VIBRONIC EXCITATION IN
ATOM-MOLECULE COLLISIONS

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A crossed molecular beam experiment has been used to investigate collisions between a superthermal primary beam of potassium atoms and a number of molecular target systems. Internal energy analysis of the colliding partners is achieved using a time-of-flight (TOF) technique. At the detector scattered potassium atoms are ionised on a warm filament and counted via a scintillator-photomultiplier assembly. A Pierce gun arrangement has been developed to improve detection performance.

Data has been collected for collisions with nitrogen, oxygen and sulphur hexafluoride, at laboratory energies of 200eV. The TOF spectra display a number of discrete peaks, with energy losses up to 14eV. These inelastic processes are interpreted in terms of atomic and molecular electronic excitation, with accompanying vibrational excitation.

A collision model is developed using the established 'harpoon' mechanism to explain observations in the low energy loss regime, corresponding to potassium excitation. Landau-Zener transitions between diabatic intermolecular potentials are assumed, with independent motion in the molecular ion. Molecular excitation is attributed to electron donation into high-lying molecular orbitals, followed by re-capture from lower normally filled orbitals.

Monte Carlo classical trajectory calculations have been carried out on the potassium-methyl iodide system, using a surface hopping technique to investigate electronic excitation in superthermal collisions. Experimental data are plentiful for alkali-alkyl halide collisions, but previous trajectory studies have been confined mainly to thermal energies. Early models based on independent intra-molecular motion have proved unsatisfactory at superthermal energies. The importance of the three body interaction is examined using a number of empirical potential hypersurfaces.
DECLARATION

I hereby declare that this Thesis has been composed by myself and that I made a substantial contribution to the work reported during my period in the Molecular Beams Group. All members of the group were involved in the data collection. I was responsible for maintenance and improvements in the experimental apparatus. I analysed the data presented in this Thesis and developed the modelling program. I carried out amendments in data collection and analysis programs and I developed the Monte Carlo surface-hopping trajectory program for the work reported in Chapter 6. The interpretation of data, as set out in Chapters 5 and 6, grew from discussions with Malcolm Fluendy and Kenneth Lawley.

GEOFFREY W. BLACK
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CHAPTER 1

INTRODUCTION

The primary importance of intermolecular collisions in determining the physical and chemical properties of fluid systems has been acknowledged for almost a century. Since Boltzmann the central theme of physical chemistry has been to relate observable bulk quantities to the basic laws of physics through the theory of molecular collisions.

In chemical experiments carried out on bulk samples, usually at thermal equilibrium with their surroundings, the Boltzmann distribution of molecules among the available states means that, if a measured property is a function of the quantum state of the molecule, then only an ensemble average can be extracted. Thus information can be interpreted only indirectly by means of elaborate theories incorporating statistical models of the bulk with the dynamics of a single collision.

The direct study of intermolecular collision processes has become possible within the last twenty five years with the development of a range of molecular beam scattering methods. These allow the selection of a given quantum state or
range of states for measurement, with the collision energy fixed routinely. Using the well established collision theories developed in the fields of nuclear and particle physics direct molecular information can be obtained from the angular and energy dependence of the associated scattering. Theory and experiment are compared at the molecular level of state-to-state cross section at a given energy rather than at the macroscopic level of rate at a given temperature. Therefore the investigation of chemical kinetics, covering an experimental field from elastic to reactive scattering, can be carried out with the degree of detail previously possible only in spectroscopy.

The earliest crossed beam experiments involved elastic scattering in the determination of intermolecular potentials from total cross-sections. These techniques evolved out of the beam-gas attenuation experiments common in physics from the 1920s, and a number of review papers are available (BUC 75), (PAU 78). Reactive scattering experiments represent the progression into chemical applications which began in the mid-fifties and developed rapidly with the improving technology of the 1960s (KIN 72), (GRI 75). Early studies involving reactions of alkali atoms with halogen-containing
molecules, e.g., (HER 61), provided new insight into molecular dynamics, unobtainable by any other means, leading to the familiar limiting reaction models, "spectator stripping", "recoil" and "complex mode" mechanisms (BER 79). The close interaction between theory and experiment established by these studies continues to be of fundamental importance in molecular beam research.

Technological innovations in the late sixties led to the development of superthermal crossed beam experiments, covering the energy range 1-1000 eV. By confining interest to the narrow angle scattering region, only glancing collisions involving energy transfers of up to about 10 eV are studied. These experiments allow the investigation of close range interactions covering the chemically important well region and repulsive potential. Over these parts of the potential surface several electronic states may be involved in the collision process.

The dynamics of a system in the vicinity of a surface crossing can be treated using either an adiabatic or nonadiabatic potential representation (NIK 74). Diabatic potentials possess a distinct electronic nature, e.g., ionic and covalent, and become degenerate at the crossing radius, where adiabatic surfaces, which represent a linear combination of such electronically characterised
potentials dependent upon nuclear geometry, experience an avoided crossing.

In previous beam experiments collision dynamics could be explained in terms of a single potential energy surface. In these processes the Born-Oppenheimer approximation (BOR 27), separating nuclear and electronic motion, holds throughout the collision. Although an avoided crossing between covalent and ionic potential surfaces is experienced, the system is limited to adiabatic motion and remains on the lower surface at thermal energies. Thus the harpoon or electron jump model (POL 32), (MAG 40), was established as the reaction mechanism (HER 66).

Electronically nonadiabatic effects, involving the breakdown of the Born-Oppenheimer approximation when electronic states closely approach each other or cross, is observed in a great number of fundamental collision processes, including collisional excitation and ionisation (JAN 78). Reviews on nonadiabatic coupling have been plentiful in recent years (BAE 75), (JAN 76), (TUL 76). It is clear that at high energies where nonadiabatic behaviour becomes important the diabatic potential scheme provides the most useful approximation to the collision system. Furthermore, the harpoon model can often produce a suitable ionic intermediate coupling ground and
electronically excited states. The probability of electronic transition at the crossing points can be found using the Landau-Zener approximation (LAN 32), (ZEN 32). A thorough discussion of the harpoon model has been presented recently by Gislason (GIS 79). In this Thesis the harpoon model is applied to experimental results for fast potassium atom collisions with a number of target molecules.

Data has been collected on potassium atom scattering with nitrogen, oxygen and sulphur hexafluoride at 200eV LAB collision energy. These target systems have undergone some investigation in recent years using molecular beam techniques. Alkali atom-nitrogen collisions have aroused interest in the "inverse" route of quenching processes (BAU 69), prior to studies on alkali atom excitation (KEM 75). The potassium-oxygen system has been employed primarily in the examination of collisional ionisation (BAE 75). However, electronic excitation has been investigated more completely over the last few years (KLE 80b), (KLE 80c) although much remains unresolved. Experimental effort in potassium-sulphur hexafluoride scattering has been directed almost exclusively towards ionisation studies (HUB 75), by virtue of the low electron affinity of SF₆ and its industrial role as an effective electron quencher (MAS 69).
By comparison of experimental data with the harpoon model fittings, a number of important scientific objectives may be achieved. Primarily, the usefulness of the harpoon mechanism in systems with large negative electron affinities, and in systems with short-lived molecular ions, may be established. Furthermore it is hoped that, where possible, more detailed mechanisms can be discovered. For example, in molecular excitation routes leading to highly excited states may be identified.

The role of internal motion can also be examined. In the high energy limit, where the collision time $t_{col}$ is very much less than the vibrational period $t_{vib}$, the molecule can be considered rigid and no vibrational effects need be taken into account. If $t_{col}$ is very much greater than $t_{vib}$, many vibrational cycles of the molecule are possible during the collision fly-by time and analysis of the collision dynamics becomes difficult, if not impossible. In the intermediate case, $t_{col}$ and $t_{vib}$ are of the same order and the effect of vibronic excitation can be investigated. The experimental results for all three systems fall into the last category. The extent of vibronic excitation is dependent upon impact parameter and so can be monitored by its angular dependence.
The collision model assumes vertical electron transitions and classical motion over the potential surfaces. Changes in the molecular bond are independent of the position of the potassium projectile and established "isolated molecule" parameters are used as far as possible. It is hoped to determine whether simple classical mechanics provides an effective description for vibrational excitation or whether quantum methods may prove more appropriate.

In short, it should be possible to discover how well a very simple harpoon model describes any given atom-molecule system. The selected collision systems each provide the model with a suitable test, particularly sulphur hexafluoride, which is considered as a "diatomic".

In Chapter 2, the apparatus used in this work is described. A new detection system has been incorporated into the experiment and is covered in some detail in this Chapter. Results in tests and in full experimental operation indicate a considerable improvement on the previous detection performance, both in energy resolution and in signal intensity. It is hoped that more successful experiments can now be achieved, particularly at low energies, where space charge effects can seriously degrade beam intensities.

Chapter 3 contains the data collected in
experiments on potassium atom scattering with nitrogen, oxygen and sulphur hexafluoride. These results are presented in the form of time-of-flight profiles at various measuring angles. Discrete energy loss processes have been identified and differential cross-sections extracted. Examination of these differential cross-sections provides information on the intermolecular potentials, crossing radii and transition probabilities. Contour maps are also shown to give an overall view of the information generated by these experiments.

The theory required in this Thesis is presented in Chapter 4. The Born-Oppenheimer approximation, the Landau-Zener model and the classical small angle formulae (FLU 73) are discussed in some detail. The importance of bond stretching in the negative molecular ion in determining the vibrational energy loss is also examined. The impact parameter harpoon model is developed and the potential surfaces involved in potassium excitation are presented for the three systems under scrutiny.

The discussion of the experimental data and the results of the model computations is contained in Chapter 5. The suitability of "isolated molecule" potential parameters in collision studies is examined and the validity of the effective diatomic model for sulphur hexafluoride is
demonstrated. Higher lying energy loss processes are attributed to molecular excitation and possible assignments are made by comparison with optical spectra although no quantitative modelling has been attempted. Other collision models are discussed in relation to the classical impact parameter description, including the "bond stretch attraction" concept (HER 81), which offers an alternative adiabatic approach challenging the validity of the harpoon mechanism. Arguments for the continued application of the harpoon model are also presented.

In the final Chapter, Monte Carlo classical trajectory calculations are applied to the important potassium-methyl iodide system, which has played a major part in the study of collision dynamics (HER 73). Over the period of this Thesis the investigation of potassium-alkyl halide collisions formed a large body of the work of the Edinburgh Molecular Beams Group (FLU 81). The bond stretching mechanism during the course of collisional excitation is of particular interest. A surface hopping trajectory (SHT) model is developed to investigate vibronic excitation using empirical potential surfaces and the Landau-Zener approximation to describe the collision processes. While work on this system, and indeed the description of nonadiabatic transitions by trajectory methods,
is rather preliminary and by its nature fairly crude, it is hoped that interest is stimulated to progress further with the available SHT model computation.
CHAPTER 2

EXPERIMENTAL

2.1 General

The results reported in this Thesis were obtained on a molecular beam apparatus designed to investigate the dynamics of collisions between alkali atoms and various target molecules in the superthermal energy range from 50eV to 1000eV. By a novel means of pulse modulation in the fast alkali beam (McC 78), a time of flight technique is employed, so allowing observation of any electronic and/or vibrational excitation taking place during the collision process. Hence the assignment of the final states of the collision system is possible.

The differential cross-sections for the collision processes were calculated from observations taken in the narrow angle region about the main beam line, where the signal intensities are sufficient to permit experiment. By confining interest to this region, however, the alkali atom trajectory can be assumed rectilinear and of constant velocity, and the model computations can make use of the small angle formulae (Chapter 4), while the high incident energy allows exploration of the regions of importance on the atom-molecule potential surfaces.
The initial construction of the apparatus has been described by Duchart (DUC 71), and modifications by Reddington (RED 73) and Kerr (KER 75). A schematic showing an improved detector design was presented by Sutton (SUT 80), and will be discussed more fully here (see figure 2.5). The experimental apparatus is shown schematically in figure 2.1. There are three main sections of the apparatus; the main beam production, the target beam formation and the means of detection of the scattered alkali atoms. A general view, such as that provided by figure 2.1, captures the important overall features; that the main beam is accelerated to the required collision energy, focussed and modulated following initial ionisation at the source, then neutralised before meeting the target beam introduced from above in the collision chamber. The scattered alkali atoms are ionised on a cool tungsten-platinum wire and are detected via a scintillator and photomultiplier in the detection chamber, which sweeps in a plane at right angles to that defined by the two beams. The signal produced stops a 50MHz crystal clock running synchronously with the beam modulation, and so the time of flight is recorded for each arrival. An on-line DEC PDP11/45 computer collects the data and monitors and controls many aspects of the experimental operation.
Figure 2.1: Apparatus Schematic

- Source oven
- Porous tungsten disc
- Extraction lens
- Lindholm Gustaffson deceleration lens
- Tof pulsing lens
- Charge exchange
- Vapour cell
- Ion dump plates
- Collision zone
- Cross beam chopper motor
- Collimating array
- Gas line
- Flexible bellows
- Cross beam monitor
- Detector
2.2 Vacuum System

The apparatus is made up of four differentially pumped chambers containing the main beam source, the cross beam unit, the scattering region and the detector. The beam production chambers and the scattering chamber are pumped by oil diffusion pumps with liquid nitrogen cryogenic baffles, backed by two rotary pumps on a single roughing line. In addition, liquid nitrogen cold trapping is employed to catch any stray condensibles, so preventing any build-up causing poorer scattered beam intensities and higher background noise. Typically pressures of $10^{-5}$ torr and $10^{-6}$ torr may be expected in the main beam production chambers and the experimental chamber respectively, with the cross beam source chamber maintaining a pressure of around $10^{-4} - 10^{-5}$ torr.

The detector chamber is connected to the bulk of the apparatus by flexible bellows with a gate valve providing entry from the collision chamber. The chamber is initially pumped out through this slit, until a low enough pressure is achieved to allow the ion pump to operate. It provides the main pumping power running continuously thereafter, with a titanium sublimation pump on stand-by to handle occasional heavy contamination, and pressures of $2 \times 10^{-8}$ torr may be maintained even during experimental runs.
2.3 Main Beam Production

Potassium ions are produced by surface ionisation on a porous tungsten disc heated radiatively to about 1500°C and bathed to the rear in potassium vapour from a reservoir oven, maintained at a steady temperature of 250°C. The source is kept at a positive voltage corresponding to the desired beam energy. The ions are extracted by a two element grid and accelerator electrostatic lens, which focuses the ions into the Lindholm - Gustaffson deceleration lens assembly. This lens, which was described by Reddington (RED 73), focuses the ion beam by means of an electrostatic field, which drops exponentially in strength over the length of the lens system. Several of the lens elements are split to allow considerable steering of the ion flux, and so any misalignments in the source may be compensated. After the Lindholm - Gustaffson lens the focused ion beam enters the pulsing lens (McC 78), where it is first X-modulated by a pulsed voltage across its path. After a suitable delay Z-modulation, i.e. velocity compression, is applied to the slice of beam passed by the X-plates. A voltage gradient is set up along the beam path such that those ions to the rear of the pulse experience a greater acceleration than those to the front, so the original pulse, with a half-width of 1.34µs, is compressed to a much narrower pulse, with a half-width of 60 - 80ns at the detector, so
making time of flight studies possible. A schematic diagram of the pulsing lens, showing the timings used, is given in figure 2.2.

The pulsed beam is neutralised by charge exchange on passing through a second oven containing potassium at 150 - 160°C, by the well known resonant process

\[ K^+(\text{fast}) + K^0(\text{slow}) \rightarrow K^0(\text{fast}) + K^+(\text{slow}), \]

which for potassium ions at 200eV has a cross-section of around 200Å², much larger than for momentum transfer (HAS 62), (KER 75), (CHA 77).

The charge exchange oven is kept as near as possible to the optimum temperatures stated above, since the intensity of the final neutral beam is rather sensitive to changes at this point (RED 73). Below about 150°C, the vapour is too diffuse to achieve any degree of neutralisation, while much above 160°C the vapour pressure is too high and the intensity is badly diminished by multiple collisions. The neutral pulsed flux passes between the dump plates, where a 100V transverse voltage deflects any residual ions out of the beam path, and is collimated on entering the collision chamber.

2.4 Cross Beam Production

The cross beam reservoir is set up in a gas line external to the main apparatus, so facilitating renewal or replacement of the cross beam material.
Figure 2.2:
Pulsing Lens Schematic and Pulse Timings
Therefore a variety of target beams may be investigated in a single experimental run without lengthy change-overs costing valuable data collection time. A schematic of the gas line is shown in figure 2.3. From the gas line, the slow, thermal cross beam is introduced into the collision chamber by effusion through a glass capillary array. It is chopped mechanically at 47Hz to enable signal plus noise, and noise to be differentiated. That is, the cross beam chopper also interrupts light from a lamp falling on a photocell, with the light cut off when the beam is off. So by monitoring the output from the photocell each arrival at the detector can be labelled according to whether the cross beam was on or off when the atom passed through the experimental zone. The target beam intensity is continuously monitored by a differential ion gauge placed directly underneath the collision zone, its output being logged into the PDP11/45 via the experiment interface to allow some degree of automatic control of the cross beam intensity.

2.5 The Detector

The detector was originally based upon a design described by Daley (DAL 60). Scattered potassium atoms entering the detector chamber impinge on a warm 92% platinum 8% tungsten wire. The resulting ions are crudely focussed onto an
Figure 2.3: The Gas Line
aluminised surface, and the secondary electrons emitted there are accelerated onto a scintillator. The photons produced by the electron pulse are detected by a photomultiplier and the output pulse is passed to the computer interface via an amplifier and discriminator. There the pulse stops a 50MHz crystal clock running synchronously with the pulse modulation and counting into a 10 bit scalar. Hence the time of arrival of the scattered atom is recorded and a time of flight spectrum is built up for each scattering angle. The detector may be varied in angle to a precision of ±0.002°, and can sweep a range of up to 7° from the main beam line. A diagram of the original detector is shown in figure 2.4.

As mentioned earlier, an improved detector design has been incorporated into the apparatus. A Pierce gun arrangement (PIE 40) including shimming plates has been developed to obtain better focussing of the potassium ions emerging from the tungsten-platinum filament onto the aluminised surface, and of the secondary electrons onto the scintillator. A schematic diagram of its final form is outlined in figure 2.6 with the initial design shown in figure 2.5.

The original detector could not focus the ions onto the aluminised plate, and the effect of the can around the filament was to smear the ions
Figure 2.4 : Original Detector Assembly
The plates P are labelled according to percentage of main EHT. F1 and F2 are the ion focussing plates and S is the filament support plate (earthed).

Plate F2 has been removed and P50 is used to shield the ion gun.
out over the surface. The resultant "burn" on the aluminised surface extended for several centimetres, and so the density of arrivals landing opposite the scintillator/photomultiplier system was much less than it might have been.

The new arrangement was hoped to achieve better detection efficiency by realising improved signal levels together with lower noise levels, and a decrease in the pulse FWHM. The improvements were expected for the following reasons. Firstly, the new detector focusses ions from the filament onto a well defined spot on the aluminised surface directly opposite the scintillator and photomultiplier housing. In the original detector, the ion flux was smeared out over a 30mm burn on the aluminised plate. Since the scintillator aperture is only about 8mm, an improvement of (at best) four times may be achieved in signal intensity. Secondly, the ions are drawn off the filament more efficiently, i.e. more quickly and in a better focussed pack, both in terms of space and time, and the same may be said of the secondary electrons. Therefore, the pulse profile should improve. This improved energy loss resolution is the most important feature hoped for in the new system. It is hoped that reference profiles with FWHM of 40ns, or 2 detection channels, may be achieved as against previous values of 80ns (4 channel) FWHM. In addition, it means
better signal to noise ratios, and makes experiment possible with beams whose intensities would have been considered too weak in the past. Another bonus offered by the new design is that, because of the presence of the shimming plates and the additional focusing lens, the contribution to the noise by residual ions in the chamber should be diminished. Lastly, higher EHTs may be applied, and so ultimately more photons should be produced. Thus the probability of detecting a neutral arrival is enhanced. Therefore, with care taken to avoid electrical breakdown between the extra plates, the noise levels should be no worse than previously, and indeed probably somewhat better, while the signal ought to improve both in intensity and shape.

This proved to be the case, although a great deal of time and effort was required to bring the new detector system to its present state. At first, very high noise levels were encountered which were traced to breakdown occurring across the small gaps around the second focusing plate. After unsuccessful attempts to shield these vulnerable points, it was decided to remove the second element and carry on with only one focusing plate. The edges of the other plates were masked with PTFE tubing at this stage. A further problem arose with the filament assembly. If the filament
lay even fractionally behind its supporting plate, the emitted ions were immediately subjected to a highly defocussing field resulting in low beam intensities and poor time of flight profiles. The insulating bearings carrying the wire were widened to ensure the filament always sat proud of its support.

With the new detector in its somewhat revised form, a field plot was made, the results of which are shown in figure 2.7. This revealed considerable field penetration from the main EHT voltage, relating to the secondary electron motion, on the aluminised plate, into the ion-focussing Pierce gun. In order to shield the focussing field from the destabilising effect, the 50% plate was extended with lugs sweeping back on each side. At the same time, the 66% shimming plate was altered to give a central 'D' gap, rather than the previously very narrow slot, which was barely wide enough to allow the ions to pass. The final technical drawings are given in figures 2.9 - 2.12, and a much improved field plot, figure 2.8, is given by this modified version.

Beam intensities are now typically 2 - 2.5MHz DC, 400kHz pulsed, at 200eV lab collision energy, with EHT settings of from 12.5kV to 16kV on the main supply, and 1.5 - 2.5kV on the focussing plate. Noise counts remain around 50Hz or less. This compares very favourably with results using the old detector, which gave signals of about 1MHz DC, 200kHz pulsed, with
Figure 2.7: Field plot of first version of new detector, with second focussing plate removed. The ion focussing plate Fl is set at a typical value of 15% of maximum voltage. Equipotentials are drawn at 5% intervals up to 50% of maximum EHT volts.
Figure 2.8: Field plot of final version of new detector. Equipotentials are drawn at 5% intervals up to 60% of maximum volts. The equipotentials between the P1 and P50 plates are no longer deformed under the influence of the electron focusing plates.
Figure 2.9
Technical Drawing of New Detector

Figures 2.9 - 2.12 have been reduced from A3
similar noise levels. Characteristics of the new detector are shown in figure 2.13 and 2.14. Figure 2.15 compares a typical time of flight profile on the new system with one taken on the previous Daley type detector.

While it is hoped that continued improvement may be made to the detection performance, it is clear that limitations do exist. With care, noise levels can be reduced without diminishing signal intensity. However, as the time of flight profile is improved by superior detector efficiency, so slight mistimings in pulsing, and small misalignments or differences in the spacings of the pulsing lens elements become obvious. Space charge effects may become noticeable. For example, a jitter of 0.1eV may result in a change of about 4ns in the arrival time, while a fluctuation of 0.5eV corresponds to a 20ns, or 1 full detection channel difference. For any of several reasons, the X-modulated potassium ion pulse may arrive within the Z-modulation region too early or too late, and so the time of flight profiles may have a poorly defined leading edge, or worse still, a sloppy trailing edge behind the elastic peak which will obscure genuine inelastic processes. Another phenomenon possibly leading to slow arrivals behind the main peak is $K(4^2P)$ formation on reneutralisation in the charge exchange chamber.
Figure 2.13(a) : Noise counts from hot filament vs. focus voltage on plate Fl. Main EHT set at 15kV.

Figure 2.13(b) : Noise counts from hot filament vs. main EHT voltage showing onset of detector operation.
Detector Characteristic

Figure 2.14: Detector Characteristic

Lines indicate region of maximum counts from a hot filament.
Figure 2.15

Typical time of flight reference profiles on old and new detector systems. Profile A shows a profile obtained from the new detector. This example is 3ch FWHM although 2ch profiles are possible. Profile B represents the typical 4ch reference obtained previously.
2.6 Data Collection and Experimental Operation

The collection of experimental data and the control of certain parameters is handled by an on-line DEC PDP11/45 computer. During a typical experimental run lasting some 120 hours, with wide angle observations taking over 10 hours to complete, the computer collects and displays the accumulating data, provides rudimentary control for variables such as the target beam intensities, count rates, signal to noise ratios and so on. Figure 2.16 provides the electronic counting schematic for the apparatus. Experimental conditions are defined at the start of the run by thirty-two experimental variables read into the collection program. These are listed in table 2.1, and a list of the PDP11 programs and their functions is given in table 2.2.

As already described, the detected signal stops a 50MHz clock counting into a 10 bit scalar in the interface, and so the flight time is recorded. With four separate scalars, four arrivals may be registered in the interface before an interrupt to the computer transfers their readings, together with the time since the previous transfer and other experimental values. Table 2.3 gives details of the data sentence sent to the PDP11/45 at each transfer. Every ten minutes the collected data is written to disc. Should experimental conditions change, for example, if the main beam intensity
Figure 2.16: Electronics Schematic
<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Date, e.g., 15th April is 15.04</td>
</tr>
<tr>
<td>2</td>
<td>Main Beam Energy, in eV</td>
</tr>
<tr>
<td>3</td>
<td>Main Beam Mass, in amu</td>
</tr>
<tr>
<td>4</td>
<td>Target Beam Temperature, in K</td>
</tr>
<tr>
<td>5</td>
<td>Target Beam Mass, in amu</td>
</tr>
<tr>
<td>6</td>
<td>Beam Centre, in teletrak units</td>
</tr>
<tr>
<td>7</td>
<td>Output File Sequence Number</td>
</tr>
<tr>
<td>8</td>
<td>CEC Slit Size, 0.015 inches</td>
</tr>
<tr>
<td>9</td>
<td>Post CEC Slit Size, 0.040 inches</td>
</tr>
<tr>
<td>10</td>
<td>Pre-scattering Centre Slit Size, 0.016 inches</td>
</tr>
<tr>
<td>11</td>
<td>Target Beam Width, 0.020 inches</td>
</tr>
<tr>
<td>12</td>
<td>Detector Width, 0.020 inches</td>
</tr>
<tr>
<td>13</td>
<td>Detector Height, 0.30 inches</td>
</tr>
<tr>
<td>14</td>
<td>Beam Height at Scattering Centre, 0.10 inches</td>
</tr>
<tr>
<td>15</td>
<td>Clock Period, in nanoseconds</td>
</tr>
<tr>
<td>16</td>
<td>= 0, for S + N - N</td>
</tr>
<tr>
<td></td>
<td>= 1, for S + N + N</td>
</tr>
<tr>
<td>17</td>
<td>Reference Angle</td>
</tr>
<tr>
<td>18</td>
<td>Unused</td>
</tr>
<tr>
<td>19</td>
<td>Minimum Angle, in teletrak units</td>
</tr>
<tr>
<td>20</td>
<td>Maximum Angle, in teletrak units</td>
</tr>
<tr>
<td>21</td>
<td>Step Size for Simple Angle Scan, in teletrak units</td>
</tr>
<tr>
<td>22</td>
<td>= 0, for angle input from keyboard</td>
</tr>
<tr>
<td></td>
<td>= 1, for simple angle scan</td>
</tr>
<tr>
<td></td>
<td>= 2, for pseudo-random scan</td>
</tr>
<tr>
<td></td>
<td>= 3, for pseudo-random scan with double step size</td>
</tr>
<tr>
<td>23</td>
<td>Number of Pulses per Cycle</td>
</tr>
<tr>
<td>24</td>
<td>Required Counts in Peak Before Angle Change</td>
</tr>
<tr>
<td>25</td>
<td>= 0, for manual control of barostat</td>
</tr>
<tr>
<td></td>
<td>= 1, for simple auto control</td>
</tr>
<tr>
<td>26</td>
<td>Minimum Acceptable Peak Counting Rate</td>
</tr>
<tr>
<td>27</td>
<td>Angle Table Entry Point One</td>
</tr>
<tr>
<td>28</td>
<td>Angle Table Entry Point Two</td>
</tr>
<tr>
<td>29</td>
<td>Main Beam Check Frequency</td>
</tr>
<tr>
<td>30</td>
<td>Main Beam Monitoring Period</td>
</tr>
<tr>
<td>31</td>
<td>= 0, no main beam monitoring</td>
</tr>
<tr>
<td></td>
<td>= 1, monitor main beam but don't suspend data collection</td>
</tr>
<tr>
<td></td>
<td>= 2, suspend data collection if main beam changes by more than 10%</td>
</tr>
<tr>
<td>32</td>
<td>As 31, but for Target Beam</td>
</tr>
</tbody>
</table>
Table 2.2. PDP11/45 Programs

*TEST* Reads the interface continuously but does not process the data. Useful for testing the interface, pulse timings, modulation lock, prior to starting data collection.

*CTF4* Carries out LAB to CM transformations for any system \( MA + MB = MC + MD \).

*CTF1* Directs transfer data sentence to line printer for inspection. Useful for checking interface and communications.

*LOAD* Loads experimental variables into the file CHEMDA, which is read by the data collection program at the start of the experiment.

*DCP5* Data collection program. The program initially flashes the filament for two minutes and then measures a reference profile. Unless the beam is very intense, this observation is made at beam centre. References are taken with experimental variable 16 set equal to 1. Afterwards, the program collects data at angles according to the conditions set by the experimental variables. After the number of blocks fixed by variable 29, the program measures another reference and flashes the filament again. After a further reference profile it returns to measuring scattered data. If the collection time at any one angle exceeds the time stated in variable 30, then the program will write the data to disc and then monitor the main beam. On restarting, the program returns to the incomplete angle. The experimenter is able to communicate with the program using manual flags on the interface.

*DDXE* Data display program. The program is used to inspect accumulating data during the experiment or data stored on disc. It is used to "MERGE" data blocks of the same angle

cont'd./...
which, with its "EDIT" facility, prepares files for transfer to EMAS.

*CONC* Concatenates files and prepares the raw data for transfer to EMAS as a CONCnn type file.
Table 2.3: Format for Data Transfer to the PDP11

<table>
<thead>
<tr>
<th>Mode</th>
<th>Manual Flags</th>
<th>Cross Beam Monitor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Units</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hundreds</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SCALAR 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SCALAR 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SCALAR 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
dropped by more than 10%, data collection is stopped and the experimenter informed. He can also communicate with the data collection program via a set of manual flags to alter the experimental situation. Table 2.4 shows the possible commands available to the flags.

The beam intensities achieved by the apparatus vary from run to run, as do the conditions required to obtain them, and with so many parameters involved it could not be otherwise. However, table 2.5 offers an indication of typical values encountered during an experiment.

2.7 Data Analysis Programs

The results accumulated on disc in the PDP11/45 computer are reviewed and edited using the facilities of DDXE after the run is completed. Appropriate reference profiles are chosen for the experimental angles and blocks collected at the same angle may be examined and merged if necessary to improve the quality of the data. Using the utility program CONC one or more files can be prepared for transfer to the Edinburgh Regional Computing Centre's EMAS system. The transfer is effected by programs generally available within the Physics Department. When the data file appears (as CONCnn) on the designated EMAS system and user process, the analysis of the raw data may proceed.

The programs used for the analysis and presentation of the data are given in figure 2.17,
<table>
<thead>
<tr>
<th>Code</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>Read new value(s) for experimental variable(s). Note that this does not alter CHEMDA, the file containing starting conditions.</td>
</tr>
<tr>
<td>010</td>
<td>Print out feedback.</td>
</tr>
<tr>
<td>011</td>
<td>Write data to disc and stop the data collection program.</td>
</tr>
</tbody>
</table>
| 100  | Receive instructions from teletype. Possible replies to prompt are:-  

R = measure reference  
F = flash filament  
L = list current experimental variables  
X = alter cross beam ideal in auto control |
| 101  | Check data but do not collect. |
| 110  | Restart data collection. |
| 111  | Write data to disc, move to new angle according to experimental variables, and start collection of new data block. |
### Table 2.5: Typical Running Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam energy</td>
<td>200 eV</td>
</tr>
<tr>
<td>Source temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Grid voltage</td>
<td>110 V</td>
</tr>
<tr>
<td>Acceleration voltage</td>
<td>-500 V</td>
</tr>
<tr>
<td>Deceleration lens voltage</td>
<td>-300 V</td>
</tr>
<tr>
<td>Ion current:</td>
<td></td>
</tr>
<tr>
<td>1st dec. lens plate</td>
<td>$10^{-5} - 10^{-6}$ A</td>
</tr>
<tr>
<td>upper quadrupole</td>
<td>$10^{-10}$ A</td>
</tr>
<tr>
<td>dump plates</td>
<td>$10^{-9} - 10^{-10}$ A</td>
</tr>
<tr>
<td>Pulser voltages:</td>
<td></td>
</tr>
<tr>
<td>focus</td>
<td>19.8 V</td>
</tr>
<tr>
<td>clear</td>
<td>30 V</td>
</tr>
<tr>
<td>C E C temperature</td>
<td>150°C</td>
</tr>
<tr>
<td>Pressures:</td>
<td></td>
</tr>
<tr>
<td>Chambers 1 and 2 (main beam production)</td>
<td>$10^{-6}$ torr</td>
</tr>
<tr>
<td>Chamber 3 (collision)</td>
<td>$10^{-6}$ torr</td>
</tr>
<tr>
<td>Chamber 4 (cross beam production)</td>
<td>$10^{-8} - 10^{-5}$ torr</td>
</tr>
<tr>
<td>Detector</td>
<td>$2 \times 10^{-8}$ torr</td>
</tr>
<tr>
<td>Detector:</td>
<td></td>
</tr>
<tr>
<td>EHT main supply</td>
<td>12-16 kV</td>
</tr>
<tr>
<td>focussing plate</td>
<td>1-2.5 kV</td>
</tr>
<tr>
<td>count rate DC</td>
<td>&gt;2 MHz</td>
</tr>
<tr>
<td>count rate pulsed</td>
<td>~400 kHz</td>
</tr>
<tr>
<td>noise rate</td>
<td>&lt;50 Hz</td>
</tr>
<tr>
<td>attenuation of main beam</td>
<td>&lt;15%</td>
</tr>
</tbody>
</table>
PDP11/45

*CONC*

prepares a "CONCnn" file for transfer

FILTER7

deconvolutes data and outputs to a "_FIL" type file

ENGLOSS3

outputs differential cross-sections

REGAL5

sets up an array of data points suitable for eventual output as a contour map and places information in a "_CON" type file

DCON1

further deconvol'n if required

TOFAVS

outputs TOF profiles

INTRTS2 → INTCN3

contour mapping sub-routine

outputs contour maps

GRAF

general graphics utility

output to 4027, graph plotter

Figure 2.17: EMAS program routes from raw data to output
together with a brief description of their functions. The possible routes from raw data to final output are also indicated in the diagram. All the programs are written in IMP, an ALGOL-type language developed at Edinburgh.

A number of improvements have been made to the data analysis and display features, partly in order to make best use of the colour graphics facilities on the recently acquired Tektronix 4027 VDU terminal. However, the most important change has been made out of a long-standing need to correlate results for the same system taken on different occasions. As mentioned in the notes accompanying figure 2.17, REGAL5 takes the filtered data and transforms it into an array suitable for contour mapping. With almost any system, there is some drifting of the profile position as experimental conditions change during the course of a run, and the effect may become considerable when data is collected over several experiments. As the channel position of the main elastic peak jitters back and forth from angle to angle, the data when presented in the form of a contour map can prove at the least untidy, and at worst misleading. In an attempt to eliminate this random effect, the program now incorporates an additional sub-routine RIGHT DRESS, which operates on each angular slice in the scheme outlined in figure 2.18. As can be
START

find maximum intensity for angle i, and its channel position j

A Elastic Peak Calculation

find channel on rising edge containing approx. 25% of max. intensity

estimate, by linear interpolation, the vel. at the 25% channel
Equation 2.1

all angles

n

? \ Y

calculate mean, stand. dev. of the velocities

set limits for search for isotopic peaks, using velocities found above

B Isotopic Peak Calculation

figure 2.18 cont'd/...
find maximum within permitted range for angle i, and its channel position j

does a maximum exist within the range?

Y

does the maximum correspond to an isotopic peak, on comparison of its relative intensity to elastic peak?

Y

estimate, by linear interpolation, the velocity at the 25% of isotope intensity position

Y

all angles?

Y

calculate mean, stand. dev. of the isotopic velocities

n

calculate nominal vel. of isotope 25% max. position Equation 2.2

n

figure 2.18 cont'd/...
calculate correct vel. for elastic peak at angle i, including the small shift in vel. (lab) with angle
Equations 2.3-2.8

calculate correct isotopic velocity, as above

calculate correction factors such that the elastic and isotopic peaks lie along the correct values
Equations 2.9, 2.10

adjust the velocity of each channel according to the correction factors
Equation 2.11

n all angles

Figure 2.18

Schematic flow diagram for the sub-routine RIGHT DRESS, which aligns data on a regular energy loss grid for INTCN3, the contour mapping program
seen from the flow diagram, the equations (2.1 to 2.11) and from REGAL5 itself, listed in Appendix A, the program also employs useful information provided in the data but hitherto ignored. That is, the relative position of the isotope with respect to the main elastic peak indicates whether there has been any expansion or contraction of the profile from angle to angle. By fixing the elastic and isotopic peaks along their average, corrected velocity positions, the inelastic data is also "straightened out" over an evenly spread energy loss grid. Thus order in the energy loss processes may be perceived more readily, particularly within the low intensity high energy loss range, and oscillations in any inelastic process may be noted with more confidence than before.

The danger in any scheme such as this is that data might be "laundered" to fit the experimenter's notional predictions. In order that such accusations could not be raised, data was always checked first in its original state following preliminary deconvolution, and the right dress operation was carried out only after careful observation of peak positions in the raw data time-of-flight profiles and considerable discussion as to its validity. In Chapter 3, contour maps are shown for data files created with and without right dressing.
As mentioned above, there have been several small changes made in the data display programs to allow presentation of results on the Tektronix 4027 colour graphics terminal. Thus time of flight profiles may be superposed for easy comparison, a particularly useful feature when focussing the pulsing lens on commencing an experiment, and preliminary analysis of data is handled relatively simply. When the final set of results is arrived at, the enhanced options of the contour mapping program, INTCN3, allow more complete examination than has been possible previously, since without colour display the contour diagrams can become "busy" and confusing.

The new options available to INTCN3 are:

- **P** - draws line connecting peaks of operator-defined specifications, i.e. upper limit (%), confidence level (%), deflection sensitivity

- **D** - data is printed for point indicated by cursors, i.e. intensity (%), angle, velocity, energy loss (CM)

- **G** - draws an extra energy loss graticule at a given CM velocity (obtained from D option)

INTCN3 can be found in Appendix B. An example of a contour map using a "peaks" option is shown in figure 3.2.
The equations required in the alignment of data are outlined here, using the notation given below.

\[ p_i = v_{i,j} + \frac{v_{i,j+1} - v_{i,j}}{a_{i,j+1} - a_{i,j}} (0.25a_i^{\text{max}} - a_{i,j}) \]  \hspace{1cm} (2.1)

estimates the velocity at the 25% of peak channel. A similar calculation applies for the isotopic peak.

The nominal velocity of the isotopic 25% channel is found from

\[ v_{i,\text{nom}} = \frac{1}{1 - \frac{l_1}{1 + l_2}} \]  \hspace{1cm} (2.2)

From the Newton diagram (figure 2.19)

\[ v_R^2 = (v_1^2 + v_2^2)^{\frac{1}{2}} \]  \hspace{1cm} (2.3)

\[ W_1 = v_R \frac{m_T}{m_T + m_M} \]  \hspace{1cm} (2.4)

\[ \cos \varepsilon = \frac{v_1}{v_R} \]  \hspace{1cm} (2.5)

\[ v_0 = (W_1^2 + v_1^2 - 2v_1W_1 \cos \varepsilon)^{\frac{1}{2}} \]  \hspace{1cm} (2.6)

\[ \alpha_1 = \cos^{-1} \left( \frac{v_1^2 + v_0^2 - W_1^2}{2v_1v_0} \right) \]  \hspace{1cm} (2.7)

Thus

\[ v_{\text{cor}} = v_0 \cos(\alpha_1 - \phi) + \left( (v_0 \cos(\alpha_1 - \phi))^2 - (v_0^2 W_1) \right)^{\frac{1}{2}} \]  \hspace{1cm} (2.8)

gives the correct velocity for the elastic peak with a similar calculation to obtain the correct isotope velocity \( v_{\text{cor}}^{\text{iso}} \).
Therefore the correction factors are

\[ C = \frac{v_{\text{cor}} - v_{\text{iso}}}{p_i - p_{\text{iso}}} \]  
(2.9)

\[ Q = v_{\text{cor}} - C p_i \]  
(2.10)

Finally,

\[ v_{i,j}^{\text{cor}} = C v_{i,j} + Q \]  
(2.11)

**Notation**

- \( a_{i,j} \): intensity at angle \( i \), channel \( j \)
- \( a_{i}^{\text{max}} \): maximum intensity at angle \( i \)
- \( C \): correction factor for profile width
- \( l_1 \): distance from collision zone to detector
- \( l_2 \): distance from pulser to collision zone
- \( m \): (elastic mass/isotopic mass)\(^{\frac{1}{2}}\)
- \( m_m, m_T \): main, target beam mass
- \( p_i \): calculated velocity of 25\% position on leading edge of elastic peak
- \( p_{\text{iso}} \): calculated or nominal velocity of 25\% position on leading edge of the isotopic peak
- \( p_{\text{nom}} \): nominal isotopic velocity
- \( Q \): correction factor for profile shift
- \( v \): LAB velocity
- \( v_0 \): correct CM velocity
- \( v_1 \): correct LAB velocity of elastic peak
\( v_2 \) correct LAB target beam velocity
\( v_R \) correct relative velocity of main and target beams
\( v_{\text{cor}} \) correct elastic velocity after scattering
\( v_{\text{iso cor}} \) correct isotopic velocity after scattering
\( v_{i,j} \) measured velocity at angle \( i \), channel \( j \)
\( v_{\text{cor}i,j} \) corrected velocity for angle \( i \), channel \( j \)
\( W_1 \) CM velocity of elastic peak
\( \alpha \)
\( \varepsilon \) see Newton diagram (figure 2.19)
\( \phi \)
Figure 2.19: Newton Diagram for the collision process
CHAPTER 3

EXPERIMENTAL RESULTS

3.1 Systems Studied

The experiment investigated energy transfer processes occurring in collisions between potassium and a number of simple molecules, using the time of flight method and the superthermal crossed molecular beam apparatus described in Chapter 2. Time of flight profiles and hence differential cross-sections were collected and are presented in this Chapter, with the discussion of these results following in Chapter 5. Table 3.1 shows the systems studied and provides some useful references to complementary work carried out by earlier workers.

Table 3.1

Systems Under Investigation

<table>
<thead>
<tr>
<th>System</th>
<th>Lab Collision Energy</th>
<th>Some previous work</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-N_2</td>
<td>200</td>
<td>MAR 79, GER 73</td>
</tr>
<tr>
<td>K-O_2</td>
<td>200</td>
<td>KLE 78, KLE 80</td>
</tr>
<tr>
<td>K-SF_6</td>
<td>200</td>
<td>OKA 80, COM 78, HUB 75</td>
</tr>
</tbody>
</table>

The possible collision pathways open to a system are detailed in Table 3.2. The importance of the harpoon mechanism (MAG 40) has
long been established with extensive investigation at both thermal (reactive scattering) and superthermal (elastic scattering) energies. Work in the field of chemi-ionisation underlines the importance of non-adiabatic behaviour at the ground-ionic state crossing (BAE 75), while the role of the ionic potential as intermediate coupling ground and excited states has been confirmed in the quenching of excited atoms (BAU 69) and in collision induced fluorescence (KEM 75). More recently this traditional framework for the collision process has been challenged by the bond-stretch attraction model (HER 81) which involves direct coupling between adiabatic potential surfaces correlating with the alkali atomic states. Discussion of both concepts is presented in Chapter 5.

Table 3.2
Exit Channels Available to the General System $A + BC$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A + BC \to A + BC(\dagger)$</td>
<td>elastic (vibrational excitation)</td>
</tr>
<tr>
<td>$A + BC \to A^+ + BC^-$</td>
<td>Chemi-ionisation (incl. similar cases e.g., electron detachment)</td>
</tr>
<tr>
<td>$A + BC \to AB + C$</td>
<td>reaction</td>
</tr>
<tr>
<td>$A + BC \to A^* + BC(\dagger)$</td>
<td>electronic (vibronic) excitation</td>
</tr>
<tr>
<td>$A + BC \to A + BC^*(\dagger)$</td>
<td>dissociation</td>
</tr>
</tbody>
</table>

57
In the present studies, investigations are confined to those channels leading to electronic and/or vibrational excitation.

In Chapter 4 a model is developed using the assumptions of non-adiabaticity and the harpoon mechanism in order to interpret the results of these investigations, in terms of differential cross-section and energy loss.

3.2 Presentation of Data

The data presented here was collected over a number of experimental runs during a period of about three years, using the techniques described in Chapter 2.

The time of flight profiles obtained at various angles for each collision system can be presented in several different ways in order to glean the maximum information on the target molecule and its interaction with the alkali atom. As in figure 3.1, which shows a plot of potassium-nitrogen scattering at 85.5eV in CM, the data can be set out in the form of a contour map, giving scattered intensity times the square of the scattering angle as a function of the scattering angle and the post collision velocity. From a contour diagram the energy loss bands corresponding to electronic excitation processes taking place during the collision can be observed fairly readily, either by eye or by using the facilities available in the contouring program.
While such plots are highly "information intensive" and are particularly valuable in identifying the behaviour of energy loss processes with angle, and hence in molecular terms with impact parameter, it is probably more useful to observe them in conjunction with the simpler angle averaged time of flight profiles, which display the grosser features of the collision system, the relative intensities of and the envelope of energy losses for the processes involved. These profiles, taken as cuts across the contour map within a small angular range, may be used to present individual experimental angles, with further deconvolution if so desired using a zero degree profile as reference. Alternatively, all angles may be summed to provide a spectrum showing the overall features of the collision, within the narrow angle region sampled by the experiment.

Once the energy losses have been established the differential cross-sections are calculated. The cross-sections for the principal exit channels are presented in this Chapter, with the tentative assignment of the states involved and the mechanism of their population being discussed in Chapter 5.

3.3 Potassium-Nitrogen Scattering

The results for potassium-nitrogen scattering at 85.5eV CM collision energy, in the narrow angle
range (0-7°), are presented here in the forms described in the previous section. Centre of mass contour maps for the system are given in figures 3.1 - 3.3, an all angles averaged time of flight profile is shown in figure 3.4, while figures 3.5 - 3.24 display the time of flight spectra for individual experimental angles. Table 3.3 summarises the results for the collision profiles, with each column indicating an assignment to a single energy loss process.

The principal features of the data are the small number of discrete energy loss processes going on during the collision, with intensity peaks in the region of up to 12eV occurring at even the narrowest angles. This would indicate the importance of strongly attractive potentials in coupling ground and excited states. The two main processes show rather small energy losses, with the elastic channel dominating, by far the most likely outcome of a collisional encounter. From the spectra, it is also seen that there is not a great deal of broadening in the elastic peak with increasing angle. The principal inelastic process can be seen on the contour maps as a broad ridge running from narrow angles in an energy loss range of between 1.6 and 3.2eV. The all angles averaged time of flight profile shows that its average peak is at 2.8eV and that it is present
at about 16% abundance. Moreover, as can be seen in figure 3.2, the peak is not constant in energy loss but displays some oscillation with angle. A change of molecular geometry is evidenced, with a strong oscillatory dependence upon impact parameter and therefore collision lifetime. The extent of the vibrational excitation is dependent upon the nature of the intermediate potential surface and the time spent on it. Since reduced scattering angle maps with impact parameter, different angular ranges sample different parts of the potential surfaces and hence different times spent on the intermediate potential. There are only very small populations in the other inelastic processes, the largest being seen as a shoulder on the main inelastic channel, at about 4.7eV, and another, indicating excitation of the target molecule, at around 8.5eV (figure 3.4). It is also seen that the spectra appear "clean". There is no substantial background count, i.e., losses are discrete occurring via specific processes rather than hard collisions. With the main energy losses identified, differential cross-sections were produced, which are displayed in figures 3.25 - 3.28. Cross-sections are expressed in arbitrary units plotted against reduced angle $E_X$, but are to the same scale unless otherwise stated. Thus it is seen that the main
Figure 3.1: Contour map of potassium nitrogen scattering at 85.5 eV in CM. Intensity times the square of the scattering angle is plotted against scattering angle and post-collision velocity. The right hand procedure ensures a regular energy loss grid. The grid marker labelled 41.00 indicates the slow $\alpha$K isotope. The elastic channel appears at the 'fast' right hand side of the plot. Contours are drawn 1% intervals from 1-5%, with some cosmetic smoothing over a 0.25° window.
Figure 3.2: As in figure 3.1, but displaying the 'peak' feature of the contour mapping program, INTCN3. The peaks, shown shaded, lie in the intensity range above 1%. It is seen that the right dress and isotopic adjustments have worked well, with both elastic and isotopic channels lying along their respective markers.
Figure 3.3: As in figures 3.1 and 3.2, but without the right dress operation. The measured velocities do not match the nominal velocities shown on the grid. The peaks accentuate the 'jitter'.
Figure 3.4:
All Angles averaged TOF Profile for K-N$_2$ scattering at 85.5eV in CM$^2$.

All TOF profiles appearing in this Thesis have undergone some right dress procedure, either by hand or by using the computing facility, prior to analysis. Unidentified spurious peaks are marked "?". They have not been assigned to any process number. TOF profiles for individual experimental angles follow in figures 3.5-3.24. Figure 3.29 is a collision process map which indicates the maxima and their allocated process numbers.
Figure 3.5

K/N2
0.92 DEGREES

Figure 3.6

K/N2
1.15 DEGREES
Figure 3.7

K/N2

1.38 DEGREES

Figure 3.8

K/N2

1.87 DEGREES
Figure 3.9

Figure 3.10
Figure 3.11

K/N2
1.891 DEGREES

Figure 3.12

K/N2
2.33 DEGREES
Figure 3.13

K/N2

2.82 DEGREES

Figure 3.14

K/N2

2.83 DEGREES
Figure 3.15

K/N2

3.29 DEGREES

Figure 3.16

K/N2

3.30 DEGREES
Figure 3.17

K/N2

3.53 DEGREES

Figure 3.18

K/N2

3.75 DEGREES
Figure 3.19

K/N2

4.23 DEGREES

Figure 3.20

K/N2

4.68 DEGREES
Figure 3.21

K/N2

5.16 DEGREES

Figure 3.22

K/N2

5.63 DEGREES
Figure 3.23: K/N2 6.10 DEGREES

Figure 3.24: K/N2 6.59 DEGREES
Figure 3.25:
Differential cross-sections for K-N\textsubscript{2} scattering at 85.5eV in CM
The intensity scale has been chosen arbitrarily with the elastic channel intensity at 330 eV taken as 100%. The same scale applies in figures 3.27 and 3.28.

Figure 3.26: differential cross-sections for K-N$_2$ scattering at 85.5 eV in CM.
Figure 3.27:
Differential cross-sections for highly inelastic processes in K-N$_2$ scattering at 85.5eV in CM. These cross-sections are very noisy and therefore only average levels have been indicated. The high noise levels can be attributed at least partly to oscillations or "wobbles" in energy loss.
Figure 3.28:
Differential cross-sections for K-N$_2$ scattering at 85.5 eV in CM. Process 3 is given for comparison of the intensity of process 7.
Figure 3.29: Collision Process Map for $K-N_2$
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inelastic process onsets at the narrowest angles and rises steadily in intensity to the limit of experimental observation at around 600eV. The "deset" in the elastic cross-section occurs at about 300eV. The high energy loss processes are of much lower intensity and consequently their cross-sectional shapes are less well defined.

3.4 Potassium-Oxygen Scattering

The results for potassium-oxygen scattering at 92.2eV CM collision energy in the narrow angle range 0-5° are similar in many respects to those of the potassium-nitrogen system, as might be expected from these light diatomics. Again, a number of discrete energy losses are observed, somewhat more than in the case of nitrogen. There is a dominant elastic channel, and at least one major inelastic process displays oscillatory behaviour with angle. The quality of the data is such that in the main energy loss process covering a range of around 1.5 - 3eV, the inelastic peak can be seen in a definite "footprints" pattern (figure 3.30). This is to some extent an artifact of the contour mapping program however. Since it interpolates from angle to angle at constant energy but does not interpolate in energy, any oscillation in energy loss is exaggerated as the peak tends to break up into "islands" or "footprints".
However, unlike the tidier spectra for potassium-nitrogen scattering, there appears to be more happening throughout the energy loss range including some apparent broadening of the elastic peak with increasing angle. This is expected given the abundance of excited states in oxygen's electronic structure compared with their relative sparcity in the nitrogen molecule. The centre of mass contour maps for the system are shown in figures 3.30-3.32, while the results of the time of flight profiles (figures 3.34-3.50) are summarised in table 3.4. Having found the most important processes, their differential cross sections were produced (figures 3.51-3.56). Thus it can be seen that the elastic channel desets at about 130eV, recovering thereafter to a wide angle intensity of about double the minimum, while the major inelastic process reaches its maximum cross-section at around 180eV, gradually declining to about one third of that value at wide angles. The all angles averaged time of flight profile is given in figure 3.33.

3.5 Potassium-Sulphur Hexafluoride Scattering

The results for potassium-sulphur hexafluoride scattering might be expected to be rather different from the previous potassium-diatom systems but in fact many common features may be noted in this data, so providing clues to
Figure 3.30: Potassium-oxygen scattering at 92.2eV in CM. The right dress operation has been carried out and contours are displayed at 1% intervals from 1-5%. Peaks are shaded for confidence limits greater than 1% and a sensitivity of 0.999. Smoothing over a 0.25° window has been used.
Figure 3.31: As in figure 3.30 but without the right dress feature.
Figure 3.32: A much simpler view of the potassium-oxygen scattering data. Heavy smoothing has been employed. Oscillatory behaviour of the inelastic channel is very pronounced.
Figure 3.33:
All Angles averaged TOF Profile for K-O scattering at 92.2eV in CM.

The individual experimental angles, figures 3.34-3.50, are summarised in figure 3.57, the collision process map.

Figure 3.33-3.50 display signal intensity vs. energy loss.
Figure 3.38

K/02

1.44 DEGREES

Figure 3.39

K/02

1.45 DEGREES
Figure 3.40

Figure 3.41
Figure 3.42

K/02

2.10 DEGREES

Figure 3.43

K/02

2.54 DEGREES
Figure 3.44

Figure 3.45
Figure 3.46

Figure 3.47
4.36 DEGREES

K/02

3.92 DEGREES

Figure 3.48

Figure 3.49
Figure 3.50
Figure 3.51: Differential cross-sections for $K - O_2$ scattering at 92.2eV in CM.
Figure 3.52:
Differential cross-sections for K-O\(_2\) scattering at 92.2eV in CM. Because of the difficulty in resolving processes in the low energy loss regime, cross-sections for processes 3 and 4 have not been given. Indeed the cross-sections shown for processes 2 and 5 may not be entirely "clear cut". The intensity scale has been chosen arbitrarily with the elastic channel (process 1) intensity at 250eV taken as 100%. The same scale applies in figures 3.53 and 3.54.
Figure 3.53: Differential cross-sections for K-O₂ scattering. Error bars are not drawn as the highly inelastic cross-sections are very noisy. Average levels only are shown, and the shapes given are rather approximate.
Figure 3.54:
Differential cross-sections for K-O$_2$ scattering. This process was extremely noisy; a very rough estimate of the cross-sectional shape is shown.
Figure 3.55:
Differential cross-sections for K-0\textsubscript{2} scattering. The scale shown is only approximate.

Figure 3.56:
Differential cross-sections for K-0\textsubscript{2} scattering. Process 10 has not been given due to the high noise levels in its energy loss range. The scale shown is only approximate.
Figure 3.57: Collision Process Map for K-O₂
Table 3.4
K-02 TOF Profiles - Summary of Results

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the behaviour of the molecule during the collision. The process is dominated by elastic scattering with the main inelastic channels showing energy losses of around 2.5–3.0eV and 4.0–4.5eV, indicating a larger degree of vibrational excitation than has been observed in the other two systems. Again there is some evidence of oscillation with angle in these energy loss processes. Further low intensity, highly inelastic processes are observed at energy losses of up to 14eV. Figures 3.58–3.78 present the scattering data for the system at 161.5eV CM collision energy in the narrow angle range 0–3.7°. Table 3.5 provides a summary of these results. Differential cross-sections have been extracted and are shown in figures 3.79–3.82. From there it is seen that the elastic channel remains at an almost constant value of cross-section (around which there appears to be some oscillation) before it begins to deset at about 460eV°. Both of the main inelastic processes remain very small in comparison.
Figure 3.58: Potassium-sulphur hexafluoride scattering at 161.5eV in CM. Peaks greater than 1% intensity are shaded, with a sensitivity of 0.1. Contours are shown at 1% intervals from 1-5%. Right dressed data has been used.
Figure 3.59: As in figure 3.58, but without the right dress procedure.
Figure 3.60:
All Angles averaged TOF Profile for K-SF$_6$ scattering at 161eV in CM.

The individual experimental angles' profiles appear in figure 3.61-3.78 and are summarised in the collision process map, figure 3.83.
Figure 3.61

K/SF6

0.49 DEGREES

Figure 3.62

K/SF6

0.73 DEGREES
Figure 3.63

K/SF6

0.76 DEGREES

Figure 3.64

K/SF6

0.87 DEGREES
Figure 3.65

K/SF6

0.96 DEGREES

Figure 3.66

K/SF6

1.17 DEGREES
Figure 3.67

K/SF6

1.18 DEGREES

Figure 3.68

K/SF6

1.47 DEGREES
K/SF6

1.67 DEGREES

K/SF6

1.90 DEGREES

Figure 3.71

Figure 3.72
Figure 3.73

K/SF6

1.95 DEGREES

Figure 3.74

K/SF6

2.12 DEGREES
Figure 3.75

K/SF6

2.15 DEGREES

Figure 3.76

K/SF6

2.53 DEGREES
Figure 3.77

K/SF6

2.90 DEGREES

Figure 3.78

K/SF6

3.64 DEGREES
Figure 3.79:
Differential cross-sections for K-SF$_6$ scattering at 161.5eV in CM. The two main inelastic processes are compared against the elastic channel. The intensity scale has been chosen arbitrarily with the elastic channel intensity at 400eV taken as 100%. The same scale applies in figures 3.80-3.82.
Figure 3.80:
Differential cross-sections for K-SF$_6$ scattering at 161.5eV in CM. Average levels only are given for these low intensity channels.
Figure 3.81:
Differential cross-sections for K-SF₆ scattering at 161.5eV in CM.

reduced scattering angle $E\chi/eV^\circ$
Figure 3.82:
Differential cross-sections for K-SF₆ scattering at 161.5 eV in CM. The intensity scale given is only approximate.
Figure 3.83: Collision Process Map for K-SF₆
Table 3.5
K-SF6 TOF Profiles - Summary of Results

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CHAPTER 4

THEORETICAL AND COMPUTATIONAL

4.1 Aims

In developing a model with which to investigate the results of the previous Chapter considerable thought must be given to what the model is hoped to achieve and how it is best set about.

In principle, the collision systems studied must be interpreted via a full close coupled quantum calculation including all the states of the systems and requiring an accurate knowledge of many of the potential surfaces, both ground and excited. In practice, though much progress has been made in the calculation of surfaces, neither the precision of the present data nor the available theoretical capability would warrant such a mammoth undertaking.

Instead, in this section it is hoped that rather simpler models can be explored, with a view to extending the physical understanding of the important parameters governing these collisions, and to link these observations with other types of information.

Thus the model should be physically plausible and as simple as possible so that this underlying aim of the scattering experiment, the interpretation of data in terms of the properties
of single collisions, can be achieved. There is little point in developing a complex theoretical treatment from the outset or in relying on a series of arbitrary parameters to improve the fit of model with experiment if a good understanding of the overall trends in the scattering data can be obtained by the application of classical mechanics to the single atom-molecule collision.

Secondly, established knowledge of the system should be used and known molecular parameters included when available, so that the model remains broadly in agreement with previous work. For example, although the electronic structure of the molecule can be expected to be perturbed by the proximity of the potassium during the collisional encounter, and different from that of the isolated molecule found by spectroscopic means, any distinctions introduced in the model must be kept within common-sense boundaries.

Finally, the developed model should be readily applicable to a number of systems, though this criterion might well be matched automatically if those of simplicity and sensibility are followed. The model used in this discussion holds true to these guidelines, particularly that it remains simple while providing adequate predictions and a readily understandable picture of the collision process. In the case of potassium-sulphur
hexafluoride scattering its flexibility is examined to some extent.

4.2 Background

The observed collisional processes fall into the category of the electronically non-adiabatic, the transitions from ground to excited states being brought about by curve crossing mechanisms rather than inter-state mixing, since the adiabatic or Massey criterion (MAS 49)

\[ \Delta E \Delta t \sim \hbar \sim \frac{\Delta E \cdot r}{v} \]  
where

- \( \Delta E \) = energy difference between the electronic states
- \( \Delta t \) = collision lifetime
- \( \hbar \) = Planck's constant
- \( v \) = projectile velocity
- \( r \) = a range parameter of molecular dimensions, e.g., the path length

is far from satisfied under the experimental conditions. Electronically adiabatic processes, for which nuclear motion can be described as evolving over a single potential energy surface, have been the subject of considerable attention, e.g., (BUN 71), being used to describe simple chemical reactions. In such processes the Born-Oppenheimer approximation is wholly valid, i.e., the electronic problem is solved with the nuclei in fixed positions, following which the nuclear motion over the potential surface
so generated may be calculated.

Non-adiabatic transitions involve the breakdown of the Born-Oppenheimer approximation when two potential energy curves describing different electronic states become degenerate, i.e., in adiabatic terms an avoided crossing. Here, if the nuclei are moving fast enough or if a component of the electronic motion has fallen to zero, the electrons do not have time to adjust to the rapidly changing nuclear geometry and the non-adiabatic transition takes place, with the system moving onto the second adiabatic potential. Such transitions are observed in a vast number of common molecular processes, even at thermal energies, including chemical reaction, quenching, charge transfer and of particular interest here, electronic excitation. A discussion of the Born-Oppenheimer approximation in adiabatic and non-adiabatic representations follows in the next section.

The electronically excited states of the potassium atom lie in the energy range up to 4.3 eV, with the lowest lying excited state, $^4P_{3/2}$, providing an energy loss of 1.62 eV. Table 4.1 shows some of the states available, although the large number of excited states results in a near continuum extending to the ionisation limit at 4.3 eV.
Table 4.1

States Available to the Potassium Atom

<table>
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<th>State</th>
<th>Potential Energy/eV</th>
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</thead>
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</tr>
<tr>
<td>$4^2p$</td>
<td>1.62</td>
</tr>
<tr>
<td>5s, 3d</td>
<td>2.64</td>
</tr>
<tr>
<td>5p</td>
<td>3.064</td>
</tr>
<tr>
<td>6s, 4d</td>
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<td>I.P.</td>
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</table>

Having established a curve crossing mechanism, it is seen that the simplest intermediate coupling these states will be of ionic character. Nitrogen, oxygen and sulphur hexafluoride have vertical electron affinities small enough for the ionic state $K^+\text{Mol}^-$ to intersect ground and electronically excited potentials. Furthermore the strongly attractive Coulomb force will lead to onset of excitation processes at narrow angles as observed, while a direct close-range interaction between the ground and excited states on their steeply repulsive potential walls would cause the processes to appear only at very large values of $E_X$. As mentioned previously the ionic intermediate has been established as the mechanism for the inverse process of quenching of excited alkali atoms by molecular nitrogen (BAU 69).
Similarly, earlier experiments provide evidence of ion pair formation in potassium-oxygen molecule collisions leading to vibronic excitation (KLE 80a), and the potassium-sulphur hexafluoride system is known to form ion pairs (HUB 75), (COM.78). Since with the exception of potassium-oxygen scattering, only excited potassium states lie within access of the ground ionic state, it was decided to develop the model using only three potential curves, representing the ground neutral, ground ionic and K(4\textsuperscript{2}P) excited states. A general schematic of the angle averaged potentials is shown in figure 4.1 and a diagram of a typical trajectory path is illustrated in figure 4.2. It is seen that an electron transition is possible both on entering the interaction region and on the way out. Therefore for all trajectories with impact parameter within the crossing radius there are two ways of reaching a specified exit channel, corresponding to "early" or "late" crossing to the ionic surface. If motion within the molecule is neglected the probability of finding the system on the ionic path as it leaves the second crossing is

\[ P = 2P_{12} (1 - P_{12}) \]  

(4.2)

where \( P_{12} \) is the probability of crossing at the ground/ionic state intersection. More generally the result is
Figure 4.1: Schematic of Intermolecular Potentials
The radius $R$ represents the foot of the ionic and covalent repulsive walls. The symbols + and 0 denote motion over the ionic and covalent paths respectively. At the first crossing, radius $R_c$, the system may behave adiabatically, crossing to the ionic surface, or diabatically, remaining on the covalent potential. In the former case, when motion within the molecular ion is included the crossing radius is changed due to the molecule's different electron affinity. The movement of the crossing radius depends on the collision lifetime and therefore on the impact parameter $b$. At the second crossing, at either $R_c^0$ (diabatic) or $R_c'$ (adiabatic at the first crossing), each path may split once again, so resulting in two routes to electronically elastic scattering and two paths leading further up the ionic surface.
\[ P = P_{12}(1 - P_{12}) + P_{12}(1 - P_{12}) \]  

where \( P_{12} \) applies to the second crossing position.

Adiabatic behaviour at the first crossing corresponds to "harpooning", the established reaction mechanism for alkali metal collision systems (HER 66), (BAE 75), although in this experiment the high collision energies exclude the reaction channel as a possible exit.

4.3 **The Born-Oppenheimer Approximation**

The Born-Oppenheimer approximation is the basic simplification applicable to almost all chemical collision processes, that electronic and nuclear motion can be separated (BOR 27). As a result of the huge difference between electronic and nuclear mass leading to fast and highly quantal behaviour in electrons and slow, nearly classical nuclei, the approximation may be considered valid in almost every case.

The separation may be shown using time independent scattering theory to find the total wave function \( \Psi(r,R) \) describing a general collision process (TUL 76). Asymptotically the wave function will behave as an incoming plane wave, corresponding to the initial state of the system, and an outgoing spherical wave, corresponding to the possible product states resulting from the collision. As
well as depending on the electronic coordinates $r$
and the nuclear positions $R$, both with respect to
the centre of mass of the system, $\psi$ will also be
a function of the initial states and the collision
energy.

The Hamiltonian operator $H$ governing the
motion of the $n$ electrons and $N$ nuclei may be
written

$$H = J_R + H_0$$

(4.4)

where $J_R$ is the nuclear kinetic energy operator,

$$J_R = \sum_{I=1}^{N-1} -\frac{h^2}{2\mu_I} \nabla_I^2$$

(4.5)

and

$$H_0 = H_{el} + H_{so}$$

(4.6)

where $H_{el}$ is the electronic Hamiltonian for
fixed positions of the nuclei,

$$H_{el} = \sum_{j=1}^{n} -\frac{\hbar^2}{2} \nabla_j^2 + \sum_{j=1}^{n-1} \sum_{k>1}^{n} \frac{1}{|r_j-r_k|}$$

$$- \sum_{j=1}^{n} \sum_{I=1}^{N} \frac{Z_I}{|r_j-R_I|} + \sum_{I=1}^{N-1} \sum_{I=1}^{N} \frac{Z_I Z_I}{|R_I-R_I|}$$

(4.7)

and $H_{so}$ is the spin orbit operator, which should
generally be included as spin-orbit interaction
effects are often as important as non-adiabatic
effects. For reasons of simplicity however, it will be neglected from the operations which follow.

At this point a basis set of electronic wave functions is chosen, which are dependent upon the nuclear positions \( R \) in a "well-behaved" functional manner but are otherwise unspecified. The total wave function is expanded in terms of the basis set \( \phi \)

\[
\Psi(r,R) = \sum \phi_e(r,R) \chi_e(R) \quad (4.8)
\]

where \( \chi_e(R) \) is the nuclear wave function describing the motion of the nuclei over the potential energy surface of electronic state \( \mathcal{E} \) and the expansion is substituted into the Schrödinger equation leading to the well known set of coupled equations in \( \chi_e(R) \), (O'MA 71)

\[
\left[ J_R + f e + U_{\mathcal{E}} \right] \chi_e = - \sum_{e' \neq e} \left[ J_{ee'} + f_{ee'} + U_{ee'} \right] \chi_e' \quad (4.9)
\]

where

\[
U_{ee'}(R) = \langle \phi_e | H_{\mathcal{E}1} | \phi_{e'} \rangle \quad (4.10)
\]

\[
J_{ee'} = \sum_{I=1}^{N-1} \left( - \frac{\hbar^2}{2\mu_I} \right) \langle \phi_e | \nabla_I \phi_{e'} | \nabla_I \rangle \quad (4.11)
\]

and

\[
J_{ee''} = \sum_{I=1}^{N-1} \left( - \frac{\hbar^2}{2\mu_I} \right) \langle \phi_e | \nabla^2_I \phi_{e'} \rangle \quad (4.12)
\]
with the integrations taking place over the electronic coordinates $r_e^e$, the non-adiabatic corrections to the potential energy surfaces $U_{ee}(R)$, are always small and normally neglected while of the off-diagonal terms which promote transitions between surfaces $T_{ee'}$ is the dominant non-adiabatic coupling term. It is also seen that the term is velocity dependent through the gradient operation on $\chi_e$, i.e., the coupling is dynamic.

Thus the separation of nuclear and electronic motion is achieved. The problem reduces to first solving the electronic part, selecting the electronic basis functions to obtain the potential energy surfaces $U_{ee}(R)$ as above, and then calculating the motion of the nuclei over the surfaces, in principle by solving the set of coupled equations. As the nuclear motion may be mapped out by classical methods, the difficulty remains chiefly in the construction of an appropriate potential hyper-surface i.e., the choice of diabatic or adiabatic representations.

In the adiabatic representation the electronic basis functions are the eigen-functions of $\mathcal{H}_e$, the electronic part of the Hamiltonian solved with "clamped" nuclei, parametrically dependent upon the nuclear coordinates and coupled by the nuclear kinetic energy terms in the total Hamiltonian. Thus the adiabatic potential energy surfaces provide
an exact description for determining the molecular behaviour; they do not correspond to any particular electronic configuration but are formed by a linear combination of such wave functions. In low energy molecular collisions non-adiabatic transitions can normally only occur if two adiabatic potential surfaces approach each other closely, resulting in an avoided crossing for states of the same symmetry (figure 4.3a). This takes place when both adiabatic states have been constructed from the same pair of simple electronic functions, whose potentials tend to degeneracy at that nuclear configuration. At the avoided crossing, if the nuclei are moving slowly the system will tend to remain on the same adiabatic surface. However, if the nuclei move quickly the non-adiabatic coupling term will no longer be negligible and the probability of a transition from one surface to the other will approach unity. Because of the velocity dependence the "width" of the non-adiabatic transition will depend upon the nuclear motion as well as the rate of divergence of the potential surface. The nature of such a collision clearly favours the selection of new electronic basis functions, moving to the simple structures corresponding to exact electronic configurations, e.g., covalent or ionic, which do cross to give a physically realistic representation of the process (figure 4.3b). This is known as the diabatic case.
Figure 4.3:
(a) adiabatic representation
(b) diabatic representation

$R_c$ internuclear distance
It must be stressed that the diabatic potential system is only a useful approximation to that of the "true process", and no formal definition of the diabatic representation exists. The potentials may be constructed either from the adiabatic potentials by extrapolation at the avoided crossing (NIK 74), or by choosing potentials of the desired electronic character.

In this Thesis the diabatic representation is chosen, since the high collision energies involved may be expected to lead to the breakdown of the Born-Oppenheimer approximation at the crossing regions. Therefore the potentials have been selected according to electronic type, using established knowledge of molecular parameters where possible.

Having established the form of the electronic part of the model, there remain the problems of finding an appropriate method of calculating the nuclear motion over the potential surfaces and of choosing a suitable means of handling the transitions. The methods for solving the nuclear motion can be placed into two categories, the "state-based" and the "trajectory-based". Some examples of the "state-based" philosophy will be mentioned in Chapter 5, but for the moment the discussion will deal only with the method chosen for the present model, which is a simple classical trajectory method.
These calculations have proved the most useful in the study of adiabatic collision processes (BUN 71), and their development in diabatic collision dynamics has achieved similar success (ATE 77a). Chapter 6 explains in some detail the classical path and surface-hopping trajectory methods, but the simple impact parameter method used here may be summarised in the following manner. The nuclei are assumed to move classically over any portion of potential surface on the collision path, and transition probabilities are calculated at each crossing point encountered en route to find the overall probability of emerging in a given exit channel. The collision trajectories are assumed to be straight line (and of constant velocity) and so the impact parameters scan through the intermolecular potential. Thus the differential cross-section may be calculated from the potentials using the formulae of section 4.5, modified by the total transition probability.

4.4 The Landau-Zener Approximation

The simplest curve crossing approximation, developed independently by Landau (LAN 32), Zener (ZEN 32) and Stuckelberg (STÜ 32), has remained the most important of the transition probability expressions, though it has frequently come under rigorous investigation, see e.g., (BAE 75).
Its assumptions are as follows:

1. There is only one external coordinate $R$.
2. Only two states, labelled 1 and 2, interact.
3. The radial velocity $v_r$ is constant around the crossing point.
4. The diabatic potentials are linearly dependent on $R$ (and therefore $t$) in the crossing region.
5. The off-diagonal coupling terms $H_{12}$ are constant.

From these assumptions, the diabatic transition probability that a system in state 1 will cross into state 2 at the crossing point $R_c$ was derived as

$$P_{12}(b) = 1 - \exp(-2\pi H_{12}^2 / \kappa v_r(b) |S_1 - S_2|_{R_c})$$

where $S_1$, $S_2$ are the gradients of the diabatic potentials at the crossing point. Thus the Landau-Zener approximation, which applies equally well to the adiabatic treatment, provides a useful and appropriate expression for these model calculations, with the third assumption fulfilled by the nature of the experiment. Although the Landau-Zener model breaks down at sufficiently high energies where the fifth assumption becomes invalid (BAT 60), alterations can be made in the overall calculation to handle this difficulty.

4.5 Description of the Model

Before discussing in detail the exact development of the model used in this Thesis, it
is useful to consider the method of calculation for the differential cross-sections which provide the link between theory and experiment. Classical mechanics yields good approximate results in the energy range in which these experiments lie, since the de Broglie wavelengths associated with the nuclear motion are small compared to the distance over which a significant variation in the potential takes place. As the measurements were made in the narrow angle region about the main beam line, it is possible to make use of the classical small angle formulae, see e.g., (FLU 73), obtaining the deflection function \( \chi(b) \) from

\[
\chi_s(b) = \frac{s}{\pi} \left[ \frac{(s+1)/2}{(s/2 + 1)} \right]^{1/2} 2E_b^s \tag{4.14}
\]

for any potential of the form

\[
V(R) = \sum S \frac{C_s}{R^{-S}} \tag{4.15}
\]

Thus the deflection function \( \chi \) is calculated by summing the contributions \( \chi_s \), and hence the classical differential cross-section may be evaluated using

\[
\sigma(\chi) = b/\sin \chi \left| \frac{d\chi}{db} \right| \tag{4.16}
\]

In passing it is worth noting that in the limiting case where a single term in the potentials provides the dominant contribution, the differential cross-section may be written.
\[ \sigma(\chi) = \frac{1}{s} \pi \left[ \frac{1}{E} \frac{((s + 1)/2) C_s}{(s/2 + 1)} \right]^{2/s} \chi^{-(2+2/s)} \]

(4.17)

for \( s \geq 3 \)

It is seen that elastic differential cross-sections measured in the narrow angle region may be used to estimate the repulsion power of the intermolecular potential, by plotting \( \log \sigma_{\text{exp}}(\chi) \cdot \chi^2 \) vs. \( \log \chi \) to obtain the gradient \( \left( -\frac{2}{s} \right) \).

Returning to the main discussion, the small angle deflection functions are found for the processes under investigation, which result via transitions from the ground state onto an intermediate ionic potential and then to the final state, by summing the contributions of each section of potential covered by the collision path. The differential cross-sections are calculated using the classical formulae, multiplied by the appropriate Landau-Zener crossing probabilities at the intersections encountered on the pathway.

At this point the model has been developed to make best use of the experimental conditions i.e., at these energies (from tens of electron volts) the potassium atom trajectories can be considered rectilinear and of constant velocity.
and the collision can be described in diabatic terms. In order to fully investigate the collision process, a decision on the role of internal motion in the target molecule is required. The simplest model would treat the molecule as rigid with the molecular bond length frozen at its equilibrium position throughout the collision. Previous results have shown this "atomic" description to be inadequate except when the collision lifetime is very much shorter than the molecular vibrational period (HUB 76), (SUT 80). In these experiments the collision lifetime is of the same order as the vibrational time, about $10^{-14}$ s, and as the vertical electron transition from the molecular ground neutral to the ionic state can generally be expected to place the negative ion in a non-equilibrium position on the repulsive wall, the molecular bond will stretch in this time. The molecular relaxation will cause drastic changes in the vertical electron affinity and hence the positions of the crossing zones. On exiting to one of the neutral channels the molecule will be left in a vibrationally excited state (figure 4.4).

Thus the moving target model gives manifestly different results compared to the frozen target treatment, both in terms of cross-section since the increasing crossing radii give the system a longer...
Following the vertical electron transition, the molecule moves classically over the negative ion potential. On return to the neutral surface, the molecule is left in a vibrationally excited state, conserving position and momentum by the Franck-Condon principle, i.e., $E_{\text{vib}} = PE + KE$. 

Figure 4.4: Calculation of Vibrational Energy Loss
path on the attractive ionic branch and a diminished crossing probability on exit, and importantly in the calculated energy losses, which now include vibrational excitation. The marked influence of bond-stretching has been investigated in experiments on ion pair formation (HUB 76), (ATE 77). Their work confirmed that diabatic behaviour becomes more likely at the second crossing, so enhancing the ion pair cross-section. An alkali atom velocity of about $4 \times 10^4 \text{ ms}^{-1}$ was considered the upper limit for bond-stretching based on typical vibrational periods. In the experiments reported in this Thesis, the potassium atom travelled at about $3 \times 10^4 \text{ ms}^{-1}$.

It is seen that the fly-by time over the ionic surface acts as a clock on the internal motion of the molecule. This lifetime is a function of impact parameter (figure 4.2) and so is related to the reduced scattering angle $E \chi$. Thus each angular range samples not only a particular set of paths over the intermolecular potentials but also covers a specific period spent on the negative ion potentials. Therefore the experiments plot the race of external and internal motion during the collisional encounter.

The potentials used to describe these processes are given later in this Chapter, but it should be noted here that in this model no
cross-terms coupling internal and intermolecular potentials are included. Motion within the negative ion is independent of the position of the potassium ion, the only connection between the two potential energy structures being via the electron affinity.

The model results were computed using the program listed in Appendix C, with a block diagram of the program structure appearing in figure 4.5. The calculated "early" and "late" crossing contributions were summed for comparison with experimental results. Computing work was carried out on the Edinburgh Regional Computing Centre's ICL 2970, 2980 (and latterly 2972) devices, a complete impact parameter scan over the possible exit channels requiring around 100s CPU typically.

4.6 Potassium-Nitrogen Potentials

As stated at the beginning of this Chapter, the potentials were constructed using established information whenever available and any deviations to obtain a good model fit on experimental data had to be kept within reason and to a minimum.

The potassium-nitrogen system has come under close investigation in recent years (KEM 75), notably by Kempter (MAR 79) who observed potassium (4^2P) excitation using a photon coincidence technique. The intermolecular potentials used successfully in that work were adopted here, but with a slightly altered ionic curve for reasons
START
↓
read potential parameters, crossing probabilities
↓
read initial impact parameter, b, channel number
↓
calculate time spent on ionic curve from crossing radii and impact parameter (fig. 4.2)
divide time into step lengths of ΔT
↓
calculate acceleration on molecular ion potential at r, increment r by Δr, find new electron affinity at end of time interval ΔT
↓
has all the n time been used?
? Y
calculate new crossing radii
↓
is difference n between old and new radii small?
? Y
calculate deflection function, differential cross-section, energy losses, using small angle formulae and Landau-Zener expression, for the path taken over the potentials
STOP

Figure 4.5:
Block Diagram of Moving Target Program
given below. These were based on potential parameters calculated from total cross-section experiments (MAL 77) and were of the form

\[ V_{K/N_2}(R) = C_s R^{-s} \]  

(4.18)

\[ V_{K+/N_2}(R) = V_{K/N_2}(R) - \frac{14.394}{R} - \frac{62.2}{R^4} + I.P. K - E.A. N_2 \text{ eV} \]

for \( R > R_c \) 

(4.19)

\[ = V_{K/N_2}(R) \]

for \( R < R_c \) 

(4.20)

The constants used are given in table 4.2. The excited potassium potential is taken to be identical in shape to the ground state but shifted asymptotically by 1.62eV. Kempter found that in order to reproduce the K \((4^2P)\) differential cross-section the attractive terms in the ionic potential had to be removed at the crossing point. To achieve this he introduced a switching function, but in the present calculations it was considered simplest to set up the ionic potential as indicated in equations 4.19 and 4.20, so retaining the use of the small angle formulae. The potential diagram is shown in figure 4.6. It is seen from table 4.2 that the repulsive exponent is increased within the crossing radius. Considerable improvement in the model fit of the elastic channel differential
Table 4.2
Potassium-Nitrogen Parameters

<table>
<thead>
<tr>
<th>System</th>
<th>Parameter</th>
<th>Value, units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-N$_2$</td>
<td>$C_s$</td>
<td>374 eV$^6.4$</td>
<td>(MAL 77)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.4 \times 10^4$ eV$^9.0$</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td>$S$</td>
<td>6.4 (1)</td>
<td>(MAL 77)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.0</td>
<td>(2)</td>
</tr>
<tr>
<td>N$_2$</td>
<td>$D_1$</td>
<td>9.8 eV</td>
<td>(GIL 65)</td>
</tr>
<tr>
<td></td>
<td>$\beta_1$</td>
<td>2.50 Å$^{-1}$</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td>$r_{01}$</td>
<td>1.10 Å</td>
<td>(HER 50), (GIL 65)</td>
</tr>
<tr>
<td></td>
<td>E.A.</td>
<td>$-1.95$ eV</td>
<td>-</td>
</tr>
<tr>
<td>N$_2^-$</td>
<td>$D_2$</td>
<td>8.5 eV</td>
<td>(GIL 65)</td>
</tr>
<tr>
<td></td>
<td>$\beta_2$</td>
<td>2.20 Å$^{-1}$</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td>$r_{02}$</td>
<td>1.185 Å</td>
<td>(4)</td>
</tr>
<tr>
<td></td>
<td>AL$_1$</td>
<td>0.3 eV</td>
<td>(GIL 65)</td>
</tr>
</tbody>
</table>

(1) initial value as selected by Kempter (MAR 79) from the results of Malerich et al. (MAL 77) which in the final set of potentials apply only for $R > R_C$

(2) revised values in final set valid in the region $R < R_C$

(3) value chosen to obtain the best fit on Gilmore potentials in the bowl region

(4) final value for equilibrium bond length of N$_2^-$. The energy loss calculations were extremely sensitive to this parameter (see Chapter 5).
KIN 2: First set of potentials

K(4^2 S)+N^2(X)

KIN 2: Best set of potentials

- K/N_2
- 3.43 K(4^2 P)+N^2(X) 2.77

Figure 4.6: Potassium-Nitrogen Potentials
cross-section was obtained by this adjustment (see figure 5.1).

The molecular potentials were chosen to fit the values given by Gilmore (GIL 65), particularly in the important bowl region. The existence of the nitrogen negative ion was previously indicated by electron scattering experiments, with a lifetime of at least $10^{-14}$ s (SCH 62). Thus it is a physically plausible species in terms of the collision time, as suggested by Bauer et al. (BAU 69). Gilmore derived the $N_2^-$ curve from the early electron scattering data and by comparison with adjacent members of the isoelectronic series, $O_2^+$, NO.

Morse type functions have been used to define the molecular potentials, equations 4.21, 4.22, which are shown in figure 4.7. The potential parameters are indicated in table 4.2.

$$V_{N_2}(r) = D_1 \left\{ 1 - \exp \left[ -\beta_1 (r - r_01) \right] \right\}^2 - D_1 \quad (4.21)$$

$$V_{N_2^-(r)} = D_2 \left\{ 1 - \exp \left[ -\beta_2 (r - r_{02}) \right] \right\}^2 - D_2 + AL_1 \quad (4.22)$$

Using these values, the potentials give a vertical electron affinity for nitrogen of about -1.9 eV, so setting the asymptotic limit of the ion pair state over the ground state at around 6.25 eV. From the
Figure 4.7: Nitrogen Potentials
relative positions and shapes of the potential wells up to 1.6eV vibrational energy may be added to any electronic energy loss sustained during the collision.

The crossing probabilities were calculated using the Landau-Zener formula (equation 4.13) with the values given in table 4.3. The matrix element coupling the ionic and excited states was fixed to allow only adiabatic behaviour at the crossing i.e., for the purposes of the three state model all encounters remaining on the ionic path after the second crossing finished up in the K \( (4^2\text{P}) \) excitation channel. This is quite reasonable since ionising collisions can be considered rather unlikely in the potassium-nitrogen system. The matrix element \( H_{12} \) coupling the ground and ionic states was also assigned a fixed value independent of the crossing radius, a major simplification which might be expected to cause difficulties.

4.7 Potassium-Oxygen Potentials

Because of the special difficulties posed by the number of possible exit channels in the potassium-oxygen system, particularly within the low energy loss regime, it was considered best to arrive at a simple set of potentials for the three state system and, having achieved rough agreement with them, seek to introduce a fourth potential describing the \( O_2(1\Delta_g) \) excitation channel.
Crossing Probabilities (1)
Used to Obtain Model Fit

<table>
<thead>
<tr>
<th>System</th>
<th>$H_{12}$/eV</th>
<th>$H_{23}$/eV</th>
<th>$H_{34}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-N$_2$</td>
<td>0.7</td>
<td>3.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(2.5 x 10$^4$)</td>
<td>(100 x 10$^4$)</td>
<td></td>
</tr>
<tr>
<td>K-O$_2$</td>
<td>0.21</td>
<td>0.37</td>
<td>0.09 (2)</td>
</tr>
<tr>
<td></td>
<td>(0.7 x 10$^4$)</td>
<td>(5.0 x 10$^4$)</td>
<td>(0.2 x 10$^4$)</td>
</tr>
<tr>
<td>K-SF$_6$</td>
<td>0.63</td>
<td>0.40</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(1.5 x 10$^4$)</td>
<td>(3.0 x 10$^4$)</td>
<td></td>
</tr>
</tbody>
</table>

(1) Crossing probabilities were calculated using the equation

$$P_{12} = 1 - \exp \left(-\frac{V_{12}}{V_r}\right)$$

with $V_{12}$ expressed in units of ms$^{-1}$, rather than using the full Landau-Zener expression. The table gives the matrix elements in the Landau-Zener formula as calculated from the initial values of $V_{12}$, which are shown in parentheses after each $H_{12}$.

(2) The coupling element for the ionic and K(4$^3$S)/O$_2$(1$^3$A$_g$) states.
The program was also modified to calculate the extent of vibrational excitation in the excited oxygen "a" state. The $O_2(1\Delta_g)$ excited state can be expected to play a part in the collision as its formation has been observed in the inverse process, the quenching of excited alkali atoms by oxygen (HER 77), (SIL 79).

The potentials were written as

$$V_{K/O_2}(R) = CS_R^{-S}$$

(4.23)


(4.24)

with the parameters provided in table 4.4. The repulsive terms were chosen arbitrarily to give a reasonable estimate for the ground state potential and consequently must be considered rather approximate. The excited potassium state corresponds to the ground neutral shifted by 1.62eV, as in the K/N$_2$ system. The $K(4^2\Sigma^+)/O_2(1\Delta_g)$ potential has the same form as the ground state curve but raised by the energy difference between the ground and excited oxygen potentials, a value dependent upon the bond length. The intermolecular potentials are shown in figure 4.8, at their positions for $r(O_2) = r_e(O_2)$. 

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### Table 4.4

#### Potassium-Oxygen Model Parameters

<table>
<thead>
<tr>
<th>System</th>
<th>Parameter</th>
<th>Value, units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1.67x10&lt;sup&gt;6&lt;/sup&gt; eV Q&lt;sub&gt;12&lt;/sub&gt;</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>12.0</td>
<td>(2)</td>
</tr>
<tr>
<td>K&lt;sup&gt;+&lt;/sup&gt;-O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C'&lt;sub&gt;s&lt;/sub&gt;</td>
<td>2.00x10&lt;sup&gt;6&lt;/sup&gt; eV Q&lt;sub&gt;12&lt;/sub&gt;</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>S'</td>
<td>12.0</td>
<td>(2)</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>D&lt;sub&gt;1&lt;/sub&gt;</td>
<td>5.11 eV</td>
<td>(HER 50) (GIL 65)</td>
</tr>
<tr>
<td></td>
<td>B&lt;sub&gt;1&lt;/sub&gt;</td>
<td>2.77 Å&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td>r&lt;sub&gt;01&lt;/sub&gt;</td>
<td>1.21 Å</td>
<td>(HER 50) (GIL 65)</td>
</tr>
<tr>
<td></td>
<td>E.A.&lt;sub&gt;v&lt;/sub&gt;</td>
<td>0.24 eV</td>
<td>-</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>D&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4.09 eV</td>
<td>(GIL 65) (CEL 72)</td>
</tr>
<tr>
<td></td>
<td>B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.96 Å&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td>r&lt;sub&gt;02&lt;/sub&gt;</td>
<td>1.31 Å</td>
<td>(ROL 64) (GIL 65)</td>
</tr>
<tr>
<td></td>
<td>AL&lt;sub&gt;1&lt;/sub&gt;</td>
<td>-1.45 eV</td>
<td>(5)</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;(&lt;sup&gt;1&lt;/sup&gt;Δ&lt;sub&gt;g&lt;/sub&gt;)</td>
<td>D&lt;sub&gt;3&lt;/sub&gt;</td>
<td>4.10 eV</td>
<td>(GIL 65)</td>
</tr>
<tr>
<td></td>
<td>B&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.60 Å&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td>r&lt;sub&gt;03&lt;/sub&gt;</td>
<td>1.21 Å</td>
<td>(GIL 65)</td>
</tr>
<tr>
<td></td>
<td>AL&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.00 eV</td>
<td>(6)</td>
</tr>
</tbody>
</table>

(1) A rather uncertain estimate of the repulsive interaction. The choice was made to provide the crossing point at around 3.5 Å i.e., the repulsion was not so strong that the relation R<sub>∞</sub> = 14.394/ΔE did not hold. However cf Kényn's estimate (KLE 80a) used for lower collision energies, which are much less repulsive.

cont'd/...
Only the repulsive term is considered of importance. Attractive exponential 6 term is neglected. Again cf (KLE 80a).

Values were chosen to provide best fit on Gilmore potentials (GIL 65) in the bowl region.

The energy loss calculations were very sensitive to changes in the ionic equilibrium bond length. The value chosen coincides with X-ray experiments on KO$_2$ (ROL 64).

An estimate of the electron affinity of the oxygen atom. This matches the value given by Gilmore (GIL 65).

The excited O$_2$(1$^1\Delta_g$) state dissociates to the same atomic products as the ground state, two O($^3$P) atoms.
Figure 4.8: Potassium-Oxygen Potentials
The internal potentials correspond to the values given by Gilmore (GIL 65), who mapped out the $O_2(\text{^1}A_g)$ curve in addition to the ground neutral and ionic states. In order to obtain agreement with experiment, some changes were made to certain molecular parameters rather than use their customary values. A notable difference is seen in the ionic equilibrium bond length, reduced from 1.34\AA as found by Celotta et al (CEL 72), to 1.31\AA, as indicated in earlier X-ray data on KO$_2$ crystals (ROL 64).

The internal potentials were written as Morse functions

\begin{align}
V_{O_2}(r) &= D_1 \left\{ 1 - \exp \left[ -\beta_1 (r - r_{01}) \right] \right\}^2 - D_1 \quad (4.25),

V_{O_2}^-(r) &= D_2 \left\{ 1 - \exp \left[ -\beta_2 (r - r_{02}) \right] \right\}^2 - D_2 + A_1 \\
V_{O_2}^*(r) &= D_3 \left\{ 1 - \exp \left[ -\beta_3 (r - r_{03}) \right] \right\}^2 - D_3 + A_2 \\
\end{align}

The parameter values are available in table 4.4 and a potential diagram of the oxygen system is shown in figure 4.9.

The matrix elements coupling neutral and ionic states were functions of the crossing radius by the relationship given in equation 4.28. The initial coupling parameters are listed in table 4.3.
Figure 4.9: Oxygen Potentials
\[ H_{ij}(R_{ij}) = H_{ij}^0 \left( \frac{R_{ij}}{R_{ij}^0} \right) \quad (4.28) \]

It is seen that the relationship is not the usual exponential dependence (HAS 62a), which was too severe to obtain a model fit. Unlike the case for potassium-nitrogen scattering, however, some dependence on the crossing radius was required to produce agreement with experimental observations. Because several possible exit channels may be contributing to an observed inelastic process it is doubtful whether the introduction of the parameter is worthwhile, and it would certainly be rash to draw any significance from it.

4.8 **Potassium-Sulphur Hexafluoride Potentials**

The potassium-sulphur hexafluoride potentials were obtained from the results of Malerich et al (MAL 77), using a slightly higher value of \( C_s \) than suggested by that work, but keeping the same repulsive exponent \( s \). Again as in the case of potassium-nitrogen and potassium-oxygen scattering, the ground neutral state is considered as purely repulsive, a good approximation for the collision conditions in this experiment. The ionic representation is constructed from the Coulomb force superposed on a strong core repulsion, plus the asymptotic limit, and once more the K(4\(^2\)P) potential runs parallel to the ground state, shifted by 1.62eV. The potentials take the form
\[ V_{K/\text{SF}_6}(R) = C_s R^{-S} \quad (4.29) \]
\[ V_{K+/\text{SF}_6^{-}}(R) = C_s' R^{-S'} - 14.394/R + \]
\[ \text{I.P.}_K - \text{E.A.}_{\text{SF}_6} \text{ eV} \quad (4.30) \]

Figure 4.10 shows the shape of the potential system and the parameters for the above equations are found in table 4.5.

The matrix elements \( H_{ij} \) were again related to the crossing radii by the equation

\[ H_{ij}(R_{cij}) = H_{ij}^0(R_{cij} / R_{cij}) \quad (4.31) \]

Details of the starting values are given in table 4.3.

At this stage the sulphur hexafluoride molecule might be considered a rather inappropriate choice for a simple diatomic model. The model's ability to handle general systems could be expected to be severely tested by such a molecule. However this is not necessarily the case, as sulphur hexafluoride has been described with some success by effective diatomic potentials (HUB 75), (OKA 80). Indeed the known behaviour of the \( \text{SF}_6^- \) ion to fragment to \( \text{SF}_5^- \) and a fluorine atom suggests that the diatomic model may be physically realistic, at least over the time scale of the collisional encounter (LEF 74), (COM 78). The \( \text{SF}_5^- \) ion has been prepared chemically and its vibrational spectrum
**Table 4.5**

Potassium-Sulphur Hexafluoride Model Parameters

<table>
<thead>
<tr>
<th>System</th>
<th>Parameter</th>
<th>Value, units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-SF$_6$</td>
<td>$C_s$</td>
<td>$2.33 \times 10^7$ eV$^3 13.7$</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>$S$</td>
<td>13.7</td>
<td>(MAL 77)</td>
</tr>
<tr>
<td></td>
<td>$C'/s'$</td>
<td>$3.44 \times 10^6$ eV$^3 13.7$</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>$S'$</td>
<td>13.7</td>
<td>(MAL 77)</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>$D_1$</td>
<td>3.38 eV</td>
<td>(COM 78)</td>
</tr>
<tr>
<td></td>
<td>$\beta_1$</td>
<td>1.58 $\AA^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td>$r_{01}$</td>
<td>1.56 $\AA$</td>
<td>(HER 67)</td>
</tr>
<tr>
<td></td>
<td>$E.A_v$</td>
<td>-0.56 eV</td>
<td>(3)</td>
</tr>
<tr>
<td>SF$_6^-$</td>
<td>$D_2$</td>
<td>1.00 eV</td>
<td>(COM 78)</td>
</tr>
<tr>
<td></td>
<td>$\beta_2$</td>
<td>1.25 $\AA^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td>$r_{02}$</td>
<td>2.12 $\AA$</td>
<td>(4)</td>
</tr>
<tr>
<td></td>
<td>$AL_1$</td>
<td>-2.9 eV</td>
<td>(COM 72)  (COM 78) (5)</td>
</tr>
<tr>
<td></td>
<td>$H$</td>
<td>0.4 eV</td>
<td>(6)</td>
</tr>
<tr>
<td></td>
<td>$a$</td>
<td>1.00 $\AA^{-1}$</td>
<td>(6)</td>
</tr>
<tr>
<td></td>
<td>$R_h$</td>
<td>3.25 $\AA$</td>
<td>(6)</td>
</tr>
</tbody>
</table>

(1) The value for the ground state repulsion $C_s$ term is of the same order as that determined by Malerich et al (MAL 77). Their work only covered the regime in $R$ outside the crossing radius ($>3.6\AA$), while these results are strongly influenced by the repulsive wall within $R$. The ionic potential $C_s$ parameter gives a softer repulsion than that of the ground neutral.

cont'd/...
(2) Value chosen to give approximate agreement with vibrational frequency measurements (HER 67) in ground state neutral. Ionic value chosen as rough estimate only.

(3) The potentials were set up such that the vertical transition arrives on the negative ion repulsive wall above the dissociation limit of SF$_6^-$. There has been a great deal of discussion on the (adiabatic) electron affinity of SF$_6^-$, (LEF 74), (HUB 75), producing results ranging from 0.3 to 1.5eV.

(4) Estimate of position of equilibrium bond length in SF$_6^-$. 

(5) The electron affinity of SF$_6$. 

(6) Arbitrarily chosen values designed to provide a retarding barrier near the "dissociation point" in the SF$_6^-$ ion, i.e., the point at which the second vertical electron transfer leaves the SF$_6$ molecule with an internal energy greater than its bond energy. The limitations imposed on these values are that they remain small and local, not providing a highly artificial construction and not interfering with the other portions of the curve.
Figure 4.10 : Potassium-Sulphur Hexafluoride Potentials
studied (CHR 72). The ion was found to be square pyramidal (C_{4v}) and with similar S-F bond lengths to sulphur hexafluoride. Thus it seems likely that dissociation is achieved by the simple extraction of a fluorine atom with little deformation in the SF_5^- remnant (COM 72). Ion pair formation studies, including investigations of the role played by internal energy (HUB 75), have shown that SF_5^- formation is the dominant process at low and medium collision energies. The question remains whether a fluorine atom can be moved a significant distance during the "fly-by" time of the potassium ion in the present experiment. A reasonable estimate of the time spent on the ionic potential may be around 1.5 \times 10^{-14} s, with the upper limit around 2.5 \times 10^{-14} s under these experimental conditions. Using the effective diatomic potentials described below the fluorine atom would move from 1\AA{} up to about 2\AA{} in the period, enough to cause some dissociation at the longer ranges. Even using the stretching mode vibrational frequencies in the SF_6 ground state, which are thought to be the only modes involved in K/SF_6 reaction (SLO 72) but which should also be considerable underestimates of the ionic motion, the fluorine atom can move 0.5\AA{} in the time available. Thus it is suggested that the effective diatomic model provides a reasonable
indication of the behaviour of the sulphur hexafluoride molecule during the collision.

The potentials chosen have remained as consistent as possible with those of earlier workers, although there has been considerable controversy over the value of the electron affinity of SF$_6$ (LEF 74), (HUB 75). Again Morse functions have been employed, but a local hyperbolic tangent term has been included as a retarding "hump" in the ionic potential, for reasons made clear in the next Chapter. The potentials are written as follows, with the parameters available in table 4.5:

\[
V_{SF_6}(r) = D_1 \left\{ 1 - \exp \left[ -\beta_1 (r - r_{01}) \right] \right\}^2 - D_1 \tag{4.31}
\]

\[
V_{SF_6}^{-}(r) = D_2 \left\{ 1 - \exp \left[ -\beta_2 (r - r_{02}) \right] \right\}^2 - D_2 + H \left\{ 1 - \tanh^2 (ar - r_h) \right\} + AL \tag{4.32}
\]

Figure 4.11 presents the internal potentials.

Table 4.6 summarises the crossing radii at the start of the collision process for all of the potassium-target molecule systems.
Figure 4.11: Sulphur Hexafluoride Potentials
**Table 4.6**

Crossing Radii taken from the Model Potentials for \( r = r_e \)

<table>
<thead>
<tr>
<th>System</th>
<th>( R_{13}/\text{\AA} )</th>
<th>( R_{23}/\text{\AA} )</th>
<th>( R_{34}/\text{\AA} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-N(_2)</td>
<td>2.77</td>
<td>3.43</td>
<td>-</td>
</tr>
<tr>
<td>K-O(_2)</td>
<td>3.55</td>
<td>5.92</td>
<td>4.71</td>
</tr>
<tr>
<td>K-SF(_6)</td>
<td>3.49</td>
<td>4.48</td>
<td>-</td>
</tr>
</tbody>
</table>
CHAPTER 5

DISCUSSION

5.1 Preamble

Model calculations were carried out for each of the collision systems according to the previous Chapter. These results are compared with the experimental data of Chapter 3 and discussed in sections 5.2, 5.3 and 5.4. In addition to the impact parameter studies of processes in the low energy loss regime, an attempt is made to identify the higher lying inelastic processes, associated with molecular excitation.

Section 5.5 contains further discussion pertinent to one or all of the target systems, and includes some comment on alternative models. Of particular interest here is the recent development of an adiabatic direct coupling mechanism, the "bond-stretch attraction" method, which now challenges the long-standing "harpoon" picture of the excitation mechanism.

5.2 The Potassium-Nitrogen System

Electronic excitation of alkali atoms through collisions with diatomic molecules has been investigated by a number of workers (KEM 75), while over the years considerable effort has been made in studying quenching in these systems,
particularly the de-excitation of sodium \( \left( 3^2P \right) \) by molecular nitrogen \((\text{BAU 69}, \ (\text{BOT 75})\). However it is only fairly recently that collisional excitation in the potassium-nitrogen system has come under scrutiny, by Gersing et al using a time of flight technique \((\text{GER 73})\), and Kempter, by fluorescence methods \((\text{KEM 73})\) and by means of a coincidence experiment \((\text{MAR 79})\). The coincidence apparatus yielded the differential cross-section for excitation to the potassium \( \left( 4^2P \right) \) state, though the extent of vibrational excitation in the molecule remained undetermined due to insufficient energy resolution.

In the results of this Thesis, although it is not possible to unambiguously assign excited states to observed exit channels, the task of identifying the low energy processes is relatively simple. Since the first excited state of nitrogen, \( A^3 \Sigma_u^+ \), occurs at 6.2eV above the ground state, the ground ionic potential can only be responsible for atomic excitation (see figure 4.6). The fluorescence experiments \((\text{KEM 73})\) have shown that potassium \( \left( 4^2P \right) \) excitation is by far the most probable, with populations of the \( \left( 5^2P \right) \) and \( \left( 6^2S \right) \) states at about 2% and 0.6% abundance in comparison. Thus the first inelastic channel, process 2 in table 3.3, ranging from 1.6 to 3.2 eV energy loss with overall maximum intensity at 2.8eV, is
assigned to $K(4^2P)$ excitation, with the excess energy due to molecular vibration. The much weaker peak at about 4.7eV, i.e. process 3, may be due to $K(5^2S)$, $K(5^2P)$ or $K(6^2S)$ excitation, again with associated vibration in the nitrogen target. Gersing et al (GER 73) assumed that vibrational excitation could be neglected on the basis that the main elastic peak did not display an inelastic contribution with increasing angle. As a result they concluded that the main inelastic peak was due to $K(5^2S)$ and $K(3^2D)$ excitation, subsequently disproved by the fluorescence results (KEM 73).

Using the potentials described in the previous Chapter, the model calculated differential cross-sections and energy losses for the $K(4^2S)$ and $K(4^2P)$ channels. Figure 5.1 shows the model fit on the experimental cross-sections using the initial set of potentials as developed by Kempter and the final best set, while figure 5.2 gives a plot of energy loss with angle for model and experiment. The model results are obtained from the sum of early and late crossing contributions. It is seen that the final set yield differential cross-sections in very good agreement with experimental observations.

Because the motion on the negative ion potential is bound, only small changes are made in
Figure 5.1:
Differential cross-sections for potassium-nitrogen scattering at 85.5 eV CM collision energy. Experimental observations are shown by the error bars. The model predictions using the Kempter set and the final set of potentials are shown by the broken and solid lines respectively.
Figure 5.2: Observed and Predicted Energy Loss Behaviour with Scattering Angle

The error bars indicate experimental energy losses for potassium-nitrogen scattering at 85.5eV CM collision energy. These have been obtained from angle averaged TOF profiles with 'right dress' carried out by inspection. The values chosen in figures 5.6 and 5.9 were achieved similarly. The model results are represented by the solid lines, with early and late crossing contributions summed to give weighted averages.
the crossing radii. As a result the energy loss
due to vibrational excitation depends almost
exclusively on the relative shapes of the \( N_2 \) and
\( N_2^+ \) potentials, while the cross-sections depend
mainly upon the intermolecular potentials. In
the case where the electron transfer is to an
unbound ionic state, this separation cannot be
made (SUT 80).

The shape of the \( K(4^2S) \) ground state
differential cross-section is determined by the
Landau-Zener formula, which is seen to work
reasonably well using a constant value for the
matrix element \( H_{12} \). In order to obtain a good
cross-sectional fit for the position of the
Landau-Zener minimum, the first set of potentials
used a higher repulsion within the crossing
radius, raised from 6.4 to 9.0.

The plot of energy loss vs. scattering
angle shows that although the \( K(4^2P) \) excitation
channel is well matched, even to the extent of
correctly predicting the oscillations, the \( K(4^2S) \)
state is populated too heavily by ionic scattering
collisions i.e. there is too much adiabatic
behaviour at the first crossing between ground and
ionic potentials and on the return intersection.
Increasingly, diabatic motion can be expected at
the second crossing as the radius moves out to
wider intermolecular distances during the time
spent on the ionic surface, so the introduction
of an $R_c$ dependence in the matrix element $H_{12}$ ought to reduce the contribution of early crossing trajectories to the ground state population. Unfortunately attempts to introduce such a dependence have failed due to their severe diminishing of the cross-section for potassium excitation. This same problem led Gersing et al to their erroneous decision (GER 73).

A further point to be noted is that early and late crossing contributions to the excited potassium channel have not been resolved in this experiment; this is not unexpected since the model predicts similar energy loss oscillations in approximately random phase to one another. Experiments at lower collision energies, where time of flight resolution is substantially improved, may be able to distinguish between the separate peaks. The importance of highly excited atomic states is mentioned briefly at the end of this Chapter.

The predicted energy losses proved very sensitive to the relative positions and shapes of the molecular potentials, a shift of around 0.01Å in the negative ion equilibrium bond length causing differences of up to 0.5eV. Furthermore the established Gilmore potentials describe the experimental observations very well, indicating that the proximity of the potassium ion does not
greatly perturb the $\text{N}_2^-$ potential. That the internal and external motions are largely decoupled is also reflected in the atom-molecule potential. The best results are obtained when the attractive terms of the ionic potential are switched off within the crossing radius, suggesting that the nitrogen molecule and ion "look" rather similar to the potassium. Once more this is in contrast to experiences in potassium-alkyl halide systems, e.g., (FLU 79), and may be attributed to the bound nature of the molecular ion.

Due to the relatively small number of states available to molecular nitrogen and their excitation energies, the spectrum for potassium-nitrogen scattering has been split rather conveniently into two sections. The energy loss processes accessible via the ground ionic potential have been discussed and assigned to atomic excitation, leaving the energy loss range above 6eV exclusively to molecular emission. The experimental results show that these processes onset at narrow angles, which, considering the extent of translational to electronic energy transfer, suggests the involvement of strongly attractive, intermediate potentials, perhaps due to transient excited negative ion states.

The electronic structure of nitrogen in its ground state, designated
$N_2$ $X^1Σ^+$ is

$\left(1σ_g^2 \left(1σ_u^2 \left(2σ_g^2 \left(2σ_u^2 \left(1π_u^4 \left(3σ_g^2 \right)^2 \right) \right) \right) \right)^2$ (lag)$^2$ (la)$^2$ (2ag)$^2$ ( 2 a)$^2$ (1)4 (3a9 ) 2

with the $N_2^-$ ground state, $X^2Π_g^-$, placing the additional electron in the lowest available orbital, $1π_g$. Table 5.1 shows the electronic configurations of some excited states of nitrogen, while figure 5.3 illustrates the potential energy curves of the nitrogen system, based on Gilmore (GIL 65).

It is seen from table 5.1 that several semi- or near-Rydberg (MUL 77) excited valence states of nitrogen, e.g., $B^3Π_g$, as well as fully Rydberg states can be accessed by electronic transitions from the ground ionic state, i.e., the electron recaptured by the potassium ion on exiting the collision is taken from a lower-lying orbital, leaving the receptor orbital occupied and a vacancy in a normally filled position. Table 5.2 shows the energy losses expected by these transitions (HER 50) and comparison with the experimental results in table 3.3 leads to the assignments given in table 5.3. Since there is little interaction between the outer electron and the positive core, the orbital energies of these states should be well-defined, but considerable mixing is expected with valence states (MUL 77) and consequently these assignments must be considered only as possible candidates. Other states which have been assigned to energy loss
Figure 5.3: Potential Energy Curves for $N_2$
### Table 5.1

Molecular Orbital Electronic Configurations of Nitrogen

<table>
<thead>
<tr>
<th>State</th>
<th>$1\sigma_g$</th>
<th>$1\sigma_u$</th>
<th>$2\sigma_g$</th>
<th>$2\sigma_u$</th>
<th>$1\pi_u$</th>
<th>$3\sigma_g$</th>
<th>$1\pi_g$</th>
<th>$3\sigma_u$</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^1\Sigma^+_g$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$A^3\Pi^+_u$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$B^3\Pi_g$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$B^3\Sigma^-_u$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$a^1\Pi_g$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$w^1\Delta_u$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$C^3\Pi_u$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$E^3\Sigma^+_g$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>$3\sigma_g$</td>
</tr>
<tr>
<td>$N_2^-$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X^2\Pi_g$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$E^2\Pi^+_g$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>$3\sigma_g$</td>
</tr>
</tbody>
</table>
### Table 5.2
Possible Energy Losses from $\text{N}_2$ Molecular Excitation

Via the Ground State Ion $\text{N}_2^-(X^2\Pi_g)$

<table>
<thead>
<tr>
<th>Orbital from which electron is re-captured</th>
<th>$1\pi_u$</th>
<th>$3\sigma_g$</th>
<th>$1\pi_u$</th>
<th>$3\sigma_g$</th>
<th>$1\pi_u$</th>
<th>$2\sigma_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final state</td>
<td>$A^3\pi_u$</td>
<td>$B^3\Pi_g$</td>
<td>$B^3\Sigma_u^-$</td>
<td>$a^1\Pi_g$</td>
<td>$w^1\Delta_u$</td>
<td>$C^3\Pi_u$</td>
</tr>
<tr>
<td>Associated electronic energy loss/eV</td>
<td>6.2</td>
<td>7.4</td>
<td>8.1</td>
<td>8.6</td>
<td>8.9</td>
<td>10.9</td>
</tr>
<tr>
<td>Maximum vibrational energy loss from vertical electron transitions (1)</td>
<td>1.5</td>
<td>0.7</td>
<td>1.4</td>
<td>0.9</td>
<td>1.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

(1) These values must be considered rather doubtful since the condition of these states may be significantly altered by the $K^+$ ion and by possible mixing between states.
<table>
<thead>
<tr>
<th>Process No.</th>
<th>relative $c_{\text{obs}}$/%</th>
<th>average energy loss/eV</th>
<th>Experimental</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>-0.1</td>
<td>$K(4^2S) + N_2(X)$</td>
<td>$\sim 0.9$</td>
</tr>
<tr>
<td>2</td>
<td>$\sim 18$</td>
<td>2.8</td>
<td>$K(4^2P) + N_2(X)$</td>
<td>$\sim 2.6$</td>
</tr>
<tr>
<td>3</td>
<td>$\sim 3$</td>
<td>4.7</td>
<td>$K(5s, 3d, 5p, 6s, 4d) + N_2(X)$</td>
<td>2.6-3.4</td>
</tr>
<tr>
<td>4</td>
<td>$\sim 2.5$</td>
<td>6.5</td>
<td>$K(4^2S) + N_2(\Sigma^+_u)$</td>
<td>6.2</td>
</tr>
<tr>
<td>5</td>
<td>$\sim 2.5$</td>
<td>8.3</td>
<td>$K(4^2S) + N_2(B^3\Pi_g, B^3\Sigma_u^-)$</td>
<td>7.4, 8.1</td>
</tr>
<tr>
<td>6</td>
<td>&lt;1</td>
<td>10.4</td>
<td>$K(4^2S) + N_2(a^1\Pi_g, a^1\Delta_u)$</td>
<td>8.6, 8.9</td>
</tr>
<tr>
<td>7</td>
<td>&lt;1</td>
<td>12.3</td>
<td>$K(4^2S) + N_2(E^3\Sigma_g^+)$</td>
<td>11.9</td>
</tr>
</tbody>
</table>

cont'd/...
Notes on Table 5.3

(1) Taken from Table 3.3.

(2) The molecule may be vibrationally excited.

(3) Model results; vibrational excitation is already accounted for in the predictions.

(4) A number of states may be involved here. These have been chosen as examples of simple population mechanisms.
processes in table 5.3 cannot be formed by removal of an inner electron from the \( \text{N}_2^- \times^{2\Pi}_g \) structure, and may instead be populated by means of an excited ion state. Table 5.4 shows a possible route, and figure 5.4 provides a schematic diagram of the potentials involved.

A detailed model of the population mechanism of excited molecular states has not been developed, as a good deal of intuition has been required even to arrive at these tentative assignments and routes. Also, while the close proximity of the potassium ion seems to have little effect on the ground state ion, the shallow excited ion potentials may be highly perturbed in its presence. The possible mixing of states casts doubt on the physical significance of associating any energy loss with a specified molecular excitation channel. Nevertheless, it is seen that the proposed assignments and mechanisms provide a reasonably good simple description for experimental observations.

5.3 The Potassium-Oxygen System

The study of alkali atom-oxygen scattering systems has been confined mainly to ionising collisions (LAC 70), in the determination of the electron affinity of oxygen (BAE 72), and total and differential cross-sections for positive (YOU 74) and negative (TAN 74) ion formation. There have also been a number of experiments where potassium
<table>
<thead>
<tr>
<th>orbital</th>
<th>state formed</th>
<th>electronic energy loss/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>electron donation</td>
<td>$3s\sigma_g$</td>
<td>$N_2 \rightarrow \Sigma^+_{2g}$</td>
</tr>
<tr>
<td>electron re-capture</td>
<td>$3\sigma_g$</td>
<td>$N_2 \rightarrow \Sigma^+_{3g}$</td>
</tr>
</tbody>
</table>
Figure 5.4:
Schematic Diagram of K-N\textsubscript{2} Potentials
Showing Involvement of an Excited Negative Ion
excitation has been observed in collisions with oxygen (KEM 75). Kempter et al (KEM 73) showed that K(4^2\text{P}) excitation is the dominant inelastic process, with the K(5P) and (6s) states populated at 1.2% and 0.3% in comparison. Evidence for the formation of an electronically excited molecular ion has been found in energy loss spectra of scattered potassium ions (GRO 76), (MOC 76), (STO 80), accessing the dissociative channel to form O + O^-.

Since the total cross-sections for O^- formation are always small, it may be assumed that mainly the ground state ion is formed on the electron jump. Previous results have shown that the internal motion of the oxygen molecular ion is responsible for the oscillatory structure on the differential cross-sections for ion pair formation in alkali atom-oxygen molecule collisions (KLE 78), which had not been explained satisfactorily by earlier suggestions (BAE 75). The importance of molecular motion in neutral scattering has also been commented upon (KLE 80). More recently a model very similar to that used in this Thesis has described vibronic excitation in potassium-oxygen collisions, see e.g., (KLE 80b), (KLE 80c).

As mentioned in Chapter 4, the model was extended to include a fourth potential representing the first electronically excited state of oxygen, \( \text{O}_2 \text{a}^1\Delta_g \), which lies 0.98eV above the ground state.
Although the $O_2 \quad b^1Σ^+$ excited state also falls within the range of the $K^+/O_2^-$ potential, transitions to it are excluded on symmetry grounds (ALE 78).

The results of the model calculations are shown in figure 5.5 detailing the differential cross-sections, and figure 5.6, giving the angular dependence of energy loss. It was found that a reasonably good fit to the experimental results could be obtained with only a very small population of the $O_2 \quad 1Δ_g$ exit channel, but it might be supposed that this state when accompanied by strong vibrational excitation may contribute to the cross-section covering the 1.6-2.5eV range, nominally attributed to $K(4^2P)$ excitation. As the dominant elastic channel prevents any detailed examination of the inelastic process in the energy loss range up to about 1eV the importance of the $O_2 \quad 1Δ_g$ state is not revealed in this work. Kleyn experienced the same problem in his results (KLE 80a), from a time of flight experiment carried out at 98.6eV and 27.7eV LAB collision energy, though with very much poorer energy resolution. As with the results of this work, it may only be concluded that, whatever the relative extent of $O_2 \quad 1Δ_g$ and $K(4^2P)$ excitation, the processes occur via the ionic surface. Since the coupling between ionic and excited states is diminished as the crossing radii move to wider internuclear distances, the
Figure 5.5: Differential Cross-Sections for Potassium-Oxygen Scattering at 92.2 eV CM Collision Energy. Experimental observations are shown by the error bars. The broken lines indicate the model predictions.
Figure 5.6: Observed and Predicted Energy Loss Behaviour Scattering Angle

The error bars indicate experimental energy losses for potassium-oxygen scattering at 92.2eV CM collision energy. Model results for electronically elastic scattering and $O_2^\text{1}\Delta_g$ state excitation are shown by the solid lines. The early and late contributions to potassium excitation are shown separately.
interaction is strongest for small radial velocities i.e., large impact parameters, so explaining the large onsets at small $E_X$ values.

Although the intermolecular potentials are not substantially different in the crossing region from previous estimates (KLE 80a), and the $O_2$ ground state potential is not changed from its usual form (HER 50) the $O_2^-$ ground state potential departs from the description given for the isolated ion (CEL 72) in order to obtain agreement with experiment. This may be interpreted as some measure of the influence of the potassium ion on the internal potential, although such a conclusion disagrees with matrix isolation experiments which suggested that the $O_2^-$ potential was not influenced by the proximity of the alkali ion (AND 76). As in the case of potassium-nitrogen scattering, the bound ionic state allows the roles of internal and intermolecular potentials to be separated, and once more the calculated energy losses are strongly influenced by relatively small changes in the ionic equilibrium bond length.

Until now only those energy loss processes accessible via the lowest ionic state have been considered. Above the ground ionic asymptotic limit there are many inelastic processes attributable to excitation of the oxygen molecule. As in the case of nitrogen these excited states may be
reached by inner electron transitions from the ground state ion, or by more speculative paths involving excited ionic states. As mentioned earlier, the existence of excited negative ion states is well known. The $^{2}\Pi_u$ excited state of $O_2^-$ has been observed in electron impact studies (SCH 73) lying about 7eV above the oxygen ground state in the Franck-Condon region. Energy loss spectra in ion-forming collisions reveal several ion excitation channels (DUR 77) and calculations confirm a host of available excited potentials (MAS 76). Since all bound excited ionic states have equilibrium bond lengths greater than the ground state, these states will be repulsive in the Franck-Condon region, leading to large negative electron affinities and hence very low cross-sections for emerging states (KRA 73). Figure 5.7 provides a schematic diagram of the $O_2$, $O_2^-$ potential system, and the electronic configuration of some excited states of oxygen are given in table 5.5. Again it is possible to identify routes to the excited states via removal of an inner electron in the ground state ion, or via an excited ion state. Table 5.6 suggests possible routes and associated energy losses and comparison with the experimental results of Chapter 3 produces the tentative assignments laid out in table 5.7.
Figure 5.7': Potential Energy Curves for $O_2$ and $O^-_2$

The broken lines indicate the ionic potentials.
### Table 5.5

**Molecular Orbital Electronic Configuration of Oxygen**

<table>
<thead>
<tr>
<th>State</th>
<th>(1\sigma_g)</th>
<th>(1\sigma_u)</th>
<th>(2\sigma_g)</th>
<th>(2\sigma_u)</th>
<th>(3\sigma_g)</th>
<th>(1\pi_u)</th>
<th>(1\pi_g)</th>
<th>(3\sigma_u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X^3\Sigma_g^-)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>(a^1\Delta_g)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>(A^3\Sigma_u^+)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>(B^3\Sigma_u^-)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
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</tr>
<tr>
<td>(^3\Pi_g)</td>
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<td>2</td>
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<td>4</td>
<td>3</td>
<td>0</td>
</tr>
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<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
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<tr>
<td>(O_2^-)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(X^2\Pi_g)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
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<td>3</td>
<td>0</td>
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</tbody>
</table>
Table 5.6
Possible Energy Losses from O₂ Molecular Excitation

<table>
<thead>
<tr>
<th>Orbital from which electron is re-captured</th>
<th>$1\pi_g$</th>
<th>$1\pi_u$</th>
<th>$1\pi_u$</th>
<th>$3\sigma_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final state</td>
<td>$^{1}\Lambda_g$</td>
<td>$^{3}\Sigma^+_u$</td>
<td>$^{3}\Sigma^-_u$</td>
<td>$^{3}\Pi_g$</td>
</tr>
<tr>
<td>Associated electronic energy loss / eV</td>
<td>0.98</td>
<td>4.5</td>
<td>6.2</td>
<td>8.0</td>
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<tr>
<td>Process No.</td>
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<td>average energy loss/eV (2)</td>
<td>Excitation (3)</td>
<td>predicted energy loss/eV</td>
</tr>
<tr>
<td>------------</td>
<td>---------------------------------</td>
<td>-----------------------------</td>
<td>----------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>-0.1</td>
<td>( K(4^2S) + O_2(X) )</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>( \approx 25 )</td>
<td>1.6, 2.4</td>
<td>( K(4^2P) + O_2(X) )</td>
<td>( \approx 2.1 )</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>( K(4^2S) + O_2(a^1\Delta_g) )</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>&lt;3</td>
<td>3.0</td>
<td>( K(5s,3d) + O_2(X) )</td>
<td>2.6</td>
</tr>
<tr>
<td>4</td>
<td>&lt;3</td>
<td>3.9</td>
<td>( K(5p,6s,4d) + O_2(X) )</td>
<td>3.4</td>
</tr>
<tr>
<td>5</td>
<td>&lt;3</td>
<td>5.0</td>
<td>( K(4^2S) + O_2(3\Sigma_u^+) )</td>
<td>4.5</td>
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<tr>
<td>6</td>
<td>&lt;1.5</td>
<td>6.4</td>
<td>( K(4^2S) + O_2(B^3\Sigma_u^-) )</td>
<td>6.2</td>
</tr>
<tr>
<td>7</td>
<td>&lt;1.5</td>
<td>7.8</td>
<td>( K(4^2S) + O_2(3\Pi_g) )</td>
<td>( \approx 8.0 )</td>
</tr>
<tr>
<td>8</td>
<td>&lt;1.5</td>
<td>9.6</td>
<td>( K(4^2S) + O_2^*(6) )</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>( \approx 0.5 )</td>
<td>10.5</td>
<td>( K(4^2S) + O_2^*(6) )</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>&lt;1.5</td>
<td>11.5</td>
<td>( K(4^2S) + O_2(L^3\Pi_u) )</td>
<td>( \approx 11 )</td>
</tr>
</tbody>
</table>

cont'd/...
Notes on Table 5.7

(1) Taken from Table 3.4.

(2) Averaged over all angles.

(3) The molecule may be vibrationally excited.

(4) Model results; vibrational excitation is already accounted for in the predictions.

(5) Repulsive states.

(6) A great number of states may contribute in this region.

(7) This process occurs via an excited ion state.
5.4 The Potassium-Sulphur Hexafluoride System

The potassium-sulphur hexafluoride results pose the simple model its most difficult test, in that it is hoped to describe the target molecule in terms of diatomic parameters. Sulphur hexafluoride has been considered in this manner by previous workers (HUB 75), (OKA 80) in order to explain qualitatively the results of ion pair formation experiments. As stated in Chapter 4, the potential parameters have never been satisfactorily established, the determination of the electron affinity of SF$_6$ proving particularly awkward (HUB 75). In this work an attempt has been made to provide semi-quantitative model fits to match experimental observations, using the set of potentials outlined in Chapter 4. The predicted differential cross-sections are compared with collected data in figure 5.8 and the angular behaviour of energy loss is given in figure 5.9. It is seen that the inelastic processes, attributed to high vibrational excitation in the ground neutral (process 2), and K(4$^2$P) excitation with a similarly large vibrational contribution (process 3), are described fairly well by the collision model, both in terms of cross-section (although "goodness of fit" is difficult to ascertain because of the low intensities) and energy loss. The elastic differential cross-section cannot be matched owing to the limitations of the Landau-Zener approximation. Hubers and Los (HUB 75)
Figure 5.8(a):
Differential cross sections for potassium-sulphur hexafluoride scattering at 161eV CM collision energy. Experimental observations are shown by the error bars. The broken lines indicate the model predictions.
The solid lines indicate average levels for observed cross-sections. The broken lines give the model predictions.
Figure 5.9: Observed and Predicted Energy Loss Behaviour With Scattering Angle

The error bars indicate experimental energy losses for potassium-sulphur hexafluoride scattering at 161eV CM collision energy. The solid lines represent the model results.
have pointed out that the first crossing is passed adiabatically, switching on the Coulomb attraction and causing rapid expansion of the S–F bond i.e., the classical "harpoon" mechanism. As a consequence of the steepness of the SF$_6^-$ potential the electron affinity is increased dramatically, moving the second crossing to much larger internuclear distances, leading to diabatic behaviour on the way out of the collision. Thus the system is "trapped" on the ionic surface, and the Landau–Zener minimum experienced when the K$^+$/SF$_6^-$ potential first becomes available is very severe indeed.

It is seen that the above argument suggests that the ionisation channel should be important even at the high collision energies used in this experiment (161eV CM). Previous calculations on superthermal data have noted anomalously low values for $s$, the repulsion exponent (KER 75), when cross-sections have been examined by the method of section 4.5. Figure 5.10 shows the scattering cross-section at 236eV CM collision energy and figure 5.11 gives the logarithmic plot of intensity and angle. The cross-section decreases too rapidly for a reasonable value of $s$, indicating that ionisation is an important competing process, even over very short collision lifetimes. Results for ion pair formation at lower energies ($\lesssim$30eV)
Figure 5.10: Potassium-Sulphur Hexafluoride Scattering at 236eV CM
For a potential of the form $V = C_s / R^{1/s}$, the slope on the log-log plot is $s^{1/2}$. Thus an estimate of $s = 6.4$ is obtained.

Figure 5.11: Logarithmic Plot for K-SF$_6$ Scattering
show that the \( \text{SF}_5^- \) cross-section rises steeply from threshold to about 6-7 times the intensity of \( \text{SF}_6^- \) production, as might be expected under conditions where the system spends long periods on the ionic surface (HUB 75). The \( \text{SF}_6^- \) cross-section rises more gently to a steady plateau, gradually decreasing with increasing collision velocities, while the \( \text{SF}_5^- \) population also diminishes steadily. However, extrapolation of these cross-sections to the high experimental energies used here shows that both ought to have reached very low values compared to their threshold maxima. Nevertheless, observations suggest that these channels remain important even at the experimental energies encountered here, although not as dominant as the simple model suggests. The collisional encounter shows more diabatic behaviour at the first crossing than suggested by the simple model, which is constrained by the requirements of excited state populations.

In order to obtain model results which did not end with dissociation it was necessary to introduce the potential barrier mentioned in Chapter 4 (equation 4.32) into the \( \text{SF}_6^- \) curve. This small and slow-rising "hump" in the potential had the effect of slowing down the expanding \( \text{SF}_5^- \)-F bond and constituted only a minor perturbation to the original form. It was only effective within
a small S–F range near the dissociation point and
did not influence the ion potential bowl region or
its repulsive wall. It may be interpreted as a
measure of the potassium ion's hindering of the
outward movement of the fluorine atom, or as a
partial back-transfer of the electron to the K
ion, or as a consequence of some stretching in the
other S–F bonds.

In conclusion, the experimental observations
in the low energy loss range show that the elastic
channel is dominant, implying that in many collisions
the first crossing is passed diabatically, but
when crossing to the ionic surface occurs, mainly
either the crossing radius moves too far for
subsequent adiabatic behaviour, or there is enough
time for the negative ion to dissociate, the
inelastic channels representing the residue.

From previous experiments involving fast
alkali beams, examination of the F− cross-section
suggests that only the ground state (2A1g) of the
negative SF6− ion is present in ionisation processes
for the energy range up to 200eV CM (TAN 74a). The
halogen hexafluoride C6F6, which is isoelectronic
with SF6−, has been shown to have O₅h symmetry, with
the unpaired electron in an antibonding a₁g* orbital
consisting of central atom ns and fluorine 2pσ
orbitals (COM 78). Thus the SF6 molecule has a
ground state electronic configuration a₁g 2l₁u 6g 42A1g

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and the ground state ion is written $a_{1g}^2 t_{1u}^6 e_g^4 a_{1g}'^*$ with SCF MO calculations indicating that the extra electron is mostly localised around the central atom (GIA 72). These computations also suggested that excited ion states would appear only at rather high energies, and so molecular excitation under 20eV can be considered as occurring via transitions in the ground ion state by removal of an inner electron. These possible highly excited states are listed in table 5.8 (HER 67), and the possible mechanisms for their population are shown in figure 5.12. From these and the results at low energy losses the tentative assignments of table 5.9 are achieved.

5.5 Further Discussion

It was shown in Chapter 4 that the problem of describing an atom-molecule collision could be separated into two parts by virtue of the large mass difference between electron and nucleus. The first part involved the choice of an appropriate set of potentials (the electronic problem) and the second dealt with the treatment of nuclear motion over these surfaces. In this section alternative descriptions are put forward for comparison with the model used. Since the harpoon model, particularly using the diabatic representation, has been regarded as the suitable choice for these systems and collision energies, differences between
<table>
<thead>
<tr>
<th>Designation</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential above ground state/eV</td>
<td>5.70</td>
<td>7.93</td>
<td>11.21</td>
<td>13.14</td>
<td>13.89</td>
<td>14.66</td>
</tr>
</tbody>
</table>

(1) from (HER 67)
Figure 5.12:
Schematic Diagram of K-SF\textsubscript{6} Potentials
Showing Possible Routes to SF\textsubscript{6} Excitation
Table 5.9

<table>
<thead>
<tr>
<th>Process No.</th>
<th>Experimental</th>
<th>Theoretical</th>
<th>Difference due to vibration/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No.</td>
<td>relative obs/°</td>
<td>average energy loss/eV</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>100</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
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<td>ν4</td>
<td>2.9</td>
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<tr>
<td>3</td>
<td>3</td>
<td>ν1.5</td>
<td>4.4</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>ν1.5</td>
<td>5.8</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>&lt;1</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>&lt;0.5</td>
<td>8.8</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>&lt;1</td>
<td>10.4</td>
</tr>
<tr>
<td>8</td>
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</tr>
<tr>
<td>9</td>
<td>9</td>
<td>&lt;1</td>
<td>12.8</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>&lt;0.5</td>
<td>13.8</td>
</tr>
</tbody>
</table>

cont'd/...
Notes on Table 5.9

(1) Taken from Table 3.5.
(2) Averaged over all angles.
(3) The molecule may be vibrationally excited.
(4) Model results; vibrational excitation is already accounted for in the predictions.
methods have generally been confined to the nuclear motion.

A number of so-called "state-based" procedures have been applied fairly successfully to alkali atom-diatom collisions (GIS 79). The Bauer-Fisher-Gilmore (BFG) model assigns a separate covalent potential surface to each vibrational level of the diatomic molecule, and correspondingly a separate ionic potential to each vibrational level of the molecular ion (BAU 69). Thus a network of intersecting curves is set up at the crossing radius. The Landau-Zener formula, modified by the appropriate Franck-Condon factor, is applied at each crossing point and the system diffuses through sets of crossings to provide a final product vibrational distribution. This is clearly a much more complicated and computationally demanding process than that employed in this Thesis, as well as rather inappropriate given the experiment's time of flight resolution.

A simpler model, the double Franck-Condon method, has been applied by Kleyn (KLE 80a) to experimental results on the quenching of metastable argon by molecular nitrogen (CUT 79). The method was developed from an earlier calculation, which assumed that the transition probabilities at the crossing point are the same for all vibrational levels and therefore determined the final vibrational state contributions from the Franck-Condon values.
In the double Franck-Condon treatment, motion in the negative ion is taken into account. As in the model used here, the intermolecular and molecular potentials are decoupled, so allowing classical development of the relative motion while now the vibrational motion is treated quantum mechanically. Following the electron jump the new time-dependent vibrational wave function is constructed from the initial function using a harmonic oscillator approximation and the Franck-Condon principle, and similar considerations apply at subsequent crossings to produce a final wave function from which the vibrational population may be calculated. Importantly this method has successfully described vibrational populations in the product channels following quenching in Ar$^+ + N_2$ collisions. This system's ionic surface, Ar$^+$ N$_2^-$ lies above both ground and excited neutral potentials, and so a direct coupling between the states is involved.

When considering the experimental arrangement here, however, it is seen that the "state-based" methods are confronted by a fundamental difficulty analogous to that of selecting diabatic or adiabatic representations in the electronic argument. This difficulty has been discussed recently by Child and Baer (CHI 81), and some attempt has been made to quantify the problem. When many,
or at least several vibrational cycles can be completed during the collision lifetime the vibrational states will be well defined and a "state-based" model can be expected to perform well (CHI 79). In the above experiment (CUT 79) the vibrationally excited nitrogen molecule oscillates about three times between transitions. In collisions characterised by high translational energies and relatively low vibrational frequencies as in the present system studied, the external coordinate can take the colliding pair to a completely different part of the potential surface during a vibrational period, or indeed a single cycle may never be completed in the intermediate state, and the vibrational state cannot be considered established. Thus the concept of discrete energy levels describing exact vibrational states is no longer physically meaningful. Here the "trajectory based" calculations are most appropriate, and as shown here the simple impact parameter model has proved an effective description.

The "state-based" close-coupling treatment, which extracts the nuclear wave functions from the coupled set of differential equations (equation 4.9) has not been considered because of the computational difficulties even in constructing a collinear collision model (TOP 75), (TUL 76). A semi-classical
impact parameter model has recently been applied to high energy $C_8 + O_2$ scattering, with some success (HIC 80).

The most recent investigation of atom-molecule collisions has challenged the validity of the harpoon model in many systems. The "bond stretch attraction" method (HER 81) proposes direct coupling between ground and excited states, discarding the concept of an ion pair mechanism. The treatment has been used to examine experimental results of thermal quenching of sodium by nitrogen (HAB 80). Adiabatic potential curves are constructed for the system in $C_{\infty v}$ and $C_{2v}$ symmetry using ab initio Hartree Fock methods. At large internuclear separations these states correlate with the atomic structure of sodium, but in the interaction region the ionic intermediate disappears, although the adiabatic potentials exhibit ionic character. Thus the collision process can be interpreted as a single non-adiabatic transition. Although such transitions are not energetically possible at thermal collision energies when the $N_2$ bond length is close to its equilibrium distance, the molecule undergoes pre-stretching under the influence of the approaching alkali atom to open a direct quenching (or excitation) channel between ground and excited states. The pre-stretching is brought about by the increasing
contribution of the partially occupied antibonding $1\pi^g$ orbital in nitrogen, which is populated by the correlated Na 3p state. This is of course an ionic contribution, and it might be suggested that it represents to some extent a "diluted" harpoon mechanism. Calculations of the interaction matrix elements between excited sodium and the ion pair states confirm that the diabatic representation is a rather crude approximation to the exact adiabatic potentials, however (HAB 80).

The direct crossing between the ground and excited alkali states occurs at much closer range than suggested by the harpoon model, at about 2 - 2.5\(\AA\). Indeed the Habitz model for the Na-N\(_2\) system suggests that the transition to the state correlating with Na 3p excitation occurs well up the repulsive wall of the ground state. Thus it might be expected that fast collisions involving such transitions would show wide deflection angle onsets, and yet observations reveal excitation processes onsetting at the narrowest angles. It may be revealing to find the predicted onset angles using the accurate potential surfaces of the bond stretch attraction model. Experiments at different collision energies may be able to determine the extent of bond stretching in the earliest phases of the collision, and compare these expansions with the requirements of the
adiabatic model. Another important difference is that the position of the sodium atom does affect the molecular potential, dependent on the symmetry of the system. It is also noted that symmetry has a commanding influence over the collision process, with transitions most favoured in the $C_{2v}$ configuration. At thermal energies the molecule has time to rotate into the desired symmetry and Coriolis coupling transitions are induced.

The mechanism is rather similar to that employed by Kleyn (KLE 80a) for the $\text{Ar}^*-\text{N}_2$ system, as mentioned above, which also relies on pre-stretching to promote transition.

Although the harpoon model is still most suitable for systems involving the formation of stable molecular ions, such as alkali-halogen collisions (LOS 79) the bond stretch attraction method seems the more likely proposition in collisions where the negative ion is unstable over the encounter lifetime. Previously in low energy collisions where the collision lifetime was longer than the expected lifetime for the ion, arguments had to be based on the stabilising effect of the alkali atom, perhaps due to partial back-bonding of the valence electron. As stated above the coupling formed by the stretching bond owes much to the ionic contribution, although the Coulomb attraction term is lost. Electron density maps
confirmed that the well formed in the excited alkali potential surface is due to substantial charge transfer (~50%) to the molecule (BOT 81), (HER 81). Therefore although the two methods start from the extremes of adiabatic and nonadiabatic formalisms they arrive at rather similar representations for the collision process. 

Thus while the ab initio potential surfaces used in the direct coupling scheme are exact, and the method is "correct", the diabatic representation has never been more than a helpful and in certain circumstances very close approximation to the actual system. It seems likely that where accurate adiabatic potentials are available collision systems will be examined by the new method, particularly at thermal energies and where vibrational distributions can be resolved from experimental data. The worth of the harpoon model rests in its ability to describe the atom-molecule collision in simple and recognisable terms.

A further problem where the harpoon model cannot be applied arises in the scattering of alkali atoms on certain hexafluorides, e.g., UF₆, WF₆. Very large electron affinities result in ionic potentials lying well below the neutral surfaces. Thus no crossings can occur yet ion pair formation is observed (ANN 78), (ANN 81).
Attempts to apply the Rosen-Zener model (ROS 32) for non-crossing potentials have failed and a collision complex theory, based on competing branches leading to fluorine abstraction or ion pair formation, has met with only very limited success (COM 78). The application of the harpoon model using an excited ion state as intermediate is not borne out by experimental observations which do not indicate appearance potentials for ion pair formation and produce cross-sections far higher than predicted (ANN 78).

A final point worth further consideration is the possible observation of highly excited potassium states in the experiment. In every set of results the peaks observed around the ionisation limit have been nominally assigned to a given excitation channel such as K(6S) or K(4d) while in reality a near continuum of states exists in this region. The collision system can be imagined as a positive alkali-molecule core with an orbiting electron (BOT 75), and this description becomes more suitable as the system moves far out on the ionic potential, approaching ion pair formation. Although the crossing probabilities will be very small at these internuclear distances the high density of states will act in the opposite sense to provide a reasonable opportunity for population. At the moment the extent of this excitation is not clear and coincidence measurements
are required to estimate the relative populations of the high lying atomic states (KEM 73).

5.6 Summary

Time of flight spectra have been collected for fast potassium atom collisions with molecular nitrogen, oxygen and sulphur hexafluoride. Discrete energy loss processes were observed and differential cross-sections were extracted.

The spectra can be divided into two regions of importance, a low energy loss range corresponding to potassium excitation and a highly inelastic region interpreted in terms of molecular excitation to valence and Rydberg states. In each case electronic excitation is accompanied by vibrational excitation.

The high energy loss molecular excitation processes onset at narrow scattering angles, indicating the involvement of strongly attractive potentials coupling ground and excited states. It is suggested that the population mechanism occurs via core excitation in the molecular ion into valence, near Rydberg or fully Rydberg states of the molecule and/or by the possible involvement of an excited molecular ion state. Tentative assignments can be made on this basis so identifying the main molecular excitation channels and their associated vibrational excitation.

For all the systems elastic scattering is
by far the most likely product channel indicating that in most collision encounters the atom-molecule pair behaves diabatically.

A simple model has been developed to explain the results in the low energy loss regime. The harpoon mechanism is invoked with an ionic intermediate coupling ground and excited alkali states. The internal motion of the molecule is included to account for vibrational excitation. External motion of the potassium atom and internal molecular motion are assumed to be independent. Differential cross-sections and energy losses have been calculated for straight line trajectories over diabatic surfaces. Good agreement with experiment is obtained with minimum adjustment of molecular parameters. In the case of nitrogen it can be concluded that the close presence of the potassium ion does not perturb the negative ion potential. In general, a separation may be effected between the role of the internal motion in determining energy losses and the role of the intermolecular motion in determining differential cross-sections.

5.7 Conclusions

The low lying energy loss processes accessible via the ground ionic state are well understood using the classical model, both in terms of energy loss and cross-section. For these experimental conditions the harpoon mechanism offers the simplest
picture of the collision event and helps provide a "feel" for the physical process. Although more accurate models are available they do not always combine simplicity of approach with applicability over the energy range or target species.

The vibrational excitation of the molecule acts as a "clock" on the collision event. Since the collision lifetime depends upon the impact parameter, which maps with reduced angle $\beta_X$, molecular motion can be observed on a sub-picosecond time scale, around $10^{-14}$ s. Changes in experimental products can be monitored over a single vibrational cycle.

The highly inelastic channels have been assigned to various molecular excited states. Although the routes leading to their population remain rather speculative it has been possible to show that recapture of the electron from a low lying orbital in the ground state molecular ion can produce the desired electronic configurations, while also providing the attractive intermediate necessary for the observed low angular onsets.

Further experiments are required to test the suitability of the various collision models available and to confirm the assignments.

Data at lower collision energies with improved time of flight resolution would be able to resolve early and late crossing contributions.
to \( K(4^2P) \) excitation and so help determine the value of the simple model.

Higher collision energies would "freeze" the molecular vibration which should produce a positive effect on the differential cross-section for potassium excitation in sulphur hexafluoride scattering. Observed energy losses would correspond more closely to values for purely electronic excitation, thus easing their interpretation. Against this is the increasing diabatic behaviour at high velocities and the expected poorer time of flight resolution.

Time of flight spectra collected at constant reduced angle \( E\chi \) at different collision energies would also yield information on the "race" of the potassium projectile against the "clock" of the molecular motion.

Similarly varying the temperature of the target beam would provide further evidence for the role of internal energy in the collision, of particular interest in the dissociative sulphur hexafluoride system.

The importance of vibrational excitation can be investigated by new collision systems. For example, ethene has the same reduced mass as nitrogen so results for potassium-ethene scattering would invite comparison.

A photon-particle coincidence experiment would allow clear assignments of product states to
observed exit channels. It would also confirm the extent of vibrational excitation in any collision process. This would be of particular importance in determining the relative intensities of the higher lying potassium states as well as in the identification of the molecular processes.

A suitable experiment must be devised to test the relative merits of the harpoon and bond stretch attraction models. The former involves relaxation on the ionic potential while the latter interprets vibrational excitation as pre-stretching during the collision approach. Accurate measurements of vibrational distributions, particularly in the ground state exit channel, may be able to point towards one method rather than the other. However the choice of method remains largely a matter of common sense. If accurate adiabatic potentials are available and the molecular ion is not a stable species over the collision lifetime then the bond stretch attraction model will be used. In any other situation the harpoon model continues to be the most useful approximation to the collision event.

Experiments on tungsten and other hexafluorides are of enormous interest, with mystery surrounding the ion formation mechanism. Time of flight data for excitation processes may provide some insight into this uncertain area.
6.1 Introduction

The classical trajectory method was developed to investigate the dynamics of reactive collisions on the assumption that such processes are adiabatic and can be described by a single potential energy surface. The potential surface can be determined by a number of methods, ranging from exact ab initio calculations to purely empirical functions. In the limit of high particle masses and high energies, trajectories can be dealt with classically except where known experimental phenomena demand a quantal or semi-classical treatment. Having made the classical assumption it is possible to track the collision from a given set of initial conditions by integration of the equations of motion.

Trajectory calculations were first performed in the 1930s but it was only with the development of the modern computer in the 1950s and of molecular beam experiments in the 1960s that they became a popular and successful tool in the study of collision dynamics (BUN 71). Larger and faster data handling facilities have produced more reliable and refined trajectory calculations and
the progress of molecular beam experiments in examining single collision events has focussed research in areas tractable to trajectory studies.

In the earliest comparison of molecular beam experiments (HER 61), (HER 62) and trajectory calculations the potassium-methyl iodide reaction was interpreted as occurring over a purely empirical potential energy surface (BLA 62), which subsequently has undergone a series of modifications by a number of authors e.g., (KAR 64), (RAF 66). These potentials form a starting point to the hypersurface used in this Thesis and will be discussed in more detail later. Reasonable agreement was achieved between theory and experiment, but more importantly the sensitivity of the trajectory results to various potential parameters provided new insight into the reaction process.

However, most classical trajectory computations have been confined to adiabatic collision systems although in one example of the above the transition from covalent CH\textsubscript{3}I to ionic K\textsuperscript{+}I\textsuperscript{-} was effected by the choice of the lower of the surfaces at any given point (RAF 66). The application of trajectory methods to electronically nonadiabatic processes involves an attempt to incorporate a quantum phenomenon, the electron transition, into a purely classical scheme. In Chapter 4 it was stated that such transitions
occur only in relatively small regions near the location of crossings (for diabatic) or avoided crossings (for adiabatic surfaces) while elsewhere the system may be described as travelling over a single potential energy surface. Thus the surface hopping trajectory (SHT) as first proposed by Tully and Preston (TUL 71) relies upon being able to locate the transition zones, having some means of calculating the crossing probabilities and having a method of passing smoothly from one surface to the other in the event of a transition. This model has been used in the present studies and will be discussed in detail in the following section.

The results of a number of sets of classical trajectories are given in this Chapter, and may be compared with experimental results for potassium-methyl iodide scattering at superthermal energies (164 eV CM). The experimental data were collected as part of the general investigation of alkyl halide systems carried out by the Edinburgh Molecular Beams Group over recent years, and have been reported elsewhere (FLU 79), (SUT 80), (FLU 81). From comparison of the computations follows some discussion on the trajectory method and on possible progress to be made towards a more complete description of the collision system.
6.2 The Surface Hopping Trajectory Model

The surface hopping trajectory model applies equally well to diabatic and adiabatic potential representations whereas previous trajectory methods were restricted to an adiabatic hypothesis. The assumptions of the SHT model can be outlined in the following manner.

Firstly, a nonadiabatic transition is represented by a hop from one potential surface to another. These hops occur only at a finite number of distinct points along the line of the trajectory e.g., in the case of diabatic potentials, at surface crossings.

Thus secondly, a relation of the form

$$S(R) = 0$$

(6.1)

must be available to define the locus of points at which hops may take place i.e., the transition zones. This is a simple procedure when the nonadiabatic coupling is restricted to narrow regions such as curve crossings but can prove awkward if coupling extends over a wider region, e.g., in close range coupling.

Thirdly, the transition probability function, dependent upon nuclear positions and velocities, is required. In general the Landau-Zener approximation is used, taking as radial coupling velocity that component perpendicular to the crossing seam. In very simple systems the
probability may be calculated directly by numerical integration of the classical path equations (MOT 31), (TUL 76). It is also important to ensure that over a single pass of the nonadiabatic coupling region the crossing probability is calculated only once.

Following a surface hop, energy and momentum must be conserved. Since the previous assumption declared that only the velocity component perpendicular to the crossing seam is effective in coupling the states, it is reasonable to make the necessary momentum correction in this component only (TUL 71).

Most importantly, a technique for handling branching trajectories must be employed. In classical trajectory calculations over a single adiabatic surface a given set of initial conditions produces a unique trajectory. There is a one to one correspondence between initial and final states which can be used to advantage in checking the accuracy of the computations by starting at the final states and "running backwards" to the initial values. In the surface hopping model this can no longer apply since at each hopping point the trajectory may split into two paths. Each branch may reach further crossing regions, leading to re-crossing, so any set of initial conditions results in a many-branched trajectory and a family
of possible final states.

There are two ways of dealing with the branching problem, which Tully and Preston dubbed the "ants" and "anteater" methods (TUL 71). In the former the transition probabilities at each hopping seam are noted and all possible trajectories are followed. Thus every non-negligible branch of the trajectory is computed together with its probability weighting. Obviously this method is efficient only where relatively few branches are involved. In the latter case, a single trajectory path is followed over the potential energy surfaces. When a crossing point is reached a pseudo-random number, in the range (0,1), is generated. If the calculated crossing probability is greater than this number the hop takes place. Therefore, there is a tendency towards the most likely path and an accurate statistical picture may be built up by computing a large number of such trajectories.

The SHT model has been applied to triatomic collision systems with excellent results e.g., (DÜR 73), (PRE 73), particularly in the H\(^+\) + H\(_2\) system, where ab initio calculations enable the use of highly accurate potentials. In the model developed here, empirical diabatic potentials were employed, and so the relationship required by equation 6.1 was simply the difference between
potentials. As soon as the difference changed in sign over an integration step the Landau-Zener transition probability was calculated. At that point the "anteater" method was used to decide on the route and a velocity correction was made in the event of a transition.

6.3 The Equations of Motion

Hamilton's equations are developed to describe the time evolution of the system. From the Cartesian coordinates \( r_i(x_i', y_i', z_i') \) the desired trajectories may in principle be generated for a N particle system using the set of 3N second order differential equations, of the form

\[
\frac{d}{dt} \left( \frac{\partial T}{\partial x_i} \right) + \frac{\partial V}{\partial x_i} = 0 \tag{6.2}
\]

where \( T \) is the kinetic energy,

\[
T = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{r}_i^2 \tag{6.3}
\]

From the Cartesian system the set of generalised coordinates \( Q_j \) are created using a point transformation, setting up the working equations for the trajectory calculations. That is, a set of 3N generalised coordinates \( q_i \) are defined such that

\[
r_i = r_i(q_1, q_2, \ldots q_{3N}, t) \tag{6.4}
\]

with the coordinate system fixed to eliminate the explicit time dependence. Following the
procedure of Porter and Raff (POR 76), the action functional

\[ S(q) = \int_{t_1}^{t_2} L(q, \dot{q}) \, dt \]  \hspace{1cm} (6.5)

is invoked, where \( L \) is an arbitrary function of the generalised coordinates and their velocities, and \( t_1, t_2 \) represent the initial and final times. The principle of least action defines the classical trajectory as the set of functions \( q_i(t) \) for which \( S \) is a minimum. Incrementing the coordinates \( q_i(t) \) by \( \delta q_i(t) \), where

\[ \delta q_i(t) = \varepsilon \sigma_i(t) \]  \hspace{1cm} (6.6)

with \( \varepsilon \) independent of \( i \) and \( \sigma_i(t) \), \( \dot{\sigma}_i(t) \) continuous and \( \sigma_i(t) \) zero at the time boundaries, it is possible to calculate the conditions for such trajectories. For a given set \( \sigma_i(t) \), the minimum \( S \) is found from

\[ \frac{d}{d \varepsilon} S(q_i + \varepsilon \sigma_i) = \sum_i \int_{t_1}^{t_2} \left( \sigma_i \frac{\partial}{\partial q_i} + \dot{\sigma}_i \frac{\partial}{\partial \dot{q}_i} \right) L(q + \varepsilon \sigma_i, \dot{q} + \varepsilon \dot{\sigma}_i) \, dt \]

\[ = 0 \]  \hspace{1cm} (6.7)

The \( \sigma_i(t) \) are considered arbitrary (but subject to the conditions above) and the equation is evaluated at \( \varepsilon = 0 \),

\[ \frac{dS}{d \varepsilon} \bigg|_{\varepsilon=0} = \sum_i \left[ \int_{t_1}^{t_2} \sigma_i \left( \frac{\partial L}{\partial \dot{q}_i} - \frac{d}{dt} \frac{\partial L}{\partial q_i} \right) dt + \int_{t_1}^{t_2} \sigma_i \frac{\partial L}{\partial \dot{q}_i} \bigg|_{t_i} \right] \]

\[ = 0 \]  \hspace{1cm} (6.8)
leading to
\[ \frac{d}{dt} \frac{\delta L}{\delta q_i} - \frac{\delta L}{\delta \dot{q}_i} = 0 \] (6.9)

Thus the trajectories \( q_i(t) \) are required to satisfy the Lagrangian equations of motion.

For equation 6.9 to reduce to Newton's law, equation 6.2, in the case of \( q_i \) as Cartesian coordinates, the Lagrangian function \( L(q,\dot{q}) \) must be of the form
\[ L(q,\dot{q}) = T - V \] (6.10)

From this point the set of \( 3N \) second order differential equations (6.9) is used to generate the required \( 6N \) first order equations. Unspecified momenta \( p_i \) are introduced and the Hamiltonian is cast
\[ H(p,q) = \sum_{i=1}^{3N} p_i \dot{q}_i - L(q,\dot{q}) \] (6.11)

Employing once more the principle of least action the turning point for \( S \) can be established from
\[
\frac{d}{d\epsilon} S(p_1 + \epsilon \tau_1, q_1 + \epsilon \sigma_1) = \sum_{i=1}^{3N} \int_{t_1}^{t_2} \left\{ \tau_i \left( \dot{q}_i - \frac{\partial H}{\partial p_i} \right) - \sigma_i \left( \dot{p}_i + \frac{\partial H}{\partial q_i} \right) \right\} dt
\]
\[ = 0 \] (6.12)

with the function \( \tau \) performing a similar role to \( \sigma \). Since the equation holds for any
$\sigma_i$ and $\tau_i$, Hamilton's equations are satisfied.

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{6.13}$$

Differentiation of the Hamiltonian and comparison with Hamilton's equations reveals

$$\dot{p}_i = \frac{\partial L}{\partial q_i} \tag{6.14}$$

Thus the momentum is chosen as

$$p_i \equiv \frac{\partial L}{\partial q_i} \tag{6.15}$$

so that $H$ is independent of $\dot{q}_i$ and

$$\frac{dH}{dt} = 0 \tag{6.16}$$

If $V$ is a function only of $q_i$ then

$$H = \sum_{i=1}^{3N} \frac{\partial T}{\partial \dot{q}_i} \dot{q}_i - T + V \tag{6.17}$$

which following from equation 6.3 and the transformation in equation 6.4 leads to the familiar definition of the Hamiltonian

$$H = T + V \equiv E \tag{6.18}$$

Any set of generalised coordinates $Q_j$, $P_j$ may be defined from $q_i$, $p_i$ using an appropriate point transformation. This can be achieved by following a similar argument to that stated above. Assuming that $Q_j(q_i)$ can be found, $p_i$ is required as a function of...
\( P_j \) and \( Q_j \) so that the transformed Hamiltonian

\[
K(Q,P) = H(q(Q), p(P, Q)) \tag{6.19}
\]

can be obtained. For \( P_j, Q_j \) to obey Hamilton's equations, the action \( R(Q, P) \) must be at a stationary value. Thus the difference of \( R(Q, P) \) and \( S(p, q) \) must be stationary.

\[
S(p, q) - R(Q, P) = \int_{t_1}^{t_2} \left( \sum_{i} p_i dq_i - \sum_{j} P_j dQ_j - (H-K) dt \right) \tag{6.20}
\]

If the integral is to be path independent, the differences in the action functionals must be zero at \( t_1 \) and \( t_2 \). Setting the differential

\[
dF_1 = \sum_{i} p_i dq_i - \sum_{j} P_j dQ_j - (H-K) dt \tag{6.21}
\]

and defining the transformation by using

\[
F_2 = \sum_{j} Q_j P_j + F_1 \tag{6.22}
\]

it follows that

\[
Q_j = \frac{\partial F_2}{\partial p_j} \tag{6.23}
\]

\[
P_i = \frac{\partial F_2}{\partial q_i} \tag{6.24}
\]

and

\[
K = H + \frac{\partial F_2}{\partial t} \tag{6.25}
\]

Since \( F_1 \) is set to zero, the final transformation is written
\[ Q_j = Q_j(q_i) \quad (6.26) \]
\[ p_i = \sum_{j=1}^{3N} p_j \frac{\partial q_j}{\partial q_i} \quad (6.27) \]

and
\[ K(Q_j, P_j) = H(q_i(Q_j), p_i(Q_j, P_j)) \quad (6.28) \]

Thus the classical trajectory calculation is developed by the following steps:

1. setting up the Hamiltonian for Cartesian coordinates;
2. transforming to generalised coordinates;
3. finding the Cartesian coordinates and momenta as functions of the generalised coordinates and momenta;
4. determining the new Hamiltonian as a function of the generalised coordinates and momenta;
5. using Hamilton's equations to set up the 6N first order differential equations,
\[ \dot{Q}_i = \frac{\partial H}{\partial p_i} = \frac{p_i}{\mu_i} \quad (6.29) \]
\[ \dot{p}_i = -\frac{\partial H}{\partial Q_i} = -\frac{\partial V(Q_i)}{\partial Q_i} \]

which comprise the working equations for the method.

The procedure has also been outlined by Miller (MIL 74) and by Bunker (BUN 71) using a matrix transformation approach.
6.4 **Integration of the Equations of Motion**

The classical trajectory is plotted by integrating the equations of motion (6.29) and incrementing the coordinates and their momenta over small intervals. The numerical integration of the equations of motion may be carried out by a number of methods, which may be classed as single step or multiple step (including variable time step). Single step methods describe the evolution of a general function $y$, where

$$\frac{dy}{dt} = f(y(t))$$  \hspace{1cm} (6.30)

by a truncated Taylor series

$$y(t_n + h) = y(t_n) + hf(y(t_n)) + \sum_{k=1}^{r} \frac{b^{k+1}}{(k+1)!} \left\{ \frac{d^k}{dt^k} f(y(t)) \right\}_{t=t_n}$$  \hspace{1cm} (6.31)

A set of Runge-Kutta methods are produced on manipulation (POR 76). While these well-known techniques have obvious advantages in that they are self-starting and relatively simple, they do not make use of information from prior steps as the trajectory proceeds. Therefore most modern trajectory calculations take advantage of starting the procedure with a Runge-Kutta routine, but quickly move over to a multi-step
method as the integration evolves. Such techniques use values of y at previous steps and so require fewer evaluations of the function f for a given step size.

Of particular interest here are the predictor-corrector methods for which an initial estimate of \( y_{n+1} \) must be supplied, i.e., the predictor, as the term \( f_{n+1} \) (\( \equiv f(y_{n+1}) \)) appears in the expression derived for evaluating \( y_{n+1} \), i.e., the corrector.

In this thesis the method used was the Hamming's predictor-corrector algorithm (HAM 59), of the form

\[
\text{predictor: } p_{n+1} = y_{n-3} + \frac{4}{3}h(2f_{n} - f_{n-1} + 2f_{n-2}) \tag{6.32}
\]

\[
\text{modifier: } m_{n+1} = p_{n+1} - \frac{112}{121}(P_{n} - c_{n}) \tag{6.33}
\]

\[
f_{n+1}^{m} = f(m_{n+1}) \tag{6.34}
\]

\[
\text{corrector: } c_{n+1} = \frac{1}{8}(9y_{n} - y_{n-2} + 3h(f_{n+1}^{m} + 2f_{n} - f_{n-1})) \tag{6.35}
\]

\[
y_{n+1} = c_{n+1} + \frac{9}{121}(P_{n+1} - c_{n+1}) \tag{6.36}
\]

In addition, a variable time step is employed. That is, the difference between predicted and corrected values is monitored as an indication of the overall error. If it becomes too large, the time interval is halved and continues to be halved until an acceptable accuracy is achieved.
Linear interpolation is used to find the earlier values of $y$ at the new step lengths, equations 6.37 and 6.38.

$$y_{n-\frac{1}{2}} = \frac{1}{256} (80y_n + 135y_{n-1} + 40y_{n-2} + y_{n-3}) + \frac{h}{256} (-15f_n + 90f_{n-1} + 15f_{n-2})$$

(6.37)

$$y_{n-\frac{3}{2}} = \frac{1}{256} (12y_n + 135y_{n-1} + 108y_{n-2} + y_{n-3}) + \frac{h}{256} (-3f_n - 54f_{n-1} + 27f_{n-2})$$

(6.38)

6.5 The Coordinate System

The model used in this Thesis was developed from a simple trajectory method, designed to investigate the reaction $O^+ + I_2$ over a single adiabatic potential energy surface at thermal energies (FER 80). In this calculation the collisions have been confined to the plane of the molecular bond, a rather drastic restriction in view of earlier comparisons of two and three dimensional calculations for the potassium-methyl iodide reaction (KAR 64). However, in view of the high collision energies and consequently short collision lifetime involved in the present computations as well as the lack of knowledge of an accurate hypersurface, the additional computational expense in moving to three
dimensional collisions cannot be warranted by anticipated results. The methyl group is considered as an atom as in most K + CH₃I calculations.

The coordinate system is given in figure 6.1 and by the equations

\[
Q_1 = R \sin \theta \\
Q_2 = R \cos \theta \\
Q_3 = -R_{BC} \\
Q_4 = 0
\]

(6.39)

and the conjugate momenta

\[
P_1 = -\mu_T R \cos (\frac{\pi}{2} - \theta + \alpha) \\
P_2 = -\mu_T R \sin (\frac{\pi}{2} - \theta + \alpha) \\
P_3 = \pm \mu_M R_{BC} \\
P_4 = \pm \mu_M \omega_{BC}
\]

(6.40)

where \(\mu_T, \mu_M\) are the reduced masses of the complete system and of the molecule respectively, \(v_R\) is the relative velocity and \(\omega\) is the molecular angular velocity.

6.6 Selecting the Starting Conditions

Initial conditions may either be scanned, i.e., assigned values which vary systematically from trajectory to trajectory, or they may be selected randomly, based on appropriate statistical distributions simulating the experimental conditions, i.e., the Monte Carlo
Figure 6.1: Coordinate System
method. By carrying out a great number of trajectory calculations, statistical averages of the resultant quantities may be established. Assuming that experimental observables correspond to such averages over the many single atom-molecule collisions, direct comparisons can be achieved. From these, conclusions can be drawn on the influence of the various potential parameters on the collision dynamics.

In this Thesis the following selections were made.

The impact parameter $b$ was scanned, stepped at intervals of 0.1 a.u. ($\sim 0.05\AA$) from 4.9 a.u. to 6.8 a.u. ($\sim 2.6 - 3.6\AA$). Thus the range of interest for collisions involving electronic excitation is covered, while those for which interaction is very small are excluded. Very wide angle scattering and dissociation can be expected for the small impact parameters.

The initial value $R$ for the distance from the potassium atom to the molecular centre of mass was fixed at about 20\AA, and $R_{BC}$, the methyl iodide bond length, was taken as the equilibrium bond length for the ground vibrational state. A method of simulating vibrational excitation was available, which set the starting values of $R_{BC}$ for $v > 1$ at those positions corresponding to maxima of the vibrational wave function probability amplitudes, with
appropriate weightings. In practice however, only the ground vibrational state was chosen, as expected in the experiment.

The initial orientation of the methyl iodide molecule is taken as the positive axis in figure 6.1, with B \equiv the iodine atom and C \equiv the methyl group. The angle \( \theta \) is obtained from

\[
\theta = 2\pi r
\]  

(6.41)

where \( r \) is a random number generated from a uniform distribution in the range \((0,1)\). The angle \( \alpha \) is of course set by

\[
\alpha = \sin^{-1}\left(\frac{b}{R}\right)
\]  

(6.42)

The program retains rotational angular momenta selection as a legacy of its development in thermal energy calculations, but these need not be discussed here.

6.7 Analysis of Final States

Final state properties are calculated when one of the groups is sufficiently far from the other two following a collisional encounter that interactions may be considered negligible. In this model a separation of about 20\( \AA \) was required to terminate the trajectory.

For the collisions under examination,
those involving elastic scattering or electronic excitation, the final relative translational energy was calculated as

\[ E = \frac{1}{2\mu_T} (P_{1f}^2 + P_{2f}^2) \quad (6.43) \]

The angle \( \chi \), for scattering in the centre of mass system is found from

\[ \chi = \cos^{-1} \left\{ \frac{P_{1i} P_{1f} + P_{2i} P_{2f}}{\sqrt{[(P_{1i}^2 + P_{2i}^2)(P_{1f}^2 + P_{2f}^2)]^2}} \right\} \quad (6.44) \]

where \( P_{ni} \), \( P_{nf} \) denote initial and final values for the momenta. The final vibrational energy is calculated from

\[ E_{vib} = \frac{1}{2\mu_M} P_{3f}^2 \quad (6.45) \]

6.8 Computing

A listing of the surface hopping trajectory program is available in Appendix D. Figure 6.2 details the flow diagram and indicates the function of each sub-routine. The integration procedure STWOD is based on the IBM sub-routine DHPCG and the random number generators G05CAF and G05DDF (uniform and Gaussian respectively) were available from the Numerical Algorithms Group (NAG) library held at the Edinburgh Regional Computing Centre.
Figure 6.2: Block Diagram for SHT Program

- **MAIN PROGRAM**
- **START**
- **SOLVE**
- **STWOD**
- **POTFUN**
- **CONTRL**
- **OPT**
- **TRANSF**
- **RMIN**
- **ABANDC**
- **ACANDB**
- **NOREAC**
- **AXES**
- **GRAPH**
- **PLOT**

**G05CAF, G05DDF** - R.N. Generators

**START** - Initial values of P, Q

**SOLVE** - Prepares values for integration

**STWOD** - Integration step

**POTFUN** - Evaluates Hamiltonians, and handles surface hopping procedure

**CONTRL** - Monitors integration, determines finish

**GRAPH** - Optional output, plots internuclear separations against collision time

**ABANDC, ACANDB** - Final state properties in reactive systems (not required here)

**NOREAC** - Final state properties for all trajectories
The surface hopping step was carried out in the sub-routine POTFUN, and figure 6.3 shows the flow diagram. The velocity correction on hopping to a new potential energy surface is found by the method of Tully and Preston (TUL 71). As stated earlier this correction takes place in the component of velocity perpendicular to the crossing seam. Since energy must be conserved during the hop the correction may be calculated as follows.

The total kinetic energy for the system A+BC is

\[ T = \frac{P_M \cdot P_M}{2\mu_M} + \frac{P_P \cdot P_P}{2\mu_T} \]  

(6.46)

where \( P_M \) is the momentum of C with respect to B and \( P_P \) is the momentum of A with respect to the centre of mass of BC. \( P_M \) may be partitioned

\[ P_M = \frac{J \cdot R_{BC}}{R_{BC}^2} + \frac{P_R \cdot R_{BC}}{|P_{BC}|} \]  

(6.47)

where \( J \) is the angular momentum of the diatomic BC and \( P_R \) is the projection of \( P_M \) on the bond axis. If \( A \) denotes the energy difference between the two electronic surfaces, and \( v_C \) represents the corrected component of velocity in the \( R_{BC} \) direction, approximately perpendicular to the crossing zone, then
ENTRY HAMPOT

CALCULATE POTENTIALS, TOTAL ENERGY, MOMENTUM

DOES CURRENT POTENTIAL APPROACH ANY OTHER POTENTIAL?

SET FLAG

END OF ENTRY HAMPOT

CALCULATE POTENTIAL GRADIENTS

CALCULATE \( \dot{q}_i \)

IS FLAG FOR CLOSE APPROACH OF POTENTIALS SET?

CALCULATE L.Z. PROBABILITY

GENERATE R.N.

IS L.Z. PROBABILITY > R.N.?

CALCULATE NEW POTENTIAL, VELOCITY CORRECTION, NEW POTENTIAL GRADIENTS

CALCULATE \( \dot{p}_i \)

RETURN

Figure 6.3

SUBROUTINE POTFUN

246
\[ v_c = \frac{p_r}{\mu_M} \]  

(6.48)

and

\[ p_r = \left[ 2T \pm 2A - \frac{J \cdot J}{\mu_M |R_{BC}|^2} - \frac{p \cdot p}{\mu_T} \right]^\frac{1}{2} \]  

(6.49)

In the coordinate system used here, the corrected component \( v_c \) is represented as \( \dot{Q}_3 \) and the momentum correction given by equation 6.49 can be re-written

\[ \text{new } p_3 = \left[ 2T \pm 2A - \frac{P^2}{\mu_M Q^2_3} - \frac{(P^2_1 + P^2_2)}{\mu_T} \right]^\frac{1}{2} \]  

(6.50)

The trajectory calculations were carried out on ICL 2970 and ICL 2980 computers at the ERCC. On the 2980 device a single trajectory could be completed in around 5s CPU with output requiring storage of about 1kbyte. The output for a typical trajectory is shown in figure 6.4, and graphical output is presented in figure 6.5.

6.9 Results and Discussion

The minimum requirements demanded of any potential energy hypersurface is that it displays the symmetry properties of the system it describes, it provides correct asymptotic descriptions at the entry and exit channels, the description of the three body interaction is
TIME AT END 10.0

FINAL HALVING STATE 0
H CONS MARKER 0
AH CONS MARKER 0
END CODE 0.0

INITIAL FINAL
HAMILTONIAN 155.8970 155.8970
POTENTIAL -2.3106 0.1477
ANG. MOM. -756.489888 -756.489888
R(A) 37.93 22.65
R(AC) 33.83 27.70
R(BC) 4.17 5.05

NON-REACTIVE

DR. ANG. MOM. -743.743184 -762.099609
ROTNL. ANG. MOM. -4.542129 5.610765
TOTAL ANG. MOM. -748.285156 -758.489770
TRANS=156.251
GROSS= 0.0208
EVIT= 1.6551
SCATTS. ANGLE= 3.4
LAW ANGLE= 2.6

WITH EXCITED POTASSIUM STATE

Figure 6.4 : Typical Output
Figure 6.5: Typical Graphical Output

+/− denotes ionisation, * denotes excitation
adequate and the potential behaves reasonably for collision processes in the region between the strong coupling zone and the asymptotes (KUN 79). The classes of potential surface available have been described as ab initio, semi-theoretical, semi-empirical and empirical (BAL 75). Ab initio calculations are as yet some way from describing heavy atom collisions, and these and semi-theoretical methods do not always produce the desired reaction products. Furthermore, they are computationally slow and, given that they were developed to handle stable molecule systems, need not be most suitable for collision processes. Of the semi-empirical methods, the "diatomics-in-molecules" (DIM) approach has become very popular in collision dynamics (KUN 76), (TUL 77), (KUN 79). However, as mentioned earlier, previous work on the potassium-methyl iodide system has been based on arbitrary functions and the development in this Thesis has been taken from here.

The Blais-Bunker potential energy surface (BLA 62) of the form

\[
V_B = D_1 \left\{ 1 - \exp \left[ -\beta_1 (R_1 - R_{01}) \right] \right\}^2 + D_2 \left\{ 1 - \exp \left[ -\beta_2 (R_2 - R_{02}) \right] \right\}^2 + D_3 \left\{ 1 - \tanh(a_1 R_1 + b_1) \right\} \exp \left[ -\beta_2 (R_2 - R_{02}) \right] + D_3' \exp \left[ -\beta_3' (R_3 - R_{03}) \right]
\]

(6.51)
was used initially to check the program's operation at thermal energies. In this potential the first and second terms are Morse potentials for the KI and CH₃I molecules respectively. The third term defines the three body interaction region, attenuating the methyl iodide attraction in the presence of the potassium atom, with \( a_1 \) and \( b_1 \) determining the range. It is clear that a corresponding attenuation term for the KI bond in the presence of the methyl group should also be included (KAR 64). The final term is purely repulsive between the potassium and the methyl group. Thus the potential fulfills the asymptotic requirements of either diatomic while the interaction region is described in terms of a switching function coupling the \( R_1 \) and \( R_2 \) coordinates. Parameter values are given in Table 6.1.

Early results confirmed that the program was operating in a sensible manner, showing similar results to previous calculations for reactive scattering at thermal energies over the two dimensional surface. The surface hopping procedure was introduced and with some alterations, e.g., initial step length, the program was prepared for superthermal operation.

Trajectories were run over the modified Blais-Bunker surface, superposing a core repulsion in K—I, with parallel surfaces at 1.62 and 3.47eV.
## Table 6.1
Parameters for Blais-Bunker Potential Energy Surface

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<th>Item</th>
<th>Value/Unit</th>
<th>Description</th>
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<th>Value/Unit</th>
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<td>$D_1$</td>
<td>3.29 eV</td>
<td>Dissociation energy of KI</td>
<td>$D_3$</td>
<td>4.34 eV</td>
<td>Morse parameter for modified K-CH$_3$ repulsion</td>
</tr>
<tr>
<td>$D_2$</td>
<td>2.34 eV</td>
<td>Dissociation energy of CH$_3$I</td>
<td>$\beta_3$</td>
<td>8.11 Å$^{-1}$</td>
<td>Morse parameter for modified K-CH$_3$ repulsion</td>
</tr>
<tr>
<td>$D_3'$</td>
<td>4.34 eV</td>
<td>Morse parameter for K-CH$_3$ repulsion</td>
<td>$R_{03}$</td>
<td>1.78 Å</td>
<td>Range parameter for modified K-CH$_3$ repulsion</td>
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<tr>
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<td>Morse B-parameter for KI</td>
<td>$\epsilon_1$</td>
<td>0.1 eV</td>
<td></td>
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<tr>
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<td>Morse B-parameter for CH$_3$I</td>
<td>$\sigma_1$</td>
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<td>Core repulsion in ground state</td>
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<td>Morse parameter for K-CH$_3$ repulsion</td>
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<th>Description</th>
<th>Item</th>
<th>Value/Unit</th>
<th>Description</th>
</tr>
</thead>
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<td>R01</td>
<td>3.23Å</td>
<td>Equilibrium bond length for KI</td>
<td>ε₂</td>
<td>0.1eV</td>
<td>core repulsion in ion state</td>
</tr>
<tr>
<td>R02</td>
<td>2.14Å</td>
<td>Equilibrium bond length for CH₃I</td>
<td>σ₂</td>
<td>2.50Å</td>
<td></td>
</tr>
<tr>
<td>R03</td>
<td>3.90Å</td>
<td>Range parameter for K-CH₃ repulsion</td>
<td>s₂</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>a₁</td>
<td>1.63Å⁻¹</td>
<td>Attenuation parameter in switching function in R₁</td>
<td>I.P.(K)</td>
<td>4.3eV</td>
<td>ionisation potential</td>
</tr>
<tr>
<td>b₁</td>
<td>-5.27</td>
<td>Attenuation parameter in switching function in R₁</td>
<td>E.A.(CH₃I)</td>
<td>-0.7eV</td>
<td>vertical electron affinity</td>
</tr>
<tr>
<td>a₂</td>
<td>1.63Å⁻¹</td>
<td>Attenuation parameter in switching function in R₂</td>
<td>H₁₂</td>
<td>0.15a.u.rs⁻¹</td>
<td>matrix elements in Landau-Zener calculation</td>
</tr>
<tr>
<td>b₂</td>
<td>variable</td>
<td>Attenuation parameter in switching function in R₂</td>
<td>H₂₃</td>
<td>1.00a.u.rs⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂₄</td>
<td>1.00a.u.rs⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

1: ground
2: ion
3: K
4: CH₃I
* signifies a specific state or condition.
representing K(4\(^2\)P) excitation and methyl iodide "A" state excitation. A simple ionic potential was included as the intermediate coupling ground and excited states. This consisted of a Coulomb attraction and a small dipole attraction in the potassium-iodine coordinate \(R_1\), together with a core repulsion in \(R_1\), the repulsive term between potassium and methyl groups, and the repulsive Wentworth potential (WEN 69) describing the \(\text{CH}_3\text{-I}^-\) interaction, of the form

\[
V_{\text{WEN}} = D_2 \left\{ \exp \left[ -2\beta_2 (R_2 - R_{02}) \right] - 2X \exp \left[ -\beta_2 (R_2 - R_{02}) \right] \right\}
\]  

(6.52)

where \(X\) is an empirical constant set to 0.075.

Results indicated that this representation was not wholly satisfactory, as only limited access to the ionic potential surface was achieved and most successful crossings led to dissociation. Examination of the potentials in a fixed \(\text{CH}_3\text{-I}\) bond representation revealed that the access "window" onto the ionic surface was very narrowly confined to the iodine "end" of the "diatomic", due to potassium-methyl repulsion (figure 6.6, table 6.2). Experiments involving the reaction of alkali atoms with oriented \(\text{CH}_3\text{I}\) molecules have shown a distinct preference for reaction at the iodine "end" (BEU 66), (BRO 66). This implies that at thermal energies the reaction proceeds by a concerted process, the
Figure 6.6; FMS Contour Map of preliminary Blais-Runker potential. The outermost contour marks the asymptotic limit. Contour values are given in eV. Access to the ionic potential is shown by the broken line.
### Table 6.2

**Potassium-Methyl Repulsion in the Original Blais-Bunker Surface**

<table>
<thead>
<tr>
<th>$R_3/\AA$</th>
<th>$V_{\text{rep}}(R_3)/\text{eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3</td>
<td>0.00</td>
</tr>
<tr>
<td>4.2</td>
<td>0.01</td>
</tr>
<tr>
<td>4.1</td>
<td>0.10</td>
</tr>
<tr>
<td>4.0</td>
<td>0.65</td>
</tr>
<tr>
<td>3.9</td>
<td>4.34</td>
</tr>
<tr>
<td>3.8</td>
<td>28.73</td>
</tr>
<tr>
<td>3.7</td>
<td>190.16</td>
</tr>
</tbody>
</table>
methyl group retreating to facilitate the approach of the potassium atom. In the sudden collision at superthermal energies there is little opportunity for such pre-stretching in the molecule.

On the other hand, the dissociative outcomes were caused by too rapid bond-stretching in the CH$_3$I$^-$ molecule. The crossing seams to the excited states move quickly to large internuclear distances, resulting in low transition probabilities, i.e., the phenomenon of ionic trapping. The CH$_3$I$^-$ Wentworth potential has been discussed in simple impact parameter calculations (SUT 80) and these also concluded that the extent of repulsion within the molecule must be modified to take account of the three body interaction.

Experimental results (FLU 79) indicate that the CH$_3$I$^-$ bond distance increases rapidly following electron transfer but the repulsion soon falls to near zero. Therefore the repulsive Wentworth potential has been amended to include a switching function in the K-I coordinate, similar to that in the ground state, to account for the presence of the potassium ion. That is, within the range specified by the $b_1$ parameter the presence of the K$^+$ ion will cause high repulsion in the CH$_3$I$^-$ molecule, cf. the concerted mechanism in K-CH$_3$I reaction. If a
measure of back-transfer of the valence electron is assumed as the potassium departs from the collision zone it would be foolish to suppose other than a reduced CH$_3$-I$^-$ repulsion. It is seen that this device might be judged running counter to previous simple models, which relied upon a potassium ion close at hand to provide the necessary molecular stability. However, for the purposes of trajectory calculations the function caters for both the provision of stability towards the end of the collisional encounter and the requirements of the reaction mechanism at low energies. Indeed this model works rather well. In fast collisions the potassium projectile traverses the interaction region very quickly. On crossing to the ionic potential a large repulsion in the CH$_3$-I$^-$ bond is switched on, which subsequently diminishes as the collision runs its course, as observed experimentally. It is certainly clear that experimental results reveal substantial neutral scattering while most models seem to indicate that dissociation should go fairly completely. It is hoped that these Monte Carlo classical trajectory calculations may discover whether experimental results are due primarily to a dynamical "trapping" effect i.e., the potassium ion physically obstructs the departing methyl group, or whether only particular
geometries may interact (though this is related to the first case) with pre-stretching predisposing the molecule to a given configuration or whether some alteration in the three body interaction is required. From even these preliminary results however, (see table 6.3) it appears that modification of the three body terms is necessary. Although access to the ionic surface can be limited to certain configurations and impact parameter ranges, intuition suggests that this is not enough. Thus it is the investigation of the role of three body interactions that is of chief importance here. The discussion is based upon these interactions rather than merely an attempt to fit experimental scattering cross-sections and energy loss distributions.

The final potentials used to describe the potassium-methyl iodide system were chosen as

\[ V_{\text{ground}} = D_1 \left\{ 1 - \exp \left[ -\beta_1 (R_1 - R_{01}) \right] \right\}^2 + D_1 \left\{ 1 - \tanh(a_2 R_2 + b_2) \right\} \exp \left[ -\beta_1 (R_1 - R_{01}) \right] + D_2 \left\{ 1 - \exp \left[ -\beta_2 (R_2 - R_{02}) \right] \right\}^2 + D_2 \left\{ 1 - \tanh(a_1 R_1 + b_1) \right\} \exp \left[ -\beta_1 (R_2 - R_{02}) \right] + D_3 \exp \left[ -\beta_3 (R_3 - R_{03}) \right] + \frac{\epsilon_1 (\sigma_1)}{R_1} S_1 - (D_1 + D_2) \]

(6.53)
<table>
<thead>
<tr>
<th>Set</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>Elastic</th>
<th>$K^*$</th>
<th>$RI^*$</th>
<th>Dissociation/ Ionisation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Set A</strong></td>
<td>$-5.27$</td>
<td>$-5.27$</td>
<td>37</td>
<td>27(70)</td>
<td>13(78)</td>
<td>23</td>
</tr>
<tr>
<td><strong>Set B</strong></td>
<td>$-6.27$</td>
<td>$-6.27$</td>
<td>51</td>
<td>15(70)</td>
<td>8(80)</td>
<td>26</td>
</tr>
<tr>
<td><strong>Set C</strong></td>
<td>$-5.27$</td>
<td></td>
<td>40</td>
<td>25(72)</td>
<td>12(70)</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>$-6.27$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Set D</strong></td>
<td>$-6.27$</td>
<td></td>
<td>51</td>
<td>11(72)</td>
<td>7(80)</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>$-5.27$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Set E</strong></td>
<td>$-3.27$</td>
<td>$-3.27$</td>
<td>70</td>
<td>14(72)</td>
<td>2(85)</td>
<td>14</td>
</tr>
<tr>
<td>Preliminary</td>
<td></td>
<td></td>
<td>$&lt;50$</td>
<td>$\approx 1-2$</td>
<td>$\approx 1-2$</td>
<td>$&gt;50$</td>
</tr>
</tbody>
</table>

Figures in parenthesis indicate the percentage scattered in the narrow angle region.
\[ V_{\text{ion}} = -\frac{14.394}{R_1} - \frac{50.4}{R_1^2} + \varepsilon_2 \left( \frac{g_2}{R_1} \right)^2_2 \]

\[ + D_2 \left[ 1 - \exp \left[ -\beta_2 (R_2 - R_{02}) \right] \right]^2 - D_2 \]

\[ + 1.85D_2 \left[ 1 - \tanh(a_1 R_1 + b_1) \right] \exp \left[ -\beta_2 (R_2 - R_{02}) \right] \]

\[ + D_3 \exp \left[ -\beta_3 (R_3 - R_{03}) \right] + \text{IP(K)} - \text{EA(CH}_3\text{I)} \]  (6.54)

for potentials in eV, R's in \( \tilde{A} \), with as usual, excited potassium and excited methyl iodide potentials of the same form as the ground state shifted by their respective asymptotic limits.

The switching function variables \( b_1 \) and \( b_2 \) were used to adjust the relative extent of the three body interaction. Table 6.1 gives details of the other parameters.

The methods of representation for potential energy surfaces, the fixed molecule (FMS) and fixed angle (FAS) surfaces, have been discussed by Kuntz (KUN 76). Figure 6.7 shows an FMS contour diagram of the ground potential surface with the molecular bond length fixed at its equilibrium value. The access window to the ionic state is indicated by the crossing seam. Because the stretching mechanism in the \( \text{CH}_3\text{I}^- \) molecule is important it is difficult to gain a realistic impression of the ionic surface from most potential diagrams. Figure 6.8 shows the ionic potential surface for the fixed molecular bond, although this situation may be somewhat different from that experienced on the first crossing due to
Figure 6.7: FMS Contour Map of Set A ground state potential.
Figure 6.8: FMS Contour Map of Set A ionic potential. Access to the $K(4^2P)$ and $CH.I"A"$ states is shown by the inner and outer broken lines respectively.
pre-stretching in the ground state.

The crossing probabilities were calculated using a Landau-Zener expression

\[ P_{12} = 1 - \exp(-\frac{H_{12}}{Q_3}) \]  

(6.55)

where \( P_{12} \) is the probability of crossing from surface 1 to surface 2, \( Q_3 \) is the velocity perpendicular to the seam and \( H_{12} \) is a matrix element with the dimensions of velocity. In the program \( H_{12} \) is expressed in atomic units per reduced second, with \( 1 \text{ rs} \) equal to \( 10^{-14} \text{s} \). Table 6.1 also gives these values. The crossing probabilities have been fixed to provide excited state populations of about the size expected from experimental observations. Since this work is concerned with electronic excitation channels, the probabilities have not been optimised to produce accurate overall intensities in comparison to the elastic channel.

Results are given for potential surfaces with the following three body b parameters:

- set A \( b_1 = -5.27 \) \( b_2 = -5.27 \)
- set B \( b_1 = -6.27 \) \( b_2 = -6.27 \)
- set C \( b_1 = -5.27 \) \( b_2 = -6.27 \)
- set D \( b_1 = -6.27 \) \( b_2 = -5.27 \)
- set E \( b_1 = -3.27 \) \( b_2 = -3.27 \)

The influence of these parameters on the potential
hypersurface can be readily interpreted. As the b value becomes more negative the hyperbolic tangent repulsion term moves to wider ranges. That is, the ground state repulsions represented by the terms

\[ D_1 \exp\left[-\beta_1(R_1-R_{01})\right]\left\{1-\tanh(a_2R_2+b_2)\right\} \]  
\[ D_2 \exp\left[-\beta_2(R_2-R_{02})\right]\left\{1-\tanh(a_1R_1+b_1)\right\} \]  

(6.56)  
(6.57)

and the ionic repulsion

\[ 1.85D_2 \exp\left[-\beta_2(R_2-R_{02})\right]\left\{1-\tanh(a_1R_1+b_1)\right\} \]  

(6.58)

remain important at larger internuclear distances \( R_1 \) and \( R_2 \). For example, increasingly negative values correspond to higher repulsion in the \( \text{CH}_3\text{I} \) molecule and molecular ion. In the ground state the approaching potassium atom induces earlier pre-stretching. On the ionic surface the repulsion in the \( \text{CH}_3\text{I}^- \) ion continues over a longer collision lifetime to wider internuclear separations. In passing it is worth noting that these potential energy surfaces have been constructed to display some degree of ionic behaviour in the ground state on approaching the collision, and some measure of re-neutralisation on the ionic surface leaving the interaction region, by virtue of these three body terms.

It is possible to increase the repulsive contributions between the methyl group and iodine
and between potassium and iodine by introducing more negative values of $b_1$ and $b_2$ respectively.

Fixed bond representations of these sets are given in figure 6.7, 6.9-6.12, which show the ground state surfaces with the crossing seams to the ionic state. As already mentioned, such representations are of limited value but here at least they serve to show the differences between these sets under frozen target conditions.

Table 6.4 summarises some important details of the hypersurfaces.

A total of 5300 trajectory calculations were carried out over these five sets of surfaces. In all cases there were still a large number of dissociative outcomes but the increase in elastic and excited state populations represented a substantial improvement on the preliminary results. In any case, dissociative trajectories are highly probable at the bottom end of the impact parameter range sampled here.

Table 6.3 indicates the relative populations for each set of trajectories. The discussion is developed only for the excited state results. It is unreasonable to complicate matters by changing core repulsions and crossing probabilities, which determine elastic channel populations and cross-sections.

These results can be compared with the
Figure 6.9: FMS Contour Map of Set B ground state potential.
Figure 6.10: FMS Contour Map for Set C ground state potential.
Figure 6.11: FMS Contour Map of Set D ground state potential.
Figure 6.12: FMS Contour Map for Set E ground state potential.
### Table 6.4

**Characteristics of the Hypersurfaces**

<table>
<thead>
<tr>
<th>Set</th>
<th>( R_c/A )</th>
<th>( V(R_c)/eV )</th>
<th>access window/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.4</td>
<td>1.00</td>
<td>160</td>
</tr>
<tr>
<td>B</td>
<td>3.2</td>
<td>0.55</td>
<td>150</td>
</tr>
<tr>
<td>C</td>
<td>3.5</td>
<td>0.70</td>
<td>160</td>
</tr>
<tr>
<td>D</td>
<td>3.2</td>
<td>5.00</td>
<td>150</td>
</tr>
<tr>
<td>E</td>
<td>3.1</td>
<td>-2.30</td>
<td>150</td>
</tr>
<tr>
<td>Preliminary</td>
<td>2.8</td>
<td>-</td>
<td>70</td>
</tr>
</tbody>
</table>

(1) Typical results for methyl iodide at equilibrium bond length. \( R_c \) and \( V(R_c) \) depend upon orientation of molecule, but are almost constant at the iodine 'end' of the bond.

(2) This is the angle between the bond axis and the position where the crossing seam moves to inaccessible potential energies, with the iodine atom as pivot. Thus the values given are one half of the full access window on the two dimensional surfaces.
available experimental data on K-CH$_3$I scattering. The Edinburgh Molecular Beams Group has carried out a large number of investigations on potassium-alkyl halide collisions in recent years, particularly on the potassium-methyl iodide system at 164eV CM collision energy. Observed cross-sections for potassium (4$^2P$) excitation and methyl iodide "A" state excitation are shown in figure 6.13 and table 6.5 lists the extent of vibrational excitation associated with these processes. Both processes display narrow angle onsets, with the potassium excitation reaching a maximum at about 400eV, declining steadily afterwards. The methyl iodide cross-section rises in intensity towards the widest angle. There are two energy loss peaks associated with each electronically excited state, corresponding to early and late crossing from the ground to ionic state. Attempts to fit observed data with simple impact parameter models have met with moderate success. "Atomic" or "frozen target" models have not been able to match experimental energy losses, due to the importance of vibrational excitation, and models allowing relaxation in the CH$_3$I$^-$ molecule revealed that the Wentworth potential did not describe the K$^+$-CH$_3$I$^-$ system well.

Figures 6.14-6.18 present the distribution of trajectories over CM scattering angle in the
Table 6.5

Range of Maximum Intensity in $E_{\text{vib}}$ distribution/eV

<table>
<thead>
<tr>
<th>Set</th>
<th>$K^*$</th>
<th>$RI^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A</td>
<td>0.5-1.0</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>Set B</td>
<td>1.0-1.5</td>
<td>0.0-0.5</td>
</tr>
<tr>
<td>Set C</td>
<td>0.0-0.5</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>Set D</td>
<td>1.5-2.0</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>Set E</td>
<td>0.0-0.5</td>
<td>-</td>
</tr>
<tr>
<td>obs. expt.</td>
<td>peaks at 0.1 and 1.2</td>
<td>peaks at 0.1 and 1.3</td>
</tr>
</tbody>
</table>
Figure 6.13: Differential cross-sections for K-CH$_3$I scattering at 164eV CM collision energy.
Figure 6.14: Scattering Distribution for Set A
Figure 6.15: Scattering Distribution for Set B
Figure 6.16: Scattering Distribution for Set C
Figure 6.17: Scattering Distribution for Set D
Figure 6.18: Scattering Distributions for Set E
narrow angle region of interest. Differences can be noted both in intensity and shape as well as certain similarities. All the trajectory sets show narrow angle onsets for both potassium and methyl iodide excitation channels. Comparison of figures 6.14 and 6.15, the angular distributions for sets A and B, suggests that the generally increased repulsion in the ground state potential of set B restricts the opportunity of crossing on to the ionic surface, and the larger repulsive term in the \( \text{CH}_3^-\text{I}^- \) coordinate "levels out" the strong peaks in the excitation channels. The relationship between scattering intensities and crossing radius \( R_c \) can be seen by comparison of these figures and table 6.4.

Set E, figure 6.18, shows relatively little excitation, though it might be expected that access to the ionic state can be readily achieved given that potassium-iodine and methyl-iodine repulsions are low. Instead however, the crossing radius is small and elastic scattering predominates. This suggests that the ground state potential is possibly too shallow. Also because there is very little repulsion in the molecular ion and consequently the crossing radii remain fairly static, there is little ionic trapping and the relative excited state populations may reflect more accurately the crossing probabilities. In
the other four cases the extent of ionic trapping remains high leading to many dissociative outcomes despite the attenuation in the CH$_3$I$^-$ repulsion.

From figures 6.16 and 6.17 it is seen that set C produces results rather similar to set A while set D shows the same features as set B, although K(4$^2$P) excitation is perhaps more noticeably peaked.

These results suggest that the methyl-iodine repulsion i.e. the switching function in $R_1$ determines the extent of surface crossing as well as the shape of the angular distribution via the CH$_3$I$^-$ repulsion. The potassium-iodine interaction has some bearing on accessing the ionic surface but because the CH$_3$I molecular bond length is usually near its equilibrium value the switching function in $R_2$ has approximately the same value for all values of $b_2$. The difference in the relative K-I repulsions will only show towards the end of the collision when the molecular bond has been stretched.

The peak in K(4$^2$P) excitation moves to narrower angles with diminishing absolute values of $b_1$, that is, less repulsion in the CH$_3$-I$^-$ coordinate. This is probably due to the shorter time spent on the repulsive part of the ion surface leading to less momentum transfer to the
methyl group.

Figures 6.19-6.23 display the energy loss distributions for the five hypersurfaces. Double peaks in vibrational excitation are present in some results, analogous to the early and late crossings of experiment and simple models. In many trajectories the potassium projectile has transferred enough energy into the molecular vibrational modes to bring about dissociation. The trajectory calculation has been terminated by the K-CH$_3$I distance rather than the degree of stretching in the methyl iodide and consequently these dissociative results are concealed. High energy loss results have been included, however, to indicate the scale of the problem. Since this is also an artifact of the impact parameter range, figure 6.24 shows the energy loss distribution for set A with only wide impact parameters.

These results show that most trajectories leading to potassium excitation display vibrational excitation within the dissociation limit of 3.38eV, typically at around 2.5eV and less. As might be expected, an increase in the potassium-iodine repulsion via an increased absolute value of $b_2$ leads to an increase in the amount of vibrational excitation imparted during potassium excitation. In methyl iodide excitation
In figures 6.19-6.24 potassium excitation is shown by the broken lines and methyl iodide excitation by the solid lines.
Figure 6.20: Vibrational Energy Loss Distribution for Set B
Figure 6.21: Vibrational Energy Loss Distribution for Set C
Figure 6.22: Vibrational Energy Loss Distribution for Set D
Figure 6.23: Vibrational Energy Loss Distribution for Set E
Figure 6.24: Vibrational Energy Loss Distribution for Set A, sampling only wide impact parameter trajectories.
however, the amount of T-V transfer is almost constant and generally lower than is the case for potassium. Since the additional time spent on the ionic surface in reaching the crossing seam to the "A" state channel can be expected only to contribute further to vibrational excitation, the observation remains rather difficult to interpret. Here the potassium ion may hinder the exiting methyl group, implying that methyl iodide excitation is more likely for a particular configuration of the atom-molecule system. Earlier impact parameter calculations (SUT 80) suggested that a freely expanding CH$_3$-I$^-$ bond would result in an ionic-excited molecule crossing seam at around 34Å. Methyl iodide excitation would be a very unlikely exit channel then, except to a small subset of trajectories involving hindrance of the bond-stretch. To support this, studies on the H$^+$+H$_2$ system have shown that computed cross-sections are little changed by alterations to the transition probabilities, indicating that final exit channel populations are determined mainly by the number of trajectories passing through certain strongly coupled regions rather than any single hopping probability on any part of the seam (KRE 74). Further calculations are required to decide upon the validity of this appealing proposition.
Investigation with greater use of graphical output may shed some light on the CH$_3$I "A" state excitation process. Some graphical output has been produced in these computations, examples of which are shown in figures 6.25 and 6.26. Table 6.5 summarises the vibrational energy losses produced by these trajectory calculations.

It must be concluded that none of the surfaces can hold a particular claim to modelling best the experimental observations. Set A displays characteristics rather similar to experiment, particularly in the second onset in methyl iodide excitation (although the scattering occurs in too narrow an angular range) and also in the vibrational contributions. Other sets can produce similar attributes however. Little more than crude comparisons can be expected since the surfaces themselves are very rudimentary. Comparison with elastic scattering may help define the core repulsions but the important three body interactions will continue to provide the chief interest and to provoke the greatest effort on the part of the experimenter.

6.10 Conclusions

A surface hopping trajectory calculation has been developed to calculate electronic excitation processes in alkali-alkyl halide collision systems. The so-called "anteater" method
Figure 6.25: CH$_3$I* Excitation

Electron recapture is at very wide separations.
The harpoon and ionic expansion are obvious.
has been used to select the trajectory path, with the Landau-Zener approximation.

A set of diabatic potential surfaces has been developed based upon the modified Blais-Bunker potassium-methyl iodide empirical description. Core repulsions have been included for fast collisions. The ground state potential surface is coupled to the K(4^2P) and CH\textsubscript{3}I (A) excited states by an ionic intermediate. The three body interactions are described by switching functions in the K-I and CH\textsubscript{3}-I coordinates. The potential surfaces are altered by adjustments to the switching functions.

Trajectories have been computed over the hypersurfaces constructed from the different switching terms. Comparisons have been made between these results and experiment for potassium and methyl iodide excitation. Elastic scattering has not been examined due to the inexact nature of the potentials, particularly in the relative importance of the three body terms and the core repulsion. The crossing probabilities also remain in some doubt. Thus comparisons are used to determine the role of the three body terms only.

It is found that the Wentworth potential describing the molecular ion state leads to rapid dissociation. Attenuation of the methyl-iodine
repulsion by the switching function in K-I reduces the amount of dissociation. There remains a high level of ionic trapping even with substantial attenuation. The switching function may be interpreted in terms of back-bonding of the valence electron to the K\(^+\) ion.

In the ground state during the approach to the collisional encounter the switching function in the K-I coordinate determines access to the ionic state and so to an extent the crossing probability. This is a methyl-iodine repulsive contribution, corresponding to pre-stretching.

The switching function in CH\(_3\)-I has little effect during the course of the collision. Thus the potassium-iodine interaction is relatively unimportant in itself; it is the effect of the potassium on the methyl-iodine interaction which plays the key role in promoting collisional excitation and in preventing the rapid decomposition of the molecular ion during the transition.

Excited methyl iodide calculations suggest a physical hindering of the fleeing methyl group by the potassium ion. Thus only trajectories in an approximate I\(^-\)-CH\(_3\)-K\(^+\) orientation may lead to molecular excitation.

Further calculations are required to firmly establish the observations made in this Thesis. The route for methyl iodide "A" state excitation
can be discovered by noting relative positions during the collision, so determining the correlation. Calculations at higher vibrational energies may also help clarify the relative importance of the molecular ion repulsion and the attenuating $K^+$ ion. More detailed computations over a large number of hypersurfaces will allow elastic scattering to be included, and core repulsions will be put on a firmer footing. Interesting calculations can be made with this model on the whole family of alkali-alkyl halide collisions. Thus the possibility arises of moving from wholly empirical potential surfaces to more exact descriptions.
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HAS 62  

HAS 62a  

HER 50  

HER 61  

HER 62  

HER 66  

HER 67  

HER 73  

HER 77  

HER 81  

HIC 80  


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(1932), 696.
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G.W.B.
FILE \ST\.VAL

COMMENT THIS IS AMENDED VERSION OF REGULAR TO HANDLE ANGLE
COMMENT FITTED DATA BY READING IN THE FITTED PARTS AND OUTPUTTING
COMMENT MATRIX FOR PLOTTING

- THIS PROGRAM TAKES FILTERED DATA AND CREATES A FILE WITH THE VIEL
  OR TRANSFORMS THEM TO X AND Y CARTESIAN COORDINATES WHICH ARE
  ACCEPTABLE TO INTCON FOR CONTOUR MAPPING OR TO SYMVU FOR 3-DIM
  INTCON NEEDS INTRTSO AND SYMVU NEEDS DATA TO RUN

ST.2--OUTPUT OF CM PARAMETERS
ST.10--INPUT
ST.14--OUTPUT OF CM ARRAY
  (ALL STREAMS ARE DEFINED WHILE THE PROGRAM IS RUNNING)

Routinespec Right Dress
Routinepro Acquireparams
Routinespec Acquiredata(\REALNAME v11, v21, v6, v11, xC
  \INTEGERNAME tJ, n, m, xC
  \REALARRAYNAME v1)
Routinespec Listarray(\INTEGERNAME nn, nm, n, k, xC
  \REALARRAYNAME c, phi, xC
  \REALNAME v1, v2, phi1, phi2, vi, v11)
Routinespec Contour(\INTEGERNAME nn, nm, n, m, l, xC
  \REALARRAYNAME a, b, x, y)
Routinespec Read File Name(\STRINGNAME NAME2)
Externalroutinespec Prompt(\STRING(15) s)
Externalroutinespec Define(\STRING(63) bc)
Externalintegerfnspec Exist(\STRING(63) file)
STRING (12) bc
INTEGER I, J, JJ, K, L, NN, MM, N, M, TJ, NEV
INTEGER ii, 12, 13, 14
REAL wifi, v111
REAL vMin, vMax, phiMin, phiMax, save
REAL ARRAY buff(1:100, 1:100), e(1:30), y, x(1:100, 1:100), phi(1:100)
REAL ARRAY a(1:129, 1:129), b(1:129, 1:129)
REAL ARRAY evl(1:10, 1:2)
REAL energy, fi, v01, vi1, v21, phi1, vi, vi1, dfly
REAL vMin, vMin, vMax, x1, y1
SWITCH SWIT(1:7)

XON: xovernt 9 Xstart
-> COMPLETE

Xfinish
LOGC: i=3 14577/150,
Xcycle i=1, 1, 100
Xcycle j=1, 1, 100
A(i,j)=55779
B(i,j)=99881: 'UNASigned Pattern

A.1
SELECT INPUT(0)

PRINT STRING ("RIGHT DRESS BY 50% OF IST (ELASTIC ?) PEAK ?")

NEWLINE

PROMPT("YES, NO:")

SKIPsymbol WHILE NEXTSYMBOL='Y' XAND NEXTSYMBOL='N'

READSYMBOL(I)

READSYMBOL(J) UNTIL J=NL

XIF I='Y' THEN ->SWIT(7)

-..j

SWIT(7): ACQUIRE PARMS ROUTINE FOR PARMS HERE

-..j

SIT: SELECT INPUT(0)

WIFI=0.0

ACQUIREDATA(VII, VS1, VI, VII, TJ, N, M, X)

COMPLETE:

SELECT INPUT(0)

PRINT STRING ("RIGHT DRESS BY 50% OF IST (ELASTIC ?) PEAK ?")

NEWLINE

PROMPT("YES, NO:")

SKIPsymbol WHILE NEXTSYMBOL='Y' XAND NEXTSYMBOL='N'

READSYMBOL(I)

READSYMBOL(J) UNTIL J=NL

XIF I='Y' THEN XSTART

RIGHT DRESS FINISH

ORDER THE PHI(I)'S

\%CYCLE I=1,1,N

L=I

\%CYCLE K=1,1,N

XIF PHI(K)<PHI(L) THEN L=K

\%REPEAT

XIF L=I THEN ->SWIT(1)

SAVE=PHI(I)

PHI(I)=PHI(L)

PHI(L)=SAVE

\%CYCLE J=1,1,M

SAVE=A(I,J)

A(I,J)=A(L,J)

A(L,J)=SAVE

SAVE=X(I,J)

X(I,J)=X(L,J)

X(L,J)=SAVE

\%REPEAT

SWIT(1):

PRINT(PHI(I), 2, 3), SPACES(2)

XIF FRACPT(I/8)=0.0 THEN NEWLINE

\%REPEAT

NEWLINE; NEWLINE; NEWLINE

PRINT STRING ("SMOOTH OVER " LAG, " ANGLE ?")

NEWLINE

A.2
I

T5:.jj

-  

11--5.  

>W 1  

E  

11=1

WYCLE  

--io p-i  

WYCLE  

rsj 

J.  

I,  

•._)  

WYCLE

WYCLE

WYCLE

WYCLE

\( \text{CYCLE } i=1, 1, N \)  
\( \text{I4=0} \)  
\( \text{I1=i-5, } \times \text{IF } \text{I1<1 } \times \text{THEN } \text{I1=1} \)  
\( \text{I2=i+5, } \times \text{IF } \text{I2>N } \times \text{THEN } \text{I2=N} \)  
\( \times \text{IF } \text{PHI(13)} \times \text{PHI(1)} \times \text{WID1 } \times \text{AND } \text{PHI(13)} \times \text{PHI(1)} \times \text{WID1 } \times \text{THEN } \times \text{START} \)  
\( \times \text{CYCLE } j=2, 1, N-1 \)  
\( \text{BUFF(i, j)=A(13, j)+BUFF(i, j)} \)  
\( \times \text{REPEAT} \)  
\( \text{I4=I4+1} \)  
\( \times \text{FINISH} \)  
\( \times \text{REPEAT} \)  
\( \times \text{CYCLE } j=2, 1, N-1 \)  
\( \text{BUFF(i, j)=BUFF(i, j)/I4} \)  
\( \times \text{REPEAT} \)  
\( \times \text{REPEAT} \)  
\( \times \text{CYCLE } i=1, 1, N \)  
\( \times \text{CYCLE } j=2, 1, N-1 \)  
\( \text{A(i, j)= BUFF(i, j)} \)  
\( \times \text{REPEAT} \)  
\( \times \text{REPEAT} \)  
\( \times \text{COMMENT ALSO AVERAGES OVER E LOSS SLIGHTLY} \)  
\( \times \text{NEWLINE} \)  
\( \times \text{NEWLINE} \)  
\( \times \text{NEWLINE} \)  
\( \times \text{PRINTSTRINGS('SMOOTHING COMPLETE')} \)  
\( \times \text{FINISH} \)  
\( \times \text{NEWLINE} \)  
\( \times \text{NEWLINE} \)  
\( \times \text{PRINT STRINGS('TRANSFORM TO THE CENTER OF MASS.')); NEWLINE} \)  
\( \times \text{TRANSFORM TO THE CENTER OF MASS} \)  
\( \times \text{XYCLE } i=1, 1, N \)  
\( \text{PHI}=\text{PHI(1)} \)  
\( \times \text{LABSCOUTPLANE(A, X, Y, M, i, N, E(3), E(5), E(3), E(5), Y11, Y21, PHI)} \)  
\( \times \text{REPEAT} \)  
\( \times \text{CYCLE } i=1, 1, N \)  
\( \text{PHI(i)=Y(I, 1)} \)  
\( \times \text{REPEAT} \)  
\( \times \text{FINISH THE MAX AND MIN OF THE CENTER OF MASS W/S AND PHI'S} \)  
\( \times \text{PRINT STRINGS('USE LINEAR INTERPOLATION BETWEEN POINTS.')) \)  
\( \times \text{NEWLINE} \)  
\( \times \text{CHANGE INTENSITY TO INTENSITY TIMES CM ANGLE SQUARED} \)  
\( \times \text{PRINT STRINGS('PARE INTENSITY=INTENSITY}\times \text{CHI}^{+}+2} \)
F

PRINT STRING('EMPHASIZE WIDE ANGLE SCATTERING

INTENSITY=(INTENSITY+CHI/2)**0.53

)

PROMPT('YES, NO: ')

SKIPSYMBOLEWHILE NEXTSYMBOLE 'Y' XAND NEXTSYMBOLE 'N'
READSYMBOLE(I)
READSYMBOLE(J) UNTIL J=NL
XIF I='N' XTHEN -3SWIT(2)
XCYCLE I=1, 1, N
XCYCLE J=1, 1, M
A(I, J)=A(I, J)*Y(I, J)**2
XREPEAT
XREPEAT

SWIT(2):

PRINT STRING('CREATE A FILE FOR CONTOUR MAP'

)

PROMPT('YES, NO: ')

SKIPSYMBOLEWHILE NEXTSYMBOLE 'Y' XAND NEXTSYMBOLE 'N'
READSYMBOLE(I)
READSYMBOLE(J) UNTIL J=NL
-3SWIT(5) XIF I='N'
NN=100
NM=100
L=0
CONTOUR(NN, NM, N, M, L, A, B, X, Y)

LIST THE ARRAY IN A CM FILE

LISTARAY(NN, NM, M, K, PHI, VMIN, VMAX, PHIMIN, PHIMAX, VI, VI1)

SWIT(5):

TRANSFORM DATA TO CARTESIAN COORDINATES BEFORE MAKING IT REGULAR

PRINT STRING('CREATE A FILE FOR A 3-DIMENSIONAL PLOT'

)

PROMPT('YES, NO: ')

SKIPSYMBOLEWHILE NEXTSYMBOLE 'Y' XAND NEXTSYMBOLE 'N'
READSYMBOLE(I)
READSYMBOLE(J) UNTIL J=NL
-3SWIT(6) XIF I='N'
NN=100
NM=100
XMAX=X(1, 1)*COS(Y(1, 1)*PI)
XMIN=X(N, M)*COS(Y(N, M)*PI)
YMAX=Y(N, 1)*SIN(Y(N, 1)*PI)
YMIN=Y(1, M)*SIN(Y(1, M)*PI)
XCYCLE I=1, 1, N
XCYCLE J=1, 1, M
L=1
CONTUR(NN, MM, N, M, L, A, B, X, Y)
LISTARRAY(NN, MM, N, R, PHI, XMIN, XMAX, YMIN, YMAX, VI, VII)
EXIT(6):

PRINTSTRING(READ NEW PAMRS OR DATA AND CONTINUE?)
NEWLINE/NEWLINE/NEWLINE
PROMPT(YES, NO:)
SKIPSsymbol XWHILE NEXTsymbol 'N' AND NEXTsymbol 'Y'
READsymbol(1)
READsymbol(1) XUNTIL J=NL
XIF I='Y' XTHEN -1L,399
X2TOP

XRoutine LABTOGROUNDPLANE (XREALARRAYNAME S, V1F, CHI, XC
XINTEGERNAME JCOUNT, J1, N, XREALNAME MASS1, MASS2, XC
MASS3, MASS4, VI1, VR1, PHI)

! THIS TRANSFORMATION ASSUMES THE LAB COLLISION ANGLE IS 90 DEGREES

XINTEGER I, G, J
XINTEGER ID
XREAL VO, CI, CHI1, CX1, FM, T1, LSC, LCD, ELOSS, TF, XC
LAMBD, GAM, W11, W1F, ALPH1, CSL1PH1, COSE
XREAL W1, COSE, VR
XREAL CSL1PH1, MASS1, VR1, VII
XREAL VO1, VII1, COSE1
XREALARRAY THETA(1:10)

LSC=49.9 + 7.9 ;!DISTANCE FROM PULSER TO COLLISION ZONE (CM)
S=1
LCD=60.1 ;!DISTANCE FROM COLLISION ZONE TO FILAMENT (CM)
TF=0.0016 ;!FLIGHT TIME FROM FILAMENT TO MULTIPLIER (MNS)
VI IS THE RELATIVE INCIDENT VELOCITY OF PARTICLE I

VR=SQRT(V2I**2+VII**2)
W1=(MASS2/(MASS1+MASS2))*VR
COSE=W1I/VR
VO=SQRT(W1**2+VII**2-2.0*W1I*VII*COSE)

! VO IS CM VELOCITY

FM=(MASS1*MASS4)/(MASS3+MASS2)
ENERGY=(MASS1*MASS2)/(MASS1+MASS2)*VR**2/2.0*5199&11
! THE UNITS OF ENERGY ARE EV

W11=W1
CSL1PH1=(VII**2-VO**2-W1I**2)/(2*VII*VO)
ALPH1=ARCCOS(CSL1PH1)

XIF J1=1 XTHEN XSTART
PRINT STRING( 'LIST CENTER OF MASS CONVERSION PARAMETERS?'
)
PROMPT(YES, NO:)
SKIPSsymbol XWHILE NEXTsymbol 'Y' XAND NEXTsymbol 'N'
READsymbol(1)
READsymbol(1) XUNTIL J=NL
XIF I='Y' XTHEN ID=1
XIF I='N' XTHEN ID=0

A.5
SW2:

THETA(0) = 0.0

CIN = PHI

PHI = PHI * 3.14159 / 180.0

CSA1 = COS(ALPH1 - THEA(0)) * COS(PH1)

C1 = COS(PH1) + COS(THETA(0))

CYCLE J = 1.1, JCOUNT

W1F = SORT(V0**2 + V1F(J1, J)**2 - 2 * V0 * V1F(J1, J) * CSA1)

CHI1 = ((W1F**2 + W1F**2 - (V1I**2 + V1F(J1, J)**2) + 2.0 * V1I * W1F(J1, J) * C1) * C1)

/ (2.0 * W1I * W1F))

IF ARCCOS %IF MOD(CHI1) <= 1.0

%IF MOD(CHI1) > 1.00001 XTHENSTART

PRINT STRING( 'ARGUMENT OF ARCCOS = ' )

PRINTFL (CHI1, 14)

PRINT STRING( 'SET EQUAL TO --- 1.0' )

XFINISH

CHI1 = -1.0 %IF CHI1 < -1.0

CHI1 = 1.0 %IF CHI1 > 1.0

ARCCOS: CHI1 = ARCCOS(CHI1)

COSEP = (W1F**2 + V1F(J1, J)**2 - V0**2) / (2.0 * W1F * V1F(J1, J))

CX1 = (W1F / V1F(J1, J))**2 * MOD(COSEP)

CH1 IS THE JACOBIAN OR THE TRANSFORMATION FROM THE LAB SYSTEM OF D2

CM COORDINATE SYSTEM OF D2(CONSQA)DH

SEE JCP 49, 187B (1938) PG. 1380

T1 = LCS / V1I + LCD / V1F(J1, J)

T1 = T1 + 1000000 + TF

i = PI

A.6
(DEFPRINT (MASS1 MASS2) = 0)
(DEFPRINT (MASS) = 1)
I=I+1
-388 XI缶 O,N
-REFGAMMA(2) XUNIT 3
REFGAMMA(0)
-REFGAMMA(1) XUNIT 4
XI缶 REFGAMMA(1) XUNIT 3
XI缶 REFGAMMA(0)
(DEFPRINT (YES, NO) = 0)
(SKIP)
(DEFPRINT (YES, NO) = 1)
I=I+1

Print STRINGS) LOCATE THE ISTOPER
NEWLINE

Print STRINGS) ANOTHER ENERGY LOSS?
NEWLINE
Print STRINGS) CM/SEC(2) NEWLINE(2)
NEWLINE
NEWLINE
NEWLINE

Print STRINGS) CONVEXT ENERGY LOSS TO CM VELOCITIES?
XI缶 I=I+1

Print STRINGS) TRANSFORMATION TO CENTRE OF MASS COMPLETE?
NEWLINE
NEWLINE
NEWLINE
NEWLINE
NEWLINE
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NEWLINE
**XROUTINE ACQUIREDATA(xrealname vi,vri,vli,vi,vii,xc***

**XINTEGERNAME JFK1,N,M,XREALARRAYNAME V**

FIRST 39 NO. S EXPERIMENTAL VARIABLES
NO. 8-39 SET BY THE EXPERIMENTER IN RUNNING CTF5

EA(1) EVENTS
EA(2) NOISE
EA(3) ANGLE
EA(4) TIME
EA(5) XBEAM
EA(6) MBEAM
EA(7) NO. BLOCKS

E(1) DATE
E(2) MB(EV)
E(3) MB(AMU)
E(4) TB(DEG)
E(5) TB(AMU)
E(6) BEAM CENTER
E(7) CLOCK PERIOD=DT
E(8) =0 FOR S+N-N, =1 FOR S+N+N
E(9) NO. PULSES/CYCLE

SECOND READ NUMBER OF CHANNELS
THIRD READ CHANNEL NUMBER AND INTENSITY
FOURTH READ CHANNEL NUMBER AND STANDARD DEVIATION

XREAL XARRAY DI,TD,TI,T(0:256),EA(1:44)
XINTEGERARRAY CH(1:256)
XINTEGER TJ, I, J, K, L, JF, IP, JI, JL, JC, JFK, DJ
XREAL X, Y, LPC, LCD, CON, TE, TCON, DT, SHIFT, SHIFT1, DA
CON=9.65199811; !ERG*MOLECULES/EV*MOLES
LPC=49.9+7.9; !DISTANCE FROM PULSER TO COLLISION (CM)
LCD=60.1; !DISTANCE FROM COLLISION TO DETECTOR (CM)
PRINT STRING('CORRECTION FOR THE APPARATUS IMPERFECTION'); NEWLINE
PROMPT('SHIFT1 (CH)=')
READ(SHIFT1)
PROMPT('SHIFT (CH/DEG)=')
READ(SHIFT)
PROMPT('INPUT FILE:')
READ FILE NAME(IG) UNTIL EXIST(IG)=1
DEFINE('ST10', IG)
SELECT INPUT(10)
CYCLE 1=1,1,100

READ THE EXPERIMENTAL VARIABLES
CYCLE K=1,1,100
READ(EA(K))
SOME VARIABLES TO BE USED IN PROCESSING THE DATA
L=0
\%CYCLE K=0, 1, 13
   L=L+1
   E(L)=EA(K)
%REPEAT
\%IF E(3)<39.3 \%AND E(3)>38.7 \%THEN XSTART
\%COMMENT FIX TO PUT IN ACCURATE MASS FOR 39 ISOTOPE OF POTASSIUM
E(3)=38.98371
%FINISH
\%FI x=E(22)
   DT=E(D)\*1E-9
   E(2)=EA(23)
   E(9)=EA(30)
   IP=INT(\{E(9)\})
   JF=1024/IP
\%IF E(2)=100. \%THEN Y=3.41
\%COMMENT USED TO BE 3.41 PROBABLY ADJUSTS ENERGY DUE
\%TO STARTING POINT IN PULSER
\%IF E(2)=200.0 \%THEN Y=4.59
\%COMMENT USED TO BE 4.59 SEE ABOVE
\%IF IP=16 \%THEN Y=0.0
VII=SGRT(2\*E(2)+Y)\*CON/E(3)) \% \% (CM/SEC)
VII=SGRT(3.0\*E32144000.0\*E(4)/E(5))
VOI=SGRT(2\*E(2)\*E(3))/E(3))
DELV=VII-VOI+4.00\%4
TE=(LPC+LDC)/VOI
! CHECK TO INSURE THE STORED VARIABLES REMAIN CONSTANT
\%FINISH \%ELSE \%START
\%IF E(2)=EA(9) \%THEN K=9 \%AND \%ERROR
\%IF E(4)=EA(11) \%THEN K=11 \%AND \%ERROR
\%IF E(5)=EA(12) \%THEN K=12 \%AND \%ERROR
\%IF E(7)=EA(22) \%THEN K=22 \%AND \%ERROR
\%IF E(9)=EA(30) \%THEN K=30 \%AND \%ERROR
\%FINISH
\% = (EA(3)-EA(13))/1000
PHI(1)=ARCTAN(28.6, X)*180./3.14159
Y = -SHIFT1 - SHIFT*PHI(1) + EA(42)
\%SW3
\%ERROR:
\%PRINT STRING('EXPERIMENTAL VARIABLE')
\%WRITE(K, 4):SPACES(3)
\%PRINT STRING('IS NOT CONSTANT AT ANGLE')
\%PRINT(EA(3), 5, 1):SPACES(3)
\%PRINT STRING('AND BLOCK')
\%WRITE(1, 4)
\%NEWLINE
\%STOP
\%IF:
\%PRINT STRING('CHANNEL NO.')
\%WRITE(K, 4):SPACES(3)
\%PRINT STRING('HAS AN ERROR AT ANGLE')
\%PRINT(EA(3), 5, 1):SPACES(3)
\%PRINT STRING('AND BLOCK')
\%WRITE(1, 4)
\%NEWLINE
\%PRINT STRING('INITIAL CHANNEL IS')
\%WRITE(J1, 4):SPACES(3)

A.9
READ THE INTENSITIES OF THE CHANNELS

READ(JPK)
XI F I=1 THEN T J=JP K
DJ = T J=JP K
READ(JC)
% CYCLE J=1, 1, JC
READ(CH(J))
CH(J)=CH(J)+DJ
READ(TI(J))
% REPEAT
% CYCLE J=1, 1, JC
READ(K)
K=K+DJ
READ(DJ(J))
% IF CH(J) THEN -> ERR
% REPEAT

PAD THE ARRAY TO SO ALL CHANNELS BETWEEN CH(1) AND CH(JC) HAVE A VALUE

% IF I=1 THEN %START
JI=JP K-19
JI=1 % IF JIC1
JL=JP K+60
JL=JP K+80 % IF E(2)=100.
% IF JL> JF+1 THEN JL= JF+1
M=JL=JI
% FINISH
% IF CH(1)< JI THEN K=CH(1) %AND -> ERR
% IF CH(JC)>JL THEN K=CH(JC) %AND -> ERR
% CYCLE JJ=1, 1, M
T(JJ)=0
% REPEAT
JJ=0
T DJ(JJ)=0
% CYCLE JJ=1, 1, JC
ANOTHER:
JJ=JJ+1
TD(JJ)=TD(J J-1)
-> ANOTHER %IF JJ=J J-1<CH(J)
T(JJ)=TI(J)
TD(JJ)=DJ(J)
% REPEAT
% IF JJ=JC %THEN %START
% CYCLE J=JJ, 1, M
TD(J)=TD(J-1)
% REPEAT
% FINISH
% IF I=1 %THEN %START

FIND TCON= THE CONSTANT TIME TO BE SUBTRACTED FROM THE CHANNEL TIME TO CONVERT TO VELOCITY
TCON= T J+DT -LCD/V11
NEWLINE
PRINTSTRING( "TIME CONSTANT IN PULSING=" )
PRINTFL(TCON,3)
PRINTSTRING("SECS")
NEWLINE
% FINISH
X=0.
LCT 1ALiZE DATA
C YCLE J=1,1, 1
J J=J-1,1
W(I, J)=LCD/V(I, J)*DT-TC0N
A(I, J)=A(I, J)*2
X=X+A(I, J)
END=T(I)+LCD/V(I, J)*2

% REPEAT
IF I=1 THEN %START
JPK=1, TJ-JI+1
VI=V(I, TJ-JI+1)
VII=V(I, TJ-JI+2)
%END
IF X=0, 0 THEN =I-1 %AND -> SW5
X=1/EA(4)

NORMALIZE DATA
% CYCLE J=1,1, 1
A(I, J)=A(I, J)/X
% REPEAT

SW5:
N=1
% REPEAT
%END ; ! ACQUIREDATA

ROUTINE RIGHT DRESS
% REAL X1, PV, PV1, PV2, VO, H.V, MR, VEL, IVR, IW1, ICOSF, ICOSY, VCOR, IVO, ULIM
% REAL LS, LCD

% REAL VR, W1, ICOSY, VCOR, COS, LLIM, CF, GF
% REALARRAY P1(1: 100), P1(1: 100), P(1: 100)

% SWITCH PS(1: 4)
% INTEGER JPK, JM, I, J, Q
LDC=60, 1
LSC=49, 9+7, 9
%COMMENT DIMENSIONS OF BEAM PATH
JPK=TJ

NEWLINE PRINTSTRING ("ROUTINE ONLY WORKS FOR POTASSIUM WHERE ISOTOPES PROVIDE A REFERENCE ")
NEWLINE PRINTSTRING (" CHECK AS ELASTIC PEAKS ROLL BY THAT THEY ARE O.K. ")
NEWLINE

%COMMENT CALCULATES AVERAGE BEAM ENERGY FROM MEAN ARRIVAL TIME
%COMENT OF 2% OF ELASTIC 0, 0 E. LOCS PEAK, THEN FINDS ARRIVAL VELOCITY
%COMMENT FOR ELASTIC AND ISOTOPES 25% POINTS . CALCULATES ENERGY AT EACH
%COMMENT ANGLE AND ZERO ERROR AND CORRECTS ALL ANGLES TO THE MEAN
%COMMENT BEAM ENERGY.
%CYCLE I=1, 1, N
M=0, 0
%CYCLE J=1, 1, M
H

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FV :

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'.OMHENT .'ELOC. I TY I N SAME NAY

:33. 	 37i>.ICRT •;' -3

4)

L

•'2, J 	 . 	 .L..

,.	 T 	 tri[:

E I-1: 1.N

A,12
XIF JH=0 XTHEN XSTART
NE ULINE
PRINTS T RING (" MAXIMUM CORRESPONDING TO ISO TOPE NOT FOUN D IN SEAR CH")
XFIN ISH
XIF A(I, JH)<A(I, JM+1) XTHEN XSTART
NEU LINE
PRINTSTR I NG(" PEAK NOT FOUN D IN SEAR CH RANG E")
XFIN ISH
XIF A(I, JH)<0.02<H(I) XOR A(I, JH)>0.293+H(I) XTHEN XSTART
PRINTSTR I NG(" FAILS TO FIND ISO TOPE PEAK AT ANGLE NO=")
PRINT (I, 3, 1)
PRINTSTRING("AMPLITUDE RATIO=")
PRINT (A(I, JM)/H(I), 3, 2); NEWLINE
PRINTSTRING("ISO TOPE TAKEN AT NOMINAL VELOCITY")

P1(I)=LCD/((LCD+LSC)/(P(I)*MR)-LSC/VII)

X COMMENT CORRECT S TO PUT VELOCITY TO ISO TOPE APPARENT VELOCITY
XCOMMENT I.E. ALLOWS FOR WAY IN WHICH VELOCITY IS COMPUTE ACQUIRE DATA
XFIN ISH
HV=0.25*A(I, JM)
XCYCLE Q=JM, -1, -12
XIF A(I, Q)CHV %AND A(I, Q+1):HV %THEN XSTART
XCOMMEN T INTERPOLATE LINEAR ELY TO FIND 25% POINT
P1(I)=X(I, Q)+((X(I, Q+1)-X(I, Q))/(A(I, Q+1)-A(I, Q)))*HV-A(I, Q)
XCOM MENT P1(I) IS ESTIMATE OF ISO TOPE VELOCITY
NEWL I NE
XCOMMENT AFTER TEST OMIT THIS PRINT SEQUENCE
PRINT (1, 3, 1); SPACES(2); PRINT (Q, 3, 1); SPACES(2)
PRINT (P1(I), 3, 3)
XFIN ISH
XREP ET
PS(4): XR EPEAT

XCOMMENT P1(I) IS NOW FILLED WITH ISO TOPE VELOCITY

XCOMMENT NOW CALCULATE MEAN AND STD. DEV OF ISO TOPE VELOCITY, COMPARE XCOMMENT WITH THAT PREDICTED AS A CHECK ON THE PROCESS

MV=0.0
MV2=0.0
XCYCLE I=1, 1, N
APPLY AND CALCULATE THE SHIFT (SMALL) IN VELOCITY PRODUCED

IN THE LAB VELOCITY BY SCATTERING THRU AN ANGLE

PV=VEL1; XCOMMENT SET ISOTOPE TO NOM. VEL.

C=V1/VEL1

W1=VR*(E(5)/(E(5)+38.96371))

CSALPH1=(V11**2+V0**2-W1**2)/(2.0*V11*V0)

CSALPH=ARCCOS(CSALPH1)

IVR=SGRT(PV**2+V2I**2)

IWI=IVR*(E(5)/(E(5)+40.984)); XCOMMENT masses set for potassium

ICOSE=PV/IVR

IVO=SGRT(W1**2+V2I**2-2.0*W1*V11*ICOSE)

ICSALPH1=(PV**2+IVO**2-IV1**2)/(2.0*PV*IVO)

ICSALPH=ARCCOS(ICSALPH)

XCOMMENT ADJUST EACH ARRIVAL SO THAT ELASTIC AND ISOTOPE

XCOMMENT LIE ALONG THE AVERAGE OF ALL THE DATA.

VCOR=VO*COS(CSALPH1-(3.14159*PHI(I)/180))

X1=(VCOR*COS(CSALPH1-(3.14159*PHI(I)/180))**2-(VCOR**2-W1**2))

XIF X1<10 XTHEN PRINT STRING ("WARNING VCORRECTION WRONG")

XIF X1<1. XTHEN X1=0.1

VCOR=VCOR+SGRT(X1); XCOMMENT CM NOMINAL VELOCITY

VCOR1=IVO*COS(ICSALPH1-(3.14159*PHI(I)/180))

VCOR1=VCOR1+SGRT(VCOR1**2-IVO**2+IW1**2)

CF=(VCOR-VCOR1)/(P(I)-P1(I))

GF=VCOR-CF*P(I)

XCOMMENT CORRECTION FACTORS CF AND GF COMPUTED NOW WE APPLY THEM

CYCLE J=1, 1, M

X(I,J)=X(I,J)*CF*GF

XREPEAT

XREPEAT

XEND

XROUTINE LISTARRAY(XINTEGERNAME NN, MM, N, K, XREALARRAYNAME C, PHI, X)

XREALNAME VMIN, VMAX, PHIMIN, PHIMAX, VI, VII)
XSTRING(30) ST1
XINTEGER I, II, JJ
PROMPT('OUTPUT FILE: ')
READ FILE NAME(ST1)
DEFINE('ST14', 'BC')
SELECT OUTPUT(14)

WRITE(NN, 4); SPACES(3)
WRITE(MM, 4); NEUILINE
XCYCLE II=1, 1, NN
XCYCLE JJ=1, 1, MM
PRINT(C(II, JJ), 4, 2); SPACES(2)
XIF FRACP(JJ/7)=0. 0 XTHEN NEUILINE
XREPEAT
NEUILINE
XREPEAT
PRINT(YMIN, 7, 2); SPACES(2)
PRINT(VMAX, 7, 2); SPACES(2)
PRINT(PHIMIN, 2, 5); SPACES(2)
PRINT(PHIMAX, 2, 5); SPACES(2)
PRINT(VI, 7, 2); SPACES(2)
PRINT(VI, 7, 2); NEUILINE
WRITE(N, 4); NEUILINE
XIF N=0 XTHEN -3. 10
XCYCLE I=1, 1, N
PRINT(PHI(I), 2, 5); SPACES(2)
XIF FRACP(I/6)=0. 0 XTHEN NEUILINE
XREPEAT
3. 10: NEUILINE
WRITE(NEV, 4); NEUILINE
XIF NEV>0 XTHEN XSTART
XCYCLE I=1, 1, NEV
XIF EVLOSS(I, 1) CO. XTHEN EVLOSS(I, 1)=-EVLOSS(I, 1)
PRINT(EVLOSS(I, 1), 2, 2); SPACES(2)
PRINT(EVLOSS(I, 2), 7, 2); SPACES(2)
XIF FRACP(I/3)=0. 0 XTHEN NEUILINE
XREPEAT
NEUILINE
XFINISH
SELECT OUTPUT(0)
PROMPT('REACTION: ')
READ FILE NAME(ST1)
SELECT OUTPUT(14)
PRINT SYMBOL(37)
PRINT STRING(ST1)
PRINT STRING(' AT')
PRINT(EVLOSS(NEV+1, 1), 3, 1)
PRINT STRING(' EV IN CM')
PRINT SYMBOL(39)
NEUILINE
SELECT OUTPUT(0)
CLOSE STREAM(14)
XEND ; ! LISTARRAY

XROUTINE CONTOUR(XINTEGER NAME NN, MM, N, M, I, XC
XREAL ARRAY NAME A, B, X, Y)

! LINEAR INTERPOLATION ROUTINE

XINTEGER I, J, II, JJ, K, L, FLAG, FJ
XREAL Y1, Y2, A1, A2, YPT, XPT, SAVE
XREAL WIDTH, DX, DY
**CODE:**

```plaintext
MAX=X(1,1)
MIN=Y(1,1)
XMAX=Y(1,1)
YMIN=Y(1,1)
XCYCLE I=1,1:N
XCYCLE J=1,1:M
IF X(I,J)=XMAX THEN XMAX=X(I,J)
IF X(I,J)=XMIN THEN XMIN=X(I,J)
IF Y(I,J)=YMAX THEN YMAX=Y(I,J)
IF Y(I,J)=YMIN THEN YMIN=Y(I,J)

XREPEAT: XREPEAT

IF WIFI=0.5 THEN %START
IF XMIN=0.94+WIFI THEN XMIN=0.94+WIFI

XFINISH
DX=(XMAX-XMIN)/NM
DY=(YMAX-YMIN)/NN
IF L=1 AND DY<DX THEN DY=DX
IF L=1 AND DX<DY THEN DX=DX
XCYCLE II=1,1:NN
XCYCLE JJ=1,1:MM

B(I,J,JU)=0,0
XREPEAT: XREPEAT

I=1
J=1
K=0
XCYCLE II=1,1:NN
YPT=YMAX-(NN-II)*DY
XCYCLE JJ=1,1:MM
XPT=XMAX-JJ*DX

LOWW:
XIF I=0 THEN I=1 AND ->OUT
XIF J=0 AND J+K=0 THEN J=1 AND K=0 AND ->OUT

HIGHW:
XIF I>=N THEN I=1-1 AND ->OUT
XIF J=M AND J+K=M THEN ->NEXT
XIF XPT<X(I,J) THEN J=J-1 AND ->LOWW
XIF XPT>CX(I,J+1) THEN J=J+1 AND ->HIGHW
XIF XPT=X(I+1,J+K) THEN K=K-1 AND ->LOWW
XIF XPT<X(I+1,J+K+1) THEN K=K+1 AND ->HIGHW

Y1=Y(I,I+1) + (Y(I,J)-Y(I,J+1))*(XPT-X(I,J+1))/(X(I,J)-X(I,J+1))
XIF Y1=0 THEN I=I+1 AND ->LOWW
Y2=Y(I+1,J+K+1) + (Y(I+1,J+K)-Y(I+1,J+K+1))*(XPT-X(I+1,J+K+1))/(X(I+1,J+K+1)-X(I+1,J+K+1))
XIF Y2=0 THEN I=I+1 AND ->HIGHW

A1=A(I,J+1)+A(I,J)-A(I,J+1)*XPT-X(I,J+1))/(X(I,J)-X(I,J+1))
A2=A(I+1,J+K+1)+A(I+1,J+K)-A(I+1,J+K+1)*XPT-X(I+1,J+K+1))/(X(I+1,J+K+1)-X(I+1,J+K+1))
B(II-II+1,MM-JJ+1)=A2+(A1-A2)*(YPT-Y2)/(Y1-Y2)

OUT:
XREPEAT
NEXT:
I=I-1 XIF I=M-1
K=0
XREPEAT

NEWLINE
PRINT STRING('XMIN =')
PRINT FL(XMIN,6):NEWLINE
PRINT STRING('XMAX =')
```

**End of Code**
SET SCALE OF MAP FOR LATER GRAPHICS

NORMALIZE ARRAY TO 100 AT THE PEAK

SAVE=0.

CYCLE II=1, 1, NN
CYCLE JJ=1, 1, MM

IF B(II, JJ):SAVE THEN SAVE=B(II, JJ)

BUFF(II, JJ)=0. 0

REPEAT; REPEAT

NEWLINE

PRINT STRING ("SMOOTH ANGLE DEPENDENCE OF MAP ?")
NEWLINE; NEWLINE; NEWLINE
PROMPT ("YES, NO:")

SKIPSYMBOL WHILE NEXTSYMBOL='Y' AND NEXTSYMBOL='N'
READSYMBOL (Q)
READ SYMBOL (J) UNTIL J=NL

FLAG=0

IF Q='Y' THEN FLAG=1

IF FLAG=0 THEN %START

CYCLE II=1, 1, NN
CYCLE JJ=1, 1, MM

B(II, JJ)=B(II, JJ)*100. /SAVE

REPEAT; REPEAT

FINISH

IF FLAG=1 THEN %START

NEWLINE; PROMPT ("WIDTH(DES)")
READ (WIDTH)

FJ=INTPT(WIDTH/50. /(YMAX-YMIN))

CYCLE II=1, 1, NN
CYCLE JJ=1, 1, MM

BUFF(II, JJ)=0. 0

Q=II-FJ: I=0

IF Q<1 THEN G=1

ELSE: BUFF(II, JJ)=B(Q, JJ)+BUFF(II, JJ)

G=G+1; I=I+1

IF Q<NN AND G<II+FJ THEN -> 1.500

BUFF(II, JJ)=BUFF(II, JJ)/I

REPEAT

REPEAT

SAVE=0. 0

CYCLE II=1, 1, NN
CYCLE JJ=1, 1, MM

IF BUFF(II, JJ):SAVE THEN SAVE = BUFF(II, JJ)

REPEAT

REPEAT

CYCLE II=1, 1, NN
CYCLE JJ=1, 1, MM
EXTERNAL ALLONGREALFNSPEC HYPTAN (XLONGREAL X)

INTEGER I, J, I1, J1, NCHAN, G, NEX, NCHN, NN, MM, NEX1, ITS, NITS

INTEGER FLAG, NANG, NPARM

XREAL ARRAY EA(1:10)
XREAL VI, VII, ANG, EE1

XSTRING (12) BC

XREAL DELTA, DANG, SUM
XREAL PHININ, PHIMAX, VMIN, VMAX, ELOSS, DA, DE, EE, AE, FM, MASS1, MASS2
XREAL RMASSE, CE, CA, W11, W1F, LAMBDA
XREAL MASS3, MASS4, ENERGY

XREAL ARRAY C(1:25, 1:70)

XREAL DEL1, CE1, CE2, CA1, CA2
L101: PRINTSTRING('INPUT FILE NAME FOR PARGS')

NEWLINE NEWLINE NEWLINE
PROMPT('FILE NAME: ') READ FILE NAME (BC) DEFINE('ST10', BC) SELECTINPUT(10)

CYCLE I=1, 1:9 READ(EA(I)) WREPEAT
READ(NCHAN), XCOMMENT NUMBER OF CHANS

J=0
FLAG=0
L00: READ(ANS)
XIF ANG < -999 XTHEN -J=1
J=J+1

PHI(J)=ANG
Y(J,1)=ANG
I=0
XCYCLE I1=1,1,NCHAN
XCYCLE J1=1,1,5
I=I+1
READO(I,J))
XREPEAT
XREPEAT
-L,30

L01: PRINTSTRING('PARAMS CAPTURED FOR ')
PRINT(J,3,1); PRINTSTRING(' ANGLES')
NEWLINE
NANG=J
K=J
XCOMMENT CAPTURE SEQUENCE COMPLETE

SELECT INPUT(0)
NEWLINE

PRINTSTRING('RANGE OF VALIDITY')
RMASS=(EA(5)+EA(3))/(EA(5)+EA(3))
RMASS=RMASS*1.6576-24
ENERGY=EA(9)*1.60206-12
FM=1
W11=(EA(5)/(EA(3)+EA(5)))*SQRT(2*ENERGY/RMASS)
XCOMMENT FIND MEAN ARRIVAL PARM FOR ELASTIC CHAN

XCOMMENT SELECT RANGE OF ANGLE CVDR WHICH ENERGY ZERO WILL
XCOMMENT BE COMPUTED
NEWLINE
PRINTSTRING('MAXIMUM ANGLE TO BE INCLUDED IN ELASTIC ZEROING')
NEWLINE; NEWLINE; NEWLINE
PROMPT('MAX. ANG. = ')
READ(DANG)
SUM=0.0
XCYCLE I1=1,1,NANG

XIF Y(I1,1)<DANG XTHEN -NL211
SUM=SUM+C(I3,11)
L211: XREPEAT
SUM=SUM/NANG
XCOMMENT CORRECT ALL CHANS AND ALL ANGLES TO MEAN ARRIVAL TIME
XCYCLE I1=1,1,NANG
DELTA=SUM-C(I3,11)
XCYCLE J1=1,1,NCHAN
G=(J1-1)*5

A.19
1:0
NEWLINE
PRINTSTRING( 'RANGE OF VALIDITY' )
NEWLINE
PROMPT( 'VMIN=' )
READ(VMIN)
NEWLINE
PROMPT( 'VMAX=' )
READ(VMAX)
NEWLINE
PRINTSTRING( 'LABEL ENERGY LOSSES?' )
NEWLINE
NEV=0
NEWLINE;NEWLINE;NEWLINE
L93: PROMPT( 'YES: NO:' )
SKIPSsymbol WHILE NEXTsymbol='Y' XAND NEXTsymbol='N'
READsymbol( Q )
READsymbol( J ) XUNTIL J=NL
->L99 IF Q='N'
I=I+1
IF I'>0 XTHEN ->L99
PROMPT( 'ELoss' )
READ(ELoss)

WIF=(EA(5)/(EA(3)+EA(5)))*SGRT(2*(ENERGY-ELoss*1.602E-12)/MASS)
EVLOSS(I,1)=ELoss
EVLOSS(I,2)=WIF
NEV=I
PRINTSTRING( 'CORRESPONDStO' )
PRINT(WIF,7,2)
PRINTSTRING( 'CM/SEC' )
PRINTSTRING( 'ANOTHER ENERGY LOSS?' )

NEWLINE;NEWLINE;NEWLINE
->L98
L99: NEWLINE;NEWLINE;NEWLINE
EVLOSS(NEV+1, 1)=EA(9)
L93: PRINTSTRING( 'CONVOLUTE FIT WITH APPARATUS FUNCTION?' )
NEWLINE;NEWLINE;NEWLINE
PROMPT( 'YES: NO:' )
SKIPSsymbol WHILE NEXTsymbol='Y' XAND NEXTsymbol='N'
READsymbol( I )
READsymbol( J ) XUNTIL J=NL
IF I='Y' XTHEN FLAG=1
NEWLINE;NEWLINE;NEWLINE
PRINTSTRING( 'TOTAL SURFACE PLOT?' )
NEWLINE;NEWLINE;NEWLINE
PROMPT( 'YES: NO:' )
SKIPSsymbol WHILE NEXTsymbol='Y' XAND NEXTsymbol='N'
READ SYMBOL( I )
READ SYMBOL( J ) XUNTIL J=NL
IF I='N' XTHEN ->L92
NEI=1; NCHN=NCHAN
%COMMENT PLOT ENTIRE SURFACE
XCYCLE I=1, 1, NANG
XCYCLE J=1, 1, 100
A(I, J)=.0
XREPEAT
XREPEAT
DELE1=0.4
EE=VMAX
XCYCLE I=1, 1, NANG
XCYCLE J=1, 1, 100
EE1=((0.5*EE*EE+(EE*2-WI+2))/1.6026-12)
EE1=-EE1
XCOMMENT GRID IS IN VELOCITY MODEL IN ENERGY
XCYCLE I1=NEX, 1, NCHN
G=Z*(II-1)
CE=((1+HYPTAN(C(2+G, I)*((EE1-C(3+G, I)))))
CA=((1+HYPTAN(C(4+G, I)*((C(5+G, I))-EE1)))))
CE=CE+CA
%IF FLAO=1 %THEN %START
CE1=((1+HYPTAN(C(2+G, I)*((EE1-DELE1-C(3+G, I)))))
CA1=((1+HYPTAN(C(4+G, I)*((C(5+G, I))-EE1+DELE1)))))
CE2=((1+HYPTAN(C(2+G, I)*((EE1+DELE1-C(3+G, I)))))
CA2=((1+HYPTAN(C(4+G, I)*((C(5+G, I))-EE1-DELE1)))))
CE=(0.333*CE1+CA1+2.333*CE+0.333*CE2+CA2)
CE=CE+DELE1/2
XFINISH
CE=CE+C(1+G, I)
XREPEAT
A(I, J)=CE+A(I, J)
XREPEAT

L110: X(I, J)=EE
Y(I, J)=Y(I, 1)
EE=EE-DE
XREPEAT
EE=VMAX
XREPEAT
NN=NANG
N=NN
MM=J
M=NN
XCOMMENT SET RANGE OF ARRAY INTO GLOBAL INTEGERS
VI=0: VI=0 %COMMENT TEMPORARILY SET PENDING FIX
XRETURN
L102: PRINTSTRING('PLOT A SINGLE STATE?')
NEWLINE
PROMPT('YES: NO:')
SKIP SYMBOL %WHILE NEXTSYMBOLE='Y' %AND NEXTSYMBOLE='N'
READ SYMBOL(G)
READ SYMBOL(J) %UNTIL J=NL
%IF G='Y' %THEN %START
NEWLINE
PROMPT('CHAN. NO. '
READ (NEX)
NCHN=NEX
-0.1103
XFINISH
XEND
XEND
APPENDIX B
FILE 'INTCONS'

! CRAP SPECS INSERTED: WENDOFLIST

X_DYNAMICROUTINESPEC STORE ON
X_DYNAMICROUTINESPEC STORE OFF
X_DYNAMICROUTINESPEC VIEWON
X_DYNAMICROUTINESPEC VIEWOFF
X_DYNAMICROUTINESPEC NEWPIC
X_DYNAMICROUTINESPEC ERASE
X_DYNAMICROUTINESPEC WINDO(XINTEGER A, B, C, D)
X_DYNAMICROUTINESPEC SWINDO(XINTEGER A, B, C, D)
X_DYNAMICROUTINESPEC FRAME
X_DYNAMICROUTINESPEC DRAWA(XINTEGER X, Y)
X_DYNAMICROUTINESPEC MOVEA(XINTEGER X, Y)
X_DYNAMICROUTINESPEC POINTA (XINTEGER X, Y)
X_DYNAMICROUTINESPEC DRAWR(XINTEGER X, Y)
X_DYNAMICROUTINESPEC MOVEK(XINTEGER X, Y)
X_DYNAMICROUTINESPEC POINTR(XINTEGER X, Y)
X_DYNAMICROUTINESPEC DEFSUB(XINTEGER NAME)
X_DYNAMICROUTINESPEC ENDSUB
X_DYNAMICROUTINESPEC CHAR(XINTEGER CVAL)
X_DYNAMICROUTINESPEC INSTAN.(XINTEGER NAME, SIZE, ORIENT, XREF, YREF)
X_DYNAMICROUTINESPEC REVU
X_DYNAMICROUTINESPEC TEXTYP(XINTEGER TYPE)
X_DYNAMICROUTINESPEC PRINT STRING(XSTRING(255) S)
X_DYNAMICROUTINESPEC DRAW TEXT (XSTRING(255) S)
X_DYNAMICROUTINESPEC PROMPT(XSTRING(63) S)
X_DYNAMICROUTINESPEC SNAPSHOT(XSTRING(20) FILE)
X_DYNAMICROUTINESPEC CURSOR(XINTEGERNAME CVAL, X, Y)
X_DYNAMICROUTINESPEC DEFHEAD(XSTRING(230) T)
X_DYNAMICROUTINESPEC DEFMENU(XSTRING(9) T, XINTEGER LINE)
X_DYNAMICROUTINESPEC BIGSTRING(XSTRING(255) S, XINTEGER ROTATION, SCALE)
X_DYNAMICROUTINESPEC TWRITE(XINTEGER NO. PLACES)
X_DYNAMICROUTINESPEC TPRI NT(XREAL NO., XINTEGER PLACES, DEC PLACES)
X_DYNAMICROUTINESPEC RTAM
X_DYNAMICROUTINESPEC CHARs(XINTEGERNAME A, B, C, D, E)
X_DYNAMICROUTINESPEC NLINE

XCOMMENT  THIS  PROGRAM  IS  ACONTOURING  INTERACTIVE  PROGRAM  FOR
XCOMMENT  USE  ON  EITHER  TEXTRONIX  4010  OR  4027(COLOUR).  IT  DISPLAYS  CONTOUT
XCOMMENT  AS  ORDERED  FINDS  PEAKS  AND  RETURNS  DATA  ABOUT  SELECTED  POINTS
XEXTERNALROUTINESPEC DEFINE(XSTRING(63) BC)
XEXTERNALROUTINESPEC DATA (XLONGREALARRAYNAME A)
XEXTERNALROUTINESPEC DEBY(XSTRING(63) S)
XEXTERNALROUTINESPEC TCONTOUR(XLONGREALARRAYNAME A, XINTEGER IMAX, JMAX, XLONGREAL LEVEL, SYMBOL, XROUTINE TRANSFORM)
XEXTERNALROUTINESPEC TRANSFORM(XLONGREALNAME X, Y)
XEXTERNALROUTINESPEC TEKS(XINTEGERNAME TEK)
XEXTERNALROUTINESPEC EXTRA PIC
XEXTERNALINTEGERFNSPEC EXIST(XSTRING(63) FILE)
XROUTINE 1. PRINTSTRING (XSTRING(25), S)
XINTEGER J, I
J=ADD(2)+1
XCYCLE I=1,1,LENGTH(S)
PRINTSTRING (BYTEINTEGER(J))
J=J+1
XREPEAT
XEND
XINTEGER 11, TEK, PIC NO

XINTEGER ARRAY COLOUR(1:10)
XINTEGER COL
XMAINSTRING (90) BUFF=""
XMAINSTRING (72) DUM
XMAINSTRING(72) S
XMAINSTRING(1) COMM="!"
XMAINSTRING(7) SEPA=";"
XMAINSTRING(7) EDFL="/;"
XMAINSTRING(7) PROM=""

XMAINSTRING(7) TERM=""

DEFINE ("ST10.PLOTCON") ;XCOMMENT STREAM FOR HARD COPY COMMANDS

XROUTINE PST(XSTRING(72) S)

XIF TEF=4027 XTHEN XRETURN
PRINTSTRING (S,"
"
NEWLINE
XEND

XROUTINE SHR (XSTRING(1) C)
S=COMM."SHR"
S=S," .C %UNLESS C=""
PST(S)
XEND

XSTRINGOFN ITOS (XINTEGER I)
XSTRING (1) SIGN
XSTRING (53) S
XIF I<0 XTHEN SIGN="-" %AND I=IMOD(I) %ELSE SIGN=""
S=""
S=TOSTRING(1-I)//10*10+"0".S %AND I=I//10 XUNTIL I=0
S=SIGN.S
XRESULT=S
XEND

XROUTINESPEC READ FILE NAME(XSTRINGNAME FILE)
XSTRING(25) FILE
XSTRING(1) BELL
XINTEGER M, N, POSN, T, J3
XINTEGER CPUTIME
CPUTIME=120
POSN=0
BELL=TO STRING(7)
PRINT STRING("Do you wish graphs plotted?
")
PRINT(1,""Yes/No: ")
SKIP SYMBOL XWHILE NEXT SYMBOL = 'Y' %AND NEXT SYMBOL = 'N'
READ SYMBOL(T)
READ SYMBOL(N) XUNTIL N = NL
XIF T = 'Y' XTHEN XSTART
PRINT STRING(""
Set graph mode (control A, G, CR)
READ FILE

READ N

XMIN = 0

XCYCLE I = 1, 1, M

XCYCLE J = 1, 1, N
VIEW OFF XIF T = 'N'

! Do not draw graphs

READ

XREPEAT

(REPEAT

RESET;

HEURISTIC

VIEW OFF XIF T = 'N'

READ

PST(COMM. "MON 5 K H")

PST (COMM. "GRA 1,2")

SELECT INPUT(0)

PROMPT(BELL, "1st Level?")

READ(FIRST)

PROMPT("Last Level?")

READ(LAST)

XIF FIRST > LAST THEN INT=FIRST AND FIRST-LAST AND LAST=LAST

PROMPT("Interval?")

READ(INT) UNTIL INT > 0

XCYCLE NO=1, 1, 50;

LEVEL shapes FIRST;

FIRST=FIRST+INT;

LEVEL shapes NEXT level

XEXIT XIF FIRST > LAST

XREPEAT

XMAX = 1

YMAX = 1

XMIN = 0

YMIN = 0

TRANSFORM(XMAX, YMAX);

TRANSFORM(XMIN, YMIN);

COREV 2;

XCYCLE I=1, 1, NO

TCOUNT (A, M, N, LEVEL(I), 0, TRANSFORM)

XREPEAT

ENDS

PROMPT(BELL, "Draw Box?")

SKIP SYMBOL XWHILE NEXT SYMBOL € 'Y' AND NEXT SYMBOL € 'N'

READ SYMBOL(1)

READ SYMBOL(J) UNTIL J = NL

XIF I = 'Y' XTHEN DRAW GRID;

MOVEA(0,0)

PST(COMM. "MON H")

XIF TEK=4027 XTHEN XSTART

PROMPT("GRID COLOUR NO=")

READ(COL)

COLOUR(I)=COL

XCOMMENT STORES GRID COLOUR FOR HARD COPY

PST(COMM. "COL C", ITOS(COL))

PST(COMM. "HOR H")

XFINISH

INSTAN(1,128,0,0,0) XIF I = 'Y';

DISPLAY grid

MOVEA(0,0)

PST (COMM. "MON H")

XIF TEK=4027 XTHEN XSTART

PROMPT("CONTOUR COL NO=")

READ(COL)

COLOUR(2)=COL

XCOMMENT STORES COLOUR OF CONTOUR FOR REPLOTTING

PST (COMM. "COL C", ITOS(COL))

PST(COMM. "HOR H")

XFINISH

INSTAN(2,128,0,0,0);

PIC NO=2

! Display contours
IF INST = "STOP" THEN ERASE X AND CLOSESTREAM(10)
IF INST="STOP" X AND TEK=4027 X THEN GREN ("PLOTCON")
IF INST= "STOP" X THEN XSTART
CYCLE I=1,1,3
REPEAT
FINISH
IF INST="STOP" X THEN XSTOP

IF INST = "H" X THEN HELP
IF INST = "D" X THEN DATA (A)
IF INST = "W" X THEN WINDOW
IF INST = "R" X THEN RETURN
IF INST = "F" X THEN FREEZE
IF INST = "L" X THEN LEVELS

IF INST = "P" X THEN PEAK

IF INST = "G" X THEN EXTRAPIC
IF INST = "E" X THEN EXTRA

IF INST = "RESET" X THEN -> RESET
REPEAT
ROUTINE HELP
IF TEK=4027 X THEN ERASE

IF TEK=4027 X THEN PST (COMM. "MON H")
PRINT STRING(""
REPLYS TO PROMPT ":;"
---------------------
"
PRINT STRING(""
STOP - STOP - Terminate programme"
)
PRINTSTRING (""
D - DATA - RETURNS DATA ABOUT POINT INDICATED BY GRATICULE
1.E VELOCITY, ENERGY LOSS, ANGLE(CM) AND INTENSITY (X"
)
PRINTSTRING(""
W - WINDOW - Window area of graph using the cross-hairs.
Strike any key to fix position of cursor"
)
PRINTSTRING ("
G - GRATICULE - PUTS A GRATICULE AT A GIVEN CM VELOCITY 1.E FROM
DATA ROUTINE")
PRINT STRING(""
R - RETURN - Return to original graph after windowing"
)
PRINT STRING(""
F - FREEZE - Send display to nominated tektronix file"
)
PRINT STRING(""
L - LEVELS - Print out values of currently displayed contours"
)
E - EXTRA - Draw an extra contour"

B.5
XINTEGER J
XINTEGER XO, YO, XT, YT, DUMP
XIF TEK=4027 THEN XSTART
CURSOR(DUMP, XO, YO)
CURSOR(DUMP, XT, YT)
XFINISH
XIF TEK=4027 THEN XSTART
CURSOR(DUMP, XO, YO)
CURSOR(DUMP, XT, YT)
XFINISH
XIF XO=XT THEN DUMP=XO XAND XO=XT XAND XT=DUMP
XIF YO=YT THEN DUMP=YO XAND YO=YT XAND YT=DUMP
VWINDOW(XO, YO, XT, YT)
SWINDOW(0, 0, 639, 330)
ERASE
POSN=0
XCOMMENT PLOTS RETAINING SPECIFIED COLOUR INFORMATION
PST(COMM. "WOR H")
XCYLE J=1, 1, PIC NO
PST(COMM. "COL C", ITOS(COLOUR(I)))
INSTANTI, 128, 0, 0, 0
XREPEAT
FRAME
PST(COMM. "MON H")
XEND
XROUTINE EXTRA
XREAL L, SYMBOL
PST(COMM. "MON H")
XIF NO<50 THEN PRINT STRING("Too many levels ") XAND XRETURN
PROMPT("Level:")
READ(L)
PROMPT("Label?"))
IF E. THEN SYMBOL = 'Y' XTHEN SYMBOL = 1 YELSE SYMBOL = 0 SKIP SYMBOL UNTIL NEXT SYMBOL = NL SKIP SYMBOL

PST(COMM. "WOR H")
NO = NO+1
PIC NO=PIC NO+1
POSN = POSN+1
LEVEL(NO) = L
DEBUG(PIC NO)
TCOUNTU(R.A.M.N.L,SYMBOL,TRANSFORM)
ENDSUB
MOVEA(O,0)

XIF TEK=4027 %THEN XSTART
PST(COMM. "WON H")
PROMPT ("COLOUR NO=")
READ (COL)
COLOUR(PIC NO)=COL
PST (COMM. "COL C", ITOS(COL))
PST (COMM. "WOR H")
XFINISH
INSTAN(PIC NO,128,0,0,0)
XEND
 Routine LEVELS
XINTEGER I
XCYCLE I=1,1.NO
 PRINT(LEVEL(I),3,0)
 NEWLINE
 POSN=POSN+1
XREPEAT
XEND
 XROUTINE RETURN
PST(COMM. "WOR H")
VWINDO(0,0,1023,1023)
SWINDO(0,0,1023,1023)
ERASE
POSN=0

XCYCLE I=1,1,PIC NO
XIF TEK=4027 %THEN XSTART
PST(COMM. 'COL C', ITOS(COLOUR(I)))
XFINISH
INSTAN(I,128,0,0,0)
XREPEAT
XCOMMENT REDRAW PICTURE WITH SPECIFIED COLOUR INFORMATION
XEND
 XROUTINE FREEZE

XINTEGER I
XSTRING(25) FIL
XSTRING(25) FILE
FILE="FILE"
XIF TEK=4027 %THEN XSTART
PROMPT('Tekfile: ')
READ FILE NAME(FILE)
SNAPSHOT(FILE)
XRETURN
XFINISH
XIF TEK=4027 %THEN XSTART
J3=J3+1
ERASE
XCYCLE I=1,1,PIC NO
PET(COMM. "MON H")
XCOMMENT PLOT OUT SERIES OF OVERPLOTS FOR EACH COLOUR PLOT
XCOMMENT EACH FREEZE CALL OPENS ST 10 AN CREATES OR ADDS TO A COMMON
XCOMMENT FILE WHICH CREATES A GP FILE OVERPLOTTING FOR UP TO FOUR CO
XCOMMENT SUBSEQUENT CALLS OF FREEZE ADD TO THIS FILE CREATING A NEW
XCOMMENT GP FILE IN THE FOUR COLOURS. ON EXIT FROM THE PROGRAM
XCOMMENT VIA STOP MENU ITEM THIS FILE IS EXECUTED. LOOK IN FILE PLOT.

SELECTOUTPUT(10)
MYPRINTSTRING(' 'CREATEGPFILE
FILE1
')
XCOMMENTTENKFILENAME

XIF J3=1 XTHEN MYPRINTSTRING('PLOT1
')
XCOMMENT PLOTTER FILE NAMES EACH CALL OF FREEZE GIVES A NEW ONE
XIF J3=2 XTHEN MYPRINTSTRING('PLOT2
')
XIF J3=3 XTHEN MYPRINTSTRING('PLOT3
')
XIF J3=4 XTHEN MYPRINTSTRING('PLOT4
')
XIF J3=5 XTHEN MYPRINTSTRING('PLOT5
')
XIF J3=6 XTHEN MYPRINTSTRING('PLOT6
')
XIF J3=7 XTHEN MYPRINTSTRING('PLOT7
')
XIF J3=8 XTHEN %START
SELECTOUTPUT(0)
MYPRINTSTRING('TOO MANY FREEZES')

XRETURN
XFINISH
XCOMMENT DELIVERY INFO SIZE(CM), PEN COLOUR (BLACK) AND NO DASHING
MYPRINTSTRING('MOLCOLEURAL BEAMS, J. C. M. B.
50
1
')
1=1
XIF I<PIC NO XTHEN %START
XCYCLE I=2, 1, PIC NO

XIF COLOUR(I)<7 XTHEN %START
XCOMMENTS OVERPLOYS IN DIFFERENT PEn COLOURS
MYPRINTSTRING('Y')

XIF I=2 XTHEN MYPRINTSTRING('FILE2')
XIF I=3 XTHEN MYPRINTSTRING('FILE3')

B.8
VIF

T'T-;EN 	 :ETAT

_•i: iLJ'jV

_J V/' COLOUR FOR 1c;:.

SELECTOUTPUT(10)

IN 1911

I)z3 WHEN HYPRINTSTRW 9  W I

F COLOUR 	 I

=1 	 :THEN 	 icrriRiNtS FINO 11

2

IF ':O CURI)=2 WHEN MYPRINTSIPING W 3

%IF COLOUR 	 I

=3

WHEN MYPRINTSTRINO 4

MYPRINTSTRING(W.

%IF 	 I(FIC 	 NO ::T-E}

IFRI

TETRIN0

!REP

EAT

FINIS}-i

NEWLINE

ELECTOUTPUT(0)

FIrUIBH

OUTINE FEj-

LONOREALAFRAY X41:100,1:100)

WEAL

___,

01 W 03, CONLEV, SENS, GFAAN

%INTEGER I J

FROnPT 'FLECTN 5E='fl

FED S4S)

PROMPT CONE.

REAWCONLEV)

;y: -pi

PEAD U_.;1

ULI=ULI -1."L0

OLEV=CO_EV/ tO

FIC C=iC: N+1

:F

;c ::o:

B.9
$\text{IF } D = u \times T \text{ THEN } X = 0.0$

$\times \text{REPEAT}

\text{XCYCLE } I = 3, 1, M-2

\text{XCYCLE } J = 2, 1, N-1

$\times \text{IF } A(I, J) > (1 + \text{GRAIN}) \times A(I, J+1) \text{ XAND } A(I, J) > (1 + \text{GRAIN}) \times A(I, J-1) \times \text{AND } C A(I, J) : \text{CONLEY} \times \text{SUM} \text{ XAND } U \times \text{ULIM} \times \text{SUM} : A(I, J) \times \text{THEN } X \times \text{START}$

$\times (I, J) = 100.01

\times (I+1, J) = 60.0 \times X(I+1, J)

\times (I+2, J) = 40.0 \times X(I+2, J)

\times (I-2, J) = 40 + X(I-2, J)

\times (I-1, J) = 60.0 \times X(I-1, J)

\times X \times \text{FINISH}

\times \text{REPEAT}

\times \text{REPEAT}

\text{FRACTO N TO SHOW POINTS OF ONFLE C TION}

$\times \text{XCYCLE } I = 3, 1, M-2

\times \text{XCYCLE } J = 2, 1, N-2

\times G1 = A(I, J) - A(I, J-1)

\times G2 = A(I, J+1) - A(I, J)

\times G3 = A(I, J-1) - A(I, J-1)

$\times \text{IF } G1 < 0 \times \text{XAND } G2 = 0 \times \text{XAND } G1 > (1 + \text{SENS}) \times G2 \times \text{XAND } G3 > (1 + \text{SENS}) \times G3 \times G2 \times A(I, J) : \text{CONLEY} \times \text{SUM} \times \text{XAND } U \times \text{ULIM} \times \text{SUM} : A(I, J) \times \text{THEN } X \times \text{START}$

$\times (I, J) = 100.01 \times X(I, J)$

$\times (I+1, J) = 60.1

\times (I-1, J) = 60.1 + X(I-1, J)

\times \text{FINISH}

$\times \text{REPEAT}

\times \text{REPEAT}

\text{TCO NTOUR } (X, M, N, 100, 0, \text{TRANSFORM})

\text{PST } \text{(COMM. "WDR H"})

\text{ENDS UB}

\text{MOVEA } (0.0)

$\times \text{IF } \text{TEK} = 4027 \times \text{THEN } X \times \text{START}

\times \text{PST } \text{(COMM. "MON H"})

\times \text{PROMPT } \text{"COLOUR } \text{NO=}"

\times \text{READ(COL)}

\times \text{COLOUR(PIC NO)} = \text{COL}

\times \text{PST } \text{(COMM. "COL C", ITOS(COL})

\times \text{PST } \text{(COMM. "WDR H"})

\times \text{FINISH}

\times \text{INSTANX(PIC NO, 128, 0, 0, 0)}

\times \text{XEND}

\times \text{XEND: } \text{! OF BLOCK}

\times \text{ROUTINE READ FILE NAME(XSTRINGNAME FILE)}

\times \text{INTEGER I}

\times \text{FILE = ’’}

\times \text{SKIP SYMBOL XWHILE NEXT SYMBOL = ’‘’ XOR NEXT SYMBOL = ’ ’ XC}

\text{B.10}
XCYLE
   READ SYMBOL(I)
   FILE = FILE, TO STRING(I)
   \%EXIT XIF NEXT SYMBOL = NL XOR NEXT SYMBOL = ""
\%REPEAT
   SKIP SYMBOL \%WHILE NEXT SYMBOL & NL
   SKIP SYMBOL
   POSN=POSN+1
\%END
\%ENDOFFPROGRAM

040615 INTCN3 14K LISTED T15 LP15
FILE 'SFRG3'
XREAL NAME XL
XBEGIN

XEXTERNAL LONGREAL FNSPEC HYPTAN(XLONGREAL X)
XREAL EPS1, EPS2, EPS3, SIG1, SIG2, SIG3, E12, E13, H12, H23
XREAL B, R1K, RELVEL, POL, RCDUM, R13, R13D, R13X, R23, R23D, CH1, SIGMA
XREAL GA1, GA2, GA3, GA4, GA5, GA6, GA7, GA8, GA9, GA10, GA11
XREAL MU, MU1, VO, ROC, DCH, PI, BETA, KIP, AL, AL1, D, RCH
XREAL DFP1, DFP2, DFP3, DFP4
XREAL GDFP1, GDFP2, GDFP3, GDFP4
XREAL EL1, EL2, EL3, EL4
XREAL DENT, TF, TVDI, DT, ACC, DROH, P1, P2, SP, NORSO, PS, ROC1, ACCMOD
XREAL DION, BETAION, BETAGSN
XREAL &SRP, IRP
XREAL L1, L2, L3, L4
XREAL H12T, H23T
XREAL DH, RH, ALP
XINTEGER PATH, I, J, K, FLAG1, CHNO
XRoutinesespec output(XREALNAME B, DFP, EL, SIGMA, RCH %INTEGER PATH)
XEXTERNAL ROUTINESPEC PROMPT(STRING(255) S)
XEXTERNAL ROUTINESPEC CAMNAMF(XREAL X)
XREALFNSPEC MTCR(XREALNAME R1, B, R2, RSTART %INTEGER PATH)
XREALFNSPEC MORSION(XREALNAME R)
XREALFNSPEC MORSPO(XREALNAME R, AL)
XREALFNSPEC CROSPT(XREALNAME E, EPS1, SIG1, EPS2, SIG2, XREALFN %C
PO1, POT2, %INTEGER FLAGS)
XREALFNSPEC LANZIE%REALNAME B, %INTEGER PATH)
XREALFNSPEC IONPO%REALNAME E, SIG, EPS)
XREALFNSPEC POWPO%REALNAME R, SIG, EPS)
XREALFNSPEC DEFO%REAL B)
XREALFNSPEC DFPow(XREAL EPS, SIG, B)
XREALFNSPEC DDEFION%REAL B)
XREALFNSPEC DDEFPO%REAL EPS, SIG, B)
PI=3. 14159
SF=SQRT(P1)
L16:
PROMPT("EPS1: ")
READ(EPS1)
PROMPT("EPS2: ")
READ(EPS2)
PROMPT("EPS3: ")
READ(EPS3)
PROMPT("SIG1: ")
READ(SIG1)
PROMPT("SIG2: ")
READ(SIG2)
PROMPT("SIG3: ")
READ(SIG3)
PROMPT("E12: ")
KIP=4. 3
PROMPT("E12: ")
READ(E12)
PROMPT("ION REP POW: ")
1. REMEMBER TO CHANGE GAMMA FNS
  GA1=GAMMAFN((GSRP+1)/2)
  GA2=GAMMAFN(GSRP/2+1)
  GA3=GAMMAFN(3.5)
  GA4=GAMMAFN(4)
  GA5=GAMMAFN(2.5)
  GA6=GAMMAFN(3)
  GA7=GAMMAFN(1)
  GA8=GAMMAFN(1.5)
  GA9=GAMMAFN((IRP+1)/2)
  GA10=GAMMAFN(IRP/2+1)

PROMPT("RED MASS: ")
READ(MU)
MU=MU*1.67252-27
PROMPT("RIKE: ")
READ(RIKE)

RELVEL=2*RIKE*1.60212-19/MU
RELVEL=SQRT(RELVEL)

PRINTSTRING("NOW PARAMETERS RELEVANT TO TARGET MOLECULE POTENTIAL")
NEWLINE
PROMPT("RED MASS: ")
READ(MU1)
MU1=MU1*1.67252-27
PROMPT("RO: ")
READ(ROCH)
ROCH=ROCH*10-10
ROCH1=ROCH
PROMPT("ROCHSSN: ")
READ(ROCH)
ROCH=ROCH*10-10
PROMPT("VO: ")
READ(VO)
PROMPT("DO: ")
READ(DCH)

IF DCH:10-10 THEN DCH=DCH*1.60212-19
PRINTSTRING("PO TENTIAL MODIFIERS")
NEWLINE
PROMPT("DION: ")
READ(DION)

IF DION:10-10 THEN DION=DION*1.60212-19
PROMPT("BETAMOD GSN: ")
READ(BETAGSN)

IF BETAGSN<1.5 THEN BETAGSN=BETAGSN*10
PROMPT("BETAION: ")
READ(BETAION)

IF BETAION<1.5 THEN BETAION=BETAON*10
BETA=VO*SQRT(2*PI*PI*MU1/DCH)
PRINTSTRING("ASSYMPOTIC LIMITS")
NEWLINE
PROMPT("GSN A. L.: ")
READ(AL)
PROMPT("ION A. L.: ")
READ(AL1)

IF MOD(AL1):10-10 THEN AL1=AL1*1.60212-19
PROMPT("POL: ")
READ(POL)
POL=POL*14.394/2
ALP=1.80*1.610
DH=0.40*1.60212-19
START OF CALCULATION

L6:
PROMPT("IMPACT PARM: ")
READ(B)
XIF BC<50 XTHEN ->L16

XIF BC<50 XTHEN %START
SELECTOUTPUT(10)
H12=H12-0.05
XIF H12< 0.0 XTHEN %STOP
PRINT (H12, 3, 3)
SELECTOUTPUT(0)
->L6
XFINISH
XIF BC<0 XTHEN ->L15
PROMPT("WHICH CHANNEL: ")
READ(CHNO)
R13D=R13
R23D=R23
XIF CHNO=1 XTHEN %START
L9:
DFP1=DEFPOW(EPS1, SIG1, B)
EL1=0.000
GDFP1=MOD(GDEFPOW(EPS1, SIG1, B))
DFP1=MOD(DFP1)
PATH=1
RCH=RCH
R13D=R13
XIF B<R13 XTHEN SIGMA=LANZEN(B, PATH)*B/(GDFP1*SIGN(DFP1))
XIF B>R13 XTHEN SIGMA=B/(GDFP1*SIGN(DFP1))
REDUM=R13
OUTPUT(B, DFP1, EL1, SIGMA, RCH, PATH)
XIF DFP1*180/PID>9 XTHEN ->L6
B=B-0.05
->L9
XFINISH
XIF CHNO=2 XTHEN %START
L10:
XIF B>R13 XTHEN ->L6
VCI=0
D=DEFPW(EPS1, SIG1, R13) / 2 + DEFPW(EPS1, SIG1, R13D) / 2
D=DEFPW(EPS1, SIG1, R13) / 2 - DEFPW(EPS2, SIG2, R23D) / 2
D=MOD(DFP3)
GDFP3=DEFPW(EPS1, SIG1, B) - GDFP(EPS1, SIG1, R13) / 2
GDFP3=DEFPW(EPS1, SIG1, R13) / 2 - DEFPW(EPS2, SIG2, R23D) / 2
GDFP3=MOD(GDFP3)
PATH=3
R13D=R13
SIGMA=L1+L2*B/(DFP2*G1N(DFP2))
OUTPUT(B, DFP2, EL2, SIGMA, RCH, PATH)
\%IF DFP2*180/P1>9 \THEN \-\L6
\-\L10
\%FINISH
\%IF CHNO=3 \THEN \%START
L11:
VCI=0
D=KIP-(MORSOT(RCH, AL)-MORSION(RCH))-E12
D=D-(MORSOT(RCH, AL)-MORSO)
RCDUM=CROSPT(D, EPS3, SIG3, EPS1, SIG1, IGMPOT, POWPOT, FLG1)
R13D=R13
L2:
\%IF RCDUM-R13D<0.025*R13D \THEN \%START
D=MTCR(R13D, B, RCDUM, RCH, 3)
R13D=RCDUM
D=KIP-(MORSOT(RCH, AL)-MORSION(RCH))-E12
D=D-(MORSOT(RCH, AL)-MORSO)
RCDUM=CROSPT(D, EPS3, SIG3, EPS1, SIG1, IGMPOT, POWPOT, FLG1)
-\L2
\%FINISH
EL2=DEMT+E12+MORSOT(RCH, AL)-MORSO
DFP3=DEFPW(EPS1, SIG1, B) - DEFPW(EPS1, SIG1, R13) / 2
DFP3=DEFPW(EPS1, SIG1, R13) / 2 - DEFPW(EPS2, SIG2, R23D) / 2
DFP3=MOD(DFP3)
GDFP3=DEFPW(EPS1, SIG1, B) - GDFP(EPS1, SIG1, R13) / 2
GDFP3=DEFPW(EPS1, SIG1, R13) / 2 - DEFPW(EPS2, SIG2, R23D) / 2
GDFP3=MOD(GDFP3)
PATH=3
R13D=R13
SIGMA=LANZEN(B, PATH)*B/(GDFP3*G1N(DFP3))
IF DFP4+150/P1=9 THEN -3L6
E=9-0.05
-3L11
XFINISH

L12:
VCI=0
DENT=MTCR(R13, B, R13, RCH, 2)
D=KIP-(MORSPO(RCH, AL)-MORSION(RCH))
D=D-(MORSPO(RCH, AL)-MORSO)
FLAG1=1
RDUM=CROSPT(D, EPS3, SIG3, EPS1, SIG1, IONPOT, POWPOT, FLAG1)
R13D=R13
PATH=2
L21=SGRT(LANZEN(B, PATH))
L21:
XIF RDUM-R13D<0.005&R13D THEN %START
DENT=MTCR(R13D, B, RDUM, RCH, 3)
D=KIP-(MORSPO(RCH, AL)-MORSION(RCH))
D=D-(MORSPO(RCH, AL)-MORSO)
FLAG1=1
R13D=RDUM
RDUM=CROSPT(D, EPS3, SIG3, EPS1, SIG1, IONPOT, POWPOT, FLAG1)
-3L21
XFINISH
PATH=1
L22=SGRT(LANZEN(B, PATH))
PATH=2
L23=SGRT(LANZEN(B, PATH))
VCI=0
DENT=MTCR(R13, B, R23, RCH, 4)
D=KIP-(MORSPO(RCH, AL)-MORSION(RCH))
D=D-E12-(MORSPO(RCH, AL)-MORSO)
FLAG1=1
RDUM=CROSPT(D, EPS3, SIG3, EPS1, SIG1, IONPOT, POWPOT, FLAG1)
R23D=R23
L3:
XIF RDUM-R23D<0.025&R23D THEN %START
DENT=MTCR(R23D, B, RDUM, RCH, 3)
R23D=RDUM
D=KIP-(MORSPO(RCH, AL)-MORSION(RCH))
D=D-E12-(MORSPO(RCH, AL)-MORSO)
RDUM=CROSPT(D, EPS3, SIG3, EPS1, SIG1, IONPOT, POWPOT, FLAG1)
-3L3
XFINISH
EL4=DEMT+E12+MORSPO(RCH, AL)-MORSO
DFP4=DEFPOW(EPS1, SIG1, R13)/2
DFP4=DFP4+DEFION(B)-DEFION(R13)/2-DEFION(R23D)/2
DFP4=MOD(DFP4+DEFPOW(EPS2, SIG2, R23D)/2)
GDFP4=GDEFPOW(EPS1, SIG1, R13)/2
GDFP4=GDFP4+GDEFP4+GDEFPION(B)-GDEFPION(R13)/2-GDEFPION(R23D)/2
GDFP4=MOD(GDFP4+GDEFP4(EPS2, SIG2, R23D)/2)
PATH=4
L24=LANZEN(B, PATH)/(L24=L24
SIGMA=L1+L24+L24+L24/(GDFP4*SIN(DFP4))
OUTPUT(B, DFP4, EL4, SIGMA, RCH, PATH)
XIF DFP4+150/P1=9 THEN -3L6
E=9-0.05
-3L12
XFINISH

! 
-3L6
XIF LG13 XTHEN XRRESULT=-999
XIF PATH=2 XTHEN XSTART
TF=(SORT(R1+R1-R+B+B)*10-10)/RELVEL
XFINISH
XIF PATH=3 XOR PATH=5 XTHEN XSTART
! CROSSING TO IONIC CURVE ON WAY OUT
TF=(SORT(R2+R2-R+B+B)*10-10-SORT(R1+R1-R+B+B)*10-10)/RELVEL
XFINISH
XIF PATH=4 XOR PATH=6 XTHEN XSTART
! CROSSING TO IONIC CURVE ON WAY IN
TF=(SORT(R1+R1-R+B+B)*10-10+SORT(R2+R2-R+B+B)*10-10)/RELVEL
XFINISH
T=0
RCH1=RSTART
! EQUILIBRIUM SF5-F BOND DISTANCE
DT=TF/1000
! STEP LENGTH FOR CALCULATION OF INCREASE IN SF5-F BOND
L30:
 ACC=2*BETAION*DION*(EXP(-BETAION*(RCH1-ROCH1)))*XC
-EXP(-2*BETAION*(RCH1-ROCH1)) - XC
2*DH=ALP*K(1-HYPTAN(ALP*RCH1-1.010*NH)*XC)
HYPTAN(ALP*RCH1-1.010*NH)) =HYPTAN(ALP*RCH1-1.010*NH)
ACC=-ACC/MU1
DRCH=VC1+DT+0.5*ACC+DT+DT
VC1=VC1+ACC+DT
RCH1=RCH1+DRCH
T=T+DT
XIF T<=TF XTHEN ->L30
! MOTION DOWN (SF5)- CURVE FINISHED
! NOW CALCULATE CHANGE IN X+/SF6- CURVE
RCH=RCH1
P1=MORSION(RCH)
P2=MORSION(RCH)
XRRESULT=P1-P2
XEND
XREALFN IONPOT(%REALNAME R,SIG,EPS)
XRRESULT=EPS*EXP((LOG(SIG)-LOG(R))*1RP)-14.394/R
XEND
XREALFN POWPOT(%REALNAME R,SIG,EPS)
XRRESULT=EPS*EXP((LOG(SIG)-LOG(R))*GSRP)
XEND
XREALFN CROSPOT(%REALNAME R,EPS1,SIG1,EPS2,SIG2,%REALFN POT1,POT2 %XINTEGER FLAGS)
  %SPEC POT1(%REALNAME R,SIG,EPS)
  %SPEC POT2(%REALNAME R,SIG,EPS)
XREAL R,V1,V2,W1,W2,0,X,Y,EE,HH
XINTEGER FLAG
! THIS FUNCTION EVALUATES THE CROSSING RADII FOR THE
! THREE NEUTRAL CURVES AND THE IONIC CURVE,
FLAG = 0
HH = 05
XIF ECO XTHEN XSTART
EE = -E/14.394
W1 = 0, W2 = 1
R = 2
->L1
XFINISH
EE = E/14.394
W1 = 0, W2 = 1
XIF FLAGS = 1 XTHEN R = 3.6
XIF FLAGS = 2 XTHEN R = 4.2
L1:  V1 = EE+POT1(R,SIG1,EPS1)/14.394
! This routine calculates the probability of exiting via a given path. \( \text{H12}, \text{H23} \) are reduced coupling parameters.

! (Units are 10**6 cm/s)

\( \text{IF BC=RI3 THEN} \%\text{START} \)

\( \text{P1}=1 \)
\( \text{P2}=0 \)

\( \text{IF} \) \%L1

\( \text{NO CHANCE OF INELASTIC BEHAVIOUR} \)

\%FINISH

\( \text{H12T=H12*(R13/R13D)} \)
\( \text{H23T=H23*(R23/R23D)} \)

\( \text{VR1}=\text{RELVEL+16-4*SGRT}((1-B+B) /(R13D*R13D)) \)
\( \text{P1}=\text{EXP}(-\text{H12T}/\text{VR1}) \)
\( \text{VR2}=16-4*\text{RELVEL+SGRT}((1-B+B) /(R23D*R23D)) \)
\( \text{P2}=\text{EXP}(-\text{H23T}/\text{VR2}) \)
L1:
%IF PATH=2 THEN %RESULT=(1-P1)*(1-P1)
%IF PATH=1 THEN %RESULT=P1*P1
%IF PATH=3 THEN %RESULT=P1*(1-P1)*(1-P2)
%IF PATH=4 THEN %RESULT=(1-P1)*P1*(1-P2)
%END
%REALFN DEFION(%REAL B)
%REAL X, Y, Z
! THIS FUNCTION EVALUATES THE CONTRIBUTION TO THE DEFLECTION
! FUNCTION FROM THE IONIC K+/SF-A- CURVE
X=IRP*EPSO*EXP(LOG(SIG3)*IRP)*SP*(GA10/GA11)
Y=X/(2*RIKE*EXP(LOG(B)*IRP))
Z=-14.364*SP*(GA7/GA8)/(2*RIKE*B)
%RESULT=X+Y+Z
%END
%REALFN MORSION(%REALNAME R)
%RESULT=(DION*(1-EXP(-BETAION*(R-ROCH)))*2+ %C
D1*(1-(HYPTAN(ALP+R-1.0*RH)*2)+AL1-DION)/1.60212-19
%END
%REALFN MORSION(%REALNAME R, AL)
%REAL V, RI
RI=R
! SI UNITS
! V=DCH*(1-EXP(-BETASN*(R1-ROCH)))**2-DCH
%RESULT=(V*AL)/1.60212-19
%END
%ROUTINE OUTPUT(%REALNAME B, DFP, EL, SIGMA, RCH %INTEGER PATH)
%REAL DFPD
SELECTOUTPUT(10)
WRITE(PATH, 2)
SPACE
PRINT(B, 5, 3)
SPACE
DFPD=DFP*180/PI
PRINT(DFPD, 4, 2)
SPACE
PRINT(EL, 3, 2)
SPACE
PRINTFL(SIGMA*DFP*DFP, 2)
SPACE
PRINT(RCH1@10, 5, 3)
SPACE
PRINTFL(RCDUM, 3)
NEWLINE
SELECTOUTPUT(0)
%END
%ENDDFFPROGRAM
FILE 'FINAL'

DOUBLE PRECISION MA, MB, MC, DAB, DAC, DBC, R01, R02
DOUBLE PRECISION ZA, A1, B1, BETAB, ETAAC, BETABC, RO3
DOUBLE PRECISION RMUAB, RMUAC, RMUBC, MTOT, MAB, MAC, MBC
COMMON/BLKD1/ MA, MB, MC, DAB, DAC, DBC, R01, R02, RO3
COMMON/BlKD3/ ETAAB, ETAAC, BETABC, DAB, DAC, DBC, R01, R02, RO3
COMMON/POTPAR/ A, B, A1, B1
COMMON/BLKD3/ TRED

DATA MA, MB, MC
/ 39. 000, 126. 900, 15. 000 /
DATA TRED/ 1. 0014/
DATA ETAAB, ETAAC, BETABC
/ .0. 6660, 4. 2700, .0. 93000 /
DATA DAB, DAC, DBC
/ .3. 2900, 4. 34000, 2. 34000 /
DATA A, B/ .0. 661200, .0. 27100 /
DATA A1, B1/ .0. 661200, .0. 27100 /
DATA R01, R02, R03
/
E N D

C FILE=UPPERV DATE=7/2/80
C PURPOSE--TO RUN BATCH TRAJECTORIES FOR DIFFERENT REACTANT
C VIBRATIONAL ENERGIES. V=0 STARTING CONDITIONS ARE TAKEN FROM
C GAUSSIAN DISTN. GOSDDF, WHICH MIMICS ZERO-POINT LEVEL.
C V=0, 1, 2, 3 STARTING CONDITIONS ARE GENERATED BY SETTING R(BC)
C EQUAL TO PEAKS IN WAVE-FN. PROBABILITY DISTN. WITH A
C PROBABILITY GIVEN BY THE APPROX. AREA UNDER THAT HUMP. THE
C PROBABILITY HERE IS NORMALISED TO UNITY & THE UNIFORM
C R. N. GENERATOR, GOSCAF, IS USED TO OBTAIN THIS.
C THE PHASE OF THE (HARMONIC) VELOC. OF B WRT C IS GENERATED
C BY GOSDDF, BEING + IF R. N.:0. 00. 00 & - OTHERWISE
C PROGRAM TRAJIC
DOUBLE PRECISION PRMT, CDOT, A, B, Y, XX, GOSCAF, GOSDDF
COMMON/BLKD9/ BB
COMMON/POTPAR/ A, B, A1, B1
DIMENSION P(4), Q(4), PFI(4), QFI(4), PRMT(5), CDOT(8)
READ(5, *) IBATCH, B, E, IV, MJ
WRITE(4) IBATCH, B, E, IV, MJ
WRITE(6, 602) E, IBATCH, B, IV, MJ
C GENERATE NEW SEQUENCE OF 'RANDOM' NOS. FOR EACH BATCH
INEG=1
IF (IBATCH. GT. 5) INEG=6
IF (IBATCH. EQ. INEG) GOTO 2
IFIN=(IBATCH-INEG)*100
DO 3 N=1, IFIN
3 Y=GOSCAF(XX)
ISUM22=(IBATCH-INEG)*200
DO 4 M=1, ISUM22
4 Y=GOSDDF(0. 000, 1. 000)
2 CONTINUE
DO 1 LOOP=1, 100
IF (LOOP. EQ. 1) BB=4. 9
IF (LOOP. GT. 1) BB=4. 9
IF (LOOP. GT. 5) BB=5. 0
IF 

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
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<tr>
<td>0.1</td>
<td>XXXX</td>
</tr>
<tr>
<td>0.2</td>
<td>XXXX</td>
</tr>
<tr>
<td>0.3</td>
<td>XXXX</td>
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<tr>
<td>0.4</td>
<td>XXXX</td>
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<tr>
<td>0.5</td>
<td>XXXX</td>
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<tr>
<td>0.6</td>
<td>XXXX</td>
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<tr>
<td>0.7</td>
<td>XXXX</td>
</tr>
<tr>
<td>0.8</td>
<td>XXXX</td>
</tr>
</tbody>
</table>

CALL START (P, Q, PRMT, CDOT, LOOP, E, IV, MJ)
WRITE(4) LOOP, BB
WRITE(6, 600) LOOP, BB
CALL SOLVE (P, Q, PRMT, CDOT)
CONTINUE

C FORMATS...

600 FORMAT('1', 75X, 'TRAJECTORY NO. ', 14/'0', 50X, 'IMPACT PARAM. ', F5.1)
602 FORMAT('1', 100/),/* 

&' 2D TRAJECTORIES--E=', F7.2, 'EV */
&' POTENTIAL PARAMETERS : */
&' BAHCH NO. ', 13, 15X, '*' /
&' A=', 15X, ' 1.00', 8X, '*'/
&' B=', 15X, 'F5.2', 7X, '*'/
&' MJ LEVEL ', 12, 14X, '*'/
&' MJ STATE ', 12, 17X, '*'/
&' STOP

SUBROUTINE CONTROL(T, C, CDOT, IHNF, NDIM, PRMT)

* PURPOSE -
* CONTROLS INTEGRATION AND DETERMINES FINISHING POINT

DOUBLE PRECISION PRMT, C, CDOT, T, HAM, DELHAM, POTNOT, RMIN, TF
DOUBLE PRECISION DELAM, AMNOT, S, SS, AM, RAB, RAC, RBC, PROD
DOUBLE PRECISION POT, Z
DIMENSION PRMT(5), C(8), CDOT(8), STORE(8), 101
DIMENSION P(4), G(4), PFI(4), GFI(4)
COMMON/BLK11/TF
COMMON/BLK14/2, SS
COMMON/BLK18/FT
COMMON/BLK22/IZ
COMMON/BLK40/IFLAG
COMMON/BLK45/IMARK, IHA
COMMON/BLK51/ISO
IFLAG=0
IMER=0
IF (IHA, EQ. 1) IMER=1
ISO=0
IF (IHNF, GT. 9) ISO=1
CALL HAM/NOT(C, HAM, POT, AM)
IFLAG=1
RBC=DSQRT(C(3)*C(3)+C(4)*C(4))
RAB=DSQRT((C(1)+S*C(3))*S+C(2)+S*C(4))*S
I MARK = 0
H: NOT = HAM
AM NOT = AM
IF (IHER. EQ. 1) GOTO 1
POT NOT = POT
RBC NOT = SNSL (RBC)
RAB Not = SNSL (RAB)
RAC NOT = SNSL (RAC)
TF = PRMT (2) / 100
L = 1
DO 2 K = 1, 101
STORE(1, K) = 0. 0
STORE(2, K) = 0. 0
STORE(3, K) = 0. 0
STORE(4, K) = 0. 0
STORE(5, K) = 20. 0
STORE(6, K) = 20. 0
STORE(7, K) = 20. 0
STORE(8, K) = 0. 0
2 CONTINUE
1 CONTINUE
IF (T. LT. (L-1) + TF) GOTO 3
STORE(1, L) = T
STORE(2, L) = HAM
STORE(3, L) = POT
STORE(4, L) = AM
STORE(5, L) = RAB
STORE(6, L) = RAC
STORE(7, L) = RBC
STORE(8, L) = IZ
L = L + 1
3 CONTINUE
C TIME HISTORY OF TRAJECTORY NOW COMPUTED
   DELHAM = DABS (HAM-HAM NOT)
   DELAM = DABS (AM-AM NOT)
C MONITOR CONSERVATION OF ENERGY & ANGULAR MOMENTUM
   IF (DELHAM. GT. 1. 0D-3) IHMARK = 1
   IF (DELHAM. GT. 1. 0D-2) IHMARK = 1
   IF (DELAM. GT. 1. 0D-3) IAMARK = 1
   IF (DELAM. GT. 1. 0D-2) IAMARK = 1
   IF (IHER. EQ. 2) PRMT (5) = 1. 0D0
   IF (T. LT. (PRMT (2) / 5)) GOTO 5
C EARLY STOP CONDITION CODE SET
   IF (RBC. GT. 3B. 0D0) PRMT (5) = 2. 0D0
   IF (RAB. GT. 3B. 0D0) PRMT (5) = 3. 0D0
   IF (RAC. GT. 3B. 0D0) PRMT (5) = 4. 0D0
5 CONTINUE
   FT = T
   RETURN
ENTRY TRANSF (IPROD. SHAM)
SHAM = SNSL (HAM)
WRITE(4) T, IHFL, IHMARK, IAMARK, PRMT (5)
WRITE(6, 500) T, IHFL, IHMARK, IAMARK, PRMT (5)
WRITE(6, 601) HAM NOT, HAM, POT NOT, POT, AM NOT, AM
WRITE(6, 602) RAB NOT, RAB, RAC NOT, RAC, RBC NOT, RBC
C NATURE OF SCATTERING PROCESS DETERMINED
   PROD = RMIN (RAB, RAC, RBC)
   IF (PROD. EQ. RAB) IPROD = 1
   IF (PROD. EQ. RAC) IPROD = 2
   IF (PROD. EQ. RBC) IPROD = 3
   IF (RAB. GT. 10. 0. AND. RAC. GT. 10. 0. AND. RBC. GT. 9. 0) IPROD = 4
RETURN
CGRAPH. IF LONG-LIVED
IF (T.LT.(FRMT(2)+0.1DO)) GOTO 6
CALL AXES
WRITE(6,604)
WRITE(6,603)((STORE(I,J),I=1,7),J=1,101,2)
DO 4 I=5,7
M=1-3
DO 4 J=1,101
IF (STORE(I,J).EQ.2) M=I+1
IF (STORE(I,J).EQ.3) M=I+4
IF (STORE(I,J).EQ.4) M=I+7
4 CALL PLOTM,STORE(I,J),J)
CALL GRAPH
6 CONTINUE
RETURN
C FORMATS.
600 FORMAT('O',25X,'TIME AT END ',F6.1/
&'FINAL HALVING STATE',I2/
&'OH CONS MARKER',I2,'OAM CONS MARKER',I2/
&'GEND CODE',F4.1)
601 FORMAT('O',20X,'INITIAL',4X,'FINAL'/
&'HAMILTONIAN',9X,F8.4,4X,F8.4/
&'POTENTIAL',11X,F8.4,4X,F8.4/
&'C.MOM.'11X,F13.6,4X,F13.6)
602 FORMAT('OR(AB)',15X,F6.2,6X,F6.2/
&'OR(AC)',15X,F6.2,6X,F6.2/
&'OR(BC)',15X,F6.2,6X,F6.2)
603 FORMAT('OCALLS TO POTFUN',16/'OCALLS TO G05DDF',16)
604 FORMAT('1',6X,'TIME',12X,'HAM',13X,'POTL',10X,
&'ANG.MOM',10X,'RAB',13X,'RAC',13X,'RBC'/O)
605 FORMAT(51',5X,F6.1,5X,F9.5,7X,F9.5,7X,F9.4,3X,
&F6.2,10X,F6.2,10X,F6.2/))
END
SUBROUTINE GRAPH

* PURPOSE -
* GRAPHS R,R1,R2,R3, AGAINST TIME
*

DOUBLE PRECISION TF,TRED
COMMON/BLK11/TF
COMMON/BLK35/TRED.
LOGICAL*1 A(115,55),MIN/-/,EYE/'I'/,PLUS/'+',BLA/'/
LOGICAL*1 DIGIT(10)/'1','2','3','4','5','6','7','8','9','0'/
LOGICAL*1 SYMBOL(14)'/G', 'C', 'B', 'A', 'F',
&'C', '-', '+', '?', '?', '?', '?', '?', '?', '?', '?
DIMENSION TIME(5)
GO TO 4
ENTRY AXES
DO 1 I=1,115
DO 1 J=1,55
1 A(I,J)=BLA
DO 2 I=1,115
2 A(I,51)=MIN
DO 3 I=1,55
3 A(10,1)=EYE
DO 7 I=6,51,15
7 A(10,1)=PLUS
DO 8 I=10,110,20
8 A(I,51)=PLUS
A(7,6)=DIGIT(1)
A(5,6)=DIGIT(5)

D.4
ENTRY PLOT(IC,Y,IX)
IX=IX+9
IY=51-INT(3,0*Y+0.5)
IF (IC.LT.1.0 OR IC.GT.14) IC=5
IF (IX.LE.0. OR IX.GE.116. OR IY.LE.0. OR IY.GE.56) RETURN
A(IX, IY)=SYMBOL(IC)
RETURN

WRITE (6,5) ((A(I,J),I=1,115),J=1,55)
FORMAT('1',51(115A1/1X),115A1)
DO 5 J=1,5
TIME(J)=TF*J*20.0E14/TRED
CONTINUE
WRITE (6,9) TIME
FORMAT(8X,'O 1',11X,G11.4,4(9X,G11.4))
WRITE (6,10) ((A(I,J),I=1,115),J=54,55)
FORMAT (1X,115A1/1X,115A1)
WRITE (6,11)
FORMAT ('OY-VALUES IN ATOMIC UNITS X-VALUES IN SECONDS. IC**14'
*O(AB)=R C (AC)=R B (BC)=A'/O')
RETURN

SUBROUTINE SWOD(Y,FCT,OUTP,PRMT,DERY)

INTEGRATION ROUTINE-

THIS IS AN EARLY VERSION OF THE IBM

SSP111 SUBROUTINE DHPCG & DETAILS OF IT CAN BE FOUND IN

THAT AUGUST PUBLICATION.

DIMENSION PRMT(5),Y(3),DERY(3),AUX(16,8)
DOUBLE PRECISION Y,DERY,PRMT,X,HE,DEL,DABS
WRITE(6,237) PRMT(5)

237 FORMAT( ' ', 'STWOD', ' ', PRMT(5)=',F6.3)
N=1
NDIM=8
IHFL=0
X=PRMT(1)
H=PRMT(3)
PRMT(5)=0. DO
DO 1 I=1,NDIM
AUX(I,1)=0. DO
AUX(15,1)=0
1 AX(I,1)=Y(I)
IF (H*(PRMT(2)-X))3,2,4
2 IHFL=12
GOTO 4
3 IHFL=13
4 CALL FCT(X,Y,DERY,PRMT)
CALL OUTP(X,Y,DERY,IHFL,NDIM,PRMT)
IF (PRMT(5))6,5,6
5 IF (IHFL)7,7,6
RETURN
7 DO 3 I=1,NDIM
3 AUX(I,1)=DERY(I)
IHFL=1
GOTO 100
7 X=X+H
DO 10 I=1,NDIM
11 X=X+H
   CALL FCT(X, Y, DERY, PRMT)
   IF(PRMT(5)) & 227, 6
227 N=2
   DO 14 I=1, NDIM
   AUX(2, I)=Y(I)
14 AUX(9, I)=DERY(I)
   ISW=3
   GOTO 100
15 DELT=0. DO
   DO 16 I=1, NDIM
   DELT=DELT+AUX(15, I)-DABS(Y(I)-AUX(4, I))
   DELT=0.66666666666667D0*DELT
   IF(DELT-PRMT(4)) & 19, 19, 17
16 IF(IHLF-10)11, 18, 18
18 IHLF=11
   X=X+H
   GOTO 4
19 X=X+H
   CALL FCT(X, Y, DERY, PRMT)
   IF(PRMT(5)) & 228, 6
228 DO 20 I=1, NDIM
   AUX(3, I)=Y(I)
20 AUX(10, I)=DERY(I)
   N=3
   ISW=4
   GOTO 100
21 N=1
   X=X+H
   CALL FCT(X, Y, DERY, PRMT)
   IF(PRMT(5)) & 229, 6
229 X=PRMT(1)
   DO 22 I=1, NDIM
   AUX(11, I)=DERY(I)
22 Y(I)=AUX(1, I)+H*(.375D0*AUX(8, I)+.791666666666667D0-AUX(4, I))
   1-.2083333333333333D0*AUX(10, I)+.0416666666666667D0*DERY(I))
23 X=X+H
   N=N+1
   CALL FCT(X, Y, DERY, PRMT)
   CALL OUTP(X, Y, DER, IHLF, NDIM, PRMT)
   IF(PRMT(5)) & 24, 6
24 IF(N-4)25, 200, 200
25 DO 26 I=1, NDIM
   AUX(N, I)=Y(I)
26 AUX(N+7, I)=DERY(I)
   IF(N-3)27, 29, 200
27 DO 28 I=1, NDIM
   DELT=AUX(9, I)+AUX(9, I)
   DELT=DELT+DELT
28 Y(I)=AUX(1, I)+.3333333333333333D0*H*(AUX(8, I)+DELT+AUX(10, I))
   GOTO 23
29 DO 30 I=1, NDIM
   DELT=AUX(9, I)+AUX(10, I)
   DELT=DELT+DELT+DELT
30 Y(I)=AUX(1, I)+.3375D0*H*(AUX(8, I)+DELT+AUX(11, I))
   GOTO 23
101 Y(1)=AUX(N, I) +. 4DCOZ
Z=Z+. 4DCO+H
CALL FCT(Z, Y, DERY, PRMT)
IF (PRMT(3)) 6, 230, 6
200 DO 102 I=1, NDIM
Z=Z+DERY(I)
AUX(I, I)=Z
102 Y(1)=AUX(N, I) +. 27697760924778359D0*AUX(5, I) +. 158739649710338350D0+Z
Z=X+. 4857372562187894D0+H
CALL FCT(Z, Y, DERY, PRMT)
IF (PRMT(3)) 6, 231, 6
231 DO 103 I=1, NDIM
Z=Z+DERY(I)
AUX(7, I)=Z
103 Y(1)=AUX(N, I) +. 2163003822392047D0*AUX(5, I) -3. 0509651486929308D0*
1AUX(6, I) +3. 8326476044701030D0+Z
Z=X+H
CALL FCT(Z, Y, DERY, PRMT)
IF (PRMT(3)) 6, 232, 6
232 DO 104 I=1, NDIM
104DY(I)=AUX(N, I) +. 17476023226269037D0*AUX(5, I) -. 55143066237873294D0*
1AUX(6, I) +1. 2055355937952355D0*AUX(7, I) +. 171184781219519030D0*
2X+DERY(I)
GOTO (9, 13, 15, 21), ISW
200 istep=3
201 IF (N-8) 204, 202, 204
202 DO 203 N=2, 7
DO 203 I=1, NDIM
AUX(N-1, I)=AUX(N, I)
203 AUX(N+6, I)=AUX(N+7, I)
N=7
204 N=N+1
DO 205 I=1, NDIM
AUX(N-1, I)=Y(I)
205 AUX(N+6, I)=DERY(I)
X=X+H
206 istep=1ISTEP+1
DO 207 I=1, NDIM
ODELT=AUX(N-4, I)+1. 33333333333333333D0+H*(AUX(N+6, I)+AUX(N+6, I) -
1AUX(N+5, I)+AUX(N+4, I)+AUX(N+4, I))
Y(I)=DELT-. 92561953471074380D0*AUX(16, I)
207 AUX(16, I)=DELT
CALL FCT(X, Y, DERY, PRMT)
IF (PRMT(5)) 6, 223, 6
233 DO 208 I=1, NDIM
ODELT=. 125D0*(9, DO*AUX(N-1, I)-AUX(N-3, I)+3. D0+H*(DERY(I)+AUX(N+6, I) 
1+AUX(N+6, I)-AUX(N+5, I)))
AUX(16, I)=AUX(16, I)-DELT
208 Y(I)=DELT-. 07436015525925620D0*AUX(16, I)
DELT=0. DO
209 DO 200 I=1, NDIM
209 DELET=DELT+AUX(15, I)+DABS(AUX(16, I))
IF (DELT-PRMT(4)) 210, 222, 222
210 CALL FCT(X, Y, DERY, PRMT)
CALL OUTP(X, Y, DERY, IHLP, NDIM, PRMT)
IF (PRMT(5)) 212, 211, 212
211 IF (IHLP-11) 213, 212, 212
212 RETURN
213 IF (H*(X-PRMT(2))) 214, 212, 212
214 IF (DABS(X-PRMT(2))-. 1D0*DABS(H)) 212, 215, 215
215 IF (DELT-. 0DE0+PRMT(4)) 215, 216, 201
216 IF (IHLP) 201, 201, 217
217 IF (N-7) 201, 218, 218
SUBROUTINE FOTFUN(T, C, CDOT, PRMT)

* * * PURPOSE - 
* * * EVALUATES DH/DG(I) AND DH/DP(I) DURING INTEGRATION 

IMPLICIT REAL*8 (A-H, L, M, O-Z) 
COMMON/BLK01/MA, MB, MC 
COMMON/BLK02/MMOL, M, MMOL, MU1, MU2, RMU1, RMU2 
COMMON/BLK05/BETAAB, BETAAC, BETAAB, DAB, DAC, DBC, RO1, RO2, RO3 
COMMON/POTPAR/A, B, A1, B1 
COMMON/BLK14/S, SS 
COMMON/BLK22/IZ 
COMMON/BLK30/P1
COMMON/XLK55/TRED
COMMON/XLK40/IFLAG
COMMON/XLK43/III
COMMON/XLK45/IMARK, IXA
COMMON/XLK45/PAR1, PAR2
COMMON/XLK47/BRACK, GMON
DIMENSION C(8), CDOT(8), DR1DG(4), DR2DG(4), DR3DG(4), PDOT(4), GDOT(4)
DIMENSION FRMT(5)

WRITE(6, 131) C

131 FORMAT(' ', GF14.5)

IXA=0
IF(IMARK.EQ.1) IXA=1
Z1=C(1)+S*C(3)
Z2=C(2)+S*C(4)
R1=DSQRT(Z1**2+Z2**2)
X1=C(1)-SS*C(3)
X2=C(2)-SS*C(4)
R2=DSQRT(X1**2+X2**2)
R1=1/R1
R2=1/R2
R3=1/R3
MORSAB=DEXP(-BETAAB*(R1-R01))
MORSAC=DEXP(-BETAC*(R3-R03))
MORSBC=DEXP(-BETABC*(R2-R02))
HYPTAB=DTANH(A*R1+B)
HYPTBC=DTANH(A1*R2+B1)
HYPTAC=DTANH(A*R3+B)
ENTRY HAMPOT(C, HAM, POT, AM)

THIS IS WRITTEN AS AN ENTRY INSTEAD OF A SUBROUTINE
TO SAVE SPACE & TIME. ITS FUNCTION IS TO CALCULATE
THE TOTAL ENERGY (HAM), THE POTENTIAL (POT) & THE
TOTAL ANGULAR MOMENTUM. THE SURFACE DETERMINING PARA-
METER, I2 IS ALSO CALCULATED.

POT1=DAB*(1-MORSAB)**2+DAB*MORSAB*(1-1-HYPTBC)+
!DBC*(1-MORSBC)**2+DBC*MORSBC*(1-HYPTAB)+
!DAC*MORSAC+0.1*(2.75/(0.529*R1))**12-(DAB+DBC)
POT2=0. 3445600D29*(-14.394/(0.529*R1))-50/(0.529*R1)**4
!+0.10*(2.50/(0.529*R1))**12*
!DBC*(1-MORSBC)**2-2-DBC+1.85*DBC*MORSBC*(1-HYPTAB)+DAC*MORSAC
POT3=POT1
POT4=POT1
POT1=POT1/0. 3445600D29
POT2=POT2/0. 3445600D29+5. 0
POT3=POT3/0. 3445600D29+1. 61
POT4=POT4/0. 3445600D29+3. 47
ETA=0. 500D0
IFL=1
IZN=1
L2PROB=1. 00000000000000000000D0
VRL2=0. 00000000000000D0
THET=0. 00000000000000D0
GR1=0. 000000000000D0
GR2=0. 000000000000D0
THENM=0. 000000000000D0
QUOT=0. 000000000000D0
DIFF=0. 000000000000D0
RQS=0. 000000001D0
H12=0. 150D0
H13=100. 00D0
H14=100. 00D0

D. 9
IF (12. EQ. 1) PUT=PUT1
IF (12. EQ. 2) PUT=PUT2
IF (12. EQ. 3) PUT=PUT3
IF (12. EQ. 4) PUT=PUT4
DIFF1=PUT-PUT1
DIFF2=PUT-PUT2
DIFF3=PUT-PUT3
DIFF4=PUT-PUT4
III=III+1
IF (IXA. EQ. 1) GOTO 10
IF (DABS(DIFF1). LE. ETA) GOTO 71
71 IF (DABS(DIFF3). LE. ETA) GOTO 73
72 IF (DABS(DIFF3). LE. ETA) GOTO 14
73 IF (DABS(DIFF4). LE. ETA) GOTO 15
GOTO 19
712 GOTO(71, 75, 19, 19), IZ
713 GOTO(78, 72, 19, 19), IZ
714 GOTO(19, 82, 73, 19), IZ
715 GOTO(19, 85, 19, 19), IZ
GOTO 19
75 IF (DIFF1. GT. 0. ODO) IFL=2
    IF (DIFF1. GT. 0. ODO) ICM1=ICM1+1
    IF (ICM1. GT. 1) IFL=1
    GOTO 19
76 IF (DIFF1. GT. 0. ODO) IFL=3
    IF (DIFF1. GT. 0. ODO) ICM2=ICM2+1
    IF (ICM2. GT. 1) IFL=1
    GOTO 19
77 IF (DIFF2. GT. 0. ODO) IFL=4
    IF (DIFF2. GT. 0. ODO) ICM3=ICM3+1
    IF (ICM3. GT. 1) IFL=1
    GOTO 19
78 IF (DIFF2. LT. 0. ODO) IFL=2
    IF (DIFF2. LT. 0. ODO) ICM4=ICM4+1
    IF (ICM4. GT. 1) IFL=1
    GOTO 19
79 IF (DIFF2. LT. 0. ODO) IFL=4
    IF (DIFF2. LT. 0. ODO) ICM5=ICM5+1
    IF (ICM5. GT. 1) IFL=1
    GOTO 19
80 IF (DIFF2. LT. 0. ODO) IFL=3
    IF (DIFF2. LT. 0. ODO) ICM6=ICM6+1
    IF (ICM6. GT. 1) IFL=1
    GOTO 19
81 IF (DIFF3. GT. 0. ODO) IFL=3
    IF (DIFF3. GT. 0. ODO) ICM7=ICM7+1
    IF (ICM7. GT. 1) IFL=1
    GOTO 19
82 IF (DIFF3. GT. 0. ODO) IFL=4
    IF (DIFF3. GT. 0. ODO) ICM8=ICM8+1
    IF (ICM8. GT. 1) IFL=1
    GOTO 19
83 IF (DIFF3. LT. 0. ODO) IFL=2
    IF (DIFF3. LT. 0. ODO) ICM9=ICM9+1
    IF (ICM9. GT. 1) IFL=1
    GOTO 19
84 IF (DIFF4. GT. 0. ODO) IFL=4
    IF (DIFF4. GT. 0. ODO) ICM10=ICM10+1
    IF (ICM10. GT. 1) IFL=1
    GOTO 19
85 IF (DIFF4. GT. 0. ODO) IFL=3
    IF (DIFF4. GT. 0. ODO) ICM11=ICM11+1
    IF (ICM11. GT. 1) IFL=1

D.10
C THIS ENTRY CALCULATES THE PERPENDICULAR GRADIENTS, THE 
C PERPENDICULAR VELOCITY, AND WORKS OUT THE LANDAU-ZENER 
C CROSSING PROBABILITIES. WHEN THESE PROBABILITIES ARE 
C SUFFICIENTLY ‘LARGE’, THE ANT-EATER STEP COMES INTO 
C OPERATION.

7 CONTINUE 
INMARK=0 
DV1DR1=-2*DAB+BETAAB*MORSAB+MORSAB*DAB+BETAAB*MORSAB*(1+HYPTAB) 
DV2DR1=0.344560327*(14.394*(1/(0.529*R1)))**2+ 
4*50*(1/(0.529*R1)))**5-12*0.10/2.50+(2.50/(0.529*R1)))**13 
!-1.85*DBC*MORSBC*A*(1-HYPTAB+HYPTAB) 
DV2DR2=-2*DBC+BETABC*MORSBC+MORSBC+ 
DBC+BETABC+MORSBC*(0.15+HYPTAB) 
DV2DR3=-DAC+BETAAC+MORSAC 
DV3DR1=DV1DR1 
DV3DR2=DV1DR2 
DV3DR3=DV1DR3 
DV4DR1=DV1DR1 
DV4DR2=DV1DR2 
DV4DR3=DV1DR3

8 DR1DG(1)=RR1*Z1 
DR1DG(2)=RR1*Z2 
SRR1=S*RR1 
DR1DG(3)=Z1*SRR1 
DR1DG(4)=Z2*SRR1 
DR2DG(1)=RR3*X1 
DR2DG(2)=RR3*X2 
SRR3=-S*RR3 
DR3DG(3)=SRR3*X1 
DR3DG(4)=SRR3*X2 
DO 1 J=1,2 
1 DR2DG(J)=0.000 
DO 2 J=3,4 
2 DR2DG(J)=C(J)+RR2 
DO 4 J=1,2 
4 DOT(J)=RMU1+C(J+4) 
DO 5 J=3,4 
5 DOT(J)=RMU2+C(J+4) 
GMDN=DOT(3) 
GOTO(35,36,37,38),1Z 
35 DVDR1=DV1DR1 
DVDR2=DV1DR2
START OF THE 'SWAP' MECHANISM

VRLZ = DABS(QMON)
GOTO(22, 23, 24, 25), 12
22 GOTO(9, 221, 222, 223), IFL
23 GOTO(9, 221, 224, 225), IFL
24 GOTO(9, 226, 222, 223), IFL
25 GOTO(9, 226, 224, 223), IFL
221 LZPROB = 1 - DEXP(-H12/VRLZ)
DIFF = POT2 - POT1
IF(IZ.EQ.1) GOTO 10
DIFF = -DIFF
GOTO 10
222 LZPROB = 1 - DEXP(-H13/VRLZ)
DIFF = POT3 - POT1
IF(IZ.EQ.1) GOTO 10
DIFF = -DIFF
GOTO 10
223 LZPROB = 1 - DEXP(-H14/VRLZ)
DIFF = POT4 - POT1
IF(IZ.EQ.1) GOTO 10
DIFF = -DIFF
GOTO 10
224 LZPROB = 1 - DEXP(-H24/VRLZ)
DIFF = POT4 - POT2
IF(IZ.EQ.2) GOTO 10
DIFF = -DIFF
GOTO 10
225 LZPROB = 1 - DEXP(-H23/VRLZ)
DIFF = POT3 - POT2
IF(IZ.EQ.2) GOTO 10
DIFF = -DIFF
GOTO 10
226 LZPROB = 1 - DEXP(-H24/VRLZ)
DIFF = POT4 - POT3
IF(IZ.EQ.3) GOTO 10
DIFF = -DIFF
10 PAR1 = ((C8)*TRED + O. 5291770 - 3) *+2)/NU2 + O. 1036410 - 11
PAR2 = G1* RNU1
EN = TKE - DIFF
DIV = RNU2* (TRED + O. 5291770 - 3) *+2* O. 1036410 - 11
GOTO 12
716 LZPROB = 1.
12 IF (LZPROB.LT. 0.0000000000) GOTO 9
Y = GOSCAF(XX)
IF (LZPROB.LT. Y) GOTO 9
EXTERNAL POTFUN, CONTROL
DOUBLE PRECISION TRED, PRMT, CDOT, C, HAM, BRACK, GMON
DIMENSION F(4), G(4), C(4), PF1(4), GFI(4), PRMT(5), CDOT(5)
COMMON/BK(0)/NMOL, N, RMOL, MU1, NU1, RMU1, RMU2

SUBROUTINE SOLVE(P, Q, PRMT, CDOT)

* PURPOSE -
* PREPARES VALUES FOR INTEGRATION BY LIBRARY SUBROUTINE

C C C C C

30 DVDR1=DV1DR1
DVDR2=DV1DR2
DVDR3=DV1DR3
GOTO60

31 DVDR1=DV2DR1
DVDR2=DV2DR2
DVDR3=DV2DR3
GOTO60

32 DVDR1=DV3DR1
DVDR2=DV3DR2
DVDR3=DV3DR3
GOTO60

33 DVDR1=DV4DR1
DVDR2=DV4DR2
DVDR3=DV4DR3
GOTO60

60 DO 3 J=1, 4
3 PDOT(J)=-DVDR1*DR1DG(J)-DVDR2*DR2DG(J)-DVDR3*DR3DG(J)
DO 6 J=1, 4
CDOT(J)=QDOT(J)

6 CDOT(J+4)=PDOT(J)/TRED*2
IF(IMARK.EQ.1) PRMT(5)=-1.000
RETURN
END
COMMON/BLK01/MA, MB, MC, RV, RMMOL, M, RMMOL, M1, MU, MRU1, MRU2, PRMT
COMMON/BLK02/MMOL, M, RMMOL, MU, MRU1, MRU2
COMMON/BLK05/BETAAB, BETAC, BETABC, DAB, DAC, DBC, A, B, R01, R02, R03
COMMON/POTPAR/A, B, A1, B1
COMMON/BLK07/BB
COMMON/BLK14/SS
COMMON/BLK18/FT
COMMON/BLK22/I2
COMMON/BLK30/PI
COMMON/BLK31/ICM1, ICM2, ICM3, ICM4, ICM5, ICM6
COMMON/BLK32/ICM7, ICM8, ICM9, ICM10, ICM11, ICM12
COMMON/BLK35/TRED
COMMON/BLK40/IFLAGS

C * PURPOSE -
C * CALCULATES STARTING VALUES OF Q(1) ... Q(4), P(1) ... P(4)

REAL*4 MDMIN
DOUBLE  PRECISION  MA, MB, MC, MMOL, M, RMMOL, M1, MU, MRU1, MRU2, PRMT
DOUBLE  PRECISION  CDOT, CONV1, BETAAB, BETAC, BETABC
DOUBLE  PRECISION  DAB, DAC, DBC, A, B, R01, R02, R03
DOUBLE  PRECISION  TRED, Y, GOSCAF, XX, S, SS
DOUBLE  PRECISION  RMM, RMMOL, M, RMMOL, M1, MU, MRU1, MRU2
COMMON/BLK01/MA, MB, MC, RV, RMMOL, M, RMMOL, M1, MU, MRU1, MRU2, PRMT
COMMON/BLK02/MMOL, M, RMMOL, MU, MRU1, MRU2
COMMON/BLK05/BETAAB, BETAC, BETABC, DAB, DAC, DBC, A, B, R01, R02, R03
COMMON/POTPAR/A, B, A1, B1
COMMON/BLK07/BB
COMMON/BLK14/SS
COMMON/BLK18/FT
COMMON/BLK22/I2
COMMON/BLK30/PI
COMMON/BLK31/ICM1, ICM2, ICM3, ICM4, ICM5, ICM6
COMMON/BLK32/ICM7, ICM8, ICM9, ICM10, ICM11, ICM12
COMMON/BLK35/TRED
COMMON/BLK40/IFLAGS

DO 1 J=1,4
   C(J)=Q(J)
   C(J+4)=P(J)/TRED
1 CONTINUE
   IND=0
   IPO=0
3 CALL STWOD(C, POTFUN, CONT, PRMT, CDOT)
   WRITE(4, P, Q)
   DO 1 J=1,4
   C(J)=Q(J)
   C(J+4)=P(J)/TRED
3 CONTINUE
   WRITE(4, P, Q)
   CALL TRANSF(IPROD, SHAM)
   HAM=DOUBLE (SHAM)
   GOTO (10, 20, 30, 30), IPROD
10 CALL ABANDC(P, Q, PFI, GFI, HAM)
   GOTO 11
20 CALL ACANDB(P, Q, PFI, GFI, HAM)
   GOTO 11
30 CALL NOREQC(P, Q, PFI, GFI, HAM, IPROD)
11 CONTINUE
   CALL OPT
   RETURN
END

SUBROUTINE START(P, Q, PRMT, CDOT, LOOP, E, IV, MJ)
TOTAL INTEGRATION TIMES ARE OBTAINED BY MULTIPLYING FLY-BY TIME BY CA. 2

ISTASK = 1000
PRMT(2) = 600. 000
IF (E. GE. 0. 100) PRMT(2) = 350. 000
IF (E. GE. 0. 250) PRMT(2) = 200. 000
IF (E. GE. 1. 000) PRMT(2) = 100. 000
IF (E. GE. 2. 500) PRMT(2) = 50. 000
IF (E. GE. 50. 0) PRMT(2) = 10. 000
IF (PRMT(2). EQ. 600. 000) ISTASK = 6000
IF (PRMT(2). EQ. 350. 000) ISTASK = 7000
PRMT(3) = PRMT(2)/ISTASK
PRMT(4) = 5. 00-3
MMOL = MB + MC
M = MA + MMOL
RMMOL = 1. 0/MMOL
MU1 = MA + MMOL/M
MU2 = MB + MC * RMMOL
RMU1 = 1. 0/MU1
RMU2 = 1. 0/MU2
RMUAB = 1. /MA + 1. /MB
RMUAC = 1. /MA + 1. /MC
RMUBC = 1. /MB + 1. /MC
MAB = MA + MB
MAC = MA + MC
MBC = MB + MC
MTOT = MA + MB + MC
S = -NC * RMMOL
SS = -MB + RMMOL
RELK = E + CONV
DAB = DAB + CONV1
DAC = DAC + CONV1
DBC = DBC + CONV1
VR = SQRT(SNGL(2. 0 + RELKE/MU1))
PI = 3. 14159
BCMAX0 = 4. 180
BCMAX1 = 4. 291
BCMAX2 = 4. 374
BCMAX3 = 4. 448
AMPO = BCMAX0 - R02

D. 15
$F_S$ and $V$ are the max. separation & the max. harmonic amplitude respectively allowed for $V$.

E-dot for 1-D rotor is $L=\omega/(2\pi)$ where $L=J\omega$.

But $L=1$ omega & if J is known omega can be obtained.

J is set at J for CH3I at 312K. --ie J=20

JAY=20

MONIN in units of AHU AU

13 CONTINUE

14 CDOT(I)=1.000/3.000

PRTN(I)=0.000

Y=605CAF(XX)

YFL=SINGL(Y)

THETA=2.0*PI*YFL

G(1)=R*SIN(THETA)

G(2)=R*COS(THETA)

LABELY=IV+1

C 10 Y=605DDF(0.000,1.000)

C PERTINENT TO V=0

AMPNOT=Y/SQRT(2*beta)

IF (ABS(AMPNOT), GT, AMP0) GOTO 10

G(3)=-R02+AMPNOT

G3DOT=ANFREG*SQRT(AMP0*AMP0-AMPNOT*AMPNOT)

GOTO 50

C 20 Y=605DDF(0.000,1.000)

C PERTINENT TO V=1

RBC=2.175

IF (Y.LE.0.000) RBC=3.979

G(3)=-RBC

AMPNOT=R02-RBC

G3DOT=ANFREG*SQRT(AMP1*AMP1-AMPNOT*AMPNOT)

GOTO 50

C 30 Y=605CAF(XX)

C PERTINENT TO V=2

RBC=R02

IF (Y.LE.0.3900) RBC=3.922

IF (Y.GE.0.6100) RBC=4.168

G(3)=-RBC

AMPNOT=R02-RBC

G3DOT=ANFREG*SQRT(AMP2*AMP2-AMPNOT*AMPNOT)

GOTO 50

C 40 Y=605CAF(XX)

C PERTINENT TO V=3

RBC=2.19

IF (Y.LE.0.37500) RBC=4.329

IF (Y.GT.0.62500) RBC=3.762

IF (Y.GT.0.37500, AND, Y.LE.0.50000) RBC=3.951

G(3)=-RBC

AMPNOT=R02-RBC

G3DOT=ANFREG*SQRT(AMP3*AMP3-AMPNOT*AMPNOT)

GOTO 50

D.16
P(4) is chosen such that rotation angle momentum is either parallel or anti-parallel with its orbital counterpart.

If \( q = 0 \) both \( P_1 \) and \( P_3 \) are zero.

General 3-D total angular momentum is given by:

\[
L = (q_1, q_2, q_3) \times (p_1, p_2, p_3) + (q_4, q_5, q_6) \times (p_4, p_5, p_6),
\]

where \( \times \) implies vector cross product.

For 2-D case with \( q_1, q_2, p_1, p_2, q_3, q_4, p_3, p_4 \) as compts. of generalised CO. ORDS, total angular momentum is given by:

\[
L = (q_1 - p_2 - q_2 \times p_1 + q_3 \times p_4),
\]

For parallel angular momenta \( (M_J = +1) \):

- If \( \theta \) is -ve, \( P_4 \) must be +ve & v. v.
- For anti-parallel angular momenta \( (M_J = -1) \):

  - If \( \theta \) is -ve, \( P_4 \) must be -ve & v. v.

  - If (\( M_J, \theta \) -ve) \( \theta = 1 \)
  - If (\( M_J, \theta \) +ve) \( \theta = -1 \)

  - GOTO 12

12 CONTINUE

\[ P(4) = I_1 \times M_2 \times q(3) \times OMEGA \]

WRITE(6,55) P

RETURN

END

C ANALYSIS ROUTINES...

REAL FUNCTION RMIN*8(A,B,C)

REAL*8 A,B,C

IF (A.LT.B AND. A.LT.C) RMIN=A

IF (B.LT.A AND. B.LT.C) RMIN=B

IF (C.LT.A AND. C.LT.B) RMIN=C

RETURN

END

SUBROUTINE ABANDC(PIN, GIN, PFI, GFI, HAM)

DOUBLE PRECISION MA, MB, MC, RMUAB, RMUAC, RMUBC, MTOT, MAB, MAC, MBC

DOUBLE PRECISION TRED, HAM

DIMENSION PIN(4), GIN(4), PFI(4), GFI(4)

COMMON/BLK01/MA, MB, MC, RMUAB, RMUAC, RMUBC, MTOT, MAB, MAC, MBC

COMMON/BLK22/I2

COMMON/BLK35/TRED

COMMON/BLK50/ALAB, ARG1, ARG2

WRITE(6,200)

200 FORMAT('0',50X,'*REACTION* AB+C FORMED')
TO EVALUATE TRANSLATIONAL ENERGY & SCATTERING ANGLE

ETRANS=0.
CHINUM=0.
CHDEN1=0.
CHDEN2=0.

DO J=1,2
TERM=PFI(J)/MBC+PFI(J+2)/MC.
ETRANS=ETRANS+0.5*MTOT+MC/MAB*TERM
CHINUM=CHINUM-PIN(J)*TERM
CHDEN1=CHDEN1+TERM
CHDEN2=CHDEN2+PIN(J)*PIN(J)

CONTINUE
ETRANS=ETRANS/0.344560E29
CHI=ARCCOS(CHINUM/SQRT(CHDEN1*CHDEN2))
ALAB=-100.0.
ARG1=0.
ARG2=0.
ARG1=SIN(CHI)
ARG2=COS(CHI)+(39.142.)
ALAB=ARG1/ARG2
ALAB=ATAN(ALAB)
ALAB=ALAB*180./3.14159
CHI=CHI*180./3.14159

ETRANS IN EV: CHI IN DEGREES
OAMI=GFI(1)*PIN(2)-GIN(2)*PIN(1)
OAMD=GFI(1)/TRED
RAMI=GFI(3)*PIN(4)-GIN(4)*PIN(3)
RAMF=GFI(3)/TRED
TAMI=OAMI+RAMI
TAMF=OAMD+RAMF
DEAB=3.290
REAB=6.106
EROT=RAMF*RAMF*RMUAB/(2.*REAB*REAB)
EROT=TRED*TRED*EROT/0.344560E29
EVIB=DEAB+HAM-ETRANS-EROT
DELTAM=(OAMF-OAMI)/0.227
IDELT=INT(DELTAM)
BIO=7.0E-6
SGJ=EROT/BIO
JAY=INT(SQRT(SGJ))
ETOT=ETRANS+EROT+EVIB
FE=(ETOT-ETRANS)/ETOT
WRITE(6,100)ETRANS,EROT,EVIB,CHI,ALAB
WRITE(6,101)OAMI,OAMD,RAMI,RAMF,TAMI,TAMF
WRITE(6,102)IDELT,JAY,FE
RETURN

101 FORMAT(’OROB. ANG. MOM.,&X,FB. 3,4X,FB. 3/
&’OROTNL. ANG. MOM.,&X,FB. 4,4X,FB. 4/
SUBROUTINE ACANDB(PIN, QIN, PFI, QFI, HAM)

* COMPUTES FINAL STATE PROPERTIES OF AC+\h
\h* AC+\h
\h* SYSTEM

DOUBLE PRECISION MA, MB, MC, RMMAB, RMMAC, RMMBC, MTOT, MAB, MAC, MBC
DOUBLE PRECISION TRED, HAM

DIMENSION PIN(4), QIN(4), PFI(4), QFI(4)

COMMON/BLK01/MA, MB, MC, RMMAB, RMMAC, RMMBC, MTOT, MAB, MAC, MBC
COMMON/BLK22/IZ
COMMON/BLK35/TRED
COMMON/BLK50/ALAB, ARG1, ARG2
WRITE(6, 300)

300 FORMAT('0', 50X, 'REACTION\h AC+B FORMED')
IF (IZ.EQ. 1) WRITE(6, 301)
IF (IZ.EQ. 2) WRITE(6, 302)
IF (IZ.EQ. 3) WRITE(6, 303)
IF (IZ.EQ. 4) WRITE(6, 304)

301 FORMAT('0', 50X, 'WITH PRODUCTS IN GROUND STATE')
302 FORMAT('0', 50X, 'WITH IONISED PRODUCTS')
303 FORMAT('0', 50X, 'WITH Excited POTASSIUM STATE')
304 FORMAT('0', 50X, 'WITH Excited METHYL IODIDE "A" STATE')

TO EVALUATE TRANSLATIONAL ENERGY & SCATTERING ANGLE

ETRANS=0.
CHNUM=0.
CHDEN1=0.
CHDEN2=0.
DO 1 J=1, 2
TERM=PFI(J)/MBC+PFI(J+2)/MB
ETRANS=ETRANS+0.5*MB*MTOT/MAC*TERM*TERM
CHNUM=CHNUM+TERM*PIN(J)
CHDEN1=CHDEN1+TERM*TERM
CHDEN2=CHDEN2+PIN(J)*PIN(J)
1 CONTINUE

CHI=ARCOS(CHNUM/SGRT(CHDEN1*CHDEN2))
ALAB=-100.0
ARG1=0.
ARG2=0.
ARG1=SIGN(CHI)
ARG2=COS(CHI)+(39./142.)
ALAB=ARG1/ARG2
ALAB=ATAN(ALAB)
ALAB=ALAB*180./3.14159
CHI=CHI*180./3.14159
ETRANS=ETRANS/0.344560E29

FINAL ORBITAL & ROTATIONAL ANGULAR MOMENTUM COMPTS

RAMP=MTOT*MB/MAC*((-MA+GFI(1)/MTOT+MC*GFI(3)/MBC)*
&((-PFI(2)/MBC+PFI(4)/MB)-(-MA+GFI(2)/MTOT+MC*GFI(4)/MBC)*
&(-PFI(1)/MBC+PFI(3)/MB))/TRED

RAMP=MA*MC/MAC*(MB*GFI(3)/MBC+GFI(1))*(PFI(4)/MC
&+PFI(2)*MTOT/MA/MBC)-(MB*GFI(4)/MBC

D.19
DEAC=4.340
REAC=7.372
EROT=RAME+RAMF+RMUAC/(2.0*REAC*REAC)
EROT=TRED+TRED*EROT/0.34450E27
EVID=DEAC+HAM+ETRANS-EROT
DELTAM=(DAMF-DAMI)/0.2271
IDELT=INT(DELTAM)
BIO=1.27E-5
SQJ=EROT/BIO
JAY=INT(SORT(SQJ))
ETOT=ETRANS+EVID+EROT
FE=(ETOT-ETRANS)/ETOT
WRITE(6,100) ETRANS,EROT,EVID,CHI,ALAB
WRITE(6,101) DAMI,DAMF,RAMI,RAMF,TAMI,TMF
WRITE(6,102) IDELT,JAY,FE
RETURN
101 FORMAT ('CULAR. ANG. MOM. ',8X,F8.3,4X,F8.3/
&'ROTATIONAL ANG. MOM. ',6X,F8.4,4X,F8.4/
&'TOTAL ANG. MOM. ',6X,F8.3,4X,F8.3)
100 FORMAT ('CETRANS=',F7.3,'/CEROT=',F7.4,'/CEVID='
&,'F7.4,'/OSCATT. ANGLE=',F6.1,'/OLAB ANGLE=',F6.1)
102 FORMAT ('O/TRANSFER OF ORB. AM (H5AR) ',I4/
&' ROTATIONAL QUANTUM NUMBER ',I4/
&' FRACTION OF ETOT INTO INTERNAL MODES ',F6.3)
END

SUBROUTINE NOREAC(PIN,GIN,PFI,GFI,HAM,JMARK)

* COMPUTES FINAL STATE PROPERTIES *
* FOR CASE OF ELASTIC/INELASTIC OR *
* DISSOCIATIVE SCATTERING *

DOUBLE PRECISION MA,MB,MC,RMUAB,RMUAC,RMUBC
INTEGER ABCDEF
DOUBLE PRECISION MTOT,MAB,MAC,MBC,HAM,TRED
DIMENSION PIN(4),GIN(4),PFI(4),GFI(4)
COMMON/BLKO1/MA,MB,MC,RMUAB,RMUAC,RMUBC,MTOT,MAB,MAC,MBC
COMMON/BLK22/I2
COMMON/BLK35/TRED
COMMON/BLK50/ALAB,ARG1,ARG2
IF (JMARK.EQ.3) WRITE(6,400)
IF (JMARK.EQ.4) WRITE(6,401)
400 FORMAT ('ONON-REACTIVE')
401 FORMAT ('ODISSOCIATION')
IF (I2.EQ.1) WRITE(6,402)
IF (I2.EQ.2) WRITE(6,403)
IF (I2.EQ.3) WRITE(6,404)
IF (I2.EQ.4) WRITE(6,405)
402 FORMAT ('O',50X,'WITH PRODUCTS IN GROUND STATE')
403 FORMAT ('O',50X,'WITH IONISED PRODUCTS')
404 FORMAT ('O',50X,'WITH EXCITED POTASSIUM STATE')
405 FORMAT ('O',50X,'WITH EXCITED METHYL IODIDE "A" STATE')

TO EVALUATE TRANSLATIONAL ENERGY & SCATTERING ANGLE
IT9, J5) 1 FE.ES

HI=U. =C

DO 1 J=1, 2
ABCDEF=2
ETRANS=ETRANS+PFI(J)*PFI(J)
WRITE(9, 808) ABCDEF, ETRANS
CHINUM=CHINUM+PIN(J)*PFI(J)
CHIDEN=CHIDEN+PIN(J)*PFIN(J)
1 CONTINUE
ABCDEF=3
CHI=ARCOS(CHINUM/SQRT(CHIDEN+ETRANS))
ARG1=0.0
ARG2=0.0
ALAB=-100.0
WRITE(9, 808) ABCDEF, CHI
ARG1=SIN(CHI)
ARG2=COS(CHI)+(39. /142.)
ALAB=ARG1/ARG2
ALAB=ATAN(ALAB)
CHI=CHI*180.0/3.14159
ALAB=ALAB*180.0/3.14159
ABCDEF=4
ETRANS=ETRANS+MTOT/(MA*MB*C)
WRITE(9, 808) ABCDEF, ETRANS
ABCDEF=5
ETRANS=ETRANS/0.344560E29
WRITE(9, 808) ABCDEF, ETRANS

C FINAL ORBITAL & ROTATIONAL ANGULAR MOMENTUM COMPONENTS

OAMF=QFI(1)*PFI(2)-QFI(2)*PFI(1)
OAMF=OAMF/TRED
RAMF=QFI(3)*PFI(4)-QFI(4)*PFI(3)
RAMF=RAMF/TRED
OAMI=QIN(1)*PIN(2)-QIN(2)*PIN(1)
OAMI=OAMI/TRED
RAMI=QIN(3)*PIN(4)-QIN(4)*PIN(3)
RAMI=RAMI/TRED
TAMI=OAMI+RAMI
TAMF=OAMF+RAMF

C SEPARATE ACCORDING TO WHETHER SCATTERING IS DISSOCIATIVE OR NOT

IF (JMARK.EQ.3) GOTO 3
EBCTR=RMUBC*(PFI(3)*PFI(3)+PFI(4)*PFI(4))/2.0
POTCK=HAM-ETRANS-EBCTR
WRITE(102) TAMF, ETRANS, EBCTR, CHI, ALAB, POTCK
102 FORMAT (80ORB. ANG. MOM. , 8X,F8. 3, 4X,F8. 3/
&'OSCATT. ANGLE=',F6. 1,'OLAB ANGLE=',F6. 1,'OPOTL. CHECK. ',F9. 5/)
GOTO 2

C APPROXIMATE ROTATIONAL ENERGY

3 REBCC=4.043
WRITE(9, 808) ABCDEF
REBCC=2.340
EROT=RAMF*RAMF*RMUBC/(2.0*REBCC*REBCC)
EROT=TRED*TRED*EROT/0.344560E29
EVIB=0.500D0*(PFI(3)*TRED)**2*RMUBC
DELTAM=(OAMF-OAMI)/0.2271
IDELT=INT(DELTAM)
JI=INT(RAMI/0.2271)
JF=INT(RAMF/0.2271)
JOEL=JF-JI
ETOT=ETRANS+EROT+EVI
FE=(ETOT-ETRANS)/ETOT
WRITE(6,101) DAMI,DAMF,RAMI,RAMF,TAMI,TAMF
101 FORMAT(’ORIR. ANG. MOM. ’,3X,F13.6,4X,F13.6/
& ’OROTNL. ANG. MOM. ’,3X,F13.6,4X,F13.6/
& ’OTOTAL ANG. MOM. ’,3X,F13.6,4X,F13.6)
WRITE(6,100) ETRANS,EROT,EVI,CHI,ALAB
WRITE(6,103) IDELT,JE,JOEL,FE
103 FORMAT(’OR//’TRANSFER OF ORB. AM=’,I4/
& ’ ROTATIONAL QUANTUM NUMBER=’,I4,10X,’RAM TRANSFER=’,I4/
& ’ FRACTION OF E(TOT) INTO INTERNAL MODES ‘,F6.3)
100 FORMAT(’ETRANS=’,F7.3/’EROT=’,F7.4/’EVI=’
& ,F7.4/’OSCATTO. ANGLE=’,F6.1/’OLAB ANGLE=’,F6.1)
803 FORMAT(’OR’,I4,5X,E10.5)
2 CONTINUE
RETURN
END
ELECTRONIC EXCITATION AND ENERGY TRANSFER IN K–N₂ COLLISIONS

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Inelastic differential scattering cross sections for the system K/N₂ have been measured in the small-angle regime for \( E_X \) in the range 80–600 eV deg. A cross beam time-of-flight technique was used to measure energy transfer effects occurring in the collision. The dominant inelastic process in the region explored was production of the K(4 \( ^2 \)P) state together with simultaneous vibrational excitation of the N₂ molecule. The observations are in excellent agreement with published potentials and a simple classical model involving an intermediate with considerable negative-ion character.

1. Introduction

The quenching of alkali atoms as a result of collisions with diatomic molecules has been of interest for a considerable time [1]; the system Na/N₂ has been of particular interest both experimentally [2] and theoretically [3,4]. The inverse process, atomic excitation as a result of energetic collisions with diatomic molecules, has also been studied [5]. More recently the system of interest here, K/N₂, has been studied by a novel coincidence technique [6] in which the differential cross section for the process K(4 \( ^2 \)S) + N₂ \( \rightarrow \) K(4 \( ^2 \)P) + N₂ was determined, the final state of the molecule not being measured in this experiment. All this work is consistent with an early suggestion that an ion-pair (K⁺/N₂⁻) state is an important intermediate.

In the present experiments the time-of-flight technique provides additional information on the excitation of other states, vibrational excitation of N₂ and elastic scattering. The combination of this data with Kempter's observations is consistent with significant ionic character in the description of the collision system both in the angular distributions and now in the vibrational excitation of the N₂.

2. Experimental

2.1. Apparatus

A schematic of the apparatus is shown in fig. 1. The beam of fast alkali atoms is produced initially as ions by surface ionisation on a porous tungsten disc heated radiatively to \( \approx 1500 \) K. The ions are accelerated to the required collision energy and electrostatically focused. The beam is then pulse-modulated, using a velocity compression technique [7], so that the time-of-flight analysis of the scattered atoms may be carried out. After modulation, the ion beam is neutralised by charge exchange in a vapour cell, and any residual ions are deflected away.

The fast neutral beam enters the collision zone where it intercepts the orthogonally introduced slow target beam, formed by effusion through a capillary array, and modulated at 47 Hz. The scattered potassium atoms are ionised on a cool tungsten wire at the detector, and arrivals are counted via a scintillator and a photomultiplier. The detector can be varied in angle with a precision of \( \pm 0.002 \) deg. The arrivals at the detector stop a 50 MHz crystal clock running in synchronism with the pulse modulation, and so their flight time is recorded. The data collection and experimental operation are controlled by an on-line computer [8], which also monitors important experimental conditions, such as beam fluxes, throughout the run. Due to
the very low count rates associated with experiments of this type, less than 0.01 s⁻¹ at wide angles, an experiment takes about five days. In these experiments the resolution in $E_X$, the reduced scattering angle, was ≈35 eV deg and the energy loss could be determined to ±0.15 eV.

2.2. Results

The results were collected over two separate experimental runs, and are presented after transformation to the c.m. reference frame. A c.m. contour map showing the variation in the product of the scattered intensity and the square of the scattering angle, $I(x)\chi^2$, as a function of scattering angle and post-collision velocity, is presented in fig. 2.

Such contour plots are highly information-intensive but the grosser features are more easily displayed in a time-of-flight profile. Fig. 3 shows such a profile averaged over all the angles of observation. It is immediately apparent that the elastic channel dominates the collision while an inelastic process with a most probable energy loss of 2.8 eV arises in ≈16% of collisions. A number of very much smaller processes are seen at greater energy losses. The $^{41}$K isotope with 6% abundance provides a useful marker.

Measurements of this type do not unambiguously identify the exit channel; however, the lowest excited state of $N_2$, $A^3\Pi_u^+$, is 6.2 eV above the incident channel, while fluorescence measurements [10] on this system revealed predominantly $K(4\,^2P)$ excitation, the $K(5\,^2P)$ and $(6\,^2S)$, states being populated to ≈2% and 0.6% in comparison. The inelastic channel observed in this experiment onsetting at 1.6 eV and having a maximum at 2.8 eV is therefore assigned to $K(4\,^2P)$ excitation with, by elimination, concurrent vibrational excitation of the $N_2$. A very weak inelastic peak with an energy loss of 4.7 eV and ≈10% of the intensity of the $K(4\,^2P)$ scattering can also be seen. This may be associated with similar excitation of the $K$ atom to $K(5\,^2S)$ or $(5\,^2P)$ states and again concurrent vibrational excitation of the $N_2$, but will not be further discussed here. The proposed assignment is supported by the success of the model based upon this interpretation of the energy loss data.

Previous time-of-flight measurements by Gersing et al. [11] on this system show similar loss profiles to those observed in this work but were interpreted solely as $K$ excitation and led to the conclusion that production of $K(5s)$ and $(3d)$ states was the main inelastic channel – an unsafe conclusion in view of the fluorescence experiments [10].
Fig. 2. Polar contour plot showing \( I(\chi) \chi^2 \) as a function of c.m. scattering angle, \( \chi \), and energy loss. The K/N\(_2\) collision energy was 85.5 eV (c.m.). Contours are drawn at 5, 10 and 15%. The angles at which observations were taken are indicated together with an energy-loss graticule. Two distinct peaks can be seen; the lowest shows an energy loss < 0.6 eV, the higher (a rather weaker one) a loss \( \approx 2.8 \) eV. The feature at the top of the figure arises from the \(^{41}\)K isotope.

Fig. 3. Energy-loss profile averaged over all angles of observation (0.9–7.5 c.m.). Collision energy 85.5 eV.

Fig. 4. Most-probable energy loss associated with K(4\(^2\)S) and K(4\(^2\)P) scattering. Experimental observations are shown as bars, two standard deviations long. Continuous curve is model prediction. Collision energy 85.5 eV.
In the coincidence experiments of Kempter et al. [6], only K(4\(^2\)P) excitation was reported. However, the flight-time resolution of their experiment, as estimated from the reported apparatus dimensions, was insufficient to distinguish the additional energy loss associated with N\(_2\) vibrational excitation and the two experiments are thus not in contention.

The differential cross sections for the electronically elastic and inelastic channels, calculated by summing appropriate regions of the individual energy loss profiles are plotted in fig. 5. They are similar to those reported by Kempter et al. In fig. 4, the most probable loss for these two channels is plotted against scattering angle.

3. Discussion

The measurements reported are confined to the narrow angle region in which the trajectories are approximately rectilinear and of constant velocity so that the deflection angle, collision lifetime and impact parameter can be simply related by small-angle formulae [12]. The collision lifetime is dependent upon the impact parameter but is of the order 10\(^{-14}\) s and so is comparable to the vibrational period of N\(_2\) and N\(_2^*\).

The potentials relevant to this system are displayed in fig. 6, 6a illustrating the potentials for N\(_2\) and N\(_2^*\) derived by Gilmore [13], while 6b shows a very simplified set of diabatic potentials for the K–N\(_2\) interaction. It can be seen that both the ground and excited K atom scattering can arise by two routes according to whether the crossing to the surface with ionic character occurs on the ingoing or outgoing phases of the collision. The electron transfer corresponding, in this simple picture, to the formation of the negative ion and the subsequent recapture of an electron to reform neutral potassium in either a ground or excited state are illustrated in fig. 6a. The transitions are assumed vertical in position and to conserve momentum. Since the potential curves for N\(_2\) and N\(_2^*\) are mutually displaced, the period spent as a negative ion results in vibrational excitation of the N\(_2\) molecule on exit from the collision.

A simple classical model based on this picture using the Landau–Zener approximation to compute the crossing probability and assuming independent motion in the N–N and (N\(_2\))–K dimensions was developed. (The model is very similar to that successfully used to describe similar processes in systems of the type K/RI [14].) In this model the only interaction permitted between these separate motions was via vertical electron transitions and changes in R\(_c\) occurring as a result.
of the variation in electron affinity as the N–N bond stretched. The model calculations were performed in a simple iterative fashion; the initial estimates of cross section, scattering angle and lifetime on the ionic surface (and hence $N_2$ vibrational excitation) were computed using the small-angle formulae based on the $u = 0$ $N_2$ electron affinity. Numerical computation of the $N_2$ motion during the collision lifetime produced a revised vertical electron affinity and $R_C$ that were used to update the small-angle scattering calculation. Iteration of this process yielded very rapid convergence.

The potentials used in this model for $N_2$ and $N_2^+$ were of Morse form fitted to the well-established Gilmore potentials \[13\] in their bowl region of importance in the calculation:

$$V_{N_2} = D_1 \left(1 - \exp\left[-\beta_1 (R - R_{01})\right]\right)^2 - D_1,$$

where

$$D_1 = 9.8 \text{ eV}, \quad \beta_1 = 2.5, \quad R_{01} = 1.10 \text{ Å};$$

$$V_{N_2^+} = D_2 \left(1 - \exp\left[-\beta_2 (R - R_{02})\right]\right)^2 - D_2 + 0.3,$$

where

$$D_2 = 8.5 \text{ eV}, \quad \beta_2 = 2.2, \quad R_{02} = 1.185 \text{ Å}$$

corresponding to a vertical electron affinity of 1.9 eV at the $N_2$ equilibrium distance.

The $K/N_2$ potentials were initially chosen to be identical to those used by Kempter et al. to fit the $K(4 \, ^2P)$ scattering. These were later modified to provide better agreement particularly with the angular distribution of $K(4 \, ^2S)$ scattering observed here, and the forms finally chosen are

$$V_{K/N_2} = \epsilon (a/R)^s, \quad \text{eqn. (3)}$$

where

$$s = 6.4 \quad (R > R_c),$$

$$= 9.0 \quad (R < R_c),$$

$$\epsilon = 0.05 \text{ eV}, \quad a = 4.03 \text{ Å},$$

$$V_{K/N_2} = V_{K/N_2}^0 - 62.2/R^4 - 14.394/R + 6.25 \text{ eV} \quad (R > R_c),$$

$$= V_{K/N_2}^0 \quad (R < R_c).$$

The crossing probability was of the usual Landau–Zener form with $V_{12} = 0.7 \text{ eV}$. The vibrational excitation predicted by this model is largely determined by, and is rather sensitive to, the difference in the $N_2$ and $N_2^+$ potentials, while the angular dependence is similarly primarily a function of the $K/N_2$ potential. This separation results from the bounded motion of the $N_2^+$ ion and the limited changes in $R_C$ which occur as the $N_2$ vibrates.

The predictions for energy loss are shown in fig. 4. The agreement in the $K(4 \, ^2P)$ channel is particularly satisfying and is certainly well within the available precision of the $N_2$ potential. The observed energy loss for $K(4 \, ^2S)$ scattering is in less satisfactory agreement — possibly as a result of changes in $V_{12}$ with the N–N distance which are not included in the present model. Increasingly diabatic behaviour can be expected as $R_{N_2}$ increases, diminishing the contribution of the ionic surface, with its attendant vibrational excitation, to scattering in the $K(4 \, ^2S)$ state, and so decreasing the average energy loss actually observed. Incorporation of such a $V_{12}$ dependence in the model would improve agreement with the observations but observations over a wider collision energy range would be required to establish its validity.

Interestingly, the model predicts that the vibrational excitation oscillates with scattering angle (i.e. collision lifetime) as the $N_2^+$ ion itself oscillates. A similar mechanism has been advanced to account for maxima in the total ionization cross section observed in Cs/O$_2$ collisions \[15\]. In the present experiments, since the early and late crossing contributions to the scattering are in an approximately random phase relation, this oscillation would be difficult to resolve. Experiments at lower collision velocities, where the energy loss resolution is substantially improved and probably adequate to resolve the predicted separate early and late crossing contributions, will be particularly interesting in testing the detailed success of this primitive classical model.

Finally, in distinction to systems of the $K/RI$ type where the RI negative ion was found to be substantially perturbed by the $K^+$ ion, the $N_2^+$ pair potential (within the limited precision with which it is known) accounts for the present results rather well.

The differential cross sections computed from the model are compared with experiment in fig. 5. The agreement is satisfactory considering the simple analytic forms used to represent the $K/N_2$ potentials. The maxima and minima calculated in the $K(4 \, ^2S)$ channel,
which is the sum of early and late crossing contributions, arises from the operation of the LZ terms in the model.

References