks in the electron energy spectrum (Boumsellek and Esaulov [25, 26], Penent et al. [123]). This contrasts with rare-gas ion collisions, in which the excitation of lower states dominates. In collisions with molecules autoionisation is often accompanied by dissociation of the molecule, generating charged molecular fragments.

Quasimolecular Auger-type Ionisation
When a state is promoted directly into the continuum, diabatic II type coupling can occur at the crossing, causing ionisation. It is the main ionisation process in rare-gas ion and atom collisions, and has been described adequately using a local complex optical potential model (Sidis [137]). The process generates a broad electron energy distribution, and becomes more important as energy increases [25].

Electron Detachment
Electron detachment is efficient in negative ion collisions, when an electron has a low binding energy. As collision partners collide, the binding energy decreases until at some point $R_c$, $A^-B$ and $AB$ curves merge. Thus a quasistationary state embedded in the continuum is formed, into which the electron can be ejected through coupling to the nuclear motion. The zero-radius potential model (Gauyacq [71]) has proved successful in treating this situation. The electron is treated as independent of $AB$ quasimolecular processes, and excitation cross sections have been reproduced by multiplying the corresponding neutral collision cross section by the calculated electron detachment probability. The
energy distribution of detached electrons have also been modelled well. Electron detachment generates a broad background in the electron spectrum, onto which peaks due to the decay of unstable autodetaching states can be seen at low energies.
3 Vibronic Phenomena

3.1 Introduction

We saw in the previous chapter how at high energies the electron dynamics of quite complex collision processes can be understood using the quasimolecular model. An implicit assumption made in these studies is that the bond is frozen during the collision, not influencing the electron dynamics. Thus transitions are 'vertical', and vibrational populations are given simply by the Franck-Condon approximation (see page 18). This approximation allowed the molecule to be considered as atom-like, and models developed for the study of atomic collisions were used and adapted to explain features that arise due to the molecule's shape. The situation becomes slightly more complex when small impact parameters are probed, as energy may be transferred impulsively to the internal coordinates (in a time much less than the duration of a collision). This is analogous to ground state vibrational excitation which is understood classically in terms of scattering by one of the atoms constituting the molecule (the 'binary model' – see [12, 142]). Electronic transitions can still be considered vertical, though, with the perturbed initial vibrational wave packet projecting onto the final state vibrational eigenstates [54].

However, at lower collision energies, the FC approximation breaks down and both vibrational and electronic quantal motions must be treated simultaneously. Here, the concept of transitions between vibronic potential surfaces emerges, where vibrational energy is considered a part of the total potential energy [13]. This concept is certainly valid when there are several vibrations of the diatomic bond during the collision, and is still useful at higher energies.

How does a non-adiabatic collision proceed when the molecule has time to vibrate during the collision? The approach of the theorist in answering this question has been to develop ways of reducing the complexity of the full Schrödinger equation (see for example eqn (2.30) on page 17) whilst retaining a proper treatment of electronic and vibrational quantal motions. By performing calculations on the simplest of processes such as ion-pair formation (diabatic curve crossing) and near-resonant charge transfer (Demkov coupling), a picture has now emerged of how factors such as the energy defect ΔE, FC factors, and the coupling potential $H_{12}$ influence non-adiabatic collisions over a range of energies.

The aim of this chapter, then, is to describe our current understanding of vibronic phenomena, and the tools that have been developed to study them. We first outline
3.2. ENERGY DEPENDENCE OF VIBRONIC PHENOMENA

how a typical non-adiabatic system will behave at different energies. Next, we look more closely at the role of vibration in higher energy collisions. A number of recent studies have shown that the use of the Franck-Condon approximation is more restricted than at first thought. We then describe the many theoretical methods that allow a quantitative study of vibronic processes. Experimentalists and theorists have worked closely over recent years, and now a variety of quite striking vibronic phenomena seen in the simplest of systems are now understood. A selection of these studies is presented in the final section, to illustrate the impressive power of current theoretical methods, and enrich our understanding of these processes.

3.2 Energy Dependence of Vibronic Phenomena

A key to the understanding of vibronic collision processes is the consideration of three characteristic times: the collision time $T_c$, the electronic period $T_{el} (= h/\Delta E)$ and the vibrational period $T_{vib} (= 1/\nu$, where $\nu$ is the vibrational frequency). Note that it is often wrongly assumed that an electronic transition is instantaneous, although it is usually smaller than the vibrational period [118]. These times define the velocity limits which classify how a vibronic system will behave. A revealing account of such behaviour was given by Klomp et al. [90] and Spalburg et al. [145]. After examining how the time-dependent vibronic coupled equations (see later) behave in high and low velocity limits for systems corresponding to ion-pair formation and near-resonant charge transfer, they concluded that

1. At high velocities, coupling between states is weak and the system behaves diabatically with the FC principle holding (no spread of the vibronic wave packet). In the case of charge transfer, cross sections are independent of $\Delta E$ and the system has merged with the resonant charge transfer mechanism. This limit is reached whenever $T_c \ll T_{el} \ll T_{vib}$.

2. In the opposite limit, where $T_c \gg T_{vib} \gg T_{el}$, the Born-Openheimer approximation holds, and the system behaves completely adiabatically as it passes through a manifold of avoided vibronic crossings. Usually, though, in low energy studies $T_c \sim T_{vib} \gg T_{el}$. Vibrational motion does not behave adiabatically here, and vibrational excitation can occur on the initial potential surface.

3. Between these two limits, where $T_c \leq T_{el}$ the Born-Openheimer approximation breaks down, and non-adiabatic transitions between vibronic states may take place. In the case of charge transfer, the energy defect is the most important factor in determining the final state distribution. Adiabatic potential shapes and coupling regions may not be related to corresponding diabatic potentials due to the presence of many close lying states which couple strongly. However, transition probabilities and coupling potentials are dependent on $T_c$. As the high velocity limit is
3.2. ENERGY DEPENDENCE OF VIBRONIC PHENOMENA

Figure 3.1. Adiabatic and diabatic potential energy curves as a function of the atom-molecule distance $R$ for the charge exchange system $\text{Ar}^+ + \text{N}_2$. The adiabatic curves (full lines) were computed from a basis containing only the six states shown. The corresponding diabatic curves are shown as dashed lines. (Taken from [145]).

approached $\Delta E$ becomes less important and Franck-Condon factors start to dominate, and the system behaves more diabatically.

To illustrate this, Spalburg et al. calculated cross sections and vibrational distributions for a simplified model of $\text{Ar}^+ + \text{N}_2$ charge transfer and spin orbit (Demkov) transitions. Their method treated vibrational and electronic motions quantally and interparticle motion classically (described later), using an adiabatic basis. At low energies they saw the expected dependence on $\Delta E$ including the excitation of states which were not coupled in a diabatic picture and of states with bad FC factors. In addition, charge transfer was enhanced by Landau-Zener transitions at avoided crossings that appeared only in an adiabatic picture, and dominated at low energies. Figure 3.1 illustrates the relation between diabatic and adiabatic potential surfaces at these energies. As energy increases, Demkov coupling takes over as the main transition mechanism, as the cross section for this mechanism peaks in the keV range in contrast to Landau-Zener coupling. At very high energies, when differences in $\Delta E$ are insignificant, they obtained FC distribution amongst vibrational states. From these studies one has a picture of the system behaving adiabatically at low energies, where avoided crossings may appear only through multistate coupling, turning into diabatic behaviour at high energies, where FC factors dominate. In addition, we must expect the orientation of the molecule to play a role throughout these energies.
3.3 Limitations of the Franck-Condon Principle

In this section, we refine our understanding of high energy collision processes. It was often thought that vibration does not play a role when $T_c \ll T_{vib}$, and certainly much understanding of non-adiabatic processes was obtained using models developed for atomic collision studies. Indeed, there was good evidence suggesting that the PC principle is obeyed at these energies. In $Ar^+ + N_2$ low keV collisions, Fernandez et al. [65] demonstrated this using plots that compared the degree of vibrational excitation in excited states to the ground state. Also, spectroscopic measurements on the same system by Moore and Doering [107] also revealed FC distributions for projectile velocities greater than $10^8$cm$^{-1}$.

However, improvement in experimental energy resolution has allowed a number of recent studies to examine more closely the role of vibration in high energy collisions, and now numerous examples are known of systems not obeying the FC principle. For example, Dhuciq et al. [50, 51] successfully measured vibrational populations in excited states of $N_2$ and CO in collisions with $He^+$ and $H^+$ (100's eV collision energies) at $0^\circ$, and later $0^\circ$ to $4^\circ$. Figure 3.2 shows typical results. Deviations from the FC distribution are clearly seen, particularly at larger angles. They concluded that necessary (but not sufficient) conditions for obtaining FC distributions are

1. Collision energies are high enough such that the vibrational sudden approximation ($T_c \ll T_{vib}$) holds.

**Figure 3.2.** Angular dependence of the relative vibrational populations of $CO(a^3\Pi, v')$ formed in $He^+ + CO$ collisions at $E = 300$eV. The data points are shown as symbols 0,1,2..., which represent relevant vibration quantum numbers $v'$. The distribution predicted by application of the FC principle is shown to the right of the figure. (Taken from [52]).
2. The transition amplitude and hence potentials and coupling parameters have a weak dependence on the diatom bond length \( r \).

3. The absence of vibrational excitation prior to (or after) the electronic transition process.

(Dhuicq et al. also derived these conditions from a time-dependent semiclassical formulation of the collision problem.)

The 'collision time' can be defined by the length traversed between the two crossing regions and will depend on the impact parameter. As a typical vibrational period for a small molecule is about \( 10^{-14} \) seconds, the first condition will be met for velocities \( v \) greater than \( 10^7 \text{cms}^{-1} \) \( (T_c > 10^{-15} \text{s}) \). Indeed, for collisions of velocity greater than \( 10^8 \text{cms}^{-1} \) the FC model works well [54], but in the range \( 10^7 < v < 10^8 \text{cms}^{-1} \) the system becomes sensitive to the nature of the collision partner, potential energy surface, transition mechanism, etc.

Parlant and Gislason [118] have expanded on this point in their discussion of the validity of the FC principle in Ar\(^+\) + N\(_2\) collisions. They performed detailed calculations on this system, and found that at 4000 eV, where \( T_c \ll T_{\text{vib}} \), charge exchange to vibrational states of N\(_2^+(X)\) obeys FC principle whereas the distribution amongst N\(_2^+(A)\) vibronic states is still skewed. (see later, page 55). They argued that the condition \( T_c \ll T_{\text{vib}} \) is not sufficient to guarantee that the FC principle is obeyed. All internal motions of the system must be considered, both vibrational and electronic. This condition can be written

\[
T_c \ll T_{\text{int}} \quad (= \frac{\hbar}{\Delta E})
\]

where \( T_{\text{int}} \) is the minimum time required for a system to undergo a transition between two states which differ in energy by \( \Delta E \). For charge transfer to N\(_2^+(A)\) states, \( \Delta E \) is relatively large (about 1eV, compared to a fraction of an electron volt for N\(_2^+(X)\) states) and so this condition is not met, explaining their result.

The second condition for obtaining a FC distribution is that the transition amplitude has a weak variation with \( r \). This in turn will depend on the nature of the colliding species, coupling potentials and the potential energy surfaces explored during the collision. Dhuicq and Sidis [52] tentatively suggested that there may be a strong \( r \)-dependence in DII transitions in the He\(^+\) + CO system, especially in the rising front of the process, where impact parameters are close to the crossing seam. This could explain departure seen at the angular thresholds for these processes all though the effect would diminish as energy increases. The case of Demkov coupling was also considered by Dhuicq and Sidis. Here, \( r \)-dependence lies in the energy defect \( \Delta E \) between the two near-resonant surfaces. As velocity decreases the range of \( r \)'s over which the transition probability is equal narrows to those closest to energy resonance. Therefore, if the main
3.3. LIMITATIONS OF THE FRANCK-CONDON PRINCIPLE

Figure 3.3. Energy spectra of H atoms produced in dissociative charge exchange collisions of H\textsuperscript{+} with Mg at 5keV. Spectra (a) and (b) correspond to H\textsuperscript{+}(v = 0) and H\textsuperscript{+}(v = 1) incident ions. Solid curves are the experimental data of De Bruijn et al. [47]; dashed curves are theoretical results of Sidis and De Bruijn [139]; dotted curves are predictions based on the Franck-Condon principle. (Taken from [47]).

contribution to the transition probability comes from a different range of r's, a non-FC distribution amongst final vibronic states will result. Another example of a system exhibiting non-FC behaviour is the dissociative charge exchange process

\[
\text{H}_2^+(X\Sigma^+_g; v = 0, 1, 2, 3) + \text{Mg} \rightarrow (H + H)_e + \text{Mg}^+
\]

Here, the final vibrational wavefunction is in the continuum, causing H\textsubscript{2}\textsuperscript{+} dissociation. As Figure 3.3 shows, the released kinetic energy departs from that predicted by the FC principle. From theoretical considerations, this was again attributed to the r-dependence of the transition amplitude [47, 139]. Clearly to assess the importance of this effect, realistic models of a transition using accurate potential surfaces are needed.

Lastly, a FC distribution will only be obtained if there is no vibrational excitation before or after the electronic transition. If long range interactions are present, this condition may not be met. The collision time is effectively increased, thwarting the use of the sudden approximation, and resulting in the modification of vibrational wave packets before and after the electronic transition. The importance of this effect depends on the strength of the interaction between collision partners, and again will decrease as collision energy increases. An example of a system in which deviations from a FC distribution have been attributed to this effect is again the excitation of CO(a\textsuperscript{3}Π) in He\textsuperscript{+} + CO collisions (at energies of 500 < E < 1000eV and scattering to 0°). Dhuicq et al. [50] arrived at this conclusion by a comparison with the excitation of electronically similar N\textsubscript{2}(B\textsuperscript{3}Π\textsubscript{g}), which shows no such deviations. The only difference between these systems is
3.4 Theoretical Techniques

We now turn our attention to the theoretical techniques that were developed to study vibronic collision processes. At energies where the vibrational sudden approximation doesn’t hold, molecules certainly don’t behave in any way like atoms in collisions. Even for the simplest situations met in atomic collisions such as diabatic curve crossing and Demkov coupling, quite complex dynamics exist with vibrational and electronic motions both correlated. Thus, theorists had to develop new techniques with which they could quantitatively unravel these dynamics. The problem proved much more challenging, with vibrational, rotational and electronic quantal motions generating a huge number of coupled equations in the partial wave expansion. However, as for atomic collision theory (described briefly in the last chapter) a succession of approximations can be made to reduce this dimensionality, and now a variety of techniques ranging from quantal to semiclassical and classical approaches have been developed. Each method varies in its range of applicability and ease of use, and some techniques have proved to be more successful than others. Molecular collision theory has been reviewed in some detail by both Kleyn [89] and very recently Sidis [141], and so only brief descriptions of the techniques are outlined here, to identify when each should be used.
3.4. THEORETICAL TECHNIQUES

3.4.1 The Infinite Order Sudden Approximation

The Schrödinger equation for triatomic systems has already been discussed on page 15. The full partial wave expansion is repeated here for convenience.

\[
\left[ \frac{d^2}{dR^2} + k_{\nu \nu j}^2 \right] F_{nuj}^{l} = \frac{l(l + 1)}{R^2} - \frac{\mu j_n(j_n + 1)}{M r_n^2} + \frac{2 \mu}{h^2} \sum_{n', \nu', j'} \Omega_{nuj, n' \nu' j'}^{l' l} (R) F_{n' \nu' j'}^{l'}
\]

\[
k_{\nu \nu j}^2 = 2 \mu (E - U_{nuj}) / h^2
\]

(Unless otherwise stated, the notation used throughout this chapter will be the same as in chapter 2.)

One way of reducing the large number of coupled equations seen above has emerged from a study of rotational transitions. Here, it is recognised that when rotational periods of the molecule are large compared to \( T_c \), it can be assumed that the collision occurs for a rotor held fixed in space – the rotational sudden approximation. Also, when the radial motion is faster than the angular relative motion, a ‘centrifugal sudden’ approximation may also be used, which allows one to assume that the \( R \) axis remains fixed in space during the collision. These two assumptions make up the infinite order sudden (IOS) approximation. They allow coupled values of \( l \) and \( j \) to be replaced by their common values \( l' \) and \( j' \), and the coupled equations reduce to a solvable form:

\[
\left[ \frac{d^2}{dR^2} + k_{\nu j}^2 \right] F_{\nu j}^{l}(R, \gamma) = \frac{l(l + 1)}{R^2} \sum_{n', \nu'} H_{\nu j, n' \nu'}^{l l'} (R, \gamma) F_{n' \nu'}^{l'} (R, \gamma)
\]

\[
k_{\nu j}^2 = \frac{2 \mu}{h^2} (E - \varepsilon_{\nu j} - \langle g_{\nu j} | \langle \Phi_n | H_{\nu j} | \Phi_{n'} \rangle - W_n (r) \delta_{nn'} \rangle | g_{\nu j'} \rangle^2)
\]

This technique was first used on vibronic transition processes by McGuire and Bellum [105] and subsequently by several other authors [8, 15, 16]. The first approximation made is likely to be valid for energies \( > 0.1 \text{eV/amu} \), but the method is expected to fall into trouble above 10\,\text{eV/amu} [141]. It is less clear when the second approximation is valid. Sidis reports that it applies best when scattering is dominated by repulsive walls and when the collision energy exceeds the potential well depths. The method is thought to have great promise for the future, and certainly the results of Baer et al. [8] on the \( \text{H}^+ + \text{H}_2 \) system illustrate its power – see Figure 3.4.

3.4.2 Time-Dependent Semiclassical Methods

It is often believed that in heavy particle collisions the nuclei have associated de Broglie wavelengths for relative motion that are smaller than typical ranges of variation of intermolecular potentials, and so may be treated using classical mechanics. This is the basis for a wide range of semiclassical techniques used in atomic (see page 11)
3.4. THEORETICAL TECHNIQUES

Figure 3.4. A comparison between experimental and theoretical integral cross sections for (a) inelastic and (b) charge transfer processes of the $\text{H}^+ + \text{H}_2$ system. (Taken from [8]).

and molecular collisions, in which the relative degree of freedom is treated classically and internal degrees of freedom (including vibration) quantally. The validity of this approximation has been discussed by Delos and Thorson [48] who concluded it was valid for energies much higher than thermal (i.e. $E > 1$eV/amu).

If in addition one assumes that there is only one trajectory for each impact parameter and that changes of internal angular motion are negligible compared to the relative angular motion, then the quantum mechanical problem reduces to solving a simpler time-dependent Schrödinger equation involving a ro-vibronic Hamiltonian $H_{\text{int}}$:

$$\frac{i\partial \chi}{\partial t} E(\{\rho\}, R(t), r) = H_{\text{int}} \chi(\{\rho\}, R(t), r)$$

$$H_{\text{int}} = H_{el} - \frac{1}{2m_b} \nabla_r$$

$$\chi(\{\rho\}, R(t), r) = \sum_{n\nu} A_{n\nu}(R(t)) G_{n\nu}(r; \ldots) \Phi_n(\{\rho\}, R(t), r)$$

where $G_{n\nu}$ and $\Phi_n$ are ro-vibronic and electronic eigenfunctions.

The number of coupled equations can again be too large due to the rapid increase with energy of rotational states associated with each vibronic state. However, at such energies, the collision time is short compared to a rotational period allowing the rotational sudden approximation to be made. Initial rotational states $|j m_j\rangle$ may thus be factored out from the time-dependent Schrödinger equation, and the number of coupled equations
are reduced to a computable level:

\[
\chi(\{\rho_i\}, R(t), r) = X(\{\rho_i\}, R(t); \mathbf{\hat{R}}) | jm_{ij}\rangle \\
X(\{\rho_i\}, R(t), r; \mathbf{\hat{R}}) = \sum_{n', \nu'} B_{n' \nu'}(R(t); \mathbf{\hat{R}}) \frac{g_{n' \nu'}(r)}{r} \Phi_{n'}(\{\rho_i\}; R, r, \gamma)
\]  

(3.3)

By determining the common trajectory (a variety of prescriptions can be used [141]) vibronic probability amplitudes and phases can be obtained from the time-dependent Schrödinger equation

\[
i \frac{\partial X(\{\rho_i\}, R(t), r; \mathbf{\hat{R}})}{\partial t} = H_{\text{vibronic}} X(\{\rho_i\}, R(t), r; \mathbf{\hat{R}})
\]

(3.4)

\[
H_{\text{vibronic}} = H_{\text{el}} - \frac{1}{2m} \frac{d^2}{dr^2}
\]

and cross sections calculated.

This form of semiclassical theory has been the basis of a number of studies on resonant charge exchange [40, 95], ion-pair formation [90, 147] and near-resonant charge exchange [73, 116, 117, 146]. In some of these studies isotropic interactions were used allowing further simplification. Also, if a centrifugal-sudden approximation is assumed (fixed molecular orientation) then a semiclassical IOS description can be formulated [116, 117].

At higher energies (100's eV/amu) the initial ro-vibrational wavepacket does not evolve during the collision (clamped bond) allowing the vibrational sudden approximation to be used. Only the electronic part of the wavefunction now remains coupled in the time-dependent equations,

\[
\chi(\{\rho_i\}, R(t), r) = Y(\{\rho_i\}, R(t); r) \frac{g_{\nu}}{r} \Phi_{\nu}(\{\rho_i\}; R, r, \gamma)
\]

(3.5)

\[
Y(\{\rho_i\}, R(t); r) = \sum_{n'} C_{n'}(\{\rho_i\}, R(t); r) \Phi_{n'}(\{\rho_i\}; R, r, \gamma)
\]

(3.6)

\[
i \frac{\partial Y(\{\rho_i\}, R(t); r)}{\partial t} = H_{\text{el}} Y(\{\rho_i\}, R(t); r)
\]

from which sudden vibronic probability amplitudes can be obtained. These equations are still more general than the Franck-Condon approximation, as no assumptions have been made on the r-dependence of the coupling potential. Sidis and De Bruijn [139] used these equations to study near-resonant and dissociative charge exchange (DCE) in \( \text{H}_2^+ + \text{Mg} \). The relationship between this formalism and the FC approximation has also been discussed by Dhuicq et al. [50].

Lastly we mention the work of Gauyacq and Sidis [72], who developed a time-dependent semiclassical technique for treating DCE processes at lower energies. Here, the vibrational sudden approximation cannot be used, and a number of coupled equations becomes infinite as the ro-vibronic basis set must include the continuum. Gauyacq
and Sidis overcame this problem by considering only the time dependence and interaction of wave packets associated with the active electron (i.e. corresponding to the two electronic states involved). The resultant number of coupled equations is reduced and the problem can be solved. Their approach was inspired from theoretical studies of electron detachment in atomic collisions. They applied the method to the $\text{H}_2^+ + \text{Mg}$ system and concluded that it gave a unified description of DCE at both low and high energy regimes. Their previous model [140] using a local complex potential (as used for ionisation processes in atomic collisions – see page 37) was shown to be inadequate in comparison, not coping with strong coupling and multiple transitions that characterise adiabatic behaviour at low energies (see later, page 60).

To summarise, time-dependent semiclassical methods are a very powerful tool for studying vibronic processes over a wide range of energies above 1eV/amu.Electronic and vibrational quantum motion are simultaneously treated and the evolution in time of probability amplitudes and phases are determined. This is considered essential for a proper treatment of vibronic processes. In addition, the technique does not rely on simple (Landau-Zener and Demkov) models of the transition. In contrast to IOSA calculations, only the rotational sudden approximation need be used, and as a classical path is determined features such as interference oscillations can more easily be interpreted. If more information can be obtained on the $r$ and orientational ($\gamma$) dependence of couplings, time-dependent semiclassical techniques will prove important in developing our understanding of vibronic processes.

3.4.3 Trajectory Surface Hopping Techniques

Perhaps the simplest theoretical approach is to treat all nuclear motions classically, and only the electronic motion quantally. This is the basis of the trajectory surface hopping (TSH) model first introduced by Tully and Preston [152], and improved upon by several authors [21, 119, 148]. In these models the equations of motion are integrated on the initial potential surface until a region of strong nonadiabatic coupling is encountered (transition seam). The probability of a ‘hop’ on to the new surface is determined using a 2 state model such as the Landau-Zener approximation, and then the system may continue on the new surface after adjusting momenta to conserve energy. At the end of the calculation, vibrational states are determined tentatively by ‘boxing’ the classical vibrational energy resulting from each trajectory. Inherent in the surface hopping technique is the assumption that avoided crossings are localised and well separated in time. For processes such as ion-pair formation and charge exchange where this condition is frequently met the technique has proved very popular.

The models differ in their prescriptions of when the hop occurs, the transition probability and the adjustment of momentum. The original model by Tully and Preston (TP) requires that a crossing seam be defined analytically prior to the calculation. Stine and Muckerman (SM) [148] later managed to remove this requirement by monitoring the
energy difference $W(t)$ between the two surfaces. If this passes through a minimum in coincidence with a zero time derivative of $W$, then a crossing seam has been identified. The direction perpendicular to this seam is then determined by a coordinate transformation. The transition probability is then calculated using the LZ approximation and momentum adjusted along this direction (as in the TP model).

The main criticism of the SM technique has been that it fails to account for the possibility of transitions away from the avoided crossing, and can only be used when intersections are trough-like. Blais and Truhlar (BT) \[21\] devised a method quite different to those of TP and SM, and designed to treat a more general class of systems. Here, the semiclassical probability for being on each surface is monitored by integrating the electronic coupled equations. Whenever the probability for being on the current surface drops below 0.5, a hop to a new surface is made. Probabilities are reset to their initial values, and momenta are adjusted along the direction $\nabla W$. However, their method has been criticised on a number of points by Stine and Muckerman \[149\] and Eaker \[59\]. The direction in which momenta is adjusted was questioned, and their choice of when a hop occurs and when to reinitialise probabilities was considered too arbitrary. Both Eaker and Stine and Muckerman demonstrated that this method could give quite different results from TP and SM methods.

Recently, Parlant and Gislason \[119, 120\] tried to answer these criticisms in a new version of the BT method. They instead decided that a transition point occurs whenever the dynamical coupling $|\Omega|$ goes through a maximum, where

$$\Omega = \dot{r} \cdot \langle \psi_i | \nabla | \psi_j \rangle$$

An accurate hopping probability is then obtained by continuing the trajectory through the entire coupling region until a minimum is reached (where probability amplitudes will be reinitialised). On hopping, momenta are adjusted along the direction of the dynamical coupling vector. They tested their model on atom-atom systems that show typical Landau-Zener and Demkov couplings, and found excellent agreement with quantum mechanical calculations.

One should also mention the Bauer-Fisher-Gilmore (BFG) model here. This model is largely similar to the TP model, except that Landau-Zener transitions between vibronic potential surfaces are considered instead. It is used in the low energy limit, when the transition time between the two crossings is large in comparison to the vibrational period, and where crossings are widely spaced \[38\].

Given the number of assumptions made, it is surprising how often $\text{TSH}$ studies have been successful. One must conclude that the motion of the vibrating atoms does behave classically, and that the approximations made in treating the transition are realistic. Frequently, the magnitudes and shapes of differential and total cross sections for processes such as ion-pair formation and charge transfer agree with experiment (e.g.
3.4. THEORETICAL TECHNIQUES

Figure 3.5. Differential cross section for ion-pair formation in K + I₂ collisions at 300eV. xxx: experimental values, -: TSH calculations. (Taken from [64]).

Evers [64] for Na,K,Cs + I₂ systems – see Figure 3.5). Here, good potential surfaces are required, but quite often calculations are found to be insensitive to the precise magnitude of the coupling potential. SHT calculations in fact were important in developing ideas such as 'prestretching' and 'bond stretching' to explain features of cross sections for ion-pair formation. Bond stretching occurs after a transition at the first crossing to the ionic potential and causes a reduction in transition probability at the second crossing. Large cross sections for ion-pair formation result, often close to the classical limit $\pi R^2$.

In Figure 3.5, the two peaks at large angles were attributed to such trajectories and the other peak to covalent trajectories (where the transition is at the second crossing). The molecular bond length can also increase before the diabatic transition seam is reached ('prestretching' due to the presence of the ionic potential), and can lead to cross sections for ion-pair formation greater than the classical value. Both of these simple ideas could be simulated using SHT methods, and cross section shapes reproduced satisfactorily. (See Kleyn's report [89] for a fuller discussion).

However, SHT methods must fail in describing the finer details of vibronic processes, as they ignore the phase of the vibronic wavefunction. Klomp et al. [90] demonstrated this by considering the time dependence of the vibronic wave packet for processes leading to ion-pair formation. They showed that the centre of the wave packet does in fact move in a classical manner. Also, in the low energy limit the BFG model does correctly predict transition probabilities. However, they showed that the wavepacket can also distort significantly about its centre when the system passes through the crossing region. Thus the motion of the centre of the wavepacket has no meaning in determining final state distribution.

This conclusion has been born out by a number of recent studies. Chapman [36] recently studied charge transfer in the Ar⁺ + H₂ system. Although the over all shape
of vibronic cross sections was reproduced the relative vibrational populations did not agree with experiment. This was similarly found by Nieder et al. [112] for the H\(^+\) + H\(_2\) charge transfer system (see Figures 3.4, 3.8 and 3.9 on pages 47, 57 and 58). In addition, their calculations of the differential cross section broke down at impact parameters corresponding to trajectories with turning points close to the crossing seam. Here, assumptions made in calculating transition probabilities are invalidated. They also of course could not reproduce interference features. Quantal IOSA calculations have been made on both these systems [8, 96] which showed much better accord with experimental results and which highlighted the problems with SHT calculations. Finally, we mention that Miller, George and co-workers developed a semiclassical version of the SHT method in which the phase of the vibronic wavefunction is calculated, thus answering the above criticisms. However, the method has the drawback of being quite difficult to use (see [89] for further details).

To conclude, then, it must be emphasised that SHT calculations are very useful for obtaining a good physical picture of electronic and reactive collision processes. The technique is the simplest to apply, and reasonable values of cross sections can be obtained. Indeed, Schlier et al. [134] recently asserted that if accurate surfaces are used then an overall accuracy of 10–20% can be expected. Of course, quantal features such as interference and rainbows in the differential cross sections cannot be reproduced. The method is restricted to systems with well separated crossing regions, but now a number of prescriptions exist for handling different types of crossing region.

SHT techniques are less successful when vibronic information is required. Recent studies have demonstrated this [36, 75, 112] – vibronic differential cross sections could not reliably be generated and predicted vibrational populations were wrong. Clearly, vibronic processes cannot reliably be treated classically, and time-dependent evolution of vibronic wave packets (including phases) must be determined in a correct calculation.

### 3.4.4 Two State Models

To calculate vibrational distributions in processes such as charge transfer, some authors have resorted to two-state models [33, 86, 92, 98]. Here, transition probabilities and cross sections are calculated by multiplying those obtained from simple two-state theories (see page 12) by Franck-Condon factors. For charge exchange, a popular approach has been to treat vibronic curves as pseudo-atomic potential curves and use the theory of Rapp and Francis [129]. Other models, such as the stationary phase method (for Landau-Zener type crossings) have also been used [37].

The validity of such methods has been discussed by Sidis [141] and Spalburg et al. [145]. From an analysis of the time-dependent coupled equations, they show that two-state models will give exact results only when all vibronic transition probabilities are weak. Also, the assumption that the coupling potential is independent of \( r \) must
be made. The condition of weak coupling is only met for example when all Franck-
Condon factors are weak, and this is unlikely for near-resonant charge transfer problems.
Spalburg et al. demonstrated quite clearly two-state models give wrong results for Ar$^+$
+ N$_2$ charge transfer and spin-orbit exchange processes due to strong coupling to the
many close states.

3.5 Case Studies

These techniques have been applied to a number of simple low energy systems where
potential surfaces can be computed. Results have been impressive, and the quite striking
and complex behaviour of some of these systems are now well understood. We end this
chapter with an account of three such studies. All are examples of the close cooperation
theorists have had recently with experimentalists. We begin with a discussion of the
(Ar+N$_2$)$^+$ system. This has already been partly described in section 3.2, so we complete
the story here.

3.5.1 Ar + N$_2^+$ Charge Exchange

At energies of 1–100 eV, the near resonant charge exchange process

$$N_2^+(X^2\Sigma_g^+, v) + Ar(^1S_0) \rightarrow N_2(X^1\Sigma_g^+, v') + Ar^+(2P_{3/2,1/2})$$  \hspace{1cm} (3.7)

has been subject to much experimental and theoretical activity (see Sidis [141] for a
review). This is partly because transitions occur at large internuclear distances (3 to 5
Å) where diabatic potentials can be considered parallel. Thus, the task of determining
the relevant potential curves and coupling potentials is simplified, and many insights
emerged from calculations based on approximations such as isotropy. A number of
theoretical studies have employed the time-dependent semiclassical method, the most
sophisticated of which used \textit{ab initio} potential surfaces (Parlant and Gislason [116]) and
included the excited N$_2^+(A, v') + Ar$ surface. Figure 3.6 shows the good agreement with
experiment of cross sections calculated by Parlant and Gislason. One trajectory surface
hopping study has also been made using anisotropic adiabatic potential surfaces [114],
but with less accord with experiment.

Experiments show that the N$_2^+(X, v = 0)$ state does not react at all at energies lower
than 20 eV cm, whereas the states N$_2^+(X, v \geq 1)$ have a relatively large cross section for
charge transfer, populating 3 to 5 states with excitation to $v' = v - 1$ clearly favoured.
Also shown to be important at these energies are transitions between the spin-orbit
states of Ar:

$$Ar^+(2P_{3/2}) + N_2(v = 0) \rightarrow Ar^+(2P_{1/2}) + N_2(v = 0)$$
3.5. CASE STUDIES

Figure 3.6. Dependence on the initial vibronic state of the integral cross section for charge transfer in \( \text{N}_2^+ (\text{X}, A; v) + \text{Ar} \) collisions at 20 eV\(_{\text{cm}}\). Theoretical results were computed by Parlant and Gislason [116] using the time-dependent semiclassical method. (Taken from [117]).

These results were at first surprising. For molecular collisions, transitions between vibronic states due to Demkov coupling are dependent on the coupling potential \( H_{12} \) and FC factors, as well as the energy defect. Yet the only state with a significantly large FC factor, namely \( \text{N}_2^+ (\text{X}, v = 0) \), does not react at all. Certainly at low energies, Demkov transitions between states of lowest energy defect are favoured (corresponding here to \( v' = v - 1 \)). Here, the asymptotic energy defect between \( \text{N}_2^+ (\text{X}, v = 0) \) and its nearest neighbour is only 0.18eV, and transitions occur between other states of comparable energy defect. Clearly, the analogy with Demkov coupling in atomic systems cannot be made, and the situation is more complex. In addition, the observed transitions between spin-orbit states were unexpected, as the diabatic coupling potential is zero.

To understand these puzzles, we must consider the vibronic curves calculated from a multistate adiabatic basis. These have been calculated by Nikitin et al. [114], and are shown in Figure 3.7. The first point to make is that the adiabatic curves deviate considerably from their (parallel) diabatic counterparts. This is because in an adiabatic basis at low energies, several electronic states may interact. Transitions between spin-orbit states are now understood, as their coupling in this basis is strong, mediated by the presence of the \( \text{Ar} + \text{N}_2^+ (A^2\Pi) \) electronic state. These processes are observed to become more important as energy increases, as is expected from a Demkov-type mechanism.
Also revealed in Figure 3.7 are crossings that are completely unrelated to any in the diabatic basis. Thus, two mechanisms contribute to the charge transfer process. Firstly, Landau-Zener transitions may occur at the crossings. Estimates by Spalburg et al. [145] show that this is the most important process at low energies, with a cross section peaking between 25 and 100eV. Amongst these crossings, FC factors and thus transition probabilities are largest for $v' = v - 1$. Hence, the propensity for the excitation of states $v' = v - 1$ is readily understood. Also, no such crossings exist with the $N(X,v=0)$ state, explaining its lack of reactivity at these low energies. At low energies, the competing Demkov mechanism is not so important in contrast to transitions between spin-orbit states, for which the energy defect and coupling potential are more favourable.

As energy increases, both experiments and calculations show that more and more states are excited (although as Figure 3.6 shows, at 20 eV$\text{cm}^{-1}$ the charge transfer cross section for $N_2^+(X,v = 0)$ is still very small). The system behaves more non-adiabatically, and Demkov coupling starts to compete the Landau-Zener transitions. Thus the energy defect is becoming less significant, and one would expect FC factors to start playing a role.

No experimental measurements have been taken at energies above 20 eV$\text{cm}^{-1}$. However, Parlant and Gislason [118] have extended their calculations up to 4000eV using the same method and surfaces as before. (They studied the reverse of eqn (3.7) with $N_2$ prepared in the state $(X,v = 0)$, and were interested also in charge transfer to the $N_2^+(A)$ state). Their results are shown in Table 3.1. At 100eV, we see that charge transfer between the
3.5. CASE STUDIES

Table 3.1. Relative state-to-state cross sections for $\text{Ar}^+({}^2P_{3/2}) + \text{N}_2(v' = 0) \rightarrow \text{Ar} + \text{N}_2^+(X, A; v)$. (Taken from [117]).

<table>
<thead>
<tr>
<th>$N_2^+$ Product</th>
<th>Relative Collision Energy (eV)</th>
<th>Franck-Condon Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion State</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>$X$ 0</td>
<td>0.060</td>
<td>0.690</td>
</tr>
<tr>
<td>$X$ 1</td>
<td>1.000</td>
<td>0.935</td>
</tr>
<tr>
<td>$X$ 2</td>
<td>0.005</td>
<td>0.013</td>
</tr>
<tr>
<td>$X$ 3</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>$A$ 0</td>
<td>0.706</td>
<td>0.671</td>
</tr>
<tr>
<td>$A$ 1</td>
<td>0.294</td>
<td>0.264</td>
</tr>
<tr>
<td>$A$ 2</td>
<td>0.064</td>
<td>0.174</td>
</tr>
<tr>
<td>$A$ 3</td>
<td>0.022</td>
<td>0.051</td>
</tr>
<tr>
<td>$A$ 4</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td>$\sigma(A)/\sigma(X)$</td>
<td>0.000</td>
<td>0.046</td>
</tr>
</tbody>
</table>

Table 3.1. Relative state-to-state cross sections for $\text{Ar}^+({}^2P_{3/2}) + \text{N}_2(v' = 0) \rightarrow \text{Ar} + \text{N}_2^+(X, A; v)$. (Taken from [117]).

$v = v' = 0$ states now has the highest cross section, reflecting the importance of the large FC factor, although the overall distribution amongst $N_2^+$ product states is still far from FC-like. At 1000eV and 4000eV, the system is behaving more diabatically. Landau-Zener transitions are not important, and the energy defect is small in comparison to the collision energy. Thus at high energies the FC factors are the dominant influence on the final vibrational distribution. We see from Table 3.1 that there is now a FC vibrational distribution for the $N_2^+(X)$ products, although the $A$ state distribution is still skewed. This difference was explained by considering the internal times of the system. Although the collision time is much smaller than the vibrational period, it is comparable to the characteristic electronic time ($\hbar/\Delta E$) for $A$ state products. A FC distribution will only be obtained when the collision time is much smaller than all the internal times of the system (see page 43).

To summarise, Spalburg’s analysis [145] described in section 3.2 is confirmed. At low energies a system will behave nearly adiabatically, with the energy defect playing an important role in determining the final state distribution. Several electronic states may interact at low energies, in this case inducing crossings that also contribute to charge exchange. As energy increases, the system will move towards diabatic behaviour, where the energy defect is insignificant and FC factors dominate. As we saw in section 3.3, the condition $T_c \ll T_{\text{vib}}$ is not enough to ensure that a FC distribution will be obtained, although the various perturbing effects will drop off as energy continues to increase.

3.5.2 $H^+ + H_2$ Charge Exchange

The $H^+ + H_2$ system is perhaps the simplest of all charge exchange reactions. Only two electrons are involved and both potential surfaces are well known. The corresponding direct channel has been much studied experimentally and theoretically. However it was
not until recently that a vibrational state-resolved study of the charge exchange channel was reported (Nieder et al. [112]). This lead to two theoretical studies using TSH and IOSA techniques [8, 112].

Nieder et al. performed their experiments at 20 eV\textsubscript{cm} (using the time-of-flight technique) and recorded state-resolved differential cross sections for both direct and charge exchange channels, which are shown in Figures 3.8 and 3.9. In the direct channel a large rainbow is seen at 10–12° for all excited vibrational states. This was attributed to the strong attractive valence forces acting at low impact parameters. In this region, vibrational excitation occurs by 'bond dilution', where $r(H_2)$ increases as the proton approaches. The second maximum seen at smaller angles is thought to be related to a minimum of the deflection function. In the charge exchange channel, they noticed a remarkable similarity in both slope and magnitude of cross sections for H\textsuperscript{+}$\rightarrow$H\textsubscript{2} ($v_f = 0,1$) with those of directly excited H\textsubscript{2}($v_f = 3,4$). This similarity was further supported when they examined the average energy transfer as a function of scattering angle.

They understood their results by suggesting that charge exchange occurs only after
Figure 3.9. As for Figure 3.9, except showing results for charge exchange excitations. (Taken from [8]).

Figure 3.10. Simplified dynamical model for charge transfer on collinear (H₃)⁺ potential surfaces, drawn here for a fixed equilibrium bond length. The approaching reactants lead to vibrationally excited H₂ (step 1), which for v_f ≥ 4 can populate H₂⁺(v_f = 0, 1) by charge transfer transitions (step 2). (Taken from [112]).
there has been vibrational excitation of H$_2$ to $v_f \geq 4$ in the incoming part of the collision. This energy is necessary for reaching the crossing seam on the outgoing part. As attractive forces around this crossing region are relatively weak, trajectories for both processes would be similar, explaining the similarities in the observed differential cross sections. Figure 3.10 graphically illustrates this model. Potential curves for the system were calculated using the DIM (diatomics-in-molecule) and supported their conclusions. The energy defect between the ground state and charge exchange surfaces is large (1.8 eV$_{cm}$) in this system, and so direct excitation from the initial state ($v_0 = 0$) to the charge exchange channels by Demkov coupling is unlikely.

The results of both TSH and IOSA calculations are also shown in Figures 3.8 and 3.9. Both these calculations used the same DIM surfaces. The use of the IOSA method was justified by the negligible rotational excitation seen in the results, and because at 20 eV$_{cm}$ reactive and dissociative channels are weak. As can be seen, the IOSA calculations generally agree very well in magnitude and shape with the experimental differential cross sections. Deviations do occur, though, for the charge transfer process at small angles. This was thought to be due to errors in the long range part of the potential. Also, the position of the rainbow is shifted by 2.5° in both cases, which could not be explained.

Differential cross sections calculated by the TSH method were generally an order of magnitude smaller than the IOSA calculations. For inelastic scattering, relative magnitudes and shapes are reasonable, with the exception of $v_f=4$. This was thought to be due to flaws in the Landau-Zener theory when trajectories barely cross the seam. For charge exchange processes, serious problems with the TSH calculations are seen.

Interestingly, one outcome of both these studies was the calculation of transition probabilities as a function of impact parameter. Whereas the TSH calculations suggested that charge transfer occurs only for head on collisions (i.e. small impact parameters), IOSA calculations revealed that it actually occurs over a wide range of impact parameters. Further dynamical insights were obtained from the IOSA results, which backed up the proposed model. A final comparison between the two calculations is made in Figure 3.4 (page 47) which show integral cross sections as a function of final vibrational state. Excellent agreement with experiment is seen for the IOSA calculations, whereas TSH results are less satisfactory. Also shown are the Franck-Condon predictions, which don't come close to the experimental results, as is expected at 20 eV$_{cm}$.

To summarise, we see here another example of a collision process proceeding adiabatically at low energies, by Landau-Zener transitions in vibronic crossing regions. This example provides a revealing comparison between IOSA and TSH methods, the latter proving on this occasion to have serious problems.
3.5.3 \( \text{H}_2^+ + \text{Mg} \) Dissociative Charge Exchange

In this last example, we consider the process

\[
\text{H}_2^+ + \text{Mg} \rightarrow (\text{H} + \text{H}) + \text{Mg}^+
\]

which belongs to the important class of collision processes in which breakup of a bond occurs simultaneously with an electronic transition.

Experimental results were first reported by De Bruijn et al. [47]. In their experiments, they collided state selected beams and recorded the momentum distribution of the released dissociation fragments using a new position and time sensitive channel plate detector. The collision energies explored were 1.5 to 6.5 keV. Three types of dissociation processes were identified, as illustrated in Figure 3.11. Process b shows a direct transition to the repulsive state \( b^3\Sigma_u^+ \). The dissociating H atoms in this case share a kinetic energy \( \varepsilon \) up to about 8eV. If an attractive surface (such as \( \text{H}_2(a^3\Sigma_g^+) \)) is populated instead, then dissociation may occur by a radiative transition to a repulsive surface, denoted as process a. The kinetic energy spectrum for process a will be shifted slightly to lower energies from process b. Lastly, predissociation from an attractive surface may occur. Process c illustrates this, in which the state \( c^3\Pi_u \) couples rotationally to the \( b^3\Sigma_u^+ \) state. A series of discrete vibrational peaks will be seen in the kinetic energy spectrum in this case.

Typical results are shown in Figure 3.11 (page 44). The broad structures at energies below 7eV are due to direct (b) and radiative (a) dissociation. Peaks at higher energy are due to predissociation (c). Departure from Franck-Condon predictions (dotted curve)
3.5. CASE STUDIES

Figure 3.12. Potential energy as a function of diatomic bondlength for the simplified H₄⁺ + Mg system. The two cases of predissociation considered by [72] correspond to the repulsive curves I and II. (Taken from [72]).

is seen, and has been discussed on page 44. Also shown are the theoretical results of Sidis and deBruijn. They modelled these processes using a time-dependent semiclassical method that assumes that the vibrational sudden approximation is valid (see page 48). Agreement with experiment is seen to be quite good (dashed curves). At these high energies, dissociative charge exchange is viewed as occurring in two steps: An electronic transition occurs first, followed after a comparatively long time by one of the above dissociation mechanisms.

At lower energies, the molecule may vibrate during the collision event. A theoretical framework for treating dissociative charge exchange at low energies was recently developed by Gauyacq and Sidis [72]. Their method is also based on the time-dependent semiclassical technique, and is described on page 48. Although they only performed calculations on a simplified model of the H₄⁺ + Mg system, and couldn’t make comparisons with experimental data, their results are still particularly interesting. Two cases of predissociation were considered, differing in the relative position of the repulsive (diabatic) curve as shown in Figure 3.12. They calculated the probability of dissociative charge exchange not occurring – i.e. that the system survives in the initial state (v=0) or undergoes vibrational excitation. Results for a collision energy of 20 eV are shown in Figure 3.13.

For case I, we see important survival probability and substantial vibrational excitation, despite the possibility of predissociation. This striking result was attributed to strong coupling which causes multiple bound-continuum transitions between the two states. Also shown are the results of an earlier calculation [140] that used a ‘local complex potential’ model [137]. Here, a first order perturbative approach is taken in which an imaginary potential is introduced to represent the decay of the initial vibronic state into the continuum. The model is only valid for weak coupling at low energies, and we see from Figure 3.13 that it totally fails to predict survival of the system. In the second case
Figure 3.13. Impact parameter dependence of the survival ($v = 0$) and total vibrational excitation ($v \neq 0$) probabilities as calculated by [72]. Left and right figures correspond to cases I and II respectively. Also shown are the survival probabilities determined using a local complex potential (LCP) approximation. (Taken from [72]).

Figure 3.14. Calculated energy spectrum of the dissociation products arising from dissociative charge exchange as a function of impact parameter $b$. Left and right diagrams correspond to collision energies of 20 and 500eV. (Taken from [72]).
that they considered, we see in contrast that both models predict that predissociation is important.

To understand these riddles, we again must consider the adiabatic picture. As $R$ decreases, the $\text{H}_1\text{H}_2$ interaction between the two states increases causing the crossing in Figure 3.12 to become more and more avoided. The initial wavepacket will split between these two adiabatic states. In case I, the upper (bound) adiabatic curve is predominantly followed, and is thereby preserved against dissociation. Vibrational excitation is understood in terms of the different shapes of the initial $E_1$ potential curve and the upper adiabatic curve. For case II, an important part of the wave packet follows the lower adiabatic curve, leading to an important dissociation probability.

Finally, Figure 3.14 illustrates the predictive power of time-dependent techniques. Here, Gauyacq and Sidis have calculated energy spectra for dissociation products in case II (see Figure 3.14). We see that at 20eV, the spectrum at large impact parameters is peaked at the resonance energy, as expected. As the impact parameter decreases, however, the peak is displaced to lower dissociation energies. This was thought to be related to the way the wavepacket evolves on the lower adiabatic surface, and wasn't predicted by the local complex potential calculations. Also shown is the spectrum calculated for a collision energy of 500eV. Here we see dramatic oscillations in intensity as a function of impact parameter. This is due to the interference of different parts of the wavefunction that have travelled along two different paths, and is a sign that the system has started to behave more diabatically.
4 Experimental Techniques

4.1 Introduction

Both experiment and theory are closely intertwined in the field of molecular collision dynamics, and the field will only move forward if both parties work closely together. It is important that the experimentalist focuses on designing new experiments which will probe more deeply our current theoretical ideas, as well as opening up new areas of study. What directions need to be followed? We saw in chapter 2 that the promotion models which were so successful in interpreting electronic excitation in atomic collisions are now being applied to molecular collisions. However, the range of applicability of these models is still not fully established, and in particular the effect of the molecule's shape on the dynamics needs to be explored. In chapter 3, we reviewed the recent successes in quantitatively treating vibronic processes, and now theories such as the IOS and vibronic semiclassical approximations are able to predict state-to-state cross sections. Thus experiments must also aim to provide more state-specific differential cross sections for these theories to be exercised and advanced. In this last part of the review we look at the current experimental techniques that can be employed in these endeavours.

Basic aims of any experimental study of a collision process are

- to identify the initial and final states of the system.
- to establish the shape and features of the potential surfaces that govern the dynamics.
- to explore the dynamics of a process by sampling a wide range of trajectories over the surfaces and looking at the dependence on kinetic energy and initial state.
- to obtain differential and total cross sections that allow a detailed comparison with theoretical calculations.

The most suited experimental arrangement for extracting this information has proved to be the molecular beams technique. Here, a well collimated beam of particles of known state and energy is collided against a target inside a vacuum. The target might take the form of a well-defined region of gas, or another beam of particles. If background pressures are favourable and the collision zone well defined, then each particle in the main beam collides only once. Information on the various collision events that may occur is then obtained by using detectors to look at the energy and angular distributions of the scattered particles and the decay products (photons, electrons, fragments). In
4.2 Exploring the Potential Surfaces

In the molecular beams technique, there is no way of initially selecting the impact parameter of a collision. However, the angle over which particles scatter does depend on the randomly chosen impact parameter. Trajectories that probe repulsive parts of the potential will scatter through large angles; similarly, attractive potentials lead to small angle scattering. Thus, recording the angular distribution of scattered particles allows one to explore different parts of the potential and look at the impact parameter dependence of a process. Indeed, it can be shown that at small angles, the quantity $E\theta$ is inversely proportional to the impact parameter ($E$ is the collision energy, $\theta$ is the scattering angle). It is for this reason, and the fact that a wide range of collision energies can be accessed, that the molecular beams technique is more suited than any other for the study of collision dynamics.

Potential surfaces and features such as the location of crossings can be experimentally determined from measurements of the intensity of scattered signal over a range of scattering angles. In the simplest experiment, the intensity of the total (elastic) scattered signal is measured as a function of $E$ and $\theta$, from which the differential (DCS) and integral (ICS) cross sections can be readily calculated:

$$\frac{d\sigma}{d\omega} = \frac{dN}{dt \, d\Omega_d} \frac{d\Omega}{d\omega} \frac{1}{n_1 \, n_2 \, v_r \, \Delta V}$$

(4.1)

$$\sigma = \int \frac{d\sigma}{d\omega} d\omega$$

(where $\frac{dN}{dt \, d\Omega_d}$ is the number of particles $dN$, per unit time interval $dt$ scattered into the solid angle $d\Omega_d$ subtended by the detector, $n_1$ and $n_2$ are the beam and target densities, $v_r$ is the relative velocity, and $\Delta V$ is the scattering volume – see also later, page 194). Results are usually expressed in the centre-of-mass (cm) frame of reference, and here the Jacobian $d\Omega/d\omega$ is used for the transformation. The total cross section arrived at mainly consists of elastically scattered signal, although in some cases it can be difficult to unravel the elastic from inelastic signals, especially at wider angles. A number of well known procedures (see [135]) can then be used to extract the ground state potential surface by inverting elastic cross sections and examining any (diffraction, glory or rainbow) oscillatory structure. The accuracy of the final potential will be dependent on the energy and angular resolution of the measurement.

For atomic collision systems, some very precise ($\pm 1\%$) potentials have been obtained,
4.2. EXPLORING THE POTENTIAL SURFACES

Figure 4.1. (a) Apparatus used by Gao et al. for their DCS measurements. (b) Total charge transfer DCS for the scattering of H$^+$ + CO, CH$_4$, NO and CO$_2$ at 1.5keV. (Taken from [70]).

and in the case of symmetric rare-gas systems, all known physical properties (both microscopic and macroscopic) can be correctly predicted from these potentials. When molecular collision partners are involved, a spherically averaged potential is arrived at, although some information on the anisotropy of the potential can be extracted if oscillatory structure is resolved. Recently, some experiments have accessed the r-dependence and anisotropy of the potential directly by using beams of selected rotational, vibrational, and $m_j$ states (using lasers, electrostatic or magnetic state selectors combined with guiding fields). Similarly, excited surfaces can be examined using beams of electronically excited particles (see [135] for a review). All of these special techniques are difficult, however, and good theoretical calculations combined with experimental measurements are normally relied upon for obtaining all the potentials needed in a dynamical study.

A recent example of an absolute total DCS measurement is the work of Gao et al. [70], who looked at the small angle scattering ($0.03^\circ$ to $0.1^\circ$) of H$^+$ and He$^{(+)}$ against a range of atomic and molecular targets. They were primarily interested in testing calculations of the potential surface and obtaining data for use in atmospheric modelling, although their results will also be of use in calibrating the relative CS data obtained in other dynamical studies. Their apparatus is shown in Figure 4.1(a). A recent trend has been the use of efficient multichannel plate detectors that allow measurements at several angles to be performed simultaneously. Here, a plate of diameter 4cm is used, located 109cm from the target cell (TC). This encodes $90 \times 90$ positions, partitioned into rings to maximise the solid angle subtended at each $\theta$. Their measurements demanded extremely high angular resolution, and two apertures of diameter 20 and $30 \mu$m separated by 49cm
ensured that the main beam is narrow and collimated to ±0.003°! This was at the expense of intensity (≈ 10^3 cs⁻¹), although the beam was stable, not fluctuating by more than 10%. To remove the noise counts, they ran the experiment with and without the target gas for the same length of time, and subtracted the results. Target cell pressures were measured using an accurate Baratron, and they determined any corrections to n₂ and V (due to gas flow at the apertures of the cell) in eqn (4.2) by investigating different geometries of the cell and performing Monte-Carlo simulations. Typical results are shown in Figure 4.1(b) for total charge transfer in H⁺ systems.

Although total scattered intensity measurements are clearly useful, they will not give direct access to the dynamics of electronically inelastic processes. This can only come from measurements of channel-specific cross sections. Then, information on potentials explored during specific processes can be extracted, and the underlying dynamics studied from the energy and angular dependence of the cross section. To measure inelastic cross sections, angular measurements need to be combined with initial and final state analysis. Preparing the initial states is usually not a problem, and standard beam sources can be used without further state selection (although we have already briefly mentioned ways of defining the initial states more exactly – see page 66). Identifying the final states is more difficult, though, and techniques for doing so are described in the following sections.

4.3 Energy-Loss Measurements

One way of identifying the different excitation channels is to measure the velocity of the scattered particles. During an inelastic collision, discrete amounts of translational energy are exchanged in exciting the internal states of the partners, and the relationship between the scattered particle velocity and the excitation energy is

\[ w'_1 = w_1 \frac{m_1 m'_2}{m'_1 m_2} \left( 1 - \frac{\Delta E}{E_0} \right)^{1/2} \quad (4.2) \]

(where \(w_1, w'_1\) are centre-of-mass velocities before and after the collision; \(m_1, m'_1, m_2, m'_2\) are the projectile and target masses before and after the collision; \(\Delta E\) is the excitation energy; \(E_0\) is the initial relative kinetic energy – see also later, page 192). Two techniques have been developed for measuring this velocity change. In the time-of-flight (TOF) technique, the main beam is pulsed (either mechanically or using electric fields), and the time taken for each packet to be detected is recorded. Alternatively, electrostatic energy analysers can be used to measure translational energy when ions are scattered.

Energy-loss techniques have the big advantage that they can in principle be applied to the study of all collision processes, and so form an important part of the armoury of the experimentalist. However, the technique cannot distinguish channels which suffer the same energy loss. Also, there is the critical problem of the resolving power. A resolution of about 1eV is required to resolve most electronic processes (although Rydberg levels
from different series for example can be much harder to identify) and about 0.1eV to resolve vibrational levels. To achieve this, not only must the final velocities after the collision be measured with high precision, but the two colliding beams must have well-defined velocity and angular distributions. In a typical experiment using either technique, electrostatic or mechanical velocity selectors are used in beam production to ensure a narrow energy distribution. Another consideration is the stability of the power supply that sets the beam energy. Crossed target beams are used in preference to collision cells, because otherwise the thermal motion of the scatterers will introduce a further broadening factor.

The Time-Of-Flight Technique

In the TOF technique, the energy resolution is given by

$$\frac{\delta(\Delta E)}{E} = \frac{\delta t}{2t}$$

(4.3)

The flight time $t$ is directly proportional to the flightpath length. Thus longer flightpaths will give a better resolution. There will be a spread in this length due to the finite size of the collision, the angular resolution of the detector and perhaps an uneven detector surface, and it is therefore important to minimise these factors. The ultimate limit on $\delta t$ will be the precision of the timing devices, which currently is of the order of a nanosecond. More likely to be a limiting factor is the time spread of each beam pulse. If electric fields are used for fast pulsing, the finite rise time of the field can also introduce a significant energy spread in the beam. Usually, though, this method is chosen in preference to mechanical (rotating disc) choppers, which are not well suited to high vacuums.

Typical energy resolutions that have been attained using the TOF technique are $\Delta E/E \approx 0.005 - 0.01$, allowing for example the identification of electronic processes at 1000eV energies. The main advantage of the TOF technique is that it can be used for analysing neutral scattered particles. Also, all energies are monitored at once, and the technique can easily be used with a multi-angle detector. The main drawback, however, is that the duty cycle is low because the main beam is pulsed, and hence experimental run times can be large. To overcome this, the beam may be chopped in a pseudo-random sequence and correlated to the scattering signal, from which flight times can be extracted. This method utilises 50% of the beam, with the drawback that regions of lower intensity are measured with lower accuracy. Alternatively, bunching fields may be used to compress a section of beam (by accelerating the tail end) and so achieve narrow pulses. Duty factors of 20-30% can be achieved at the expense of impact parameter precision, due to the spread in energy within each pulse [104] (see also later, page 173).
4.3. ENERGY-LOSS MEASUREMENTS

Energy Analysers

An alternative technique for measuring the kinetic energy of ions is to use electrostatic energy analysers, either in the form of 127° coaxial cylinders, 180° concentric spheres or parallel plates. Now the energy resolution is fixed by the geometry of the analyser

$$\frac{\delta E}{E} = \frac{\delta R}{R} \quad 127^\circ \text{analyser} \quad (4.4)$$

(where $\delta R$ is the exit slit width, $R$ is the mean radius of the analyser). Typical resolutions are now 0.001-0.01, depending on the angular acceptance of the analyser. However, ions may be decelerated before entering the analyser (with perhaps some loss in signal), allowing energies to be determined with much higher precision than the TOF technique, and often measurements will be limited by the finite energy spread of the beam. With this technique, there are no limitations on the duty cycle, although usually only one energy measurement is made at a time and so experiments can still have very long run times.

Some of the best energy-loss measurements have been made at the Atomic and Molecular Collision Laboratory, Paris-Sud University (Orsay) [29, 50, 52, 54]. They used both TOF and energy analyser techniques to study direct and charge exchange processes in a range of atomic and molecular systems at 100-1000eV. Their TOF apparatus is shown in Figure 4.2. The glow discharge ion source generated beams of a tolerably low energy spread for their earlier experiments on atomic systems, and so no further initial energy selection was needed. To ensure sufficient energy resolution over a range of collision energies, the flightpath $L$ could be varied between 1.25 and 7.50 meters. Ions or neutrals were detected using an electron multiplier with an angular resolution of $\Delta \theta = 0.2^\circ$. The best energy resolution they achieved with this apparatus was $\Delta E = 0.3eV \ (E = 1000eV)$, which was limited by the beam energy spread. This allowed

![Figure 4.2. Schematic diagram of the TOF apparatus and electronics used by Brenot et al. for the study of ion-atom collisions. (Taken from [29]).](image-url)
4.4. STUDYING THE DECAY CHANNELS

them to distinguish different excited electronic states and identify different excitation mechanisms from the corresponding differential cross sections.

For the study of molecular processes they built a much more precise apparatus using a 127° energy analyser (see Figure 4.3). Now, the main beam is mass and energy analysed, giving a final beam energy spread of 80meV. Scattered ions are decelerated to 20eV before entering a 127° energy analyser and are detected using an electron multiplier ($\Delta \theta = 0.4^\circ$). This gave an energy resolution of about 100meV allowing them now to resolve vibronic levels. Resolution is again limited by the beam energy spread and worsened at wider angles due to the thermal motion of the targets. They later replaced their detector by a multichannel plate device placed at the exit of the analyser. As the radial position of the ions leaving the analyser is dependent on energy, they could make several energy measurements at once, reducing the experimental run time by a factor of 15. They also switched to a crossed beam target, allowing precision measurements to be made at wider angles.

4.4 Studying the Decay Channels

Indirect information on the dynamics of a collision process and the nature of the excited state can come from studying how this state decays. As Figure 4.4 illustrates, this may be by ionisation, photon emission or dissociation, and a large number of experiments have employed photon, electron and ion detectors to monitor these competing 'half collisions'. The energy resolution attained in such measurements is usually good, and in some cases total cross sections for each decay channel can be obtained. This allows the relative importance and energy dependence of different channels to be studied, giving insights into both the excitation and decay dynamics. In the following we shall give examples of these measurements, to indicate the variety of information that can be obtained and
Figure 4.4. Collisionally excited states may decay by photon emission ($10^{-9}$ sec.), electron emission ($10^{-13} - 10^{-15}$ sec.) or dissociation. The excited state may also be populated by cascading from higher excited states.

the problems associated with each technique.

4.4.1 Optical Spectroscopy

One of the ways in which an excited state may decay is by photon emission. If this decay is fast (typically $10^{-9}$ sec.), emanating from the collision zone before secondary collisions occur, then recording the radiation provides a way of establishing what states are excited through collisions. In some cases, radiation emitted during the collision has been observed, giving information on quasimolecular states (see [155]). Also, because the number of photons emitted is proportional to the number of atoms formed in that excited state, it is in principle possible to extract a total cross section for the collision process and thus probe the energy dependence of the dynamics.

The technique is attractive because very high resolution can be obtained, and in favourable cases the rotational structure of each vibrational band can be resolved. Thus the relative population of vibrational levels of the excited state can be established, allowing the role of vibration in the collisions to be studied. There is also the possibility through polarisation or angular measurements of extracting information on the population of the degenerate magnetic sublevels. For molecules, orientational information is also obtained as the alignment of these levels is referenced to the internuclear axis. As Figure 4.5 shows, the experimental set up is simple. The energy and angular spread of the beam is not critical, and the detector consisting of a monochromator and photomultiplier (possibly position sensitive) is well understood and commercially available. The optics are focused on the collision zone, and shields must be employed to eliminate other light sources.

There are, however, a number of serious problems associated with the technique, which has made its use rather limited, especially in the case of collisions involving
4.4. STUDYING THE DECAY CHANNELS

molecules. One cannot guarantee that the radiating state observed was populated directly through a collision. Cascading from the decay of higher levels to that state can be a problem, and care must also be taken to ensure measurements were made under single collision conditions. The extraction of the total cross section is particularly fraught with difficulties. Several measurements are required, to determine the emission cross section for both the radiative state and any cascading states, to check the polarisation of the emission, and to check for any anisotropy. The detection system must be accurately calibrated and the efficiency as a function of wavelength established. And lastly, all other competing decay mechanisms must be accounted for. (For a fuller discussion, see ref. [41], page 35).

Nevertheless, measurements have been reported on a wide range of collision systems involving molecules, including H₂ [82], N₂ [14, 18, 78, 87, 88, 132], O₂ [19, 88], NO [14, 19], CO [14], CO₂ [19, 28], N₂O, OCS [19]. In some cases, excitation cross sections could be obtained, and comparisons were made with Franck-Condon distributions [18, 19, 88]. Often, the stimulus for these studies is to obtain an understanding of atmospheric processes.

4.4.2 Electron Spectroscopy

Ionisation is a much faster decay mechanism than photon emission, occurring on a time scale of $10^{-13}-10^{-15}$ seconds. Recording the ejected-electron energy spectra therefore provides a more direct way of probing the initial collision event, with minimal problems of cascading from higher excited states. The energy resolution that can be attained is also good (50meV), and a number of recent studies have combined results from both TOF and electron spectroscopy experiments to look at collisional excitation of open shell
4.4. STUDYING THE DECAY CHANNELS

Figure 4.6. Schematic diagram of the experimental setup used by Boumsellek et al. for electron spectroscopy measurements. The diagram shows the ion source (IS), Wien filter (W), quadrupole deflector (Q), electrostatic lenses (L1-L3), deflectors (D1-D5), Faraday cage (FC), parallel plate analyser (EA) and the associated data-handling arrangement. (Taken from [24]).

atoms and ions (see [25] for a review).

Figure 4.6 shows a typical experimental setup used by Boumsellek et al. [24, 25, 26]. A mass analysed ion beam is produced which can be passed through a charge exchange chamber to generate a neutral beam. Less demands are made on the angular and energy spread of the main beam in these experiments, although it is important to have a well-defined collision zone. Here, an effusive gas beam is used as a target. Electrons ejected in collisions (with energies ranging from meV to a few eV) can be detected over a wide range of angles (±5°) by a detector consisting of zoom optics, a 45° parallel plate energy analyser and an electron multiplier. The optics are used to accelerate the electrons to a convenient energy (~ 2.5eV) and focus them onto the entrance of the analyser. The overall energy resolution was about 50meV.

It is important in electron spectroscopy to remove any magnetic fields or surface contact potentials that might influence the electron trajectories. Another more difficult problem is the determination of the transmission function of the detector i.e. the transmitted electron intensity for a given electron energy. In this case, the use of zoom optics resulted in strong sensitivity of the shape of the acquired spectrum to the size of the collision zone and variations in the beam position. This prevented them from determining the transmission function, although care was taken to ensure it did not change between experiments. Other workers [122] could establish the transmission function by measuring the electron spectrum in ionising electron-helium collisions, and comparing
it to the known spectrum. Without knowing the transmission function, the absolute magnitudes of different peaks cannot be compared, although relative magnitudes can be compared as a function of collision energy.

As was discussed on page 36, different ionisation mechanisms can be identified from their characteristic shape in the ejected electron spectra. For example, autoionisation gives well-defined peaks, whereas direct electron detachment (in negative ion collisions) has a broad energy distribution. Also, because an electron emitted from the projectile will have a doppler shift in energy, taking measurements as a function of angle is a way of assigning a feature to a particular collision partner. Thus, electron spectroscopy is a useful method for establishing what ionising states are excited in collisions, and how they decayed. Indeed, new autoionising states that are optically inaccessible have been identified by this technique. The energy dependence and relative magnitudes of the processes also give information on the initial excitation dynamics, with which Boumsellek et al. could test the predictions of state correlation diagrams. In F,F+ He collisions, there was general agreement seen between the relative populations of autoionising states observed, and those predicted by radial and rotational coupling mechanisms. In addition, the prediction made on statistical grounds that the Rydberg states $^1D_{nl}$ would dominate over $^1S_{nl}$ states was born out experimentally. Lastly, a DII-type ionisation mechanism was predicted for F scattering only. This could account well for a broad continuum seen in the corresponding electron spectrum, which became more important as energy increased.

4.4.3 Ion Fragment Measurements

The last competing way an excited state may decay is by dissociation, either directly if the excited state is unstable, by predissociation (coupling to a repulsive state) or after electron or photon emission to an unstable state. Again the study of dissociation channels is a big subject in itself, and complementary information can come from studies in which electron or photon bombardment is used to excite the initial state. In a collision study, it is of interest to establish what the parentage of each fragment is, the kinetic energy released during fragmentation, and what the preferred orientation of the collision is. Information can thus be obtained on the nature of the excited state and the location on the potential surface on which it is formed.

How are these measurements made? Firstly, momentum analysers (e.g. mass quadrupole spectrometers) can be used, or flight-time measurements made to identify each fragment ion. The fragmentation energy can be determined by looking at the velocity distribution of the fragments, for instance using electrostatic energy analysers (as for electron spectroscopy). Lastly, orientational dependence can be probed by looking at the angular distribution of the fragments.

There have only been a few studies of collision-induced dissociation, most of which have centred on H₂, because of its importance in plasmas. An example is the work of
4.5. COINCIDENCE TECHNIQUES

We have seen so far how energy-loss techniques can be used to identify different collision processes and probe their dynamics, and how photon, electron and ion emission measurements can be used to obtain complementary information and to determine how collisionally excited states decay. A summary is given in Table 4.1. These measurements alone are usually sufficient for obtaining a broad understanding of many collision
4.5. COINCIDENCE TECHNIQUES

Experimental Techniques

Total Angular Scattering Measurements
Used for extracting ground state potentials. Absolute total cross sections are useful for calibrating other relative CS measurements. The simplest experimental arrangement. However, as no state selection is made, no dynamical information on specific process can be obtained.

Energy-Loss Measurements
Used for identifying different excitation channels, and exploring collision dynamics through DCS measurements. Resolution at 1000eV is sufficient to resolve valence electronic levels (TOF) or vibronic levels (analysers). No restriction on process or target type. However, well-defined beams must be used, and low duty cycles are involved. Cannot distinguish processes suffering same energy loss.

Photon Spectroscopy
A means of identifying radiating states with high resolution. Polarisation measurements allow investigation of magnetic sublevel populations and orientation (in the case of molecules). Beam performance is less critical. However, extraction of ICS is difficult due to the contribution from cascading states and overlapping spectral lines.

Electron Spectroscopy
Used to identify ionising states and to study the dynamics of decay. Resolution can be good (50meV). However, it is difficult to determine the transmission function and hence the ICS.

Ion Spectroscopy
Used for studying processes that lead to fragmentation. Orientation dependence is probed by the angular distribution of fragments. However, identifying the parent state and hence the ICS can be difficult.

Coincidence Techniques
Involves correlating two signals (particle-particle, e^- -particle, e^- -hν etc.) and so combines the advantages of the two measurements, with the additional bonus that information is unambiguously process specific. Can also be used to probe orientational dependence. However, coincidence signal rates are small, and so long experimental run times are involved.

Table 4.1.
phenomena, but there are limitations on the amount of scientific information that can be obtained using each technique individually. In the case of energy-loss measurements, the energy resolution attained may not be sufficient to resolve all of the processes being investigated and indeed it is impossible to distinguish two channels that suffer the same energy loss. Optical, electron and ion emission measurements on the other hand do give much better energy resolution, but now there is the problem of relating the measurements to the original collision process. To overcome these problems and fully characterise a process one may turn to the coincidence technique, the most powerful (but most difficult to use!) tool available to an experimentalist.

The coincidence technique makes use of the fact that the flight-time difference between detecting one scattered particle (or photon, electron) A and another (B) is fixed if A and B emanate from the same collision. A time-of-flight experiment is set up by using the signal from one detector as a reference for recording flight times to the other detector. A typical timing arrangement is shown in Figure 4.8.

Two pieces of information on a geometrically well-defined collision process are obtained, and in principle the process can be nearly completely characterised. Also, many of the problems associated with each individual measurement are removed. For example two processes that suffer the same energy loss are distinguished if the scattered projectile is detected in coincidence with the corresponding electron or photon emission. Now the angular information from the energy-loss measurement is coupled with the superior energy resolution of the other measurement, allowing the DCS for the process and the excited state to be accurately determined.

The main problem with the technique is that coincidence count rates are often small and so long counting times are required to obtain a sufficient signal-to-noise ratio. Because experiments cannot be run indefinitely care must go into their design before measurements become feasible. Consider the signal and noise rates in a coincidence.
4.5. COINCIDENCE TECHNIQUES

An experiment involving detection of the scattered particle:

\[ N_s(\theta) = (n \times \text{vol}) \times (F \times \Delta \theta \times \Delta \phi \times \frac{\partial \sigma_i}{\partial \theta \partial \phi}) \times f \times q \]  

(4.5)

\[ B = (N_i + B_i) \times (N_s(\theta) + B_n) \times \tau \]

(where \(\frac{\partial \sigma_i}{\partial \theta \partial \phi}\) is the differential cross section for the process; \(\Delta \theta, \Delta \phi, f, q\) are solid angles subtended by the projectile and secondary detectors and their efficiencies; \(F\) is the projectile beam flux; \(n\) is the target number density; \(\text{vol}\) is the volume of the collision zone; \(B_i, B_n\) are the background counts in the two detectors). The coincidence count rate is ultimately determined by the DCS for the process, but can be maximised by using efficient detectors subtending as large as possible a solid angle (the upper limit being set by the quality of angular information required). Also, beam intensities can be set to an optimum value beyond which noise counts (proportional to the square of \(nF\)) will swamp the signal. Random coincidences depend on the detector count rates \((R_i, R_n)\) and can be reduced if charge or energy selection is performed before detection. Another consideration is the coincidence resolving time \(\tau\) which depends on the beam energy spread, the emission time of the electron or photon and the geometry of the experiment. Lastly, we note that the signal-to-noise ratio increases as the square root of the counting time:

\[ S/N = \frac{N_c t}{(N_c t + B t)^{1/2}} \]  

(4.6)

Figure 4.9(a) shows the apparatus used by Eriksen and Jaecks [63] for measuring photon-ion coincidences (with and without polarisation) from the process

\[ \text{He}^+(1s) + \text{H}_2(X^1\Sigma_g^+; v = 0) \rightarrow \text{He}^*(3^3P) + \text{H}_2^+(n'; v') \]

The particle detector consists of a parallel-plate analyser with 3 slits, allowing either neutral or ionic species to be detected. For this experiment, only He was of interest, and a deflecting field was used to prevent \(\text{He}^+\) being detected at S3. The \(\text{He}(3^3p)\) state has a lifetime of 100ns, and decays by emitting a photon. These photons were detected in coincidence with scattered He by the optics system. The coincidence electronics consisted of a single-channel analyser with a time resolution of 100ns. Thus transitions involving different vibrational states of \(\text{H}_2^+\) could not be resolved, although because more channels are seen the corresponding coincidence count rate is higher. An interference filter is used to single out photons of the correct wavelength, although there was noise from a closely-lying line of H (estimated to be 12% of the total signal). Noise from cascading states which can contribute as much as 20% in a standard emission measurement was much reduced here because of the longer lifetime of cascading states (150ns). Experimental run times were long, however, with each coincidence peak taking 24hrs to collect!
Using this apparatus, Eriksen and Jaecks recorded both the differential cross section for the process and the polarisation of the photons. Polarisation measurements are of interest as they allow the relative importance of different coupling mechanisms (rotational or radial) to be investigated by looking at the final distribution amongst magnetic sublevels. (In the case of molecules, polarisation is referenced to the molecular axis, and thus orientational information can be obtained). Their most striking result was that at some energies and angles He(3^3P) was observed to be in an almost pure (m=0) state, despite the fact that the radiation is summed over a large number of unresolved ro-vibronic states of H\textsubscript{2}. They also deduced that this radiation was aligned to the momentum transfer axis. This behaviour is very similar to the atomic He\textsuperscript{+} + He system (although here the momentum transfer axis proves to be unimportant), and emphasises the atom-like behaviour of H\textsubscript{2} in these collisions. They tentatively suggested that the underlying mechanisms were independent of both the orientation and any ro-vibrational excitation of the molecule.

Similar experiments were performed by Yenen et al. [84, 156, 157] to look at polarisation of Lyman-\alpha radiation produced in collisions of H\textsubscript{2}\textsuperscript{+} + He, Ne and H\textsubscript{3}\textsuperscript{+} + He. The geometry of their coincidence measurements is shown in Figure 4.9(b). They were able to obtain information on both the orientation of the molecule during the collision and the alignment of the radiation produced as H(2p) decays 1.6ns after dissociation. Thus the H\textsubscript{2}\textsuperscript{+} (H\textsubscript{3}\textsuperscript{+}) state excited in these collisions is fully identified for specific collision orientations, allowing important tests of the quasimolecular model to be made (see page 34).

Other molecular systems that have been studied using the photon-particle coincidence technique include K + N\textsubscript{2}, CO [100], H\textsuperscript{+} + N\textsubscript{2} [154], Li + H\textsubscript{2}, N\textsubscript{2} [22] and He\textsuperscript{+} + H\textsubscript{2}, D\textsubscript{2}[61, 74]. Many more atomic systems have been studied and the reader is referred to [7, 41] for reviews.
There are numerous other examples of two measurements being combined by coincidence technique to study molecular collision dynamics. Dissociation channels can be studied by detecting the fragments in coincidence with each other. Parent excited states can then be identified from the measured fragmentation energy. Also, if the event is fast relative to rotation then the angular distribution of fragments can give information on any orientational dependence of the collision process. Such measurements have been made on the systems $H^+ + H_2$, $N_2$ [159, 160], $H_2$ + He, Ar [153] and $H^+_2$ + Ar, Mg, Na, Cs [47]. DeBruijn et al. [47] used an impressive position- and time-sensitive channel plate detector in their measurements, and could determine most of the dissociative charge exchange channels from their well resolved energy spectra. Also, by manipulating the electron energy in the discharge source, they could select to a certain degree the initial vibrational state of the molecule, and thus probe vibrational energy dependence in these collisions.

In the study of vibronic phenomena, there is an increasing demand placed on the experimentalist to obtain differential cross sections that are closer to being fully state resolved, if the theoretical models developed for treating vibronic processes are to be advanced. One step towards this is the recent use of the PEPICO (photoelectron-photoion coincidence) technique for selecting the initial states of the system. Here, projectile ions produced by photoionisation are scattered and the products detected in coincidence with the energy analysed (and hence state-specifying) photoelectrons. Figure 4.10 shows the PEPICO apparatus of Campbell et al. [33, 98]. Helium I radiation crosses and ionises...
the primary gas (A) jet, and the photoelectrons corresponding to different spin-orbit or vibrational states of A⁺ are analysed using an efficient wide aperture retarding lens system ($\Delta \theta = \pm 18^\circ, \Delta E = \pm 50\text{meV}$). When an electron is detected, a pulsed field is applied to extract the corresponding ions, which are then accelerated to the desired energy and collided against the target beam B. Both primary ions A⁺ and charge exchange products B⁺ may then be detected in coincidence with the photoelectrons, from which cross sections as a function of internal state can be obtained. With this apparatus, state specified primary beam intensities were low (50-150cs⁻¹) and data accumulation times were very long (100 hours per coincidence peak!). Recent studies that have used similar techniques are [75, 86].

In conclusion, the experimentalist will increasingly have to make imaginative use of the coincidence technique if the models described in chapters 2 and 3 are to be advanced. These experiments are difficult to perform, but the quality of information that is potentially available is high. Measurements using the PEPICO and polarised photon-ion coincidence techniques exemplify this. In the rest of this thesis, our attempts at performing both atom-fragment ion and photon-ion coincidence experiments is described.
K-CH₃I Coincidence Study

5.1 Background to the Experiment

The experimental work described here is a continuation of a study in this laboratory of inelastic processes in collisions between potassium atoms and methyl iodide molecules.

This system provides a good example of the electron harpooning collision process, and has played an important role in the development of chemical reaction dynamics – the reaction channel has been much studied and is now quite well understood. Because CH₃I has a small negative electron affinity (compared to the halogens) non-adiabatic effects occur at shorter ranges and consequently there are more avoided crossings before the ionic exit channel. Thus a selection of states are accessible via harpooning and these inelastic channels have been studied using the time-of-flight technique [35, 43, 67].

Measurements were made in the small angle, high energy (100's eV) regime where the reactive channel is closed, and as Figure 5.1 shows, large inelasticity is seen extending to over 12eV, beyond which an isotope of K obscured measurements. Several distinct channels could be identified, including vibrational excitation, K(4²P) excitation, and excitation of valence and Rydberg states of the molecule (see Figure 5.2 and Table 5.1). The most striking features seen were that all processes appeared to onset at low angles (although only small portions of the DCS were recorded), and that in many cases the energy loss was independent of scattering angle. This suggests that an electron harpoon process is operating, in which an attractive intermediate ion-pair potential scatters particles to small angles and provides a ‘gateway’ to further crossings. One consequence of this model is that the ionic surface would be repulsive in the C-I coordinate, causing the bond to stretch. Also, the Rydberg channels cannot be reached from the ground ionic surface, and so excited ionic intermediate surfaces containing a valence shell vacancy and two Rydberg electrons may be involved. Figure 5.3 shows cuts through the relevant potential surfaces.

5.1.1 Vibrational, Alkali Atom and A State Excitation

To test the harpoon mechanism, a simple trajectory surface hopping model was developed [43] containing a minimum number of adjustable parameters, and tested on the four lowest observed processes (see Figure 5.2).Significantly, it was found necessary to include a three-body polarisation term in the ground ionic surface, which had the effect of reducing the repulsive strength of the C-I⁻ interaction whenever K⁺ is adjacent. Excellent agreement with both the energy loss data and the DCS is seen, confirming
5.1. BACKGROUND TO THE EXPERIMENT

Figure 5.1. Typical contour diagram showing $I(\chi)\chi^2$ for the scattering of K atoms off CH$_3$I ($E = 164$ eV$_{cm}$) as a function of energy loss and deflection angle ($\chi$). Note the growth of inelastic scattering with increasing angle, together with a drop in elastic scattering. (Taken from [67]).

Figure 5.2. Observed energy losses as a function of scattering angle ($E_{cm} = 164$eV). Solid lines show the quasiclassical trajectory model predictions. (Taken from [43]).
5.1. BACKGROUND TO THE EXPERIMENT

Figure 5.3. (a) K-CH₃I/ diabatic potentials displayed as a cut through the surface with the molecule in its equilibrium geometry. Ionic states are drawn dashed. (b) CH₃—I potentials. (Taken from [43]).

<table>
<thead>
<tr>
<th>Process Number</th>
<th>Proposed Assignment</th>
<th>Predicted energy loss (eV)</th>
<th>Observed energy loss (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K(4s) + CH₃I</td>
<td>Elastic</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>K(4s) + CH₃I(v)</td>
<td>Vibrational excitation</td>
<td>0.0 + vib</td>
</tr>
<tr>
<td>3</td>
<td>K(4p) + CH₃I(v)</td>
<td>Early and late</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>K(4s) + CH₃I(A)</td>
<td>A State excitation (4 states)</td>
<td>3.5-5.5</td>
</tr>
<tr>
<td>5</td>
<td>K⁺ + CH₃I⁻</td>
<td>Ground ion pair</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>K(4s) + CH₃I(6s)</td>
<td>n(I) → 6s Rydberg</td>
<td>6.5</td>
</tr>
<tr>
<td>7</td>
<td>K⁺ + (CH₃I⁻)**</td>
<td>1st excited ion pair</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>K(4s) + CH₃I(7s)</td>
<td>n(I) → 7s Rydberg</td>
<td>8.2</td>
</tr>
<tr>
<td>9</td>
<td>K⁺ + (CH₃I⁻)**</td>
<td>2nd excited ion pair</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>K(4s) + CH₃I(6s)</td>
<td>σC-H → 6s Rydberg</td>
<td>11.0</td>
</tr>
<tr>
<td>11</td>
<td>K⁺ + (CH₃I⁻)**</td>
<td>3rd excited ion pair</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>K(4s) + CH₃I(7s)</td>
<td>σC-H → 7s Rydberg</td>
<td>12.9</td>
</tr>
<tr>
<td>13</td>
<td>K⁺ + (CH₃I⁻)**</td>
<td>4th excited ion pair</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>K(4s) + CH₃I*</td>
<td>n(I) → σ*(C-H)</td>
<td>~ 6.0</td>
</tr>
</tbody>
</table>

Table 5.1.
that the ground state ionic intermediate is involved in these processes\(^1\). Crossings to the ionic surface may either occur on the incoming or outgoing parts of the trajectory, and lead to different amounts of vibrational excitation because of the repulsive nature of the surface in the C-I\(^-\) coordinate. This is seen in Figure 5.2 as two branches in energy loss for both channels 2 and 3. Note that as the bond stretches, one expects the electron affinity of the molecule to increase, pushing the second crossing point with channels 2 and 3 out to larger distances. This results in a lower transition probability, a picture confirmed by the lower DCS for vibrationally hot branches over a range of alkyl halide targets.

Excitation of the repulsive A states are also thought to be mediated by the ground ionic potential, despite the fact that at equilibrium, the second crossing point is already at large distances. Now, however, the electron affinity can decrease as the bond stretches (depending on the relative shapes of the ionic and A state surfaces), lowering the crossing radius and providing a mechanism for excitation. This conjecture was supported by the model results, which again could reproduce the observations (including the low angular onset) rather well.

Some questions concerning these processes still remain. For instance, the origin of the second sharp fall off at 600 eV in the elastic DCS is still uncertain (see Figure 5.4). One interpretation is that it marks the onset of transitions to a second excited ionic surface which might also contribute to the feeding of inelastic channels. Alternatively, the fall off may simply reflect the anisotropy of the ground potential surface. (Both of these possibilities could be modelled convincingly). However, it can be concluded from this work that the underlying physics governing these channels, in which early harpooning to the ground ionic surface mediates the collision, is understood.

5.1.2 Molecular Rydberg Excitation

Our understanding of the channels that lead to larger energy losses (channels 6,8,10,12) in contrast is much less complete. Firstly, we note that there is still uncertainty over how to assign these peaks. The comparison with UV and photoelectron spectroscopy data made in Table 5.1 seems to suggest that Rydberg states (or even excited positive ions) characterised by a hole in a previously doubly occupied orbital are excited. Such states would probably decay by fast autoionisation, and the observation of positive fragment ions formed in these collisions [32, 68] (see later) lends support to their assignment. However, the large uncertainty in the observed energy loss makes any assignment very difficult, and one also cannot rule out the possibility that both partners are simultaneously excited or that one peak is hiding several unresolved processes.

What is the mechanism for exciting molecular Rydberg states? Given the shape of the DCS shown in Figure 5.4, one is again tempted to suggest that a harpoon mechanism

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\(^1\)However, a mistake has since been found in their trajectory model. See later, page 124.
Figure 5.4. DCS for the processes listed in Table 5.1. The solid and dashed curves in the top figure show the results of a simple model of the system. (Taken from [35, 67]).
is operating. The ionic intermediate surface would now be highly excited, containing a valence shell vacancy and accommodating two electrons in the Rydberg levels (curves 7, 9, 11, 13 in Figure 5.3). Evidence for the existence of such states has come from differential negative ion production measurements [43, 127], to which CH$_3$I$^-$ ions mainly contribute. As Figure 5.5 shows, the peak in the DCS shifts to wider angles as energy increases, and in some cases (using Cs projectiles) a series of distinct rainbow peaks can be seen. Modelling the three lowest ionic surfaces (assuming that these states do not dissociate) could account well for the observations, although there is no experimental evidence in support of curves 11 and 13. Similar core excited ionic states have been observed in HCl and the rare-gases as resonances in electron scattering [102, 110, 133].

Of course, other mechanisms can be thought of that can lead to the production of core excited states. Radial or rotational coupling far up the repulsive wall could be a competing mechanism, especially at higher collision energies. A more gradual onset in the DCS would be expected, and as the DCS has only been recorded over a limited angular range, this mechanism cannot be ruled out. However, given the fact that excited negative ion states have been observed, and that other channels have been shown to proceed via the ground ionic surface, it seems reasonable to suggest that these channels are also populated by a similar harpooning mechanism.

5.1.3 Positive Ion Production

The most recent published work on the K + CH$_3$I collision system has examined the fate of these Rydberg excited molecular states [32, 68]. One would expect autionisation to be the most probable decay channel, and thus the observation of positive ions from these collisions provides another way of studying these channels. Experiments performed using
5.1. BACKGROUND TO THE EXPERIMENT

Figure 5.6. Energy dependence of the relative total cross section for the production of positive ions in \( \text{K} + \text{CH}_3\text{I} \) collisions (a) and \( \text{K} + \text{CF}_3\text{I} \). (Taken from [68]).

A mass quadrupole spectrometer confirmed this expectation, and revealed a significant cross section \((10^3 - 10^4\text{ pm}^2)\) for positive molecular ion production. As Figure 5.6 shows, the major fraction of the ions observed were the fragments \( \text{CH}_2^+ \) and \( \text{I}^+ \), consistent with the formation of excited dissociative states of \( \text{CH}_3\text{I}^+ \). Also shown are the results obtained when \( \text{CF}_3\text{I} \) was used as a target, and all fragment ions are now fully resolved.

Useful comparisons can be made with photodissociation experiments performed using the PEPICO technique [126]. Here, fragment ions result from transitions to electronically excited states of the positive ion. These states are repulsive in character, and the product ions are characteristic of where the inner vacancy was. It is found that the ions \( \text{CH}_3\text{I}^+ \), \( \text{I}^+ \) and \( \text{CH}_2\text{I}^+ \) can only arise from dissociation of the parent ion states \( \tilde{X} \), \( \tilde{A} \) and \( \tilde{B} \) respectively, whereas \( \text{CH}_3^+ \) can arise from all three (although mainly the \( \tilde{A} \) state), depending where on the potential surface the parent ion is formed. Table 5.2 summarises the information obtained from the PEPICO experiments. Based on these conclusions, rough estimates were made of branching ratios for initial ion states produced by collisions [68], although all that one can say with certainty is that excitation of the \( \tilde{X} \) state appears to be the least likely. Note also that in the collision study, a considerable fraction of highly fragmented ions \( (\text{CF}_2^+, \text{CF}^+) \) were seen. These could be accounted for if parent \( (\tilde{B}/\tilde{C} \text{ state}) \) ions are formed with significant vibrational excitation in the C-I bond, which would be consistent with the involvement of the ground ionic surface. The
effect of direct momentum transfer cannot be ruled out, though.

It is difficult to link this work to the earlier TOF work, where experiments were run at lower collision energies and probed only a limited range of impact parameters. However, the positive ion measurements do support the hypothesis that the excited molecular states seen in the earlier experiments contained a low-lying vacancy. Also, the expectation that decay occurs mainly by fast ionisation with conservation of the core vacancy, rather than by some shakedown mechanism (which would lead to more parent state ions), is confirmed. Finally, in Table 5.2, the higher K energy loss channels are compared with the PEPICO results, suggesting plausible alternative assignments.

### 5.1.4 The \( K + \text{CH}_3\text{I} \) Coincidence Experiment

It is clear from the discussion so far that the mechanisms by which core vacancies are produced in \( K + \text{CH}_3\text{I} \) collisions is still unclear, although it seems likely to involve an ionic intermediate surface. An abundance of positive fragment ions that correspond to core excited parent ion states have also been seen in these collisions, but whether they result from the same processes that produce large neutral atom energy losses (as opposed to, say, some charge exchange process) is still unknown. Given the large cross section for positive ions seen, and assuming the processes involve forward scattering, it was decided that an experiment in which the fragment ions and scattered K atoms are detected in coincidence would be feasible. Such an experiment would then allow an unambiguous assignment of the excited molecular states, and their decay channel. Also, from measurements of channel-specific differential cross sections, much information on the dynamics of these processes and the potential surfaces involved can be obtained.

Without special precautions, the energy resolution of the experiment would be seriously limited by the spread in flight times due to the finite size of the collision zone. To overcome this, a custom built ion detector was designed that achieves ‘time-focusing’ and mass selection through the choice of accelerating voltages. This, and the rest of the apparatus is described in the following sections. The chapter then ends with a discussion of the feasibility of the experiment. Results are presented and discussed in chapter 6.

<table>
<thead>
<tr>
<th>Electronic state and symmetry of ( \text{CH}_3\text{I}^+ )</th>
<th>Location of electron vacancy</th>
<th>State Energy/eV (U.V. PES data)</th>
<th>PEPICO dominant ion and observed appearance potential/eV</th>
<th>K energy loss/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \overline{X} \quad ^2E_2,^2E_1 )</td>
<td>I non-bonding</td>
<td>9.54, 10.17</td>
<td>( \text{CH}_3\text{I}^+ )</td>
<td>9.5</td>
</tr>
<tr>
<td>( \tilde{A} \quad ^2A_1 )</td>
<td>( \sigma_{\text{C-I}} ) bonding</td>
<td>11.95</td>
<td>( \text{CH}^+ )</td>
<td>12.2</td>
</tr>
<tr>
<td>( \tilde{B},\tilde{C} \quad ^2E )</td>
<td>( \sigma_{\text{C-H}} ) bonding</td>
<td>13.90</td>
<td>( \text{I}^+ )</td>
<td>12.9</td>
</tr>
<tr>
<td>( \text{CH}_2\text{I}^+ )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.2.** States of \( \text{CH}_3\text{I}^+ \) and their dissociation products. (Adapted from [68]).
5.2 Apparatus

Essentially the same apparatus described in [34] is used in this experiment, to which a newly designed ion detector has been incorporated. A brief description follows but consult [34] for further details.

5.2.1 General Description

The vacuum apparatus is shown in Figure 5.7 and consists of four differentially pumped chambers containing the main beam source, cross beam unit, scattering region and the alkali atom detector. Oil diffusion pumps with nitrogen cold traps backed with three rotary pumps generate a vacuum of $10^{-5}$, $10^{-5}$, and $10^{-6}$ torr in the cross beam, main beam and scattering chambers respectively. The alkali detection chamber is connected by flexible bellows to the bulk of the apparatus and maintained at $10^{-7}$ torr using an ion pump.

Potassium ions are produced by surface ionisation on a porous tungsten disc heated radiatively to 1500K and bathed in potassium vapour from a heated oven (250°C). Ions are extracted, accelerated and focused using a two element lens into a Lindholm-Gustaffson deceleration lens. This focuses the beam using an exponentially decaying electric field, and split lens elements allow steering of the beam to compensate for any misalignments. The beam emerges from the deceleration lens at its final energy and enters the neutralisation oven containing potassium vapour at 160°C.

Neutralisation occurs by resonant charge transfer. This is an efficient process occurring over large distances and so the ions are not deflected significantly. The emergent neutral beam is collimated after any remaining ions have been deflected away, and enters the collision chamber.

The cross beam is produced by diffusing CH$_3$I vapour along a gas line and through a glass capillary array of length 1mm and channel width 5μm. For a typical backing pressure regulated to 15 torr, the mean free path of molecules (5mm) is greater than the array length, ensuring the source is effusive. Note that capillary array sources are superior to slit aperture or single capillary tube sources in projecting an effusive beam in the forward direction, and so are a good choice for ensuring a small collision zone [66]. In this apparatus, the collision zone is designed to have dimensions $5 \times 1 \times 5$mm. The pressure in the collision chamber when both beams are running is typically $3 \times 10^{-5}$ torr, and the main beam is attenuated by $< 15\%$, ensuring single collision conditions.

Scattered potassium atoms can be detected 601mm away from the collision zone in the third differentially pumped chamber over a range of angles (0 to 12°). The atoms are ionised on hitting a warm tungsten/platinum filament, and then accelerated to hit a well defined spot on an aluminised surface. Secondary electrons are emitted, accelerated and detected using a scintillator/photomultiplier arrangement.

Positive fragment ions are detected in a similar fashion after being extracted from
Figure 5.7. Schematic diagram of the K + CH₃I crossed beam apparatus. Also shown is the coincidence timing arrangement.
Typical Experimental Running Conditions

<table>
<thead>
<tr>
<th>Main Beam Production</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>source oven temperature</td>
<td>230°C</td>
</tr>
<tr>
<td>C.E.C. temperature</td>
<td>160°C</td>
</tr>
<tr>
<td>beam energy</td>
<td>600eV</td>
</tr>
<tr>
<td>grid voltage</td>
<td>-200V</td>
</tr>
<tr>
<td>accelerator voltage</td>
<td>-600V</td>
</tr>
<tr>
<td>deceleration lens voltage</td>
<td>-450V</td>
</tr>
<tr>
<td>ion current at 1st dec. lens plate</td>
<td>$10^{-6}$ A</td>
</tr>
<tr>
<td>ion current on dump plates</td>
<td>$10^{-9} - 10^{-10}$ A</td>
</tr>
<tr>
<td>count rate at detector</td>
<td>&gt; $10^6$cs$^{-1}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pressures</th>
</tr>
</thead>
<tbody>
<tr>
<td>main beam chamber</td>
</tr>
<tr>
<td>target chamber</td>
</tr>
<tr>
<td>target gas line</td>
</tr>
<tr>
<td>collision chamber (without target)</td>
</tr>
<tr>
<td>collision chamber (with target)</td>
</tr>
<tr>
<td>detector chamber</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Detector count rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>main beam attenuation</td>
</tr>
<tr>
<td>atom counts at 3° (S+N)</td>
</tr>
<tr>
<td>atom counts (N)</td>
</tr>
<tr>
<td>ion counts (S+N)</td>
</tr>
<tr>
<td>ion counts (N)</td>
</tr>
</tbody>
</table>

Table 5.3.

the collision zone and accelerated. The design of the ion detector is described in detail in the next section. Because the detector and collision chambers were made of glass, blackout material was placed around the outside of the apparatus to exclude light and minimise the photomultiplier noise.

Table 5.3 summarises the running conditions for a typical experiment.

5.2.2 Coincidence Timing Arrangement

In this experiment the time delay between pulses from the ion and atom detectors is measured. If this falls within a defined ‘coincidence window’ then a pulse of proportional height is produced by the time-to-amplitude converter (TAC). These pulses are analysed by the multichannel analyser (MCA), and a ‘coincidence spectrum’ is generated in which numbers of counts are plotted as a function of time. Scattered atoms and ions produced in the same collisions will be correlated in time, and will give a peak in the spectrum growing above a statistical noise baseline generated by accidental coincidences. Figure 5.7 illustrates the arrangement of coincidence timing electronics. As shown, delays can be set on either signal in order to position a coincidence peak within a time window.
5.2.3 Running the Experiment

A computer model was written to calculate the detector voltages and delay times needed to observe a narrow coincidence peak corresponding to a chosen fragment ion. These values must be accurately set in an experiment, requiring the careful calibration of both the MCA and a voltage probe. Also, while running the experiment, it was important to ensure that the peak does not shift in position, and so critical voltages were frequently monitored. To maintain a good signal-to-noise ratio for the duration of a long experiment, the main beam was refocused regularly, which also provided a convenient time for transferring data from the MCA to the computer. Experiments were usually run in a darkened room to minimise noise in the ion detector. Lastly, we note that the experimental run time is an important parameter in the analysis of results, and so careful records were kept.

5.2.4 Problems with the Apparatus

The main problems experienced with this apparatus were with the routine production of a stable, intense atom beam. Contaminants would frequently condense on the insulators separating the extraction lens plates, causing electrical short circuits. Applying a high voltage between the lens plates to burn off the material proved to be a short term solution, but the problem was never really overcome. Shields were attached to the lens plates to screen the insulators from any ions scattered off the lens plates, without success. The source of the problem was therefore probably material diffusing out of the nozzle (e.g. potassium or oil) or perhaps vapourising off the radiation heater.

Problems were also encountered with the diffusion pumps. No water cooled baffles were attached to the pumps, and electrical shorts between the plates of the ion detector and main beam lenses due to oil vapour was a recurrent problem. Also, on several occasions the water cooling lines around the diffusion pumps blocked, overheating the pump and causing frustrating setbacks to the work! The cause of this was the gradual build up of contamination from a badly filtered (recirculated) water supply.

5.3 Ion Detector

Dr Keenan designed and built the ion detector in this laboratory, and a schematic diagram of it is shown in Figure 5.8. The detector was designed to generate three linear field gradient regions for extracting positive ions from the collision zone, separating their masses, and accelerating them to hit an aluminium surface. The ejected electrons are then detected using a scintillator/photomultiplier arrangement. The overall efficiency of the detector is expected to be about 10%.

Later inspection showed the region between A and B in Figure 5.8 actually produces several slightly different field gradients due to resistor mismatch. Table 5.4 gives a
5.3. ION DETECTOR

summary of the distances and resistances that define the geometry of both detectors that were used. Note that the resistance chain to which $V_{ms}$ is applied actually terminates with a variable resistor. This allows the voltage $V_{pcp}$ on plate that immediately follows $V_{ext}$ to be set to an appropriate value.

5.3.1 Design Principle

As mentioned earlier, the aim in designing the detector was to cancel the broadening of a coincidence peak due to the collision zone size. If no precautions were taken, the coincidence peak would be at least 100ns broad (for a 500eV beam), resulting in unacceptably long data collection times, as well as poor energy resolution. To see how the geometry of the detector shown in Figure 5.8 can improve on this, consider first the possibilities of an atom having a collision in either in the extreme right (forming ion 1) or left (2) ends of the collision zone (different X coordinate, same Y coordinate). Ion 2 is created $\Delta t$ seconds after ion 1, where $\Delta t$ is the flight time of K across the collision zone. However we see in Figure 5.8 that ion 1 has further to travel to before hitting the Al plate at D, and in fact if accelerating voltages $V_{ext}$ and $V_{ms}$ are correctly chosen, all ions formed along the collision zone can be detected with the same coincidence time.
### Table 5.4

<table>
<thead>
<tr>
<th>Region</th>
<th>Length (mm)</th>
<th>Resistance (MΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion Detector</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0) → $V_{\text{ext}}$ (A)</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>$V_{\text{ext}}$ → $V_{\text{pcp}}$</td>
<td>1.0</td>
<td>$\infty$</td>
</tr>
<tr>
<td>gnd → $V_{\text{pcp}}$</td>
<td>variable</td>
<td></td>
</tr>
<tr>
<td>$V_{\text{pcp}}$ → $V_{20}$</td>
<td>50.2</td>
<td>8.39</td>
</tr>
<tr>
<td>$V_{20}$ → $V_{21}$</td>
<td>3.42</td>
<td>0.51</td>
</tr>
<tr>
<td>$V_{21}$ → $V_{28}$</td>
<td>21.6</td>
<td>3.56</td>
</tr>
<tr>
<td>$V_{28}$ → $V_{\text{ms}}$ (B)</td>
<td>207.7</td>
<td>43.80</td>
</tr>
<tr>
<td>$V_{\text{ms}}$ (B) → $V_{\text{ms}}$ (C)</td>
<td>61.7</td>
<td>0.00</td>
</tr>
<tr>
<td>$V_{\text{ms}}$ (C) → $V_{\text{HV}}$ (D)</td>
<td>27.0</td>
<td></td>
</tr>
<tr>
<td>$V_{\text{HV}}$ (D) → scintillator</td>
<td>131.0</td>
<td></td>
</tr>
<tr>
<td>Atom Detector</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C.Z. → filament</td>
<td>601</td>
<td></td>
</tr>
<tr>
<td>filament → 15% (HV)</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>15% (HV) → 50% (HV)</td>
<td>10.1</td>
<td></td>
</tr>
<tr>
<td>50% (HV) → 100% (HV)</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>100% (HV) → scintillator</td>
<td>25.3</td>
<td></td>
</tr>
</tbody>
</table>

Thus 'time-focusing' in the X-direction can be achieved.

Note also that an ion formed at the back (ion 3) of the collision zone has further to travel before being detected than one formed at the front (4). However, this effect can be cancelled, because the ions experience more than one field gradient before being detected. Thus, although ion 3 arrives at A later than ion 4, it has been accelerated to a higher velocity, and if the correct voltages are chosen both can be arranged to arrive at D at the same time. Thus time-focusing in the Y-direction can also be achieved.

In principle, it is possible for a specific pair of voltages $V_{\text{ext}}$ and $V_{\text{ms}}$ to cancel all coincidence peak broadening effects due to the finite size of the collision zone.

### 5.3.2 Model and Properties of the Detector

A computer program was developed for investigating the properties of the detector and for calculating the voltages and delay times needed for running the experiment. The collision and dissociation event were modelled by conserving energy and momentum to give the initial ion and atom directions and velocities. Equations of motion were then derived that govern the passage of the scattered particles along both detectors, and atom and fragment ion flight times combine to give the coincidence time. By comparing times for events occurring in each of the XY-plane corners of the collision zone, the time-focusing property of the detector could be examined. Assumptions made in the calculation were that dissociation occurs instantaneously, and the target molecule is initially at rest. Also it was assumed that all field gradients were linear, and that
5.3. ION DETECTOR

Figure 5.9. Graph illustrating that a unique pair \((V_{ext}, V_{ms})\) can be chosen that cancels the peak broadening effect of the collision zone.

trajectories are not influenced by gravity or any stray magnetic fields.

As the program forms the backbone of the experiment, it was important to ensure that it contains no mistakes and gives a realistic model of the experiment. Comparisons with a ‘pencil on paper’ calculation showed that the programming was bug free. Results of a simple time-of-flight measurement also confirmed that the physics had been correctly modelled (see later, page 102). Careful examination of the built detector later showed that the electric field defined by applying \(V_{ms}\) actually consisted of several slightly different linear field regions (due to mismatching of resistors), and so a refinement to the model was made. Versions of the program were written for inverting experimental results to obtain the collision energy loss, and for modelling the fragmentation event. These were combined to give a menu in the final program, a listing of which can be found in appendix A.1, page 228.

In the following sections, we discuss the different properties of the detector that were investigated.

**Time Focusing**

Figures 5.10(a) and (b) show the effect of varying \(V_{ext}\) and \(V_{ms}\) on the spread in coincidence times. As expected, time spreads pass through a minimum, and in fact a unique pair \((V_{ext}, V_{ms})\) can be found that eliminates this spread. Figure 5.9 illustrates this by
5.3. ION DETECTOR

(a) $V_{ext}$ v's Peak Width

Fragment ion: CH$_3^+$
Beam Energy: 500eV (lab)
Energy Loss: 10eV (cm)
Scattering Angle: $3^\circ$
$V_{ms}$: 2000V
$V_{hv}$: 15kV

(b) $V_{ms}$ v's Peak Width

Fragment ion: CH$_3^+$
Beam Energy: 500eV (lab)
Energy Loss: 10eV (cm)
Scattering Angle: $3^\circ$
$V_{ext}$: 30V
$V_{hv}$: 15kV

Figure 5.10. Graphs illustrating the time-focusing property of the ion detector.
5.3. ION DETECTOR

showing how varying $V_{\text{ext}}$ (while keeping $V_{\text{ms}}$ optimised) affects the time spread. From these graphs, we also note that to ensure a time spread of less than 10ns, voltages must be set with a precision of ±5%.

Further checks showed that time-focusing of the detector is independent of the energy loss of the process (which is not known prior to an experiment) as well as the scattering angle, beam energy and $V_{\text{HV}}$.

Mass Separation

Thus, the detector can be set up by choosing a unique pair $(V_{\text{ext}}, V_{\text{ms}})$ to focus all coincidence peaks that correspond to a particular fragment ion. However, the behaviour of ions in an electric field is mass dependent, and so peaks corresponding to other ions will be broader. Figures 5.11(a) and (b) illustrates this, showing the mass dependence of the peak position and width for a detector focused on CH$_3$I$^+$. In fact, it is found that only a range of masses can be separated by careful focusing of the detector, and this range worsens as mass increases. For instance, clusters of peaks due to CH$_n$I$^+$ and CH$_4$I$^+$ (for various values of $n$) cannot be separated. Also, longer data collection times will be required to observe broader peaks.

Ion Fragmentation

A further peak broadening effect emerges if one considers the consequences of the dissociation event. Here, the velocity imparted on an ion by fragmentation is dependent on the energy of dissociation, the orientation of the molecule during the collision and the ions mass. Fragmentation parallel to the direction of extraction will lead to a split in coincidence times, whereas fragmentation perpendicular to extraction will not affect flight times (although this will lead to spatial separation of ions at D). Figure 5.12 illustrates the dependence of the coincidence time on molecular orientation for the case of CH$_3$I$^+$ fragmenting with energy 0.1eV to give I$^+$.

Thus, we expect for fragment ions to see a coincidence peak that is convoluted to form two peaks. The separation of these peaks gives a measure of the dissociation energy. Also, any asymmetry between the peaks would be an indication of orientational dependence of fragmentation. One could envisage future experiments in which the orientational dependence of collisions is probed by incorporating a position sensitive multichannel plate into the detector to look at the spatial distribution of ions. The peak broadening effect is quite large, though (a peak correlating to I$^+$ is broadened by ±50ns for a fragmentation energy of 0.1eV), and so experiments presented here were all performed with a detector set up to see CH$_3$I$^+$. 
Figure 5.11. Graphs showing how the coincidence peak position (a) and width (b) vary with ion mass for a detector focused on CH$_3$I.
5.3. Molecular Orientation vs Coincidence Time

**Figure 5.12.** Graph showing how the coincidence time varies with the orientation in the XY plane at which CH$_3$I$^+$ fragments. In this example, CH$_3$I$^+$ fragments with an energy 0.1eV to give I$^+$.

**Corner Turning**

Finally, the position of the collision zone image at D as a function of V$_{HV}$ was checked and is shown in Figure 5.13. As can be seen, the image is 5mm across and is centred 12mm from the central axis at D (when V$_{HV}$ = 13kV). Thus no reduction in the efficiency of the detector due to drift as ions turn the corner is expected.

5.3.3 Setting Time Delays and Windows

To perform the experiment, we need to calculate the range of times over which a coincidence peak is guaranteed to appear, and its likely width. Only then can we know what time delays and coincidence window to set, and how long the experiment must be run for. The uncertainty in the peak position will be determined by the precision with which relevant distances are measured and voltages set during the experiment. This was fully investigated using the computer model. Results for voltages that were actually set during an experiment are given later in chapter 6 (Table 6.2). Here we mention that the focusing of the detector is most sensitive to the geometry around the extraction region (especially between $V_{ext}$ and $V_{pex}$ where there is a change in field gradient), limiting the certainty to which we know a peak will be focused to ±30ns. Uncertainty in the peak position mainly arises from the unknown energy loss of the process and the longer...
5.3. ION DETECTOR

5.3.1 Fragment Ion: CH$_3^+$
Beam Energy: 500eV (lab)
Energy Loss: 10eV (cm)
Scattering Angle: $3^\circ$
Vext: 28.2V
Vms: 1573V
Vhv: 15kV

**Figure 5.13.** Graph showing how the image of the collision zone at D varies with V$_{HV}$. The edge of the sensitive area at D is 25mm from the centre of the plate, and thus no significant loss in detection sensitivity due to corner turning at C is expected for the values of V$_{HV}$ shown.

ion and atom flightpath lengths, and amounts to about $0.5\mu$s. Thus, we conclude that a coincidence window of no smaller than $2\mu$s must be set to guarantee seeing a coincidence peak.

5.3.4 Modifications to the Detector

It was found that ions were deflected along the detector, thought to be caused by the distortion of electric field due to grounded surfaces near the extraction region. To overcome this, strips of metal were strategically positioned and given voltages to correct the linear extraction field. Steering plates positioned along the detector were not found necessary after this.

Noise generated by the high field gradient between C and D was a more serious problem. Here, ions are stripped off dirty surfaces, especially near sharp edges where fields are particularly strong. Smoothing all edges and corners and gold plating the electrode plates helped to reduce the noise to acceptable levels, although the problem was never completely eliminated.

5.3.5 Positive Ion Time-of-Flight Spectra
To check various aspects of the detector, a TOF experiment was run, in which the extraction voltage $V_{\text{ext}}$ across the collision zone was pulsed (a square wave of width 1 $\mu$s and height 30V) and the resultant TOF spectrum recorded on the MCA. Figure 5.14 shows a typical spectrum that was obtained, and Table 5.5 compares the recorded fragment ion flight times with the predicted times over a range of detector voltages. The reasonable agreement seen confirms that CH$_3^+$, K$^+$, I$^+$, and CH$_3$I$^+$ ions are formed in the collision zone and that the computer program is largely correct. Discrepancies in the predicted times were probably due to the badly defined extraction pulse shape that was used. A better way of recording the TOF spectrum would be to pulse the atomic beam (for instance by applying a 10V pulse across the deflection plates). Smaller pulse widths could then be achieved without disturbing the electric fields in the detector, providing a more rigorous test of the computer model. These measurements were not pursued, however, and work was instead focused on attempting the coincidence experiment.

Note that with a gas line pressure of 20 torr, large amounts of both CH$_3$I$^+$ and I$_2^+$ were observed, presumably formed in multiple collisions due to a flooded collision chamber. Even for backing pressures of 9 torr where the beam attenuation was 15%, a small amount of I$_2^+$ is still seen (see Figure 5.14), suggesting perhaps that the collision zone is not as well defined as was first thought.

Figure 5.14. Example TOF spectrum. Four peaks are seen, identified from the left as CH$_3^+$, K$^+$, I$^+$, CH$_3$I$^+$ and I$_2^+$.
### Table 5.5.
Comparison between observed and predicted fragment ion flight times for different $V_{\text{ms}}$ voltages. Measurements were all taken for $V_{\text{ext}} = 0 - 30\text{V}$, $V_{\text{pcp}} = 33\text{V}$ and $V_{\text{HV}} = 12\text{kV}$ with a beam energy of $500\text{V}$. The delay on the START pulse delay was about $1.68\mu\text{s}$.

<table>
<thead>
<tr>
<th>$V_{\text{ms}}$ (volts)</th>
<th>Observed (predicted) ion flight time ($\mu\text{s}$)</th>
<th>CH$_3^+$</th>
<th>K$^+$</th>
<th>I$^+$</th>
<th>CH$_3$I$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>9.57 (9.42)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>6.54 (6.07)</td>
<td>10.94 (10.79)</td>
<td>20.07 (20.71)</td>
<td>21.48 (21.99)</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>5.27 (4.74)</td>
<td>8.79 (8.66)</td>
<td>16.70 (16.90)</td>
<td>17.58 (17.97)</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>4.12 (3.78)</td>
<td>7.27 (7.12)</td>
<td>13.57 (14.14)</td>
<td>14.45 (15.04)</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>3.42 (2.97)</td>
<td>6.00 (5.81)</td>
<td>11.52 (11.78)</td>
<td>12.36 (12.56)</td>
<td></td>
</tr>
<tr>
<td>2500</td>
<td>2.85 (2.40)</td>
<td>5.27 (4.89)</td>
<td>-</td>
<td>10.70 (10.82)</td>
<td></td>
</tr>
</tbody>
</table>

#### 5.4 Feasibility of the Coincidence Experiment

It is important before running a coincidence experiment to perform a feasibility calculation to predict the required data collection time and to highlight areas for improvement in the experiment. The calculation relates detector count rates to scattering cross sections, and so is also very useful in analysing the results of a coincidence experiment. In this final section, we describe such a calculation. Symbols that are used are defined in Table 5.6.

#### 5.4.1 The Feasibility Calculation

A scattering differential cross section is defined as

$$\sigma(\theta) \Delta \theta = \frac{\text{no. scattered into } \Delta \theta/\text{sec}}{\text{flux}}$$  \hspace{1cm} (5.1)

Signal counts in the atom and ion detectors are thus given by

$$N_a(\theta) = (n \times \text{vol}) \times (F \times \Delta \theta \times \sigma_{\text{tot}}(\theta)) \times f$$  \hspace{1cm} (5.2)

$$N_i = (n \times \text{vol}) \times (F \times \sigma_{\text{tot}}) \times q$$  \hspace{1cm} (5.3)

Similarly, the coincidence signal rate is

$$N_c(\theta) = (n \times \text{vol}) \times (F \times \Delta \theta \times \sigma_i(\theta)) \times f \times q$$  \hspace{1cm} (5.4)

Or, combining with eqn (5.3),

$$N_c(\theta) = (\text{frac} \times N_i) \times f \times \Delta \theta \times (\sigma_i(\theta)/\sigma_{\text{tot}})$$  \hspace{1cm} (5.5)

where $\text{frac} \times N_i$ is the number of ions produced by channel $i$. 


5.4. FEASIBILITY OF THE COINCIDENCE EXPERIMENT

Symbols used in the Feasibility Calculation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>number density of target molecules</td>
</tr>
<tr>
<td>$F$</td>
<td>flux of main beam</td>
</tr>
<tr>
<td>$f, q$</td>
<td>atom/ion detector efficiencies</td>
</tr>
<tr>
<td>$\Delta \theta$</td>
<td>solid angle subtended by atom detector</td>
</tr>
<tr>
<td>$\text{vol}$</td>
<td>volume of collision zone</td>
</tr>
<tr>
<td>$\sigma_{i\text{tot}}$</td>
<td>total cross section for channel i</td>
</tr>
<tr>
<td>$\sigma_i(\theta)$</td>
<td>differential cross section for channel i</td>
</tr>
<tr>
<td>$\sigma_{i\text{tot}}(\theta)$</td>
<td>total differential cross section</td>
</tr>
<tr>
<td>$\sigma_{ei}(\theta)$</td>
<td>elastic differential cross section</td>
</tr>
<tr>
<td>$B_i, B_a$</td>
<td>background counts in detectors</td>
</tr>
<tr>
<td>$\tau$</td>
<td>width of coincidence peak</td>
</tr>
</tbody>
</table>

Table 5.6.

The background count rate in a coincidence experiment results from random coincidences between signals due to other scattering processes and the detector noise counts. This can be written

$$B = (N_i + B_t) \times (N_a(\theta) + B_a) \times \tau$$

(5.6)

There are two requirements in the coincidence experiment. Firstly, we require a sufficiently large signal-to-background ratio after a time $t$ for the peak to be statistically significant. For a white noise (normal) distribution containing 1000 points (the number of channels in our experiments), 99.9% of all points will lie within 3 standard deviations of the mean $Bt$. The standard deviation of the distribution is $(Bt)^{1/2}$ (using De Moivre’s theorem), and hence our requirement can be written

$$S/B = N_c t / (Bt)^{1/2} > 3$$

(5.7)

The second requirement is that the number of coincidence signal counts is measured with sufficient precision. It can be shown that the standard deviation of the measured coincidence counts is $(N_c t + 2Bt)^{1/2}$, and hence the measurement precision is given by

$$\text{precision} = \frac{N_c t}{(N_c t + 2Bt)^{1/2}}$$

(5.8)

This requirement only becomes more important than the first when the background count rate is much smaller than the signal rate. For the feasibility calculations given in this thesis, we shall use a compromise between the two, the signal-to-noise ratio:

$$S/N = \frac{N_c t}{(N_c t + Bt)^{1/2}}$$

(5.9)
This expression is approximately the same as the signal to background ratio when \( B \gg N_c \), and also contains information on the precision of the measured peak height.

Now, rearranging eqn (5.9), we obtain the observation time required to collect a peak that is \( k \) standard deviations above the noise:

\[
t \geq \frac{k^2(N_c + B)}{N_c^2}
\]

**5.4.2 Example Calculation**

Using estimates of the parameters in eqns (5.5) and (5.6) we can calculate how long an experiment must be run before a coincidence peak 3 standard deviations above the noise level is seen:

\[
\Delta \theta = 2 \times 10^{-5} \text{ str. Measured by [23].}
\]

\[ f = q = 0.2 \quad \text{Typical for these types of detectors.} \]

\[ \tau = 50\text{ns} \quad \text{Easily obtainable with our design of ion detector.} \]

\[ N_i = 5000\text{cs}^{-1} \quad \text{Typical ion signal rate.} \]

\[ N_s = 700\text{cs}^{-1} \quad \text{Typical scattered atom signal rate} \]

\[ frac = 0.1 \quad \text{Pessimistic guess of branching ratio for \( CH_3I^+ \) formation [68].} \]

\[ B_i = B_a = 0 \quad \text{Compared to our signal rates.} \]

Hence, the coincidence signal and noise rates are

\[
N_c = 2 \times 10^{-3} \times (\sigma_i(\theta)/\sigma_{itot}) \text{cs}^{-1}
\]

\[ B = 0.175\text{cs}^{-1} \]

and so the time required to collect a peak 3 standard deviations above the noise level is

\[
t = \frac{109 \text{ hours}}{(\sigma_i(\theta)/\sigma_{itot})^2}
\]

We see that the feasibility of this experiment hinges on the shape of the differential cross section. If there is isotropic scattering across all angles, then

\[
\sigma_i(\theta)/\sigma_{itot} = \frac{1}{4\pi}
\]

and the experiment is not feasible. However, we expect forward-peaked scattering, and thus the required data collection time is

\[
\sigma_i(\theta)/\sigma_{itot} \approx 3 \quad \Rightarrow \quad t = 12 \text{ hours}
\]
5.4.3 Discussion

Comments on the feasibility of coincidence experiments have already been made on page 77. It was noted that the beam intensity can be set to an optimum value beyond which noise counts swamp the signal. In our example calculation, the noise rate is in fact much higher than the signal rate, and the required observation time has become independent of the beam intensity (as eqn (5.10) contains the ratio $N_a N_i / N_j^2$). Much more important is our ability to minimise $\tau$ by correctly choosing the ion detector focusing voltages, and to maximise $\sigma_i(\theta) / \sigma_{\text{tot}}$, by careful selection of the scattering angles. Also, the detectors must be operated as efficiently as possible, although unfortunately it was not possible to increase the solid angle subtended by the atom detector. The biggest contribution to the noise in this experiment comes from the elastically scattered atoms. At first sight, one might expect small gains to be made at larger scattering angles, where the inelastic to elastic DCS ratio improves. However, these are offset by the losses in $\sigma_i(\theta) / \sigma_{\text{tot}}$, as $\sigma_i(\theta)$ decreases markedly towards larger scattering angles. Nevertheless, the example calculation clearly indicates that our experiment is feasible.

Finally we mention that $\sigma_i(\theta)$ can be directly extracted from eqn (5.4) if an accurate record of the detector signal count rates are kept during an experiment. Martin et al. [100] demonstrate this from the results of a photon-scattered ion coincidence experiment on the $K + N_2$ system.
6

Results and Discussion

6.1 Introduction

Eventually, a stable and intense potassium beam was obtained with the rest of the apparatus in working order, and so a series of experiments were run successively over a period of 5 days. Because the fragmentation event causes extra broadening of the coincidence peak, all the experiments were set up for observing coincidences with the parent ion, CH$_3$I$^+$. Based on knowledge of the onset positions in the DCS for these processes, (see Figure 5.4, page 86), scattering angles of 3° and 4° were chosen for a beam energy of 700eV, hopefully to coincide with any maximum in the DCS. All relevant voltages were monitored during each experiment, to ensure that coincidence peaks would not shift in time. Alas, early on during the course of these runs, a short appeared in the detector between the plates $V_{ext}$ and $V_{pcp}$ (see Figure 5.8). Although this remained stable for the rest of the measurements, it did mean that the focusing conditions of the detector were bad, and as we shall show, any coincidence peak may have been broadened by up to ±100ns.

In this chapter, results of two of these runs, labeled 5 and 6, will be discussed. These were performed over the longest periods of time (36 and 28 hours, respectively), and so provide the most stringent test of the experiment. In both cases, data was transferred to a computer approximately half way through the run, generating four independent data sets, 51, 52, 61 and 62. Running conditions for these measurements are given in Table 6.1. Figures 6.1, 6.2 and 6.3 show the spectra that were recorded. One notices immediately that there are no obvious peaks in the spectra that can be attributed to coincidences. In the following section, we confirm this by taking a closer look at the spectra, and also show that if any coincidences were to appear, they would definitely have been positioned within the time window that was set.

What can one conclude from these measurements? Returning to the feasibility calculation, we show that an upper estimate for the cross section ratio $\sigma_i(\theta)/\sigma_{tot}$ can be set, and we examine the implication of this result on the original hypothesis that the collisions are mediated by an attractive ionic intermediate surface. The chapter then ends with a discussion of alternative mechanisms for molecular Rydberg excitation in these collisions, through an examination of the MO correlation diagram for the system.
(a) Experiment 5

(b) Experiment 6

Figure 6.1. Results of coincidence experiments 5 and 6. The dotted lines show the average background levels and the 2 and 3 standard deviation limits.
Figure 6.2. Results of coincidence experiments 51 and 52, collected under identical conditions. Also shown are the curves that result from passing a noise filter through the data, and the associated 2 and 3 standard deviation levels.
Figure 6.3. Results of coincidence experiments 61 and 62, collected under identical conditions. Also shown are the curves that result from passing a noise filter through the data, and the associated 2 and 3 standard deviation levels.
6.2 Analysing the Spectra

6.2.1 Predicted Peak Position and Width

First of all, it is important to see if there is any chance that a coincidence peak for CH₃I⁺ may have appeared outside the time window. Also, it is important to see what the consequences of the electrical short were on the detector focusing fields. The computer program was modified to take the short into account, and an investigation was made into the dependence of coincidence times on the precision with which distances and voltages were known for these experiments. Results are given in Table 6.2, and final computer predictions are summarised below.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Position (ns)</th>
<th>Width (ns)</th>
<th>Position (channels)</th>
<th>Width (channels)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt 5</td>
<td>1824 ± 360</td>
<td>±(63 + 40)ns</td>
<td>765 ± 76</td>
<td>±(13 + 9)</td>
</tr>
<tr>
<td>Expt 6</td>
<td>1748 ± 360</td>
<td>±(61 + 40)ns</td>
<td>659 ± 76</td>
<td>±(13 + 9)</td>
</tr>
</tbody>
</table>

It can be concluded that the coincidence signal for CH₃I⁺ should certainly have fallen within the rather large time window that was set. This ‘worst case’ calculation shows also that coincidence counts would certainly have been spread out over ±63ns, and possibly over ±103ns.

It is interesting to note from Table 6.2 that the region around detector plates V_{ext} and V_{pcp} (where the short occurred) is quite critical in determining how broad a coincidence peak will be. The region is important because a precise change in field gradient is set up across it which determines the focusing of the detector. Ions are travelling relatively slowly over this short region, and thus their calculated flight times are particularly sensitive to the geometry of the region. Perhaps this is the biggest drawback of the
6.2. ANALYSING THE SPECTRA

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Deviation from predicted position</th>
<th>Additional increase in peak width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltages</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_{\text{ext}} \pm 1$V</td>
<td>$\pm 8.4$ ns</td>
<td>7.1 ns</td>
</tr>
<tr>
<td>$V_{\text{pcp}} \pm 2$</td>
<td>67.5</td>
<td>14.2</td>
</tr>
<tr>
<td>$V_{\text{ms}} \pm 100$</td>
<td>211</td>
<td>5.8</td>
</tr>
<tr>
<td>$V_{\text{HV}}$ (atom detector) $\pm 1000$</td>
<td>11.5</td>
<td>0</td>
</tr>
<tr>
<td>$V_{\text{HV}}$ (ion detector) $\pm 1000$</td>
<td>2.5</td>
<td>0</td>
</tr>
<tr>
<td>Beam Energy $\pm 1$eV</td>
<td>7.4</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta E \pm 10$eV</td>
<td>124</td>
<td>0.6 ns</td>
</tr>
<tr>
<td>Distances</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(0) \rightarrow V_{\text{ext}}(A) \pm 1$mm</td>
<td>150</td>
<td>34.8</td>
</tr>
<tr>
<td>$V_{\text{ext}}(A) \rightarrow V_{\text{pcp}} \pm 0.5$</td>
<td>101</td>
<td>11.9</td>
</tr>
<tr>
<td>$V_{\text{pcp}} \rightarrow V_{20} \pm 1$</td>
<td>73.6</td>
<td>2.1</td>
</tr>
<tr>
<td>$V_{20} \rightarrow V_{21} \pm 1$</td>
<td>43.9</td>
<td>0.2</td>
</tr>
<tr>
<td>$V_{21} \rightarrow V_{28} \pm 1$</td>
<td>40.2</td>
<td>0.2</td>
</tr>
<tr>
<td>$V_{28} \rightarrow V_{\text{ms}}(B) \pm 5$</td>
<td>118</td>
<td>0.2</td>
</tr>
<tr>
<td>$V_{\text{ms}}(B) \rightarrow V_{\text{ms}}(C) \pm 1$</td>
<td>17.3</td>
<td>0</td>
</tr>
<tr>
<td>$V_{\text{ms}}(C) \rightarrow V_{\text{HV}}(D) \pm 1$</td>
<td>11.2</td>
<td>0</td>
</tr>
<tr>
<td>$V_{\text{ms}}(D) \rightarrow$ scintillator(E) $\pm 1$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$CZ \rightarrow$ atom detector $\pm 5$</td>
<td>86.1</td>
<td>0</td>
</tr>
<tr>
<td>scattering angle $\pm 0.5^\circ$</td>
<td>34.3</td>
<td>0.9</td>
</tr>
<tr>
<td>Total Changes</td>
<td>$\pm 360$ns</td>
<td>40 + 63 = $\pm 103$ns</td>
</tr>
</tbody>
</table>

Table 6.2. Dependence of coincidence times and widths on the measurement precision of experimental voltages and distances. The geometry of the extraction field region (where the short occurred in experiments 5 and 6) is seen to be quite critical.

detector design, and extending the length of the extraction field region would be an improvement.

6.2.2 Gaussian Noise Filter

A visual inspection of Figure 6.1 shows that there are no peaks 3 standard deviations high above the background level falling within the ranges calculated above. Here, the background level is defined by fitting an exponentially decaying curve to the whole spectrum. A check was also made to see if there are any broad peaks hidden within the background noise that could be attributed to coincidences. To do this, a ‘noise filter’ was used, in which each point in the spectrum is adjusted to the average of its surrounding points:

$$\bar{x} = \frac{1}{25} \sum_{x_j = \bar{x} - 12}^{x_j = \bar{x} + 12} x_j$$

$$\sigma(\bar{x}) = \sqrt{\frac{25}{25}} \times \sqrt{\text{background}}$$
Here, the size of the filtering 'box' is set at 25 channels. The standard deviation $\sigma(\bar{x})$ appropriate to the filtered spectrum is calculated from the exponentially decaying background level.

The resulting curves are also shown in Figures 6.2 and 6.3. Comparing (independent) results from identical experiments (expt61 with expt62 etc.), it can be seen that there are no correlated peaks above the background noise level. Thus we conclude that although coincidence counts (possibly spread over ±100 ns) should certainly have fallen within the time window set for experiments 5 and 6, no correlated peaks greater than 2 standard deviations above the noise level were seen.

### 6.3 Estimating the Ratio $\sigma_i(\theta)/\sigma_{itot}$

It seems unlikely that there is an experimental reason that can account for not seeing a coincidence peak. Real scattering signals were seen as care was taken to ensure that beams were pure, and signal was only seen when beams were crossing. There was no other source of scattering, and at the scattering angles chosen there was no interfering signal from the main beam. The cross beam was run so that there was no more than about 20% main beam attenuation, and background pressures were maintained at less than $3 \times 10^{-5}$ torr. Thus it is unlikely that there were multiple collisions that prevented atoms and ions from reaching their detectors. Lastly, noise produced by the counting electronics was insignificant, and the inherent photomultiplier and detector noise was at an acceptable level. We return therefore to the feasibility calculation to explain the result and its implication on the hypothesised collision dynamics.

Recall that the time taken to collect a coincidence peak $k$ standard deviations above the noise is given by

$$t_{obs} \geq \frac{k^2(N_c + B\tau)}{N_c^2} \approx \frac{k^2 \times N_a(\theta) \times N_i \times \tau}{N_i^2}$$

(6.3)

where $N_c = (\text{frac} \times N_i) \times f \times \Delta\theta \times \sigma_i(\theta)/\sigma_{itot}$

(For convenience, we've defined $B$ here as $N_a(\theta) \times N_i$). As values for $t_{obs}$, $N_a(\theta)$ and $N_i$ have been measured, and the peak width $\tau$ estimated, we can set an upper limit on the value of $\sigma_i(\theta)/\sigma_{itot}$.

The total number of counts in each spectrum equals the product $N_i \times N_a(\theta) \times t_{obs} \times t_{window}$, from which $N_i$, $B$ and $N_c$ can be estimated. Ion and atom count rates were also measured directly during these experiments, and these rates are expected to be consistent with the spectra. A comparison made in Table 6.3 between the measured and calculated product $N_i \times N_a(\theta)$ shows that in fact this is not the case. The discrepancies are probably due to the fluctuation of count rates during the experiments, and it is realistic to assume that atom and ion count rates were overestimated by equal proportion. Values of $N_i$ and $N_a(\theta)$ deduced in this way are given in Table 6.3.
6.4. IMPLICATIONS OF RESULT ON THE ORIGINAL HYPOTHESIS

Recall that the hypothesis being tested in this experiment is that positive fragment ions originate from collisions in which molecular Rydberg states are excited, which in turn occurs by a mechanism that involves harpooning to excited ionic surfaces (see page 85). The main evidence supporting this mechanism is the low angular onset seen in the DCS for these processes, and also that doubly excited negative ion states have been observed, which may act as intermediates in this scheme. If negative ion states are involved in

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experiment 5</th>
<th>Experiment 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_iN_a(\theta)$ (from spectra)</td>
<td>$4.57 \times 10^6 c^2 s^{-2}$</td>
<td>$2.53 \times 10^5 c^2 s^{-2}$</td>
</tr>
<tr>
<td>$N_iN_a(\theta)$ (measured)</td>
<td>$10.80 \times 10^6 c^2 s^{-2}$</td>
<td>$3.50 \times 10^6 c^2 s^{-2}$</td>
</tr>
<tr>
<td>$N_a(\theta)$</td>
<td>$1171 \text{ cs}^{-1}$</td>
<td>$595 \text{ cs}^{-1}$</td>
</tr>
<tr>
<td>$N_i$</td>
<td>$3902 \text{ cs}^{-1}$</td>
<td>$4251 \text{ cs}^{-1}$</td>
</tr>
<tr>
<td>$B$</td>
<td>$0.0218 \text{ cs}^{-1} \text{ cnl}^{-1}$</td>
<td>$0.0121 \text{ cs}^{-1} \text{ cnl}^{-1}$</td>
</tr>
<tr>
<td>$N_i/(\sigma_i(\theta)/\sigma_{\text{tot}})$ (worst)</td>
<td>$3.90 \times 10^{-4} \text{ cs}^{-1}$</td>
<td>$4.25 \times 10^{-4} \text{ cs}^{-1}$</td>
</tr>
<tr>
<td>$N_e/(\sigma_i(\theta)/\sigma_{\text{tot}})$ (best)</td>
<td>$1.56 \times 10^{-3} \text{ cs}^{-1}$</td>
<td>$1.70 \times 10^{-3} \text{ cs}^{-1}$</td>
</tr>
</tbody>
</table>

Table 6.3. Table showing various count rates that were deduced from the spectra.

Values for $B$ and $N_e$ can now be obtained using eqn (6.3). The solid angle subtended by the atom detector, $\Delta \theta$, is known to be $2 \times 10^{-5}$ steradians [23]. Comparisons made by Duchart [57] between this and another detector suggest that the detection efficiency is around 20%, although in the worst case, it could be as low as 5%. Branching ratios for positive ion formation in these collisions have been measured previously by Fluendy and Ryall [68] (see Figure 5.6, page 88). Their work suggests that for a beam energy of 700eV, only 10% of positive ions formed are the parent ion, and hence the appropriate value for $frac$ in the above equations is 0.1. Table 6.3 gives values of $N_e$ and $B$ calculated using these numbers. We did not see a peak 2 standard deviations above the background level. Hence,

$$t_{\text{obs}} < \frac{4 \times B \times \tau}{N_e^2}$$

$$\Rightarrow \frac{\sigma_i(\theta)}{\sigma_{\text{tot}}} < \left[ \frac{4 \times B \times \tau}{t_{\text{obs}} \times N_e^2} \right]^{1/2} \text{ where } n_e = N_e \div \frac{\sigma_i(\theta)}{\sigma_{\text{tot}}}$$

Substituting in our values for $N_e$, $t_{\text{obs}}$, $B$, and assuming in the best (worst) case that the coincidence peak is ±13(22) channels broad, we finally obtain upper estimates for the cross section ratio:

$$\frac{\sigma_i(\theta)}{\sigma_{\text{tot}}} < 2.7 \text{ (14) } \text{ (experiment 5)}$$

$$\frac{\sigma_i(\theta)}{\sigma_{\text{tot}}} < 2.1 \text{ (11) } \text{ (experiment 6)}$$
these collisions, one would expect there to be a very low angular onset, with the largest contribution to the total cross section coming from small angles. Assuming that the experimental measurements were made near the peak in the cross section at low angles one would expect the cross section ratio to be relatively large.

The other possibility, assuming that the positive fragment ions do form coincidences with scattered neutral potassium, is that only neutral molecular states are involved, with coupling occurring on the repulsive wall. In this case, we would expect the cross section to onset at wider angles, with the main contribution to the total cross section coming from a larger angular range. Hence the cross section ratio would be smaller. Because we have set an upper estimate on the cross section ratio, we can set a limit on how 'peaked' the DCS might be, and so determine whether the harpoon mechanism is plausible.

6.4.1 Exploratory Calculations

To test these ideas, it was assumed to start with that the reduced DCS onsets and peaks at small angles, and various decay shapes were considered to see how 'peaked' the reduced DCS must be before it is ruled out. Cross section ratios for scattering to 3.94 degrees ranged from $11.95 \left( \sigma(\theta) \sin(\theta) = (\theta - A)^{-2}, A=-1^\circ, \text{onset}=800 \text{eV}^* \right)$ to $1.0 \left( \sigma(\theta) \sin(\theta) = (\theta - A)^{-3}, A=1^\circ, \text{onset}=800 \text{eV}^* \right)$, the first lying above the upper estimate set experimentally.

Figure 6.4(a) shows the reduced DCS measured by Martin et al. [100] for the excitation of K($4^2P$) in collisions with N$_2$. This system is similar to the K + CH$_3$I system, with excitation occurring by harpooning to an intermediate ground ion-pair state, and the reduced DCS shape shown was taken as a model. Figure 6.4(b) illustrates how the cross section ratio changes as the onset of this DCS is moved out to beyond where experiments 5 and 6 were run. For experiment 5, the calculated ratio lies just above the experimentally set 'best case' upper estimate (but not the 'worst case' estimate) over nearly the whole range of possible onset angles. Thus doubt is cast as to whether the DCS shape shown in Figure 6.4 is a good model for the K + CH$_3$I system. To obtain a ratio within the (best) upper estimate, the DCS would have to peak and decay much faster, with a rather flat shape near where our measurements were made. Alternatively, the DCS could be rather flat over the whole angular range. Certainly, one can conclude that measurements were not made near any peak in the DCS.

6.4.2 A Model of the Collision System

A more rigorous test of the hypothesis is to follow the approach of Cowan et al. [43] and use classical mechanics to calculate for typical potential surfaces the cross section ratio via the classical deflection function. This would allow us to see what the restrictions are on the possible mechanisms and potential surface shapes. There are eight different paths that can be followed, if the model is restricted to the four potential surfaces shown...
6.4. IMPLICATIONS OF RESULT ON THE ORIGINAL HYPOTHESIS

Figure 6.4. (a) Reduced differential cross section for the excitation of $K(4^2P)$ in collisions with $N_2$. (Taken from [100]). Taking this as a model for the reduced DCS shape for $K + CH_3I$ collisions, we see in (b) how the cross section ratio changes as a function of the DCS onset position. As the upper estimates set experimentally fall in the range 2.7-14 and 2.1-11 (for expts 5 and 6), these possibilities can only tentatively be ruled out.
6.4. IMPLICATIONS OF RESULT ON THE ORIGINAL HYPOTHESIS

Figure 6.5. The four potential surfaces considered in the model of the K + CH\textsubscript{3}I collision system. The x-axis here is \( R \), the interparticle separation.

in Figure 6.5.

path 11 \( \text{gnd(neu)} \rightarrow \text{ex(neu)} \), early crossing.

path 12 \( \text{gnd(neu)} \rightarrow \text{ex(neu)} \), late crossing.

path 21 \( \text{gnd(neu)} \rightarrow \text{ex(ion)} \rightarrow \text{ex(neu)} \), early crossing.

path 22 \( \text{gnd(neu)} \rightarrow \text{ex(ion)} \rightarrow \text{ex(neu)} \), late crossing.

path 31 \( \text{gnd(neu)} \rightarrow \text{gnd(ion)} \rightarrow \text{ex(ion)} \rightarrow \text{ex(neu)} \), early crossing.

path 32 \( \text{gnd(neu)} \rightarrow \text{gnd(ion)} \rightarrow \text{ex(ion)} \rightarrow \text{ex(neu)} \), late crossing.

path 41 \( \text{gnd(neu)} \rightarrow \text{gnd(ion)} \rightarrow \text{ex(neu)} \), early crossing.

path 42 \( \text{gnd(neu)} \rightarrow \text{gnd(ion)} \rightarrow \text{ex(neu)} \), late crossing.

A computer program was developed to see how the cross section ratio depends upon the position of the crossings shown in the figure, and the potential surface parameters for each path.
6.4. IMPLICATIONS OF RESULT ON THE ORIGINAL HYPOTHESIS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ground Surface</th>
<th>Excited Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$</td>
<td>0.11 eV</td>
<td>0.11 eV</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>3.2 Å</td>
<td>3.2 Å</td>
</tr>
<tr>
<td>$A'$</td>
<td>1.5 eV</td>
<td>0.75 eV</td>
</tr>
<tr>
<td>$R_m$</td>
<td>3.2 Å</td>
<td>3.2 Å</td>
</tr>
<tr>
<td>$\alpha'$</td>
<td>4.0 Å$^4$</td>
<td>6.25 Å$^4$</td>
</tr>
</tbody>
</table>

Table 6.4. Table showing the potential parameters that were used in the model. The ground state parameters have been experimentally measured by the references given in [43], and the adjustable excited state parameters are set to the values used by [43].

Method of Calculation

The potential surfaces used in these calculations are the same as those reported by [43]. Neutral surfaces are given by the Lennard-Jones 6-12 potential,

$$V(R)_{K-CH_3I} = 4\epsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^{6} \right] + E_{exc}$$

(6.4)

and ionic surfaces by the power series

$$V(R)_{K^+-CH_3I^-} = A' \left( \frac{R_m}{R} \right)^5 - 14.4 \left( \frac{\alpha'}{R^4} \right) + I.P. + E_{exc}$$

(6.5)

where $I.P.$ is the ionisation potential of the potassium atom (4.3 eV) and $E_{exc}$ is the excitation energy of the molecule. Values of the potential parameters are given in Table 6.4.

To calculate the differential cross section for each path, firstly the deflection function is required. Because the main contribution to the total cross section comes from small angles, and high collision energies are involved, the small angle formula [66] that assumes straight line trajectories was used:

$$\chi(b) = \frac{b}{2E} \int_{R_{ci}}^{R_{ci+1}} \frac{dV}{dR} \left( R^2 - b^2 \right)^{-1/2} dR$$

(6.6)

Here, the integration ranging between ±∞ is split up into different sections, $\chi$ is the angle of deflection, $E$ is the collision energy, $b$ is the impact parameter and $V$ is the potential for section $i$ of the branch considered. (Note that in [43], the formula is incorrectly given, with the factor 2 needed because integration is between ±∞, being omitted). Because in our model only inverse power potentials ($V = CR^{-\alpha}$) are used, the contribution from each section $i$ can be evaluated analytically using the result

$$b^\alpha \chi_i(b) = \frac{sc}{2E} \int_{\arcsin(b/R_{ci}+1)}^{\arcsin(b/R_{ci})} \sin^\alpha \theta d\theta$$

(6.7)
The classical differential cross section is then given by
\[ \sigma(\chi) = \frac{\text{prob} \times b}{\sin \chi |d\chi/db|} \]  
(6.8)

from which the integral cross section and the cross section ratio can be calculated.

To keep the model as simple as possible, the crossing probability \( \text{prob} \) in eqn (6.8) is assumed to have no impact parameter dependence. This in fact is incorrect, as can be seen by examining the Landau-Zener equations on page 13, and one would expect the crossing probability \( \text{prob}(1 - \text{prob}) \) for each branch to decrease exponentially with \( b \). Thus differential cross sections calculated by the program will be slightly less peaked than a correct calculation would produce. A listing of the program can be found in appendix A.2, page 234.

Although the model is very basic, with assumptions of straight line trajectories and unit crossing probabilities, the results of the model should still be reasonably meaningful. The failure of the small angle formula at small impact parameters should not lead to large errors in the calculation of the cross section ratio, as the main contribution to the total cross section comes from small angles, where the calculation is valid. For the same reason, the calculation of the DCS onset position will also be reasonably accurate. Here, the biggest error may come from the assumption that only distances of closest approach smaller than the curve crossing position contribute to the DCS. In fact, there is a finite probability that trajectories that do not reach the curve crossing may also lead to excitation, especially for the case of rotational coupling.

The range of validity of the small angle formula was checked by computing the deflection function for a Lennard-Jones potential and comparing the results with those of a fuller classical calculation given in [66]. It was found that the small angle formula is safe to just beyond the rainbow. For smaller impact parameters, the calculation clearly goes wrong, with the deflection function failing to converge to \( \pi \) radians at a zero impact parameter. In the program, extrapolation routines are used to cover the angular region that the small angle formula cannot cope with. Finally, one must be aware of the limitations of classical mechanics, and expect certain regions such as the rainbow to be inadequately described. Care was taken when using the model to prevent classical singularities appearing in the DCS from dominating the calculation of the total cross section.

**Scattering on Repulsive Surfaces**

For scattering on a Lennard-Jones potential at 700eV, the rainbow position depends on the well depth \( \epsilon \) and for the values given in Table 6.4 it in fact appears at very low angles (\( < 50 \text{ eV}^\circ \)). For paths 11 and 12, the position of the crossing R3 restricts the DCS to onset beyond this rainbow, where the DCS is relatively featureless and flat. An example of the DCS calculated for these paths is given in Figure 6.6(a). Table 6.5 shows
6.4. IMPLICATIONS OF RESULT ON THE ORIGINAL HYPOTHESIS

Table 6.5. Computed DCS onsets and cross section ratios for different paths and crossing positions, using the parameters given in table 6.4. The upper estimates for the cross section ratios set by the coincidence experiment fall in the range 2.7–14 (expt5) and 2.1–11 (expt6). The DCS have been measured to onset typically at around 100 eV°, with a steep rise at 500 eV°. (Note that for crossing positions outside the ranges given, results from the computer program could not be trusted).

<table>
<thead>
<tr>
<th>Path</th>
<th>Crossing position</th>
<th>DCS Onset</th>
<th>$\sigma_i(\theta)/\sigma_{i\text{tot}}$ (Expt 5)</th>
<th>$\sigma_i(\theta)/\sigma_{i\text{tot}}$ (Expt6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11, 12</td>
<td>2.8Å</td>
<td>327 eV°</td>
<td>3.12</td>
<td>1.78</td>
</tr>
<tr>
<td>2</td>
<td>2.6</td>
<td>851</td>
<td>3.28</td>
<td>1.87</td>
</tr>
<tr>
<td>2.4</td>
<td>2105</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.3</td>
<td>3307</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>21</td>
<td>2.8</td>
<td>0</td>
<td>3.48</td>
<td>2.56</td>
</tr>
<tr>
<td>2.6</td>
<td>74</td>
<td>3.63</td>
<td>2.67</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>326</td>
<td>3.38</td>
<td>2.48</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>2575</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>2.8</td>
<td>71</td>
<td>1.95</td>
<td>1.44</td>
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<td>41</td>
<td>2.8</td>
<td>266</td>
<td>1.95</td>
<td>1.45</td>
</tr>
<tr>
<td>2.6</td>
<td>570</td>
<td>1.96</td>
<td>1.46</td>
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</tr>
<tr>
<td>2.4</td>
<td>1250</td>
<td>1.98</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>2916</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>474</td>
<td>2.84</td>
<td>2.10</td>
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</tr>
<tr>
<td>2.4</td>
<td>978</td>
<td>3.33</td>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>2916</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>0</td>
<td>3.30</td>
<td>2.43</td>
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<td>2.5</td>
<td>5.39</td>
<td>3.62</td>
<td>2.66</td>
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</tr>
<tr>
<td>2.3</td>
<td>108</td>
<td>3.65</td>
<td>2.68</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>2.7</td>
<td>4.54</td>
<td>1.94</td>
<td>1.44</td>
</tr>
<tr>
<td>2.5</td>
<td>68</td>
<td>1.95</td>
<td>1.44</td>
<td></td>
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<tr>
<td>2.3</td>
<td>164</td>
<td>1.95</td>
<td>1.45</td>
<td></td>
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<tr>
<td>2.1</td>
<td>298</td>
<td>1.95</td>
<td>1.45</td>
<td></td>
</tr>
</tbody>
</table>

how the cross section ratio and DCS onset varies with the crossing position. We see that the cross section ratio is small, and therefore the mechanism cannot be ruled out by the upper estimates set experimentally.

The onset positions are more interesting, and we see that for R3 less than 2.7Å the DCS onsets beyond 500 eV°, and at 2.3Å, the onset has moved to beyond where our measurements were made. Experimentally, however, these processes appear at around 100 eV° and show a steep rise at 500 eV°. Given that we would expect the crossing on the repulsive surface to be well within 2.87Å (the position of the first crossing with the ground ion-pair state [43]), it is unlikely that scattering occurs solely on repulsive surfaces, and the early onsets of these processes are a powerful argument for the involvement of ionic intermediate potentials.
6.4. IMPLICATIONS OF RESULT ON THE ORIGINAL HYPOTHESIS

Figure 6.6. Typical DCS computed by the program. (a) corresponds to pure repulsive scattering. In (b), attractive forces produce a rainbow at the onset angle. In (c), the attractive forces are strong enough to pull trajectories to negative deflections, causing DCS to onset at 0°.
Scattering Over Ionic Intermediate Surfaces

When attractive potentials are involved with the key crossing still occurring on the repulsive part of the surface, two possibilities emerge. If the attractive force is strong enough, some trajectories can be pulled in to negative deflections. Scattering will be seen to onset from 0°, and a rainbow maximum will be seen at some wider angle. Beyond this rainbow, the cross section will be relatively small, corresponding to pure repulsive scattering. The second possibility is that repulsive forces are sufficiently strong over all impact parameters to prevent scattering to negative deflections. Attractive forces may still have the effect of pulling in trajectories, in which case the onset angle seen in the DCS will coincide with the rainbow. Examples of the DCS that result from these two situations are shown in Figure 6.6(c) and (b).

It was found that most of the paths considered that involve an ionic intermediate surface correspond to this latter case. Table 6.5 shows how the onset positions and cross section ratios depend on the crossing positions. In most cases we see that the cross section ratios are only just below the range of upper estimates set experimentally, which is not surprising, given the shapes of the DCS in Figure 6.6(b). Failure of the small angle formula at small impact parameters prevented the investigation of smaller crossing positions. The largest cross section ratio that was computed was for path 21, with \( R_c = 2.5 \) and \( A' = 6 \). The onset in the DCS in this case is 1737 eV°, close to where experiment 5 was run, producing a cross section ratio of 5.6. In fact it was hard to find any configurations of potential surfaces that are completely ruled out by the experimentally set upper estimate!

For the parameters given in Table 6.4, we see that for all but the smallest crossing positions considered, the early onset in the DCS is reproduced if attractive intermediate surfaces are involved. For paths 31 and 32, two attractive surfaces are involved, and the onset in the DCS is seen to occur at small angles, even for very small crossing positions \( (R_c = 2.1\text{Å}) \). A general result is that the onset position increases as \( A' \) and \( R_c \) increase, and as \( A' \) decreases. The requirement that the DCS should onset before 500 eV° does then restrict the possibilities if larger values of \( A' \) are taken for the ionic intermediate surfaces. For example, for paths 21 and 22, potentials that had a crossing at \( < 2.5\text{Å} \), with \( A' > 1.5 \) all gave onsets in the DCS greater than 500 eV°. For paths 31 and 32, the DCS onset only moves to unreasonably large angles when the upper intermediate surface is quite repulsive, e.g. for \( A' = 3.0 \), \( R_c = 2.3 \) the onset is at 830 eV°.

6.4.3 Summary

To summarise, it is found that for DCS shapes similar to that reported for K + N₂ [100], cross section ratios lie within the range of upper estimates set by the coincidence experiment. It is difficult to draw any definite conclusions from this except that a rerun of the coincidence experiment would be interesting. Problems with the small angle formula
and with classical mechanics near the rainbow angle prevented useful comparisons being made with the classical model of the collision system. The model, however, did prove useful when reanalysing the DCS recorded for these processes (the previous model used by [43] was found to contain a number of mistakes). This work supports the previous hypothesis that attractive surfaces must be involved to account for the early onsets seen.

6.5 Conclusions Drawn from the Coincidence Experiment

The reasons why these experiments failed becomes clear when experimental (best case) count rates are compared to those in the example calculation:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Example Calculation</th>
<th>Experiment 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_c$ (cs$^{-1}$)</td>
<td>$2 \times 10^{-3} \times (\sigma_t(\theta)/\sigma_{tot})$</td>
<td>$3.4 \times 10^{-3} \times (\sigma_t(\theta)/\sigma_{tot})$</td>
</tr>
<tr>
<td>$B$ (cs$^{-1}$cm$^{-1}$)</td>
<td>0.0175</td>
<td>0.0121</td>
</tr>
<tr>
<td>$\tau$ (ns)</td>
<td>$\pm 25$</td>
<td>$&gt; \pm 61$</td>
</tr>
</tbody>
</table>

The detector had obviously performed badly. The unfortunate short that occurred and the resultant peak broadening may have caused a two fold increase in the required run time (see eqn (6.3)). In fact, repeating the feasibility calculation using the experimentally estimated values above, and assuming a cross section ratio of 2 (to be consistent with upper estimate calculation), suggests that a peak 3 standard deviations high would only have been seen if the experiment had been run for 68 hours!

Otherwise, the experiment was run with count rates close to those given in the example calculation. If anything, running the beam with a smaller intensity might have helped, bringing the large background count rate closer to the coincidence rate. Gains in the coincidence count rate may have been achieved if smaller scattering angles were chosen. The DCS falls off rapidly with $\theta$, and so ideally the experiments should have been run much closer to the onset angle for these processes, thought to be around 500 eV°. Also, the formation of CH$_3$I$^+$ is reported to have a low branching ratio (0.1), so it perhaps might have been better to look for coincidences with other more abundant ions (although for these ions there may be an increase in peak broadening resulting from the fragmentation event).

To summarise then, it's clear that the apparatus had under performed for these experiments, and that a rerun may still be successful. Some time was spent trying to repeat these experiments, but the problems faced with the vacuum system and main beam eventually forced us to abandon our study.

A number of lessons were learnt from this work. Firstly, it is essential when beginning work on a new apparatus, to confirm basic aspects of the apparatus, such as the nature of the collision zone, the performance of the ion detector, or the efficiencies of the detectors. This could be by repeating previously well described simple experiments. The size of the collision zone and the possibility of multiple collisions was a problem that was never tackled properly. Ultimately, progress was hampered by the age of the apparatus, and
perhaps it was a mistake to attempt such an ambitious experiment without custom-built apparatus. For example, one of the key experimental parameters, the acceptance angle of the atom detector, could not be widened because of the inaccessibility of the slits.

One of the achievements of the work was the design and use of a 'time-focusing' ion detector. Although the time-focusing property could never be tested, a simple time-of-flight experiment showed that it could detect ions with reasonable efficiency (compared to the previous detector used in the fragment ion experiments), with flight times that could be modelled. The design could be improved by increasing the length of the extraction region, so that the geometry of the region at which there is a critical change in field gradient is known with better accuracy. Ions would then be travelling faster across this region, and so be less influenced by any imperfections in the electric fields.

6.6 Molecular Rydberg Excitation Mechanisms

What is the mechanism that governs the excitation of molecular Rydberg levels in these collisions? As we have seen, the results of the coincidence experiment shed no new light on these processes. However, this work did prompt a fresh examination of the physics of this collision system, as well as a critical look at the previous proposals [43].

The hypothesis being tested by the coincidence experiment is that molecular Rydberg levels are excited by a mechanism involving excited ionic intermediate surfaces (see page 85). The main basis for this hypothesis was the low angular onsets observed for these processes. Support came from the observation of excited molecular negative ion states, identified from structure seen in negative ion total DCS measurements. A simple Landau-Zener surface hopping model designed to test the hypothesis (using the potential scheme shown in Figure 5.3, page 84) also gave an encouraging fit to the experimental data. Finally, an abundance of positive ions was seen in these collisions, supporting the original identification of the larger K atom energy-loss processes as Rydberg excitation channels.

This earlier work however can be criticised on a number of points. A re-examination of the computer model used [43] showed that a mistake was made in their calculation of the deflection function, using the small angle formula (as described on page 118). This may have implications, for example, on our interpretation of features of the DCS for elastic scattering and K(4\textsuperscript{2}P) excitation, and more significantly molecular negative ion production. However as we saw in section 6.4, the main result, that the experimental DCS onsets can be accounted for if attractive intermediate states are involved, remains intact.

Secondly, the potential scheme shown in Figure 5.3 is perhaps misleading when considering mechanisms for Rydberg excitation. It seems unlikely that the double Rydberg ionic surfaces (e.g. curve 7) are populated directly via crossings with the ground neutral or ionic surfaces as suggested by the figure, as this would require an uncorrelated two
electron rearrangement which one would expect to be weak, in contrast to correlated two-electron (DII) processes. An initial crossing with singly excited ionic surfaces (e.g. \( K^+(3p^6) + CH_3I^-(5p^66s) \)) that are not shown in the figure might provide an alternative route: \( K + CH_3I(5p^6) \rightarrow K^+ + CH_3I^-(5p^66s) \rightarrow K^+ + CH_3I^-(5p^66s^2) \), with the final crossing occurring on the potential wall.

Thus, whether or not ionic intermediate surfaces are involved, molecular Rydberg excitation will occur through the interaction of both the potassium and atom cores, with key crossings located on the potential wall. To understand more deeply how these cores interact, one must turn to the MO correlation diagram for the system.

### 6.6.1 \( K + CH_3I \) Correlation Diagram

It is known that Xenon provides a good model for the excited states of \( CH_3I \) [9, 43, 45]. As a starting point, then, the MO correlation diagram for the K/Xe collision system was constructed by applying the Barat and Lichten rules given on page 19, and is shown in Figure 6.7. Certain K and Xe energy levels of the same values of \( m \) and \( n-l \) have changed their relative order from the slightly asymmetric case (Figure 2.7, page 19) and therefore their correlations have been swapped. The MO correlation diagram previously reported for this system [43] failed to take this rule into account, and is therefore incorrect. Note also that to be consistent with Brenot’s rule, the correlations of \( Xe(5p) \) and \( K(3p) \) have also been swapped, with the outer \( Xe(5p) \) orbitals preferentially promoted. Finally, it should be mentioned that the ordering of the UA and SA Rydberg levels given in the diagram may not be accurate, although the correlations should be correct.

As can be seen, the diagram is very complex because of the high atomic numbers involved. However, the key feature is that both the \( Xe(5p) \) and \( K(4s) \) orbitals are highly promoted, correlating to UA orbitals of Rydberg character. These orbitals undergo a series of crossings with less promoted K and Xe Rydberg orbitals. Radial or rotational coupling at these crossings would then induce transitions, providing us with a mechanism for atomic and molecular Rydberg excitation.

The different possibilities become clearer when the state correlation diagram shown in Figure 6.8 is considered. This diagram was constructed from the MO correlation diagram by considering how different electron configurations correlate between the UA and SA limits, and only the relevant states are included. At large internuclear distances, an attempt has been made to show how the potential curves might appear. The main feature of the diagram is that the entrance channels are highly promoted, correlating to a united atom with the highly excited core configuration \( 5f^7\pi^46g\sigma^2 \), and pass through at least three different regions of crossings.

The first set of crossings encountered are with the singly excited ion-pair states at large internuclear distances. Harpooning to the ground ionic surface has a relatively high probability, and provides an efficient route for the excitation of K(4p), higher excited atomic states and possibly even the \( CH_3I(A) \) states (see page 82).
Figure 6.7. Diabatic MO correlation diagram for the K + Xe collision system. The significant CH₃I orbitals are also shown, with n(1) and 2σ molecular orbitals correlating to Xe 5pσ and 5pσ respectively. — σ orbitals; - - π orbitals; ..... δ orbitals; - - - - ε orbitals.
Figure 6.8. Schematic state correlation diagram for the K + CH₃I collision system. Only the relevant states are given, and at large internuclear distances the crossings with the ionic surfaces (not predicted by the MO diagram) are also shown. The insert illustrates in more detail the first grid of crossings seen on the repulsive wall, and crossings at which DI transitions are allowed are circled. These provide a route for the excitation of molecular states containing an n(I) vacancy. The second grid of crossings are with states containing a vacancy in 2σ.
At smaller internuclear distances, the neutral or ionic entrance channels pass through at least two more sets of crossings, probably on the repulsive wall. These crossings arise because the molecular Rydberg states and doubly excited ionic states (and various other Rydberg series) correlate to united atom states with a less excited core, e.g. \(6g\sigma^15f\pi^4\). Diabatic I transitions at these crossings provide a route for the excitation of molecular Rydberg levels.

We see from the insert in Figure 6.8 that molecular Rydberg states may be populated either directly via the ground neutral entrance channel, or via the singly excited ionic surfaces. Thus the harpooning hypothesis [43] that accounts for the early onsets for these processes may still be accommodated within this scheme, assuming that harpooning to excited ionic surfaces has a significant probability. On the repulsive wall, both radial and rotational transitions are predicted, and one might expect rotational coupling to become more important at higher collision energies (see page 14). The diagram also predicts that crossings with a series of states having a \(n(I)\) core vacancy (i.e. \(6g\sigma^15f\pi^4\)) are passed before those with \(\sigma_{C-I}\) and \(\sigma_{C-H}\) core vacancies (\(6g\sigma^25f\pi^3\)). This apparently is in contradiction with the results of the positive ion production measurements, although one cannot conclude too much without knowing details of the relative positions of these crossings or the coupling potentials. Finally, in the outgoing part of the trajectory, the populations between molecular Rydberg states will become mixed at crossings with the excited ionic surfaces, and by configuration interaction.

We should of course be aware of the limitations of quasidiatomic state correlation diagrams. The molecule has shape, and at small internuclear distances we can expect the features of the potential surfaces to be highly orientationally dependent. Crossing positions and coupling potentials will also be dependent on the internal geometry of the molecule, which will change during these close collisions. However, the main feature, that the entrance channels pass through a grid of crossings at small internuclear distances that can lead to molecular Rydberg excitation, should remain intact.

To summarise, we can understand the mechanism for molecular Rydberg excitation as involving primary DI transitions at a complex grid of crossings on the repulsive surface, followed by population sharing at further crossings as the core dissociates, or possibly by configuration interaction. The entrance channel will be the ground neutral state, or the singly excited ionic surfaces if there has been harpooning at larger internuclear distances.

### 6.6.2 The Alkali–Rare-Gas Collision Systems

So far, we have discussed the possible excitation mechanisms for the K-CH\(_3\)I collision system using a quasidiatomic correlation diagram that chooses Xe as a model for the molecule, and using some additional knowledge of the potential curves for the molecular system. A comparison with the actual K-Xe collision system and other alkali–rare-gas systems is also instructive, highlighting the similarities and differences between the
6.6. MOLECULAR RYDBERG EXCITATION MECHANISMS

atomic and molecular collision systems.

Alkali–rare-gas collision systems were intensively investigated in the late 1970’s using photon emission spectroscopy and polarised photon-atom coincidence techniques. It is generally found that excitation of the resonant atomic $^2P$ state dominates by as much as 1000 times over other atomic states, at keV collision energies [6]. In the case of K-Xe, photon emission is also seen from K(5p), K(3d,6s) and K+(5p), the latter arising from two electron excitation. Varying degrees of target excitation are seen, ranging from an insignificant amount in K-He to an equal amount (compared to K(4p) excitation) in the ‘quasisymmetric’ K-Ar system. In the case of K-Xe, the only important target state exited is Xe(6p) (25% of the total emission), with little else seen except Xe+(6p), which again arises from two electron excitation. It is observed that the emission from ionic states strongly increases with energy in contrast to the neutral emission, indicating a different excitation mechanism. Figure 6.9 displays the emission cross sections for K(4p) and Xe(6s) (which is shown to be populated by cascading from Xe(6p)). A threshold is seen in both cases at around 60eV where the cross section rises steeply. This is somewhat surprising considering that the excitation energy of K(4p) is only 1.6eV, although a small but significant cross section is seen below 60eV. The cross section shape for K(4p) is seen to be rather undulatory, which is observed generally in other collision systems.

Most of the work has centred around understanding the mechanism for alkali $P$ state excitation. Two completely different approaches have been taken, one invoking the familiar quasimolecular model, and the other treating the collision as scattering of the valence electron from the rare-gas target. The first approach has similarities with our discussion of K-CH$_3$I collisions, and is discussed first.

The shape of the emission cross section suggests that two mechanisms are operating. At low energies, K(4p) excitation is mediated by the relatively well localised curve crossings involving the promotion of rare-gas electrons. These crossings occur on the repulsive wall (as predicted in Figure 6.8 for the case of K-Xe) and are only reached in low impact parameter encounters. Thus a threshold and maximum at 1keV is seen in the emission cross section, and the strong excitation of rare-gas electrons is also explained. For softer collisions, where the impact parameter is large enough so that the cores do not interact, the 4s electron can interact directly with the rare-gas atom. This mechanism accounts for the maximum seen in the cross section at large energies (20keV in the case of K-Xe), which is in approximate agreement with the Massey criterion (see page 6).

Further evidence in support of these ideas came from the DCS recorded for both potassium and sodium systems [4, 81, 161]. Figure 6.10(a) shows the DCS for Na-Ne. At 2keV, there is a well localised impact parameter threshold for excitation, indicating that only the curve crossing mechanism is important; with increasing energy, excitation gradually shows up at larger impact parameters, indicating the onset of the second mechanism. For potassium systems, the situation is more complex, with a second maximum appearing beyond the curve crossing threshold. This is again associated with the
Figure 6.9. Integral cross sections for the excitation of K(4p) (a) and Xe(6s) (b). (Taken from [6]).
Figure 6.10. Differential cross section (a) and total cross section (c) for the excitation of Na(3p) in collisions with Ne. Theoretical results are also seen in (b) and (c). (Taken from [81]).

direct excitation mechanism, and shows up as a maximum in the total cross section at 3–5 keV [5].

Figure 6.11 shows the diabatic state correlation diagram for the Na-Ne system. Calculations have been performed on both mechanisms for this system [42, 81]. The curve crossing problem is particularly difficult, due to the large number of states that are involved in the crossing region. A basis set consisting of the four most important states from the A series plus the entrance and exit channels were included in the close coupling calculation. These states were built from single configuration ‘frozen’ SCF molecular orbitals. The direct excitation mechanism was modelled instead using states built from a more appropriate set of perturbed atomic orbitals. The calculation included the 3s and 3p orbitals of both Na and Ne.

Figure 6.10(b) compares the theoretical calculations with the experimental DCS.
Good agreement is seen in the position of the threshold, although the absolute values are shown to be only semiquantitatively correct. Figure 6.10(c) also compares the theoretical calculation of the total cross section with experiment. At low energies, the agreement is good, but at high energies, the cross section is overestimated by a factor of three. These calculations are considered to give a solid foundation to the proposed models, in particular for the first mechanism. Discrepancies between theory and experiment are thought to be due to problems with the potentials at large energies, and insufficiently large basis sets. Improvements were made by using a larger basis set in the first case.

6.6.3 Comparisons with the Molecular System

It seems likely that the K-CH$_3$I collision system belongs to this general class of quasi-one electron collision systems, which all feature a grid of localised crossings on the repulsive wall. However, there are a number of important differences between the molecular system and the atomic systems. In the molecular case, a large range of collision channels are excited at quite low energies (up to 12 distinct channels were identified at 164 eV$_{cm}$), in contrast to the atomic systems, where only the first excited alkali and target P states are important. Also, the K-CH$_3$I channels onset at much lower angles (see Figure 5.4, page 86) than in the atomic case. K(4p) excitation is a good example; for a beam energy of 164 eV$_{cm}$, an onset is seen at 200 eV$^*$ in collisions with CH$_3$I, whereas for collisions with rare-gas atoms, the onset is at 5000 eV$^*$. Even in the case of molecular Rydberg excitation, excitation is definitely seen at 500 eV$^*$, even though it is not clear whether
the threshold is sharp or gradual.

The most obvious explanation for these differences is the involvement of ionic intermediate surfaces, in which attractive forces pull in trajectories to smaller angles. The case of K(4p) excitation is a well known example of the harpooning mechanism. It seems likely, also, that molecular Rydberg excitation occurs by a similar mechanism. As described earlier, this can be realised by an initial crossing to a singly excited ionic surface at large internuclear distances followed by a second crossing with the doubly excited ionic surfaces at smaller distances. This second crossing is related to the grid of crossings predicted by the state correlation diagram and is probably well localised, although its exact position cannot be predicted without knowing the potential curves for the system. Interestingly, the DCS for a number of molecular excitation channels rise steeply at around 500 eV, which also coincides with a second fall off in the elastic DCS, indicating perhaps that a second crossing region has been reached (see Figure 5.4, page 86).

The lack of involvement of ionic intermediate states in the case of atomic scattering can be understood in terms of orbital overlap. The Xe 5d, 6s, 7s orbitals are quite diffuse compared to their CH$_3$I counterparts, particularly in the case of 5d which correlates to an antibonding orbital. Thus, for the atomic system, the coupling potentials are small at crossings with the ionic surfaces, and thus the harpooning mechanism does not apply. A similar argument might also explain why so few excitation channels are populated in the case of atomic scattering. In the molecular system, crossings at the second grid are with a molecule of changed geometry with less diffuse Rydberg orbitals, and thus the coupling potential is quite strong, in contrast with the atomic system.

In atomic scattering, a direct excitation mechanism is invoked at high energies to explain the undulations in the total cross section, and the scattering seen at reduced scattering angles that are lower than the curve crossing onset. The importance of this mechanism is dependent on the excitation energy, and hence it is unlikely that molecular Rydberg levels are excited in a similar way at the low energies involved here. Thus we conclude from our analysis that molecular Rydberg excitation can be understood in terms of the quasimolecular model as occurring through localised crossings on the repulsive wall, probably with involvement of ionic intermediate surfaces.

### 6.6.4 Excitation in Quasi-One Electron Systems: An Alternative View

In alkali–rare-gas collisions, a number of results have always been difficult to explain. Firstly, the extreme dominance (by a factor of $10^3$) of the excitation of the alkali resonant $^2P$ state over other alkali states, even at keV collision energies. If the excitation is via a dense grid of states, one would instead expect comparable excitation at high energies. Secondly, to reproduce the undulations in the total cross sections, potential shapes had to be assumed in some cases, which could not be accounted for [58]. Lastly, the interpretation of the behaviour of the total cross section at low energies as a ‘threshold’
has been questioned. Experimentally, for K(4p) excitation in collisions with Xe, one observes a small but significant excitation between 10 and 60eV, followed by a sharp rise in the total cross section above 60eV. This is usually interpreted as a threshold, with two mechanisms invoked to account for the low and high energy parts. However, it is questionable whether the Massey criterion is safely satisfied at such low energies.

To interpret their extensive emission cross section data for potassium systems, Andresen et al. [6] investigated various versions of the quasimolecular model, but finally came to use a substantially different one. They considered the alkali valence electron to be carried along by the alkali core, and visualised the excitation process as a scattering process of this electron from the rare-gas target. By performing calculations in the Born approximation, they could reproduce the key features of experimental results. Their model only required the states directly involved, in contrast to molecular calculations, which require a very large expansion set.

The Born approximation is applicable whenever the electronic excitation process is fast, with a small coupling potential, as in the case discussed here. The key equations used in their calculations of excitation cross sections are

\[
\sigma_{12}(E) = \frac{A}{k^2} \int_{q_{-}(E)}^{q_{+}(E)} dq \, q |V_{eX}(q)|^2 |F_{nL'n'L'}(q)|^2
\]

(6.9)

\[
q_{\pm}(E) = \left(2\mu/k^2\right)[E^{1/2} \pm (E - \Delta E)^{1/2}]
\]

(6.10)

where \(V_{eX}(q)\) is the valence electron–rare-gas interaction potential, and \(F(q)\) is the radial form factor for the alkali atom, dependent on the overlap of the initial and final states. (\(A\) is a group of constants, including the quantum number \(L'\)). Thus, two key factors govern the shape of the cross section, the form factor which depends only on the alkali atom, and the interaction potential. Undulations in the cross section arise whenever there are zeros in the form factor. Thus, one expects to see the same number and positions of minima and maxima for different rare-gas targets. The effect of different interaction potentials will only appear in the absolute size of the cross sections. These predictions are born out experimentally, as is seen in Figure 6.12 for potassium systems, and similarly for other alkalis.

Results of theoretical calculations of the cross section are also seen in Figure 6.12. We see that the agreement with experiment is quite good. Both the 'threshold' behaviour and the undulations are well reproduced. The late rise in the cross section can thus be understood as arising from the behaviour of the form factor at low energies, rather than some curve crossing phenomenon. Calculations were also performed for the excitation of different atomic levels of Xe. It is found that K(4p) excitation dominates by at least a factor of 10 over other levels, in accord with experiment. This again results from differences in the form factor for different processes.

Quantitative agreement with experiment is not found, with the absolute size of the cross sections worsening at higher energies. The results shown in Figure 6.12 used an
interaction potential that included a polarisation term with one adjustable parameter. This gave an improvement on previous calculations, although in the case of Ne, agreement is still not good. However, bearing in mind that their calculations were performed in an ab initio manner, and that the key features of the experimental results are reproduced, their work provides a compelling alternative interpretation of excitation in alkali–rare-gas collisions in which the valence electron scatters from the target.

Is it possible that the excitation of molecular Rydberg states can also be described as an electron scattering process? Excitation would then occur for larger impact parameters without the interaction of atomic cores, and thus could also account for the scattering seen at low reduced scattering angles. It is difficult to account for the shape of the differential cross sections for these processes using the molecular model (see Figure 5.4, page 86). In all cases, a small but significant amount of excitation is seen at very low reduced scattering angles, followed in some cases by a steep rise at around 500 eV\textsubscript{cm}. Thus, it is difficult to identify exactly where the curve crossing threshold is, and to account for the scattering at very low reduced scattering angles. Reinterpreting the collision as an electron scattering process instead gives a natural explanation for this behaviour. In this model it is possible for excitation to be seen for any collision energy.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure6.12.png}
\caption{Comparison of the experimental and calculated energy dependence of K(4p) excitation in collision with Ne, Kr and Xe. The calculations were performed in the Born approximation, treating the collision process as a scattering of the electron from the rare-gas target. (Taken from [6]).}
\end{figure}
above the excitation energy (where the integration interval in eqn (6.10) becomes non-zero), and then the behaviour of the cross section will be dependent on the form factor for the process. No 'threshold' is required by the model.

Of course, one is reluctant to dismiss the quasimolecular description of the collision. Certainly K(4p) excitation is well described by the harpoon mechanism, and so it is reasonable to assume the quasimolecular model applies equally well to other scattering processes. Also, two electron processes such as the formation of doubly excited Rydberg states are harder to explain by the electron scattering mechanism. In the case of K-Xe, these processes were observed to have a completely different energy dependence, suggesting that another excitation mechanism (such as curve crossing) is operating, and Andresen et al. made no attempt to model it. However, it should be remembered that two electron processes have been seen in electron scattering from rare-gases [93].

To summarise, the excitation of molecular Rydberg levels may also be understood as an electron scattering process. Here, the electron is carried along by the alkali atom and can interact at large impact parameters directly with the target. This model gave a convincing account of scattering in K-rare-gas collisions, and perhaps can also account for scattering to small angles seen in K-CH$_3$I collisions. Relative excitation probabilities and features of the cross section are governed mainly by the form factor for the system.

6.6.5 Concluding Comments

It's clear that the K + CH$_3$I collision system is of some importance. To explain experimental data, a new class of excitation mechanism has to be hypothesised, in which Rydberg excitation is described either by some electron scattering process, or by a complex quasimolecular curve crossing mechanism involving ionic surfaces. It is apparent from these two chapters that there is a lack of experimental evidence relating to these processes. Only small portions of the DCS have been reported, with a TOF energy resolution not sufficient for identifying the upper excited states. Indirect evidence has been obtained through ion-pair and positive ion cross section measurements, but again the excited states cannot be identified with certainty, and it is difficult to link this work to the earlier work. The fragment ion-scattered atom coincidence experiment certainly would have bridged this gap, and still appears to be feasible on paper, but in practice the experiment proved to be too difficult.

What other experiments can be attempted? As we saw in chapter 4, differential cross section measurements are rich in information, and it would perhaps be worth extending these measurements to wider angles. Previously, the isotope of potassium obscured measurements beyond 1000 eV, and the use of isotopically pure alkali metals may be a way of overcoming this problem. Perhaps the best way of identifying the excited states is to look at the fate of the excited products. In the case of atomic excitation, this can easily be achieved using optical methods. For autoionising molecular
species, electron and fragment ion energy analysis would be the best choice. An electron-fragment ion coincidence experiment would allow a complete identification of the excited molecular states and their associated fragments. As we saw in chapter 4, this technique has already been applied to other molecular systems, and one exciting way our work could be continued might be a collaboration with these research groups.
7
Photon-Scattered Ion Coincidence
Apparatus

7.1 Introduction

In the following three chapters, the work performed on a more recently built crossed beam apparatus is described. As we saw in chapter 4, the coincidence technique is a powerful tool for obtaining state-specific information on inelastic collisions. The polarised photon-scattered particle coincidence experiment in particular is one of the few methods of probing excited state sublevel populations, and in the case of molecular collisions, the orientational dependence of electronic processes. The technique is difficult, requiring long data collection times, and the apparatus discussed here was built specifically for performing such experiments.

The apparatus features a low noise multi-angle ion detector that simultaneously monitors 45 different angles between -1 and 7°. The pulsed nozzle target beam, the ion beam, and the vacuum system were designed to produce high signal rates. Sufficient flexibility was built into the design to allow a wide range of collision systems to be studied. At present, rare-gas ion beams (He+, Ar+) are generated by a ‘Coultron’ plasma source, but it would be possible to interchange sources and incorporate charge exchange ovens, allowing the use of different projectile beams. Different pulsed nozzle target gases can also easily be selected. At present, the target gas is N₂, although Ar and HCl have been used previously.

Progress towards performing coincidence experiments so far has been slow. The apparatus was originally assembled between 1980 and 1986. Details of the apparatus have been well documented by Abbas [2] and Sheach [143]. So far, only optical measurements on the systems He⁺ + Ar, He⁺ + HCl, He⁺ + N₂ [143], and differential cross section measurements on the system He⁺ + Ar [2] have been performed. One attempt was made at a coincidence experiment [2] on the He⁺ + N₂ system, with inconclusive results.

My aims were to set up the apparatus to perform both time-of-flight measurements and the coincidence experiment. This work involved the installation and testing of two new ion beam pulsing units, and is described in chapters 8 and 9. Frustratingly, these experiments could not be run because of a number of problems encountered with the apparatus. It was found that the ion beam underperformed, and was unstable. Considerable effort was therefore put into improving the performance of the apparatus. The ion beam still remains a problem, but the efficiency of the ion detector has been
improved, and a new data collection system installed. (This work was undertaken partly with the help of Dr Poradzisz). The aim of these final three chapters is to detail the recent changes to the apparatus, establish the current performance of the apparatus, and to highlight the work that still has to be done. In the following sections of this chapter, the apparatus is described and details are given on the new data collection system. Finally, the performance of the ion beam and the ion detector are discussed.

7.2 Description of the Apparatus

Figure 7.1 illustrates the layout of the apparatus. The left of the diagram shows the plasma ion source, an energy analyser, and various ion optics. At the centre lies the collision zone, the photon optics, and the pulsed nozzle target source. On the right is the multi-angle ion detector. The whole apparatus is about 4 meters long, with the ion detector positioned 1.6 meters from the collision zone. Not shown in the figure is the data collection system, used for correlating the photon and scattered ion signals in the coincidence experiment. Descriptions of each component of the apparatus follow, but consult [2, 143] for further details.

7.2.1 Vacuum Pumping

The whole apparatus is grouped into 9 different aluminium walled chambers, differentially pumped by 10 oil diffusion pumps and 5 rotary pumps. One of the requirements of the coincidence experiment is that the repetition rate of the pulsed target beam is high so as to maximise the signal rates. The largest diffusion pumps are therefore positioned below the collision chamber (Edwards 1203, 12") and the nozzle chamber (Edwards 18B, 18", 6000ls⁻¹). The head of each diffusion pump is fitted with cooling vails to prevent oil from diffusing into the chambers. These vails were formerly cooled by a freon based refrigeration system, but because of problems with leaks, this has now been replaced by a recirculating water system. Liquid nitrogen cold traps, including a new one positioned over the source chamber, help most chambers maintain a good vacuum.

Typical pressures are given in Table 7.1, and range from $1-4 \times 10^{-6}$ mbar throughout the apparatus when no beams are running. The best vacuum is maintained in the steel-walled ion detector chamber ($7 \times 10^{-7}$ mbar), allowing the detector to be run with maximum efficiency. With beams running, it is found that the time-averaged pressure in the collision chamber can be allowed to rise to $4 \times 10^{-5}$ mbar whilst still maintaining single collision conditions. Finally, we note that all the diffusion pumps are fitted with thermal cutout switches, and that the water pressure circulating around the diffusion pumps is monitored, to prevent the pumps from overheating.
Figure 7.1. Schematic layout of the coincidence apparatus.
7.2 DESCRIPTION OF THE APPARATUS

<table>
<thead>
<tr>
<th>Chamber</th>
<th>Pressure (mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion source (no gas)</td>
<td>$1 \times 10^{-6}$</td>
</tr>
<tr>
<td>Ion source (gas)</td>
<td>$1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Analyser</td>
<td>$3 \times 10^{-6}$</td>
</tr>
<tr>
<td>Exchange</td>
<td>$2.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>Collision (no gas)</td>
<td>$2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Collision (gas)</td>
<td>$1.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>Ion detector</td>
<td>$7 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Table 7.1. Pressures maintained in the vacuum system.

7.2.2 Ion Beam Production

For the coincidence experiment to be feasible, it is essential to have an ion beam that is intense, reliable, and of low angular divergence. The apparatus was therefore designed to generate an ion beam with the following characteristics:

- $E = 100-1000\text{eV}$
- $\Delta E = 0.2\text{eV}$ (for resolving vibronic processes)
- Intensity at the collision zone = $1 \times 10^{-6}$ Amps
- cross section at the collision zone = $0.3 \times 10^\text{mm}$
- Angular divergence = $0.2-0.3^\circ$
- Stability over long experimental runs

Ion Source

Figure 7.2 shows in more detail the ‘Coultron’ plasma ion source, which is based on a design first reported by Menzinger in 1969 [103]. Electrons are thermionically emitted from a tungsten filament and accelerated towards the anode. Target gas flows across this region, and collisions with the electrons result in the formation of a plasma near the extraction slit. A sharp potential drop occurs near the cathode, whereas across the plasma the potential should be approximately constant. Positive ions are then extracted and accelerated using ion optics, with an energy spread determined by the thermal motion in the plasma.

Ionisation of rare-gas atoms by electron impact has for a long time been known as an efficient method for generating ions [101]. For Argon, the process onsets for electron energies of $15.8\text{eV}$, and has a maximum in the cross section at energies of $40-80\text{eV}$ [115]. In the ion source, the accelerating electrons have a spectrum of energies between the filament and the cathode. Of course, there will be other competing collision processes, the most serious of which is the formation of metastable states $\text{Ar}^+(4D, 4F, 2F, 2G)$
7.2. DESCRIPTION OF THE APPARATUS

Figure 7.2. The plasma discharge ion source. The extraction lens is positioned 2–4mm from the anode slit.

[27]. In practice, however, one expects these to form less than 1% of the total beam, and can be eliminated entirely, if the electrons have energies lower than the onset of 32eV.

The stability of the plasma depends on the target gas pressure and the filament-to-anode distance. As will be discussed later, plasma stability was found to be a problem. Typical settings for the target gas pressure, the anode voltage, the filament current and the discharge voltage can be found in Table 7.2.

The Extraction Lens

Figure 7.3 shows schematically the various ion lenses in used the apparatus. The extraction lens is designed to extract maximum current from the ion source and focus the beam as a narrow slit image on the analyser entrance. The plates $V_0$ and $V_1$ are of slit geometry, and are positioned a few millimeters from the source slit. These plates act as a Pierce gun, extracting ions from the plasma, and projecting them as a parallel beam. Plates $V_2$ and $V_3$ are cylindrically symmetric, and act as a two element aperture lens, focusing and accelerating the beam onto the analyser entrance slit. The two steering
Figure 7.3. The ion lens system. (Taken from [143].)
plates $V_{3a}$ and $V_{3p}$, used for maximising the current entering the analyser, were usually not found necessary.

Typical operating voltages are given in Table 7.2. Note that the source and extraction lenses are all floated to the beam energy, and so at the entrance to the analyser, ions have been accelerated to an energy of $V_3$.

**Energy Analyser**

The electrostatic energy analyser consists of two hemispherical plates of radii 74mm and 96mm, and is contained in a second differentially pumped chamber. The function of the analyser is to clean the beam of doubly charged species, and define the beam energy resolution. The analyser also acts as a light baffle, preventing light from the glowing source filament from being detected in the collision chamber.

The operation of the analyser is simple. Ions of correct energy at the entrance slit are bent through 90°, and refocused onto the exit slit. Ions of incorrect energy arrive off-axis, and thus the slit width defines the energy resolution. If the energy of the ions entering the analyser is $V_3$, then to transmit the ions along the centre of the analyser, the inner and outer analyser voltages should be set to

\[
V_{\text{inner}} = V_3 - V_3(1 - R_1/R_2) \quad (7.1)
\]
\[
V_{\text{outer}} = V_3 + V_3(1 - R_2/R_1)
\]

Normally, the voltage ratio between the two hemispheres is fixed, and the voltage difference $V_g$ adjusted to the desired energy:

\[
V_g = V_3(R_2/R_1 - R_1/R_2) \quad (7.2)
\]
\[
= 0.5265 \times V_3
\]

The energy resolution of the analyser is given by

\[
\frac{\delta E}{E} = \frac{S_1 + S_2}{2 \times R_0} \quad (7.3)
\]

where $S_1$ and $S_2$ are the slit widths, and $R_0$ is the mean analyser radius. Thus the energy resolution of the beam depends upon the voltage $V_3$, and for $V_3$ equal to 700V (400V), the energy resolution has been measured to be 3eV (1.5eV) Experimentally, a compromise must be sought between the desired resolution and the beam intensity.

**Ion Optics**

After energy analysis, the ion beam is shaped by four more ion lenses, before emerging as a parallel beam at the collision zone – see Figure 7.3. The first of these, $V_4$, is
7.2. DESCRIPTION OF THE APPARATUS

Table 7.2. Typical settings for the ion source and lenses. The extraction lens (V2), the analyser (Vg) and the acceleration lens (V4) operate as designed. Problems were found, however, with the other lenses. The predicted values are taken from [2], and from recent SIMION modelling (see later).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Typical Setting</th>
<th>Predicted Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source gas pressure</td>
<td>0.6 torr</td>
<td>–</td>
</tr>
<tr>
<td>Filament current</td>
<td>5–6 A</td>
<td>–</td>
</tr>
<tr>
<td>Anode voltage</td>
<td>35V</td>
<td>–</td>
</tr>
<tr>
<td>Discharge current</td>
<td>50mA</td>
<td>–</td>
</tr>
<tr>
<td>Beam Energy</td>
<td>900V</td>
<td>–</td>
</tr>
<tr>
<td>V0</td>
<td>-23V</td>
<td>–</td>
</tr>
<tr>
<td>V1</td>
<td>-100V</td>
<td>50V (≈ 2 × V0)</td>
</tr>
<tr>
<td>V2</td>
<td>-3.3kV</td>
<td>-3.1kV (≈ 3-4 × V3)</td>
</tr>
<tr>
<td>V3</td>
<td>-800V</td>
<td>–</td>
</tr>
<tr>
<td>Vg</td>
<td>-417V</td>
<td>-421V (≈ 0.5265 × BE)</td>
</tr>
<tr>
<td>V4</td>
<td>-8.2kV</td>
<td>-8.75kV (≈ 10 × V3)</td>
</tr>
<tr>
<td>V5</td>
<td>-2.0kV</td>
<td>–</td>
</tr>
<tr>
<td>V6</td>
<td>-4.6kV</td>
<td>~ -8kV</td>
</tr>
<tr>
<td>V8</td>
<td>+200V</td>
<td>~ -3kV</td>
</tr>
<tr>
<td>V9</td>
<td>+100-300V</td>
<td>+100 (≈ 0.1-0.5 × BE)</td>
</tr>
</tbody>
</table>

Table 7.2. Typical settings for the ion source and lenses. The extraction lens (V2), the analyser (Vg) and the acceleration lens (V4) operate as designed. Problems were found, however, with the other lenses. The predicted values are taken from [2], and from recent SIMION modelling (see later).

an accelerating asymmetric three element cylindrical lens (diameter 60mm), which is designed to accelerate the beam to keV energies and form an image on the differential pumping slit 3. Figure 7.4 illustrates the ion trajectories that were computed by Abbas [2] using an ion lens simulation program (SIMION, written by D.C.McGilvey, Latrobe University, Dept. of Physics and Chemistry, Australia (1977). PC/PS2 version 3.1, developed at the Idaho National Engineering Laboratory). Currently, slit 3 is set at 3mm.

The next lens, V6, is a decelerating asymmetric 3 element cylindrical lens (diameter 135mm). Both this, and the following Einzel lens V8 are designed to decelerate the beam to the beam energy, and form an image at the entrance to the slit lens V9. The transport lens V8 has elements of diameter 20mm, and can be run in either an accelerating or a decelerating mode. Figure 7.4(b) shows the trajectories predicted by SIMION. The distance between the object (at slit 3) and the image is approximately 670mm, and in this region, space is provided for a beam pulsing unit (for TOF measurements) or a charge exchange oven.

The slit lens is designed to take an image some 4mm behind the entrance, and by acting as a decelerating Einzel lens, project a parallel beam of width 0.3mm and height 10mm into the collision zone. At present, the beam width is probably larger, as the adjustable final slit width has been set at 2mm.

The predicted voltages and typically set voltages are listed in Table 7.2. The performance of these lenses will be discussed later. Here we mention that difficulty was found in using some of these lenses as designed, leading to problems with beam divergence and
Figure 7.4. Ion trajectories through the ion optics system, as computed using the SIMION program. (a) illustrates the focusing of the acceleration lens. (b) shows how $V_6$ and $V_8$ can be used to bring the beam to focus in front of the slit lens. (Taken from [2]).
7.2. DESCRIPTION OF THE APPARATUS

<table>
<thead>
<tr>
<th>Beam Monitor</th>
<th>Typical Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer analyser hemisphere</td>
<td>$1 - 2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Acceleration lens entrance slit</td>
<td>$1 - 4 \times 10^{-7}$</td>
</tr>
<tr>
<td>Final monitor (3 x 10mm, flightpath chamber)</td>
<td>$1 - 3 \times 10^{-9}$</td>
</tr>
<tr>
<td>Ion detector angular element</td>
<td>$&gt; 10^6 \text{cs}^{-1}$</td>
</tr>
</tbody>
</table>

**Table 7.3.** Typical beam intensities along the beam path.

stability. Typical currents measured along the beam path and at the ion detector are shown in Table 7.3.

### 7.2.3 The Target Beam

To ensure good time resolution and large signal rates in the coincidence experiment, the target beam is required to be narrow at the collision zone, and intense enough to cause 10% attenuation of the ion beam. It is also important that the pulsed beam is reliable and has a high repetition rate.

To achieve these requirements, a pulsed supersonic nozzle source was chosen. As Figure 7.5 shows, this consists of a nozzle unit and skimmer slits. The nozzle position is adjustable in all directions, and has an orifice of 0.1mm diameter. The skimmer slits are constructed from razor blades angled at 60° and width 0.04mm, and are positioned at least 5mm from the nozzle. A calibration of the nozzle (back/forward) stepping motor is given in Figure 7.6, and the normal target beam operating conditions are given in Table 7.4.

The nozzle can be operated with a backing pressure of 1-6 bar, usually with a repetition rate of 40Hz and pulse width of 0.9ms. Under these conditions, the gas expands supersonically towards the skimmer, with a mach number around 20 for a diatomic. A useful summary of the theory of supersonic nozzles is given by [143]. Here we mention that a considerable degree of vibrational and rotational cooling occurs in the expanded beam (with a local temperature < 4K). An intense beam emerges from the skimmer, that is highly directed and designed to have a cross section of $0.3 \times 10^{mm}$ at the collision zone.

To remove gas efficiently from the collision chamber, ensuring that the collision chamber pressure does not rise to more than $5 \times 10^{-6}$ mbar, a dump tank is employed (see Figure 7.5). This is a differentially pumped chamber with an entrance slit of width 0.6mm positioned directly opposite the nozzle skimmer. To prevent gases from leaving the chamber again after hitting the chamber walls, these slits are baffled. Contained within the dump tank is a target beam monitor, which operates as a double ionisation gauge. One side of the gauge gives a measure of the gas intensity entering the tank, with the other giving a background pressure reading. The device is used for optimising the position of the nozzle pulser and the pulse duration, in order to obtain the most intense
7.2. DESCRIPTION OF THE APPARATUS

Figure 7.5. Diagram of the nozzle (A), skimmer (B), dump tank (C) and the optics system (D). (Taken from [2]).

Calibration of the Nozzle Stepping Motor

Figure 7.6. Nozzle stepping motor calibration.
Target Beam Operating Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stagnation pressure</td>
<td>1–6 bar</td>
</tr>
<tr>
<td>Nozzle to skimmer distance</td>
<td>&gt; 5mm</td>
</tr>
<tr>
<td>Mach number</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>Target temperature</td>
<td>&lt; 4K</td>
</tr>
<tr>
<td>Pulse rate</td>
<td>20 – 40Hz</td>
</tr>
<tr>
<td>Target pulse width</td>
<td>0.9 – 1.1ms</td>
</tr>
<tr>
<td>Signal pulse delay</td>
<td>1.6ms</td>
</tr>
<tr>
<td>Noise pulse delay</td>
<td>25ms</td>
</tr>
<tr>
<td>Collision chamber pressure</td>
<td>$1-4 \times 10^{-6}$ mbar</td>
</tr>
</tbody>
</table>

Table 7.4.

and well-defined beam possible.

7.2.4 Optical Detection System

Optics are installed in the apparatus to detect fluorescence of wavelength 200–800nm emitted from collisionally excited species in the collision zone. The system consists of three components, an optics cone and slit, a holographic diffraction grating, and an imaging photon detector (IPD) – see Figure 7.5.

The optics cone allows only light emitted from the collision zone to be seen by the grating. Slits at the end of the cone had to be removed to allow a beam blanking device (described in chapter 9) to be accommodated. The cone entrance now has dimensions 5×10mm, positioned 3–5mm from the collision zone with an offset orientation. The solid angle subtended by the optics is thus approximately 1.5 steradians.

The diffraction grating collects the light from the collision zone (or slit) and disperses it according to wavelength towards the IPD. The whole grating can be rotated to select the desired wavelength. Characteristics of the grating are given in Table 7.5. The grating has the capability of resolving lines up to 0.002nm apart. In this apparatus, however, this is not achieved (nor desirable), as the total resolution also depends on the size of the emitting collision zone, and the dimensions of the focused image. The resolution achieved in practice is about 0.5nm. The efficiency of the grating varies with wavelength, and is expected to be around 30–50%. Finally, we note that the signal-to-noise ratio of light dispersed by a holographic grating is much better than that for conventional grooved gratings. Holographic gratings are manufactured by a highly accurate lithographic-type approach, and so the random flaws that cause ghosting and stray light scatter in conventional gratings are avoided.

The diffracted light is detected by the imaging photon detector, which has a photocathode head of 18mm diameter. Electrons are ejected from the photocathode, amplified by a series of stacked channel plates, and focused onto a resistive anode. The gain achieved is of the order of $10^7$. Four discrete collectors on the anode record both the XY
Properties of the Holographic Grating

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>lines per mm</td>
<td>1484</td>
</tr>
<tr>
<td>Dispersion (nm/mm)</td>
<td>2.2</td>
</tr>
<tr>
<td>Diameter of ruled area</td>
<td>145mm</td>
</tr>
<tr>
<td>Aperture</td>
<td>f/2</td>
</tr>
<tr>
<td>Coating</td>
<td>Al + MgF₂</td>
</tr>
<tr>
<td>Spectral range</td>
<td>200–800nm</td>
</tr>
<tr>
<td>Absolute efficiency</td>
<td>25%</td>
</tr>
<tr>
<td>Relative efficiency</td>
<td>32%</td>
</tr>
</tbody>
</table>

Table 7.5.

Diffraction Grating Calibration

Figure 7.7. Calibration of the diffraction grating. Both zinc-cadmium and sodium lamps were used for this measurement, and the identity of the observed lines are given in the figure.
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Figure 7.8. Outline of the ion detector, showing a vertical section along the direction of the scattered ions. Details of the field shimming plates are shown in the insert. Type B has superior performance, and is used throughout.

coordinates of the signal and the time of arrival. For the purposes of the coincidence experiment, the electronics were modified to improve the response time of the IPD from 80ns to 20ns. Two signals are generated – one for recording the detection time, and the other containing the encoded XY information. The latter is decoded using an interface unit, and the two signals correlated using the coincidence technique.

Finally, we mention that the whole optics can be conveniently calibrated by shining light from a sodium or zinc-cadmium lamp from a port in the analyser chamber onto a nylon line suspended at the collision zone. Figure 7.7 gives a calibration of the diffraction grating.

7.2.5 The Scattered Ion Detector

For the coincidence experiment, an efficient detector is required that has a fast response time. In this apparatus, a sophisticated multi-angle detector is employed, that monitors simultaneously 45 angles between -0.9° to 7.0° with a resolution of 0.07°. The detector
7.2. DESCRIPTION OF THE APPARATUS

is of a Daley-type [46], and because a binary coincidence technique is used, the detector has a high signal-to-noise ratio. The performance of the detector is discussed in a later section, and a recent paper details the design [1]. Here we describe the principle of operation.

Before entering the detector, scattered ions pass through two sets of ion lenses (see Figure 7.3). The first of these is a rectangular lens \(V_{10}\) that is used for focusing ions in the vertical plane to increase (2 to 4 times) the solid angle subtended by the detector \((5.4 \times 10^{-6}\) steradians, defined by a 4mm differential slit, 1215mm from the collision zone). The second lens, \(V_{11}\), then focuses the ions onto the entrance of the detector.

Figure 7.8 illustrates the detector. Ions are accelerated by a Pierce gun to 50kV, and deflected by a strong vertical electric field onto an aluminium coated strip. The area of impact is positioned precisely 1671(±5)mm from the collision zone. At least 10 secondary electrons are ejected at 50kV [43], which are accelerated and focused (after steering corrections) onto an array of 45 scintillator elements.

Each scintillator element is 2mm in diameter, separated by 5mm, and produces 250 photons per electron (at 50kV). Y-shaped fibre optics connect each element to two photomultipliers. When an electron burst occurs at some specific element, simultaneous signals are produced in the two photomultipliers, which can be observed by correlating the signals in a coincidence unit. A total of ten photomultipliers are used to encode the 45 different scintillator elements. The great advantage of this binary coincidence technique is that all uncorrelated noise produced by the photomultiplier dark counts and the background light is eliminated from the signal. One expects the total detection efficiency to be high, and Abbas et al. [1] report that efficiencies as high as 90% can be achieved. The biggest losses in signal occur at the fibre optics couplings.

7.2.6 Data Collection System

A new data collection system has been installed into the apparatus, which at present can process data from both the time-of-flight and coincidence experiments. The main change from the former system has been to replace the elderly PS11 computer by an IBM ps/2, fitted with a high speed 32 bit parallel digital I/O interface (MC-DIO-32F expansion board, manufactured by National Instruments). Memory space is larger than our former system, and much faster signal rates can be processed (up to 300K 16 bit words/sec). Thus, the experiment run time is not restricted by the speed of data processing, as it was formerly. Computer programs were written by Dr Fluenedy to handle the data analysis, and are reported in more detail in chapters 8 and 9.

Figure 7.9 illustrates how data from the photon and ion detectors is processed and correlated in the coincidence experiment. Two signals are produced by the photon detector – a fast (discriminated) nim pulse for timing purposes and a slower signal containing the wavelength information. These pulses are correlated again by an interface unit. If successful, then an ‘accepted’ pulse is generated (about 1.4\(\mu\)s after the fast
Figure 7.9. Timing arrangements for data collection in the coincidence experiment.
photons), and the wavelength information is processed. Note that for the duration that the photon pulses are being correlated, the photon detector is switched off by the "inhibit" pulse.

For the coincidence measurement, START and STOP pulses are required. The accept pulse produced by the interface is too broad for the measurement, and so a fast photon pulse is used as a START pulse, after being gated by the 'accepted' pulse. Delays T2 and T3 are set to ensure proper gating, and to position coincidence peaks within the time window. Outputs from the 10 ion detector photomultipliers are passed through discriminators, correlated to recover the signals at each angle, and the outputs sent to the interface. These are used as STOP pulses.

The interface unit records the correlations between START and STOP pulses at each angle, and sends the information to the computer in the form of a 32 bit word. 16 bits contain information about the photon wavelength, and the other 16 bits encode the angle, the coincidence time and the signal or noise flag (the whole system is gated by the signal and noise pulses set by the target beam pulsing box). To speed up the data processing, a large buffer (temporary memory space) is used. While the buffer fills, the data is simultaneously processed by the programs and stored in the computer memory. At selected time intervals, a permanent record of the results is stored on computer disc (halting the data collection).

Note that in Figure 7.9, a fast photon pulse is also sent through a delay to the coincidence blanker. This device consists of a pair of deflection plates positioned after the collision zone, and can be used to improve the signal-to-noise ratio in the coincidence experiment — see later, chapter 9. The timing arrangement for the time-of-flight experiment is similar to Figure 7.9. The photon detector is not used, and the delayed TOF START pulses are instead sent directly to the interface unit. A computer program is used to analyse only 16 bits of the 32 bit word. The performance of the data collection system is discussed in chapters 8 and 9.

7.3 Performance of the Ion Beam

The angular-resolved coincidence experiment places stringent requirements on the ion beam. It should have a well-defined geometry with a low angular divergence, as well as being intense and stable over many hours (see page 141). As has been mentioned, with the design outlined in the last section these requirements are not achieved. Typically, one finds that the beam is unstable, requiring frequent retuning of the energy analyser. Investigations using deflection plates also showed that the angular divergence of the beam is larger than designed, and occasionally the beam was observed to swing.

Why does the beam perform so badly in this apparatus? Several causes can be identified:

- Charging up of any oil that is coating slits and lenses can distort lens field gradients,
causing poor focusing and beam swinging.

- Misalignments of the ion optics.
- Instabilities in the plasma. Any movement of the plasma has the effect of switching the beam on and off after energy analysis.
- Faults in the design of the ion optics. Problems were found in getting the extraction lens system and the final combination of lenses ($V_6, V_8, V_9$) to perform as designed.

Oil escaping into vacuum chambers is frequently a problem when oil diffusion pumps are used, especially when large pressure fluctuations occur. In this apparatus, water-cooled baffles (attached to all diffusion pumps) and cold traps help to prevent oil from reaching the chambers. Nevertheless, the ion optics still frequently required cleaning. Some of the ion optics chambers currently do not employ cold traps, and it would be sensible to install traps. This has already been done for the source chamber, at an inexpensive cost.

Misalignments in the ion optics can also lead to beam instabilities and bad focusing. Bed bars running through the ion optics and source chambers ensure that the majority of lenses (the extraction, acceleration and deceleration lenses) are aligned precisely. The other lenses and the ion source were aligned by shining a He-Ne laser through windows in the analyser along the beam lines. The analyser in particular was found to be incorrectly positioned. For correct focusing, the slits have to be positioned so that the relationship

$$R^2 = l_0 \times l_1$$

is satisfied (where $R$ is the mean radius of the hemispheres, and $l_0$ and $l_1$ are the distances from the analyser slits to the centre of the hemispheres). This involved moving the source chamber some 5mm back from the analyser! Thus, the alignment of the ion optics was thoroughly checked, and cannot account for our problems with beam stability.

The other two problems listed above are more difficult to solve, and suggest a redesigning of the ion source and ion optics. In the following sections, the work that was done that leads us to this conclusion is described.

### 7.3.1 Performance of the Plasma Ion Source

In the original paper describing the ion source, Menzinger et al. [103] reported that stable beams of intensity $1 \times 10^{-6}$ A at 200eV energy could be obtained, with an energy spread of 0.11eV. This energy spread is limited only by the thermal motion of the ions, as the plasma is localised at the anode in a region of near constant potential. They were able to focus the beam down to a spot of diameter 1mm, 40cm away from the ion source, which is close to the space-charge limit. They reported also that a larger version of the
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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Menzinger et al.</th>
<th>Us</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode voltage</td>
<td>30–70V</td>
<td>30–50V</td>
</tr>
<tr>
<td>Filament current</td>
<td>6–6.5A</td>
<td>6A</td>
</tr>
<tr>
<td>Source Pressure</td>
<td>(\sim 10^{-3}) torr</td>
<td>0.1–0.9 torr</td>
</tr>
<tr>
<td>Discharge Current</td>
<td>100–200mA</td>
<td>40–100mA</td>
</tr>
<tr>
<td>Filament-anode distance</td>
<td>3–4mm</td>
<td>1–3mm</td>
</tr>
<tr>
<td>Anode-extraction lens distance</td>
<td>(\sim 7)mm</td>
<td>2–4mm</td>
</tr>
<tr>
<td>Geometry of aperture</td>
<td>circular</td>
<td>slit</td>
</tr>
<tr>
<td>Beam Current</td>
<td>(1 \times 10^{-6})A</td>
<td>0.5–2 \times 10^{-6})A</td>
</tr>
<tr>
<td>Energy spread</td>
<td>0.1eV</td>
<td>several eV</td>
</tr>
</tbody>
</table>

Table 7.6. Table comparing the performance of our ion source to the original design reported by [103].

source was successfully employed in a Coultron, generating precision beams of 0.2mA intensity at 25kV energies.

In our apparatus, a source of identical dimensions is used. The main differences are that an extraction slit of dimensions 10 \(\times\) 0.25mm is used rather than an aperture of 0.3mm diameter. Consequently, our filament design is different from the tapered spiral shape used by [103]. Also, in our design, an extraction lens comprising of 4 elements, rather than a 3 element (decelerating) cylindrical lens, is used. In Table 7.6, a comparison is made between the operating conditions of our source and the original design.

Although intensities compare favourably before energy analysis, we find that after energy analysis, the beam is often unstable and very sensitive to the source conditions. The cause of this is most probably instabilities in the plasma. When the source is run at low gas pressures in an electron-impact mode (i.e. without forming a plasma), very stable currents (100 times less intense) are observed after energy analysis. Thus, the beam instabilities are unlikely to be caused by the charging of surfaces, and can only be attributed to instabilities in the plasma. The energy spread of the beam can been measured using a time-of-flight pulsing technique (see later, chapter 8). Typically the energy spread is found to be several eV (for 900eV beams), much larger than the 0.11eV reported by [103]. This supports the conclusion that the plasma is not localised and stable near the anode. If ions are extracted from different regions between the filament and anode, there will be a spectrum of different energies at the analyser. Changes in the mean energy of the extracted ions will be seen as instabilities in the beam intensity after energy analysis.

The shape, position and age of the filament, the filament current, the gas pressure and the anode voltage are all factors that affect the stability of the plasma. Although on several occasions stable and intense beams have been seen, no successful combination of parameters were found that were repeatable, except that low discharge currents seemed to be preferred. Different filament shapes were experimented with; at present, a spiraled design is used, with the spirals aligned with the slit. The filament is normally positioned
approximately 1–3mm from the extraction slit. Alumina sleeves and a ring allow only a small portion of the anode to be ‘seen’ by the plasma, which helps to localise and stabilise the plasma. After long use of the filament, the inside of the alumina becomes coated with conducting material which probably affects the plasma stability, and certainly new filaments performed better. Running the source with and without the alumina ring was experimented with, but no definite preferences were seen. A wire mesh was installed close the anode slit, in an attempt to set up a region of uniform potential and stabilise the plasma. Again, it was difficult to see any improvement, and certainly the energy spread in the beam remained the same.

The extraction field also has an influence on the plasma. Normally, the first two elements of the extraction lens form a Pierce gun of slit symmetry. Recently, these two elements have been replaced by lenses of cylindrical symmetry, which gave slight improvement. Improvements may also be seen if the anode extraction slit is replaced by an aperture. Our source could then be set up to be identical to the original design, with the filament shape and position precisely copied. Also, it is possible that symmetry is an important factor, and a cylindrically symmetric electron flux and electric field within the anode cup may help the plasma to stabilise. There is a case anyway for having the same symmetry throughout the ion optics, as we shall see later.

A survey of the literature shows that in fact this design of source has been a very popular choice! The design is very simple, requiring no magnetic fields, and when used correctly it delivers strong currents of low energy spreads. Moreover, a wide range of gaseous and solid source materials has been used as a source including the rare-gases, Be, Cd, C, O, CO, N₂, H, and recently Zn (see for example [3, 17, 39, 76, 85, 121]). The source is commercially available, manufactured by Coultron Inc. The best approach in this laboratory is therefore to pursue using the design. Improvements can be made by changing from a slit to a circular aperture (of diameter 0.3–0.5mm) on the anode plate. Screening of the anode using alumina is important for localising the plasma, and positioning the filament further back from the anode (to 5mm) could be experimented with. Also, the filament shape reported by [103] should be used.

7.3.2 Performance of the Extraction Lens

The extraction lens comprises of four elements (see Figure 7.3). The first two elements \(V₀\) and \(V₁\) are designed to act as a Pierce gun, extracting ions from the anode slit, and projecting a parallel beam. The last two elements \(V₂\) and \(V₃\) then accelerate and focus the beam onto the entrance slits of the analyser. Experimentally, it is found that \(V₀\) and \(V₁\) show little focusing preferences, although for \(V₂\) focusing solutions can be found. Table 7.7 lists the experimentally determined values of \(V₀\), \(V₁\) and \(V₂\) for a range of \(V₃\) that produce a sharp focus at slit S3.

The lens system was modelled using the SIMION simulation program. Two possibilities were considered as illustrated in Figure 7.10. In the first, the object for the \(V₂\)
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<table>
<thead>
<tr>
<th>$V_3$</th>
<th>$V_2$</th>
<th>$V_1$</th>
<th>$V_4$</th>
<th>$V_5$</th>
<th>Predicted $V_3$</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>-800</td>
<td>-3.1kV</td>
<td>-100V</td>
<td>-7.5kV</td>
<td>417V</td>
<td>-792V</td>
<td>$3 \times 10^{-7}$A</td>
</tr>
<tr>
<td>-700</td>
<td>-2.6kV</td>
<td>-80V</td>
<td>-6.6</td>
<td>369</td>
<td>-701</td>
<td>$1 \times 10^{-7}$</td>
</tr>
<tr>
<td>-600</td>
<td>-2.4</td>
<td>-86</td>
<td>-5.2</td>
<td>321</td>
<td>-610</td>
<td>$1 \times 10^{-7}$</td>
</tr>
<tr>
<td>-500</td>
<td>-2.2</td>
<td>-87</td>
<td>-4.1</td>
<td>269</td>
<td>-511</td>
<td>$0.3 \times 10^{-7}$</td>
</tr>
<tr>
<td>-400</td>
<td>-1.9</td>
<td>-87</td>
<td>-3.1</td>
<td>215</td>
<td>-408</td>
<td>$0.15 \times 10^{-7}$</td>
</tr>
<tr>
<td>-300</td>
<td>-1.5</td>
<td>-74</td>
<td>-2.1</td>
<td>162</td>
<td>-308</td>
<td>$0.05 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Table 7.7. Table giving for different $V_3$ the values of $V_1$, $V_2$ and $V_4$ that lead to sharp focusing at the entrance of the analyser and at slit 3. For these measurements, $V_0$ was set to -30V and $V_5$ to -2.5kV. Note that voltages $V_0$, $V_1$, $V_2$ and $V_3$ are given with respect to the beam energy of 900V.

Thus, we conclude that the extraction lens does not perform as designed. Also, the change in symmetry from rectangular to cylindrical in this lens system is probably not a good idea. Ions emerge from slit $V_1$ with a range of positions off the central beam axis, and so the beam can never be brought to a tight focus. Those ions straying off the beam axis will cause spherical aberrations in the focusing of the subsequent lenses. Changing the geometry of the source aperture to a circle would allow a consistent symmetry to be used throughout the lens system, and sharp focusing could then be achieved. Also, changing the extraction lens from a four element design to a simple three element lens would be an improvement. It was noted in the literature survey that the most common extraction lens used consisted of three elements. In the original paper describing the Coultron ion source, Menzinger et al. also used a three element cylindrical lens system.

7.3.3 The Analyser and Lens $V_4$

As well as instability, problems were experienced in obtaining sufficient intensity at the collision zone, and maintaining a low angular divergence. Measurements using a probe placed at the exit of the slit lens ($V_9$) suggest that the beam intensity is $0.5 - 1 \times 10^{-7}$amps (for a 900eV beam), over 10 times smaller than that required in the design specifications (see page 141). Beam divergence is a more serious problem in angular-resolved experiments. Measurements using deflection plates suggest that the full-width-half-maximum (FWHM) angular divergence of the beam is $0.25^\circ$. This is worse than the design requirement of $0.2-0.3^\circ$, for the full beam intensity. To tackle these problems, the performance of the analyser and ion optics was investigated.

The focusing properties of the energy analyser and the acceleration lens $V_4$ were checked by placing a copper wire (diameter 2mm) in front of slit 3 (see Figure 7.3). The
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Figure 7.10. Operation of the extraction lens $V_0$ and $V_1$. The lens is designed to operate as shown in (A). Experimentally, the alternative solution (B) is preferred.

Performance of $V_2$ Lens

Figure 7.11. Performance of the $V_2$ lens. The SIMION results were obtained by modelling the second possibility in Figure 7.10 and assuming $V_1$ is fixed at -100V. The experimental results are taken from Table 7.7.
Table 7.8. SIMION model results for the voltages required to bring the beam to a focus at the slit lens entrance, and then to project a parallel beam (of energy 900eV). Alternative \( V_9 \) values are 0.1-0.2\( \times \) BE (from the Harting and Read tables [77]).

The analyser should be focused when the voltage difference between the hemispheres is set at \( 0.5265 \times V_3 \) (see eqn (7.2)). As Figure 7.12 shows, the experimental values do follow this relationship. A slight offset is seen between the chosen energy of the beam \( (V_3) \) and that measured by the analyser. This is partly accounted for by inaccuracies in setting \( V_3 \). Also, the actual beam energy will always be slightly larger than the voltage difference between the source anode and the analyser (or ground potential), because ions have kinetic energy as they emerge from the extraction slit. In an experiment, therefore, care must be taken to measure the actual beam energy using the analyser, rather than relying on the voltage settings.

To check the performance of the acceleration lens \( (V_4) \), a SIMION simulation was run, and results are compared with the experimental values in Figure 7.13. The agreement is good.

Also shown in Table 7.7 is the current measured at slit 3. As expected, the current decreases as \( V_3 \) is lowered. Thus, the selection of the energy spread in the beam must be balanced against the final beam intensity required at the collision zone.

### 7.3.4 \( V_6, V_8 \) and \( V_9 \) Lenses

The focusing of the final set of lenses \( V_6, V_8 \) and \( V_9 \) have the greatest influence on the final beam divergence. The lenses can operate together in several different ways:

- \( V_6 \) can bring the beam to a focus just before the \( V_8 \) lens. \( V_8 \) then takes this object and forms an image at the slit lens \( (V_9) \) entrance.

- \( V_6 \) can project a converging beam into the \( V_8 \) lens, which then focuses the beam at the slit lens entrance.

- \( V_6 \) can project a near parallel beam through the apparatus, with \( V_8 \) and \( V_9 \) slightly modifying the angular divergence.

The lens system was modelled using SIMION, for the second case given above. Three solutions are given in Table 7.8. For values of \( V_6 \) larger that -10kV, the beam is converging too fast as it enters \( V_8 \) for the image to be positioned close to the slit lens.
Figure 7.12. Performance of the analyser. A slight offset is seen in the experimental values, corresponding to beam energies possibly up to 10eV higher than the set voltage.

Figure 7.13. Performance of the V₄ lens system. Experimental data is taken from Table 7.7. Both the experimental and SIMION values are given for V₅ = -2.5kV and BE = 900V.
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Performance of $V_6$, $V_8$ and $V_9$ Lenses

Experimentally, it is found that the values of both $V_6$ and $V_8$ do influence each other and show weak focusing behaviour as expected. However, no focusing solutions could be found for $V_6$, $V_8$ and $V_9$ that were close to those predicted by SIMION or the Harting and Read tables [2]. Furthermore, it is found that $V_9$ shows little or no focusing effect on the beam intensity. The most favoured solutions of $V_6$ that give large beam intensities seem to be voltages that project a parallel beam from the object slit at $V_5$ (i.e. about half the value predicted by SIMION – see Table 7.2, page 145). $V_8$ and $V_9$ then act by fine tuning the angular divergence of the beam, and show little effect on the intensity of the monitored beam. Why has it been found difficult to focus the beam as designed, using lenses $V_6$, $V_8$ and $V_9$? One reason might be that poor focusing prior to these lenses, particularly at the entrance of the analyser, prevents effective focusing at $V_9$.

The angular divergence of the beam was checked using the ion detector, and using deflection plates. In addition, a coating of fluorescent material was placed next to the final beam monitor in the flightpath chamber, and a small glass window installed into the wall of the chamber. This allowed us to see the beam profile when intensities were large. As mentioned earlier, when the beam is well focused, the angular divergence is $0.25^\circ$ (FWHM), larger than that specified in the design requirements. However, the angular divergence of the beam and consequently the signal-to-noise ratio of scattered ions is very sensitive to small changes in $V_6$, $V_8$, $V_9$, and on several occasions, the beam was observed to swing. Thus, in an angular-resolved time-of-flight or coincidence experiment, data collection would have to be halted every time the beam required tuning.

Other problems were experienced with the ion lenses. It was found that when using the time-of-flight compressor lens (described in chapter 8), compressed beam pulse widths were also sensitive to the focusing conditions of $V_4$ and $V_6$. This is because the compressor lens is positioned next to the $V_6$ lens system, where the beam is still converging. It is possible that the field lines of the $V_6$ distort those of the compressor, although a wire mesh was installed at the entrance of the compressor to prevent this.

Alternative Lens Designs

The bad experimental performance of the $V_6$, $V_8$, and $V_9$ lens system and the problems experienced with beam divergence, beam swinging and the time-of-flight pulsing suggest that the lens system should be redesigned. If a charge exchange oven was installed in the apparatus in place of the compressor, the lens system would have to be redesigned anyway. The oven would have entrance and exit slits, and thus the beam would have to be parallel as it enters the oven, rather than converging as it is now.

What are the options? No work has been done to design alternative ion optics for this apparatus, although here we offer some ideas. The best way of ensuring that the beam has an angular divergence of $< 0.2^\circ$ and does not swing is to use a combination
7.3. PERFORMANCE OF THE ION BEAM

Figure 7.14. Alternative lens designs that could replace V₄, V₆, V₈ and V₉ in the
current apparatus. (a) One lens projects a parallel beam through two collimating slits.
The TOF compressor and/or a charge exchange oven could be placed between these slits.
(b) Two lenses are used, the first forming a demagnified image in front of the second.
Again, two slits collimate the beam to ensure low angular divergence.

Lenses are required to accelerate/decelerate the ions emerging from the analyser slits,
and project a parallel beam onto the collimating slits. The simplest design is to use only
one lens positioned after the analyser to project a parallel beam, as shown in Figure
7.14(a). The only problem here is that the geometrical cross section of the beam might
be too large, causing losses in intensity after collimation. A more sophisticated design
would use two lenses. The first would form a demagnified image of the beam emerging
from the analyser. The second would then take this image, and project a parallel beam
of smaller cross section onto the collimating apertures – see Figure 7.14(b).

Finally, we mention that when designing ion optics, one must be aware of the limita-
tions on what can be achieved. The brightness to energy ratio is a conserved property
in ion optics:

$$\frac{\beta_1}{E_1} = \frac{\beta_2}{E_2}$$  

(7.5)
Here, the brightness $\beta$ of a luminous object (usually an aperture) is defined as being the differential current $dI$, which passes through an incremental area $dA$ and shines into solid angle $d\Omega$:

$$\beta = \frac{dI}{dAd\Omega} \quad (7.6)$$

Thus, the maximum current that can be expected along different sections of the optics depends upon the geometry and energy of the beam, and the original brightness of the source. Also, the space-charge limit, arising from the mutual repulsion of ions in the beam, places a limit on how tightly a beam of given current can be focused [108, 124]. This limit is not normally reached, though, as geometric aberrations (resulting from deviations from the paraxial assumption) and chromatic aberrations (resulting from the energy spread in the beam) also restrict the size to which the beam can be focused.

### 7.4 Performance of the Ion Detector

The ion detector has already been reported in detail by Abbas et al. [1] and Campbell [34]. It is designed to monitor 45 angles simultaneously, and uses a binary coincidence technique to ensure high signal-to-noise ratios. In this section we describe recent tests of the detector performance. The focusing properties of the various lenses used in the detector were measured, and checks were made of the sensitivity of each angular element. Firstly, however, changes to the geometry of the detector are described.

#### 7.4.1 Detector Geometry

One of the key experimental parameters in any angular-resolved experiment is the distance from the collision zone to the detector and the scattering angle. Inspection of the detector revealed that it had previously been positioned badly – only the angular range 4.0–8.1° was covered, with 'shadows' occurring over 18 channels, caused by the edge of the nozzle chamber (8.1°) and an incorrectly designed flange (4°). It was thus necessary to reposition the detector chamber and replace the flange to make full use of the 45 detector elements. Careful measurements were also made of the flightpath length.

Figure 7.15 illustrates the new positioning of the detector chamber. The flange B at the entrance of the detector chamber contains a differential pumping slit of height 4mm. This flange is connected by flexible bellows to flange A at the end of the flightpath region, and as illustrated these flanges are arranged so that the central axis is aligned parallel with the beam axis. With this arrangement, the detector covers an angular range of -0.98° to 7.04°. At present, a beam stopper has been positioned on the edge of flange A. This is to prevent the main beam from swamping individual angular elements with signal, which caused problems with the data collection system. It also proved to be a convenient place to position the final beam monitor. A shadow is cast over 8 of
the angular elements, and the remaining 37 elements cover an angular range of 0.91°
to 7.04°. Table 7.9 lists the encoded name and the angular position of each scintillator
element. As each scintillator has a circular cross section of diameter 2mm, the angular
resolution of each element is 0.07°, and the solid angle subtended is 5.4 × 10⁻⁶ steradians.

The flightpath length at different stages between the collision zone and the aluminium
strip in the detector is shown in the figure. These measurements were made simply using
a length of flexible thin wire, and the accumulated measurement uncertainty is about
±5mm. A computer program was written that calculates the flight times of ions from
the TOF pulsing lens to the detector. As we shall see in the next chapter, the program
correctly predicts experimentally measured flight times to the detector to within ±150ns,
confirming that the flightpath length was correctly measured to within ±14mm.

7.4.2 Detector Focusing

In the coincidence experiment, it is important to maximise the signal rates in both
detectors. The ion detector high voltage, the ion and electron lenses $V_{10}$, $V_{11}$ and the
electron focus (see Figure 7.8) are powered by separate supplies and thus their effect
on the ion signal rate could easily be investigated. Focusing of the Pierce gun and the
effect of electron steering was not checked. These plates are set internally to be 0, 10%,
and 50% of $V_{HV}$ for the 3 Pierce gun plates, and ground for the steering plates.

Figure 7.16(a) shows the effect of varying $V_{HV}$ on the ion signal for a 900eV beam.
### Table 7.9. Angular position of each of the 48 angular elements. Ten photomultipliers encode 45 of these elements, and the encoded names are given. (x) indicates which elements are not working. (S) indicates which elements are in shadow.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>AB</td>
<td>7.04°</td>
<td>25</td>
<td>DE</td>
<td>(x) 2.96</td>
</tr>
<tr>
<td>2</td>
<td>AC</td>
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<td>DF</td>
<td>2.79</td>
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<tr>
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<td>AD</td>
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<td>27</td>
<td>DG</td>
<td>2.62</td>
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<td>AE</td>
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<td>DI</td>
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<tr>
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<td>6.37</td>
<td>29</td>
<td>DH</td>
<td>2.28</td>
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<td>AG</td>
<td>6.20</td>
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<td>DL</td>
<td>2.11</td>
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</tr>
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<td>AI</td>
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<td>EG</td>
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<tr>
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<td>FH</td>
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<td>FL</td>
<td>(S) 0.54</td>
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<td>GH</td>
<td>(S) 0.39</td>
</tr>
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<td>41</td>
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</tr>
<tr>
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<td>GL</td>
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</tr>
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<td>CE</td>
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<td>HI</td>
<td>(S) -0.12</td>
</tr>
<tr>
<td>20</td>
<td>CF</td>
<td>3.82</td>
<td>44</td>
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</tr>
<tr>
<td>21</td>
<td>CG</td>
<td>3.65</td>
<td>45</td>
<td>IL</td>
<td>(S) -0.46</td>
</tr>
<tr>
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<td>CH</td>
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<td>(S)  -0.63</td>
<td></td>
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<tr>
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<td>(S)  -0.81</td>
<td></td>
</tr>
<tr>
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<td>CL</td>
<td>3.13</td>
<td>48</td>
<td>(S)  -0.98</td>
<td></td>
</tr>
</tbody>
</table>
7.4. PERFORMANCE OF THE ION DETECTOR

(a) Detector HV v's Ion Counts

(b) Electron Focus v's Ion Counts

Figure 7.16. Effect on the signal rates of varying (a) $V_{HV}$ and (b) the electron focus lens.
Count rates begin to level off above 55kV, although contrary to Abbas et al. [1] no plateau region is seen above 50kV. A 2 times gain in signal is seen when increasing the voltage from 50kV to 60kV. At present, electrical arcing outside the chamber, particularly on humid days, places an upper limit on the voltage that can be set.

The focusing effect of the electron lens is shown in Figure 7.16(b). Voltages of 40–50% of $V_{HV}$ are required to focus electrons emitted from the aluminium surface onto the scintillator strip, which is in good agreement with the Harting and Read tables [77] and with Abbas et al.. We see that the focusing is sharp, and gains of 2 times can be made to the signal rates. The effect of the electron steering plates was not checked here, although Abbas et al. demonstrate that steering is sharp, with approximately a 20% gain in signal if a voltage difference of 2–3kV is applied.

The performance of the lens $V_{11}$ has not been reported before, and is shown in Figure 7.17 for a beam energy of 900eV. We see that a 2 times gain in signal can be achieved. The lens is designed to bring the scattered beam to a focus in front of the Pierce gun lens, which then projects a parallel beam onto the aluminium plate. To achieve this, the Harting and Read tables suggest that voltages of 3 to 4 times the beam energy must be applied. We see however that signal is maximised when a voltage of about 1 times the beam energy is applied. Thus the lens does not operate as designed, and the scattered signal is probably being brought to a focus at the aluminium plate instead. In light of this, it is possible that the Pierce gun settings could be further optimised, as the present
settings were determined by placing an ion source close to the entrance of the gun.

Finally, the focusing property of the rectangular lens $V_{10}$ was checked. This lens is designed to focus a greater angular spread of ions into the detector, and thus increase the effective solid angle and the signal. It is found that applying a voltage of 300–400V increases the signal by about 2 times (for a 900eV beam). It was noted, however, that a different focusing voltage is required to focus ions onto the final beam monitor, and thus care must be taken when using this lens in an experiment.

It is clear that the detector efficiency is very sensitive to the focusing of the ion optics, and these lenses must be carefully set in a coincidence experiment to ensure optimum detector efficiency.

### 7.4.3 Angular Element Sensitivities

The final sensitivity of each angular element depends on a variety of factors, including:

- The transparency of each scintillator
- The coupling of fibre optics to each scintillator and photomultiplier.
- The performance of each photomultiplier tube.
- The setting of the discriminators for each photomultiplier.

Because of problems with vacuum leaks, a new array of scintillator elements was installed. Originally, the conical tips of each scintillator element were aluminised by vacuum sputtering to improve reflectivity, and provide electrical grounding. In the new array, this was omitted, to improve the efficiency of scintillation. No problems were experienced with the electrical charging of the scintillators, and a definite improvement in performance was seen.

Experimentally, the only factor that can be easily changed that effects the final sensitivity of the scintillators is the discrimination level of the photomultiplier tubes. As Figure 7.18 shows, a wide variation in sensitivity is seen over each angular element. These measurements were made by applying a saw-tooth shaped pulse to deflector plates to sweep the beam into the detector uniformly over all angles. Thus, a calibration over the angular range must be performed before results from different angular elements can be compared. This will only be meaningful if the variation over time is stable. Abbas et al. [1] report that stability is only obtained after data is collected for more than 8 hours, and that performance is improved at high detector voltages. Our experiences were that large variations in sensitivity could occur if the photomultipliers had been switched off for some time. Thus, the main factor affecting the stability of the detector is the photomultiplier performance, and improvements may be found by changing some of the tubes.

At present, the detector must be recalibrated before running a time-of-flight or coincidence experiment, after the photomultipliers and detector high voltage have been
left on for a period of several hours. Light emitted from an ion gauge in the detector chamber has been shown to give a uniform intensity across the scintillator array, and thus can be used for this measurement. The variations in sensitivity across the angular elements is the biggest drawback of the detector design, and may devalue the quality of scientific information that can be obtained in the coincidence experiment.

7.5 Summary

In this chapter we have discussed the performance of the apparatus, and described the improvements made. The apparatus is designed to perform the coincidence experiment. High beam intensities are required to ensure good signal rates. Efficient detectors are needed with a good signal-to-noise ratio. Also, the apparatus must be reliable, as experiments would be run over a number of hours.

It is found that the majority of the apparatus does operate as designed. The vacuum system is good, although cold traps would be useful in all of the ion optics chambers. No problems were found with the target beam or the photon optics, and the data collection facility has been improved.

The detector is also shown to operate efficiently, as long as care is taken to optimise to all of the ion and electron optics. Furthermore, the use of a binary coincidence technique
eliminates the background noise level. The drawback of the design is the wide variation in sensitivity over the angular elements.

The only problems experienced with this apparatus were with the generation of a stable and intense ion beam of low angular divergence. At present the plasma ion source is not operating stably, and improvements may be seen by bringing our design closer to the original. The extraction lens is also not performing as designed. If the anode slit is replaced by an anode aperture, and a three element lens used instead, sharp focusing should be achievable. Finally, redesigning the ion optics after the energy analyser should be considered. At present, the $V_6$, $V_8$ and $V_9$ lenses do not operate as designed, and it is found that the angular divergence of the beam is very sensitive to these voltages.

With these changes, it is hoped that future workers will have more luck in attempting the time-of-flight and coincidence experiments. The groundwork to these experiments are described in the next two chapters.
The TOF Technique

8.1 Introduction

In this chapter, the work done to set up the apparatus for time-of-flight experiments is described. As discussed in chapter 4 (page 68), the TOF technique is used for obtaining angular and energetic information on inelastic scattering processes. The technique is direct, can be applied to 'dark' processes, and has none of the problems of cascades that other techniques have, such as photon spectroscopy. Our first experiments would repeat previous measurements made on ion-atom and ion-molecule collision systems by other groups [29, 50, 53, 56, 138], as a way of testing the apparatus. Experiments exploring new collision systems involving molecules could then be pursued.

In the TOF technique, the projectile beam is pulsed. The kinetic energy of the scattered projectile can then be measured, allowing different inelastic processes to be identified. Resolution is determined by the length in time of the pulsed beam, and a resolution of 0.5eV (0.1eV) is needed to resolve electronic (vibronic) processes.

As mentioned on page 68, there are different ways of pulsing the beam. Switching the beam on and off using deflection plates is the simplest method, but has the drawback that beam utility is low. A cross-correlation technique in which the beam is chopped with a pseudo-random sequence can utilise up to 50% of the beam. The drawback here is that regions of low intensity are measured with lower accuracy, and so the method is not suited to our work. We have chosen to use another technique in which the beam is pulsed using bunching fields, so that the tail end of a pulse is accelerated to catch up with the leading edge at the time of detection. A spread in kinetic energy is introduced, but as we shall see, this does not limit the scientific information that is available. The advantage of the method is that up to 50% of the beam can be utilised.

My work has involved the installation, modelling and testing of the compression lens, and this is reported in the following sections. A program that controls the data collection has been written by Dr Fluendy, and is also described. From the results of a TOF experiment, the excitation energy and differential cross section of an inelastic process can be determined. Useful equations that aid this calculation are given. Finally, we give a feasibility calculation for the experiment. No experiments could be run for the reasons given in the last chapter, but the work described here will allow TOF experiments to be run in the near future.
8.2 The Velocity Modulation Technique

Our velocity modulation technique has already been reported in detail by McCall and Fluendy [104]. Here we repeat the important results.

8.2.1 The Principle

Two scientific requirements of the TOF experiment are that different scattering channels can be resolved, and that impact parameter resolution is sufficient to allow information on the potential surfaces to be extracted. These requirements can be related to the experimental variables in the following way:

\[
\frac{\delta t}{t} = \frac{\delta(\Delta E)}{2E} \quad (8.1)
\]

\[
\frac{\delta \tau}{\tau} = \frac{\delta E}{E} + \frac{\delta \chi}{\chi} \quad (8.2)
\]

where \(\delta(\Delta E)\) is the energy loss resolution needed, and \(\delta E/E\) and \(\delta \chi/\chi\) are the FWHM resolutions in energy and scattering angle. The impact parameter resolution depends on both the angular and energy resolution. In our apparatus, \(\delta \chi/\chi \sim 0.03\), and usually in angular-resolved measurements it is desirable to choose \(\delta E/E\) to be similar, to maximise the beam intensity, which varies approximately linearly with \(\delta E/E\). However, the time resolution is limited by the energy spread \(\delta E\) in the beam, set by the energy analyser. With the standard pulsing technique (deflection plates), eqns (8.1) and (8.2) are both satisfied only when a low intensity beam is run with a low duty cycle.

In contrast, the velocity modulation technique allows these conditions to be met simultaneously. An initial beam pulse of duration \(\delta t'\) and energy spread \(\delta E'\) is modulated using linear compression fields to produce a pulse of duration \(\delta t''\) (satisfying eqn (8.1)) and an increased energy spread \(\delta E''\) (afforded by eqn (8.2)), where

\[
\delta E' \delta t' = \delta E'' \delta t'' \quad (8.3)
\]

Thus phase space is manipulated, and the required time resolution is obtained with enhanced beam utilisation.

8.2.2 Design Considerations

Figure 8.1 shows the geometry of the velocity modulation system in our apparatus. A pair of X deflection plates are positioned between the analyser and the acceleration lens, and the Z pulsing lens is positioned between \(V_6\) and \(V_8\) (see also Figure 7.3, page 143). The X deflection plates are used to chop the beam of well-defined velocity \(v_0\) into segments that fill the length of the compressor. The aim is to apply a field between \(Z_1\) and \(Z_2\) that ‘focuses’ all ions in this region so that they arrive at the detector nearly simultaneously.
Figure 8.1. Geometry of the compressor and the X deflection plates installed in our apparatus.

Consider an ion located between Z1 and Z2 at time \( t = 0 \), when the field is applied. At Z2, its initial energy \( E = \frac{1}{2}mv_0^2 \) will be incremented by an amount \( \epsilon(t_c) \), where \( t_c \) is the time-of-flight in the field. For this ion to arrive at the detector at the same time as one positioned at Z2 when \( t = 0 \), the following equation must be satisfied [104]:

\[
\epsilon(t_c) = E \left( \frac{l_d/v_0}{l_d/v_0 - t_c} \right)^2 - 1 \quad (8.4)
\]

(where \( l_d \) is the distance from Z2 to the detector). Since the time \( t_c \) taken to pass through the compressor will be much smaller than the time taken to reach the detector \( (t_d) \), eqn (8.4) yields

\[
\epsilon(t_c) = 2E(t_c/t_d) \quad (8.5)
\]

Also, \( \epsilon(t_c) \ll E \), and so \( t_c \approx x/v_0 \), where \( x \) is the distance of the ion from Z2 at \( t = 0 \). This gives

\[
\epsilon(t_c) \approx 2Ex/l_d \approx exF \quad (8.6)
\]

Thus, the electric field \( F \) applied between Z1 and Z2 at \( t = 0 \) that is required to time-focus ions is

\[
F = 2E/el_d \quad (8.7)
\]

(where \( e \) is the electronic charge). The duration of the voltage pulse and hence the
8.2. THE VELOCITY MODULATION TECHNIQUE

Figure 8.2. The predicted time profiles the beam at the particle detector. (a) A DC beam is passed through the compressor. (b) Chopping the beam using the X deflection plates. (c) Applying both X and Z pulses.

length \( l_c \) of the compressor are determined by the energy resolution \( \delta E/E \) needed:

\[
t_z = \left( \frac{l_d}{v_0} \right) \delta E/E \tag{8.8}
\]

\[
l_c = l_d(\delta E/E) \tag{8.9}
\]

Lastly, the enhancement in signal intensity achieved by the compression technique will be

\[
\text{Enhancement} = \frac{\delta E/E \text{ after modulation}}{\delta E/E \text{ before modulation}} \tag{8.10}
\]

If a DC beam is passed through the compressor, the beam train arriving at the detector will appear as shown in Figure 8.2(a). Application of the Z voltage accelerates ions within the compressor, and at the detector a narrow peak in intensity will be seen followed by a blank period. The peak will be positioned at \( t_d \), the flight time of ions travelling from the end of the compressor (Z2) to the detector, and the blank period will be of length \( t_c \), the flight time through the compressor. Those ions that have not reached the compressor (Z1) at \( t = 0 \) will feel a retarding potential, creating a second peak after the blank period and resulting in some noise within the blank period. To remove this noise, a pulsed voltage must be applied to the X deflection plates (Figure 8.2(b)) to chop the beam into compressor-sized lengths. Application of both X and Z pulsed voltages (after careful setting of pulse delays) will result in the clean profile seen in Figure 8.2(c).
The pulse repetition rate will depend on the arrival time of the inelastic scattering signal. If this occurs within the time $t_c$, then beam utilisation could approach 50%. McCall and Fluendy [104] report a duty cycle of 25%. They found that the finite rise time of the voltage applied to the X deflection plates could cause a slight energy modulation of the beam. After compression, this is seen as broadening of the peak at the detector. To remove this noise, they found it necessary to apply a 'clearing' voltage directly after the Z voltage. Ions trailing behind the beam pulse are then accelerated to arrive before the main peak at the detector, at a time of no physical interest. Lastly, we note that the time-focusing property of the compressor depends on the kinetic energy of the ions, and so it may be necessary to alter the focus the Z pulse voltage to bring ions suffering large energy losses into focus.

### 8.3 Modelling and Construction of the Compressor

#### 8.3.1 Geometry

As shown in Figure 8.1, the length of our compressor is 108mm, positioned 1615mm from the entrance to the detector (172 ±1mm from the collision zone). The compressor consists of 8 parallel plates, with holes ranging from 92 to 40mm diameter centred on the beam path. Tapering of the diameter is necessary, because the compressor is positioned just after the deceleration lens ($V_6$), where the beam is converging towards a focus beyond the $V_8$ lens. A grid is positioned at the entrance of the compressor to prevent distortion of the Z field by the $V_6$ lens. The X deflection plates are of length 10mm, separated by about 8mm. They are positioned after the analyser exit slit, 679mm from the start of the compressor (Z$_i$).

With this geometry, the final energy resolution of the beam after compression will be $\delta E/E = 0.066$ (eqn (8.9)). This compares favourably with the angular resolution of 0.01–0.07. Assuming that the energy spread of the beam before compression is 0.5eV, the enhancement in the signal will be 120 (eqn (8.10)), for a 900eV beam.

Using eqns (8.7) and (8.8), we can also predict that the voltage required to achieve time-focusing is 120V, which must be applied for a duration of 1.64μs.

#### 8.3.2 Modelling the Compressor

To establish more precisely the pulsing requirements of the system over a range of energies and energy losses, and to check the performance of the compressor and our knowledge of the geometry of the apparatus, a computer program was written. The program will also prove useful when analysing results of an experiment. The passage of ions through the apparatus and the inelastic collision was modelled simply using classical mechanics. Not taken into account are the processing time of the photomultipliers and electronics, and the internal time delay of the Z pulse generator. A listing of the program
MODELLING AND CONSTRUCTION OF THE COMPRESSOR

<table>
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<tr>
<th>B.E.</th>
<th>X-Z Delay</th>
<th>Z Width</th>
<th>$V_z$</th>
<th>Avtech</th>
<th>$T_{\text{elastic}}$</th>
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<td>30.898µs (9.783)</td>
<td>4.748µs (1.503)</td>
<td>14.24V</td>
<td>16.28V</td>
<td>75.074µs (23.737)</td>
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<td>21.848 (6.918)</td>
<td>3.357 (1.063)</td>
<td>28.47</td>
<td>32.54</td>
<td>53.483 (16.911)</td>
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<td>2.741 (0.868)</td>
<td>42.70</td>
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<td>1.795 (0.568)</td>
<td>99.51</td>
<td>113.7</td>
<td>29.202 (9.235)</td>
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<tr>
<td>800</td>
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<td>1.679 (0.532)</td>
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<td>129.9</td>
<td>27.399 (8.665)</td>
</tr>
<tr>
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<td>127.9</td>
<td>146.1</td>
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<tr>
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<td>1.501 (0.475)</td>
<td>142.1</td>
<td>162.3</td>
<td>24.642 (7.794)</td>
</tr>
</tbody>
</table>

Table 8.1. Voltages and time delays required for time-focusing of elastically scattered Ar$^+(\text{He}^+)$ at different beam energies. Because of the arrangement of resistors, the Avtech voltage is $8/7 \times V_z$. These values were calculated for a scattering angle of 3°, and a detector voltage of 50kV. The scattering target was chosen to be N$_2$.

can be found in appendix A.3 (page 240).

Table 8.1 gives the voltages, pulse widths and time delays that are predicted for focusing of elastically scattered particles. Experimentally, it is found that a focusing voltage of $146 \pm 2.5V$ is required to focus the ions at the detector, for a 900eV beam. This agrees very well with the calculated value of 146.1V, confirming that the program contains no mistakes. Also, in a later section we demonstrate that flight times are correct to ±150ns.

The flight time resolution requirements were investigated using the program, and it is found that eqn (8.1) is correct to ±10%, and Figure 8.3 gives the results for a 900eV beam. We see that an energy resolution of 0.5eV (0.2eV) is obtained if the spread in arrival times is no more than 7ns (2.5ns). To achieve this, the focusing voltage must be set with an accuracy of ±0.5eV (±0.2eV). Time resolution also varies with the energy loss of the process. Figure 8.4 shows how the spread in arrival times varies with energy loss, for a compressor focused on the elastic peak. For an energy loss of 10eV, the peak width has risen to 22ns, corresponding to an energy resolution of 1.6eV. To focus on this energy loss, a voltage adjustment of +2eV would be required. Notice that inelastic processes up to 20eV energy loss all arrive within 220ns after the elastic peak. As this is much less than the flight time of an ion through the compressor (1.6µs), large duty cycles are possible.

8.3.3 Experimental setup

We see from Table 8.1 that the Z pulse power supply must be capable of delivering 10–200V pulses of width 0.5–5µs. An Avtech supply was bought for this purpose (Model AVR-4A-PW-PS, Lyons Instruments), which can generate 400V pulses of width 0.1–5µs and rise time 2–3ns. The maximum average output power of the supply is 16W, which limits the average repetition frequency to 1000cs$^{-1}$. In our experiments, however, this
Figure 8.3. The dependence of energy resolution on peak width for the case of a 900eV beam.

Figure 8.4. The arrival time of inelastic peaks after the elastic peak. The beam energy is 900eV and the compressor is focused on the elastic peak. As seen, the time resolution worsens with increasing energy loss.
Figure 8.5. A timing box is used to control the sequence of beam pulsing. For the duration that signal or noise pulses are received, TTL triggers are sent to the X pulse and Avtech supplies. A nim pulse is also sent to the particle interface (or a time-to-amplitude converter) to start the flight time measurement.

does not place a restriction on the experimental duty cycle, as pulses of smaller height and width are used. The supply was modified slightly to allow the Z voltage to be fine-tuned with greater control. The internal delay of the supply is designed to be varied between 100ns and 500ns, but at present is 0.486\mu s (see later, page 185).

The compressor acts as a 50\Omega terminator, preventing ringing along the signal cables. This is achieved by wiring eight 6.25\Omega resistors between the eight plates of the compressor. The pulse must therefore pass through a 6.25\Omega resistor before reaching the first plate, and so the voltage set must be 8/7 times the value of V_x given in Table 8.1. As the average power dissipated by the 8 resistor stages will be up to 16W, with a peak power of 50W per stage, resistors of large power rating were needed. Three metal oxide resistors in parallel were therefore used (12\Omega, 15\Omega and 100\Omega), each rated at 2W.

Calculations suggest that the X deflector plates require 50V to switch the beam off. In fact it is found experimentally that 20V is sufficient. Pulses are generated using a purpose-built supply. The arrangement of resistors ensures that the pulse is correctly terminated to 50\Omega, and that the voltage is supplied symmetrically, i.e. \pm 10V to each plate (relative to V_3). When operating, the beam remains switched off except for the duration of a TTL trigger pulse that is sent to the supply.

To control the sequence of pulsing (given the requirements of Table 8.1), a timing box was built – see Figure 8.5. Signal and noise gates set by the target pulser are inputed into the timing box. For the duration that these gates are received, X and Z trigger pulses (TTL and nim) are generated and sent to the X and Z pulse generators and the
8.3. MODELLING AND CONSTRUCTION OF THE COMPRESSOR

Figure 8.6. (a) The sequence of X and Z trigger pulses produced by the timing box. (b) An alternative sequence that would give higher duty factors.

data collection system. Figure 8.6 shows the sequence of pulsing. Both X and Z pulse widths can be adjusted over the range 0.5 to 10µs. The critical timing between the X and Z pulses is controlled by a variable ‘X delay’ (0.5 to 28µs). The repetition rate is set by the ‘Z delay’ controlling the time between the Z pulse and the next X pulse (4.2 to 23µs). With these ranges of settings, we will be able to perform experiments with Ar and He in the energy ranges 150–1000eV and 100–800eV respectively. (from Table 8.1).

The duty cycle of the experiment is limited by the timing box and the target beam pulsing. When the ‘Z delay’ is set to its smallest value (4.2µs), with the ‘X delay’ and the X and Z pulse widths set according to Table 8.1 (1.5µs widths, 9.77µs delay for 1000eV Ar beam), the duty cycle of the beam during gating is maximised to 9.67%. If the target beam is run with a repetition rate of 40Hz, with signal and noise gate widths set at 1ms, the duty cycle of the target beam is 4.0%. Thus, the total experimental duty cycle is 0.39%.

Much larger duty cycles can be achieved if the timing box pulsing sequence is altered to allow more than one X trigger pulse to occur before the Z pulse is fired (see Figure 8.6(b)). As inelastic pulses arrive within the time $t_x$, the duty cycle of the projectile beam during gating could in principle approach 50%, with the total experimental duty cycle increasing to 2%. However, care would have to be taken to ensure that the power dissipated by the Avtech supply does not exceed 16W. As power $= V^2/R$, the average Z pulse repetition rate must not exceed

$$Z\text{ pulse rep. rate} = \frac{800}{V_z^2 \times t_z}$$
8.4. PERFORMANCE OF THE COMPRESSOR

The effect of changing the timing parameters and the focusing voltages was investigated by using a time-to-amplitude converter and a multichannel analyser to record the time profiles of the 900eV beam at the detector. Delayed Z trigger pulses produced by the timing box were used as START pulses, with the signal recorded at one detector angle stopping the TAC. No target beam was necessary for these measurements.

Figure 8.7 shows the effect of applying a Z pulse when a DC current is passing through the compressor. The spectra shown are for Z pulse voltages ranging from 130 to 162V. The sharpest profile seen has a width of 40ns, recorded when $V_z$ is set to 146V.

Finally, we remark that if pulsing of the main beam was performed instead using a conventional deflection plate technique, the duty cycle during the signal and noise gates would not exceed 4.7% (10ns pulses separated by 215ns, the inelastic/elastic separation for a 1000eV beam, $\Delta E = 20$eV), and with a 4% target beam cycle, the total experimental duty would be 0.18%. Thus, our velocity modulation technique currently allows us to run the experiment with a doubled duty cycle, and with modification of our timing pulse sequence, the gain could approach 10 times.

8.4 Performance of the Compressor

where $V_z$ and $\ell_z$ are the height and width of the Avtech pulse.
Figure 8.8. Time profiles collected when only the X deflection plates are used. (a) shows the effect of varying the width of the X trigger pulse. In (b), the delay between the X and Z trigger pulses is changed. The time window is 8μs in both cases (8ns per channel), and other settings are the same as for Figure 8.7.
8.4. PERFORMANCE OF THE COMPRESSOR

X and Z Pulses: Varying the X Delay

Figure 8.9. Here, both the X deflectors and the compressor lens are pulsed, and the graph shows the effect of varying the delay between these pulses. The time window is $4\mu s$ (4ns per channel), and other settings are the same as for Figure 8.7.

This corresponds to a beam energy resolution of 2.8eV (from Figure 8.3). $V_3$ was set at 700eV in this example, and the energy analyser gives better resolution (at the expense of beam intensity) if lower values of $V_3$ are set. The narrowest peak recorded so far is 22ns (FWHM) for $V_3$ set at 450V. This corresponds to a FWHM beam energy spread of 1.5eV, just sufficient for resolving electronically inelastic peaks in the TOF experiment.

Beam counts are seen to the right of the main peak, caused by slower ions entering the compressor after the Z pulse is applied, and other effects. This is intolerable in the TOF experiment, where the inelastic signals are weak, and so both the compressor and the X deflection plates must be used in combination. Figures 8.8(a) and (b) show the beam profiles that result when only the X deflection plates are used. The first graph illustrates how the X plates can chop the beam into sections of different lengths. The aim is to choose a beam section length that just fills the compressor lens, but without causing noise after the main peak.

The timing between applying the X and Z pulses is critical – the Z pulse must be fired when the chopped section of beam exactly fills the compressor. Figure 8.8(b) demonstrates how the delay between the X and Z pulses can be varied. The point at which the main peak would appear if the Z pulse was applied is marked. Ideally, the delay is set so that the pulse lies just to the right of this point – i.e. the section of beam just fills the compressor when $V_z$ is applied.
Finally, in Figure 8.9 we see the beam profiles that result when both X and Z pulses are applied. The graph furthest to the right in the figure was taken when the Z pulse is fired too late. The section of beam had already partly emerged out of the compressor when the Z voltage was applied, and appears as signal to the left of the main peak. Moving from left to right, the delay between the X and Z pulses is decreased, and we see that more of the beam section lies within the compressor when the Z voltage is applied. Experimentally, this is found to be the best way of setting the pulse timing.

Thus, we conclude that the technique does work as designed. At present, weak beam intensities after energy analysis limits the energy resolution that can be achieved, although crude experiments with a resolution of 1.5eV can still be run. Improving the ion source would help here (see chapter 7).

Some other problems were found. When the beam is chopped by the X deflection plates, the count rate at the detector is small (typically 1000cs⁻¹, for a 10⁻⁹A beam). This makes the refocusing of the beam during an experiment difficult, and the experiment would probably have to be temporarily halted. Also, it was found that the beam was more prone to instabilities when chopped, due possibly to the charging of dirty surfaces when the beam is deflected. Some dependency of the beam profile on the ion optics focusing conditions has been seen. Small changes in the beam energy occur when the analyser is tuned, and possibly the Z pulsing field is distorted by the $V_\theta$ lens.

### 8.5 Calibrating the Apparatus

The compressor lens is a valuable tool in a crossed beams apparatus, as it can be used to check flightpath lengths, timing arrangements in a coincidence experiment (see chapter 9), as well as of course allowing TOF experiments to be run. A series of measurements were made using the compressor to establish how accurate the computer model is in predicting flight times, and thus to check our knowledge of the flightpath from the compressor to the detector.

Experimental flight times were measured by pulsing the beam using the compressor, and recording the arrival time of the (deflected) pulse at the detector. The deflection angle was chosen to be 2.94°, and the detector high voltage was 50kV. No target beam was necessary for the measurement, and the X deflectors were not used. The timing arrangement was identical to that shown in Figure 8.5, with Z ním pulses from the timing box (width 0.4μs, dial setting 0.63) used to start a time-to-amplitude converter and Z TTL pulses sent to the Avtech supply. Signal from the detector was used to stop the TAC and no delay was set on either start or stop pulses. The time window was set to be 40μs, and the resulting time spectrum was collected using a calibrated multichannel analyser.

Measurements were made at four different beam energies, and results are summarised in Table 8.2. The 'beam energy' listed is the voltage that was set on the appropriate
8.5. CALIBRATING THE APPARATUS

<table>
<thead>
<tr>
<th>Beam Energy</th>
<th>Avtech Voltage</th>
<th>Measured Time</th>
<th>Flight Time</th>
<th>Predicted Time</th>
<th>Corrected Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>600.5eV</td>
<td>97.5V</td>
<td>32.041µs</td>
<td>31.228µs</td>
<td>31.372µs</td>
<td>31.088µs</td>
</tr>
<tr>
<td>700.5</td>
<td>108.5</td>
<td>29.894</td>
<td>29.081</td>
<td>29.181</td>
<td>28.954</td>
</tr>
<tr>
<td>800.5</td>
<td>130.5</td>
<td>27.997</td>
<td>27.184</td>
<td>27.342</td>
<td>27.156</td>
</tr>
<tr>
<td>900.5</td>
<td>145.9</td>
<td>26.462</td>
<td>25.649</td>
<td>25.857</td>
<td>25.701</td>
</tr>
</tbody>
</table>

Table 8.2. Experimental and Predicted flight times of Ar$^+$ from the compressor to the detector (50kV, 2.94°). The 4th column gives the measured flight time after subtracting 0.813µs, the delay between the start pulse and the Avtech output. The last column gives the computer predictions, assuming a correction of +13eV to the beam energy.

Power supply. $V_3$ was set at about 750V during the measurements. Avtech focusing voltages were taken from Table 8.1, and peaks in the time spectrum were spread over 2 to 3 channels (80-120ns FWHH). This is about what one would expect for correctly focussed peaks with a beam energy spread of ±5eV. (see Figure 8.3). The uncertainty in the recorded peak arrival times listed in Table 8.2 is about ±80ns (±2 channels).

To obtain the actual flight times of the ions from the compressor to the detector, corrections must be made for the delay between the start pulse and the response of the Avtech supply, as well as the photomultiplier and electronics response time (about 30ns). The former could be directly measured using the same timing arrangement, by passing the Avtech output pulse (of TTL height) through a small delay to stop the TAC. After calibrating the MCA and the additional delay, the time delay between the Z nim start pulse and the Avtech output was measured to be 0.813 ± 0.002µs. Hence, the actual flight time of the ions is the measured time minus 0.813µs (before the second small correction is made). These flight times are also listed in Table 8.2. (The delay between the Z TTL and Z nim pulses produced by the timing box was also measured, and found to be 0.326µs. Hence the internal delay of the Avtech supply is 0.486µs.)

A modified version of the computer program was used to predict flight times. The only changes made were to remove the modelling of the collision (as no target beam was used in the experimental measurements), and to change the point at which ions are deflected to 61.5mm beyond the collision zone (where the deflection plates are). Experimentally, the times recorded correspond to the position of the peak in intensity in the time spectrum. In the computer program, the position of the peak is modelled to be the average time of arrival of ions that are positioned between $Z_1$ and $Z_2$ when the compressor was fired. The predicted times are given in the second last column in the table.

How closely do the experimental and computed flight times agree? This is best seen in Figure 8.10(a), which plots the difference between computed ($t_p$) and experimental ($t_{ex}$) times against $(1/BE)^{1/2}$:

$$t_p - t_{ex} = (d_p - d_{ex}) \times (m/2e)^{1/2} \times (1/BE)^{1/2} - \text{PM response time} \quad (8.11)$$
8.5. CALIBRATING THE APPARATUS

Flight—Time Calibration

Figure 8.10. Comparison between experimental and computed flight times. (a) Assuming the beam energy to be the values in Table 8.2. (b) After a correction of 13eV is made. The error bars correspond to an uncertainty of ±83ns in the measured flight times.

On average, \( t_p - t_{ex} \) is about 153 ± 44ns. The most likely cause of this discrepancy is uncertainty in the beam energy. It has already been remarked on page 160 that the actual beam energy is larger than the beam voltage applied to the source anode, due to the kinetic energy of the ions emerging from the anode slit. To check this, the required analyser focusing voltage \( V_g \) was carefully measured for two different values of \( V_3 \), for an ion source that was run under identical conditions as in the flight time measurements. For \( V_3 = -992 \pm 0.5V \), \( V_g \) was -530 ± 1V, and hence the correction to the beam energy is 15 ± 2eV (eqn (7.2), page 144). For \( V_3 = -878V \), \( V_g \) was -468V, and hence the correction is 11 ± 2eV. Taking the average correction to the beam energy to be +13eV, new predicted flight times are given in the last column of Table 8.2, and a comparison is made with the experimental values in Figure 8.10(b). Now \( t_p - t_{ex} \) is on average -73 ± 93ns

Conclusions

From these measurements, one can conclude that the computer model contains no mistakes, and can predict flight times correctly to within ±150ns. From a plot of \( t_p - t_{ex} \) vs \((1/BE)^{1/2}\), the gradient of the least-mean-squares straight line that passes through the data gives in principle the correction required to the measured flightpath length \( d_p - d_{ex} \)
(see eqn (8.11)), and the intercept gives the response time of the photomultipliers. In Figure 8.10, the large error bars associated with the experimental measurements prevent any detailed analysis, although it is possible to set error bounds on the measured flightpath length. Choosing data set (a) in Figure 8.10 (the worst case), and forcing the least-mean-squares straight line to intercept the y axis at -30ns, \( d_p - d_{ex} \) is calculated to be \( 10 \pm 4mm \). Hence the flightpath length from the compressor to the entrance to the detector is \( 1615 \pm 14mm \).

8.6 TOF Data Collection

During a TOF experiment both beams are collided and a flight time spectrum is accumulated in which peaks emerge corresponding to different inelastic processes. The timing arrangement that allows this measurement to be taken has already been described on page 154. Briefly, the particle interface records the flight times between delayed Z trigger pulses and the 45 scattered particle signals. The timing window is \( 2.56\mu s \), and contains 256 channels. Flight time and angular information is encoded into a 16 bit word (2 bits: signal/noise flag, 6 bits: scattering angle (1 to 45), 8 bits: flight time (1 to 256)) and sent to the computer.

A new IBM ps/2 computer fitted with a high speed 32 bit parallel I/O interface (MC-DIO-32F, National Instruments) has been installed to process this information, and a sophisticated program was written by Dr Fluendy to control the data collection. In this section, we describe the operation of this software, in the form of a short ‘user’s guide’. Details of the program and a listing can be found in appendix A.5 (page 245).

8.6.1 Design Philosophy

The computer interface is designed to operate in parallel with the data processing program. Thus, at all times the interface receives data from the experiment, storing the 16 bit words in a large temporary buffer (having a capacity of 32000 words). Simultaneously, the computer program takes data from this buffer, processes it, and returns to the buffer to take all the new data that arrived. With this arrangement, the program should be able to keep up with the rate at which data is received, keeping the experimental ‘dead time’ to a minimum. The only time that data collection halts is when the buffer becomes full. A short pause occurs while the program catches up in processing the remaining data, and only then is the buffer emptied and new data from the experiment collected. In a typical TOF experiment, in which the scattering signal is small (e.g. \( 100cs^{-1} \) in each angular element), the buffer takes several minutes to fill, and the experimental dead time is insignificant in comparison. Lastly, it should be mentioned that the computer interface runs an accurate clock, which the program uses for timing the experiment, and determining the data count rates.
8.6. TOF DATA COLLECTION

8.6.2 The Data Collection Program

The program was written in BASIC (Microsoft Corp.), using Labwindows, a software writing package (National Instruments). The aims of the program are to take data from the buffer, decode it, and store it on the hard disc. In addition the program is designed to provide the user with on-line information about how the experiment is progressing, including graphs showing time and angle profiles of the scattered signal, tables showing the performance of the ion detector, and data used for tuning the beam.

Starting the Program

The program is run simply by switching on the computer and typing the program name, currently TOFN. On entering the program, the user is asked for:

Experiment I.D. A name attached to the results when data is dumped to the hard disk.

Update rate The number of data points that are processed before the user is provided with information on various experimental parameters.

Data dump time The time interval (seconds) between dumping data to the computer hard disc.

Tune Rate Similar to the update rate, and used when the program is in a ‘tune mode’ (see later).

The program then runs, taking data from the buffer, and decoding the words to reveal the angle and time position, and signal/noise period that scattered particles were detected at (one count corresponding to one word). At regular intervals (the update rate), information on the state of the experiment is sent to the screen:

- The total number of data points processed since the experiment started.
- The current number of events contained in the buffer.
- The current ‘global’ time on the computer interface clock (s)
- The ‘elapsed time’ of the experiment (s)
- The event rate \((s^{-1})\) received from the experiment.
- The signal and noise rates \((s^{-1})\).
- The scattered signal (i.e. signal – noise) rate.
- The dead time that occurred since the buffer was last cleared.
In addition, after the ‘dump time’ has elapsed, the data processing halts (but not the data collection by the computer interface), and all of the decoded data is written to the file ‘\data\tof.dat’. This takes about 10 seconds. At present, the file lists the experiment I.D., date and time, followed by the particle detector correction factors (see later) and finally two columns of numbers giving the data received in the signal and noise periods. There is clearly room for improvement here: the data could be organised better in the file, and at present the experimental run time and total dead time are not written. Indeed, the program does not calculate the accumulated dead time, and this should be changed.

The Function Keys

At any time while the program is running in this fashion, the user can ask for a number of different tasks to be performed by pressing one of the function keys of the keyboard. This temporarily halts the data decoding, although whenever the program has a chance, for example when waiting for a response from the keyboard, data decoding continues.

**F1: Time Distribution**  A graph is plotted on the screen displaying the time-of-flight spectrum. The data displayed may be that received in the signal or noise periods, or the difference between these (scattered signal), and counts are summed over a chosen angular range (between 0 to 44). After plotting, the graph is left on the screen, and the program returns to processing the data.

**F2: Angular Distribution**  A graph may also be plotted showing the distribution in counts over the 45 angular elements. Again, this may be the signal, noise or scattered signal, and the time range (between channels 0 to 255) over which data is summed is chosen.

**F3: Live 2D Plot**  This function goes one step further and runs a ‘live’ two-dimensional plot of the intensity received at each (angle, time) location! The number of counts is represented by one of 15 colours ranging from black (no counts) to ‘bright white’ (see page 175 of the Microsoft ‘Programming in Basic’ manual), and the plot is continually updated as data is processed. Again, either the signal, noise or scattered signal data is plotted. A ‘history’ or ‘update’ mode is also chosen, which determines whether or not all previous data collected is to be plotted. Lastly, the sensitivity of the display is determined by a scale setting, and can be increased by pressing key F11, and decreased by pressing key F14. To exit from 2D plotting, F3 must be pressed again.

**F4: ID and Logging Data**  The experiment ID, update rate, dump time and tune rate can be changed by pressing key F4. This has no effect on the experimental data that has already been collected.
F5: Initialise  Pressing key F5 clears all program arrays and variables to allow a new set of data to be collected. As all data that has not already been dumped to a file is lost, the key should be used with great caution! (It would be sensible to change the program so that the user is asked to confirm this choice).

F6: Engineer  In Engineer, a range of information can be accessed on the performance of the particle detector and the main beam. On first entering engineer, the user is asked to select between Beam Hist., Angle Norm. or P/M Tube.

If Beam Hist. is selected, a plot is given showing how the signal and noise rates have varied over a time spanning back 100 update periods. This is a useful way of monitoring the stability of both crossed beams.

Angle Norm. is used for setting the correction factors that are needed to ensure a uniform sensitivity across the 45 scintillators. These factors can be set to 1.0, read in from a file, or measured. To a measure the factors, a uniform signal must be applied across the scintillators, for example by sweeping the beam into the detector using a saw-tooth waveform, or by switching on the ion gauge (see page 169). The correction factors are then calculated by dividing the mean number of counts by the actual counts collected at each angle. If the actual counts recorded at some angle are lower than a chosen threshold, the angle is deemed to be too insensitive, and a factor of 0 is set. Finally, the factors and their mean and standard deviations are printed on the screen, and the factors are written to a file on the hard disc.

P/M Tube is used to examine the performance of the ten detector photomultiplier tubes. Again, a uniform signal must be inputed to the detector, and a table is listed on the screen showing the sensitivity (before correction) of each angular element and the mean sensitivity in the photomultiplier tubes. Here 'sensitivity' is calculated as the actual counts at each element (or P/M tube) divided by the mean number of counts. The option proves useful, for example, when setting the discriminator levels of the photomultipliers.

F7: Tuning the Beam  Lastly, a facility is provided to monitor the performance of the beam when it is being tuned to give a narrow time and angle profile. As all data stores are cleared when F7 is pressed, the tune mode is only used when setting up an experiment. (Again, the program should be altered to provide some protection against accidents). The user then has the choice of tuning either the angular divergence of the beam, or the time profile. When running, information is given on the mean arrival time (or angle) and its standard deviation. This is repeated on the screen at a fast rate (the tune rate, set by F4) to allow the user to see the effect of tuning the ion beam focusing and pulsing parameters.

F8: Writing Data to a File  At any time, the user can save the experimental data on the hard disc by selecting key F8. This of course is in addition to the automatic
saving, which occurs at time intervals set by the ‘dump time’.

**F9: Terminate** If F9 is selected, the program ends and experimental data is stored on the disc (if requested).

**F10: Help** The help selection simply lists on the screen the function of each of these keys.

### 8.6.3 Performance of the TOF Data Collection System

At present, it is thought that the computer software contains no mistakes, but the whole data collection system has not yet been tested using simulated signals. This is necessary to confirm that no data is lost during the processing by the interfaces and program, and that the data is not modified in anyway.

All of the various functions of the program listed in the last subsection have been fully explored, and any problems found have been sorted out. Also, tests have confirmed that channel and scintillator numbers identified in the program agree with those in the experiment, and so the important decoding part of the program is correct. As identified in the last subsection, the program can be improved in a number of ways. At present, no record is kept of the accumulated dead time in the experiment. Also, the data that is written to a file could be better organised, and a record included of the experimental run time and dead time. Lastly, some protection should be offered to keys F5 and F7, to prevent accidental loss of data in an experiment.

Problems were found, however, with the communication between the computer interface and the particle detector interface. Originally, if any of the angular elements received large count rates the particle interface would hang. To fix this problem, the electronic workshop (Chemistry Department, Edinburgh University) have had to make a major modification to the design of the particle interface, causing a delay of almost a year. In addition, it was discovered recently that in the short time that data collection is halted, while the remaining data in the full buffer is processed by the program, the computer interface sends stray signals back to the particle interface. This is a fault not detailed in the computer expansion board specifications, and to overcome the problems that are caused, further modifications are required of the particle interface! At present, the problem is in hand, and final tests of the TOF data collection system are anticipated in several weeks time.

### 8.7 Extracting Scientific Information from TOF Data

With our apparatus, TOF measurements are made over a range of scattering angles simultaneously. From such an experiment, the excitation energy of different inelastic
8.7. EXTRACTING SCIENTIFIC INFORMATION FROM TOF DATA

Figure 8.11. Newton diagram for an inelastic collision between two particles.

processes and their differential cross sections can be determined. To extract this scientific information, a conversion from the lab-frame to the centre-of-mass (CM) frame of reference is necessary. The endothermicity of a collision $\Delta E$, defined as the change in relative kinetic energies, can easily be calculated knowing the initial velocities of the beams, and the scattering angle and velocity of the projectile. Extracting differential cross sections is harder, as knowledge of the geometry of the detector, collision zone size and beam number densities is required. Relative differential cross sections, on the other hand can be readily calculated.

The equations used for performing these calculations have of course been well documented in the literature (see for example [66, 109]). Here we give a summary of these equations for future reference.

8.7.1 Calculating the Excitation Energy

The Newton diagram shown in Figure 8.11 illustrates the geometrical relationship between the lab and CM frames of references for two colliding beams. In the lab-frame, the initial projectile (mass $m_1$) and target (mass $m_2$) velocities are $v_1$ and $v_2$. The relative velocity is $v_r = v_1 + v_2$, and its magnitude is

$$v_r = \sqrt{v_1^2 + v_2^2 - 2v_1v_2 \cos \lambda}^{1/2} \quad (8.12)$$

where $\lambda$ is the angle between the two incident beams (in our apparatus, $\lambda = 90^\circ$). Hence, the initial relative kinetic energy of the collision $E_0$ is

$$E_0 = \frac{1}{2} \mu v_r^2 \quad (8.13)$$
where \( \mu = (m_1 + m_2)/m_1 m_2 \) \hspace{1cm} (8.14)

The projectile scatters inelastically with velocity \( v'_1 \) through polar angles of \( \theta \) and \( \Phi \) (with respect to \( v_1 \)). In our apparatus, the detector is positioned in the scattering plane, and so \( \Phi \) is zero.

In the centre-of-mass frame, the initial velocity of the projectile is \( w_1 \), relative to the centre of mass; its magnitude is

\[
w_1 = v_r m_2 / (m_1 + m_2)
\hspace{1cm} (8.15)
\]

(and similarly for \( w_2 \)). The speed of the CM frame is given most conveniently in terms of Cartesian components of the initial particle velocities:

\[
v_{cm} = \sqrt{ \left( (m_1 v_{1x} + m_2 v_{2x})^2 + m_1^2 v_{1y}^2 \right) / (m_1 + m_2)}
\hspace{1cm} (8.16)
\]

In the case of right-angled crossed beams, this simplifies to

\[
v_{cm} = \sqrt{ (m_1^2 v_1^2 + m_2^2 v_2^2) / (m_1 + m_2)}
\hspace{1cm} (8.17)
\]

The CM velocity is oriented with an angle \( \gamma \) to \( v_1 \), which can be calculated using the cosine rule:

\[
\gamma = \arccos \left( \frac{v_1^2 + v_{cm}^2 - w_1^2}{2v_1 v_{cm}} \right)
\hspace{1cm} (8.18)
\]

\( \Delta E \) is defined as the endothermicity of the inelastic collision:

\[
\Delta E = \frac{1}{2} \left[ m_1 v_1^2 + m_2 v_2^2 - m_1' v_1'^2 - m_2' v_2'^2 \right]
\hspace{1cm} (8.19)
\]

(where \( m_1' \) and \( m_2' \) are the masses after the collision). As we know the initial velocities \( v_1, v_2 \), the final velocity \( v'_1 \), and scattering angle \( \theta, \Phi \) of the projectile, we have enough information to determine \( \Delta E \). Firstly, we must calculate the final projectile velocity in the CM frame, \( w'_1 \). The magnitude of \( w'_1 \) can be obtained from

\[
w'_1 = v'_1 \left[ \cos \alpha \pm \sqrt{ \frac{v_{cm}^2}{v_1} - \sin^2 \alpha } \right]
\hspace{1cm} (8.20)
\]

(the sign is chosen by inspection of the Newton diagram). Here, \( \alpha \) is the angle between \( v'_1 \) and \( w'_1 \). Using eqns (8.17) and (8.18) to obtain the Cartesian coordinates of \( v_{cm}, \alpha \)
8.7. EXTRACTING SCIENTIFIC INFORMATION FROM TOF DATA

can be calculated from

\[ \cos \alpha = \frac{v_1^x(v_1^x - v_{cm}^x) + v_1^y(v_1^y - v_{cm}^y) + v_1^z}{|v_1||[(v_1^x - v_{cm}^x)^2 + (v_1^y - v_{cm}^y)^2 + v_1^z]|^{1/2}} \]  

(8.21)

Knowing \( w_1' \), we can finally calculate \( \Delta E \) from

\[ w_1' = w_1 \frac{m_1 m_2'}{m_1' m_2} \left( 1 - \frac{\Delta E}{E_0} \right)^{1/2} \]  

(8.22)

where \( E_0 \) is the initial relative kinetic energy, given by eqn (8.14).

8.7.2 Calculating the Differential Cross Section

In addition to the flight time, the intensity of scattered particles over a range of angles is measured in the TOF experiment. From this, the differential cross section of different inelastic processes can be obtained, providing rich information on the dynamics of these processes. The flux \( \Delta F_i(\theta, \Phi) \) (number per unit time) of particles of process \( i \) recorded by the detector located at \( (\theta, \Phi) \), is related to the lab-frame DCS by

\[ \frac{\Delta F_i(\theta, \Phi)}{\Delta \omega_d} = I_i(\theta, \Phi) = f n_1 n_2 v_r \Delta V \frac{d\sigma_i(\theta, \Phi)}{d\omega_L} \]  

(8.23)

where \( I_i(\theta, \Phi) \) is the detected intensity (number per unit time per unit of solid angle), \( n_1 \) and \( n_2 \) are the number densities of the colliding particles, \( \Delta V \) is the volume of the collision zone, \( f \) is the particle detector efficiency, \( \Delta \omega_d \) is the solid angle subtended by the detector, and \( d\sigma_i(\theta, \Phi)/d\omega_L \) is the DCS in the lab-frame.

Results are normally expressed in the CM frame. The CM scattering angle \( \chi \) can be calculated from

\[ \chi = \arccos \left[ \frac{w_1^2 + w_2^2 - (v_1^2 + v_2^2)}{2w_1 w_2} \cos \theta \cos \Phi \right] \]  

(8.24)

The CM frame DCS is related to the lab-frame DCS by

\[ \frac{\sigma_i(\theta)}{d\omega} = \frac{d\sigma_i(\theta, \Phi)}{d\omega_L} \frac{d\omega_L}{d\omega} \]  

(8.25)

Here, \( d\omega_L/d\omega \) is the Jacobian of the system, the ratio of unit solid angles in the lab and CM frames. With the help of eqns (8.20) and (8.21), the Jacobian can be calculated using

\[ d\omega_L/d\omega = (w_1'/v_1)^2 |\cos \alpha| \]  

(8.26)
In practice, the calculation of the absolute DCS is fraught with difficulty, as the terms \( f, n_1, n_2 \) and \( \Delta V \) are difficult to measure. Assuming, however, that these quantities remain the same for different inelastic processes (as they should in a multi-angle experiment), and that the detector remains uniformly normalised over all angles, relative DCS for different processes can be calculated and compared.

Because of the way the scintillators are oriented in our detector, care must be taken in evaluating the solid angle subtended by each element \( \Delta \omega_d \). Also, if the \( V_{10} \) lens is used in the experiment to increase the solid angle, a further correction would be required. Lastly, as ions pass through an accelerating Pierce gun lens in the detector, refraction will occur, and a correction to the geometric scattering angle is needed. Such calculations have been performed for our apparatus by Abbas [2].

### 8.8 Feasibility of the TOF Experiment

Measurements have been made of the scattered signal and noise rates seen in the ion detector when both beams are running. For a DC beam intensity of \( 3-5 \times 10^{-9} \text{A} \) measured on the final beam monitor and a pulsed target beam repetition rate of 40Hz, width 0.8ms, gated signals of \( 1100 \text{cs}^{-1} \) and \( 3000 \text{cs}^{-1} \) have been recorded in the photon and scattered particle detector (3 angular elements at about 2.2°), with a signal-to-noise ratio of 27:1 and 6:1, respectively. From this measure of the performance, we can estimate the feasibility of the TOF experiment.

#### Signal Rate

In the worst case, for a DC beam one might only see a gated scattered signal rate of \( 100 \text{cs}^{-1} \) scattered into one angular element. If TOF pulsing is run with a gated duty cycle of 10% (see page 180), the scattered signal reduces to \( 10 \text{cs}^{-1} \). One might expect the differential cross section for the inelastic process of interest to be 1000 times smaller than the total DCS at the chosen angle. Hence, in the worst case, the inelastic signal rate will be \( 0.01 \text{cs}^{-1} \). For a 900eV beam, the narrowest profile seen so far is 25ns (page 183). Our data collection system has a time window of 2.56\( \mu \text{s} \) spanning 256 channels, and so the peak will be broadened over 3 channels, with a count rate per channel of \( 3.3 \times 10^{-3} \text{cs}^{-1} \text{cnl}^{-1} \).

#### Noise Rate

The noise rates in the TOF experiment should be very low. Unlike the coincidence experiment, the ion beam is pulsed and so the elastic signal is separated in time from the inelastic, not contributing to the noise. Background noise in our detector should also be insignificant, because a binary coincidence technique is used (see page 151). Even if the gated DC noise rate was \( 50 \text{cs}^{-1} \) (i.e. 2:1 signal-to-noise ratio), the noise per channel
would only be $5 \times 10^{-5} \text{cs}^{-1} \text{cnl}^{-1}$, 1000 times smaller than the inelastic signal rate. A much larger contribution to the noise could come from the elastic peak itself. During the switching period of the X pulsed voltage, slight energy modulation of the leading and trailing edge of the beam can occur, broadening of the far wings of the detected pulse.

To give some idea of how important this effect might be, the spectra shown in Figure 8.9 were examined closely. In one example, the main peak was 400 counts high, and broadened over 20 channels (4ns per channel), with a small tail extending beyond this. We shall take this as a model for the elastic peak shape. An inelastically scattered particle suffering 5eV energy loss would appear 60ns from this peak, where 10 noise counts are seen. As the total number of elastic counts is 4000, received at a rate of 10cs$^{-1}$, the noise rate per channel is $(10/4000) \times 10 \times 2.5 = 62.5 \times 10^{-3} \text{cs}^{-1} \text{cnl}^{-1}$ (where the factor 2.5 arises because one channel corresponds to 10ns in our experiment). Two noise counts are seen where we expect a 10eV peak to appear, and so the appropriate noise rate in this case is $19 \times 10^{-3} \text{cs}^{-1} \text{cnl}^{-1}$. At 20eV, no noise counts are seen.

**Experiment Run Time**

The time taken to collect a peak $k$ standard deviations above the noise level (see page 105) is

$$t \geq \frac{k^2 (N_i + B\tau)}{N_i^2}$$

where $\tau$ is the width of the peak. For the signal and noise rates given above, and a peak width of 3 channels, the time taken to collect a peak 3 standard deviations high will be

- 10eV loss: time = 14 hours
- 5eV loss: time = 44 hours

### 8.9 Summary

In this chapter I have described how the apparatus is set up for performing the TOF experiment. We use a velocity modulation technique to pulse the main beam, and the deflection plates, compressor and timing box are shown to work as designed. The narrowest beam profile recorded so far is 22ns (for a 900eV beam), corresponding to an energy resolution of 1.5eV.

Also, a new data collection system has been installed, and a computer program written to control the collection. The operation of the program is described, and a few minor suggestions are made for improvement. The program is believed to be operating correctly, although as yet a final test of the whole system has not been made. Repairs
to the particle interface are currently in progress.

Thus, all the elements required for running a TOF experiment have been assembled. The feasibility of the experiment depends largely on the performance of the ion beam. The main source of noise in the experiment comes from the tail of the elastic peak itself, and a pessimistic feasibility calculation suggests that the experiment may take up to 44 hours to run. Gains can be made by improving the ion source and hence the beam profile. If necessary, a 'clearing voltage' could be applied, to clean up the elastic peak tail. Also, the current experimental duty cycle of 0.39% can be improved up to 5 times by modifying the pulsing arrangement.

The best energy resolution seen so far is 1.5eV, just sufficient for resolving electronically inelastic processes. With improvements to the ion source, resolutions of 0.5eV should easily be attainable. Thus useful TOF experiments are certainly feasible with improvements to our ion beam, and the technique will prove an excellent back up to the coincidence measurement, allowing new collision systems to be fully explored.
9

The Coincidence Technique

9.1 Introduction

In this final chapter, we return to the elusive coincidence experiment, which the present apparatus was designed to run. Our reasons for wanting to perform this experiment have already been well documented in this thesis. As we saw in chapters 2 and 3, there is an increasing demand for the experimentalist to provide more state-specific data on inelastic collisions. In addition, a deeper understanding of non-adiabatic molecular collisions will only come from experiments that probe the orientational dependence of the collision. One of the few techniques that can provide us with this information is the coincidence measurement. Some of the most valuable measurements made so far are those on the H$_2^+$ + He, Ne and H$_2^+$ + He collision systems by Jaecks et al. [84, 156, 157, 158], using the polarised photon-scattered particle coincidence technique (see pages 34 and 78 for a review).

The coincidence experiment is also one of the hardest to perform. Kessel et al. [41] recommends that

"these coincidence methods are worth using only for critical experiments, particularly where other methods such as total cross section measurements, conventional spectroscopy, and conventional scattered-particle energy-loss measurements are inadequate. Usually it is wise to apply these simpler methods first before beginning a detailed coincidence study on any given collision system"

These warnings are given because coincidence count rates are often small, so long counting times are required, over which the apparatus must remain stable, to obtain a sufficient signal-to-noise ratio. For example, Jaecks et al. [83], in their pioneering Lyman α-scattered (charge exchange) particle coincidence experiment, collected real and random coincidence counts at rates of only 20/hr$^{-1}$ and 200/hr$^{-1}$, despite a main beam current of 10$^{-8}$A (their main problem was the low efficiency of their photon detector). Measurements in which the scattered main beam is monitored without any prior mass, charge or energy selection, are more difficult, as many scattering channels contribute to the random coincidences, including the strong elastic scattering channel. The experiment described in chapters 5 and 6 falls into this category.

It is obviously preferable to run a coincidence experiment which involves some form of initial filtering of the signal, to reduce the random coincidences that occur. In this chapter, a device is described, consisting simply of a pair of deflection plates positioned close to the collision zone, that can remove the elastically scattered particles which make
the biggest contribution to the noise in a scattered ion-photon coincidence experiment. In the following section, the principle behind ‘coincidence blanking’ is revealed, and results of a model illustrate how the device installed in our apparatus can be used. Next, we complete our report of the new data collection system by briefly describing the software that has been written for the coincidence experiment.

Previous workers were in fact able to run a coincidence experiment on our apparatus. They looked at the excitation of $N_2(C^3Π_u)$ in collisions of $He^+ + N_2$, and after 22 hours a baseline of about 24 counts per channel was collected [2]. A peak of four standard deviations was seen above this noise level, although there is still some doubt as to whether this is a true coincidence signal [143]. At that time, the experiment could only be run at a single scattering angle, chosen by guessing where the maximum in the DCS lies. Since then, our aims have been to tackle the problems of high noise and multi-angle detection, and then repeat the measurement. The first two aims have been met by installing the coincidence blanker and the new data collection system, but so far we have not been able to repeat the experiment (although two brief attempts were made). The final two sections then describes in more detail the early experiment, and summarises the work that still has to be done before repeating this measurement.

### 9.2 Coincidence Blanking

#### 9.2.1 Principle

Unlike the TOF experiment, the coincidence experiment is run with a DC beam. Thus, there will always be some particles a certain distance behind the collision zone at the time of the inelastic event, that subsequently scatter elastically and catch up with the inelastic particle at the time of detection. These result in the largest contribution to the random coincidence rate, and the aim in ‘coincidence blanking’ is to remove (or at least diminish) elastic noise using a pair of deflection plates.

To see how this can be achieved, consider inelastic and elastic particles passing through the collision zone, depicted in Figure 9.1. At $t = 0$, the inelastic collision occurs, signified by the detection of a photon shortly afterwards ($t_{hv}$). The particles that will contribute to noise are well separated from the inelastic particle at this stage. After a time ($t_b - t_{hv}$), the inelastic particle has passed through the blanker and so a voltage is applied to the deflection plates. This remains on until the elastically scattered particles have passed through the plates and been deflected, i.e. for a duration ($t'_b - t_b$), where $t'_b$ is the time taken for the elastic particle to reach B2.

As we shall discuss later, the feasibility of coincidence blanking hinges on the separation of elastic and inelastic particles at the blanker. As a rough guide, this can be
9.2. COINCIDENCE BLANKING

\[ t = \frac{\text{Ad}}{\sqrt{B_E \cdot E}} \]

\[ \Delta d = d_{det} \left[ \left( \frac{B_E}{B_E - \Delta E} \right)^{1/2} - 1 \right] \quad (9.1) \]

where \( d_{det} \) is the distance from the collision zone to the detector, 1443mm in our apparatus. (Here, the energy of the inelastic ions has been taken to be \( B_E - \Delta E \), which is not quite correct – see page 192). For a 300eV Ar\(^+\) beam, and an energy loss of 11.05eV, the separation is calculated to be 27mm. Notice that this separation is independent of ion mass, and is directly proportional to \( d_{det} \).

The required delay time \( t_b - t_{hu} \) and pulse width \( t'_b - t_b \) can also be estimated using the equations

\[ t_b = d_{B2} \times \left( \frac{m}{2e(B_E - \Delta E)} \right)^{1/2} \quad (9.2) \]

\[ t'_b = (d_{B2} + \Delta d) \times \left( \frac{m}{2eB_E} \right)^{1/2} \quad (9.3) \]

where \( d_{B2} \) is the distance from the collision zone to B2 (56mm), and \( m \) is the ion mass. For a 300eV Ar\(^+\) beam, taking \( t_{hu} \) to be 30ns, the required delay time is 1498 - 30 = 1468ns, and the pulse width is 2179 - 1498 = 681ns.

Elastic scattering has a cross section that is typically 100–1000 times the inelastic
9.2. COINCIDENCE BLANKING

Figure 9.2. Geometry of the coincidence blanker installed in our apparatus. Also shown is the timing arrangement.

cross section. Because the signal-to-noise ratio is

\[
S/N = \frac{\text{signal count rate}}{\left(\text{noise count rate}\right)^{1/2}}
\]

gains of 10 to 32 times can be achieved using the blanking technique.

9.2.2 Construction of the Blanker

Figure 9.2 shows the geometry of the blanker installed in our apparatus. The left/right deflection plates of length 20mm are positioned 36mm from the collision zone. These plates are boxed in by two surfaces at ground potential containing slits of height several centimetres and width shown in the figure. It is important that when a voltage is applied to one of the deflectors, the electric field does not influence any inelastic ion that has already passed through the blanker, and the grounded plates help to prevent this. The dimensions of the whole device have been chosen to match the solid angle subtended by the ion detector. To install the blanker, some modifications had to be made to the optics cone, and the adjustable slit attached to the cone was removed (see page 149).

Calculations suggest that at least 150V is required to deflect ions away from the ion detector, for all scattering angles and beam energies (up to 1000eV). This can easily be supplied by our Avtech pulsed voltage generator (see page 177). Another consideration is the rise time of the voltage pulse, and again the 3ns rise time of the Avtech voltage pulses is sufficient. To terminate the pulses, two grounded 100Ω resistors of high power rating are attached in parallel to one of the deflectors. A shielded electrical vacuum
9.2. COINCIDENCE BLANKING

feed-through was also constructed.

The timing arrangement for using the coincidence blanker is shown in Figure 9.2. Fast signal pulses from the IPD detector are passed through a delay, and used to trigger the Avtech pulse generator. When setting the time delay, account must be taken of the decay time of the photon (around 30ns), the response time of the IPD (about 20ns), and the internal delay of the Avtech voltage supply (which is designed to be varied between between 100ns and 500ns, but at present is fixed at 0.486µs – see page 185). As we expect photon count rates to be around 1000cs⁻¹, the Avtech generator will run safely below its maximum power output, and also the duty cycle of the experiment will not be affected.

9.2.3 Modelling the Blanker

Two requirements that must be satisfied when using the coincidence blanker are:

1. The elastic particle must be a sufficient distance from the end of the blanker (B2) when the voltage is applied, to ensure that it will be deflected completely out of the detector.

2. The inelastic particle must be a sufficient distance away from B2 when the voltage is applied to prevent its trajectory from being distorted.

Thus, the feasibility of using the device hinges on the separation of the elastic and inelastic particles as the inelastic passes through the blanker. Exactly how far the elastic particle must be from B2 when the voltage is applied will depend on the height of the voltage pulse, and is probably best estimated experimentally. Ideally, the elastic particle will not have reached the blanker (B1) when the voltage is applied, with the inelastic particle several millimeters from (B2).

The timing of the voltage pulse is of course critical; it would be a disaster if an incorrect setting of the delay resulted in loss of the signal as well as the noise! In calculating this time, consideration must be given to uncertainties in the size of the collision zone, the detection time of the photon and the energy spread of the beam.

To investigate the feasibility of coincidence blanking and to calculate accurately the delay time and width of the voltage pulse, a computer program was written. The program is a modified version of the TOF program described on page 176, with the collision and the passage of ions to the detector modelled as before. As reported on page 184, this modelling has already been demonstrated to be accurate, with a range of experimental flight times of reproduced with an accuracy of ±150ns. A listing the program can be found in appendix A.4, page 242.
9.2. COINCIDENCE BLANKING

Figure 9.3. Separation between the elastic and inelastic particles when the inelastic particle is at B2. The target molecule is $N_2$, the scattering angle is $3^\circ$, and the detector high voltage is 50kV.

Feasibility of Coincidence Blanking

Figure 9.3 shows how the gap between the elastic and inelastic particle (positioned at B2) varies with the beam energy, for various $\Delta E$. The scattering partner is taken to be $N_2$, and the scattering angle and detector high voltage are $3^\circ$ and 50kV. The position of B1 and the collision zone are also marked in the diagram.

We see from the figure that the requirement that the elastic particle be outside the blanker when the voltage is applied places a big restriction on the range of beam energies that can be studied. Consider, for example, an energy loss of 11.05eV, the excitation energy of $N_2(C^3\Pi_u)$. For energies greater than 500eV, the elastic particle has already passed B1 when the inelastic is at B2, and so use of the blanker is questionable.

Also taken into account should be the size of the collision zone, and the requirement that the inelastic be some distance beyond B2 when the blanker is fired, as well as uncertainty in the beam energy and photon emission time. Thus, there will in fact be a range in possible inelastic flight times, $t_b$. To guarantee that the inelastic particle is not perturbed by the deflection voltage, the largest delay time in this range should be set. On the other hand, the shortest distance that the elastic particle will be from B2 when the voltage is applied will correspond to the shortest possible inelastic flight time, i.e. for a particle of the highest possible energy suffering an inelastic collision at the front...
9.2. COINCIDENCE BLANKING

<table>
<thead>
<tr>
<th>BE</th>
<th>$t_b$ (ns)</th>
<th>$t'_b - t_b$ (ns)</th>
<th>Gap (mm)</th>
<th>Detection Time ($\mu$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2718 (856)</td>
<td>4031 (1212)</td>
<td>92 (88)</td>
<td>71.424 (22.514)</td>
</tr>
<tr>
<td>200</td>
<td>1860 (588)</td>
<td>1326 (409)</td>
<td>45 (44)</td>
<td>49.316 (15.580)</td>
</tr>
<tr>
<td>300</td>
<td>1504 (475)</td>
<td>706 (219)</td>
<td>31 (30)</td>
<td>40.120 (14.360)</td>
</tr>
<tr>
<td>400</td>
<td>1296 (409)</td>
<td>454 (141)</td>
<td>23.9</td>
<td>34.759 (10.988)</td>
</tr>
<tr>
<td>500</td>
<td>1156 (365)</td>
<td>323 (101)</td>
<td>19.8</td>
<td>31.141 (9.845)</td>
</tr>
<tr>
<td>600</td>
<td>1053 (333)</td>
<td>245 (76)</td>
<td>17.1</td>
<td>28.490 (9.008)</td>
</tr>
<tr>
<td>700</td>
<td>973 (308)</td>
<td>194 (61)</td>
<td>15.2</td>
<td>26.439 (8.360)</td>
</tr>
<tr>
<td>800</td>
<td>910 (287)</td>
<td>158 (50)</td>
<td>13.8</td>
<td>24.791 (7.839)</td>
</tr>
<tr>
<td>900</td>
<td>857 (271)</td>
<td>132 (41)</td>
<td>12.7</td>
<td>23.429 (7.409)</td>
</tr>
<tr>
<td>1000</td>
<td>812 (257)</td>
<td>113 (35)</td>
<td>11.8</td>
<td>22.279 (7.045)</td>
</tr>
</tbody>
</table>

Table 9.1. Table giving $t_b$ and $(t'_b - t_b)$, for different Ar$^+$ beam energies. Also given is the separation of the inelastic and elastic particles at $t_b$, and the time taken for the inelastic to reach the detector. Values in brackets are for He$^+$. The target molecule is taken to be N$_2$, and the energy loss is 11.05eV (the excitation energy of N$_2$(C$^3$I$_u$)). The scattering angle is 3°, and the detector high voltage is 50kV.

of the collision zone.

The collision zone in our apparatus is designed to have dimensions 0.3 $\times$ 0.3 $\times$ 10mm. In fact, we know from measurements made using the optics system that the collision zone is probably larger than this, say 1mm. Assume also that the inelastic particle must be 5mm from B2 when the blanker is fired. For a 500eV beam, the energy spread will be about $\pm 1$eV, introducing a small spread in flight times of about $\pm 1.5$ns. This is negligible compared to the uncertainty in $t_h$ of $\pm 30$ns, which leads to an uncertainty of $\pm 1.5$mm in the flightpath length. Summing these contributions, the closest distance that the elastic particle can be from B2 when the blanker is fired is 20 (from Table 9.1) $-$ 1mm (CZ) $-$ 5mm (B2) $-$ 1.5mm ($t_h$) = 12.5mm. The feasibility of using the blanker at this energy is thus borderline, depending on whether a high enough voltage can be applied to the deflectors without perturbing the inelastic ion that is 5mm in front of B2 when the voltage is applied. At 700eV, the gap reduces to about 7.5mm, and it is unlikely that an experiment can be run.

We conclude therefore that coincidence blanking is certainly feasible for beam energies up to 400eV, and impossible for energies higher than 700eV.

Using the Coincidence Blanker

Table 9.1 lists the time that an inelastic particle takes to reach B2 ($t_b$) and the subsequent times that the elastic particle takes to pass through the blanker ($t'_b - t_b$), for various beam energies. Also given is the separation between elastic and inelastic particles at the time of blanking, and the detection time of the inelastic particle.

To set the Avtech time delay, other factors must be considered including the photon detection time, the length of the collision zone, the position of the inelastic from B2 when the voltage is applied, and finally the beam energy spread. For the case of a beam
energy of 300eV, an energy spread of ±1eV introduces a small uncertainty of ±3ns in the time delays and widths given in the table. A collision zone length of 1mm introduces an additional uncertainty of ±13ns in $t_0$, and the inelastic particle will take an extra 134ns to reach 5mm beyond B2. Assuming the photon emission time is 30 ±20ns, and knowing that the response time of the IPD is about 20ns, the required time delay is

$$\text{time delay} = 1504 - 10(h\nu) - 20(IPD) + 13(CZ) + 134(B2) + 3(\Delta BE)$$

$$= 1624\text{ns}$$

This time delay will ensure that there is no chance of the inelastic particle trajectory being perturbed when the blanker voltage is applied. The setting of the pulse width is less critical; the voltage should be on for the duration that the elastic takes to pass through the blanker, and not so long that the next inelastic event is perturbed. From Table 9.1, the minimum time that should be set is 706ns.

In fact, the coincidence time and the blanker delay time can be measured experimentally if a pulsed beam is passed through the apparatus. For example, accurate coincidence times can be measured if the beam is pulsed using the TOF compressor (chapter 8), with the timing started by the detection of a photon from the collision zone. By pulsing the beam instead using the blanker deflection plates, the flight time from the blanker to the detector can be measured, and the difference between the two measurements will give a check of the blanker time delay.

The deflection voltage required should be sufficient to deflect ions that have scattered through the largest scattering angles entering the blanker (about 8.5°) across to negative angles (i.e. out of the detector). As has been mentioned, this is probably best set experimentally, although calculations suggest that for a 900eV beam, about 150V is required. Consideration must also be given to where the elastic particle is when the voltage is applied. If it lies within the blanker, then a larger voltage must be set to compensate for the shorter time traversing the field gradient. This can be calculated using the approximate relation

$$\tan(\theta) = \text{constant} \times \frac{V \times l}{BE} \quad (9.4)$$

where $\theta$ is the angle through which the ion is deflected, $l$ is the length traversed in the electric field and $V$ is the blanker voltage. For example, if 50V is found experimentally to be sufficient to deflect a 500eV particle that traverses the full length of the blanker (20mm), then for a 900eV particle traversing only 13mm, the voltage required is $(900/500) \times (20/13) \times 50 = 138V$, approximately.
9.3. COINCIDENCE DATA COLLECTION

9.2.4 Summary

In this section we have seen how a pair of deflection plates can be used to 'clean' the scattered ion signal in a coincidence experiment. The feasibility of coincidence blanking hinges on the separation of the elastic and inelastic particles when the blanker is fired, as well as a host of experimental uncertainties such as the size of the collision zone, the detection time of the photon, the required clearance of the inelastic ion from B2 and the beam energy spread. A computer model suggests that blanking will be feasible in our apparatus for beam energies up to 400eV, and impossible for energies greater than 700eV.

To use the device, the time at which the blanker is fired is critical, and account must be taken of the experimental uncertainties involved. A computer program has been written to aid this calculation. The time that the deflection voltage should be left on for, and the voltage that should be applied are less critical. The model suggests settings for the pulse width, and the required voltage can be measured experimentally.

Although use of the coincidence blanker is rather restricted in our apparatus, it will nevertheless prove to be a valuable tool in our coincidence experiment. Gains of up to 10 times in the signal-to-noise ratio can be expected, allowing us to extend coincidence measurements to lower beam energies, where total cross sections for inelastic processes are smaller.

Finally, we remark that the ultimate limit on the range of useful beam energies is set by the flightpath length to the detector. In our apparatus, this is about 1.4m, although in the literature flightpaths of up to 7.5m have been reported [29]. For a given detector position, the range of useful energies is determined by our ability to confine the strong electric field to between the deflectors, to prevent inelastic trajectories from being influenced. This in turn is set by the exit slit size, and the only factor preventing us from placing the device very close to the collision zone, where small slits could be used, is the emission time of the photon. Lastly, we note that there are alternative ways of removing the elastic signal in the experiment. A velocity-modulation lens could also be used to accelerate the elastic noise to times of no interest. With this device, the inelastic particle outside the lens would be less influenced by the electric field, as the final plate of the lens is at ground potential.

9.3 Coincidence Data Collection

The timing arrangement for collecting data in the coincidence experiment has already been described on page 152. Briefly, the ion detector interface records the time difference between receiving a (delayed) fast photon pulse and detecting a ion in any of the 45 angular elements. A 32 bit word is then sent to the computer, encoding the photon wavelength (16 bits: 0–255 channels), the flight time (8 bits: 0–255 channels), the
scattering angle (6 bits: 0–44) and the signal/noise flag (2 bits). The same computer and parallel I/O interface that was described on page 154 stores these words in a large buffer, and a program has been written (COINCDA) to decode and analyse the words.

In this section, we complete the report on our data collection arrangement by describing the operation of the new computer program COINCDA. Much of the program is identical to the program TOFN used in TOF data collection. The data, however, has extra dimensionality because of the wavelength information, and so a number of small changes and new features have been included in the program. Here, we detail these changes. A listing of the program can be found in appendix A.6, page 255.

9.3.1 The Data Collection Program

Starting the Program

The program is started by switching on the computer and typing the program name, COINCDA. As before (page 188), the user is asked for the experiment I.D., the update rate and the data dump time. In addition, ‘lower and upper wavelength limits (0–126)’ must be specified. The range given corresponds to the number of channels across the sensitive area of the IPD, and can be converted to wavelength after calibrating the optics. During an experiment, the observed spectral line will only span a number of these channels, and so the limits returned are used to determine which events correspond to true coincidences.

The program then begins the process of decoding the words in the buffer. The important difference from the TOF program here is that it is assumed from the outset that only the scattered signal (signal-noise) is of interest. Thus, no permanent record is kept of the individual events occurring in each signal and noise period. Only events with wavelengths occurring within the specified range are recorded as coincidences. The coincidence wavelength range is further divided into 10, and a record is kept of where each coincidence occurs within this range.

At regular time intervals set by the update rate and the data dump time, selected information is sent to the screen (see page 188), and coincidence data is stored in the file ‘\data\con.data’. This file lists the experiment I.D., the particle detector correction factors, the spectrum collected (over the entire 128 channels) and finally the coincidence data (in two columns).

The Function Keys

At any time while the program is running, function keys can be pressed to ask the computer to perform a number of different tasks:
9.3. COINCIDENCE DATA COLLECTION

F1 Time-of-flight distribution.
F2 Angular distribution.
F3 Live 2D plot.
F4 ID and logging data.
F5 Initialise data stores.
F6 Engineer (hasn’t been installed yet).
F7 Wavelength distribution.
F8 Write data to a file.
F9 Terminate the program.
F10 Help.
F11 Scale up (used in 2D plotting).
F12 Scale down.

Most of these functions (F4, F8, F9, F10, F11, F14) are identical to those in TOFN (see page 189), and the main change has been to replace the ‘tune up mode’ by a plot of the wavelength distribution. When plotting the angle (F1), time (F2) or wavelength (F7) distribution, only the scattered signal is plotted. The user is asked whether the coincidence or the full spectrum is to be plotted. If the full spectrum is asked for, then all of the events that arrive at each time (0-255) / angle (0-44) / wavelength (0-127) are plotted. If the coincidence spectrum is required, then a selection is made of the ranges of the other two variables, and in the case of wavelength, only the coincidence range (0-10) is offered or plotted.

The ‘live 2D plotting’ (F3) is also slightly different in this program. Only the scattered signal at each time and angle location is plotted (summing over the coincidence wavelength range), and an ‘update’ is not offered, with the entire spectrum collected (the ‘history’) shown on the screen. Again, keys F11 and F14 are used to change the sensitivity of the display, and the mode is terminated by pressing F3.

9.3.2 Performance of the Coincidence Data Collection

The same comments given on the TOF data collection system apply here, as well. After a thorough exploration of the different program functions, it is thought that the program COINCDA contains no mistakes. Thus, photon, angular, and time distributions have been reproduced accurately on the screen, and the 32 bit words are decoded correctly. However, the most important test, to check that there is no data lost or altered during analysis, and that count rates are reproduced accurately, has not yet been made. Repairs to the particle interface are currently in progress, and final tests are envisaged in several weeks time.

A number of improvements can be made to COINCDA. At the moment, no permanent record is kept of the events received in each signal and noise period, and from the outset, the difference between these is taken. This makes the analysis of the random coincidence count rate more difficult at the end of an experiment. Other small problems have already been commented on. The data could be better organised in the permanent file, and records should be kept of the experimental run time and the total ‘dead’ time. Also, protection should be offered to certain function keys to prevent loss of data.
9.4 Attempts at the Coincidence Experiment

To test the apparatus, a well documented collision process must be found, in which the electronically excited state decays by emission of a photon in the range 200–800nm. There should be only small contributions from cascading states, and the scattering should onset at narrow angles and have a reasonable cross section. The collision systems we have chosen that satisfy these criteria are:

\[ \text{He}^+(\text{Ar}^+) + \text{N}_2(X^1\Sigma_g^+, \nu = 0) \rightarrow \text{He}^+(\text{Ar}^+) + \text{N}_2(C^3\Pi_u, \nu = 0, 1) \]

In this section, we describe 3 attempts at detecting coincidences between the \( \text{N}_2(C^3\Pi_u \rightarrow B^3\Pi_g) \) photon and a scattered ion. We begin by reviewing the available data on the \( \text{He}^+(\text{Ar}^+) + \text{N}_2 \) collision systems. This has come from energy loss and spectroscopic measurements. A feasibility calculation is then given before our measurements are described.

9.4.1 Available Data on \( \text{He}^+(\text{Ar}^+) + \text{N}_2 \) Systems

Energy Loss Measurements

The most complete measurements on the \( \text{He}^+ + \text{N}_2 \) collision system have been reported by Dowek et al. [50, 52, 54]. Only excitation of the target \( \text{N}_2 \) is seen, and at least 6 distinct direct excitation channels can be identified, as well as a range of exothermic and endothermic charge exchange channels – see Figure 9.4. In some cases, vibronic levels were resolved [50, 52]. Excitation of \( \text{N}_2(C^3\Pi_u) \) is marked by the symbol \( \gamma \).

Differential cross sections for these processes are seen in Figures 9.5(a) and (b). We see from (a) that the charge exchange channels are by far the most important, accounting for some 80\% of all collisions that scatter into the angular range 0.5-2.5keV°. Inelastic scattering, in contrast, occurs in only 1\% of these collisions, onsetting in the range 0.5-1keV°. Figure 9.5(b) shows in more detail the DCS for the inelastic channels, relative to the ‘quasielastic’ channel. The figure neglects to show the DCS for the \( \text{N}_2(C^3\Pi_u) \) state, which probably lies between the \( \beta \) and \( \epsilon \) curves. Thus, at 2keV°, the ratio \( \sigma_{el}(\theta)/\sigma_{\epsilon}(\theta) \) is around 0.01, and \( \sigma_{\epsilon}(\theta) \) is still rising beyond 2.5keV°.

Energy loss data for the \( \text{Ar}^+ + \text{N}_2 \) collision system is less complete [65]. Again, it is found that the charge exchange channels dominate over all other inelastic channels [65]; the probability of charge exchange rises rapidly at 2keV° to 50\%, where it remains constant up to angles above 6keV°. Fernandez et al. [65] managed to resolve two peaks and a shoulder in the energy loss spectra for direct excitation. The first corresponds to ro-vibrational excitation of \( \text{N}_2 \) in its ground electronic state. The second at around 10eV arises from the excitation of a range of \( \text{N}_2 \) electronic states, of which \( A^3\Sigma_u^+ \) and \( B^3\Pi_g \) were tentatively identified. The shoulder, positioned at around 16eV is due to the
Figure 9.4. Potential energy curves and typical energy loss spectra recorded by Dowek et al. for the He$^+ + \text{N}_2$ collision system. A range of electronic states are excited through direct and charge exchange collisions. Excitation of $\text{N}_2(C^3\Pi_u)$ is denoted by $\gamma$. (Taken from [54]).
9.4. ATTEMPTS AT THE COINCIDENCE EXPERIMENT

Figure 9.5. (a) Reduced DCS for the He$^+ + N_2$ collision system. The curves $\rho_e$, $\rho_{el}$ and $\rho_{inel}$ refer to charge exchange processes, elastic scattering and electronic excitation of $N_2$. (b) Relative probabilities of direct electronic excitation of $N_2$. X refers to elastic scattering. (Taken from [54]).

ionisation of $N_2$. No DCS are available for this collision system.

Spectroscopic Measurements

There have been a number of spectral scans reported on the He$^+(Ar^+) + N_2$ systems [78, 87, 88] and related systems [14, 18, 132]. Generally it is found that the $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ emission dominates the spectra (300-450nm). The most intense fluorescence from $N_2$ are the $N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g) (0,0)$ and (1,1) emission lines, at 333 and 337nm. The $C$ state is populated directly from inelastic collisions, and fluorescence is rapid, about 30ns. There are also small contributions from cascading states, for example from the $E^3\Sigma_g^+$ state [18]. Other weak emissions are seen from N and the collision partner, and from $N_2^+(C \rightarrow X)$ and $N_2(B \rightarrow X)$.

Spectroscopic measurements have been made with our apparatus as well. Figure 9.6(a), shows the emission spectra recorded from He$^+ + N_2$ collisions over the range 320-350nm. The strongest emission is from the $N_2^+(B)$ state, and an atomic $N^+$ line is also seen. Spectra were recorded over a range of beam energies, and it is found that the ratio of the $N_2C(0,0)$ and $N_2^+B(2,0)$ line intensities increases with collision energy (see Figure 9.6(b)). Thus, for the coincidence experiment, there is significant advantage in working at higher collision energies.
Figure 9.6. (a) Fluorescence spectrum recorded from He$^+$ + N$_2$, for a beam energy of 850eV. (b) Ratio of N$_2$C(0,0)/N$_2^+$B(2,0) fluorescence observed in He$^+$ + N$_2$ collisions as a function of the He$^+$ beam energy.
9.4.2 Feasibility of the Experiment

Before running a coincidence experiment, it is important to run through the feasibility calculation, to see how long the experiment must be run for. The worst case calculation we give here is based on the same equations given on page 103, and the same symbols are used.

The rates at which atoms and ions are detected are

\[ N_i = (n \times vol) \times (F \times \Delta \theta \times \sigma_{tot}(\theta)) \times f \]  
(9.5)

\[ N_{h\nu} = (n \times vol) \times (F \times \sigma_{tot}) \times (q \times (\Delta \phi/4\pi) \times frac) \]  
(9.6)

where \( \Delta \phi \) is the solid angle subtended by the photon detector, and \( frac \) is the fraction of photons emitted from excited state \( i \) that contribute to the spectral line observed. The number of coincidences is

\[ N_c(\theta) = (n \times vol) \times (F \times \Delta \theta \times \sigma_i(\theta)) \times f \times (q \times \Delta \phi/4\pi \times frac) \]  
(9.7)

which combines with eqn (9.6) to give

\[ N_c(\theta) = N_{h\nu} \times \Delta \theta \times \sigma_i(\theta)/\sigma_{tot} \]  
(9.8)

The random coincidence rate is

\[ B = (N_{h\nu} + B_{h\nu}) \times N_i(\theta) \times \tau \]  
(9.9)

where \( B_{h\nu} \) is the background noise of the photon detector and contributions from other processes. Hence the time required to collect a peak with a signal-to-noise ratio of \( k \) is

\[ t_{obs} \geq \frac{k^2(N_c + B)}{N_c^2} \]  
(9.10)

In the experiments we shall be describing, the photon and ion count rates were approximately the same, ranging from 250\( cs^{-1} \) to 1000\( cs^{-1} \). In the worst case, let us take \( N_{h\nu} \) and \( N_i \) to be 200\( cs^{-1} \), and assume that only 75% of the photons observed contribute to the emission time. The geometric solid angle subtended by the ion detector, \( \Delta \theta \) is \( 5.4 \times 10^{-6} \) steradians. Let us assume that this doubles with the use of lens \( V_{10} \). The efficiency of the detector in the worst case might be 25%. Finally, we expect the coincidence peak to be only about 40ns broad, due to the beam energy spread and the emission time of the fast photon. Substituting these numbers into eqn (9.10), and taking
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$k$ to be 3, we obtain

\[ t_{\text{obs}} \geq \frac{30.6 \text{ hours}}{(\sigma_i(\theta)/\sigma_{\text{tot}})^2} \]

Again, we see that the feasibility hinges on the cross section ratio, which rapidly worsens for larger scattering angles. In chapter 6 (page 114), the likely value of the ratio for forward peaked scattering was discussed at length, typical ratios $\sigma_i(\theta)/\sigma_{\text{tot}}$ were seen to range from 1 to 5 for reduced scattering angles of 2000eV. If this is the case, our experiment is feasible. In the unlikely case that scattering has an isotropic distribution, the ratio is $1/4\pi$ and our experiment is not feasible.

A discussion of the feasibility of coincidence experiments has already been given on page 106. As in the K-CH₃I coincidence experiment, here the noise rate is much larger than the signal rate, and so one cannot expect to make gains by increasing the beam intensity. Much more important is the efficiency of the detectors, and large gains can be made by optimising $f \times \Delta \theta$. The maximum ion detector efficiency possible is 50%, rising to 70% if the high voltage is increased above 50kV [34]. Also, it is essential to use the $V_{10}$ lens to increase $\Delta \theta$, and gains of more than two times (assumed in this calculation) are possible.

Finally, we note that if the coincidence blanker is used, the noise due to elastic scattering is removed, and the only other contribution to the noise will come from other inelastic processes. The random coincidence rate is thus reduced by up to 100 times and at best can be ignored in comparison to $N_c$. Hence, required observation time is

\[ t_{\text{obs}} \geq \frac{k^2}{N_c} \frac{6.7 \text{ hours}}{\sigma_i(\theta)/\sigma_{\text{tot}}} \]

9.4.3 The Preliminary Experiment

We have seen so far that the excitation of the N₂($C^3Π_u$) state produces the strongest fluorescence in the He⁺(Ar⁺) + N₂ collision systems, and that this process onsets at small scattering angles, peaking beyond 2000 eV. In addition, the inelastic to elastic cross section ratio is typical at 0.01. For a 900eV He⁺ beam, Abbas [2] measured photon count rates during the signal (noise) gates of $87\text{cs}^{-1}$ ($9\text{cs}^{-1}$). At 2.1°, the corresponding scattered particle rates (in 3 angular elements) were $240\text{cs}^{-1}$ ($120\text{cs}^{-1}$). With these signals, a coincidence experiment was run.

The experiment was certainly not run under optimum conditions. As the particle interface unit had not been built at that time, only one angular measurement at 2.1° could be taken. Also, the photons collected over the spectral range of 330–340nm included some photons from other transitions, as well as the two $C$ state emissions. A photon signal rate of $0.5 \times 87\text{cs}^{-1}$ might be realistic. Notice that the ion detector noise
He$^+$ + N$_2$ Coincidence Spectrum

Figure 9.7. Coincidence spectrum collected by Abbas [2], after 21.8 hours. Also shown is the curve that results from passing a noise filter through the data, and the appropriate 3 and 4 standard deviation levels.

The rate was high (120cs$^{-1}$). The detector is designed to eliminate background noise, and so the noise seen is probably due to the bad angular divergence of the main beam. Lastly, the ion detector could have been run more efficiently, as the lenses V$_{10}$ and V$_{11}$ were not used. Assuming the ion detector efficiency is 0.25, and taking $\sigma_i(\theta)/\sigma_{tot}$ to be 2, the feasibility calculation suggests that a run time of 20.4 hours is required to see a significant peak 3 standard deviations high. In fact, the experiment was run for 21.8 hours, and the spectrum collected with a multichannel analyser is shown in Figure 9.7.

The mean counts per channel is 24, with a standard deviation of 7. A peak is seen at channel 198, containing 57 counts. Is this peak significant? A noise filter with a ‘box’ size of 3 channels (see page 112) was passed through the data and is also shown in Figure 9.7. The peak is now seen clearly, and lies more than 4 standard deviations above the white noise. A check showed that the background noise has a normal distribution, and so the peak is statistically significant.

The peak width of 30ns is approximately what one would expect. The fluorescence lifetime is around 30ns, and an additional broadening of 10ns is introduced by a beam energy spread of ±2eV. The position of the peak at 6.97μs is also approximately where it should appear, although calculations in 3 different reports [2, 69, 143] give predictions ranging from 6.26μs to 7.15μs!

However, there are a number of problems with the result. Figure 9.7 shows only
200 channels, the data reported by Abbas [2]. The original measurement would have spanned more channels, and no clear record has been kept of this original raw data. Data has been found on a computer file, but this appears to have been corrupted, with 4000 counts added to the first 300 channels. Careful comparisons between the two sources suggest that some preliminary data 'smoothing' had been performed, although this is not reported by Abbas. Hence, we cannot have confidence that the peak seen in Figure 9.7 is a coincidence, despite the fact that its size and position is what we would expect. Another run of the experiment is clearly required.

9.4.4 Further Attempts at the Coincidence Experiment

Careful measurements of the \( \text{N}_2(\text{C} \rightarrow \text{B}) \) count rate suggested that a 50\% gain in signal (at 900eV) could be obtained if an Ar\(^+\) beam was used instead of He\(^+\). Thus, our work since the preliminary experiment has concentrated on the Ar\(^+\) + N\(_2\) collision system.

Two attempts were made to repeat the coincidence measurement. Unfortunately, neither the data collection system nor the coincidence blanker had been installed at the time of these measurements, and so as before a multichannel analyser was used to collect the data. To increase the scattered ion signal, three angular elements (\( \sim 3^\circ \)) were multiplexed together. The MCA was gated so that separate spectra during the signal and noise periods were collected. In both attempted experiments, the beam energy was 900eV.

Experiment 1

In the first experiment, photons and scattered ions were detected with a gated rate of about 870cs\(^{-1}\) (S:N = 22:1) and 1200cs\(^{-1}\) (3.5:1). The noise rate in the ion detector was large because of the angular spread in the main beam. The beam intensity was measured on the final beam monitor to be \( 4.4 \times 10^{-9} \text{A} \), which was attenuated by 20\% (ungated) when both beams were running. The optics were centred at around 337\text{ns} to collect light from the N\(_2\)C(1, 0) line. The fast photon signal was passed through a delay of 20.48\text{\mu s}, and the coincidence window was 5\text{\mu s}, containing 256 channels. Making the same 'worst case' assumptions as before, the feasibility calculation suggested that a run time of about 9.12 hours was required.

After 3.9 hours, problems with the apparatus forced the experiment to be stopped. Baselines of 2670ccnl\(^{-1}\) and 43ccnl\(^{-1}\) had been collected during the signal and noise periods. This is 10 times more than is predicted from the count rates measured at the start of the experiment, suggesting that count rates in the ion and photon detectors had increased to 2256cs\(^{-1}\) and 4296cs\(^{-1}\) during the course of the experiment. No peaks were seen in the spectrum more than 3 standard deviations above the noise. The predicted height after 4 hours is 1.7 standard deviations.
9.5. THE FUTURE

Experiment 2

A second attempt at the experiment was made, with the aim of running the experiment for a much longer time. At the start of the experiment, the photon and ion count rates were $1100\text{cs}^{-1}$ (27:1) and $3000\text{cs}^{-1}$ (6:1), respectively. All other settings were identical to before. However, during the run problems were experienced with sparking inside the ion detector chamber, and after 11 hours the measurement had to be abandoned because the signal-to-noise ratio in the ion detector had deteriorated to 0.8:1!

9.5 The Future

The apparatus has certainly been improved since the early measurement of Abbas [2]. A new data collection system has been installed, and is almost ready for final testing. The system will allow measurements at 45 angles to be made simultaneously. Also, a coincidence blanker has been built, which for energies up to $700\text{eV}$ can be used to significantly reduce the noise. The success of the experiment now depends on the reliability of the apparatus.

Problems With the Apparatus

The main problem with the apparatus, which has prevented us from performing successful experiments, is the stability of the ion beam. As has been fully discussed in chapter 7, the ion source needs a small modification, and the extraction lens and post-analyser lenses require redesigning. The optics and the target beam have always been reliable. The ion detector is found to be rather difficult to use, as all ion lenses ($V_{10}$, $V_{11}$, Pierce gun, electron focus, electron deflectors) as well as 10 photomultiplier discriminators require optimising before the detector can run with maximum efficiency. Also, there is a wide variation in sensitivity across the angular elements.

Running An Experiment

Before running the experiment, a number of careful measurements must be made.

1. The angular sensitivity of the detector must be normalised. However, this will only become stable after the photomultipliers have been left on for over 8 hours. Normalisation of the detector is described on page 169, and requires the beam to be swept using a saw-tooth wave form.

2. The beam energy must be carefully measured. This is probably best done by calibrating the energy analyser. The accelerating voltage cannot be relied upon, because of contact potentials and more importantly the local potential in the plasma region (see page 160).
3. By pulsing the ion beam, the arrival position of the elastic and hence the inelastic particles can actually be measured (see page 205), allowing the time delay to be set accurately. The delay and the coincidence time window must be accurately calibrated prior to an experiment.

Also, during the experimental run, careful records should be kept of the ion and photon counts collected, and of the experimental run time.

Concluding Comments

Although the coincidence technique is clearly difficult, our apparatus does have much promise for the future, after simple improvements to the ion source and optics have been made. The apparatus has the advantage that both detectors are efficient, and that data at different scattering angles can be collected simultaneously. The experiments are feasible, especially if the coincidence blanker is used. A wide range of collision systems can be studied, and the acquired data is rich in information. It is hoped that funding can be found to allow future workers to complete this work.
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Appendix A
Computer Programs

A.1 FLIGHT

A.1.1 Purpose
Program FLIGHT is used to predict coincidence times in the K + CH₃I coincidence experiment.

A.1.2 Description
The program actually consists of 4 separate subprograms DET1, DET2, DET3 and DET4. The main part of the program offers a menu to the user, calls the appropriate subprogram, and then prints out results to the screen and to a file.

DET1 calculates coincidence times given the ion mass and excitation energy. After initialising variables, subroutines BASH and TIMES are called which model the collision and the two detectors. DET2 is an extension of DET1, with the fragmentation of the parent ion modelled by calling subroutine SPLIT. DET3 is used to calculate the time-focusing voltages $V_{\text{ext}}$ and $V_{\text{ms}}$ (given the excitation energy). Both OPTV1 and OPTV2 are called to run the optimisation algorithms. Finally, DET4 was written to calculate the excitation energy from the results of a coincidence experiment. Here, the optimisation of $\Delta E$ is handled by subroutine OPTEL. A description of the model is given on page 95.

A.1.3 Example Input/Output

menu

[1] calculate coincidence time for ion given $v_1, v_2, v_3$ & $e_{\text{loss}}$
[2] as [1], but modelling fragmentation
[3] find $v_1$ & $v_2$ to focus detector, given $v_3$ & $e_{\text{loss}}$
[4] find $e_{\text{loss}}$ for an ion, given a coincidence time

please select 1 to 4

1

enter k atom energy (eV)
500

enter molecular weight of ion (amu)
141.939
  enter trial eloss (eV) & scattering angle (deg)
  15 0
  enter trial voltages v1,v2,v3
  30 1800 12000
  enter Vpcpo (0 gives ideal Vpcpo)
  33
  enter atom detector voltage
  18000

RESULTS

K atom energy = 500.000 eV
weight of ion = 141.939 amu
Eloss = 15.000 eV
scatt. angle = 0.000
a-det voltage = 18000.00 V
a-det time = 95.840 ns
Vpcpo = 33.0000000000

(x,y) Tion Tatom Tcoin (xx,zz)

-2.5,-0.5 : 14242.013 : 12291.601 : 1950.412 : -8.3,-2.7
-2.5, 0.5 : 14229.007 : 12291.601 : 1937.406 : -8.3,-7.7
 2.5,-0.5 : 14242.506 : 12293.150 : 1949.356 : -15.3,-2.8
 2.5, 0.5 : 14229.347 : 12293.150 : 1936.197 : -15.4,-7.8

Average coincidence time = 1847.503 +/- 7.146 ns
run again? (y/n) n

A.1.4 The listing
program menu

10 print 1000,'(1) calculate coincidence time for ion given v1,v2
10 print 1000,'(2) as (1), but modelling fragmentation'
10 print 1000,'(3) find v1 & v2 to focus detector, given v3 & eloss'
10 print 1000,'(4) find eloss for an ion, given a coincidence time'

c display menu.....
10 print 1000,'menu'

print*,'(1) calculate coincidence time for ion given v1,v2
print*,'(2) as (1), but modelling fragmentation'
print*,'(3) find v1 & v2 to focus detector, given v3 & eloss'
print*,'(4) find eloss for an ion, given a coincidence time'

read *,num

if ((again.eq.'y').or (again.eq.'Y')) goto 10
print*,run again ?
read '(al)',again

common/mvar/fg2128,fg28ms,fgmshv
common/mvar/fge,fgep,fgp20,fg2021
implicit double precision (a-h,m,p-z)

subroutine detl(vl,v2,v3,v15)

write(jj,1000) time(1)*1d9,tatom
write(jj,1001) time(1+4)*1d9,time(1+8)*1d9,
1 time(16+1),time(20+1)

if (num.eq.1) call det1(vl,v2,v3,v15)
endif
if (num.eq.2) call det2(vl,v2,v3,expl,ang4,ang5)
if (num.eq.3) call det3(vl,v2,v3,v15)
if (num.eq.4) call det4(vl,v2,v3,v15)
c calculate atom detection time
write(jj,1001) time(1)*1d9,tatom

end subroutine detl(vl,v2,v3,v15)

implicit double precision (a-h,m,p-z)
common/mvar/fg2128,fg28ms,fgmshv
common/mvar/fge,fgep,fgp20,fg2021
implicit double precision (a-h,m,p-z)

subroutine detl(vl,v2,v3,v15)

write(jj,1000) time(1)*1d9,tatom
write(jj,1001) time(1+4)*1d9,time(1+8)*1d9,
1 time(16+1),time(20+1)

if (num.eq.1) call det1(vl,v2,v3,v15)
endif
if (num.eq.2) call det2(vl,v2,v3,expl,ang4,ang5)
if (num.eq.3) call det3(vl,v2,v3,v15)
if (num.eq.4) call det4(vl,v2,v3,v15)
c calculate atom detection time
write(jj,1001) time(1)*1d9,tatom

end subroutine detl(vl,v2,v3,v15)
133 c call times to calculate coincidence times......
134 call times(v1,v2,v3,v15,flag)
135 c convert back angl......
136 angl=angl*57.29578
137 c return to menu and display results......
138 return
139 end

140 subroutine det2(v1,v2,v3,expl,ang4,ang5)
141 implicit double precision(a-h,m,p-z)
142 common/mvar/fge,fgep,fgp20,fg2021
143 common/mvar/fg2128,fg28ms,fgmsnv
144 common/mvar/ekl,emf,angl,ang2
145 common/mvar/ekl,eloss,ml,time(30)
146 common/mvar/mm,mk,emz,rpmco
147 print *,enter trial e loos (eV) & scattering angle (deg)'
148 read *,ml
149 print *,enter molecular weight of ion (amu)'
150 read *,mi
151 print *,what is fragmentation energy & orientation angles 2 ' 2
152 read *,expl,ang4,ang5
153 convert anq4,ang5 to radians
154 angl=ang4/57.29578
155 eloss=expl
156 c call split to calculate initial fragment velocities
157 c call optel to compute close
158 call split (expl,ang4,ang5) 235
159 c call bash to give initial molecular velocities
160 call bash
161 print *,enter trial voltages v1,v2,v3'
162 read *,v1,v2,v3
163 c ask for starting values......
164 print *,enter k atom energy (ev)'
165 read *,eki
166 print *,enter molecular weight of ion (amu)'
167 read *,mi
168 print *,enter trial voltages vl,v2,v3 '
169 read *,vl,v2,v3
170 c convert angl to radians
171 call times(v1,v2,v3,v15,flag) 237
172 c return to menu and display results......
173 return
174 end

175 subroutine det3(v1,v2,v3,v15)
176 implicit double precision(a-h,m,p-z)
177 common/mvar/fge,fgep,fgp20,fg2021
178 common/mvar/fg2128,fg28ms,fgmsnv
179 common/mvar/ekl,emf,angl,ang2
180 common/mvar/ekl,eloss,ml,time(30)
181 common/mvar/mm,mk,emz,rpmco
182 print *,enter trial voltages vl,v2,v3'
183 read *,vl,v2,v3
184 c ask for starting values......
185 print *,enter k atom energy (ev)'
186 read *,eki
187 print *,enter molecular weight of ion (amu)'
188 read *,mi
189 print *,enter trial e loos (eV) & scattering angle (deg)'
190 read *,eloss,angl
191 convert angl to radians
192 angl=angl*57.29578
193 c return to menu and display results......
194 return
195 end

196 subroutine det4(vl,v2,v3,v15)
197 implicit double precision(a-h,m,p-z)
198 common/mvar/mm,mk,emz,rpmco
199 common/mvar/fge,fgep,fgp20,fg2021
200 common/mvar/fg2128,fg28ms,fgmsnv
201 common/mvar/ekl,emf,angl,ang2
202 common/mvar/ekl,eloss,ml,time(30)
203 common/mvar/mm,mk,emz,rpmco
204 print *,enter trial voltages vl,v2,v3'
205 read *,vl,v2,v3
206 c ask for starting values......
207 print *,enter k atom energy (ev)'
208 read *,eki
209 print *,enter molecular weight of ion (amu)'
210 read *,mi
211 print *,enter trial voltages vl,v2,v3'
212 read *,vl,v2,v3
213 c convert angl to radians
214 call times(v1,v2,v3,v15,flag) 237
215 c return to menu and display results......
216 return
217 end

218 subroutine det1(v1,v2,v3,expl,ang4,ang5)
219 implicit double precision(a-h,m,p-z)
220 common/mvar/fge,fgep,fgp20,fg2021
221 common/mvar/fg2128,fg28ms,fgmsnv
222 common/mvar/ekl,emf,angl,ang2
223 common/mvar/ekl,eloss,ml,time(30)
224 common/mvar/mm,mk,emz,rpmco
225 c calculate the various constants....
226 data ee,const/1.602e-19,2.30630427577d-23/
227 pki=((n lk*ekj)**0.5)*const
228 b(2*pki*cos(angl))
229 mel2=eloss*mm*const*const
230 c__(pki*pki*(1_mm/rnk)+mel2)/(m jn / m k+1)
231 d=(b*b_4*c(**0.5
232 pkf=(b+d(/2
233 pmf=((nin/mk)*(pki*pki_pkf*pkf)_mel2)**0.5
234 ang2=asin((pkf/pmf)*sin(angl))
235 ang2=sign(ang2,angl)
236 ekf(pki*pkf)/(mk*const*const)
237 emf=(pmf*pmf) / (j*coflst*coflst)
238 c calculate energy of fragment after splitting
239 c ready to compute pkf,pmf & ang2....
240 pkf=(b+c)/(d+e)
241 pmf=((mm/mk)*pkf*(pkf+pkf)*me12)/(mm/mk+1)
242 d=(b+c)***0.5
243 c ready to compute pkf,pmf & ang2....
244 pkf=(b+c)/(d+e)
245 pmf=((mm/mk)*pkf*(pkf+pkf)*me12)/(mm/mk+1)
246 c ready to compute pkf,pmf & ang2....
247 pkf=(b+c)/(d+e)
248 pmf=((mm/mk)*pkf*(pkf+pkf)*me12)/(mm/mk+1)
249 c ready to compute pkf,pmf & ang2....
250 c calculate the various constants....
251 pkf=(m*ekl)**0.5
252 b(2*pkf*cos(angl))/(mm/mk+1)
253 me12=eloss*(mm*const*const
254 c(pki*pkf*(1-mm/mk+me12))/(mm/mk+1)
255 d=(b+c)**0.5
256 c ready to compute pkf,pmf & ang2....
257 pkf=(b+c)/(d+e)
258 pmf=((mm/mk)*pkf*(pkf+pkf)*me12)**0.5
259 ang2=asin(pkf/pmfsin(angl))
260 ang2=sin(angel(2,angl))
261 c convert final momenta to energy (ev) units....
262 ekf=(pkf*pkf)/(mk*const*const)
263 emf=(pmf*pmf)/(mm*const*const)
264 c calculate energy of fragment after splitting.....

265 subroutine det(v1,v2,v3,v15)
266 implicit double precision(a-h,m,p-z)
267 common/mvar/fge,fgep,fgp20,fg2021
268 common/mvar/fg2128,fg28ms,fgmsnv
269 common/mvar/ekl,emf,angl,ang2
270 common/mvar/ekl,eloss,ml,time(30)
271 common/mvar/mm,mk,emz,rpmco
272 c call bash to give initial molecular velocities
273 call bash
274 print *,enter molecular weight of ion (amu)'
275 read *,mi
276 print *,enter scattering angle (deg)'
277 read *,angl
278 convert angl to radians
279 angl=angl*57.29578
280 print *,enter trial voltages v1,v2,v3'
281 read *,v1,v2,v3
282 c ask for starting values......
283 print *,enter k atom energy (ev)'
284 read *,eki
285 print *,enter molecular weight of ion (amu)'
286 read *,mi
287 print *,enter trial voltages v1,v2,v3'
288 read *,v1,v2,v3
289 c convert angl to radians
289 angl=angl/57.29578
290 print *,what is fragmentation energy & orientation angles 2 '
291 read *,expl,ang4,ang5
292 convert anq4,ang5 to radians
293 angl=ang4/57.29578
294 eloss=expl
295 c a...
265 \[ emf = em' \times (m/m) \]
266 \[ emz = em' \times (m/m) \]
267 return
268 end
269 subroutine split(expl, ang4, ang5)
270 implicit double precision(a-h,m-p-z)
271 common/mvar/fge, fg20, v20, v21
272 common/mvar/fg2128, fg28ms, fgmshv
273 common/mvar/fk1, floss, nm, time(30)
274 common/mvar/mm, mk, emz, rpccp
275 convert back emf,...
276 \[ emf = em' \times (m/m) \]
277 \[ emz = em' \times (m/m) \]
278 \[ v20 = (v20 - vms) / (m/m) \]
279 \[ v21 = (v21 - vms) / (m/m) \]
280 c calculate new velocity components...
281 v20 = (v20 - vms) / (m/m) * cos(ang4) * sin(ang5)
282 v21 = (v21 - vms) / (m/m) * cos(ang4) * sin(ang5)
283 \[ v20 = v20 \times \cos \theta \]
284 \[ v21 = v21 \times \cos \theta \]
285 \[ v28 = v28 \times \cos \theta \]
286 c calculate field gradients...
287 \[ fge = v20 / d20 \]
288 \[ fgep = v21 / d20 \]
289 \[ fgp20 = v20 / d20 \]
290 \[ fgp21 = v21 / d20 \]
291 c calculate ion flight time...
292 if (flag.eq.0) then
293 \[ \text{time} = \text{time} + \text{time}(\text{calc}) \]
294 \[ \text{time} = \text{time} + \text{time}(\text{calc}) \]
295 \[ \text{time} = \text{time} + \text{time}(\text{calc}) \]
296 \[ \text{time} = \text{time} + \text{time}(\text{calc}) \]
297 \[ \text{time} = \text{time} + \text{time}(\text{calc}) \]
298 end subroutine split
397 time(1l+8)=time(1l)-time(1l+4)
398 time(1l+16)=xxx
399 time(1l+20)=zzz
400 z=z
401 130 continue
402 150 continue
403 c calculate average coincidence time & max time diff......
404 time(25)=(time(9)+time(10)+time(11)+time(12))/4
405 time(26)=0
406 do 170,11=9,12
407 if ( (abs(time(i1) -time(25) ) ) .gt.time(26)  )then
408 time(26)=abs(time(i1) -time(25))
409 endif
410 continue
411 return
412 end
413 subroutine optvl(vl,v2,v3,v15)
414 implicit double precision(a-h,m,p-z)
415 common/mvar fg,fge,fgep,fgp20,fg2021
416 common/mvar fge,fgep,fgp20,fg2021
417 common/mvar fg2128,fg28ms,fgmshv
418 common/mvar ekf,emf,ang1,ang2
419 common/mvar ek1,loss,ml,time(30)
420 common/mvar/mm,emz,rpcpo
421 c initialise variables before entering loop.....
422 flag=0
423 call times(vl,v2,v3,v15,flag)
424 ttt=time(26)
425 xx=vl/3
426 vlv1
427 10 vlvl+xx
428 if (abs(v2/vlv-1).lt.ld-5) goto 20
429 call optv2(vl,v2,v3,v15)
430 if (time(26).gt.ttt) xx=xx/3
431 vlvvl
432 goto 10
433 goto 10
434 20 return
435 end
436 subroutine optv2(vl,v2,v3,v15)
437 implicit double precision(a-h,m,p-z)
438 common/mvar fg,fge,fgep,fgp20,fg2021
439 common/mvar fg2128,fg28ms,fgmshv
440 common/mvar ek1,loss,ml,time(30)
441 c initialise variables before entering loop.....
442 flag=0
443 call times(vl,v2,v3,v15,flag)
444 ttt=time(26)
445 x=x/2
446 v2v1
447 10 v2v2+x
448 if (abs(v2/vv2-1).lt.ld-6) goto 20
449 flag=0
450 call times(vl,v2,v3,v15,flag)
451 if (time(26).gt.ttt) x=x/2
452 ttt=time(26)
453 v2v2
454 goto 10
455 20 return
456 end
457 subroutine optel(vl,v2,v3,tcoin)
458 implicit double precision(a-h,m,p-z)
A.2 RATIO

A.2.1 Purpose

This program was written to compute the DCS onsets and cross section ratios in the K + CH$_3$I coincidence experiment. A description of the model is given on page 115. Four potential surfaces are considered, and the classical deflection function for different paths is computed using the small angle formula.

A.2.2 Description

The strategy is to compute the DCS up to the point at which the small angle formula begins to fail (identified by monitoring the shape of the deflection function). Extrapolation routines are then used to extend the cross section to larger angles.

The program begins by asking the user to choose the trajectory path and enter initial parameters. A loop is then set up in which the impact parameter is stepped from the crossing point (where the excitation channel opens) to zero. Subroutine CALCULATE is called to return the deflection function and cross section for each impact parameter. This routine evaluates eqns (6.7) and (6.8), which involves calling CLOSE to calculate the distance of closest approach, and DEFNEU and DEFION, which evaluate the integral for neutral and ionic surfaces. In the main program, results from different branches of the deflection function are separated, because different impact parameters can contribute to the same scattering angle. ANALYSE is then called to extrapolate the cross section to wide angles and compute the cross section ratio (at 2.94° and 3.94°). Final results are printed to the screen and to a file. The calculated DCS shape is also printed to a file.
A.2.3 Example Input/Output

path11: ->ex(neu), early crossing
path12: ->ex(neu), late crossing
path21: ->ex(ion) ->ex(neu), early crossing
path22: ->ex(ion) ->ex(neu), late crossing
path31: ->(ion) ->ex(ion) ->ex(neu), early crossing
path32: ->(ion) ->ex(ion) ->ex(neu), late crossing
path41: ->(ion) ->ex(neu), early crossing
path42: ->(ion) ->ex(neu), late crossing
path5: ionic surface only
path6: neutral surface only

Rc1,Rc2,Rc3,Rc4,Rc5,Rc6  ......
  2.86800003051758   2.56399989128113   2.4639998664856
  2.29999995231628   2.27999997138977   5.00000000000000

which path do you want to compute?
32
adash1,adash2,alpha1,alpha2 (1.5,0.75,4.0,6.25)
1.5 0.75 4 6.25
rm1,rm2? (3.2,3.2)
3.2 3.2
impact parameter step? (-0.001)
-0.001
rdcsmax? (1000) (prevent class. mech. failure)
1000
Rc, onset angle (eVdeg), ratio(2.94), ratio(3.94)
RDCS peak position, height:-
  2.300 163.95 1.948 1.446 165.929 46.284

A.2.4 The Listing
endif 199 call defneu(l, epsl, sigl, b, dca, rmax, defa)
100 call defneu(l, epsl, sigl, b, dca, rc3, defb)
101 call defneu(l, epsl, sigl, b, dca, rc3, defc)
102 call defneu(l, epsl, sigl, b, dca, rc3, defd)
103 def=defa+defb+defc+defd
104 gdef=(defbit-def)/db
105 if (path.eq.31) then 106 prob=1
107 sig=prob*b/(abs(gdef)*sin(abs(def)))
108 endif
109 c path12 = ->ex(neu), late crossing 110 c calculate the def function
111 call defneu(1, epsl, sigl, b, dca, rmax, defa)
112 call defneu(1, epsl, sigl, b, dca, rc3, defb)
113 call defneu(1, epsl, sigl, b, dca, rc3, defc)
114 call defneu(1, epsl, sigl, b, dca, rc3, defd)
115 def=defa+defb+defc+defd
116 gdef=(defbit-def)/db
117 gde=defbit-def/db
118 if (path.eq.21) then 119 prob=1
120 sig=prob*b/(abs(gdef)*sin(abs(def)))
121 endif
122 123 call defneu(1, epsl, sigl, b, dca, rmax, defa)
124 call defneu(1, epsl, sigl, b, dca, rc3, defb)
125 call defneu(1, epsl, sigl, b, dca, rc3, defc)
126 call defneu(1, epsl, sigl, b, dca, rc3, defd)
127 def=defa+defb+defc+defd
128 def=defa+defb+defc+defd
129 gdef=(defbit-def)/db
130 if (path.eq.22) then 131 prob=1
132 sig=prob*b/(abs(gdef)*sin(abs(def)))
133 endif
134 135 call defneu(1, epsl, sigl, b, dca, rmax, defa)
136 call defneu(1, epsl, sigl, b, dca, rc3, defb)
137 call defneu(1, epsl, sigl, b, dca, rc3, defc)
138 call defneu(1, epsl, sigl, b, dca, rc3, defd)
139 def=defa+defb+defc+defd
140 gdef=(defbit-def)/db
141 prob=1 142 sig=prob*b/(abs(gdef)*sin(abs(def)))
143 endif
144 145 call defneu(1, epsl, sigl, b, dca, rmax, defa)
146 call defneu(1, epsl, sigl, b, dca, rc3, defb)
147 call defneu(1, epsl, sigl, b, dca, rc3, defc)
148 call defneu(1, epsl, sigl, b, dca, rc3, defd)
149 def=defa+defb+defc+defd
150 gdef=(defbit-def)/db
151 if (path.eq.22) then 152 prob=1
153 sig=prob*b/(abs(gdef)*sin(abs(def)))
154 endif
**Note:** The image contains a block of code that appears to be written in a FORTRAN-like programming language. The code segments are numbered from 265 to 338, and they include various mathematical and logical operations, which seem to be part of a larger algorithmic process. The code is structured into several functions and subroutines, each performing specific calculations related to ion-neutral interaction and potential calculations.

### Key Concepts and Code Snippets

- **Function Definitions:** Subroutines such as `defneu`, `defion`, `close`, and others, which perform calculations related to deflection functions, potential calculations, and boundary conditions.
- **Mathematical Expressions:** Use of trigonometric functions like sine, cosine, and exponential functions.
- **Loop Statements:** Use of `DO` loops to iterate through calculations.
- **Conditional Statements:** `IF` statements to conditionally execute different code blocks based on input parameters.

### Example Snippet

```fortran
265 c path4l = ->(ion) ->ex(neu), early crossing
266 if (path.eq.41) then
267 c calculate the def function
268 call defneu(l,eps,l,sigl,b,dca,rmax,defa)
269 call defneu(l,eps,l,sigl,b,dca,rmax,defb)
270 call defion(adashl,rml,alphal,b,rcl,rmax,defa)
271 call defion(adashl,rml,alphal,b,dca,rmax,defd)
272 defbit=defa+defb+defc+defd
273 c calculate d(def)/db
274 call close(bbit,dca)
275 call defneu(l,eps,l,sigl,bbit,dca,rmax,defa)
276 call defneu(l,eps,l,sigl,bbit,dca,rmax,defb)
277 call defion(adashl,rml,alphal,bbit,dca,rmax,defc)
278 call defion(adashl,rml,alphal,bbit,dca,rmax,defd)
279 defbit=defa+defb+defc+defd
280 goto 273
281 gdef=(defbit-def)/db
282 c calculate the DCS
283 prob=1
284 sigma=prob*b/(abs(gdef) * sin(abs(def)))
285 endif
```

### Additional Notes

- **Function Calls:** The code calls various subroutines like `close`, `defneu`, and `defion` to carry out the calculations.
- **Mathematical Formulas:** Use of formulas involving trigonometric functions and logarithms to calculate the deflection and potential functions.

This code snippet is part of a larger program that likely deals with simulations or calculations in a physics or engineering context, possibly related to plasma physics or quantum mechanics.
y1 = 0.3125*t1 - 0.3125*sin(t1)*cos(t1)  
if (jfail.eq.1) goto 5

y2 = 0.3125*t2 - 0.3125*sin(t2)*cos(t2)

y = y2 - y1

return

end

subroutine deflon(adash,rrn,alpha,b,rl,r2,def)
imPLICIT DOUBLE Precision(a-h,p-z)
common/const/pi,be

... subroutine calculations ...

calculate the cross section ratio...

calculate the cross section ratio...
A.3 COMPRESSOR

A.3.1 Purpose

Program COMPRESSOR models the TOF compression lens. The optimum Z pulse voltage is calculated, as well as flight times from the X plates to the compressor, and from the compressor to the detector.

A.3.2 Description

The computation involves calculating the detection time of ions positioned at both the front (A) and the back (B) of the compressor when $V_z$ is applied. In the main program, after various parameters have been asked for, the flight time from B to A is calculated (an acceleration region). Subroutine TOF is then called, to obtain the flight time from A to the detector. On return, the average time and the spread in times is calculated. An iteration is set up to find the voltage $V_z$ that is required to minimise the spread in times. Final results are then printed to the screen and to a file.

In subroutine TOF, the calculation of the detection time of an ion at A is broken into several stages: $A \rightarrow CZ$, $CZ \rightarrow S1$, $S1 \rightarrow S2$, $S2 \rightarrow S3$ (S1, S2 and S3 are the pierce gun plates), $S3 \rightarrow Al$ (the aluminium plate), $Al \rightarrow G$ (a grounded plate that electrons are accelerated to), $G \rightarrow Sc$ (the scintillators). The routine calls subroutine BASH to get the final beam energy (eV) of the projectile after a collision with N$_2$. The collision is treated classically, and assumes the N$_2$ target is stationary. Relevant equations of motion were taken from Morse and Bernstein [109], and are reproduced on page 192.

A.3.3 Example Input/Output

He or Ar beam ? (1/2) 2
Beam energy, detector high voltage ? 900 50000
Scattering angle, Eloss (cm) ? 3 11.05
BE (eV) = 900.00 detector HV (V) = 50000.0 ion = 2
eloss (eV) = 11.05 scatang (deg) = 3.000
B to A time (uS) = 1.5835
vcomp (V) = 125.75 Vcomp*8/7 (V) = 143.72
width (ns) = -0.01
detection time (uS) = 26.0437 X to Z time (uS) = 10.2994

A.3.4 The listing
block data
implict double precision(a-h,m,p-z)
common/mvar/mtarg,mion,scatang
common/mvar/eloss,constl,hv
data mtarg/28/
end

program compressor
implict double precision(a-h,m,p-z)
common/mvar/mtarg,mion,scatang
common/mvar/eloss,constl,hv
data he,ar,dcomp,const/4,39.9,108,13.89133d3/ c cOflst = (2e/amu)**0.5
else mion=he endif const2=const/melec**0.5 c convert scatang from degrees to radians.... print*,Beam energy, 	detector high voltage ?' scatangr = scatang*17.45329d_3
data dczsl,dsls2,ds2s3,ds3al, dalg,dgsc/1443, 18, 10, 200, 13.89133d3/ vcomp=145 c call BASH to calculate post collision beam energy.... call bash(be,bescat) flag=0
vla=const* (be/mb) **0.5 c time from x plates to compressor
wl=mt*vl/(mb+mt)
txpulse=679.5d3/vb
e1=(vl/const)**2*nib*mt/(mb+mt)
wlf=wl*(1_eloss/e1)**0.5 c add up total time (us) & return........
te=tac*tcs+tal+ta2+ta3+tal+tgsc*1d3 vcm=(mb*vl)/(mt+mb)
open (unit=10,file='coinpressor.out') do 800, 
write (iunit,992) be,ion 801 write (iunit,993) vcomp,vcompbit
802 write (iunit,994) tav,twidth 803 write (iunit,995) epulse	 continue
804 format (lx,'BE 	 (eV) 	 = ',f7.2,15x,'ion 
805 format (lx,'detector HV 	 (V) 	 = ',f7.1,15x,'scatang (deg) 
806 format (lx,'eloss 	 (eV) 	 = ',f5.2,14x,'B to A time 	 (uS) 	 = ',f7.4,4x,'Width 	 (nS) 	 = ',f5.2)
807 format (lx,'X to Z time 	 (US) 	 = ',f7.4)
c print out results.....
open unit=991,file='compressor.out')
do 800, 
write (iunit,990) be,ion 801 write (iunit,991) hv,scatang 802 end
A.4 BLANKER

A.4.1 Purpose

Program models the coincidence blanker that is installed in our apparatus. The deflection voltage time delay and pulse width that are required to use the device are calculated, and the coincidence time is also given. No corrections are made in the program for the response times of the photon and ion detector electronics, the internal delay of the Avtech pulse generator, or the photon emission time.

A.4.2 Description

Much of the program is the same as in program COMPRESSOR. In the main program, a loop is set up to determine the position of the elastic particle behind the collision zone ($d_{acx}$) when the inelastic event occurs. Both subroutine TOF and BASH are called within this loop, to calculate flight times to the detector. After $d_{acx}$ has been found, the required time delay and width are calculated. Subroutine POSITION is then called to compute the gap between the elastic and inelastic ions when the inelastic has reached B2. Final results are printed to the screen and to a file.

A.4.3 Example Input/Output

He or Ar beam? (1/2)  
2  
detector high voltage, scatt. angle, eloss ?  
50000 3 11.04  
be? 900  
BE = 900.000000000000 ion= 2  
detector HV = 50000.0000000000 scatang = 3.00000000000000  
eloss = 11.0400000000000  
flight time from cz = 23.4289020006074  
position of elastic from cz at t=0 (mm) = 9.07211303710938  
Blanker voltage delay (ns) = 856.957693907851  
Blanker voltage width (ns) = 132.187491353480  
elastic to B2 distance (mm) = 12.6920871513589  
again? (0/1) 0

A.4.4 The Listing
block data
  implicit double precision(a-h,m,p-z)
  common/mvar/mtarg,mion, scatang
  common/mvar/constl, hv
  data mtarg/28/
end

program blanker
  implicit double precision(a-h,m,p-z)
  common /mvar/mtarg,mion, scatang
  common/mvar/constl, hv
  data he,ar,const/4,39.9,13.89133d3/

  c \t const = (2e/amu(0.5
  c \t ask for initial parameters ......
read 5
  if (ion.eq.2 ) then
  mion ar
else
  mionhe
endif
  constl=const/mion**0.5
  print','detector high voltage, scatt. angle, 
read',hv,scatang, eloss
  c \t convert scatang to radians .......
  scatang = scatang*17.45329d_3
  print 5
  read*, be
  C
  B1 is 36mm from cz, B2 is 20mm from B1
  c \t first calculate the arrival time of inelastic
  call tof(be,eloss,0,tinel,tinelb2)
  c \t setup a loop to calculate position of noisey elastic
  flag=0
dacz50
daczbit=dacz/4
  c \t call tof to calculate time for elastic....
90 \t call tof(be,0,dacz,tel,telb2)
  C
  compare timings (nanosec), and decide whether dacz is ok...
  tnoise=(tel-tinel) 5 ld3
  if 	 (abs(tnoise).gt.0.01) 	 then
  if 	 (tnoise.gt .0) 	 then
  if 	 (flageq.0) 	 daczbit=daczbit/4
  f1ag1
dacz=dacz-daczbit
  endif
  if 	 (tnoise.1t.0) 	 then
  if 	 (flag.eq.1) 	 daczbit=daczbit/4
dacz=dacz+daczbit
flagO
  endif
else
  goto 100
endif
90 continue
  c now can calculate the required delay
  c taken for the inelastic to reach B2, and the pulse voltage width
50 \t (defined as telb2-tinelb2)
tdelay= (telb2-tinelb2)*1d3
50 \t width= (telb2-tinelb2)*1d3
50 \t call position(tinelb2,dacz,BE,delb2)
50 \t now print out results and finish
open (unit=10, file='blanker.out')
do 310, 10, 10
write (unit,*) 'BE = ',BE,'ion=',ion
write (unit,*) 'detector HV = ',hv,'scatang = '
100 continue
}

time from A -> C1
vcz=constl*be**0.5
tacz=dacz/vcz
if (tacz*1d3.gt.tinelb2) then
  separation=dczbl+dblb2+(dacz-vcz*tinelb2*1d-3)
goto 100
endif
elastic lies somewhere between Cz and B2
call BASH to calculate post collision beam energy....
call bash (be,bescat,eloss)
Cz -> B1.....
vs1=constl*bescat**0.5
separation=dczb1+dblb2-((tinelb2/1d3-tacz)*vs1
1 *cos(scatang)
sep2 = (telb2-tinelb2)*1d-3*vs1*cos(scatang)
100 return
end

subroutine bash (be,bescat,eloss)
implicit double precision(a-h,m-p-z)
common/mt,mb,scatang
common/const1,hv
data const/13.89133d3/
v1=const* (be/mb) **05
wl=mt*vl/ (mb+rnt)
e1 (vl/const) **2**mt/ (mb+mt)
w1fwl*(1+loss/el)**0.5
vcm=mb*vl/(mt+mb)
v1f=vcm*cos(scatang)+(vcm**2*(cos(scatang)**2-1)+w1f**2)**0.5
bescat=(v1f/const)**2*mb
return
end
A.5 TOFN

A.5.1 Purpose

Program TOFN is used to control data collection in the TOF experiment. Words stored in the computer interface buffer are decoded, and the data is displayed on the screen during the experiment and stored in a file at the end of the experiment – see page 187. The program was written by Dr Fluendy.

A.5.2 Description

The program is huge, containing 30 separate subroutines (!), and is written in Microsoft BASIC.

After initialising all variables (via INITIALISE), the user is asked to input various running parameters (via IDDATA). The computer interface and various ports are then set up (CONFIGDIO, CONFIGTIMEPLOT, CONFIGANGLEPLOT, CONFIGDISPLAY), the buffer is initialised (via START), and data collection begins.

Data collection and decoding are controlled by a loop – lines 101 to 130. Firstly, the contents of the buffer are checked (PROGRESS), and all unprocessed words are analysed by DECODE. If the buffer is found to be full, with all the words decoded, START is called again. In the remaining part of the loop, data can be sent to the screen (via RUNNINGDATA), the ‘live 2d plot’ is updated (in DECODE), or the ‘tune’ data is updated (via TIMEPROFILE or ANGLECHECK).

While the loop is in progress, function keys can be pressed, and the program diverts temporarily to perform other tasks. Function ENTRYKB$ ensures that data collection continues if the computer is waiting for some response from the keyboard (by again setting up a loop: PROGRESS → DECODE → START). The routines that are called by each function key can be identified on lines 64 to 75. These routines in turn call other routines, and signposts are given in the listing.

A.5.3 The Listing
Program TOFN
rem written by Dr. Flynnady, documented by A. Cooke

rem order of the routines: MAIN, INITIALISE, CONFIGDIO, CONFIGTIMEPLOT, CONFIGANGLEPLOT, 
rem IDDATA, ENGINEER, PERFORMANCEPLOT, CONFPERFORMANCEPLOT, 
rem NORMALISE, DIAGNOSIS, PHOTO, TUNE (F7), DUMP (F8), TERMINATE

rem (F9), HELPP (F10), SCALEUP (F11), SCALEDOWN (F14), CLGRAPH
rem
rem $DYNAMIC
rem $INCLUDE: 'C:\LW\INCLUDE\LWSSYSTEM.INC'
rem $INCLUDE: 'C:\LW\INCLUDE\GPIB.INC'
rem $INCLUDE: 'C:\LW\INCLUDE\FORMATT.INC'
rem $INCLUDE: 'C:\LW\INCLUDE\GRAPHICS.INC'
rem $INCLUDE: 'C:\LW\INCLUDE\ANALYSIS.INC'
rem $INCLUDE: 'C:\LW\INCLUDE\DATAACQ.INC'
rem $INCLUDE: 'C:\LW\INCLUDE\RS232.INC'
rem common shared /prev.cnt/ prev.cnt&
rem common shared /curr.cnt/ curr.cnt&
rem common shared /total.cnt/ total.cnt!
rem common shared /oldupdate/ oldupdate&
rem common shared /dataupdate/ dataupdate&
rem common shared /tstcnt/ tstd.cnt&
rem common shared /angcnt/ ang.cnt%
rem common shared /tflag/ tflag%
rem common shared /live.tflag/ live.tflag%
rem common shared /code/ code%
rem common shared /noise.cnt/ noise.cnt&
rem common shared /sig.cnt/ sig.cnt%
rem common shared /currt.cnt/ currt.cnt!
rem common shared /old.tcnt/ old.tcnt%
rem common shared /store.cnt/ store.cnt&
rem common shared /dead.tcnt/ dead.tcnt!
rem common shared /store.time/ store.time&
rem common shared /profile.time/ profile.time!
rem common shared /time.time/ time.time%
rem common shared /estart.time/ estart.time!
rem common shared /store.timestore.cnt!(100), storenoise.rat%(100)
rem common shared /storetime!(100)
rem common shared /store.data(32000), tof.data(45,256,1)
rem common shared /time.data(256), angle.data(45), angnc.data(45)
rem common shared /time.data(256), angle.data(45)
rem common shared /corr.fct(45)
rem call start
rem buffer full
rem call start
rem note only counts dead time at end of buffer
rem i.e. operator use of plotting etc not included
rem accumulates dead time in processing
rem 40 long string
rem time of flight data capture from DIO32f board
rem rem time of flight data capture from DIO32f board
rem
rem 40 long string
rem key 15, chr(0)+chr$(72)
rem key 16, chr(0)+chr$(80)
rem rem and down keys for scaling 2d display
rem for cnt% = 0 to 45
rem corr.fct(cnt%) = 1.0
rem next
rem starts off collecting at unormalised condition
rem on key(1) gosub plottime
rem on key(2) gosub plotangle
rem on key(3) gosub plot2d
rem called by MAIN, F5, TUNE
rem clears all arrays and variables before prog start
Initialisa:
for cnt%=0 to 32700
buffer.dat%(cnt%)=0
next
for cnt%<4 to 44
for acnt%=0 to 44
for tcnt%=0 to 255
tof.dat%(acnt%, tcnt%, cnt%)=0
next
next
cnt%=0 to 255
time.dat%(cnt%)=0
next
cnt%=0 to 44
CANG.DAT&(cnt%)=0
iangle.dat&(cnt%)=0
angle.dat&(cnt%)=0.0
next
cnt%=0 to 255
itime.dat&(cnt%)=0
time.dat&(cnt%)=0.0
next
cnt%=0
currcnt&=0
total.cnt!0
sample.cnt&=0
prev.cnt&=0
dead.time!0.0
print " all tof data stores initialised -"
print "play "t180 o2 p2 p8 l8 qgg 12 e- p24 p8 l8 fff 12 d"
for t%=1 to 100
storetime!(t%)=0
storenois.rate!(t%)=0
storesig.rate!(t%)=0
next
tint.fct%=1
live.flag%=0
return

rem subroutine CONFIGDIO
rem called by MAIN
rem configure interface pulse +ve edge invert ack.
sub configdio
board.dat%8
err.num1%=init.da.brds (1,board.dat%) err.num2%=dig.grp.config(1,1,2,0,0)
err.num3%=dig.grp.mode(1,1,1,0,0,1,1)
end sub

rem subroutine CONFIGTIMEPLOT
rem called by MAIN
rem configures port ready for time plot
sub configtimeplot
call grfreset(4)
time.port %=createport (0,25,100,70)
call setportvisibility(time.port%,0)
call settitle("TIME OF FLIGHT")
call setplotmode(0)
call setpointstyle(1)
call SETDATATYPE(2)
call SETDATATYPE(1)
call setaxauto(0)
call setaxrange(0,0,45,9)
call setaxauto(1,21)
call setaxname(0,"ANGLE")
call setaxname(1,"COUNTS")
end sub

rem subroutine CONFIGDISPLAY
rem called by MAIN, PLOT21), ENGINEER
SUB CONFIGDISPLAY
SCREEN 12
REM VIEW (20,21)-(620,272), 1
REM WINDOW (0,0)-(620,272)
REM SET GRAPHICS AREA
VIEW PRINT 23 TO 30
REM PUS TEXT INTO BOTTOM OF SCREEN
rem
rem
rem subroutine START
rem called by MAIN, DIAGNOSE, ENTRYKB$
sub start
err.num4%=diq.b1ock.in (1,1,buffer.dat%,32000)
if tflag%<1 then
print "Collecting data!
endif
total.cnt!=curr.cnt&+total.cnt'
prev.cnt&0
curr.cnt&=0
sample.cnt&=0
end sub

rem subroutine PROGRESS
rem called by MAIN, ENTRYKB$
sub progress
rem checks for sufficient data or completion
prev.cnt&=curr.cnt&
remain%=0
err.num1%=dig.block.check (1,1,remain%)
curr.cnt%=32000-remain%
end sub

rem subroutine DECODE
rem called by MAIN, ENTRYKB$
sub decode
rem decodes 16 bit unsigned integer to angle,time, code
rem works from prev.cnti-1 to curr.cnt&
rem code=1 is noise; code=0 is signal
if prev.cnt&=curr.cnt& then
exit sub

endif

a%prevcnt&+l
for count%a% to curr.cnt&
remubb%0
temp%buffer.dat%(count%-1)
if temp%<16384 then
rem take 2a complement
temp%=32767+temp%
rem noise
tcode.dat%=0
else
tcode.dat%=1
while tcode.dat%=0
rem rubbish
endif
if tcode.dat%<0 then
tangle.dat%=(temp%/256.)-0.5
if tangle.dat%<45 then
temrubb%=temrubb%+1
endif
rem ALL TESTS FOR OFLO IN DECODE REMOVED CAUTION
rem if tangle.dat%<0 then
rem ternrubb%=temrubb%+1
rem endif
rem if ttime.dat% > 256 then
rem temrubb%=temrubb%+1
rem endif
rem if ttime.dat%<0 then
rem temrubb%=temrubb%+1
rem endif
if tangle.dat%45 then
tangle.dat%=0
endif
if temrubb%>0 then
rubbish%=rubbish%fl
endif
next
decode

entrykbs
ENTRY KB$ = NT RY KB$
end function

timeprofile
rem subroutine TIMEPROFILE
rem called by MAIN
rem calculates posn and width of time peak in noise mode
sum%=0.0
sumt%=0.0
plast.time%=profile.time!
for cnt%=0 to 255
in!=cnt%
sumt!=time.dat&(cnt%)*jn!*10+swnt!
next
if sumt%>0 then
Tmean ! sumt /sum!
suint
tadev! sumt! mum!
tsdev! =sqr(tadev!)
if p.time!>0.0001 then
arr.rate!=sum!/p.time!
endif
print "arrival rate(s-1) =",arr.rate!
endif
print "mean arrival time(elastic) =",Tmean!
profile.time!="profile.time!-plast.time!
plast.time!=profile.time!
for cnt%=0 to 255
x%=10.0*in!-tmean!
x%=x%*x%
sum%=time.dat&(cnt%)*x%+sum!
next
Tadev!=sum!/sum!
tadev!=sqr(tadev!)
print "mean=",x%
print "std.dev=",tadev!
if p.time%!0.0001 then
arr.rate!=sum!/p.time!
print "arrival rate(s-1) =",arr.rate!
end function
print "mean arrival time(elastic) =",Tmean!
print "std.dev of arrival time=",Tadev!
rem clear time.dat store before next clk
for cnt%=0 to 255
time.dat&(cnt%)=0
next
decode
end sub
rem subroutine ANGLECHECK
if e.tlme'<>0 then
rem called by MAIN
count.rate!=(curr.cnt&-sample.cnt&)/e.tlme'
SIG_RATE!=(sig.cnt&/e.tlme')
SIG_RATE(S-I)= SIG_RATE;
PRINT "GLOBAL TIME (S)";curr.time!;
ELAPSED TIME(SECS)=e.tlme!
print "EVENT RATE(S-1)";count.rate!;
SIG_RATE(S-I)= SIG_RATE;
SIG_RATE(S-I)= SIG_RATE;
noise.rate!=noise.cnt&/e.tlme'
noise.rate=SIG_RATE(S-I);
noise.rate=SIG_RATE(S-I);
noise.rate=SIG_RATE(S-I);
SIG.RATE!=SIG.CNT/(E.TIME!)
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SIG.RATE!=SIG.CNT/(E.T...
for ang.cnt%<= 44
for time.cnt%<lint% to topinct%
Cang.data(ang.cnt%)=Cang.data(ang.cnt%)+tof.data(ang.cnt%,time.cnt%,time.cnt%,
chosenencode%)
TANGLE.data (ANG.CNT%)=CANG.data(ANG.CNT%)*CORR.FCT(ANG.CNT%)
next
call config2d
if answer$="N" then
rem scattered signal as difference
for ang.cnt%<0 to 44
for time.cnt%<lint% to topinct%
Cang.data(ang.cnt%)=Cang.data(ang.cnt%)+tof.data(ang.cnt%,time.cnt%,
0)-tof.data(ang.cnt%,time.cnt%,1)))*CORR.FCT(time.cnt%)
next
call gfrfreset(0,flag%,0,3)
print "Angular Distribution"
PRINT "Cond code(Signal,N=Noise,D=scatt.signal)?";
ANSWER$ENTRYKB$
subprogram PLOT2D (F3)
IF ANSWER$="S" THEN  
call configdisplay,ENTRYKB$,CONFIG2D
rem plots tof in 2 dims as points
plot2d:
rem ENABLES LIVE DISPLAY
CRL 0
CLS 1
if live.flag% < 1 then
print "Live Display in 2 D" 
print "Signal(S),Difference signal(D) or Noise(N)? 
answer$=Entrykb$
if answer$="S" then
code%=O 
input "Time range from"; lint%
if lint%<0 then
lint%=0
endif
if topinct%<255 then
topinct%=255
endif
if chosenencode%<2 then
for cnta%=0 to 44
if code%=2 then
print "CONTROL DATA"
else if code%=2 then
print "Current update rate(obs)=",update6;
if code%=0 then
input "New value for data points between updates?", update&
tint% = tof.dat%(cnta%,cntt%,0)*corr.fct!(cnta%)
endif
if store.time&<30 then
print "Dump takes 10 seconds time set to 30s -"
tint%=tint%/tint.fct%
endif
y1%=y1%*6
xl%2=(xl%2+1)*2
line (xl%,y1%)-(x2%,y2%),tint%,bf
next
rem subroutine ENGINEER (F6)
rem called by F6
engineer;
answer$="B"
if answer$="B" then
return
call performanceplot
call normalise
call Diagnose
call phototube
call config2d
endif
end sub}

CALL CONFIGDISPLAY
rem need to reset palette at this point (how?)
return
rem called by PLOT2D
sub config2d
dim palettearray(16) as long
palettearray(0)=0
palettearray(1)=+65536
palettearray(2)=32*65536
palettearray(3)=68*65536
palettearray(4)=104*65536
palettearray(5)=140*65536 + 16*256
palettearray(6)=176*65536 + 32*256
palettearray(7)=212*65536 + 48*256
palettearray(8)=248*65536 + 64*256
palettearray(9)=284*65536 + 80*256
palettearray(10)=320*65536 + 96*256
palettearray(11)=356*65536 + 112*256
palettearray(12)=392*65536 + 128*256
palettearray(13)=428*65536 + 144*256
palettearray(14)=464*65536 + 160*256
palettearray(15)=496*65536 + 176*256
palettearray(16)=532*65536 + 192*256
screen 12
line (20,2)-(540,280),,b
view print 22 to 29
end sub
rem subroutine IDDATA (F4)
rem called by F4, MAIN
rem enters and stores id & control data
iddata:
print "ID and LOGGING DATA"
print "Current ID string",exptld$,
line input exptld$
CALL GRFRESET(4)
engineer.port% = createport(0, 25, 100, 70)
call setportvisibility(engineer.port%, 0)
call settitle("BEAM INTENSITY v ELAPSED TIME")
call setxdatatype(3)
call setydatatype(3)
call setplotmode(0)
call setaxauto(0, 21)
call setaxauto(1, 21)
call setaxname(0, "ELAPSED TIME/S")
call setaxname(1, "COUNT RATE/S")
END SUB
rem subroutine NORMALISE
rem called by ENGINEER
rem calls ENTRYKB$
sub normalise

dim an! (45)
rem normalizes angle detector performance needs uniform signal
answer$ = ""
while answer$ <> "0"
print " Angle Normalisation Options"
print "Set 	 factor = 1.0 	 (S),Read in factors(R),Measure factors(M),Quit(Q)"
answer$ = ENTRYKB$
if answer$ = "R" then
print " Element No. 	 Corrn.factor"
input "Name of corn. file?", Name$
open Name$ for input as #25
for cnt% = 0 to 44
input #25, cnt%, corr.fct! (cnt%)
print cnt%, " 	 	 	", corr.fct! (cnt%) 
next
close #25
endif
if answer$ = "S" then
for cnt% = 0 to 44
corr.fct! (cnt%) = 1.D
next
print "All corrn. factors set to 1.0"
endif
if answer$ = "M" then
rem normalize by measuring uniform flux
print "Angle normalization start - 
print " A uniform signal must be input at all angles"

tau! = 0.0
tau! = 0.0
print "Required count at any angle"
input tau!
numb% = tau!
sum! = 0.0
for cnt% = 0 to 44
an!(cnt%) = 0.0
if angle.dat& (cnt%) > tau! then
an!(cnt%) = angle.dat& (cnt%)
sum! = sum! + an!(cnt%)
endif
next
if numb% = 0 then
print "No qualifying angles"
exit sub
endif
an! = sum!/numb%
print " Element No. 	 Corrn.factor"
sun! = 0.0
for cnt% = 0 to 44
CORR.FCT! (cnt%) = 0.0
if an!(cnt%) > tau! then
rem sets very insensitive angle off > 1 below average, < 1 above
corr.fct! (cnt%) = an!/an!(cnt%)
sun! = sum! + corr.fct! (cnt%)
sun! = sum!
endif
next
mean corr! = sum!/numb%
for cnt% = 0 to 44
print cnt%, spec(5) + corr.fct! (cnt%)
next
numb% = 0
sumsqc! = 0.0
PRINT "Defective angles are:";
for cnt% = 0 to 44
if corr.fct! (cnt%) > 0.0001 then
numb% = numb% + 1
sumsqc! = (corr.fct! (cnt%)) ** 2 + sumsqc!
else
print cnt%; " 
endif
next
meancorr! = sumsqc! / numb%
for cnt% = 0 to 44
print cnt%; " 	 	 	", corr.fct! (cnt%)
next
numb% = 0
sumsqc! = 0.0
PRINT "Defective angles are:"
for cnt% = 0 to 44
if corr.fct! (cnt%) > 0.0001 then
numb% = numb% + 1
sumsqc! = (corr.fct! (cnt%)) ** 2 + sumsqc!
else
print cnt%; " 
endif
next
sumsqc! = (sumsqc! / numb%) - (meancorr!) ** 2
suznsqc! = sqr (abs (sumsqc!))
PRINT "Std.Devn.of corrn factors="; suznsqc!
PRINT "Mean value of corrn.factors="; meancorr!
PRINT "List to data file (Y/N)?";
answer$ = ENTRYKB$
if answer$ = "Y" then
input "Name of file for corrn. factors?", Name$
open Name$ for output as #21
for cnt% = 0 to 44
write #21, cnt%, corr.fct! (cnt%)
next
close #21
endif
endif
wend
end sub
rem subroutine DIAGNOSE
rem called by ENGINEER
rem reports current values and kickstarts
sub diagnose
print "Current event count=", curr.cnt&
err.num!%= diag, block.check (1, 1, remain%)
PRINT "Number remaing in buffer to be collected="; remain%
print "Data colln. kickstarted"
call start
end sub
rem subroutine PHOTOTUBE
rem called by ENGINEER
rem analyses performance of phototube
sub phototube
dim an! (45)
CALL GRFRESET(0, 0, 0, 2)
SCREEN 9
VIEW PRINT 1 TO 25
print " Input uniform flux"
print " A B C D E F G H I J K L M N O P Q R S T U V W X Y Z"
sump! = 0.0
numb! = 0
for cnt%=0 to 44
if corr.fct! (cnt%) > 0.0 then
  an! (cnt%) = angle.dat (cnt%)/numb!
  sump! = sump! + an! (cnt%)
  numb! = numb! + 1
endif
next
if sump! < 100 then
  print "Not enough Counts collected"
  sump! = 1
endif

numb! = numb! / sump!
for cnt%=1 to 45
  an! (cnt%) = an! (cnt%) / sump!
next
mrk! = 99.000
PRINT "A ";
  print using "1#.###", mrk!, an! (1), an! (2), an! (3), an! (4), an! (5), an! (6),
  an! (7), an! (8), an! (9);
  meanaa! = (an! (1) + an! (2) + an! (3) + an! (4) + an! (5) + an! (6) +
  an! (7) + an! (8) + an! (9))/9;
  PRINT "B ";
  print using "##.###", mrk!, meanaa!, an! (10), an! (11), an! (12), an! (13), an! (14), an! (15), an! (16);
  meanbb! = (an! (10) + an! (11) + an! (12) + an! (13) + an! (14) + an! (15) + an! (16))/9;
  PRINT "C ";
  print using "##.###", an! (17), an! (18), an! (19), an! (20), an! (21), an! (22), an! (23), an! (24);
  meancc! = (an! (17) + an! (18) + an! (19) + an! (20) + an! (21) + an! (22) + an! (23) +
  an! (24))/9;
  PRINT "D ";
  print using "##.###", an! (25), an! (26), an! (27), an! (28), an! (29), an! (30), an! (31), an! (32);
  meandd! = (an! (25) + an! (26) + an! (27) + an! (28) + an! (29) + an! (30) +
  an! (31) + an! (32))/9;
  PRINT "E ";
  print using "##.###", an! (33), an! (34), an! (35), an! (36), an! (37), an! (38), an! (39), an! (40);
  meanee! = (an! (33) + an! (34) + an! (35) + an! (36) + an! (37) + an! (38) + an! (39) +
  an! (40))/9;
  PRINT "F ";
  print using "##.###", an! (41), an! (42), an! (43), an! (44), an! (45), an! (46), an! (47), an! (48);
  meanff! = (an! (41) + an! (42) + an! (43) + an! (44) + an! (45) + an! (46) + an! (47) +
  an! (48))/9;
  PRINT "G ";
  print using "##.###", an! (49), an! (50), an! (51), an! (52), an! (53), an! (54), an! (55), an! (56);
  meangg! = (an! (49) + an! (50) + an! (51) + an! (52) + an! (53) + an! (54) + an! (55) +
  an! (56))/9;
  PRINT "H ";
  print using "##.###", an! (57), an! (58), an! (59), an! (60), an! (61), an! (62), an! (63), an! (64);
  meanhh! = (an! (57) + an! (58) + an! (59) + an! (60) + an! (61) + an! (62) + an! (63) +
  an! (64))/9;
  PRINT "I ";
  print using "##.###", an! (65), an! (66), an! (67), an! (68), an! (69), an! (70), an! (71), an! (72);
  meanii! = (an! (65) + an! (66) + an! (67) + an! (68) + an! (69) + an! (70) + an! (71) +
  an! (72))/9;
  PRINT "J ";
  print using "##.###", an! (73), an! (74), an! (75), an! (76), an! (77), an! (78), an! (79), an! (80);
  meanjj! = (an! (73) + an! (74) + an! (75) + an! (76) + an! (77) + an! (78) + an! (79) +
  an! (80))/9;
1057 rem called by F9
1058 1059 rem stores data if asked and terminates program
1060 rem stop board data acquisition
1061 1062 terminate:
1063 1064 err. num5%=dig. block. clear (1,1)
1065 CALL GrfLReset (0, 0, 0, 2)
1066 1. .dumy% = 010.Block.Clear (1, 1)
1067 print "termination requested"
1068 CLS
1069 1070 rem 	 subprogram HELP (PlO)
1071 1072 help:
1073 print "Commands to interupt at KB are:";
1074 print 	 F1=Plot angular distribution";" ";
1075 print 	 F2=Plot time of flight distribution"
1076 print 	 F3=Plot live two dimensional time angle display";" ";
1077 print 	 F5=Initialise all data in ram"
1078 print 	 F6=Engineer,history of beam,angle detector normalise etc.";
1079 print 	 F7=Tune up,fast info on beam time profile(locn, width and strength"
1080 print 	 also mean signal at each operating angle and std.dev of signals"
1081 print 	 F8=Dump tof data to disk file";" ";
1082 print 	 F9=Terminate program "y" ";
1083 print 	 F10=Help,thls help information"
1084 print 	 Angular corrn factors are initially set to 1.0 but may be read in"
1085 print 	 or measured if a uniform signal is available"
1086 return
1087 1088 rem 	 subprogram SCALEUP (Pl1)
1089 1090 scaleup:
1091 tint.fct%=tint.fct%*2
1092 print 	 "scale up",tint.fct%
1093 return
1094 1095 rem 	 subprogram SCALEdown (Pl4)
1096 1097 scaledown:
1098 tint.fct%=0.5*tint.fct%
1099 1099 if tint.fct%<0 then
1100 tint.fct%=1
1101 endif
1102 print 	 "SCALE DOWN=",tint.fct%
1103 return
1104 1105 rem 	 subprogram CLRGRAPH
1106 1107 rem not being used!
1108 clrgraph:
1109 rem clears time and angle graphs
1110 call setportvisibility(time.port%,0)
1111 call setportvisibility(angle.port%,0)
1112 print 	 "clear graph requested"
1113 return
A.6 COINCDA

A.6.1 Purpose

Program COINCDA is used to control data collection in the coincidence experiment – see page 206. The program was written by Dr Fluendy

A.6.2 Description

Much of the program is identical to program TOFN, and the structure and many of the subroutines are the same. The main change has been to use different arrays to store the information that is decoded from the 32 bit words taken from the buffer, and new routines have been written to display the wavelength distribution. As in TOFN, signposts are given in the listing to guide the reader through the ?? subroutines.

A.6.3 The Listing
rem written by Dr. Fluendy, documented by A.Cooke
rem S15m: same as COINCIDE
rem order of the routines:
rem MAIN, INITIALISE(F5), CONFIGDIO, CONFIGTIMEPLOT, CONFIGANGLEPLOT
rem CONFIGDISPLAY, START, PROGRESS, DECODE, PARTMESSAGE, PHOTONDECODE
rem ENTRYEOF, RUNNINGDATA, PLOTTIME(F1), PLOTPLOT(F2), PLOTPLOT(F3),
rem CONFIGDIO, IDDATA(F4), ENGINEER(F6), PERFORMANCEPLOT,
rem CONFIGPERFORMANCEPLOT, NORMALIZE, PLOTWAVE(F7), CONFIGWAVELENGTHPLOT
rem DUMP(F8), TERMINATE(F9), HELP(F10), SCALEUP(F11), SCALEDOWN(F14)
rem SOTYMIC
rem INCLUDE: \C:\\\ INCLUDE\\\ SYSTEM. INC
rem INCLUDE: \C:\\\ INCLUDE\\\IPB. INC
rem INCLUDE: \C:\\\ INCLUDE\\\FORMATIO. INC
rem INCLUDE: \C:\\\ INCLUDE\\\GRAPHICS. INC
rem INCLUDE: \C:\\\ INCLUDE\\\ANALYSIS. INC
rem INCLUDE: \C:\\\ INCLUDE\\\DATAACQ. INC
rem INCLUDE: \C:\\\ INCLUDE\\\RS232. INC
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!, old. time!, store. time!, dead. time!
rem COMMON SHARED /sig. cnt/ sigcnt%
rem COMMON SHARED /noise. cnt/ noise. cnt%
rem COMMON SHARED /tflag/ tflag%
rem COMMON SHARED /tflag/ tflag%
rem COMMON SHARED /live. flag/ live. flag%
rem COMMON SHARED /dflag/ dflag%
rem COMMON SHARED /front/ front%
rem COMMON SHARED /back/ back%
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
rem COMMON SHARED /exptid/ exptidS
rem COMMON SHARED /time/ curr. time!
rem COMMON SHARED /profile. cnt/ profile. cnt%
rem COMMON SHARED /buffer. cnt/ buffer. cnt%
rem COMMON SHARED /storetime/ storetime!
rem COMMON SHARED /storesig. rate/ storesig. rate!
rem COMMON SHARED /storenoise. rate/ storenoise. rate!
133 next
134 next
135 for cnt%=0 to 44
136 angle.dat%(cnt%)=0
137 angle.dat%(cnt%)=0
138 next
139 for cnt%=0 to 255
140 time.dat%(cnt%)=0
141 time.dat%(cnt%)=0
142 next
143 for cnt%=0 to 255
144 wave.dat%(cnt%)=0
145 wave.dat%(cnt%)=0
146 next
147 curr.cnt%=0
148 total.cnt%=0
149 sample.cnt%=0
150 prev.cnt%=0
151 dead.time=0.0
152 print " all coincidence data stores initialised ">
153 rem play "t180 o2 p2 p8 18 ggg 12 e- p24 p8 18 fff 12 d" 
154 for t%=1 to 100
155 storetlme!(t%)=0
156 storenoise.rate!(t%)=0
157 storesig.rate!(t%)=0
158 next
159 LIVE.FLAG%=0
160 print " collectin data!"
161 return
162 rem subroutine CONFIGDIO
163 rem called by MAIN
164 rem config for 32 bits
165 rem configure interface pulse +ve edge invert ack.
166 rem config interface pulse +ve edge invert ack.
167 rem config board.dat%8
168 board.dat%=8
169 err.num1%=init.da.brds(l,board.dat%)
170 err.num2%=dig.grp.config(1,1,1,0,0,0)
171 err.num3%=dig.grp.mode(l,1,0,0,0)
172 end sub
173 rem subroutine CONFIGTIMEPLOT
174 rem called by PLOT
175 rem config time ready for time plot
176 rem config for time ready for time plot
177 rem config for time ready for time plot
178 call grfreset(4)
179 time.port%createport(0,25,100,70)
180 call setportvisibility(time.port%,0)
181 call settitle("TIME OF FLIGHT")
182 call setplotmode("TIME OF FLIGHT")
183 call setplotmode(0)
184 call setplotstyle(1)
185 call setdatementype(1)
186 call setaxauto(0,0)
187 call setaxrange(0,0,255,5)
188 call setaxrange(0,255,5)
189 call setaxrange(0,255,5)
190 call setaxrange(0,255,5)
191 end sub
192 rem subroutine CONFIGANGLEPLOT
193 rem called by PLOT
194 rem config for angle plot
195 rem config for angle plot
196 rem config for angle plot
197 call grfreset(4)
198 angle.port%createport(0,25,100,75)
265 rem signal
266 part.word% = part.word% - 16384
267 tcode.dat% = -1
268 else tcode.dat% = -5
269 rem rubbish
270 rem note signal code carried by part.word
271 endif
272 if tcode.dat% = 2 then
273 call partdecode
274 call photondecode
275 if tempubb% > 0 then
276 rubbish = rubbish + 1
277 tempubb% = 0
278 else
279 iwave.dat%(1%) = iwave.dat%(1%) + corr.fct!(a%) * tcode.dat% 
280 rem stores all wavelengths in coincidence adding signal subtract noise
281 if l% < llim% then
282 l% = ((llim% - llim%)/(del%)) * 10 + 0.99
283 rem increments the various arrays used to store the data
284 con.dat%(a%, t%, l%) = con.dat%(a%, t%, l%) + tcode.dat%
285 rem section enabling live display but not of photons
286 if live.flag% = 1 then
287 t% = t% + t% * corr.fct!(a%) + tint% 
288 yl% = yl% + (a% * l% + 1) * corr.fct!(a%) + tint% 
289 x1% = x1% + t% 
290 y2% = y2% + t% 
291 x2% = x2% + 1
292 line(x1%, y1%) - (x2%, y2%), tint%, bf
293 endif
294 rem adds to buffer only if photon in set range
295 end if
296 endif
297 endif
298 rem profile for angle and time
299 time.dat!(t%) = time.dat!(t%) + 1 * corr.fct!(a%) * tcode.dat% 
300 rem angle profile hopefully flat
301 angle.dat!(a%) = angle.dat!(a%) + 1 * corr.fct!(a%) * tcode.dat% 
302 wave.dat%(ls%) = wave.dat%(ls%) + 1 * corr.fct!(a%) * tcode.dat% 
303 if tcode.dat% = 1 then
304 sig.cnt% = sig.cnt% + 1
305 endif
306 if tcode.dat% = -1 then
307 noise.cnt% = noise.cnt% + 1
308 endif
309 next
310 sample.cnt% = sample.cnt% + curr.cnt% - prev.cnt%
311 prev.cnt% = curr.cnt%
312 end sub
313 rem subroutine PARdecode
314 rem called by DECODE
315 rem decodes particle word for angle and time
316 a% = (part.word% * 256) - 0.5
317 if a% > 45 then
318 tempubb% = 1
319 exit sub
320 endif
321 if a% < 0 then
322 tempubb% = 1
323 exit sub
324 endif
325 t% = part.word% * 14256
397 count_rate! = (curr.cnt% - sample.cnt%)/e.time! 463 time.cnt% = corr.fct! (temp.cnt%)
398 print "GLOBAL TIME (S)=" curr.time!; " 464 next
399 print "ELAPSED TIME (SEC)=" e.time! 465 next
400 print "EVENT RATE (S-1)" count_rate!; 466 next
401 noise_rate! = noise.cnt% / e.time! 467 ENDIF
402 SIG_RATE! = SIG.CNT% / E.TIME! 468 call setportvisibility(wave.port%, 0)
403 print "SCATTERED SIGNAL RATE (S-l)=" ss_rate!; 469 call setportvisibility(angle.port%, 0)
404 print "DEAD TIME=", dead.time! 470 call setactiveport(time.port%)
408 dead.time=0.0 471 call setcurv2d(time.dat%, 0)
409 rem roll oldest data out of data stream 472 call setdisplayport(time.port%)
410 for t%2 to 100 473 call grfcurv2d(time.dat%, 0)
411 stores ig.rate! (t%-1) = stores ig.rate! (t%) 474 call displayport(time.port%)
412 storenoise.rate! (t%-1) = storenoise.rate! (t%) 475 call grfcurv2d(time.dat%, 1, time.cnt%)
413 storetime! (t%-1) = storetime! (t%) 476 call displayport(time.port%)
414 next 477 call grfreset(1, flag%0, 2)
415 stores ig.rate! (100) = igrate! 478 return
416 storenoise.rate! (100) = noise_rate! 479 rem subprogram PLOTTIME (F1)
417 storetime! (100) = curr.time! - estart.time! 480 rem called by F1
418 endif 481 next
419 noise.cnt% = 0 482 rem called COFIGANGLEPLOT, ENTRYKB$ 483 sig.cnt% = 0 484 end sub
421 end sub
422 rem subprogram PLOTTIME (F1) 485 rem called by F2
423 rem called by F1 486 rem calls COFIGTIMEPLOT, ENTRYKB$ 425 rem calls COFIGTIMEPLOT, ENTRYKB$ 426 plottime:
427 rem plots prepared port 428 cls 1
429 call configtimeplot 430 for tignecnt% = 0 to 255 431 itime.dat% (time.cnt%) = 0
433 print "Time Profile Display" 432 next
434 PRINT "COINCIDENCE OR FULL SPECTRUM(C/F)?" 433 for ang.cnt% = 0 to 44
435 TFL$=ENTRYKB$ 434 next
436 IF TFL$="F" THEN 435 Angle.dat% = Angle.dat% (ang.cnt%)
437 FOR TIME.CNT%=0 TO 255 436 IF APLS="F" THEN
438 ITIME.DAT% (TIME.CNT%) = TIME.DAT% (TIME.CNT%)
439 NEXT 437 FOR ANG.CNT%=4 TO 44
439 ENDIF 438 JANGLE.DAT% (ANG.CNT%) = JANGLE.DAT% (ANG.CNT%)
443 IF TFL$="C" THEN 440 NEXT
444 FOR TIME,CNT%=0 TO 255 441 ENDIF 444 JANGLE.DAT% (ANG.CNT%) = JANGLE.DAT% (ANG.CNT%)
449 TITIME,DAT% (TIME,CNT%) = TIME,DAT% (TIME,CNT%)
453 IF topint% = 255 then 448 flag% = 0
455 IF topint% < 255 then 449 input "Time range from", lint%
457 IF lint% < 0 then 450 if lint%<0 then
459 if lint%=0 then 500 lint%=0
461 if llim%=1 then 501 input "Angle range from", lang%
462 end if 502 input "Angle range to", topang%
464 flag% = 0 503 input "Time range from", lint%
466 end if 505 if lint%<0 then
468 end if 506 input "Wavelength range (0-10) from ", lim%
469 end if 507 input "to ", lup%
471 end if 508 if lim%=0 then
473 end if 509 if lim%=1 then
475 end if 510 llim%=1
477 end if 511 if lup%>10 then
479 end if 512 lup%=10
481 end if 513 end if
483 end if 515 for l.cnt% = lim% to lup% 516 for ang.cnt% = 0 to 44
485 ENDIF 517 for time.cnt% = lint% to topint% 518 for l.cnt% = lim% to topint% 519 llim% = corr.fct! (ang.cnt%)
487 call setportvisibility(wave.port%, 0) 520 next 521 next 523 ENDIF
488 call setportvisibility(angle.port%, 0) 524 call setportvisibility(time.port%, 0) 525 call setportvisibility(angle.port%, 1) 526 call setactiveport(angle.port%)
489 call setportvisibility(time.port%, 0) 527 call setcurv2d(2)
490 call setportvisibility(wave.port%, 0) 528 call setportvisibility(angle.port%, 1)
529 call displayport(angle.port%)
530 call grfcycurv2d(lamang.dat%,angle.cnt%)
531 call displayport(angle.port%)
532 call grffreset(1,flag%,0,2)
533 return
534
535 rem 	 subprogram PLOT2D (F3)
536 rem called by F3
537 rem calls ENTRYKBS, CONFIG2GD
538 plot2d:
539 rem plots coin in 2 dims as points
540 rem ENABLES LIVE DISPLAY
541 if live.flag% < 1 then
542 print 11
543 line 0
544 call config2d
545 rem plot all 2d space
546 for cnta%=0 to 44
547 for cntt%=0 to 255
548 tint%=0
549 for l.cnt%0 to 10
550 tint%=con.dat%(cnta%,cntt%,l.cnt%)*corr.fct%
551 next
552 tint'=tint%/tInt.fct%
553 yl%=9*(cnta%-1)
554 xi%=2*cntt%
555 y2%=yi%+5
556 x2%=xi%-i-2
557 line (xi%,yl%)-(x2%,y2%),tint%,bf
558 next
559 next
560 live.flag%=1
561 f1ag%=0
562 else live.flag%>1 then
563 print "Display in 2D Terminated "
564 live.flag%=0
565 f1ag%=1
566 view print 1 to 10
567 call GrfLReset(1,0,1,2)
568 cls 0
569 screen
570 call grffreset(4)
571 call Defaultgrssettings
572 call setDisplaymode(0)
573 endif
574 return
575
576 rem 	 subroutine CONFIG2GD
577 rem called by PLOT2D
578 sub config2d
579 dim palettearray(16) as long
580 palettearray(0)=0
581 palettearray(1)=16*65536
582 palettearray(2)=32*65536
583 palettearray(3)=48*65536
584 palettearray(4)=64*65536
585 palettearray(5)=80*65536
586 palettearray(6)=96*65536
587 palettearray(7)=112*65536
588 palettearray(8)=128*65536
589 palettearray(9)=144*65536
590 palettearray(10)=160*65536
591 palettearray(11)=176*65536
592 palettearray(12)=192*65536
593 palettearray(13)=208*65536
594 palettearray(14)=224*65536
595 palettearray(15)=240*65536
596 palettearray(16)=256*65536
597 call grffreset(4)
598 cls 0
599 screen 12
600 palette using palettearray(0)
601 call setDisplaymode(0)
602 print " Angle vs Flight Time"
603 line (10,12)-(522,405),bf
604 view (10,12)-(522,405)
605 view print 27 to 30
606 print "scale"=tint.fct%
607 end sub
608
609 rem 	 subprogram I/DDATA (F4)
610 rem called by F4, MAIN
611 iddata:
612 rem enters and stores id & control data
613 print "ID and LOGGING DAT"
614 input exptid$
615 print "CONTROL DATA"
616 input "data points between updates?", update%
617 input "time (secs) between disc stores of data",store.time&
618 if store.time&<30 then
619 print "Dump takes 10 seconds time set to 30s "
620 store.time%=30
621 endif
622 print "Lower and Upper Wavelength Limits (0-255) ,Lower= ",llim%
623 print "Upper= ",ul%
624 return
625
626 rem 	 subprogram ENGINEER (F6)
627 rem called by MAIN
628 rem calls ENTRYKBS, PERFORMANCEPLOT, NORMALISE
629 engineer:
630 rem handles beam history,angle corrn and p/rm tubes
631 answer9=""
632 while answer$ <>"
633 print "Reduced Engineer Facilities In Coincidence program -
634 print " Engineer on line, Beam history(B).Angle Norm(A), or Quit(Q)
635 answer$=Entrykb$
636 if answer$=B then
637 call performanceplot
638 else if answer$="A" then
639 print "Normalise"
640 endif
641 wend
642 return
643
644 rem 	 subroutine PERFORMANCEPLOT
645 rem called by ENGINEER
646 rem calls CONFIGPERFORMANCEPLOT
647 sub performanceplot
648 dim stor.rate!(100)
649 rem plots beam count rate versus elapsed time
650 for cnt%=1 to 100
651 stor.rate!(cnt%)=storesig.rate!(cnt%)*tInt.fct%
652 next
653 call configperformanceplot
654 call setactiveport(engineer.port%)
655 call setcurv2d(1)
656 call setportvisibility(engineer.port%,1)
657 call setpointstyle (0)
658 call setxdatatype(3)
659 call setxdatatype(3)
660 call grfcycurv2d(stor.time!,stor.rate!(),100)
call setpointstyle(1)
call grfcurv2d(storetime!0,storenoise.rate!(),100)
call displayport(engineer.port%)
call grfreset(1,0,2)
end sub
rem subroutine CONFIGPERFORMANCEPLOT
rem called by PERFORMANCEPLOT
sub configperformanceplot
engineer.port%=createport(0,25,100,75)
call setportvisibility(engineer.port%,0)
call settitle("BEAM INTENSITY v ELAPSED TIME ">
call setxdatatype(4)
call setydatatype(4)
call setplotmode (0)
call setaxauto(0,21)
call setaxauto(1,21)
call setaxname (0, 'ELAPSED TIME/S")
call setaxname(1, "COUNT RATE/S")
end sub
rem subroutine NORMALISE
rem called by ENGINEER
rem calls ENTRYKB$
dim an! (46)
rem normalises angle detector performance needs uniform signal
answer$=""
while answer$ <> "Q"
print " Angle Normalisation Options"
print "Set factor = 1.0 (S),Read in factors(R) or Quit (0)"
anwer$= ENTRYKB$
if answerS"R" then
print " Element No. Corrn.factor"
open "corrn.fct" for input as #25
for cnt%O to 44
input #25,cnt%, corr.fct! (cnt%)
print cnt%," ",corr.fct! (cnt%)
next
close #25
endif
if answer$="S" then
for cnt%=O to 44
corr.fct! (cnt%)=l.0
next
print "All corrn. factors set to 1.0"
endif
wend
end sub
rem subroutine PLOTWAVE (17)
rem called by F7
rem calls CONFIGWAVELENGTHPLOT
plotwave:
call setportvisibility(angle,port%,0)
call setportvisibility(time.port%,0)
call setactiveport(wave.port%)
call setcurv2d(1)
call setcurv2d(wave.dat%(j,cnt%)
if wfl$="C" then
for l.cnt%=O to 10
for time.cnt%=lint% to topint%
for ang.cnt%=lanq% to topang%
twave.dat%(l.cnt%)=twave.dat%(l.cnt%)
corr.fct! (ang.cnt%)
call setportvisibility(angle.port%,0)
call setportvisibility(time.port%,0)
call setactiveport(wave.port%)
call setcurv2d(1)
call setcurv2d(wave.dat%(j,cnt%)
call displayport (engineer.port%)
call grfreset(1,flag%,0,2)
return
rem subroutine CONFIGWAVELENGTHPLOT
rem called by PLOTWAVE
sub configwavelengthplot
engineer.port%=createport(0,25,100,70)
call setportvisibility(engineer.port%,0)
call settitle("WAVELENGTH v NUMBER OF COUNTS")
call setplotmode (0)
call setpointstyle(10)
call setxdatatype(1)
call set�性type(1)
call setactiveport(0,0)
call setaxrange(0,0,INUM%,8)
call setaxname (0,"WAVELENGTH")
call setaxname(1, "COUNTS")
end sub
rem subroutine DUMP (18)
rem called by F8
rem called by F7
rem called by F8 MAIN
dump:
rem dumps coincidence data to disc file
print "Coincidence Data dumped to file data\con.data"
dump.time!=timer
dump.time=dump.time!
last.time!=last.time!
open "con.dat" for append as #30
data.at=expitd="",".dat=",".time=
write #30, data, st$
for cnt%=0 to 44
write #30, corr.fct!(cnt%)
next
for l.cnt%=0 to 12?
write #30, iwave.dat%(l.cnt%)
next
for l.cnt%=0 to 10
for angle.cnt%=0 to 255 step 2
for time.cnt%=0 to 255 step 2
write #30, con.dat%(angle.cnt%,time.cnt%,1, l.cnt%), con.dat%(angle.cnt%,
time.cnt%+1, l.cnt%)
next
next
next
close #30
sample.cnt%=curr.cnt%
return
rem subprogram TERMINATE (F9)
terminate:
terminate:
rem stores data if asked and terminates program
rem stop board data acquisition
err.num5%=dig.block.clear(l, 1)
CALL GrfLReset (0, 0, 0, 0)
i.dummy% = DIGBlock.Clear (1, 1)
print "termination requested"
cls
stop
return
rem subprogram HELP (F10)
help:
rem called by F10, MAIN
print "Commands to interrupt at KB are:
print " F1=Plot angular distribution"
print " F2=Plot time of flight distribution"
print " F3=Plot live two dimensional time angle display"
print " F4=Note up and down arrow keys change the intensity scale by 2"
print " F5=Initialise all data in ram"
print " F6=Engineer,history of beam,angle detector normalise etc." 
print " F7=Plot Wavelength distribution"
print " F8=Dump coincidence data to disk file"
print " F9=Terminate program"
print " F10=Help, this help information"
print " Angular corr factors are initially set to 1,0 but may be read in"
print " or measured if a uniform signal is available"
return
rem subprogram SCALEG (F11)
scalend:
tint.fct%=tint.fct%*2
print "scale up",tint.fct%
return