to Audrey and Peter
DECLARATION

This thesis has been composed entirely by myself. Where reference to the work of others has been made the proper acknowledgements have been given in full.

Signed

Date 6th Feb '80
ACKNOWLEDGEMENTS

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I am indebted to Alastair Rae for his creative genius, especially during the laser construction and to Robert Donovan for his irrepressible enthusiasm. The experience of Malcolm Fluendy aided greatly the 'beams' and 'trajectories' side of things whilst myself, Robert Glen, David Sutton (John Weston), and Charlotte Sholeen enjoyed many memorable discourses related our experiences with M.A.D.F.. To all persons mentioned above, I am deeply grateful for their respective contributions.

Since the majority of this thesis was written after 1977 my employers during that time deserve special mention. Much of the spadework for Chap. 4 was done during my stay at the Royal Institution of Gt. Britain and I am grateful to its managers through Dr. M.A. West for unrestricted use of its library facilities. Finally, the hardest aspect of this thesis (the writing) was done whilst employed as 'post-doc.' in the Dept. of Chemistry at the University of Manchester. I am especially indebted to Prof. R Grice, Dr. J.C. Whitehead, Dr. P.A. Gorry and the beams group at Manchester for essential guidance and discussions.
This thesis is concerned with the determination of internal quantum state distributions obtained under single collision conditions from crossed beam reactive molecular scattering. Specifically, the reaction \( \text{O} (^3\text{P}_g) + \text{I}_2 (^1\Sigma^+_g) \rightarrow \text{IO} (^2\Pi_{3/2}) + \text{I} (^2\text{P}_{3/2}) \) is considered at experimental and theoretical levels. Chapter 1 introduces briefly the development of reactive scattering with an emphasis on the role of optical detection. The technique of laser induced fluorescence (LIF) as such a detector is detailed in Chapter 2 for most of the experimental regimes which arise in practice and the superiority of continuous wave over pulsed excitation is highlighted. In addition, the feasibility of LIF detection of the radical IO from the above reaction is demonstrated. In Chapter 3, the apparatus intended to carry out such a study is described in detail. Unfortunately, due to a prolonged breakdown of the nitrogen laser, the author was not successful here. Consequently, a theoretical study of the reaction under various conditions was made using the classical trajectory technique and a detailed discussion of this along with the results is presented in Chapter 4. It is seen that the reaction ostensibly behaves in the manner expected for a long-lived-complex at low collision energies tending to stripping dynamics at higher energies. More detailed examination of the results suggests that dynamical rather than statistical factors determine trajectory outcomes and this is attributed to the anomalous behaviour of systems with mass combination 'L + HH' on attractive surfaces.
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\[ O + I_2 \rightarrow OI + I \]

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CHAPTER 1

SOME RECENT LIGHT ON MOLECULAR

REACTION DYNAMICS
CHAPTER 1

SOME RECENT LIGHT ON MOLECULAR REACTION DYNAMICS

1.1 INTRODUCTION

To gauge the expansion in the general field of reaction dynamics it is instructive to compare the present state of the art for the laser induced fluorescence technique (LIF) with the state prevailing in early 1977. Kinsey\(^1\) noted that the ground covered between the first report in 1972\(^2\) and January 1977 was an order of magnitude above that of (alkali) reactive scattering at the same age. Inspection of Appendix 2 below reveals over 100 separate reactions studied via LIF to date compared with twenty when Kinsey wrote his review - a fivefold increase in yearly output. Similar remarks apply to the visible chemiluminescence (VCL) technique: the first report\(^3\) of single collision VCL appeared in 1970 and since then some eighty systems (see Appendix 1) have been investigated with a current productivity level three times that of two years ago.

The reasons for this expansion are largely technological. During the last decade, the development of superior apparatus and techniques has meant that tighter control on experimental variables is possible and this, in turn, has permitted extraction of more detailed information. Some notable examples include the preparation of oriented molecules\(^5, 6\) and the

\(^1\)Strictly speaking, Moulton and Herschbach were first here but they required two distinct single collisions to obtain VCL\(^4\).
direct observation of steric\textsuperscript{7} and specific energy\textsuperscript{8} requirements for reaction, notably in vibration. In conjunction with these advances, signal retrieval and analysis has been improved by on-line recording, by cross-correlation techniques\textsuperscript{9} and by various forms of multiplexing. Thus, the use of Fourier transform spectroscopy has facilitated and extended measurements of infra-red chemiluminescence\textsuperscript{10, 11} such that rotational relaxation is a minor perturbation on the nascent distributions. Similarly, the Fourier Transform Doppler Spectroscopy (FTDS) technique resurrected by Kinsey\textsuperscript{12} holds considerable potential for mapping out velocity/angle contours of single internal (diatomic) states in favourable circumstances\textsuperscript{13}.

In addition to available technology, there are those currently unavailable which are vigorously sought. Thus, although efficient isotope separation methods and visible chemical lasers, once developed, are unlikely to draw on single collision environments for their implementation, the understanding of the individual contributory processes is essential - it is far less expensive to model potential systems computationally than to build prototypes which may not work.

It seems reasonable to assert that optical and, in particular, laser techniques have made the most significant contributions to molecular beam reaction dynamics in the last decade. In the future we can look forward to laser induced chemiluminescence, photodissociation and photo-ionisation as standard diagnostic devices in molecular beams work. The low cross-sections for the latter can be offset by powerful U.V. and vacuum-U.V. lasers and in conjunction with time-of-flight mass spectrometry (without the inefficient electron bombardment ioniser) can be more efficient than "universal" detection\textsuperscript{14} whilst being equally universal. Indeed, the use of multi-photon ionisation by lasers of modest power has recently\textsuperscript{15}
been demonstrated both as a beams characterisation device and as a detector of reactive scattering. More exotic yet is the proposal by Letokhov\textsuperscript{16} that the shift in I.R. frequency of molecular vibrations brought about by nuclear excitation (through $E = \Delta mc^2$) can be used to separate nuclei and lead to gamma ray laser action.

In the spirit of the advances in reaction dynamics which depend on light for their elucidation, an overview of the field is presented below. Interest is confined to single collision investigations (crossed beam and beam/gas) only. The state of the art of crossed beam reactive scattering is not reviewed since this has recently been covered in a number of reviews\textsuperscript{17}.

1.2 \textbf{VISIBLE CHEMILUMINESCENCE (VCL)}

This field has been thoroughly reviewed up to early 1978 by Campbell and Baulch\textsuperscript{18} and a potted bibliography has recently been given by Engelke\textsuperscript{19}. Accordingly the subject will be reviewed only briefly for 1970-1978 and in more detail for 1978 to date since the forthcoming review of Menzinger\textsuperscript{20} is not yet available. A complete list of all single collision systems studied \textit{via} VCL is presented in Appendix 1.

The vast majority of these reactions are metal oxidations. The excited state reactions of $\text{Hg}^* (3P_{0,2})$ and $\text{Xe}^* (3P_{0,2})$ are both analogous to corresponding alkali atom ($2P$) reactions. The former presents a theoretical challenge since a marked difference in reactivity with spin-orbit state is observed, the $3P_2$ state being 30 times more reactive with $\text{Br}_2$ than the $3P_0$ state\textsuperscript{21, 22}. The mechanism with $\text{Hg}^* (3P_2)$ is expected to be ionic with long range electron transfer ($q_R \sim 100 \text{ Å}^2$) whilst $3P_0$ appears more covalent and hindered by a potential barrier\textsuperscript{22}. For the reaction of
NO \((^2\Pi_{1/2}, \, 3/2)\) with ozone similar differences in reactivity have been reported\(^{23}\). On the other hand, the work of the Birmingham group\(^{24}\) with \(\text{Xe} \,(^3\text{P}_{0,2})\) does not seem to follow the reactivity trends of \(\text{Hg}^*\) and \(\text{NO}\) but does indicate the strong similarity of \(\text{Xe}^* \,(^3\text{P}_{0,2})\) with \(\text{Cs} \,(^2\text{P})\).

Here, the use of the rotor beam technique\(^{24}\) permits more detailed investigation of reaction dynamics via the VCL excitation function and polarisation.

1.2.1 NON METAL REACTIONS

These consist of the following:

\[
\begin{align*}
\text{R1:} & \quad \text{C}_2^* + \text{NO} \rightarrow \text{CN}^* + \text{CO} \\
\text{R2:} & \quad \text{H} + (\text{NO})_2 \rightarrow \text{HNO}^* + \text{NO} \\
\text{R3:} & \quad \text{O} + (\text{NO})_2 \rightarrow \text{NO}_2^* + \text{NO} \\
\text{R4:} & \quad \text{O} + \text{NO} \rightarrow \text{NO}_2^* \\
\text{R5:} & \quad \text{O}_2^* + \text{R}_1\text{R}_2\text{C} = \text{CR}_3\text{R}_4 \rightarrow \text{R}_1\text{R}_2\text{C} = \text{O}^* + \text{R}_3\text{R}_4\text{C} = \text{O} \\
\text{R6:} & \quad \text{O}_3 + \text{NO}^* \rightarrow \text{NO}_2^* + \text{O}_2 \\
\text{R7:} & \quad \text{I}_2^* + \text{F}_2 \rightarrow \text{IF}^* + \text{IF}
\end{align*}
\]

The reactions of carbon polymers are of fundamental importance in most natural combustion processes. It emerged from Krause's work on R1\(^{25}\) that the reaction proceeded without activation energy on a single adiabatic \(^2\text{A}'\) surface via a facile four-centre mechanism. The internal state distributions of \(\text{CN}^*\) were characterised by temperatures indicating complex formation which was supported by dynamically derived CO internal distributions. In addition, the specificity of the reaction to \(\text{C}_2^* \,(X', \, ^3\Pi_u)\) constitutes an extremely sensitive test for its presence.
The preassociation reaction (R4) of \( \text{O} (^3P) + \text{NO} (^2\Pi) \) which is responsible for airglow in the night sky has been a source of controversy for some time\(^{26}\). The work of Ibaraki et al.\(^{27}\) has removed some of the uncertainty concerning the stabilizing effect of NO dimers. By controlling the NO nozzle temperature they were able to show that preassociation was of negligible importance in comparison to dimer reactions, R3, which exhibited a cross-section, \( \sigma_R \), of either 100 or 340 \( \text{Å}^2 \) depending on the dimerization equilibrium constant value. Such enormous cross-sections suggest long range electron jump mechanisms but little supporting data are available to support this. The vastly lower \( \sigma_R \) for R2 can be accounted for in two ways: firstly, the probability of electron jump in this reaction is negligible and secondly branching characteristics of the intermediate may be entirely different. Although a subsequent re-analysis of the \( \text{O} + \text{NO} \) reaction has been carried out in a sensitive crossed beams apparatus\(^{28}\) it was not conclusively shown that the VCL was due to binary collisions. The enigma of the background stabilized "immortal complex"\(^{29}\) of \( \text{BaCl}_2^* \) formed in "single collisions" of \( \text{Ba} + \text{Cl}_2 \) indicates very high cross-sections for energy transfer and casts some doubt on "two body" radiative recombinations.

The only reaction of organic importance thus far studied has been the dioxetane reaction\(^{31}, \text{R5}\). Application of orbital symmetry rules\(^{32}\) indicate that formation of ground state dioxetanes from ground state reactions is forbidden. The observation of activation barriers with various substituents which could only be overcome by translational energy implied an entrance channel barrier. This was rationalized in terms of an avoided intersection between excited and ground dioxetane states which was brought about by vibronic mixing.
Lastly, the 4-centre reaction of $I_2^* \rightarrow \Pi^2(0^+_g)$ with $F_2$ ($1^+_g$), R7, has much in common with the dioxetane reaction since it is forbidden by orbital symmetry considerations. Although VCL is energetically possible with ground and excited state $I_2^*$, it is only with the latter that any is observed, the cross-section being comparatively high ($10 - 50 \text{ A}^2$).  

Three possible explanations for this behaviour were proposed:

1) symmetry considerations for non-$C_2v$ configurations may be relaxed especially for $I_2^* + F_2$.

2) as in the dioxetane reaction, forbidden concerted reactions may become allowed by vibronic mixing - in this case the $I_2^* + F_2$ barrier will be reduced sufficiently to permit reaction at thermal energies.

3) an ionic mechanism may be operating.

The possibilities will exhibit a dependence with $I_2^*$ vibrational state and the authors suggest use of a tunable excitation laser (they used an $\text{Ar}^+$ laser) to examine this. However, it is possible that reaction in this case is assisted by translational energy as in the dioxetane reaction and a study of its excitation function would also yield considerable information.

1.2.2 REACTIONS CONTAINING ALKALI SPECIES.

Of the reactions involving metals, the most widely studied are the group 2A oxidations. More recently, groups 3A and 3B have been investigated. In addition, the transition element Ti has been observed via its excited oxide $^{34}$ and the lanthanides Sm, Ho and Eu as well as the group 4A metal Pb have also been studied$^{38}$. The atomic alkali metals which dominated the reactive scattering scene in the '60's do not give rise to chemiluminescence but instead to vibrationally excited salt molecules particularly with halogen containing molecules. However,
Moulton and Herschbach\textsuperscript{4} have shown that these excited halides can subsequently react with atomic alkalis to produce alkali atom chemiluminescence thereby substantiating Magee's\textsuperscript{37} mechanism for alkali emission in alkali-halogen flames:

\[
M + X_2 \rightarrow MX^\dagger + X
\]

\[
M, M' = \text{alkali}
\]

\[
X + M_2 \rightarrow MX^\dagger + M
\]

\[
X = \text{halogen}
\]

\[
M' + MX^\dagger \rightarrow M'X + M^*
\]

\[
* = \text{electronically excited}
\]

\[
\dagger = \text{vibrationally excited.}
\]

However, the definitive work of Struve et al.\textsuperscript{35} has shown that the original Polanyi (direct) mechanism\textsuperscript{35} also contributes here:

\[
M + X_2 \rightarrow MX + X
\]

\[
X + M_2 \rightarrow MX^* + M
\]

Consequently, work on alkali metals has revolved around their dimers. This is summarised in Table 1.1 below. For the $M_2 + X$ reactions\textsuperscript{35}, alkali atom emission is seen for all accessible states up to and just beyond the exoergicity limit with extremely large VCL cross-sections ($10 - 100 \AA^2$). This is interpreted in terms of an electron-jump (E-J) mechanism which takes place near the inner surface crossings and consequently gives rise to many excited states. The distribution of exoergicity amongst these states is seen to be nearly statistical with a characteristic temperature $\sim 5000 \text{K}$. The $M_2 + X_2$ reactions\textsuperscript{35, 36} on the other hand display much lower VCL cross-sections although the total reaction cross-sections are similar ($50 - 150 \AA^2$). The emission here however is from both excited
Table 1.1 - Alkali dimer reactions studied via VCL

'X' ~ studied, '-' ~ not studied.

atomic and molecular product and, in contrast to the $X + M_2$ reactions, chemionisation has a substantial cross-section ($1 - 10 \AA^2$). The mechanisms here are complicated but involve

(a) $M_2 + X_2 \rightarrow M + M^+ X^- + X$
(b) $\rightarrow M^+ X^- + M^+ X^-$
(c) $\rightarrow M^+ + M^+ X^- + X^-$
(d) $\rightarrow M_2 X^+ + X^-$

and the intermediate proposed is the biradical ion-pair.

$$M . M^+ \cdots \cdot X^- . X$$

The latter can explain the forward scattering of the salt molecules and
the chemionisation process (d) in terms of its modes of decomposition. For pathways (b) and (c) a 2nd electron jump is necessary and the instant shape of the intermediate then determines the pathway (bent configurations produce two salt molecules). The major difference between the X and X₂ series of reactions is that for X, VCL accounts for the majority of reactive scattering whereas the reverse applies to X₂. The phenomenon of orbital degeneracy originally proposed by Magee is invoked to explain this. Thus, 2/3 of the X + M₂ collisions yield M⁺ whilst essentially none obtains from X₂ + M₂. The existence of VCL from the latter is due to surface crossings in the ionic intermediate and is unrelated to orbital degeneracy which is absent (both reactants are ¹Σ⁺).

1.2.3 REACTIONS OF GROUP 2A METALS

These reactions lend themselves well to analysis by VCL. Unlike the alkali reactions, the excited states of group 2A salts are stable and well defined and the observed VCL is not quasi-continuous. However, since the behaviour of 1A and 2A metals is chemically similar as a consequence of their comparable ionisation potentials much comparison with the early alkali work is possible. Nonetheless it is unfortunate that little crossed beam scattering has been done with group 2A metals since their divalent character does give rise to pronounced differences in mechanism which are difficult to interpret on the basis of LIF/VCL work alone.
The reactions studied to date are tabulated below.

<table>
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<tr>
<th></th>
<th>F₂</th>
<th>Cl₂</th>
<th>Br₂</th>
<th>I₂</th>
<th>O₂</th>
<th>O₃</th>
<th>N₂O</th>
<th>NO₂</th>
<th>ClO₂</th>
<th>CO₂</th>
<th>S₂Cl₂</th>
<th>HCl</th>
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<tr>
<td>Be</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>G,E</td>
<td>E</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>G</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sr</td>
<td>G,E</td>
<td>E</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>E</td>
<td>G</td>
<td>G</td>
<td>-</td>
<td>G</td>
<td>-</td>
</tr>
<tr>
<td>Ba</td>
<td>G,E</td>
<td>G</td>
<td>E</td>
<td>G</td>
<td>-</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>-</td>
<td>G</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1.2 Reactions of group 2A metals

- ~ not studied
G ~ ground state reactants
E ~ excited atomic reactant.

For both ground and excited state (metal) reactants, the predominant mechanism is harpooning. For reactions with halogens, Menzinger has observed that Ca + Cl₂, Br₂ proceeds via a long-lived-complex for CaX* production and that the species CaCl₂* is formed with a very long radiative lifetime suggesting complex stabilisation by background gas collisions. The same report showed that Ca + F₂ proceeded in a direct fashion analogous to the alkali case. This has been supported by
Engelke\textsuperscript{19, 39} who has established the E-J mechanism on the basis of high total cross-sections (70, 115; 74, 125; 90, 160 \AA\textsuperscript{2} for Ca, Ca\textsuperscript{*}; Sr, Sr\textsuperscript{*}; Ba, Ba\textsuperscript{*} respectively). For the reactions of Ca\textsubscript{2} with excited atoms, the cross-sections and mechanisms are again similar, non-adiabatic transitions being necessary to yield excited products\textsuperscript{40, 41}.

The reactions of Ca, Sr, Ba with the oxidisers N\textsubscript{2}O, NO\textsubscript{2} and C\textsubscript{2}O\textsubscript{2} form a contrasting set. With NO\textsubscript{2}, all proceed by a straightforward electron jump\textsuperscript{42} whereas for N\textsubscript{2}O the situation is complicated by the negative electron affinity when the \nu\textsubscript{2} bending vibration is unexcited. This leads to a very short range electron jump or possibly a covalent mechanism\textsuperscript{43} similar to that of K + CH\textsubscript{3}I. However, excitation of \nu\textsubscript{2} has been shown to have a dramatic effect on the VCL cross-section\textsuperscript{44} and provides strong evidence in favour of the E-J mechanism. This is further supported by reaction of the excited atoms with N\textsubscript{2}O which is characterised by very large VCL cross-sections (Sr\textsuperscript{*}, Ca\textsuperscript{*} (\textsuperscript{3}P) \sim 27, 6 \AA\textsuperscript{2} respectively)\textsuperscript{45, 46}

The E-J cross-section, \( q^E-J \), is given by

\[
q^E-J = \pi r_c^2 \\
\text{.................. (1.1a)}
\]

where

\[
r_c (\text{A}) \sim \frac{14.4 \text{ (A)}}{\text{I.P. (eV)} - \text{E.A. (eV)}} \\
\text{.................. (1.1b)}
\]

is the crossing radius. The enhancement of the VCL cross-section (and, almost certainly, the reaction cross-section) noted above corresponds to decreasing (increasing) the ionisation potential (electron affinity).
In the case of $\text{ClO}_2^*$, both excited chloride and oxide have been observed\textsuperscript{47} with comparable cross-sections. The 'snap-out' reaction to form $\text{MCl}^*$ led the authors here to propose an electron jump into a half-full anti-bonding molecular orbital centred on the Cl atom which caused attraction of the O-atoms with product formation in a single direct encounter. The oxide formation was a consequence of the geometry of the intermediate.

Perhaps the most interesting of all the VCL reactions studied to date are those of Ba, Sr, Ca + $S_2\text{Cl}_2$. The odd feature here is that the VCL comes largely from the "old" $S_2$ bond with only a small contribution from $\text{MC}^*$ and $\text{MC}_2^*$. The total reaction cross-sections were 160, 105 and 92 Å\textsuperscript{2} respectively indicating an E-J mechanism once more. The intermediate proposed which could account for the observations was

and the reaction was expected to proceed by a concerted mechanism in a single collision. Although such mechanisms are rare in the gas phase, they are nonetheless known and the authors cited 11 instances of these involving Ba. That most of the exoergicity of this reaction ends up in $S_2^*$ internal excitation is presumably a reflection of the strain in the ring. The spin-forbidden nature of the reaction may again be a consequence of vibronic coupling.
1.2.4 REACTIONS OF GROUP 3A METALS

The laser induced chemiluminescence of In, Tl + I₂* has demonstrated directly a preferential collinear orientation for reaction since the total VCL signal (compensated for polarisation) was shown to be a smooth function of the polarisation of the excitation laser with respect to the metal beam. The same simple experiment was able to show a reaction-induced product rotational polarisation which was independent of laser polarisation. Since the reactants were not polarised in these experiments, the product polarisation must be a direct consequence of the potential which must be highly non-spherical in order to give rise to measurable anisotropy after experimental averaging. Such measurements can be inverted to yield information on the preferred geometry for reaction.

Of the other group 3A studies, little information on the reaction dynamics was obtained. However, in ref. 49 the use of laser vapourisation of a thin metal containing substrate to yield fast pulsed beams was demonstrated. The oxidation of B and NO by N₂O showed that while the total reactive cross-section decreased with increasing collision energy, the VCL cross-section did the reverse quite decisively. Although no explanations were forwarded it seems that a surface crossing may be responsible for this.
1.2.5 REACTIONS OF GROUP 3B METALS

The group 3B metals Sc, Y, La have similar ionisation potentials to the alkaline earths and alkalis and are therefore expected to form ionic bonds in oxidation reactions via an E-J mechanism. The cross-sections for oxide formation have been tabulated using known oxidant electron affinities and equation (1.1). In a detailed thermodynamic study of the reactions Sc, Y, La + O₂, N₂O, NO₂, Gole and Preuss have deduced that the observed activation energies reflect rearrangement of the ground state ionic complex to the excited emitting state. Such a mechanism is consistent with the generally low efficiency of single collision VCL processes (10⁻³ - 1%) since the ground state reactants tend to form ground state intermediates initially. This idea is further supported by Dagdigian who reported extremely large VCL cross-sections for excited state reactants where considerably less rearrangement is required. An important point arising from the thermodynamic work is the interpretative difficulty introduced by the complicated relationships between VCL intensity, latent heat of vapourisation and activation energy, A.E., for the various states populated in the source. This was seen to lead to an anomalously low A.E. for the La + N₂O reaction.

The distribution of exoergicity amongst ground and excited states has been shown to vary markedly for the 3B metals depending on the oxidant. For M + O₂, Manos and Parson showed that the partitioning in the excited state was well reproduced by a prior distribution based only on translational state density over a wide range of collision energy. This is in contrast to the ground state partitioning in ScO and YO studied by LIF which was seen to be statistical in vibration but "cold" in
rotation. On increasing the collision energy, the fraction into rotation was reduced at the expense of translation whilst that into vibration remained constant. This behaviour is unlike that of direct interactions on a single surface and the authors concluded that indirect collisions on a variety of surfaces were responsible since this was consistent with the statistical distributions observed and the large number of surfaces correlating with reactants.

Although less well characterised, the other oxidants appeared to give rise to far from statistical distributions in the excited state, notably from Sc + NO₂.

1.3 INFRA-RED CHEMILUMINESCENCE (IRCL)

This technique measures relative rate constants for formation of a particular (v) or (v, J) state of the ground electronic state. The corresponding populations $N_v$ and $N_{vJ}$ characterise the nascent internal distributions of the reaction under study. There are two variants of the method in current use: the Southampton group utilises the "measured relaxation" technique in which relatively fast flows of reagents are used at high pressure (> $10^{-3}$ Torr). This way, diffusion is minimised and the correction for vibrational relaxation is straightforward. In the "arrested relaxation" method the apparatus more resembles a large crossed molecular beams machine with reagents forming "sprays" and intersecting at a fairly well defined region in the field of view of the detector. Unlike the high pressure variant, only translation is completely thermalised here and rotational relaxation can be accounted for with precision.
However, the low signal: noise properties of IR photodetectors is low compared to photomultipliers even when operated at liquid He temperatures and this in conjunction with the low Einstein 'A' coefficients in the IR means that the technique is limited only to species with large vibrational and rotational quanta, namely hydrides. Consequently the vast majority of this research has been devoted to the reactions

\[ \text{H} + \text{XY} \rightarrow \text{HY} + \text{Y} \text{ or } \text{HY} + \text{X} \]

\[ \text{X} + \text{HY} \rightarrow \text{HX} + \text{Y} \]

where X and Y are halogens. This is not a serious restriction however since there is intense interest in such reactions because of their chemical laser applications. In addition, the range of mass combinations displayed above means that quantitative comparisons with metathetical trajectory studies can be made. This is greatly facilitated by the tendency of these systems to be electronically adiabatic.

The main drawback of IRCL is that for low vibrational levels the precision is low (cascade effects are greatest) and for the zero-point level, no information can be gained unless self-absorption of the \( v = 1 \rightarrow v = 0 \) emission is studied. However, chemical laser methods, notably the grating-selection method\textsuperscript{56b}, can supply this information.
The whole field of IRCL has been reviewed by Campbell and Baulch and will not be detailed. One recent experiment of note however has produced evidence of two-sided attack in an \( H + XY \) reaction, one direct and one indirect\(^{57} \). The vibrational population distributions are seen to be bimodal with the low \( v \) peak corresponding to direct attack (repulsive energy release) and the high \( v \) peak arising from the migratory nature of the indirect reaction. Although eminently reasonable, the actual demonstration of bimodal mechanisms has proved very difficult to date due to "washing out" of the nascent product distributions by initial condition averaging and other analytical difficulties.

### 1.4 LASER INDUCED FLUORESCENCE

A complete list of all single collision systems studied by LIF is presented in Appendix 2. Like VCL, LIF requires a stable excited molecular state which must also be accessible by presently available lasers. Since the optical signal is related to populations and ultimately cross-sections in both cases, interest is confined almost exclusively to diatomic products. Polyatomic molecules are very poorly characterised at the quantitative level required by LIF (some exceptions exist eg. \( \text{NH}_2 \)) and in addition are prone to radiationless processes which makes population analysis untenable. However, \( \text{Ca}, \text{Sr} \) and \( \text{Ba} \) cyanides produced in the \( M + \text{BrCN} \) reactions have been studied subject to the limited spectroscopic information\(^{58} \). The tightly bound \( \text{CN}^- \) ion could be treated as a single particle with properties similar to halide ions. Indeed, this similarity is nearly complete except for the \( C \) states\(^{58} \).
At the other extreme, Polanyi's group have recently used atomic fluorescence excited by a complex vacuum-U.V. laser whose output, tunable from 140 - 160 nm, was produced by resonantly enhanced 4-wave mixing in Mg or Sr vapour. The reaction studied here was

$$R8: \ H(D) + Br_2 \rightarrow HBr(DBr) + Br$$

and the variation in $Br^*$ emission with collision energy gave directly the excitation function for the reaction (this is not so easily derived from molecular fluorescence). From this study, R8 appeared to have no threshold thereby setting an upper limit of 1 k. cal. mol$^{-1}$ for the activation energy. The most important outcomes however were the agreement with previous trajectory studies and the demonstration of a purely mechanical mass effect (ie. H or D). Both vindicated the classical trajectory technique.

Breakdown of the reactions studied by LIF is simpler than for VCL. The early studies with the exception of the $H + NO_2$ system were exclusively of group 2A metal salts, particularly Ba salts. Since 1977, the field has flourished and the group 3B metal oxides have been investigated in various reactions. More recently yet, reactions of F, O and Yb atoms have been studied. In the vast majority of cases, the excitation laser has been pulsed but within the last 2 years, five reactions using CW excitation have been reported. It is notable that no reports involving alkali atom or dimer reactions have appeared, this being a reflection of the unsuitability of alkali halide excited states for quantitative LIF.
On a cautionary note, Farrar and Lee have criticised the ability of LIF to provide detailed cross-sections. Since the technique measures number density and not flux (to which cross-sections and hence rate constants are related) it is always desirable to draw on velocity/angle contour maps to effect the transformation to flux. However, for the majority of reactions studied by LIF to date these have not been available and the approximation

\[ F = n \bar{v} \quad F = \text{flux} \]
\[ n = \text{no. density} \]
\[ \bar{v} = \text{mean (lab) velocity} \]

\[ \text{......................... (1.2)} \]

has been used with \( \bar{v} \) corresponding to the most probable Newton diagram. If the reaction has appreciable activation energy then this relation would be clearly inappropriate in the threshold region which often arises for thermal beams. Even if angular distributions are established the transformation is complicated by the presence of two contributory branches at each LAB angle whose relative importance is a strong function of scattering angle as a consequence of the transformation Jacobian. Further uncertainty arises from the spread in centroid vectors which further highlights the importance of using beams with low velocity and angular spreads especially in reactions of modest exoergicity.
The state of the art in LIF has been reviewed up to January 1977. Accordingly, systems discussed therein will not be considered below unless necessitated by comparison. In addition, purely spectroscopic and beam diagnostic applications of the technique will not be discussed.

1.4.1 REACTIONS OF GROUP 2A METALS

These are summarised below in Table 1.3:

<table>
<thead>
<tr>
<th></th>
<th>CX₄</th>
<th>CHₓ₃</th>
<th>CH₂X₂</th>
<th>CHₓX</th>
<th>CFₓX</th>
<th>CCₓ₂X</th>
<th>HX</th>
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<td>Sr, Sr*</td>
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</tbody>
</table>

Table 1.3 Reactions of group 2A metals - *~ excited atomic reactant.
A: Reactions with substituted halomethanes

Along the Br row of Table 1.3 there is some disagreement regarding energy disposal. Rommel and Schultz\textsuperscript{74} have reported a convincing trend towards high BaBr vibrational excitation with increasing N in CH\textsubscript{4-N}Br\textsubscript{N}, the distributions being decidedly non-statistical and heavily inverted. Similarly for CF\textsubscript{3}Br, Solarz and Johnson\textsuperscript{75} reported that 88\% of the available energy ended up in BaBr vibration in accord with the above trend. The explanation offered was that the halomethyl product retained its shape if completely halogenated whilst the CH\textsubscript{3} product suffered a change in geometry from pyramidal to planar thereby invoking the inversion vibrations to the detriment of the diatomic product excitation. In contrast, the reactions of F atoms with CH\textsubscript{3}I and CF\textsubscript{3}I\textsuperscript{76} exhibited very low vibrational excitation of IF (\(\tilde{f}_v = 0.15\) and 0.11 respectively) which the authors attributed to the low values of the CF\textsubscript{3} quanta with consequent ease of energy transfer. However, comparison with the K + CH\textsubscript{3}I/CF\textsubscript{3}I reactions indicate that an E-J mechanism would prevail for Ba + CF\textsubscript{3}Br whilst the CH\textsubscript{3}Br reaction would be covalent leading to repulsive energy release. The trend in the data is perhaps more reconcilable with a gradation from ionic (stripping) to covalent (rebound) dynamics. Indeed, the early work on Ba + CCl\textsubscript{4}\textsuperscript{77} suggests this since it displays a large cross-section, an inverted vibrational distribution with \(\tilde{f}_v = 0.75\) and a very "cold" rotational distribution all of which are consistent with a spectator stripping interaction. Similarly, the Ca + CCl\textsubscript{4} system studied by CW excitation displays strong vibrational inversion\textsuperscript{78a} as does the Sr + CCl\textsubscript{4} reaction\textsuperscript{75}. 
The sequence of reactions of Ba with CH$_2$I$_2$, CH$_3$I$^{79}$ and CF$_3$I$^{64, 80}$ displays trends similar to those of the brominated species. All show inverted vibrational distributions with $f_v$'s of 0.18, 0.29 and $\sim$ 0.7 respectively. The earlier bimodal distribution for the CF$_3$I reaction$^{64}$ has been disclaimed after re-analysis$^{80}$ and only the high quantum number peak remains. The interpretation of these trends assumes an E-J mechanism which is in the entrance channel for CF$_3$I and the exit channel for CH$_3$I leading to high internal excitation of the CH$_3$ fragment in a repulsive interaction. A general trend of all the ground state (atom) reactions is vibrational excitation of MX in the order Ba > Sr > Ca for a given collision partner as expected on the basis of an E-J mechanism. A similar mechanism is expected to apply to the Yb + CHBr$_3$ reaction recently reported$^{81}$.

B: Reactions with hydrogen halides

The ground state reactions of Ba + HX$^{82}$ indicate straightforward repulsive energy release which becomes slightly mixed with increasing halogen mass. The reaction cross-section correlates with the fraction of $E_{\text{tot}}$ into vibration; polarisability considerations suggest more attractive character with heavier halogen. The Ba + HI reaction appears to be inconsistent with the above but no explanation was given of this. The recent revision of the Ba - F and Ba - Cl bond energies$^{83}$ now indicates more mixed release in the HF/HCl reactions but it remains predominantly repulsive. Thus, since the H + H' L $\rightarrow$ HH' + L mass combination favours mixed release, it would appear that the surfaces themselves control the reaction character and that these are highly repulsive.
A contrasting situation arises for reactions with HF (v = 1) where the reactant is prepared by HF laser excitation\textsuperscript{84}. For Ba, the BaF product becomes more vibrationally excited some 57% of the excitation energy being retained in vibration. Overall, $f_v$ changes from 19% for $v = 0$ to 33% for $v = 1$ indicating more mixed release. This can be readily explained in terms of "corner cutting trajectories" where the reactant vibration enables the system to cross into the product valley "from the side".

For Ca and Sr, the reactions are endoergic with HF (v = 0) but exoergic with HF (v = 1) and the rate of reaction ratio\textsuperscript{85}, $k_{v=1} : k_{v=0}$, is $\sim 10^4$. This is to be expected since endoergic reactions have barriers in the exit channel which are more readily overcome by vibration. The partitioning of the exoergicity in these reactions is similar to that of Ba + HF (v = 1) with 30 - 40% in product vibration and slightly more in translation. This is similar to the alkali + HX cases in which most of the exoergicity ends up in product translation. The surfaces involved, although ionic, must be repulsive as for K + CH$_3$I with an electron jump in the exit channel.

More detailed dynamical information has recently been reported for this category. Karny and Zare\textsuperscript{86} established on two counts that for Sr + HF (v = 1) the preferred reaction geometry was bent. Firstly, the electric vector of the HF laser orientated the v = 1 molecules either parallel or perpendicular to the Ba beam with a larger signal for the latter and secondly, tuning the HF laser to populate J = 1, 2, 3 etc. also produced an increased signal with increasing J. This was the complete reverse of the findings of Brooks' group for the K + HCl (v = 1) reaction\textsuperscript{87} where the reactivity decreased with increasing J.
Neither effect can be statistical because of the small change in accessible phase space and must therefore be dynamic. If a preferred geometry for reaction does arise it seems that increasing J would reduce the probability of favourable orientation especially at low J. Thus the explanation of Brooks et al appears most plausible at this stage.

The relative efficacy of translational over vibrational energy in bringing about the endothermic Sr + HF (v = 0, I respectively) reaction has been investigated using a seeded HF beam. Contrary to expectation, the latter was only 1 - 10 times more effective in agreement with work on K + HCl. This was interpreted in terms of a mass effect since H + H'L → HH' + L is known to favour vibrational enhancement of endothermic reactions least. The skewed axes of this mass combination (see Chapter 4) tends to scramble V and T modes and promotes multiple "clouting" encounters. That phase space theory could account for the observations here substantiates this; the reaction mechanism, although by no means complex, exhibited highly snarled trajectories.

Similarly, for Ba + HF (v = 0), snarled trajectories were invoked to account for the low collision energy observations whilst at high energy the mechanism appeared to change to a classic rebound type. This was not seen in trajectory calculations on Ba + HCl, HBr where repulsive release was always the case. It was therefore speculated that although technically exoergic the Ba + HF barrier may still be in the exit channel since, referred to equilibrium potentials rather than zero-point levels, it was endoergic. In addition, the H + H'L mass combination is not entirely appropriate to Ba + HF.
Both factors detract from a model description of the system and, as such, a mixture of two energy dependent extremes is not unreasonable.

C: Reactions with excited atoms

The reactions of metastable Ba (3D, 1) and Sr (3P1) with halomethanes are surprising in their general lack of reactivity. Two striking exceptions arise in that with CH3Cl and CF3Cl, Ba (3D) does react but not Ba (1S0) or Sr (1S0, 3P). The simple E-J model predicts the reverse since Ba (3D) has a higher ionisation potential than Sr (3P). The detailed mechanisms are not simple but the similarity of the energy disposal to that in related reactions of ground state species suggests an attractive interaction. The apparently equal reactivity of the Ba* spin-orbit states is accounted for in terms of covalent + ionic surface crossings at the same radius, unlike in Hg*.

Further contrast is provided by the reactions

R9: Sr* (3P1) + HF, HCl → SrF, SrCl + H

in which electronic excitation of Sr bestows reactivity on otherwise endoergic systems. The vibrational disposal in SrF is highly inverted and very narrow (v = 26 - 31) accounting for 70% of E_tot whilst for SrCl the figure is 40%. Both are considerably more vibrationally excited from the Ba + HX ground state reactions which the authors attribute to the more attractive nature of the triplet surface combined with its ability to adiabatically mix in ionic character.
The only other report concerning excited species\textsuperscript{122} discusses the reactions

\[
\text{Ca}^* (^3P) + \text{O}_2, \text{CO}_2 \rightarrow \text{CaO} (X, A', a) + \text{O, CO}
\]

which present yet another theoretical challenge. For the \text{O}_2 case, the branching ratio for excited state (A', a) formation over ground state (X) is \(\sim 2\) whilst that for \text{CO}_2 is \(\sim 0.3\). Both results, whilst subject to considerable uncertainty, imply highly non-statistical energy partitioning in contrast to the \text{Ba} (^1S_o) + \text{O}_2, \text{CO}_2 reactions which are confidently expected to proceed \textit{via} long-lived-complex formation\textsuperscript{92}. Likewise, the spin-forbidden reaction

\[
\text{Ba} (^1S_o) + \text{SO}_2 (^1A_1) \rightarrow \text{BaO} (^1\Sigma^+) + \text{SO} (^3\Sigma^-)
\]

has been shown\textsuperscript{93-95} to proceed by complex dynamics with near statistical partitioning at thermal energies. However, its cross-section is much higher than for \text{Ba} + \text{CO}_2, \text{O}_2 being \(\sim 70\) \(\text{A}^2\), symptomatic of a long-range E-J mechanism with a facile singlet \(\rightarrow\) triplet crossover due to spin-adiabaticity relaxation\textsuperscript{136}.

On the basis of the \text{Ba} + \text{O}_2, \text{CO}_2, \text{SO}_2 results, an ionic mechanism with ensuing complex dynamics would be expected \textit{a priori} for the \text{Ca}^* reactions (although Solarz and Johnson found otherwise\textsuperscript{75}). The detailed nature of the potential surfaces sampled in these reactions may well hold the key to their differing dynamics. Indeed, some hint of this has already been given in Herm \textit{et al}\textsuperscript{93} who reported an anomalous dependence of angular distribution on kinematics and the possible existence of a singlet \(\rightarrow\) triplet threshold.
1.4.2 OXIDATIONS OF GROUP 3B METALS; Y, Sc + O₂, NO, SO₂

The group 3B metal monoxides are isoelectronic with the 2A monohalides and exhibit similar spectroscopic properties. They are therefore eminently suitable for LIF detection because of their high "A" coefficients and, unlike the 2A monohalides, their rotationally resolved spectra.

The use of computer simulation of the spectra both in LIF and VCL has been emphasised by Parson's group. The results are necessarily non-unique but physical intuition overcomes this and by demonstrating insensitivity to dynamic and kinematic variations, considerable confidence can be placed in this approach. Thus, for the above reactions, the simulations are invariant with angular scattering assumptions and in close agreement with the data. Further, the NO and SO₂ cases give rise to statistical rotational distributions whilst the O₂ reactions are decidedly "cold"; in all cases, the vibrational distributions were statistical. Analysis of the O₂ system using dynamically constrained phase-space theories suggest that it is not angular momentum constrained. It is therefore concluded that the NO, SO₂ reactions proceed by complex formation whilst for O₂ the mechanism is direct. However, VCL work suggests that the excited monoxides display statistical dynamics. This is another indication of "hermaphroditism" in that the excited state follows complex dynamics whilst the ground state proceeds directly.
1.4.3 REACTIONS OF METALS WITH ORGANIC MOLECULES

The fluorescence spectra of organic species are generally confined to condensed phases which prejudices their application in single collision LIF. However, reactions of these molecules with metals leading to metal salt formation can directly provide information on their reaction dynamics. The example of the re-arrangement of the o-tolyl radical\(^{98}\) is exceptional since the resulting benzyl radical is known spectroscopically from flash photolysis. Thus, Ba reacts with both benzyl chloride \((C_6H_5.CH_2.Cl)\) and o-, m-, p- chlorotoluene \((C_6H_4.Cl.CH_3)\) to yield BaCl with roughly the same internal excitation in each case. However, the greater exoergicity of the former means that the benzyl radical must take up more energy either collisionally or internally. In addition, the non-appearance of a benzyl radical spectrum for the meta and para reactions indicates inability of these systems to transfer an H-atom to the site vacated by Cl. This is seen\(^ {98}\) to be due to an activation barrier to migration which is small but significant in the ortho case. There is, however, some danger in making an interpretation based on relative intensities (as was done here) since the organic radicals may well be subject to variable radiationless deactivation even in the gas phase.

In another report\(^ {99}\) the problem of replacement of H-atoms by alkyl groups and its effect on reactivity has been addressed together with that of concerted abstraction processes - an essential mechanism in organic chemistry. For the sequence of reactions
R: 12  Sc, Y, La + H - OH, R - OH
       → ScO, Yo, LaO + products
R = CH$_3$, C$_2$H$_5$, iso - C$_3$H$_7$, n - C$_3$H$_7$

the most striking observation is that the metal oxide is formed in abundance (the hydroxide could be formed but be undetectable). The reaction cross-section for H$_2$O is substantially higher than for D$_2$O for all metals, and for Yo, the H$_2$O and D$_2$O cross-sections are decidedly larger than for R-OH especially CH$_3$OH.

The formation of oxide only from H$_2$O and D$_2$O is interpreted in terms of a more facile redistribution of electron density from both OH bonds to the O-atom. Excitation of asymmetric vibrations is more difficult than for the symmetric ones and, in addition, results in electron density being concentrated in the OH bond which is not conducive to oxide or hydroxide formation.

The alcohol reactions are expected to proceed via a ring mechanism

R: 13  H
      \  C - C - O + M → MO + H$_2$ + C - C
      /   H

with concerted bond formation to form products. This would explain the vastly higher cross-sections for the C$_2$ and C$_3$ groups since for CH$_3$OH this mechanism would be sterically hindered. The internal state
distributions of MO imply that the iso-C$_3$H$_7$OH reaction proceeds by a similar mechanism to that of C$_2$H$_5$OH but markedly different than the n-C$_3$H$_7$OH case which appears to proceed via 6-membered ring formation which closes to produce cyclopropane. All of the proposed mechanisms are supported by surprisal analyses with prior distributions corresponding to expected products.

Continuing this work, Liu and Parson$^{100}$ have studied the corresponding carbonyl and carboxylic acid oxygen atom abstractions. The outstanding feature of this series is the "coldness" of the rotational distributions compared to prior distributions for both ground and excited state diradical formation. The occurrence of the most exoergic pathway was rejected since this would have resulted in vibrationally "hot" distributions unlike those observed which resembled the prior distributions.

The reaction dynamics here, by comparison with other 3B oxidations, are most likely to be complex - a direct mechanism would yield "hotter" than statistical distributions rather than the reverse. Despite considerable interpretative uncertainty, the authors propose a complex mechanism with both exit and entrance channel dynamical constraints to account for cross-section variations and apparently repulsive release.
The OH radical lends itself very well to LIF detection since its spectrum is well resolved due to its high rotational and vibrational quanta and well characterised as a consequence of its atmospheric and astrophysical importance.

Two studies of the H + NO₂ reaction have been reported [60, 101] which arrive at significantly different conclusions regarding the dynamics. Although the LIF evidence was not unambiguous, the respective groups based their ultimate conclusions on the molecular beams studies of Haberland et al. [102] which changed from forward peaking to isotropic when a simultaneous velocity/angle analysis was made (sic). The later LIF study [102] was able to resolve contributions from Λ-doublet states which proved to be essential to the vibrational populations and energy partitioning. In addition, the higher quality of the data for OH (v = 1) showed both vibrational levels (v = 0, 1) to have the same rotational surprisal. The effect of these was to reduce the energy partitioning to values more attributable to complex dynamics. By using seeded supersonic beams to rotationally cool the NO₂, no difference was seen from the "hot" case indicating freedom from entrance channel effects. This exercise also yielded $\tilde{r}_{\text{rot}}$ and $\tilde{r}_{\text{vib}}$ for the NO product since the products' rotational angular momenta were constrained to be antiparallel.
The dynamics were therefore shown to be complex by energetic considerations. This was strongly supported by the \( \Lambda \)-doublet populations which for planar complexes correlating with HONO (\(^1A'\)) would favour \( \Pi^+ \) over \( \Pi^- \). Thus, although a complex model accounted for Haberland's results\(^{102b} \) and most of the IBM results\(^{101} \), the authors pointed out that the energy partitioning was somewhat less than statistical. The idea of separate time constants for angular and energy randomisation proposed by Zare\(^{63} \) is brought to mind once more.

The other reaction studied by the IBM group replaced NO\(_2\) by C\(_2\)\(_3\). The \( \Lambda \)-doublets were again produced unstatistically implying a planar intermediate but the energy partitioning was expressly non-statistical. The qualitative similarity to the H + NO\(_2\) system in combination with the dissimilarity to H + O\(_3\) led the authors\(^{101} \) to propose a stable HOC\(_3\)O intermediate which has yet to be experimentally verified.

A completely different approach to OH formation involving abstraction of H-atoms in saturated hydrocarbons by atomic oxygen, O (\(^3P\)), has recently been reported\(^{103} \). The rates of these reactions were small indicating small but effective barriers and abstraction, although predominant, was not the only mechanism. Variation of the environment of the H-atom was seen to markedly alter the OH vibrational disposal. Thus, primary H-atom abstraction led exclusively to OH (\( v = 0 \)); secondary, to OH (\( v = 0, 1 \)) in roughly equal proportions and tertiary, to OH (\( v = 1 \)) exclusively. Further, only a small fraction of the exoergicity was channelled into the organic radical product. Modelling
these systems using classical trajectories was seen to be quite successful if a 3-body (R, H, O) interaction on LEPS surfaces which differed only in the R-H bond dissociation energy adopted.

1.4.5 F-ATOM REACTIONS WITH IODIDES

The exemplary work of Clyne et al.\textsuperscript{104} on the spectroscopy of the IF molecule has made study of this sequence of reactions possible. Unlike the other interhalogens, IF is relatively free from predissociation and is a strong emitter. Its absorptions extend from ~450 - 650 nm which can be readily covered by CW dye lasers.

A complete study of the F + CH\textsubscript{3}I, CF\textsubscript{3}I reactions has been made by the Garching group \textsuperscript{105} as well as a brief report on the F + IC\textsubscript{2} reaction \textsuperscript{78b}. A more restricted study of the F + I\textsubscript{2} reaction has been made using pulsed excitation \textsuperscript{106}. Unfortunately, excitation here above 500 nm was precluded in the latter work because of I\textsubscript{2} fluorescence which could not be easily removed.

The reactions with CH\textsubscript{3}I and CF\textsubscript{3}I yielded IF internal distributions in agreement with those expected assuming a long-lived complex. This was seen to agree with earlier crossed-beams results by Lee's group \textsuperscript{107}. The low vibrational partitioning with CF\textsubscript{3}I is in contrast to the reactions Ba + CF\textsubscript{3}I \textsuperscript{64}, CC\textsubscript{2} \textsubscript{4}, \textsuperscript{77, 75, 78a}, CBr\textsubscript{4} \textsuperscript{74} and Yb + CHBr\textsubscript{3} \textsuperscript{81} and strengthens the complex argument. The slightly lower \( f_v \) (IF) for CF\textsubscript{3}I is probably due to more facile energy transfer to CF\textsubscript{3} inversion vibrations in the complex.
In complete contrast, the $F + I_2$ \cite{106}, IC\textsubscript{2} \cite{78b} reactions proceed directly and exhibit strong vibrational inversion. The existence of a weakly bound $FI_2$ species by Lee's group \cite{108} is likely to create an attractive surface for this reaction. However, as demonstrated below, (see Chapter 4) direct dynamics are not essential for producing vibrational inversions (see also reference \citenum{57}). Similar remarks apply to the IC\textsubscript{2} reaction but the cross-section here is not likely to be as large since $F–Cl–I$ approaches would, on a molecular orbital basis, be repulsive.

1.4.6 MISCELLANEOUS

The reaction $A\lambda + O_2 \rightarrow A\lambda O + O$ has been repeated \cite{109} using time-of-flight LIF \cite{110}. The first report here \citenum{68} suffered deductive uncertainty because the collision energy spread was comparable to the exoergicity. Unfortunately, the TOF work still suffered since intensity considerations mandated a beam-gas arrangement. Nonetheless, it was seen that both vibrational and rotational excitation increased with collision energy. The fraction of $E_{\text{tot}}$ into vibration was $\sim 20\%$ throughout whilst rotation accounted for $30\%$. This disposal is curious since it cannot be reconciled with the Polanyi classifications. A recent quantum mechanical model \cite{111} which exhibited similar characteristics on an attractive surface was therefore invoked to explain the observations and the authors tentatively established that, on the basis of Walsh's rules, the $A\lambda + O_2$ interactions could not be repulsive.
In summary, the $\text{Al} + \text{O}_2$ reaction and others could be interpreted with much greater confidence if tighter control on experimental variables is made. In addition, much benefit would accrue from supporting angle/velocity maps from crossed beams studies.
### APPENDIX 1 - CHEMILUMINESCENT REACTIONS UNDER SINGLE COLLISION CONDITIONS

<table>
<thead>
<tr>
<th>#</th>
<th>REACTANTS</th>
<th>PRODUCTS</th>
<th>REFS.</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>$A^0 + O_3$</td>
<td>$A^0O^* + O_2$</td>
<td>112</td>
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<tr>
<td>2</td>
<td>$B + N_2O$</td>
<td>$BO^* + N_2$</td>
<td>49, 50</td>
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<tr>
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<td>$Ba^* + Br_2$</td>
<td>$BaBr^* + Br$</td>
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<td>5</td>
<td>$Ba + Cl_2$</td>
<td>$BaCl^* + Cl$</td>
<td>29, 30, 114-116</td>
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<td>6</td>
<td>$Ba, Ba^* + F_2$</td>
<td>$BaF^* + F$</td>
<td>19, 39</td>
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<td>7</td>
<td>$Ba + I_2$</td>
<td>$BaI^* + I$</td>
<td>113, 117</td>
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<td>8</td>
<td>$Ba + ClO_2$</td>
<td>$BaO^* + ClO$</td>
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<td>9</td>
<td>$Ba + O_3$</td>
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<td>12</td>
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<td>$S_2^* + BaCl_2$</td>
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<td>$BaCl^* + S_2Cl$</td>
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<tr>
<td>13</td>
<td>$Br + K_2$</td>
<td>$K^* + KBr$</td>
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<td>14</td>
<td>$Br + Na_2$</td>
<td>$Na^* + NaBr$</td>
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<td>15</td>
<td>$Br + Rb_2$</td>
<td>$Rb^* + RbBr$</td>
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<td>16</td>
<td>$C_2^* + NO$</td>
<td>$CN^* + CO$</td>
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<td>17</td>
<td>$Ca + Br_2$</td>
<td>$CaBr^* + Br$</td>
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<td>$CaCl^* + O_2$</td>
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<td>20</td>
<td>$Ca^* + CO_2$</td>
<td>$CaO^* + CO$</td>
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<tr>
<td>21</td>
<td>$Ca, Ca^* + F_2$</td>
<td>$CaF^* + F$</td>
<td>19, 39</td>
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</table>
22. \( \text{Ca}^* + \text{HCle} \rightarrow \text{CaCl}^* + \text{H} \)
23. \( \text{Ca} + \text{N}_2\text{O} \rightarrow \text{CaO}^* + \text{N}_2 \)
24. \( \text{Ca} + \text{NO}_2 \rightarrow \text{CaO}^* + \text{NO} \)
25. \( \text{Ca}^* + \text{O}_2 \rightarrow \text{CaO}^* + \text{O} \)
26. \( \text{Ca} + \text{S}_2\text{Cl}_2 \rightarrow \text{S}_2^* + \text{CaCl}_2 \)
27. \( \text{Cl} + \text{K}_2 \rightarrow \text{K}^* + \text{KCl} \)
28. \( \text{Cl} + \text{Na}_2 \rightarrow \text{Na}^* + \text{NaCl} \)
29. \( \text{Cl} + \text{Rb}_2 \rightarrow \text{Rb}^* + \text{RbCl} \)
30. \( \text{Cs}_2 + \text{Br}_2 \rightarrow \text{CsBr}^* + \text{CsBr} \)
31. \( \text{Cs}_2 + \text{Cl}_2 \rightarrow \text{CsCl}^* + \text{CsCl} \)
32. \( \text{Cs}_2 + \text{ClF} \rightarrow \text{CsCl}^* + \text{CsF} \)
33. \( \text{Cs}_2 + \text{ICl} \rightarrow \text{CsI}^* + \text{CsCl} \)
34. \( \text{Cs}_2 + \text{IBr} \rightarrow \text{CsI}^* + \text{CsBr} \)
35. \( \text{Cs}_2 + \text{I}_2 \rightarrow \text{CsI}^* + \text{CsI} \)
36. \( \text{Cs}_2 + \text{F} \rightarrow \text{Cs}^* + \text{CsF} \)
37. \( \text{Eu} + \text{O}_3 \rightarrow \text{EuO}^* + \text{O}_2 \)
38. \( \text{Eu} + \text{N}_2\text{O} \rightarrow \text{EuO}^* + \text{N}_2 \)
39. \( \text{Eu} + \text{NO}_2 \rightarrow \text{EuO}^* + \text{NO} \)
40. \( \text{Eu} + \text{F}_2 \rightarrow \text{EuF}^* + \text{F} \)
41. \( \text{H} + (\text{NO})_2 \rightarrow \text{HNO}^* + \text{NO} \)
42. \( \text{H} + \text{Li}_2 \rightarrow \text{Li}^* + \text{LiH} \)
43. \( \text{Hg}^* + \text{Br}_2 \rightarrow \text{HgBr}^* + \text{Br} \)
44. \( \text{Hg}^* + \text{CCl}_4 \rightarrow \text{HgCl}^* + \text{CCl}_4 \)
45. \( \text{Hg}^* + \text{CHCl}_3 \rightarrow \text{HgCl}^* + \text{CCl}_3 \)
46. \( \text{Hg}^* + \text{Cl}_2 \rightarrow \text{HgCl}^* + \text{Cl} \)
47. \( \text{Ho} + \text{N}_2\text{O} \rightarrow \text{HoO}^* + \text{N}_2 \)
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<tr>
<th>Reaction</th>
<th>Products</th>
<th>Refs</th>
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<td>48. I + K₂</td>
<td>K⁺ + KI</td>
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<td>IF⁺ + IF</td>
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<td>50. I₂⁺ + In</td>
<td>In⁺⁺ + I</td>
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<td>51. I₂⁺ + Tl</td>
<td>Tl⁺⁺ + I</td>
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<td>52. K₂ + Br₂</td>
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<td>63. La + NO₂</td>
<td>LaO⁺⁺ + NO⁻</td>
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<td>64. La + N₂O</td>
<td>LaO⁺⁺ + N₂⁻</td>
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<td>66. Mg + ClO₂</td>
<td>MgO⁺ + ClO⁻</td>
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<td>67. Mg, Mg⁺⁺ + F₂</td>
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<td>69. Na₂ + Cl₂</td>
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<td>70. NO⁺ + O₃</td>
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71. $O + NO \rightarrow NO_2^*$ 28
72. $O + (NO)_2 \rightarrow NO_2^* + NO$ 27
73. $O_2^* + R_1R_2C=CR_3R_4 \rightarrow R_1R_2CO^* + R_3R_4CO$ 31
74. $Pb + N_2O \rightarrow PbO^* + N_2$ 130
75. $Pb + O_3 \rightarrow PbO^* + O_2$ 131
76. $Rb_2 + Br_2 \rightarrow RbBr^* + RbBr$ 35, 36, 121, 124
77. $Rb_2 + Cl_2 \rightarrow RbCl^* + RbCl$ 36, 124
78. $Rb_2 + ClF \rightarrow RbCl^* + RbF$ ” ”
79. $Rb_2 + IC\ell \rightarrow RbI^* + RbCl$ ” ”
80. $Rb_2 + IBr \rightarrow RbI^* + RbBr$ ” ”
81. $Rb_2 + I_2 \rightarrow RbI^* + RbI$ ” ”
82. $Sc + F_2 \rightarrow ScF^* + F$ 128
83. $Sc + ClF \rightarrow ScCl^* + F$ ” ”
84. $Sc + SF_6 \rightarrow ScF^* + SF_5$ ” ”
85. $Sc + Cl_2 \rightarrow ScCl^* + Cl$ ” ”
86. $Sc + NO_2 \rightarrow ScO^* + NO$ 51, 54
87. $Sc + N_2O \rightarrow ScO^* + N_2$ ” ”
88. $Sc + O_3 \rightarrow ScO^* + O_2$ ” ”
89. $Sc + O_2 \rightarrow ScO^* + O$ 52-54, 132
90. $Sm + O_3 \rightarrow SmO^* + O_2$ 125
91. $Sm + N_2O \rightarrow SmO^* + N_2$ 125, 133
92. $Sm + NO_2 \rightarrow SmO^* + NO$ 125
93. $Sm + F_2 \rightarrow SmF^* + F$ 125
94. $Sr, Sr^* + F_2 \rightarrow SrF^* + F$ 19, 39
95. $Sr + NO_2 \rightarrow SrO^* + NO$ 42
96. $Sr + N_2O \rightarrow SrO^* + N_2$ 42, 46
97. $Sr + S_2Cl_2 \rightarrow S_2^* + SrCl_2$ 48
+ $SrCl^* + S_2Cl$ ”
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<th>Reaction</th>
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<th>products</th>
<th>References</th>
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<td>99. Sr + Cl₂O₂</td>
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<td>SrCl₂* + O₂</td>
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<td>101. Ti* + N₂O</td>
<td>TiO₂* + N₂</td>
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<td>102. Ti* + O₂</td>
<td>TiO₂* + O</td>
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<td>103. Xe* + Br₂</td>
<td>XeBr₂* + Br</td>
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<td>XeBr₂* + CN</td>
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<td>XeCl₂* + CCl₃</td>
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<td>106. Y + F₂</td>
<td>YF₂* + F</td>
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<td>107. Y + Cl₂F</td>
<td>YCl₂* + F</td>
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<td>108. Y + SF₆</td>
<td>YF₂* + SF₅</td>
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<td>109. Y + Cl₂</td>
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<td>110. Y + NO₂</td>
<td>YO₂* + NO</td>
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<td>111. Y + N₂O</td>
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<td>112. Y + O₃</td>
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<td>113. Y + O₂</td>
<td>YO₂* + O</td>
<td>52-54, 132</td>
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# APPENDIX 2 - REACTIONS STUDIED BY LASER INDUCED FLUORESCENCE UNDER SINGLE COLLISION CONDITIONS

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<tr>
<th>Reactants</th>
<th>Products</th>
<th>Refs.</th>
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<tbody>
<tr>
<td>1. Al + O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>AlO + O</td>
<td>68, 109</td>
</tr>
<tr>
<td>2. Ba + BrCN</td>
<td>BaBr + CN</td>
<td>58</td>
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<tr>
<td></td>
<td>BaCN + Br</td>
<td></td>
</tr>
<tr>
<td>3. Ba + CBr&lt;sub&gt;4&lt;/sub&gt;</td>
<td>BaBr + CBr&lt;sub&gt;3&lt;/sub&gt;</td>
<td>74</td>
</tr>
<tr>
<td>4. Ba, Ba* + CCl&lt;sub&gt;3&lt;/sub&gt;F</td>
<td>BaCl + CCl&lt;sub&gt;2&lt;/sub&gt;F</td>
<td>75</td>
</tr>
<tr>
<td>5. Ba, Ba* + CCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>BaCl + CCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>75, 77</td>
</tr>
<tr>
<td>6. Ba + CHBr&lt;sub&gt;3&lt;/sub&gt;</td>
<td>BaBr + CHBr&lt;sub&gt;2&lt;/sub&gt;</td>
<td>74</td>
</tr>
<tr>
<td>7. Ba + CH&lt;sub&gt;2&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>BaBr + CH&lt;sub&gt;2&lt;/sub&gt;Br</td>
<td>74</td>
</tr>
<tr>
<td>8. Ba + CH&lt;sub&gt;2&lt;/sub&gt;I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>BaI + CH&lt;sub&gt;2&lt;/sub&gt;I</td>
<td>69, 79</td>
</tr>
<tr>
<td>9. Ba, Ba* + CH&lt;sub&gt;3&lt;/sub&gt;F</td>
<td>BaF + CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>75</td>
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<td>10. Ba, Ba* + CH&lt;sub&gt;3&lt;/sub&gt;Cl</td>
<td>BaCl + CH&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>11. Ba, Ba* + CH&lt;sub&gt;3&lt;/sub&gt;Br</td>
<td>BaBr + CH&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>12. Ba + CH&lt;sub&gt;3&lt;/sub&gt;I</td>
<td>BaI + CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>69, 79</td>
</tr>
<tr>
<td>13. Ba + C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Cl</td>
<td>BaCl + C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>98</td>
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<tr>
<td>14. Ba + o-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>BaCl + C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>15. Ba + m-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>BaCl + C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>16. Ba + p-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>BaCl + C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>17. Ba + CF&lt;sub&gt;3&lt;/sub&gt;I</td>
<td>BaI + CF&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>18. Ba + CF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>BaF + CF&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>19. Ba + CF&lt;sub&gt;3&lt;/sub&gt;Cl</td>
<td>BaCl + CF&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>20. Ba + CF&lt;sub&gt;3&lt;/sub&gt;Br</td>
<td>BaBr + CF&lt;sub&gt;3&lt;/sub&gt;</td>
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**Refs.**: 68, 74, 75, 77, 69, 79, 98
21. Ba + CO₂ → BaO + CO  67, 92, 94
22. Ba + DCl → BaCl₂ + D  82
23. Ba + HBr → BaBr₂ + H  69, 82
24. Ba + HCl₂ → BaCl₂ + H  69, 82
25. Ba + HF → BaF₂ + H  82, 84, 89
26. Ba + HI → BaI₂ + H  82
27. Ba + KCl → BaCl₂ + K  63
28. Ba + LiCl → BaCl₂ + Li  62
29. Ba + O₂ → BaO + O  2, 92
30. Ba + SF₆ → BaF₂ + SF₅  69
31. Ba + SO₂ → BaO₂ + SO  78c, 94, 95
32. Ca + BrCN → CaBr + CN  58
→ CaCN + Br
33. Ca⁺ + CO₂ → CaO + CO  122
→ CaO⁺ + CO
34. Ca⁺ + O₂ → CaO₂ + O  122
→ CaO⁺ + O
35. Ca + CCl₄ → CaCl₂ + CCl₃  78a
36. Ca + DF → CaF + D  85
37. Ca + HBr → CaBr₂ + H  69
38. Ca + HCl₂ → CaCl₂ + H  69
39. Ca + HF → CaF₂ + H  85
40. Ca + NaCl → CaCl₂ + Na  65
41. D + Br₂ → Br + DBr  59
42. F + CH₃I → IF + CH₃  76, 78b
43. F + CF₃I → IF + CF₃  78b
44. F + Cl₂ → IF + Cl₂  78b
45. F + I₂ → IF + I  106
46. \( H + CO_2 \rightarrow OH + CO \) 101
47. \( H + NO_2 \rightarrow OH + NO \) 60, 73, 101, 134, 135
48. \( H + Br_2 \rightarrow Br + HBr \) 59
49. \( La + H_2O \rightarrow LaO + H_2 \) 99
50. \( La + D_2O \rightarrow LaO + D_2 \) 99
51. \( La + RO \rightarrow LaO + R \) 100
52. \( La + ROH \rightarrow LaO + RH \) 99, 100
53. \( O + CS_2 \rightarrow CS + SO \) 70
54. \( O + RH \rightarrow OH + R \) 103
55. \( Sc + H_2O \rightarrow ScO + H_2 \) 99
56. \( Sc + D_2O \rightarrow ScO + D_2 \) 99
57. \( Sc + RO \rightarrow ScO + R \) 100
58. \( Sc + ROH \rightarrow ScO + RH \) 99, 100
59. \( Sc + O_2 \rightarrow ScO + O \) 96
60. \( Sc + NO \rightarrow ScO + N \) "
61. \( Sc + SO_2 \rightarrow ScO + SO \) "
62. \( Sr + BrCN \rightarrow SrBr + CN \) 58
\[ \rightarrow SrCN + Br \] "
63. \( Sr, Sr^* + CCl_4 \rightarrow SrCl + CCl_3 \) 75
64. \( Sr, Sr^* + CCl_3F \rightarrow SrCl + CCl_2F \) "
65. \( Sr, Sr^* + CH_3F \rightarrow SrF + CH_3 \) "
66. \( Sr, Sr^* + CH_3Cl \rightarrow SrCl + CH_3 \) "
67. \( Sr, Sr^* + CH_3Br \rightarrow SrBr + CH_3 \) "
68. \( Sr + CH_3I \rightarrow SrI + CH_3 \) 69
69. \( Sr, Sr^* + CF_4 \rightarrow SrF + CF_3 \) 75
70. \( Sr, Sr^* + CF_3Cl \rightarrow SrCl + CF_3 \) "
71. \( Sr, Sr^* + CF_3Br \rightarrow SrBr + CF_3 \) "
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
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<tr>
<td>72. Sr + DF⁺</td>
<td>SrF + D</td>
</tr>
<tr>
<td>73. Sr + HBr</td>
<td>SrBr + H</td>
</tr>
<tr>
<td>74. Sr + HCl</td>
<td>SrCl + H</td>
</tr>
<tr>
<td>75. Sr, Sr* + HF⁺</td>
<td>SrF + H</td>
</tr>
<tr>
<td>76. Y + O₂</td>
<td>YO + O</td>
</tr>
<tr>
<td>77. Y + NO</td>
<td>YO + N</td>
</tr>
<tr>
<td>78. Y + SO₂</td>
<td>YO + SO</td>
</tr>
<tr>
<td>79. Y + ROH</td>
<td>YO + RH</td>
</tr>
<tr>
<td>80. Y + RO</td>
<td>YO + R</td>
</tr>
<tr>
<td>81. Yb + CHBr₃</td>
<td>YbBr + CHBr₂</td>
</tr>
</tbody>
</table>

**NOTES**

(1) Probed product is listed first.
(2) If both products can be probed, those actually probed are underlined.
(3) '*' ~ excited atomic reactant or molecular product.
(4) '+' ~ vibrationally excited reactant.
CHAPTER ONE

REFERENCES

   (b) M.R. Levy, Prog. Reaction Kinetics, 10, 1, (1979).


(b) L. Stein, J. Wanner, H. Figger and H. Walther, ibid, p. 232.

(c) R. Discherl and H.U. Lee, ibid, p. 239.

(b) Same authors, ibid., 16, 124, (1976).


88. A. Gupta, D.S. Perry and R.N. Zare, J. Chem. Phys., to be published.

89. A. Gupta, D.S. Perry and R.N. Zare, J. Chem. Phys., to be published.


(b) See also ref. 78c.


(b) H. Haberland - private communication to Mariella et al, cited in ref. 101.


CHAPTER 2

LASER INDUCED FLUORESCENCE FROM CROSSED BEAM REACTIVE SCATTERING
CHAPTER 2

LASER INDUCED FLUORESCENCE FROM CROSSED BEAM REACTIVE SCATTERING

2.1 GENERAL INTRODUCTION

Since the first L.I.F. review\(^1\) much progress in this technique has been made with extension to angular distributions and to velocity resolution. The state of the art up to 1977 has been reviewed by Kinsey\(^2\) who categorised areas of interest into four groups:

1. Beam - beam total
2. Beam - beam differential
3. Beam - gas total
4. Fourier Transform Doppler Spectroscopy (FTDS)

Since then, FTDS has been accomplished although with limited success\(^3\) and categories 1 and 3 remain predominant. The most notable advance since 1977 has been the more widespread use of continuous-wave (C.W.) dye lasers in place of the "traditional" \(\text{N}_2\) laser pumped dye laser and preliminary accounts of this approach are given in Reference 4. Much of the early spectroscopic interest has now lost ground in favour of only dynamical interest, at least in molecular beams systems. The wealth of detailed spectroscopic information which the technique is capable of producing seems to be back in the physicists' hands\(^5\) whilst molecular spectroscopy is ordinarily confined to discharge flow systems using pseudo molecular beam sampling techniques.
A measure of the progress made is afforded by the reported sensitivity of the technique. Recently, LIF has been used to characterise the reactions of H-atoms with NO$_2$ and ClO$_2$. The minimum detectable OH concentration here was cited as $5 \times 10^3$ cm$^{-3}$ in a single resolvable $(v, J)$ quantum state corresponding to only 50 molecules in the intersection zone of the three beams. This is a factor of ten more sensitive than reported for BaO from Ba + O$_2$. However, the actual improvement in sensitivity exceeded this since OH is a decidedly poorer emitter and absorber than BaO.

Perhaps more striking than this is the claim of $10^2$ cm$^{-3}$ sensitivity by the Garching group using CW excitation of IF. This corresponds to only one or two molecules in the interaction region and is comparable to the sensitivity of atomic detection. When converted to an equivalent pressure, $10^2$ cm$^{-3}$ corresponds to $\sim 10^{-15}$ Torr which is the maximum sensitivity of the "universal" detector discussed in Chapter 3. Although the information content is higher from internal state distributions than velocity angle contour maps, the LIF technique is still severely prejudiced by the requirement that the spectroscopy of the species being probed be well known and is generally less applicable than universal detection.

2.2 MODEL DESCRIPTION OF LIF PROCESS

An idealised scheme for crossed beam LIF detection is presented in Figure 2.1 below.

*This has recently been reduced 50-fold (J. Wanner Private communication).
Figure 2.1 - Two level scheme describing crossed beams L.I.F. process

Here, $\alpha$ and $\beta$ represent individual quantum states of the ground and excited electronic states (atomic or molecular) respectively. The intersection region of the three beams is assumed to lie in a region of space free from static fields such that magnetic sublevels are degenerate. The rate constants describing the process are as follows:

- $k_0$ rate of formation of state $\alpha$ from the crossed beams
- $k_1$ rate of photon absorption due to $\beta \rightarrow \alpha$ transition
- $k_2$ rate of stimulated emission from $\beta \rightarrow \alpha$
- $k_3$ rate of spontaneous emission from $\beta \rightarrow \alpha$
- $k_4$ non-radiative loss rate - in the following analysis, this is assumed to arise from predissociation only.
- $k_5$ depletion rate of probed species from the reaction zone.

In the absence of laser excitation, the rate equation for the system is

$$\frac{dn_\alpha}{dt} = k_0 - k_5 n_\alpha$$  \hspace{1cm} (2.1)
which, in the steady state \( (n_\alpha = n_\alpha^0) \) yields

\[
n_\alpha^0 = \frac{k_0}{k_5} \quad \text{............ (2.2)}
\]

If, at an instant \( t_0 \), the laser field is applied at the reaction zone, the master equations for the system become

\[
\frac{dn_\alpha}{dt} = k_0 - k_1 n_\alpha + k_2 n_\beta + k_3 n_\beta - k_5 n_\alpha \quad \text{............ (2.3a)}
\]

\[
\frac{dn_\beta}{dt} = k_1 n_\alpha - k_2 n_\beta - k_3 n_\beta - k_4 n_\beta - k_5 n_\beta \quad \text{.... (2.3b)}
\]

The laser intensity, \( I(\lambda_{\alpha\beta}) \), is in general a function of time and this is reflected in \( k_1(t) \) and \( k_2(t) \). In practice however this time dependence separates into two distinct regimes: fast-pulsed and C.W. The only reported exception to this has been the relatively slow (\( \sim 80 \) ns) FWHM. system of Kinsey et al.\(^{10}\). The approximation is therefore made that the laser intensity is a square wave of duration \( \Delta t \) where \( \Delta t \cdot k_i \ll 1 \), \( i = 1 - 5 \) for fast-pulsed excitation and \( \Delta t \to \infty \) for C.W. excitation. The time scales under consideration are illustrated below in Figure 2.2. The square wave approximation can be justified in the fast-pulsed régime since detailed calculations with various assumed pulse shapes but the same energy content arrive at essentially the same results.\(^{10}\) The benefit of the approximation is that (2.3) can be solved analytically since a linear, homogeneous form is thereby obtained. The solutions for \( n_\alpha \) and \( n_\beta \) are:
The laser is fired at $t=t_0$ referred to an arbitrary origin at $t=0$ (eg sync. pulse from $N_2$ laser).

The detector gate opens at $t=t_2$.

Figure 2.2 - Excitation and detection timing scheme

\[ n_\alpha = \exp\left(-\frac{Kt}{2}\right)\{A \exp(FT) + B \exp(-FT)\} + (P.I.)_\alpha \] \hspace{1cm} \text{(2.4a)}

and

\[ n_\beta = \exp\left(-\frac{Kt}{2}\right)\{C \exp(FT) + D \exp(-FT)\} + (P.I.)_\beta \] \hspace{1cm} \text{(2.4b)}

The coefficients $A, B, C, D, K, F$ are given by

\[ A = \frac{1}{2F} \left[ \left(F + K - K_o\right) n_o^o - \frac{(F + K) k_o (k_2 + k_3 + k_4 + k_5)}{(k_1 + k_5)(k_2 + k_3 + k_4 + k_5) - k_1(k_2 + k_3)^2} \right] \] \hspace{1cm} \text{(2.5a)}
\[ B = \frac{1}{2F} \left[ (F - K + k_1) n_\alpha^0 - \frac{(F - K) k_0 (k_2 + k_3 + k_4 + k_5)}{((k_1 + k_5)(k_2 + k_3 + k_4 + k_5) - k_1(k_2 + k_3))} \right] \]

\[ C = \frac{1}{2F} \left[ k_1 n_\alpha^0 - \frac{(F + K) k_0 k_1}{((k_1 + k_5)(k_2 + k_3 + k_4 + k_5) - k_1(k_2 + k_3))} \right] \]

\[ D = -\frac{1}{2F} \left[ k_1 n_\alpha^0 - \frac{(F - K) k_0 k_1}{((k_1 + k_5)(k_2 + k_3 + k_4 + k_5) - k_1(k_2 + k_3))} \right] \]

\[ K = k_1 + k_2 + k_3 + k_4 + k_5 \]

\[ F = \frac{1}{2} \left( K_0^2 - 4(k_1 + k_5)(k_2 + k_3 + k_4 + k_5) + 4 k_1(k_2 + k_3) \right)^\frac{1}{2} \]

using the conditions (at \( t = t_0 \))

\( n_\alpha = n_\alpha^0 \; ; \; \dot{n}_\alpha = -k_1 n_\alpha^0 \) \hspace{1cm} (2.6a)

\( n_\beta = 0 \; ; \; \dot{n}_\beta = k_1 n_\alpha^0 \) \hspace{1cm} (2.6b)

The particular integral solutions are

\[ (P.I.)_\alpha = \frac{k_0 (k_2 + k_3 + k_4 + k_5)}{((k_1 + k_5)(k_2 + k_3 + k_4 + k_5) - k_1(k_2 + k_3))} \] \hspace{1cm} (2.7a)
(P.I.)_β = \frac{k_1k_0}{((k_1 + k_5)(k_2 + k_3 + k_4 + k_5) - k_1(k_2 + k_3))} \quad \ldots (2.7b)

It can be readily shown that F < K such that for t \to \infty, the time dependent parts of the solutions vanish and only the particular integrals remain.

These solutions are considered in detail in Sections 2.3 and 2.4.

Since k_1 and k_2 are given by

\begin{align*}
k_1 &= B_\alpha I (\lambda_\alpha) \quad \ldots (2.8a) \\
k_2 &= B_\beta I (\lambda_\beta) \quad \ldots (2.8b)
\end{align*}

it is instructive to consider the ranges of I (λ) presently available.

Separate consideration of the Einstein 'B' coefficients in (2.8) will be given later. For both pulsed and C.W. lasers, I(λ)\textsuperscript{†}, the spectral energy density, is given by

\begin{equation}
I (\lambda) = \frac{4P}{(\text{B.W.}) \cdot \pi \omega^2 \cdot c} \quad \ldots (2.9)
\end{equation}

where P is the output power in Watts (peak or C.W.), B.W. is the laser spectral bandwidth in Hz, \omega is the laser beam "waist" in m (to 1/e\textsuperscript{2} intensity points) and c, the speed of light. Values of I (λ) are presented in Table 2.1 for λ = 450 nm and an assumed beam waist of 5 mm.

\textsuperscript{†} I(λ) is also a measure of the laser intensity and both terms are used interchangeably here.
Table 2.1 - Values of $I(\lambda)$ in J Hz$^{-1}$ m$^{-3}$ for $\lambda = 450$ nm and $\omega = 5$ mm.

2.3 FAST-PULSED EXCITATION

In practice, this refers to laser pulses of 1 - 10 ns FWHM normally from a N$_2$ laser pumped dye laser. More recently, Nd$^{3+}$ : YAG and rare gas halide "excimer" have also been used as pumps but little change in $\Delta t$ from the above has resulted. Since the time constants associated with formation and depletion of the reaction zone are typically $10^{-4}$ - $10^{-5}$ s, the populations in that zone can be considered as frozen on the time scale of the laser excitation. This approximation does not usefully simplify (2.4) - (2.7) unless two explicit sub-divisions are considered:

(a) low/high predissociation ($k_4$)
(b) low/high excitation ($k_1, k_2$)
2.3.1 LOW PREDISSOCIATION, LOW EXCITATION INTENSITY

Here, $k_1, k_2, k_4 \ll k_3$ and (2.4) simplifies to

\[ n_\alpha = n_\alpha^0 - \frac{k_1}{k_3} n_\alpha^0 (1 - \exp(-k_3 t)) \quad \text{(2.10a)} \]

\[ n_\beta = \frac{k_1}{k_3} n_\alpha^0 (1 - \exp(-k_3 t)) \quad \text{(2.10b)} \]

where (2.10b) is formally identical to equation 2 of Reference 10. The appearance of $k_1$ in the numerator above signifies linearity of $n_\beta$ and the resultant LIF signal with laser intensity. The populations $n_\alpha^0$ are then simply proportional to the nascent product internal state distributions.

The fluorescence emission, $N_Y$, is given by

\[ N_Y = V_{RZ} \left( \int_{t_0}^{t_1} n_\alpha^0 k_1 (1 - \exp(-k_3 (t - t_0))) \, dt + n_\beta (\Delta t) \right) \]

\[ \text{with } n_\beta (\Delta t) \text{ given by (2.10b), } V_{RZ} \text{ being the volume of the reaction zone.} \]

Substitution in (2.11a) and integration yields

\[ N_Y = k_1 n_\alpha^0 V_{RZ} \Delta t \quad \text{................. (2.11b)} \]

However, in many real systems, it is necessary to exclude detection during the laser pulse and for some time after to exclude laser induced noise. In such cases the gate is opened at $t_2$ and

\[ N_Y = k_3 V_{RZ} \int_{t_2}^{t_3} n_\beta (\Delta t) \exp(-k_3 (t - t_1)) \, dt \]
where \( t_3 \) is assumed large enough (a few radiative lifetimes) to capture the majority of the fluorescence. The choice of \( t_2 \) depends on the radiative lifetime of the state \( \beta \): if this is small such that \( k_3 \Delta t \sim 1 \) then fluorescence collection must be made both during and after laser excitation for optimal efficiency; if the radiative lifetime is large then little signal is lost by excluding the period \( (t_2 - t_0) \) from observation and in this case since \( k_3 \Delta t \ll 1 \)

\[
N_Y = k_1 n_0 \nu_{RZ} \Delta t \exp (-k_3 (t_2 - t_1)) \]  

Equation (2.11b) is appropriate to the \( \text{Ba} + \text{HX} \) reactions\(^{11} \) whilst (2.11d) applies in the cases of \( \text{H} + \text{NO}_2, \text{ClO}_2 \)^6,10 amongst others. Insertion of appropriate values into (2.11b) and (2.11d) reveals that signal levels for fast radiative lifetimes (strong emitters/absorbers) are 1 - 3 orders of magnitude above those for common radical radiative lifetimes (>1\( \mu \)s)

2.3.2 LOW PREDISSOCIATION, HIGH EXCITATION INTENSITY

The dye laser described in Chapter 3 has a value of \( I \sim 10^{-12} \) J. Hz\(^{-1} \) m\(^{-3} \). Similar lasers can have \( I(\lambda) \) values up to \( 10^{-8} \) J. Hz\(^{-1} \) m\(^{-3} \). Thus, since

\[
B_{\alpha\beta} = B_{\beta\alpha} = \frac{\lambda^3 A_{\alpha\beta}}{8\pi h} \]  

when \( \alpha \) and \( \beta \) have the same electronic degeneracy, substitution in (2.8) yields
\[ k_1 = k_2 = \frac{\lambda^3 A_{\beta\alpha} I (\lambda_{\alpha\beta})}{8\pi n} \]  
............... (2.12b)

where \( A_{\beta\alpha} \) is the Einstein A coefficient. Typically \( A_{\beta\alpha} \) (= \( k_3 \)) is \( 10^5 - 10^8 \) s\(^{-1}\) and the range of values accessible to \( k_1 \), \( k_2 \) is \( 10^5 - 10^{15} \) s\(^{-1}\), with values of \( 10^6 - 10^8 \) s\(^{-1}\) being common. For \( k_1, k_2 \gg 10^8 \) s\(^{-1}\)

\[ n_\alpha = \frac{1}{2} n_\alpha^0 \]  
............... (2.13a)

\[ n_\beta = n_\alpha^0 \quad \text{.............. (2.13b)} \]

these values being established early in the laser pulse. The integrated fluorescence signal in this extreme is:

\[ N_\gamma = \frac{1}{2} n_\alpha^0 V_{RZ} (k_3 \Delta t + 1) \]  
............... (2.14a)

if the gate is open during excitation. For gate opening at \( t_2 \)

\[ N_\gamma = \frac{1}{2} n_\alpha^0 V_{RZ} \exp (-k_3 (t_2 - t_1)) \]  
............... (2.14b)

In both cases, the signal is independent of laser intensity and essentially only dependent on the initial population of state \( \alpha \). This corresponds to complete saturation of the \( \beta-\alpha \) transition.
Between the low and high intensity regimes, an intermediate exists which is characterised by a non-linear dependence of the signal on the laser intensity. Here the equations for $n_{\alpha}$ and $n_{\beta}$ are

$$n_{\alpha} = n_{\alpha}^0 \left(1 - \frac{k_1}{(k_1 + k_2 + k_3)} (1 - \exp \left( - (k_1 + k_2 + k_3) t \right)) \right)$$

(2.15a)

$$n_{\beta} = n_{\alpha}^0 \cdot \frac{k_1}{(k_1 + k_2 + k_3)} (1 - \exp \left( - (k_1 + k_2 + k_3) t \right))$$

(2.15b)

Irrespective of the gate timing, the appearance of $k_1$ and $k_2$ in the exponent of (2.15) means that signal non-linearity in $I(\lambda)$ occurs. This situation corresponds to partial saturation (sometimes called optical pumping). The case of $k_1, k_2 \gg k_3$ has been treated by Liu and Parson\textsuperscript{12} whose equation (A8) can be derived from (2.15b), i.e.

$$n_{\beta} = n_{\alpha}^0 \cdot \frac{k_1}{(k_1 + k_2)} (1 - \exp \left( - (k_1 + k_2) t \right))$$

(2.15c)

Substitution of (2.12b) in (2.15c) yields

$$n_{\beta} = \frac{1}{2} n_{\alpha}^0 (1 - \exp \left( - \text{const.} k_3 I(\lambda_{\beta\alpha}) t \right))$$

(2.15d)

which demonstrates the non-linearity.
In order to extract population information from the LIF excitation spectrum, the use of the "saturation parameter" method is necessary. This complication can be overcome at the expense of signal by reducing \( I(\lambda_{AB}) \) sufficiently to regain the linearity of (2.11). The alternative of raising the laser intensity to achieve complete saturation, although possible with current lasers, has not been reported so far.

2.3.3 HIGH PREDISSOCIATION, LOW EXCITATION INTENSITY

Analysis of spectral line broadening shows that predissociation rates of \( 10^{10} - 10^{12} \text{ s}^{-1} \) occur and in such cases

\[
k_4 \gg k_1, k_2, k_3, k_5
\]

and the solutions to the rate equations are

\[
n_\alpha = n_\alpha^0 \hspace{2cm} \text{(2.16a)}
\]

\[
n_\beta = \frac{k_1}{k_4} n_\alpha^0 (1 - \exp(-k_4 t)) \hspace{2cm} \text{(2.16b)}
\]

The corresponding fluorescence photon yield is

\[
N_\gamma = \frac{k_1}{k_4} \cdot \frac{k_3}{k_4} n_\alpha^0 \cdot v_{RZ} \hspace{2cm} \text{(2.16c)}
\]

indicating that, at best, only \( 10^{-3}\% \) of \( n_\alpha^0 \) give rise to photon emission, a factor ca. \( 10^4 \) below that expected when no predissociation occurs. The effect of this is to preclude observation of LIF where predissociation is
strong and this is well demonstrated in the case of $\text{C}_2\text{O}^{14}$ where even in "bulk" concentrations, no fluorescence could be seen.

### 2.3.4 HIGH PREDISSOCIATION, HIGH EXCITATION INTENSITY

The range of values accessible to $k_1$ and $k_2$ has been shown (Section 2.3.2) to be $10^5 - 10^{15} \text{ s}^{-1}$. For predissociation in the range $10^{10} - 10^{12} \text{ s}^{-1}$, three classifications arise here

(i) $k_1, k_2 \sim 10^8 - 10^{10} \text{ s}^{-1}$

(ii) $k_1, k_2 \sim k_4$

(iii) $k_1, k_2 > 10^{12} \text{ s}^{-1}$.

Case (i) is effectively identical to the low intensity limit of the previous section. However, in case (iii), the integrated photon signal is

$$N_\gamma = \frac{k_3}{2k_4} n_\alpha^0 V_{\text{RZ}} \quad \text{(2.17)}$$

indicating that the conditions for measurable signal are

(a) high rate of ground state formation and

(b) short radiative lifetime.

At best however only $\sim \frac{1}{2}%$ of the photons absorbed will be re-emitted as fluorescence. Substituting $10^4 \text{ cm}^{-3}$ for $n_\alpha^0$ and $10^{-2} \text{ cm}^3$ for $V_{\text{RZ}}$ yields for $N_\gamma$ one fluorescence photon in two laser pulses. Since the overall collection efficiency of detection systems is $\sim 10^{-3}$ this means that integration periods of 10 - 100 hours would be required for pulse repetition
frequencies in the range 10 - 100 Hz to achieve a signal: noise ratio of only unity. (This assumes 1 photoelectron/pulse noise which is typical). Clearly, such an experiment would fail in practice due to other noise sources.

The intermediate case (ii) does not lend itself to simplification but for \( k_1 = k_2 = k_4 = k \), only the particular integrals contribute appreciably. Thus, for \( k = 10^{11} \text{ s}^{-1} \) (correspond to an excimer/Nd\(^{3+}\) YAG pumped dye laser).

\[
\begin{align*}
n_\alpha &= \frac{2k_5 n_\alpha^0}{k} \quad (2.18a) \\
n_\beta &= \frac{k_5 n_\alpha^0}{k} \quad (2.18b)
\end{align*}
\]

which for realistic values of \( k_5 (10^4 - 10^6 \text{ s}^{-1}) \) yields an immeasurably low result.

### 2.4 CONTINUOUS-WAVE EXCITATION

Although the instantaneous power of pulsed dye lasers greatly exceeds that of C.W. lasers, the average power is generally larger for the latter being typically 100 mW or more. The bandwidth of C.W. dye lasers can be actively narrowed to a few MHz over long periods, a feat not possible in pulsed lasers without considerable pulse stretching to satisfy the uncertainty principle. However, both lasers have typically been operated with bandwidths in the \( 10^9 - 10^{11} \text{ Hz} \) region (0.01 - 1.0 Å in the visible) and although this is well below the ultimate performance of the C.W. laser no need to increase \( I(\lambda) \) has been found necessary since signals
levels have been so much higher than in the pulsed case. The main reason for this is that the C.W. duty factor (ratio of 'on' time to 'on + off' time) is unity whereas in the pulsed case it seldom exceeds $10^{-6}$.

The solutions to the rate equations for C.W. excitation are simply the particular integrals of (2.4).

\[ n_\alpha = \frac{k_0 (k_2 + k_3 + k_4 + k_5)}{(k_1 + k_5)(k_2 + k_3 + k_4 + k_5) - k_1(k_2 + k_3)} \quad \cdots (2.19a) \]

\[ n_\beta = \frac{k_1 k_0}{(k_1 + k_5)(k_2 + k_3 + k_4 + k_5) - k_1(k_2 + k_3)} \quad \cdots (2.19b) \]

2.4.1 LOW PREDISSOCIATION, LOW EXCITATION FIELD

Here, $k_1, k_2, k_4 \ll k_3, k_5$, a situation occurring readily for many of the C.W. systems thus far reported. In this case

\[ n_\alpha = n_\alpha^0 \quad \cdots \cdots \cdots \cdots (2.20a) \]

\[ n_\beta = \frac{k_1 n_\alpha^0}{(k_3 + k_5)} \quad \cdots \cdots \cdots \cdots (2.20b) \]

and the photon emission rate, $N_\gamma$, is

\[ N_\gamma = k_3 n_\beta V_{RZ} \quad \cdots \cdots \cdots \cdots (2.20c) \]

\[ = \frac{k_3 k_1}{(k_3 + k_5)} n_\alpha^0 V_{RZ} \quad \cdots \cdots \cdots \cdots (2.20d) \]
It is more likely that (2.20d) will be controlled by $k_3$ rather than $k_5$ since extremely high recoil velocities are uncommon. Thus

$$N_\alpha = k_1 \eta_\alpha^0 V_{RZ} \quad \text{(2.20e)}$$

which is similar to the result for the pulsed case in (2.11). On substituting reasonable minimum values in (2.20e) a photon signal rate of at least $10^4 \text{ s}^{-1}$ arises which is probably just below the threshold for detectability. However with sufficiently strong absorbers present in quantity, photon signal rates of $10^6 - 10^8 \text{ s}^{-1}$ become accessible well above the noise level of the experiment.

The enhancement, $E$, in sensitivity of CW over pulsed excitation is given by

$$E = \frac{I(\lambda)}{I(\lambda)_{\text{Pulsed. \Delta t. PRF}}} \quad \text{(2.21)}$$

which for the minimum values of each given in Table 2.1 gives $E = 10^2$ for a 100 Hz repetition frequency. This has been verified in practice where integration to a signal : noise ratio of 3.5 has been achieved in one second.
2.4.2 LOW PREDISSOCIATION, HIGH EXCITATION INTENSITY

For transitions of short radiative lifetime realisable values of $k_1, k_2$ lie in the range $10^6 - 10^8$ s$^{-1}$. Indeed, from (2.8), (2.9) and (2.12), it is evident that $k_1$ and $k_2$ are bounded by $k_3$, i.e.

$$k_1, k_2 \leq k_3$$ ............... (2.22)

which contrasts with pulsed excitation where $k_1$ and $k_2$ vastly exceed $k_3$ for all but the lowest $I(\lambda)$ values. The population densities for this extreme are given by

$$n_\alpha = \frac{(k_2 + k_3)}{(k_1 + k_2 + k_3)} n_\alpha^0$$ ............... (2.23a)

$$n_\beta = \frac{k_1 n_\alpha^0}{(k_1 + k_2 + k_3)}$$ ............... (2.23b)

and the photon emission rate by

$$N_Y = \frac{k_1 k_3 n_\alpha^0 V_{RZ}}{(k_1 + k_2 + k_3)}$$ ............... (2.23c)

and for sufficiently large $k_3$ this becomes

$$N_Y = k_1 n_\alpha^0 V_{RZ}$$ ............... (2.23d)

as in the low excitation intensity case. Minimum values for $N_Y$ of $10^5$ s$^{-1}$ for $n_\alpha^0 = 10^2$ cm$^{-3}$ are predicted in keeping with the minimum detectable concentration proposed by Wanner et al. The application of
this method to study of reactions of low cross-section is immediately evident.

Unlike in pulsed excitation, complete saturation cannot be realised using C.W. lasers being a consequence of (2.22). However, partial saturation does occur and resort to a similar procedure already discussed for pulsed excitation will be necessary. Since the non-linearity in the C.W. case is not contained in an exponent, the corrections to the derived populations will in general be smaller. For the high intensity extreme, the relative sensitivity of C.W. : pulsed detection is

\[ E \gg \frac{k_1}{PRF} \]  

(2.24)

which can exceed \(10^4\), two orders of magnitude above the low power enhancement.

2.4.3 HIGH PREDISSOCIATION, LOW EXCITATION INTENSITY

As for the pulsed case \(k_4 \gg k_1, k_2, k_3, k_5\) and the steady state populations are

\[ n_\alpha = \frac{k_5 n_\alpha^0}{(k_1 + k_5)} \]  

(2.25a)

\[ n_\beta = \frac{k_1 k_5 n_\alpha^0}{(k_1 + k_5) k_4} \]  

(2.25b)

Since \(k_5 (10^4 - 10^6\, s^{-1})\) predominates over \(k_1\) in the low intensity régime, the photon emission rate is
and over the accessible range of parameter values in (2.25c), \( N_y \) values in the range \( 10^{-4} - 10^5 \, \text{s}^{-1} \) are predicted. As an example, the C\(_2\)O radical formed in the (supersonic) crossed beams reaction of O + C\(_2\) could yield up to \( 10^3 \) photons/sec in the (0, 19) band using a sufficiently intense laser (for C\(_2\)O, \( k_3 \sim 10^6 \, \text{s}^{-1} \) \(^{14}\) and \( k_4 \sim 10^{10} \, \text{s}^{-1} \) \(^{13}\)). Thus, unlike the pulsed case, C.W. excitation can in principle yield LIF data providing that predissociation is not overwhelming i.e. \( k_4 \ll 10^{12} \, \text{s}^{-1} \). In practice however it is most unlikely that this will be realised at low power levels.

### 2.4.4 HIGH PREDISSOCIATION, HIGH EXCITATION INTENSITY

Again, \( k_4 \) is dominant over all other rate constants and equations (2.25a) and (2.25b) hold here also. However, \( k_1 \) will now predominate over \( k_5 \) and

\[
N_y = \frac{k_3 k_5 n_0 V}{k_4} \alpha \ \text{RZ} \hspace{3cm} \text{(2.26)}
\]

which, predicts a range of \( 10^{-1} - 10^6 \, \text{s}^{-1} \) for \( N_y \). The conditions for observation of a LIF signal are again the same as for pulsed excitation namely high reaction cross-section and short radiative lifetime. The ratio of sensitivity for each case is now given by

\[
E = 2k_5/\text{PRF} \hspace{3cm} \text{(2.27)}
\]
which is in the range $10^2 - 10^4$. It is therefore predicted that only for high intensity C.W. excitation will a resolvable LIF spectrum be obtained and even then, only in very selective reactions.

2.5 EXTENSION TO REAL SYSTEMS

The approximation inherent in the rate process analysis of the previous section was that fluorescence was resonant only. In reality, each excited state $\beta$ is optically connected with a finite number of states $\alpha_i$, the extent of this depending on the line strengths of the $\alpha_i + \beta$ transitions. The rate of fluorescence from $\beta$ is now given by

$$ \dot{N}_Y = k_{\text{rad}} n_\beta V_{RZ} \quad \text{................. (2.28a)} $$

where

$$ k_{\text{rad}} = \sum_i k_{\text{rad}}^i \quad \text{................. (2.28b)} $$

and

$$ k_{\text{rad}}^i = A_{\beta\alpha_i} = \frac{64\pi^4}{3(4\pi\varepsilon_0)} \cdot \frac{1}{g_\beta} \cdot \frac{S_{\beta\alpha_i}}{\lambda_{\beta\alpha_i}} \quad \text{................. (2.28c)} $$

$S_{\beta\alpha_i}$ is the line strength for the $\beta_{\alpha_i}$ transition given in the Born-Oppenheimer approximation by

$$ S_{\beta\alpha_i} = \frac{|R_{\beta\alpha_i}^e|^2 q_{\beta\alpha_i} \rho_{\beta\alpha_i}}{g_{\alpha_i}(2J_{\alpha_i} + 1)} \quad \text{................. (2.28d)} $$

The electronic transition moment $R_{\beta\alpha_i}^e$ is normally assumed constant but variation with vibration and rotation quantum state does occur and in such cases this can be accounted for by the r-centroid approximation.
using rotationally perturbed RKR potential curves. The term $p_{\beta\alpha_i}^+$ is the rotational line strength which embodies the selection rules for the transition as well as the relative intensity. An extensive bibliography of these is presented in Kovacs' book.

Since photomultiplier tubes are characterised by an energy sensitive response, $Q(\lambda)$, normally in mA/W, it has been customary in the case of pulsed excitation and analogue (boxcar) detection to consider the optical power of the emitted fluorescence rather than the number or rate of photons emitted. Thus, the fluorescence signal at any time $t > t_2$, $P_Y(t)$, is

$$P_Y(t) = n_B(t) \cdot \sum_{\alpha_i} \frac{64\pi^4}{3(4\pi\epsilon_0)} \cdot \frac{1}{g_\beta} \cdot \frac{S_{\beta\alpha_i}}{\lambda_{\beta\alpha_i}^4} \cdot Q(\lambda_{\beta\alpha_i}) \quad \text{(2.29a)}$$

However, $n_B$ is exponentially decaying when the detector gate is opened and in order to account for this, (2.29a) is divided by $k_{\text{rad}}$ to yield the integrated (eg boxcar) signal, $P_Y$

$$P_Y = \sum_{\alpha_i} \frac{64\pi^4}{3(4\pi\epsilon_0)h} \cdot \frac{1}{g_\beta} \cdot \frac{S_{\beta\alpha_i}}{\lambda_{\beta\alpha_i}^3} \quad \text{(2.29b)}$$

Some simplification of (2.29) is possible if the bands are not extensively spread by rotation i.e. for "parallel" potential energy curves. In this case, $\lambda_{\beta\alpha_i}$ is assumed roughly constant and the rotational sum rule is invoked resulting in

$\dagger$ The remaining terms in (2.28d) are $q_{\beta\alpha_i}$, the Franck-Condon factor and $g_{\alpha_i}$, the electronic degeneracy of the lower state.
\[ P_Y = \frac{\sum_{\alpha} (S_{\beta \alpha_i} Q(\lambda_{\beta \alpha_i}) \lambda_{\beta \alpha_i}^{-4})}{\sum_{\alpha} (q_{\beta \alpha} \bar{\lambda}_{\beta \alpha}^{-3})} \]  

(2.29c)

where the constant of proportionality embodies the electronic transition moment, geometrical and optical factors and the excited state population. \( \bar{\lambda}_{\beta \alpha} \) is normally taken as the band head since this carries the greatest statistical weight.

Alternatively, if the function \( Q(\lambda) \) represents a quantum efficiency instead of the more common energy sensitivity, the numerators of (2.29) should be multiplied by \( \lambda_{\beta \alpha_i} \) to reconvert to a photon signal. This applies in both excitation cases. For C.W. excitation, however, no normalisation of (2.29a) is necessary since \( n_\beta \) is constant.

Although the C.W. approach gives better statistics than the pulsed mode there is one serious limitation here which must be overcome. This is brought about by the cavity mode structure inherent in C.W. lasers and absent in fast pulsed lasers. If the gain profile of the laser is not uniformly filled with a large number of cavity modes, most of the output energy will be contained in a few very narrow emission lines and this can cause saturation when resonant with a given transition. Equally serious are the phenomena of mode pulling and hopping which arise from a variety of environmental effects and cause wavelength instability. In general the pulsed approach lends itself more readily to the rigours of laboratory environments whereas C.W. systems require special precautions.
To obtain relative state populations from the excitation spectrum it is customary to simulate it rather than invert it since considerable error will arise in the latter case. Descriptions of this procedure have already been outlined\textsuperscript{2, 12, 19, 20} and a detailed account is presented by Glen\textsuperscript{21}. Basically, the prescription is as follows: first a "stick" spectrum of the fluorescing species is constructed using the available spectroscopic information. For each transition in this spectrum the components of $S_{\beta\alpha_i}$, the line strength, must be established from experimental data and/or calculation. The spectral bandwidth of the laser is then given an assumed form approximating to its measured profile (normally Gaussian/triangular) and this is superimposed on the stick spectrum to determine which absorptions contribute to the signal; this process is often termed "convolution". Finally, a form must be assumed for the rotational distribution within each vibrational level if the experiment cannot resolve this directly. The only parameters left are then the relative vibrational populations and variation of these is made to fit the observed data. If a fit is not possible then the assumptions about the rotational distributions must be revised until a satisfactory fit obtains. In certain cases it is necessary to iterate to a solution if the rotational distributions for different vibrational levels varies significantly\textsuperscript{19}. 
2.6 LIF STUDY OF THE CROSSED BEAM REACTION: \( \text{O} + \text{I}_2 \rightarrow \text{IO} + \text{I} \)

- A FEASIBILITY ANALYSIS.

The dynamics of this reaction are fully described in Chapter 4 and the experimental arrangement for its investigation detailed in Chapter 3. The values quoted in the following analysis are established in these chapters.

Figure 2.3 presents the most probable Newton diagram for the experimental arrangement. At the thermal velocities encountered the total cross-section for reaction into all accessible internal states is \( \sim 1 \, \text{A}^2 \). The total rate of formation of \( \text{IO} \) is therefore given by

\[
\frac{d\{\text{IO}\}}{dt} = n_0 \cdot n_{\text{I}_2} \cdot v_{\text{rel}} \cdot \sigma_R^{\text{tot}} \quad \text{.................................. (2.30a)}
\]

\[
\frac{\frac{F_0}{v_0}}{\frac{F_{\text{I}_2}}{v_{\text{I}_2}}} \cdot v_{\text{rel}} \cdot \sigma_R^{\text{tot}} \quad \text{.................................. (2.30b)}
\]

where the forward fluxes divided by the most probable source velocity replace the reaction zone number densities. Using the following values:

\[
F_0 = 1.5 \times 10^{15} \, \text{cm}^{-2} \, \text{s}^{-1}
\]

\[
F_{\text{I}_2} = 1 \times 10^{17} \, \text{cm}^{-2} \, \text{s}^{-1}
\]

\[
v_0 = 6.8 \times 10^4 \, \text{cm} \, \text{s}^{-1}
\]

\[
v_{\text{I}_2} = 1.7 \times 10^4 \, \text{cm} \, \text{s}^{-1}
\]

\[
v_{\text{rel}} = 7.6 \times 10^4 \, \text{cm} \, \text{s}^{-1}
\]

... gives for (2.30)
Figure 2.3 - Most probable Newton diagram for thermal 0/12 system.

\[ v''(10) = 10 \]

\[ v_0 \]

\[ 500 \text{ m/s} \]
\[
\frac{d\{\text{IO}\}}{dt} = k_0 = 10^{12} \text{ cm}^{-3} \text{s}^{-1}
\]

The volume of the reaction zone is at least $10^{-2}$ cm$^3$ indicating a total IO production rate of $10^{10}$ s$^{-1}$.

Since the reaction is 17.4 kcal mol$^{-1}$ exothermic, there is on average 19.5 kcal mol$^{-1}$ available for redistribution amongst the motions of the products when relative translation and reactant internal energy are taken into account. This is capable of populating up to $v'' = 10$ of IO. For $v'' = 0$, a total of $\sim 140$ rotational states can be populated in the rigid rotor approximation and for $v'' = 10$, 21 rotational levels are accessible. The total number of vibration-rotation states energetically accessible is very nearly 1000 and since a uniform distribution amongst these is most unlikely, a fraction of at least $10^{-3}$ of any statistical sample will be in a state which is observable by LIF. Thus, a single vibration-rotation state is produced in the reaction zone at a minimum rate of $10^7$ s$^{-1}$.

To estimate the lifetime of an IO molecule in the reaction zone, the laboratory distributions of Radlein et al$^{22}$ are used. From these data, the laboratory velocity range is 100 - 900 m/s peaking at $\sim 300$ m/s in the centroid direction. Away from the centroid, these velocities are slightly reduced. Taking 300 m/s as a representative velocity, the residence time in the reaction zone (strictly speaking, this should be the field of view of the detector) will be $10^{-5}$ s which translates into a $k_5$ value centred around $10^5$ s$^{-1}$. For the highest internal states populated $k_5 \approx 5 \times 10^4$ s$^{-1}$, whilst for the lowest $k_5 \approx 3 \times 10^5$ s$^{-1}$. The steady state population in the reaction zone for ground state level $\alpha$ is
given by (2.2) which predicts a value for \( n_0 \) of \( 10^4 \) cm\(^{-3} \) in the present case. In view of the approximations involved, this is probably a lower limit.

The analysis of Section 2.3 implies that LIF is only observable for pulsed excitation if the emitting state is not heavily predissociated. This confines excitation to \( v' = 0, 2 \) of IO since all other levels are predissociated with lifetimes < \( 10^{-10} \) s \(^{23}\). Since the resolution of the spectrometers used to determine the absorption \(^{23}\) and emission \(^{24}\) spectra of IO was at best 0.1 cm\(^{-1}\) (\( \sim 3 \times 10^9 \) Hz) then even the sharp bands originating (in emission) on \( v' = 0, 2 \) may still be predissociated with a lifetime at least \( 10^{-9} \) s. The extent of this is entirely unknown but comparison with BrO \(^{23}\) and ClO \(^{13}\) \(^{25}\) suggests that it remains appreciable. Accordingly, the rate constant \( k_4 \) will be treated parametrically below.

To estimate the values of \( k_1, k_2 \) and \( k_3 \), the line strengths \( S_{\beta \alpha_i} \) must be known. For the bands originating on \( v' = 0, 2 \), these must be estimated since lifetime data are not available. The Franck-Condon factor array for \( v' = 0 - 4/v'' = 0 - 6 \) has been obtained\(^{26}\) using accurate RKR curves (shown in Figure 2.4), and, since the A-X transition of IO corresponds to pure case (a) - case (a) coupling\(^{23}\), the rotational line strengths are well known\(^{17, 18, 27}\). For a \( \Delta \Lambda = 0 \) transition, these are

\[
\rho(R) = \frac{(J'' + 1 + \Lambda'')(J'' + 1 - \Lambda'')}{{J''} + 1} = \frac{(J' + \Lambda')(J' - \Lambda')}{J'} \]

........................ (2.31a)
Figure 2.4 - R.K.R. curves for A and X states of IO

$A(^2\Pi_{3/2})$

$X(^2\Pi_{3/2})$

$T_e = 21565 \text{ cm}^{-1}$

5000 cm$^{-1}$
\[ \rho(Q) = \frac{(2J'' + 1)(A'')^2}{J''(J'' + 1)} = \frac{(2J' + 1)(A')^2}{J'(J' + 1)} \quad \ldots \quad (2.31b) \]

\[ \rho(P) = \frac{(J'' + A'')(J'' - A'')}{J''(J'' + 1)} = \frac{(J' + 1 + A')}{J' + 1} \quad \ldots \quad (2.31c) \]

for the P, Q and R branch transitions. From (2.31) it is evident that the intensity of Q-branch transitions for \( J > 7/2 \) is < 10% of the P, R intensity (which explains their absence in the observed spectra) and justifies their neglect. For the P and R branches above \( J = 7/2 \)

\[ \frac{\rho(P)}{2J + 1} = \frac{\rho(R)}{2J + 1} = \frac{1}{2} \]

The last remaining spectroscopic information necessary is the electronic transition moment. This is related to the oscillator strength, \( f \), for the transition by

\[ |R^e|^2 = 3.6 \times 10^{-3} f \lambda(\AA) \quad \ldots \quad (2.32a) \]

where \( R^e \) is in units of \( a_o \text{e} \). Since \( 10^{-2} < f < 1 \) for allowed electric dipole transitions then

\[ 6 \times 10^{-3} < \frac{R^e}{\lambda^2} < 6 \times 10^{-2} \quad \ldots \quad (2.32b) \]

which for \( \lambda \approx 4500 \text{Å} \) yields
The transition moment for C₂O which is spectroscopically similar has been measured\textsuperscript{28, 29} and found to be \(1.0 \pm 0.1 \text{ a}_0\text{e}\) and \(1.1 \pm 0.2 \text{ a}_0\text{e}\) respectively. For comparison, Liu and Parson\textsuperscript{12} have tabulated \(R\text{e}\) values for the Gp. III B metal oxides and have obtained values in the range \(1.2 - 1.9 \text{ a}_0\text{e}\) for these comparatively strong transitions. In view of this, a reasonable estimate for \(R\text{e}\) (I0) is \(1 \text{ a}_0\text{e}\) for the A-X transition which would result in radiative lifetimes of the (0, 0), (2, 0) and (2, 1) bands of 10 \(\mu\text{s}\), 1.0 \(\mu\text{s}\) and 0.4 \(\mu\text{s}\) respectively using the available Franck-Condon factors\textsuperscript{26}.

A complication which arises in pulsed excitation is background LIF from reactants and "cold" residual products which cannot be separated from the signal without considerable increase in integration time. In the present case, I\textsubscript{2}, which is present in concentrations three orders of magnitude above I0, is excited to fluorescence above 500 nm\textsuperscript{30} and consequently excitation is limited to \(v'' = 0, 1, 2\) of the ground state since excitation of the bands (0, \(v'' > 3\)) and (2, \(v'' > 4\)) leads to I\textsubscript{2} fluorescence, the (2, 3) band being so weak (\(q_{23} = 0.003\)) that its emission spectrum has not been recorded.

The higher signal levels inherent in C.W. excitation permit modulation of both the molecular beam and the laser beam to remove this background by on/off subtraction. Therefore, in the pulsed case, only information concerning the relative populations of \(v'' = 0, 1, 2\) is possible.
The spectral profile of the dye laser described in Chapter 3 is roughly bell-shaped with an FWHM, $\sigma$, of $\sim 2\lambda$. Accordingly, this is best modelled by a Gaussian intensity profile

$$I(\lambda) = I_0 \exp \left[ -\frac{1}{2} \left( \frac{\lambda - \lambda_0}{\sigma} \right)^2 \right]$$  \hspace{1cm} (2.33)

where $I_0 = 1 \times 10^{-12}$ J Hz$^{-1}$ m$^{-3}$. This function is shown below super-imposed on the $(2, 0)$ spectrum to indicate the number of rotational lines excited at various wavelengths. Near the band head, a total of 22 lines (15R and 7P) can be accommodated by the laser bandwidth whilst at higher J near to the overlapping $(3, 1)$ bandhead, only 4 lines (2 P/R doublets) can be packed in.

Figure 2.5 - (2,0) band of IO ($X^2\Pi_{3/2} - A^2\Pi_{3/2}$) on linear wavelength scale.
Since \( k_1 \) and \( k_2 \) for the present system are both \( \sim 5 \times 10^6 \, \text{s}^{-1} \) for the (2, 0) band, they fall mid-way between the low and high intensity categories discussed in Section 2.3. To simplify the analysis, the assumption of a two-state system is again invoked and the rate equation solved assuming no losses from the excited state \( \beta \). This gives

\[
\eta_\beta = \eta_\alpha^0 (1 - \exp(-kt)) \quad \cdots \cdots \cdots \quad (2.34a)
\]

and since \( kt < 2.5 \times 10^{-2} \) for a 5 ns FWHM laser pulse, the small exponent approximation is valid and

\[
\eta_\beta = 2.5 \times 10^{-2} \eta_\alpha^0 \quad \cdots \cdots \cdots \quad (2.34b)
\]

Since the excited state population is so low stimulated emission is negligible and, on the time scale of the laser, the same is true of spontaneous emission. It is therefore reasonable to assume that the levels excited in practice do not interact with the levels depleted to a first order approximation. This justifies the two-level scheme and obviates solution of a large number of simultaneous equations corresponding to each optically connected state. Since the P and R branch intensities are equal and sum to unity, (2.28a) can be approximated to

\[
S_{\beta \alpha_i} = |R_{\beta \alpha_i}^e|^2 q_{\beta \alpha_i} \quad \cdots \cdots \cdots \quad (2.35)
\]

for the line strength of all rotational lines in a given band. Since to a very good approximation \( |R_{\beta \alpha_i}^e|^2 \) is constant for \( 10^{26} \), the radiative lifetime of the upper state \( \beta \) in (2.28c) is given by
\[ k_{rad}^\beta = \sum_\alpha A_\alpha^\beta = \frac{64\pi^4}{3(4\pi\varepsilon_0)} \cdot |R_{\beta\alpha}\rangle^2 \sum_\alpha q_{\beta\alpha} \lambda_{\beta\alpha}^{-3} \quad \ldots \ldots \quad (2.36) \]

\[
= 8 \times 10^6 \text{ s}^{-1} \quad \text{for } v' = 2
\]

and \[ \approx 11 \times 10^6 \text{ s}^{-1} \quad \text{for } v' = 0 \]

To estimate the photon yield of fluorescence per excitation pulse, the two-level scheme above is used with parameter values.

\[
k_0 = 10^7 \times (\text{no. of rotational lines excited}) \text{ s}^{-1}
\]
\[
k_1 = \frac{1}{2} \times 5 \times 10^6 \text{ s}^{-1}
\]
\[
k_2 = k_1
\]
\[
k_3 = 10^7 \text{ s}^{-1}
\]
\[
k_4 = 0 \quad \text{and} \quad 10^9 \text{ s}^{-1}
\]
\[
k_5 = 10^5 \text{ s}^{-1}
\]

(a) \[ k_4 = 0 \]

\[
N_Y = k_1 n_0^\alpha V_{RZ} \Delta t
\]

\[
> 5 - 30 \quad \gamma/\text{pulse for (2, 0) excitation}
\]

(b) \[ k_4 = 10^9 \text{ s}^{-1} : \]

\[
N_Y = \frac{k_1}{k_4} \cdot \frac{k_3}{k_4} \cdot n_0^\alpha V_{RZ}
\]

\[
= (1 - 6) \times 10^{-2} \quad \gamma/\text{pulse for excitation of the (2, 0) band.}
\]
Evidently, the experiment is only feasible providing the predissociation lifetime is substantially greater than the radiative lifetime (i.e. $k_4 \ll k_3$). The photon + photoelectron conversion efficiency of the apparatus described in Chapter 3 is $1 - 1\%$ and for a pessimistically large noise figure of 5 photoelectrons/pulse an integration time of $10 - 100$ minutes per wavelength is necessary for $100$ Hz PRF. However since the signal level calculated errs on the low side and the noise count on the high side more realistic integration times of 1 minute are approached.

It is instructive to note that small improvements in e.g. fluorescence collection efficiency can have a dramatic effect on integration time for the same $S : N$ ratio - a tenfold improvement is capable of reducing integration time by a factor up to 100! Also evident is the fact that even with moderate predissociation this experiment is feasible with C.W. excitation.
CHAPTER 2

REFERENCES

1. R.N. Zare and P.J. Dagdigian; Science, 185, 739, (1974).
   (b) A. Schultz and W. Schmidt, ibid, p. 236.
   (c) R.Dirscherl and H.U. Lee, ibid, p. 239.
CHAPTER 3

EXPERIMENTAL
CHAPTER 3

EXPERIMENTAL

3.1 GENERAL INTRODUCTION

Until the late '60's, reactive scattering invariably employed an alkali species as one of the beams with a cross beam of an equally condensable nature, normally a halogen, an alkyl halide or a halogen containing molecule. The beam sources used were the low pressure effusive type and the main body of pumping was cryogenic. The low beam intensities realised meant that velocity selection of both reactants and products was not feasible despite the large total cross-sections encountered ($\sim 100 \text{ A}^2$) and the high efficiency of differential surface ionisation detection.

The introduction in 1969 of the so-called "universal" beams machine by the Harvard group was highly significant in that for the first time the reaction of non alkali and, indeed, non-condensable species could be studied in beams. This was made possible by the simultaneous use of differential pumping, supersonic beams, extensive cryo-pumping and a mass-spectrometric time-of-flight (T.O.F.) detection system maintained, where possible, at liquid nitrogen (helium) temperatures. The whole detector was pumped out to U.H.V. pressures ($< \sim 10^{-9}$ Torr) by various getter-type pumps capable of pumping He, Ne and Ar which were used as buffer gases for supersonic beams. Further refinements to this apparatus have since been made by Grice et al. in which the detection efficiency has been increased by a factor of 10 - 20. Improvements in associated beam production have meant that reactions with high activation energies ($\sim 25 \text{ k. cal. mol}^{-1}$)
involving radicals or radical atoms are now possible\textsuperscript{5, 6, 7} thus extending the range of accessible reactions to those of a more practical nature such as the reaction of \( 0 + C_2F_4 \)\textsuperscript{8} which is of considerable general importance in organic chemistry.

As well as the "universal" machine, other recent innovations include a pulsed beam system\textsuperscript{9} which produces extremely intense supersonic beam pulses of some microseconds duration. The high intensity of these sources offsets the low duty factor (\( \sim 10^{-3} \)) compared to continuous beams and greatly simplifies (and cheapens) the vacuum requirements. The similar repetition frequency of this source and pulsed laser sources makes this combination ideal in e.g. detailed photodissociation studies. Perhaps not an innovation but a renaissance is the rotor-accelerated technique of Moon \textit{et al}\textsuperscript{10}. Here, developments in carbon-fibre composites for the rotors have meant that rotor tip speeds of the order of \( 2 - 3 \) km/sec. can be achieved. This permits observation of reaction cross-sections as a smooth function of collision energy without the expense of seeded beams. Again, the vacuum requirements for such a system are minimal.

In 1972 a complementary approach to reactive scattering appeared in which the nascent product internal state distributions were probed by observing fluorescence induced by a pulsed, tunable dye laser\textsuperscript{12}. The early experiments using this technique were confined to reactions of alkaline earth metals with halogen and oxygen containing molecules which were characterised by large total cross-sections (\( > 10 \text{ Å}^2 \)) and low-lying excited states optically connected with the ground electronic state such that absorption and emission were strong\textsuperscript{12}. The first departure from this was
by Kinsey et al. who succeeded in measuring rotational and vibrational distributions of OH produced from the reaction of H + NO₂. Unlike the earlier work of Zare's group this work used a hydrogen discharge atom source in conjunction with a complex (twice frequency doubled) laser system and a gated photon counting system, all of which was controlled by a dedicated minicomputer. The need for this arose since the beam intensities were lower than previous work as was the total cross-section for reaction (≈ 1Å²) and the absorption/emission strength. This work together with more recent work on the same product from O (1D) + H₂ is perhaps unique in that it cannot easily be done in a "universal" machine due to interference contributed by H₂O and O₂ backgrounds. In addition, since internal distributions can only be inferred from T.O.F. measurements, the observations of Luntz et al. of an inverted rotational distribution from a reaction which proceeds via the H₂O (1A) intermediate presents a severe challenge to existing theories.

In the last few years the laser-induced-fluorescence (L.I.F.) technique has flourished and improved experimental arrangements using continuous wave (C.W.) dye lasers (which can be actively stabilised in terms of amplitude and bandwidth) have emerged. As improvements to C.W. lasers emitting in the U.V. occur, it is likely that the traditional pulsed nitrogen laser will be finally eased out since the improvements in signal acquisition are enormous for the former. To date, less emphasis on beam sources in L.I.F. has been made, most beams being thermal and effusive. However, with a general interest in reactive scattering tending towards reactions of high activation energy, it is likely that this trend will soon end.
The L.I.F./beams system to be described below was the result of work started in 1973. The first reactive system chosen was $O + I_2 \rightarrow OI + I$ which was a significant departure from the metal beam work of Zare's group since, like $H + NO_2$, a radical atom beam was being used in a reaction of low total cross-section ($\sim 1\AA^2$). The use of $F_2$, $Cl_2$ or $Br_2$ although easier and less unpleasant was precluded by increasing activation energies, decreasing absorption wavelengths and in particular extensive predissociation in the upper state of the product. The attraction of the $O + I_2$ system was its simplicity in terms of beam production although considerable uncertainty as to the detailed spectroscopy of the $A-X$ transition in $IO$ existed (and still does!)

A schematic view of the complete apparatus is given in Figure 3.1. The $O$-atom beam is derived from an extra-vacuum microwave discharge in "pure" $O_2$ at $\sim 1$ Torr total pressure whilst the $I_2$ beam is generated from an intra-vacuum oven assembly. The laser beam is steered by mirrors into the chamber through vacuum windows whence through a set of pre-aligned baffles, the three beams ($O$, $I_2$, laser) meeting at a well defined "point". Fluorescence is collected by a light guide and photomultiplier at right angles to the laser beam whose intensity is monitored by a second, identical photomultiplier at the exit window. The entire apparatus is protected against mains electricity and cooling water failure and against occurrence of high temperatures and pressures. The data collection and laser wavelength is controlled on-line by a time-shared minicomputer (PDP 11/45) under teletype control from the laboratory. Details of each major aspect of the apparatus are presented below.
Gas handling

![Diagram of complete apparatus]

Key:

- L - Silica lens
- M - Plane aluminised mirror
- B.M. - Laser beam monitor

Figure 3.1 - Schematic of complete apparatus
3.2 VACUUM AND BEAMS SYSTEM

3.2.1 GENERAL CONSIDERATIONS

A fundamental requirement for the vacuum system in crossed-beam experiments is that the pressure in the background is acceptably less than the "pressure in the beam". Failure to meet this will inevitably result in relaxation of the translational, rotational and vibrational distributions in that order of probability and higher noise in the angular distribution measurements. The following argument underlines this:

The number of collisions, $Z$, per unit time in unit volume is

$$Z = n_1 n_2 v_{12} \sigma_{12}$$ \hspace{1cm} (3.1)

with $n$ = number density; $v$ = relative velocity and $\sigma$ = total collision cross-section. For a beam/beam system, $n$ can be approximated by

$$n = \frac{F}{v}$$ \hspace{1cm} (3.2)

where $F$ = beam flux (molecules/unit area/unit time) and $v$ = (Lab.) velocity. Since the relation

$$n = \frac{N}{V} = \frac{P}{kT}$$ \hspace{1cm} (3.3)

is a good working approximation, substitution in (3.1) yields
\[ Z \propto \frac{P_1}{T_1} \cdot \frac{P_2}{T_2} \cdot V_{12} \cdot \sigma_{12} \] \hspace{1cm} \ldots \ldots \ldots (3.4)

and this is the basis for the above requirement. For air at ambient temperature the following backgrounds are expected:

<table>
<thead>
<tr>
<th>$P$ (Torr)</th>
<th>$n$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4}$</td>
<td>$3 \times 10^{12}$</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>$3 \times 10^{11}$</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>$3 \times 10^{10}$</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>$3 \times 10^{9}$</td>
</tr>
</tbody>
</table>

This covers the pressure range used in most experiments from "beam/beam" to "beam/gas".

Anticipating equation (3.18), the minimum density of beam species used is ca. $10^{11}$ cm$^{-3}$ and this sets a working pressure region of $10^{-5}$ - $10^{-6}$ Torr with both beams running. The value of $\sigma_{12}$ in (3.4) may be larger for product-background energy transfer than it is for product formation and this means that in general operation at or less than $10^{-6}$ Torr should be sought in order to minimise perturbation of the nascent distributions. If, on the other hand, the resolution of the experiment does not yield rotational and translational distributions (as in infra-red chemiluminescence) the constraint on the vacuum system is considerably relaxed and operation at or less than $10^{-4}$ Torr is normally acceptable.
A further requirement arises from the necessity to have intense, collimated beams. The attenuation of a beam is given by

\[ F = F_0 \exp(-n \sigma L) \]  \hspace{1cm} (3.5)

where \( L \) is the beam path length. For an operating pressure of \( 3 \times 10^{-5} \) Torr \( (n = 10^{12} \text{ cm}^{-3}) \) and a total (elastic) cross-section of \( 100 \text{ A}^2 \), the small exponent approximation to (3.5)

\[ F = F_0 (1 - n \sigma L) \]  \hspace{1cm} (3.6)

is only valid for \( L < 10 \) cm. For \( L = 1 \) cm, only 1% attenuation of the beam results and collision induced spread is negligible.

Given a vacuum chamber of volume \( V \), net pumping speed \( S \) and gas load \( N \), the equation describing the system is

\[ V \frac{dP}{dt} = \dot{N} k T - P S \]  \hspace{1cm} (3.7a)

i.e.

\[ \frac{dP}{dt} = A - BP \]  \hspace{1cm} (3.7b)

with

\[ A = \frac{\dot{N} k T}{V} \text{ and } B = \frac{S}{V} \]  \hspace{1cm} (3.7c)

The solution to (3.7) is

\[ P = A \left(1 - \exp(-Bt)\right) \]  \hspace{1cm} (3.8a)
with the ultimate attainable pressure $P_\infty$ being given by

$$P_\infty = \frac{A}{B} \quad \text{(3.8b)}$$

and the response of the system to a sudden pressure rise having a time-constant given by

$$\tau \sim \frac{1}{B} \quad \text{(3.8c)}$$

For a typical gas load of $5 \times 10^{17} \text{ s}^{-1}$, a net pumping speed of 400 l/s and a volume of 300 l, (3.8) yields

$$P_\infty \sim 4 \times 10^{-5} \text{ Torr} \quad \text{and} \quad \tau \sim 1 \text{ s}$$

Thus, a system with the above characteristics (such as the one described below) would be unsuitable for high resolution beams work but be quite acceptable for LIF determination of vibrational distributions. In addition, to minimise the effects of "drift" on the results, beam modulation should be performed at a frequency $>> 1 \text{ Hz}$.

The appearance of temperature in some of the preceding equations emphasises the utility of cryo-pumping in beams systems. If used sufficiently, the load on diffusion pumps particularly of condensable material is considerably reduced. Alternatively, use of cryo-pumping and large diffusion pumps permits experiments using non-condensable materials. If, in addition, the use of differential pumping is made then the gas load to the main scattering chamber can be dramatically reduced at little extra cost in terms of vacuum hardware. This enables high resolution work to be
carried out using non-condensables\textsuperscript{18} since freedom from multiple collisions is ensured.

3.2.2 DESCRIPTION OF VACUUM SYSTEM

A schematic perspective of the scattering chamber is shown in Figure 3.2. This is a cylinder of diameter 100 cm and height 45 cm constructed of \( \frac{\text{1}}{4} \)" stainless steel sheet (EN58J) rolled into cylindrical form and seam-welded. The base and lid are also of stainless steel each being 2" thick to minimise distortion under vacuum. Eight "mushroom" ports are arranged symmetrically in a plane 25 cm above the base and these were used to mount the two baffle and photomultiplier assemblies as well as various vacuum feedthroughs. Limited cryopumping is possible from liquid nitrogen reservoirs suspended from the lid, the total cooled area being ca. 1 m\textsuperscript{2}. Otherwise, the main pumping is by four 6" oil diffusion pumps (3 Edwards E06 (1300 l/s) and a Leybold D0501 (600 l/s) using M.S. 704 oil (Edwards)). The backing pumps comprise three rotary mechanical pumps (2 x Edwards ED250 (250 l/min) and 1 Edwards EDM12 (200 l/min) and these are protected from attack by iodine using liquid nitrogen cooled foreline traps and activated alumina sieve traps. All vacuum connections conform to the 1" "Speedivac" series (Edwards). Since optical components are present in the vacuum chamber, "backstreaming" of oil vapour from the diffusion pumps must be eliminated. This is especially applicable to the baffle assembly whose effect could be ruined by condensation of oil droplets. Consequently, each diffusion pump is accompanied by two Chevron baffles through which cooling water is passed and under these conditions, no detectable backstreaming occurs. No steps were taken to prevent laser scatter from the walls and components in the tank, the blackening procedure of Cruse et al not being practical in this instance.
Key:  
A Woods horns  
B Microwave cavity  
C L N₂ cryotrap  
D Differential pumping chamber  
E Iodine oven  
F Iodine beam trap  
G Laser baffle assembly  
H Fluorescence collection assembly  
I Optical bench  
J Cooled chevron baffles  
K Ports (4x6") to diffusion pumps

Figure 3.2 - Schematic of vacuum chamber
To lighten the gas load on the system, the O-atom source is contained within a separate, differentially pumped chamber (Figure 3.3) with an estimated\(^{19}\) net pumping speed of 140 \(\ell/s\) resulting in an ultimate pressure of \(\sim 5 \times 10^{-5}\) Torr. The \(I_2\) source is also mounted inside this chamber on a machined plate which rests on three adjustable legs. The combined \(O/I_2\) beam assembly is shown in Figure 3.4. The O-atom supply originates from a microwave discharge in "pure" O\(_2\) the products of which are fed into the scattering chamber by a glass delivery tube compression sealed to a flange on the lid. Immediately below the source assembly is another separately pumped chamber (net pumping speed \(\sim 230 \ell/s\)) which removes the majority of the unattenuated O-atom beam and the attendant O\(_2\) beam through an aperture in the "optical bench" (Figure 3.3b). The \(I_2\) beam is trapped by a liquid nitrogen cooled, "venetian blind" trap constructed of copper.

3.2.3 IODINE BEAM SOURCE

The vapour pressure/temperature curve for \(I_2\) is given below. For source pressures in the range 1 - 10 Torr, the required operating temperature range is 0 - 60\(^\circ\)C which makes for a comparatively simple source.
Figure 3.3 (a) Plan of D.P.C. and optical bench
(b) Section of (a) through A-A'
From O2 discharge

Figure 3.4 - Atomic & molecular beams assembly

Key
A - Glass delivery tube
B - Support for A
C - Oven supports
D - Beams assembly supports
The main requirement for the I$_2$ source is in collimation since intensity can be increased easily by a small increase in source temperature. The cosine intensity distribution characteristic of an orifice source$^{20}$ is unsuitable since the majority of the beam ($\sim 75\%$) misses the reaction zone and is deposited over a wide area of the scattering chamber. A better arrangement utilises capillary arrays which enhance the fraction in the forward direction and generally reduce the angular spread permitting easier cryo-trapping. The physical characteristics of these arrays are well documented$^{21-24}$. 

Figure 3.5

VAPOUR PRESSURE OF IODINE
The construction of the $I_2$ source is detailed in Figure 3.6 and the operational arrangement in Figure 3.4. The body is constructed of stainless steel with recesses to accommodate six heater elements (24 V/25 W GEC. Henley) which are held firmly in position by a stainless steel cover plate. The source temperature is monitored by two Cu/constantan thermocouples, one in the source body and one in the nozzle. The delivery tube to the nozzle extends well into the source to prevent blockage on filling and this is welded to the source base. The nozzle end is separately heated to a temperature a few degrees above the body to prevent blockage by condensation and the beam is collimated by a capillary array plate (25 $\mu$m x 1 mm; Teknis Ltd.) held in position by epoxy resin and covered by stainless steel plate with a 2 mm defining aperture. The iodine charge is admitted through a threaded inlet on the oven top which is tightly shut after filling to maintain a compression seal against the PTFE gasket. Each charge of $\sim$250 g is sufficient for 3 - 4 weeks running.

To estimate the intensity and width of the emergent beam, the following considerations were made:

(a) **Collision diameter of $I_2$:**

This can be obtained approximately from bulk kinetic data such as viscosity, self-diffusion and van der Waals co-efficients. For the former $\eta = 1.84 \times 10^{-4}$ Poise at 124°C \(^{25}\). The value at 40°C (the $I_2$ oven temperature) can be obtained from \(^{26}\)

\[
\frac{\eta_T}{\eta_o} = \left(\frac{T}{T_o}\right)^{1/2} \frac{(1 + C/T_o)}{(1 + C/T)}
\]

\[\text{........................................ (3.9)}\]
Key

A - P.T.F.E. gasket
B - Groove for mounting pins
C - Glass capillary array
D - Cover plate/aperture
E - Groove for heater elements & cover plates
F - Nozzle heater groove & plate
G - 'O'-ring seal (main chamber/D.P.C.)

Figure 3.6 - Iodine oven assembly
The yields

\[ \eta \left( 313 \, ^0\text{K} \right) \sim 1.47 \times 10^{-4} \, \text{Poise} \]

which, when inserted into the equation for the mean free path, \( \lambda \) (cm)

\[ \lambda \sim 8.6 \cdot \frac{\eta \, (\text{Poise})}{P \, (\text{Torr})} \cdot \frac{T \, (\text{K})}{M \, (\text{gm})}^{\frac{1}{3}} \quad \text{............ (3.10)} \]

gives \( \lambda \approx 4 \, \mu\text{m} \) corresponding to an effective collision cross-section of \( 163 \, \text{Å}^2 \) and to a collision diameter of 7.2 Å.

(b) **Critical length of capillary**

The separation of flow regimes into three groups by Giordmaine and Wang are defined by the relationship between capillary dimensions and average mean free path along the capillary. For the present case, their mode II obtains and the application of the equations for gas load, \( \dot{N} \), forward intensity, \( I(0) \), and angular spread, \( \Delta\theta \)

\[ \dot{N} = \frac{2\pi}{3} \cdot \frac{n_0 \, c \, a^3}{L} \quad \text{................. (3.11)} \]

\[ I(0) = \frac{\left( \frac{3 \cdot c \, a}{2^{1/4} \cdot \pi^{1/2} \cdot 8.1} \right)^{1/2} \cdot \dot{N}^{1/2}}{21/4 \cdot \pi^{1/2} \cdot 8.1} \quad \text{................. (3.12)} \]

\[ \Delta\theta = \frac{2^{7/4} \cdot 3^{1/2} \cdot d \cdot \dot{N}^{1/2}}{1.78 \cdot (a \cdot c)^{1/2}} \quad \text{................. (3.13)} \]

rely on the condition:
Substituting in (3.14) for $T = 313 \, ^0K$ requires $L > 0.13 \, \text{mm}$ which is well met by a capillary length of 1 mm.

The resulting values from equations (3.11) - (3.13) have been modified by Johnstone et al.\textsuperscript{22} such that

$$N_{\text{obs}} \sim \frac{1}{2} N_{\text{calc}} \sim 5 \times 10^{16} \, \text{s}^{-1}$$

$$I(0)_{\text{obs}} \sim \frac{3}{4} I(0)_{\text{calc}} \sim 1 \times 10^{17} \, \text{cm}^{-2} \, \text{s}^{-1}$$

and

$$\Delta \theta_{\text{obs}} \sim 2 \Delta \theta_{\text{calc}} \sim 13^0$$

The number density of I\textsubscript{2} at the reaction zone (1 cm from nozzle) was ca. $5 \times 10^{12} \, \text{cm}^{-3}$. Finally, since the I\textsubscript{2} beam was purely effusive, no cooling of its degrees of freedom were likely to have occurred at these low pressures\textsuperscript{27}. The internal and translational distributions were therefore represented by Boltzmann forms corresponding to the nozzle temperature of $\sim 320 \, ^0K$. The peak translational velocity was 175 m/s with a half-width of $\sim 170 \, \text{m/s}$ (95%) assuming a $v^3$ Maxwellian distribution\textsuperscript{23}. The peak
rotational quantum number was $J \sim 55$ with a half-width of $88 \, \hbar$ and the vibrational distribution was

$$v'' = 0 : 1 : 2 : 3 : 4 = 1.00 : 0.37 : 0.14 : 0.05 : 0.01$$

with only $\sim 64\%$ in the $v'' = 0$ state.

3.2.4 OXYGEN ATOM SOURCE

The production of atomic oxygen has been a pre-occupation of many chemists and physicists over the last three decades. A number of methods exist for its production notably by electrical discharge, thermal dissociation, and by pyrolysis or photolysis of ozone. Whilst the latter yields $\text{O} \left( ^1\text{D} \right)$ and $\text{O} \left( ^3\text{P} \right)$ depending on photolysis wavelength, such a source is best suited to $\text{O} \left( ^1\text{D} \right)$ production since its production in electrical discharge is followed by its immediate collisional deactivation by $\text{O}_2 \left( ^3\Sigma_g^- \right)$ on a sub-microsecond time scale. Recent advances in $\text{O} \left( ^3\text{P} \right)$ production have meant that both photolysis and pyrolysis are no longer attractive propositions.

Since the dissociation energy of ground state $\text{O}_2$ is $\sim 5 \, \text{eV}$, the temperature of a thermal dissociation source (e.g. iridium oven) needs to be above $2000 \, ^\circ \text{C}$ for appreciable dissociation at $\sim 1$ Torr. At these temperatures, the $\text{O}$-atoms have a broad velocity distribution centred round $1750 \, \text{m/s}$ which is often unsuitable in molecular beams work unless velocity selection is made. In L.I.F. experiments, close positioning of the source (electrical/thermal) to the reaction zone can introduce problems of stray light from the source which is above the time signal level of the reaction.
Of the electrical discharges, only two are currently of any importance notably the RF type (1 - 30 MHz) and the microwave type (2450 MHz). It was established early on \(^{28}\) that electrode discharges caused sputtering of the electrodes and immediate discharge tube to the detriment of the atom production. Thus, choice of the atomic oxygen source rested on the "electrodeless" discharges which had similar performances\(^{31, 33}\). A comparison of the two methods has been given by Horne\(^{37}\) (for halogen dissociation) who found the RF type more suitable at the low pressures (< 0.5 Torr) he employed although claiming that the microwave discharge gives higher dissociation over a wider pressure range above \(\approx 1\) Torr.

To test the suitability of each, a direct comparison using the chemiluminescent titration reaction

\[
0 + NO \rightarrow NO_2^* \rightarrow NO_2 + h\nu \text{ (green/yellow)}
\]

was made. This study substantiated the earlier ideas that the RF discharge (27 MHz, 200 W) was most suitable below 1 Torr and that the microwave discharge was unstable in this regime, the stability improving with increasing pressure. The degree of dissociation, although not obtainable absolutely, was always greater for the microwave discharge, this being evident from the titration figures\(^{\dagger}\) as well as the visual intensity of the emission. This may well have been due to the inherent difficulty of coupling the RF into the load efficiently; all attempts to match the load

\(^{\dagger}\)No quantitative results are presented since it was only found possible to reproduce trends due to uncontrollable drifts in signal levels. Attempts to calibrate the flow through capillaries (Poiseuille) were unsuccessful thus precluding absolute dissociation figures.
to the generator were unsuccessful largely and power measurement via a standing wave meter was not possible.

One of the most serious limitations of the R.F. discharge was the tendency for it to spread to the low pressure end of the flow system irrespective of power coupling mode (capacitative/inductive). Below \( \sim 1 \) Torr, discharges often extended \( \sim 150 \) cm into the rotary pump whereupon the pump oil fluoresced blue! Since the presence of a light source close to the interaction region in a L.I.F. experiment is not desirable, this method of atom production was rejected.

The arrangement of the discharge source is shown schematically in Figure 3.1. The power source was a 2450 MHz magnetron (Electro Medical Supplies Ltd. EMS 200 Mk II) from a diathermy unit feeding a standard Evenson (no. 5) cavity (West X-Ray, Edinburgh). The discharge tube was of clean fused quartz connected to a clean pyrex delivery tube of total length ca. 60 cm having two Woods horns to eliminate stray light. The nozzle (Figure 3.4) was ground from a rounded glass tube to a diameter of \( \sim 20 \) thou. (1/2 mm) taking care to ensure no regions of high surface area: volume ratio occurred which would cause considerable recombination of the O-atoms. It seems that untreated pyrex does not lead to high rates of wall recombination although the most recent report considers only pyrex tubes coated with O-phosphoric acid as originally recommended for halogen atom sources. The 0/0\(_2\) beam from the orifice was collimated and skimmed by a 2 mm aperture in the \( \text{I}_2 \)-oven mounting plate, the excess being differentially pumped.

\[^{\dagger}\text{Another effect of the RF source was to radiate high noise levels in the immediate vicinity which could be picked up in distant laboratories.}\]
The above arrangement is essentially similar to that of Radlein et al.\textsuperscript{43} and similar remarks were expected to apply to it. It was not possible to directly measure the degree of dissociation \textit{in situ} since a suitable mass spectrometer was not readily available. The predominant species were therefore expected to be

\begin{align*}
&O_2\left(^3\Sigma_g^+\right) \sim 90\% \\
&O_2\left(^1\Delta_g\right) \sim 1\% \text{ \textsuperscript{43}} \\
&O_2\left(^1\Sigma_g^+\right) \sim 10^{-2}\% \text{ \textsuperscript{31}} \\
&O\left(^3p_g\right) \sim 10\% \text{ \textsuperscript{41, 43}}
\end{align*}

with no appreciable ionic contribution\textsuperscript{18, 28, 37} or O\left(^1D\right)\textsuperscript{36}. Since the vibrational excitation of the molecular species was not expected to be high\textsuperscript{28} the contribution of these to the overall reaction was considered negligible.

The oxygen used was commercial grade (99.5\% purity) and was not further purified. The main impurities present are N\textsubscript{2} and H\textsubscript{2}O and these are known to be positively beneficial to efficient O-atom production\textsuperscript{30, 31} compared to clean discharges in pure O\textsubscript{2}. Input power to the discharge was 100 W with < 5 W reflected (total resonance results in "hot spots" on the discharge tube and reduces its lifetime). Under these conditions the source throughput, \( \dot{N} \), and the forward intensity, I(0), given by

\[
\dot{N} = \frac{1}{4} n_0 \bar{c} A_s; \quad \text{............... (3.15)}
\]
\[ I(0) = \frac{N}{\pi r^2} \] ........................ (3.16)

is

\[ N \sim 5 \times 10^{17} \text{ s}^{-1} \] and \[ I(0) \sim 5 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1} \]

for an orifice-reaction zone distance, \( r \), of 2 cm. If 10% of the forward intensity is due to \( \text{O} \)-atoms (corresponding to \( \sim 5\% \) dissociation of \( \text{O}_2 \)), then the figure is reduced to \( I(0) \sim 5 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1} \). The peak velocity of the \( \text{O} \)-atom beam given by

\[ v_{pk} = \left[ \frac{3RT}{M} \right]^\frac{1}{2} \] ........................ (3.17)

which, for an effective source temperature of 350 \( ^\circ \text{K} \) gives \( v_{pk} = 740 \text{ m/s} \) and the corresponding number density of \( \text{O} \)-atoms in the reaction zone is given by

\[ \bar{n} = \frac{\int_0^\infty P(v) n(v) \, dv}{\int_0^\infty P(v) \, dv} \] ........................ (3.18a)

where

\[ n(v) = \frac{I(0)}{v} \] ........................ (3.18b)

and

\[ P(v) = v^3 \exp \left( -\frac{mv^2}{2kT} \right) \] ........................ (3.18c)

i.e.

\[ \bar{n} = \frac{I(0) \int_0^\infty v^2 \exp \left( -\frac{mv^2}{2kT} \right) \, dv}{\int_0^\infty v^3 \exp \left( -\frac{mv^2}{2kT} \right) \, dv} \]

\[ = I(0) \cdot \frac{1}{c} \] ........................ (3.18d)
with \( \bar{c} \) given in equation (3.14). This corresponds to \( \bar{n} \sim 7 \times 10^{10} \text{ cm}^{-3} \).

3.2.5 COMMENTS

The vacuum system described above is obviously far from ideally suited to the job in hand and this stems from its previous history. To obtain better vacuum performance and beam characteristics (particularly \( 0/0_2 \)) the chevron baffles in the pumps serving the D.P.C. and the gas beam dump (Figure 3.3) could be completely removed since backstreaming from these pumps is not likely to be serious. The pumping speed in each chamber can in practice be increased by factors of \( \sim 5 \) and \( \sim 3 \) respectively. Likewise, in the main chamber, the two-stage water cooled chevrons could more effectively be replaced by single stage refrigerated baffles allowing an increase in the net pumping speed of \( \sim 50\% \) without added backstreaming. In addition to this, replacement of the existing liquid nitrogen reservoirs on the lid by coppers cold shields (plated with Nickel for protection) throughout the tank. This step alone would greatly reduce "cold" background of both condensable reactants and products as recently observed 44.

For the beam sources, considerable improvement in \( 0 \)-atom production could be realised using an intra-vacuum microwave discharge 5, 32. The author has recently observed dissociation of up to 30\% in a pure \( 0_2 \) and a helium seeded \( 0_2 \) discharge at oxygen pressures from 1 to 20 Torr. This represents a hundred-fold increase in atom flux. The iodine source was found in practice to be difficult to set up and align accurately. A better arrangement would have an extra vacuum oven (glass bulb) feeding a heated glass pipe fed through the vacuum wall to the reaction zone. This approach offers some degree of modularity since it could also be used for \( \text{Br}_2 \) unlike the present arrangement. Ordinary "pyrex" glass is far more resistant to halogen attack than all of the common metals.
3.3 LASER SYSTEM

3.3.1 INTRODUCTION

The requirements on the dye laser beam which irradiates the reaction zone are:

1. High stability in its spatial, spectral and temporal characteristics
2. High average spectral power density
3. Low bandwidth (for rotational resolution)
4. High reproducibility.

These requirements in turn set performance limits on the pumping source. If, in addition to dynamical information, spectroscopic information is sought, the most appropriate laser system is a short pulsed one (for lifetime studies). In this case, a major source of noise stems from the associated pulsed discharges which produce mainly radio-frequency interference (R.F.I.) and steps must be taken to eliminate this. A number of possible contenders exist for this type of work and their relative merits are considered below.

(a) Flashlamp pumped dye-lasers

These pulsed lasers are characterised by high energy output (0.001 - 10 J/pulse) and comparatively long pulse lengths (∼1 μs). The pumping source is either a linear or co-axial (Xe) flashlamp emitting black body radiation (with superimposed lines) of characteristic temperature 7000 - 12000 °K. Due to the practical difficulty of filtering both the
harmful U.V. (photo-degrading) and I.R. (heating) regions, this type of laser suffers from excessive consumption of dye solution. This in conjunction with the heating effect requires a large dye reservoir to feed a fast flow cavity with the inclusion of micropore filters to clean the dye. The pulse length of this type of laser is invariably too long for lifetime studies & to obviate this electro-optic chopping of the output beam is necessary. The stability of the output beam is not very high due to thermal effects in the active region, and the ability of flashlamps to pump U.V./blue dyes is severely hindered by photo-degradation to the extent that frequency doubling of rhodamines is usually employed. The operating pulse repetition rates (P.R.F.) are $10^{-1} - 10^2$ Hz but at the higher end the system lifetime is considerably shortened by the flashlamps, $10^6$ shots being a high figure here.

The long pulse length and consequent mode structure places stiff engineering tolerances on the construction of this type of dye laser. The cost of a complete system (before liquidation of Electro-Photonics Ltd) was £20 - 30 and the cost of running and replacing flashtubes is generally high. Although there has recently been some resurgence in activity in this field lately with some respectable designs being published, the flashlamp pumped dye laser has not yet found its way into L.I.F. in molecular beams and, indeed, is not likely to do so in the future.
Continuous-Wave (CW) dye lasers

These are the best developed types of dye laser at least commercially. They offer high spectral power and stability but do not easily allow lifetime determination. For the present application, they are undoubtedly the best since beam quality is very good (low scattered noise) and derived signals are high even at high resolution\(^\text{15}\). Most C.W. dye lasers are pumped "all line" by \(\text{Ar}^+\) lasers (488 and 514 nm) and can achieve conversion efficiencies of up to 35% with Rhodamine 6G. However, efficiency in the blue is much less (\(\sim 8\%\)) and it is more common to use \(\text{Kr}^+\) lasers here (\(\text{E} \sim 18\%\)). The \(\text{Kr}^+\) pump has the added advantage of being very efficient at pumping I.R. dyes (\(\sim 35\%\)) as well. Although basic C.W. (Jet Stream) dye lasers are "cheap" in comparison to pulsed dye lasers (< £10 k), the pump laser is expensive (\(£10\, k - 20\, k\)) and is particularly prone to damage in transit and operational failure. In addition, the high optical quality of this type of laser mandates clean room operation free from vacuum pump oil vapours which progressively coat the delicate optics. The recent development and commercial production of a British argon laser and jet stream dye laser in conjunction with the new Coherent Radiation Ltd. production facility at Cambridge is likely to stimulate greater use of these lasers in the future. However, despite their suitability, their considerable price could not be met at the outset.
Rare gas halide excimer lasers\textsuperscript{46a, b}

This mis-named laser was announced in late 1975 in the West although it was available in the East five years previous to this. The operation of this laser is very similar to that of double-discharge TEA CO\textsubscript{2} lasers and the well-developed technology of the latter was fairly straightforwardly adapted to it. They do not lend themselves so readily to home-construction as N\textsubscript{2} or CO\textsubscript{2} lasers since the use of fluorine containing gases requires safe gas handling and passivated discharge cavities. Despite this, they have advanced enormously since 1975 with "Multi-Gas" versions being very popular. Laser action at discrete wavelengths from 193 nm to 10.6 \textmu m including 337 nm (N\textsubscript{2}) is available now at very high power (0.1 - 1 J/pulse) and high PRF (< 200 Hz). Their high power does not readily permit high power dye laser construction without resort to oscillator/double amplifier configurations to prevent super-radiance. The alternative of attenuating the pump beam is wasteful. Nonetheless, their rapid exploitation has meant that they are now cheaper than nitrogen lasers as well as being more efficient at lasing on 337 nm than the latter! However, there is still a lot of development work to be done on dye lasers to match these, none being commercially available and few being published\textsuperscript{46c}.

Nd: YAG pumped dye lasers.

This type was not well known at the outset of this project with only one very expensive commercial version being available. This is particularly curious since solid state lasers, especially the Nd\textsuperscript{3+} based ones, are the best developed of all lasers and, indeed, always have been. Operation of Nd: YAG lasers in Q-switched mode can produce pulses of 10 - 100 ns at up to a few kHz PRF with high reproducibility. In addition, efficient
frequency mixing to give output wavelengths of 266, 355, 532 and 1064 nm has long been possible with the result that the entire spectrum of presently available dyes can be pumped. Despite this, it was only around 1977 that these unique properties were exploited and presently around half a dozen are commercially available. However, most work here has been done on pumping Rhodamine dyes at 532 nm and little on pumping at 266 and 355 nm. Evidently excited state absorption limits the usefulness of this pump (which is necessarily longitudinal) for blue emitting dyes although conflicting reports also occur on this point.

(e) Nitrogen laser pumped dye lasers.

This has been by far the most popular choice of system by virtue of its ease of home construction and the wealth of detailed information on both components which exists in the literature. The dye laser invariably used is the Hansch type although a simpler variant using achromatic prism beam expanders is gaining increasing popularity. Moderate resolution (few Å) is readily achievable without elaborate engineering and very high resolution (< 50 MHz) is obtainable by pressure tuning again without complex engineering.

As for the pump laser, many hundreds of design orientated papers have appeared since its inception in 1963 but the scene is dominated by a few notable ones of which only three were known in 1973 all of which suffered severe reduction in output peak power at high repetition rates. We therefore set out to build a nitrogen laser which did not suffer from this reduction at high P.R.F. hoping that the average power (which determines S: N) was also high. Both lasers are described in detail below.
3.3.2 NITROGEN LASER

A primary design consideration here was the choice of energy storage medium and fast switch. For the former, use of high voltage ceramic (doorknob) capacitors tends to limit the laser lifetime by high frequency heating and their discrete distribution along the laser cavity gives rise to non-uniform discharges. Use of co-axial transmission lines \( Z_0 \sim 17 - 70 \Omega \) requires many parallel cables to provide a high enough capacitance \( (\sim 10 \text{ nF}) \) and low enough impedance \( (< 0.5 \Omega) \) and inductance \( (< 5 \text{ nH}) \). In practice some 50 - 100 cables are necessary giving rise to engineering problems. In view of this, a Blumlein\(^6\) arrangement was used since this allowed a uniform discharge and some control on the optical pulse length via the two-way transit time.

Having had previous experience with a spark-gap switched \( \text{N}_2 \) laser, the choice of hydrogen thyatron switching was immediate since operation over long runs without degradation of the switch and consequent cleaning was essential. Although carefully designed spark gaps can have very low inductances \((1 - 2 \text{ nH})\)\(^6\), a major requirement for a fast-rising excitation pulse \((10^{11} - 10^{12} \text{ A/s})\), the near independence of the actual laser discharge on this quantity\(^5\) relaxes the inductance constraint and in practice 5 - 20 nH is acceptable. The general advantages of thyatron switching are

\[\begin{align*}
(1) & \quad \text{lower trigger voltage than spark gap} \\
(2) & \quad \text{less timing jitter} \\
(3) & \quad \text{greater shot-shot reproducibility of the laser output} \\
(4) & \quad \text{higher PRF} \\
(5) & \quad \text{longer lifetime.}
\end{align*}\]
To facilitate high PRF operation without loss of peak power, a sandwich type of laser discharge gap was adopted with transverse flow of N₂ between the electrodes. This arrangement had been previously noted for its high PRF performance. In addition to permitting diffusion of metastables (N₂ A²Π) to the glass walls in 1 - 10 ms, the transverse flow ensured freedom from pressure gradients along the length of the discharge tube which obtain with longitudinal pumping and give rise to non-uniformities. In addition to cooling by diffusion, pumping also contributes here but to a much lesser extent such that complete renewal of the gas between shots is unnecessary. Indeed, residual ionisation in the cavity is beneficial since this contributes to discharge uniformity and output reproducibility. The increasing cost of oxygen-free N₂ is another factor in this respect. In practice the throughput of gas should be the minimum necessary to preserve maximum output power.

3.3.3 MECHANICAL

The construction of the laser is detailed in Figure 3.7. The cavity consists of two 2 mm thick, 100 cm long dural electrodes sandwiched between two sheets of float glass of thickness 5 mm (upper) and 11 mm. The electrode spacing was set at 5 cm. A vacuum seal is maintained by sealing the glass plates to perspex supports with silicone rubber compound (RTV) and by using extruded silicone cord 'O'-rings to seal the electrodes and end windows. The latter (not shown) are composed of quartz slides (6 cm x 1 cm x 2 mm) cemented to machineable ceramic plates with epoxy resin. These plates complete with 'O'-ring are screwed into place against the ends of the perspex cavity surrounds. The arrangement shown was the end result of a number of previous failures using progressively
Fig. 3.7
MECHANICAL

Material: Dural (cavity and line); brass (thyatron housing)

Cavity:
Length 100 cm
Electrode gap 5 cm
Glass plate spacing 0.2 cm

Blumlein:
Outer plates 110 x 100 x 0.25 cm
Inner plates 95 x 95 x 0.16 cm
Plate separation 0.32 cm

Thyratron Housing:
Length 15.6 cm
i.d. 10.2 cm

ELECTRICAL

Dielectric: Polyethylene (K = 2.3; strength = 50 kV/mm)
Total Capacitance: 27 nF
Total (line) inductance: 1 nH
Thyratron inductance (est.): ~ 10 - 20 nH
Line impedance: 0.37 Ω
Two-way transit time: 10 ns
Charging: Full-wave rectified a.c.
Triggering: On zero-crossover of charging voltage
Thyratrons:
Laser - EEV CX 1180
Trigger - Mullard EN91

OPTICAL

Peak power: ~ 45 kW
Width: 14 ns FWHM
Jitter: < ± 2 ns
Reproducibility: < ± 3%

Table 3.1 - Description of $N_2$ Laser
thinner float glass which inevitably cracked under the combined effects of differential expansion and atmospheric forces. The entire cavity was sandwiched between two dural cover plates, the window ends being covered with dural plates tightly screwed onto the cover plates and slotted to pass the laser beam.

The $N_2$ gas was admitted through a series of glass capillary tubes and subsequently flowed through 101 $\frac{1}{1}$ mm holes in the H.V. electrode spaced at 1 cm intervals. The spent gas was exhausted through some 40 $2$ mm saw cuts in the earth electrode to a rotary pump (Edwards EDM6, 100 $l/min$) via 20 $\frac{1}{2}$ cm glass tubes protruding through the top dural cover plate. Cavity pressure was read by an aneroid capsule gauge (Edwards) and was varied by throttling the inlet. The volume of the cavity was $100 \text{ cm}^3$ and at working pressures of $\sim 30$ Torr, a standard $O_2$-free $N_2$ cylinder (99.9% purity) lasted 2 - 4 weeks. At 100 Hz PRF, a maximum of 17% of the previous fill was exhausted but when the finite conductance of the connecting tubes is considered, a figure nearer 10% is probably more appropriate. Calculations of diffusional transfer rates, supported by 1-D random walk estimates, imply a 1 - 10 ms transit time to the walls. Thus, the gas conditioning is diffusion controlled largely although atoms and atomic ions which require three-body collisions for their removal can be seen via the Lewis Rayleigh afterglow in the exhaust pipes. On switching off the laser, this glow is extinguished in substantially less than one second.
The Blumlein pulse forming line/energy storage capacitor was constructed from five Al plates and is shown in section in Figure 3.7. The outer plates were 100 cm wide and \( \frac{1}{6} \)" thick whilst the inner plates were 96 cm wide and 1/16" thick. The dielectric used (polythene) was in the form of 1/16" sheet, each plate in the assembly being separated by two thicknesses. The inner plates were insulated from the vertical supporting bars (not shown) by allowing the excess dielectric to fill in the 2 cm gap. The innermost H.V. plate was attached by 40 6 BA brass screws to the H.V. electrode as shown and the screws covered by silicone rubber and further protected from arcing to the outer Al plate by a double layer of dielectric. The other two H.V. plates were connected at the base by a threaded dural bar to which they were screwed. This same bar forms the connection to the thyatron anode by means of a brass connector. The base of the Blumlein assembly is firmly held together by another dural bar of 100 cm length as shown. Thus, the entire laser assembly is held at earth potential to reduce RFI and effectively forms its own integral Faraday cage.

The thyatron housing is also indicated in Figure 3.7 although not to scale. The brass connector to the inner H.V. plates is a four quadrant hollow cylinder which is machined to tightly accommodate a male connector screwed to the thyatron anode. The housing is screwed onto the outer Blumlein plate as shown and a seal is maintained by a 1/4" PTFE gasket disc which supports and isolates the anode connector. The thyatron itself is bolted to the cover flange of the housing and sealed by an 'O'-ring to prevent cooling oil leakage, the flange being similarly bolted and sealed to the housing. The entire assembly is constructed from brass which,
although heavy, provides good protection from X-ray emission and facilitates construction by soldering flanges to the tube. The coolant used is untreated (cf. ref. 55) transformer oil pumped through the housing by a diaphragm pump (Capex III, Charles Austin Ltd.). Provision to cool the oil by heat exchanger was made but found in practice to be unnecessary. The electrical connections to the thyatron were made by 'O'-ring sealed feedthroughs on the cover plate.

Two important points arose from the laser construction. Firstly, it was crucial to avoid undue stress on the discharge cavity which led to the glass cracking. Any 'play' was taken up by layers of Al foil such that tight fitting joints could be achieved without stress in order to minimise RFI. The second point concerns sharp points on any high voltage component particularly screws and solder joints. These had to be smoothed by filing or scraping and further protected by an insulating layer. The Blumlein assembly required considerable care and time in construction which could be lost by a single defective element causing breakdown. Successful construction however resulted in faultless operation for considerable periods of time (> 1 year).

3.3.3 ELECTRICAL

The nature of the Blumlein element represented below plays a major part in the laser characteristics and to a first approximation, the performance of the laser can be projected at the design stage.
A choice of ~10 ns for the two way transit time was made to result in a dye laser pulse of 5 - 8 ns, not too long to lose gain by spontaneous emission and not too short to ensure a high ratio of laser emission to super-radiant background. Thus, for a dielectric constant, $K$

$$\tau_{2\text{-way}} = \frac{2L}{C} = \frac{2K^{\frac{3}{2}}L}{C} \quad \text{ .............. (3.19)}$$

$\sim 10 \text{ ns}$

For $K \sim 2.5$, (3.19) requires a line length of 94 cm and a working value of 100 cm was chosen.
In order to achieve peak powers in excess of 100 kW (1 mJ/pulse) the energy storage of the line must exceed a value given by

\[
E_{\text{line}} = \frac{E}{\text{pulse}} \frac{1}{\text{Efficiency}} \quad \text{(3.20)}
\]

The electrical efficiency of N\textsubscript{2} lasers is commonly 0.05% such that a stored energy of \(\sim 2J\) is required. Now,

\[
E_{\text{line}} = \frac{1}{2} CV^2
\]

\[
= \frac{1}{2} \frac{L \cdot W \cdot K \varepsilon_0}{d} V^2 \quad \text{(3.21)}
\]

which for \(K = 2.5, V = 10 \text{kV}, L = 1 \text{ m}\) requires \(W/d \sim 2 \times 10^3\).

The inductance of the line is of major importance and should be ca. 1 nH to ensure minimum back-emf when the laser fires. For the Blumlein

\[
L = 4\pi \frac{9}{4} 10^2 \frac{d \text{ (nH)}}{W} \quad \text{(3.22)}
\]

and a value for \(W/d\) of \(\sim 1 \times 10^3\) is necessary, roughly consistent with the energy storage.
To complete the selection of parameters, a choice of \( W \sim 1 \) m for the length of the cavity was made since this represented a compromise between practicality and the requirement for high shot-shot reproducibility which is not met by short cavities. This required the plate spacing, \( d \), to be 0.5 - 1 mm a value too low for safe operation. To obviate this however, four capacitors were folded together in parallel with a plate spacing of \( \frac{1}{8} \) (3.2 mm) to provide the required capacitance whilst reducing the inductance. This is shown in section in Figure 3.7. Polythene sheet which was readily available in quantity was used as the dielectric (\( K = 2.3 \)). It has one of the highest breakdown strengths known (50 kV/mm) and consequently relaxes the stringent constraints on the Blumlein construction.

The final electrical parameters of the line are listed in Table 3.1.

The complete electrical circuit for the laser is shown in Figure 3.9 and details of individual electrical processes are given in the appendix. The design stemmed from the group's inheritance of a 30 kV/300 mA full-wave-rectified a.c. power supply. Rather than go to the expense and potential danger of a large L-C smoothing network, it was decided to fix the laser frequency at 50 or 100 Hz corresponding to zero crossings in the output waveform. This approach although not entirely original was adopted to minimise current surges in the H.V. supply since the output voltage at the instant of discharge is zero. This in turn helps reduce interference in the power lines. The scheme is as follows: First, the output from the H.V. rectifier is sampled by the 10K, 1M, 100M resistor network resulting in two positive portions of a sine wave being presented to the input of the 741 difference amplifier, the output being a reconstructed sine wave in phase with the H.V. transformer secondary. This waveform is sampled by the two 710 comparators which are set for 0-\( \delta \) and 0 + \( \delta \) volts giving a level
change at their output when every zero is crossed. This is converted to a fast, negative-going 5V pulse by the 7412 N monostable whose output time constant is set in accordance with the specifications of the trigger thyratron (Mullard EN91) i.e. RC \( \sim 10 \) \( \mu \)s. This TTL pulse is inverted and raised to 12V by the 7406 inverter/driver and fed capacitatively to grid one of the trigger thyratron which is normally held off at \(-10\) V.

The trigger thyratron then discharges a pulse-forming network (P.F.N.) and a positive going pulse is transmitted to the main thyratron (CX 1180, English Electric Valve Co.) through the pulse transformer. This pulse gates "on" this thyratron and subsequently initiates the laser discharge. This pulsing scheme is superior to previous ones in that timing jitter is minimised by using fast rising TTL pulses to drive a thyratron. The use of silicon controlled rectifiers (SCR) in this application results in poorer jitter performance and limited lifetime due to the high peak currents involved. One drawback of the circuit shown however is the tendency for capacitative pickup on the grid of the trigger thyratron to be fed back into the low level circuitry via the 470 pF coupling capacitor. Although untried during the author's time, the inclusion of a voltage dependent resistor should eliminate this.

3.3.4 OPTICAL

The laser pulses emitted were fairly symmetrical approximating a sine-squared waveform with a full width at half height (FWHM) of \( \sim 14\) ns. A representative example reproduced from an oscilloscope photograph is shown in Figure 3.13 (b). The exact pulse shape depended on operating conditions with double pulse formation similar to that reported by Godard\(^6\) and by Geller et al.\(^5\) occurring both at low pressure and high voltage. The peak
separation here was reproducibly \( \sim 4 \) ns which did not correspond to any characteristic time of the system. In view of this it seems most likely that laser action occurs preferentially at one site along the cavity closely followed by the remainder. This is further substantiated by the observation of pulse shape variation with lateral sampling position at the laser output.

In addition, it was also noted that the majority of the laser output was concentrated in two lines parallel to the cavity walls. This has also been previously reported\(^{64, 65}\) although with conflicting claims as to its usefulness. The mechanism responsible is dielectric pre-ionisation of the gas by the glass walls leading to preferential discharge along their surfaces. In this particular case it had both good and bad attributes: the low \( (\sim 7 \) kV) threshold and corresponding low optimum \( (\sim 10 \) kV) voltages meant that voltage induced stress on all electrical components, particularly the thyratron, was considerably lower than in most other \( N_2 \) lasers. However, a maximum voltage of only 15 kV could be applied without onset of serious timing jitter and amplitude instability. Beyond this, arcing set in and stopped any laser action. It was evident after prolonged running that arcing took place where accumulation of dirt occurred emphasising the need for a clean cavity and avoidance of dust and moisture intake from the \( N_2 \) gas supply.

The peak output power was measured using a calibrated neutral density filter and a biplanar photodiode (I.T.L. Ltd.) with an Si response the output of which was displayed on a Tektronix 7904 oscilloscope using the 7A21 (1 GHz) plug in (risetime 0.35 ns). A value of \( \sim 45 \) kW obtained which was seen to increase only very slightly \( (< 15\% ) \) as the PRF was
reduced from 100 Hz to single shot. This is again consistent with the idea of dielectric preionisation: the charging voltage at low PRF's tends to the peak a.c. voltage (ca. 1.4 x V_{meter} - see Appendix) and it was expected that this would increase the peak power by at least 20%. The fact that it did not implies the discharge was struck before maximum voltage is reached in the pulse forming line.

The variation of peak power with running voltage and cavity pressure is shown in Figure 3.10. The latter takes on a very familiar form \textsuperscript{53, 54, 66} with the peak shifting towards higher voltages as the pressure is raised. The broadening observed above 12 kV in the pressure curves is consistent with dielectric preionisation. The dependence of peak power on voltage emphasises the insensitivity of the present laser to this variable above \(\sim 10\) kV over a wide pressure range. This is peculiar to few other \(\text{N}_2\) lasers reported most of which display a monotonic increasing dependence. The optimum operating condition is 10 kV, 25 Torr, the lower pressure being chosen to reduce gas consumption. Under these conditions, the electrical efficiency is 0.045%, the wall plug efficiency being \(\sim 0.02\)% due to charging resistor losses. This figure is comparatively high for this type of laser\textsuperscript{60} being higher than that of the capacitor-transfer type with thyratron\textsuperscript{56} and similar to the spark gap version of the latter\textsuperscript{54}. The mean power however is comparatively low being \(\sim 60\) mW at 100 Hz PRF.

The performance of the laser with respect to amplitude reproducibility, stability and timing jitter is very good. The former was not detectable beyond the thickness of the oscilloscope traces and sets a limit of \(\pm 3\)% when working optimally whilst the jitter seldom exceeded \(\pm 2\) ns referred to the monostable output (Figure 3.9)
Figure 3.10 - N₂ laser output power characteristics
One effect seen by chance was the variation in pulse onset delay (w.r.t. monostable) seen on the 'scope when the pressure was varied (at fixed voltage) or the voltage varied (at fixed pressure). The results for this are shown in Figure 3.11 for optimum pressure and voltage. More physical insight is derived from the accompanying reduced plot of delay vs. V/P (or E/P). A limiting operative value for V/P of 250 V/Torr is evident from the vertical asymptote corresponding to a limiting field of 50-80 V cm\(^{-1}\) Torr\(^{-1}\) taking correction of the voltmeter reading into account. This is below the limiting value of 80 V cm\(^{-1}\) Torr\(^{-1}\) proposed elsewhere\(^54,66\) and is strong evidence in favour of dielectric preionisation. The optimum running conditions occur for E/P \(\sim\) 100 V cm\(^{-1}\) Torr\(^{-1}\) which is substantially lower than previous reports\(^50,54,63,66\).

The variation of pulse onset delay with voltage, all other variables held fixed, indicates that the laser does not discharge at the peak of the charging cycle (see Appendix) for the thyatron Blumlein combination since no variation would occur in this case. In this respect, the laser is therefore not functioning optimally\(^55,67\). In the absence of detailed knowledge of the thyatron and laser discharge processes, the time scale for the above effect cannot be confidently related to the temporal behaviour of the discharge. However, the conformation of the independent variations to a single reduced plot indicates that the delay is due to the build-up of electron density and subsequent population inversion in the cavity. If this is the case then it must extend to other operationally similar pulsed gas lasers, exhibiting a similar but displaced reduced plot.
Figure 3.11 - Time delay characteristics of N\textsubscript{2} laser emission

Pulse onset delay (ns)

- 10 kV
- 25 Torr

P/Torr

V/V\text{p} (kV/Torr)
3.3.5 DYE LASER

Since a wealth of design information is readily available for pulsed dye lasers it is good economy to home-build these since commercial ones are enormously expensive. The ease of short-pulsed dye laser construction over C.W. versions stems from their lack of cavity mode structure. The \( \text{N}_2 \)-laser-pumped dye laser is not an oscillator as it is often termed but a wavelength selective amplifier. The design chosen was the much acclaimed one due to H"ansch and is detailed in Figure 3.12.

The complete laser assembly occupies an area \( \sim 90 \times 40 \text{ cm}^2 \) and is mounted on a rigid metal table. The basic elements include a spherical (silica) lens to focus the pump beam, an optical bench containing the dye laser and beam-steering optics, a grating assembly with drive unit and a dye circulator.

The optical bench (Oriel; B-16-202) supports the laser optics on movable carriages (Oriel; B-23-62/52) with dovetailed bases. The output coupler is a dielectric coated mirror of \( \frac{1}{2} \text{ m} \) radius of curvature (Oriel; B45-40; \( R = 0.6 \text{ in} \lambda(400, 600 \text{ nm}) \)) held in an optical mounting (Oriel: B-45-40-02). This is followed by a 400 \( \mu \text{m} \) pinhole (Ealing) whose function is to suppress amplified super-radiance and generally improve the output beam quality by removing stray reflections.

The dye cell consists of a milled channel in a perspex block (3.5 x 1.0 x 1.0 cm) bounded on its three open sides by a quartz window (\( \text{N}_2 \)-laser) and two glass windows. The latter are deliberately offset with respect to each other and the cavity axis to avoid internal "etalon" effects. The three windows were carefully cemented to the perspex body using cyanoacrylate adhesive, ensuring none entered the cell. The complete
cell is mounted in a custom-made carriage which permits rotation, translation \((x, y, z)\) and tilting to correct for optical axis variations brought about by refraction at the dye cell as well as general utility. Dye solution is circulated in the cell via two brass tubes as indicated coupled to a novel pump (created by A.G.A. Rae). This consists of a nylon (or PTFE) impeller connected by a shaft to a ferrite bead. The latter is spun by an external rotating magnetic field (a horseshoe magnet mounted on a fan induction motor). The pump body consists of two parts; one containing the impeller and the other, the ferrite bead. These are bolted together and compression sealed with a suitable 'O'-ring. Dye is delivered to/from the pump by silicone rubber tubing and any "ripple" in the flow caused by the impeller is "smoothe\(d\)" by passage through a reservoir of dye solution \((\sim 5\) cm of dye solution in a test tube). The peak-to-peak output power variation using this arrangement was < 5%.

The beam expanding optics consisted of a commercial Galilean telescope (Oriel; B-34-40) of 10X magnification, the eyepiece being an 8 mm f.\(\lambda\) negative lens and the objective a positive achromatic doublet of 80 mm f.\(\lambda\). Both elements were anti-reflection coated in the 450 - 700 nm range to minimise internal etalon effects. The telescope was mounted in a piece of extruded Al 'C'-tube bolted to a movable carriage and alignment was possible via four micrometer screws.

The grating (P.T.R. Optics) was an aluminised replica blazed at 500 nm in first order (blaze angle = 17.5°), having a line density of 1200 \(\text{mm}^{-1}\). This was mounted in a precision mount (Oriel; B-44-60) on a rotary table (Unislide A4757 TSP) separate from the cavity. The minimum step angle of the table (0.08°) was reduced by an anti-backlash gearbox
to 0.004° corresponding to a minimum wavelength step of 0.6 A. The stepping motor drive could be controlled manually through a variable speed control box or remotely by an on-line minicomputer.

Finally, the beam steering optics comprised two aluminised glass plates on adjustable mounts as shown, their relative heights being determined by the optical height of the vacuum chamber above the laser axis.

The laser's performance is illustrated in Figure 3.13, captions (a) and (b) showing the temporal profile and its absolute synchronism with respect to the N₂ laser. It is evident from the modulation displayed that at least four double passes of the cavity are taking place since the peak separation (2.3 ns) corresponds to twice the cavity length (∼35 cm). This has been previously reported ⁷¹, ⁴⁷a, the latter reference criticising it on the grounds that it constituted a source of timing error due to its dependence on excitation power and wavelength. There was some indication of the latter but it was not significant (c.f. (a) and (b) in Figure 3.13) particularly since accurate timing measurements were not sought.

The spectral profile of the laser at optimum setting is shown in Figure 3.13(c). This curve has not been deconvoluted to remove the instrumental response of the spectrometer used (McKee Pederson ½ m, reciprocal dispersion 17. A/mm) and a value for the FWHM of 2 A is reasonable since the Hg and Cd lines at 4358 A and 4678 A were both broadened to ∼0.5 A at the same spectrometer slitwidth. The bandwidth seemed to depend quite heavily on the configuration of the cavity, particularly the dye cell and telescope. Subsequent determinations of the bandwidth using a scanning Fabry-Perot have yielded larger values than
Figure 3.13 - Spectral and temporal laser characteristics

(a) Typical dye laser pulse

(b) Nitrogen (full) and dye (dotted) laser pulse profiles. These are synchronised with respect to the $N_2$ laser to show absolute delay between the pumping- and emission pulse of the dye laser

(c) Lineshape of dye laser emission

(d) Tuning curve (uncorrected) of Coumarin 2 dye laser
above ($\sim 3$ Å) again subject to optical configuration.

The tuning performance of the laser using Coumarin 2 dye (Applied Photophysics Ltd.) in ethanol is shown in Figure 3.13(d). This is again uncorrected but conveys the essential laser performance since the recording instruments varied little over this wavelength range. The effects of super-radiance were most marked at the tuning extremes and operation here is best done with other dyes. As regards the optical quality of the output beam, projection onto a distant whiteboard showed this to be decidedly non-Gaussian with corresponding beam divergence of $3 - 5$ m rad close to the diffraction limit of $\sim 2$ m rad.

The bandwidth, $\Delta \lambda$, of the laser can be estimated from the optical constants of the cavity$^{48a, 74}$:

$$\Delta \lambda = \frac{\Delta \theta}{D} \quad \ldots \ldots \quad (3.23)$$

where $\Delta \theta$ is the divergence of the beam striking the grating and $D$, the grating dispersion. For a grating used in autocollimation

$$D = \frac{2 \tan \theta}{\lambda} \quad \ldots \ldots \quad (3.24)$$

where $\theta$ is the angle between the grating normal and the cavity axis.

The angular divergence of the expanded beam is given by$^{75}$

$$\Delta \theta = \frac{\lambda}{\pi \omega_2} \quad \ldots \ldots \quad (3.25)$$
where $\omega_2$ is the beam "waist" ($e^{-2}$ intensity point) given by

$$
\omega_2^2 = M^2 (\omega_1^2 + (f_1 - d_1)^2 (\lambda/\pi\omega_1)^2) \quad \ldots \quad (3.26)
$$

with $M = $ telescope magnification ($= \frac{f\text{obj}}{f\text{eye}}$), $d_1$, the distance of the dye cell from the telescope eyepiece and $\omega_1$ the "waist" of the unexpanded beam. Substituting

$$
\lambda = 450 \text{ nm}
$$
$$
d_1 = 72 \text{ mm}
$$
$$
f_2 = 80 \text{ mm}
$$
$$
f_1 = 8 \text{ mm}
$$
$$
\omega_1 = 0.08 \text{ mm} \quad \ldots \quad 48, 69
$$

in $(3.23) - (3.26)$ yields $\Delta \lambda = 0.8 \text{ A}$.

The above analysis assumes a Gaussian beam which does not arise in practice with the H"{a}nsch laser due to the gain distribution in the dye cell and its dependence on the pumping laser spatial profile. This departure could be easily observed in the distribution of scatter from the grating and is a fundamental limitation of the H"{a}nsch design. To improve the beam quality the use of an amplifier stage is generally necessary with intermediate shaping optics. This has the added benefit of higher conversion efficiency and lower bandwidth. Thus, the estimated value of $\Delta \lambda$ above is probably a lower limit indicating that the observed behaviour is close to diffraction limited.
The peak power at 450 nm was measured to be \( \sim 5 \text{ kW} \) representing an energy conversion efficiency of \( \sim 5\% \) in close agreement with the similar system of Perry et al\textsuperscript{72}. This figure could be improved upon by using a "holographic" grating and high optical quality dye cuvette. Similarly, the output bandwidth could be reduced by a factor of 2 to 4 depending on the grating line density.

3.4 DETECTION SYSTEM

3.4.1 GENERAL CONSIDERATIONS

The feasibility analysis of the previous chapter indicates that the expected signal from the \( \text{O} + \text{I}_2 \rightarrow \text{O} + \text{I} + \text{I} \) system is very small and of the order of the photomultiplier (PMT) dark current. The preferred detection method in such a case\textsuperscript{13, 76, 77} is that of single photon counting (SPC) rather than d.c. or analogue methods although both have been used in L.I.F. work of this type, especially the latter. In the present case however, the anticipated signal is considerably lower than in previous work such that the high leakage and drift associated with analogue device inputs precludes their use. Unlike pulse or scintillation counting as in nuclear physics and mass spectrometry, S.P.C. is considerably more difficult at low light levels since it is characterised by a pulse height distribution (P.H.D.) identical to that for thermionic emission from the photocathode. In pulse counting, a well defined hump appears in its P.H.D. at large pulse heights due to the larger number of photoelectrons emitted making pulse height discrimination relatively easy. The signal: noise ratio (S.N.R.) in such a case can be independent of dark noise even at low signal rates whilst for S.P.C. this is emphatically not the case and long counting times and special techniques are necessary to achieve acceptable S.N.R.\textsuperscript{5}. 
Of these special techniques, spectral resolution of the L.I.F. has been employed (though not in molecular beams work) to increase the optical S.N.R. by effectively isolating the true signal. However, at very low light levels this approach decreases S.N.R. since the noise is not "noise-in-signal". In addition, the loss of multiplex advantage means longer acquisition times for each excitation spectrum. In practice, only detailed spectroscopic information is obtained this way, excitation spectra derived from undispersed L.I.F. being acceptable if the spectroscopy is previously known.

The most widespread S.N.R. enhancement method is signal gating in which only a small portion of the L.I.F. is viewed at a specific delay with respect to the excitation pulse (for CW excitation, lock-in detection is used). The signal which gets through this "gate" is generally free from laser-induced background and the dark signal negligible. However, the exponential characteristic of L.I.F. signals means that some compromise between gate-width and delay is necessary and it is necessary to optimise this for each experimental situation. If gating is carried out on the electronics rather than the P.M.T., the ultimate S.N.R. depends on the extent of laser scatter which if serious causes "afterpulsing" in the P.M.T. This is due to residual ionisation in the tube and is characterised by onsets ~ 0.1 μs after the parent pulse and decay times of 10 - 50 μs. The end result of this is to swamp the true fluorescence signal and no amount of gating or other method can retrieve it. It is therefore necessary to gate the P.M.T. itself in addition to the electronics or to eliminate laser scatter to a level well below that of the signal. Of the arsenal of P.M.T. gating methods which exist few are applicable at very low signal levels since most tend to introduce a certain amount of noise but the method
using conducting mesh over the P.M.T. end window\textsuperscript{79} seems to be promising.

For transitions of low lifetime it is essential to eliminate scatter and view the L.I.F. both during and after the laser pulse\textsuperscript{11}. However these transitions are characterised by strong absorption and emission which favour their observation (see equation 2.11). Low lifetimes can also arise from predissociation in the upper state which reduces the L.I.F. signal by the ratio of radiative: predissociate lifetime. In such cases, \textsuperscript{69} (C\textsubscript{2}O \textit{and} I\textsubscript{2} are good examples!) elimination of laser scatter and dark noise is paramount and in addition the optical detection efficiency must be maximal. The signal once detected should then be preserved by impedance matching and amplification before driving any lines to counting equipment such that pick-up in transit is reduced. This is particularly important in pulsed laser excitation.

From the general considerations above it is evident that CW excitation is inherently better suited to L.I.F. work in beams since

1. little R.F.I. is generated.
2. dye laser beam quality is very high ensuring facile baffling.
3. average spectral power densities are higher than for pulsed lasers even at high resolution leading to high data rates.
3.4.2 LASER BAFFLING AND FLUORESCENCE COLLECTION.

Schematic representations of the optical system are included in Figures 3.1 and 3.2 and detailed drawings of the baffle assembly and detector are shown in Figure 3.14.

Although many reports$^{11, 13, 81, 82}$ have detailed their baffle systems and stressed their importance it seems that trial and error is the key to success here. However, there are a number of ground rules which must be observed.

1. Surfaces capable of high Fresnel diffraction should be avoided.

2. Sharp edges on baffle elements should be ground away.

3. The classical path of the laser should avoid any reflecting surfaces.

4. The baffle assembly should be coated with an absorbing substance to avoid multiple reflections.

5. Clean, optical quality windows for coupling the laser beam in and out of the vacuum chamber are necessary to minimise scatter.

The assembly shown to scale in Figure 3.14(a) was the first attempt at baffling whilst adhering to the basic rules above.
Figure 3.14

(a) - Baffle assembly
(b) - Fluorescence collection assembly

KEY
A. Window flange
B. mating flanges
C. Threaded rod (support and adjustment)
D. Flexible bellows
E. Flange to vacuum chamber
F. Vacuum chamber wall
G. Positioning screws \((2 \times 3 \; \theta \; 120^\circ)\)
H. Baffle tube (removable)
I. Baffles and spacers
J. P.M.T. and \(\mu\)-metal shield
K. Fused quartz light guide
L. Reaction zone centre
The baffles are turned from Ag rod and are 16 mm in diameter with a 3.5 mm central aperture. These are fitted into a 16 cm long stainless steel tube (19 mm o.d. x 16 mm i.d.) and separated by paxolin spacers to produce a robust assembly. All elements were chamfered and ground to remove both sharp and straight edges and were coated by absorbing paint (Nextel, 3-M Co.). The assembled baffle was then mounted in a stainless steel tube (35 mm o.d.) with a 4½" conflat flange vacuum-brazed to it at one end to provide a vacuum seal as indicated. Each baffle (entrance and exit) was individually aligned by adjustment of the supporting screws using a 2 mW He-Ne laser. The criterion for alignment was that both tubes were co-axial.

Both baffles were mounted as close to the reaction zone as possible to reduce to probability of scattered light emerging. Unfortunately, the large size of the tank and consequently low engineering tolerances meant that both assemblies were not co-axial and their axes did not project through the reaction zone. To correct this, each baffle arm was connected to a flexible bellows which allowed some movement in the baffle. Despite this, complete co-incidence could not be achieved and although the author was unable to test this under experimental conditions, subsequent work proved this arrangement to be unsatisfactory. The development of a successful baffle assembly was done by Glen 83.

The approach adopted for fluorescence collection is shown in Figure 3.14(b). Here, a light guide is optically coupled to the end window of the P.M.T. Using silicone grease or oil to index match. The P.M.T. end window forms a compression seal against an 'O'-ring to provide a vacuum seal. In this way, the P.M.T. base is at atmospheric pressure allowing easier heat dissipation from the interdynode resistors and freedom from arcing at low pressure. The mounting assembly is similar to that for
the baffles with the added advantage of being able to advance/retract the
light guide from the reaction zone by way of the flexible bellows. The
final position of the guide should be such that the subtended solid angle
is maximised subject to the extent of scattered laser light.

Previous reports \(^{11, 81}\) have used converging lenses to capture
fluorescence and transmit it to an extra-vacuum P.M.T. However, the
vacuum chamber did not readily permit this here and it was felt that the
light guide was lead to higher collection efficiency both geometrically
and optically since only vacuum/quartz interface arose.

The guide was constructed from fused silica rod 90 mm long x 17 mm
diameter (Thermal Syndicate Ltd.) and was chamfered at the edges to prevent
chipping. The ends were successively ground with carborundum grades and
finally with diamond paste\(^{+}\) to yield an optically smooth surface. The
surfaces of the guide were thoroughly degreased before assembly to avoid
frustrating its total internal reflection properties. At a distance of
25 mm from the reaction zone the fractional solid angle viewed was 2.1% for
an aperture diameter of 15 mm. The maximum deviation from normal incidence
is 17\(^{\circ}\) for which the reflectivity is 3.5% as for normal incidence. The
optical collection efficiency is therefore 2\%, absorption and scattering
along the guide being negligible. The critical angle for the guide (\(n = 1.46\)
is 43\(^{\circ}\) and consequently any ray refracted at the front face will be trans-
mitted without loss. Rays entering from the sides of the guide will not be
transmitted except for incidence angles above 84.7\(^{\circ}\) for which transmission
is negligible. The shielding properties of the guide however are very poor

\(^{+}\)The author is grateful to the Geology Department of Edinburgh University
for the use of their lapping facility.
since the transmission probability exceeds 50% for all incidence angles below 80° at the front face. The use of a smaller diameter guide (1 cm say) may have been superior since collection efficiency could have been increased to 10 - 15% by the relaxation of space limitations with no increase in scattered noise. Such a device is described by Imhof.\textsuperscript{84}

A later method introduced by Clyne \textit{et al} \textsuperscript{85} used 2 aspheric lenses to capture \~11% of the fluorescence while discriminating against noise by vignetting the image produced to include only the immediate region of the source. This method is only effective if the scattered noise lies without the field of view of the detector. Thus, for a given collection efficiency, the light guide method is superior over the lens assembly due to the smaller reflection loss (4\% c.f. \~20% for a two lens system) providing the field of view contains no other light except the fluorescence signal. To ensure this condition, all surfaces viewed by the detector must be black - a condition which was impractical in the present case. Further increase in collection efficiency can be obtained by use of a concave mirror to reflect light travelling from the light guide and total collection efficiencies of up to 50% have been reported \textsuperscript{86, 87} by this method. However this may produce more noise by scatter and it is first necessary to baffle the laser effectively.
3.4.3 ELECTRONICS

(a) Photomultiplier: The choice of P.M.T. was straightforward for this work; since the fluorescence expected lay below 500 nm only two tubes, S20 or bialkali, merited consideration due to their high quantum efficiency. The S20 tube however has a very pronounced red response and consequently high dark current. The bialkali tube on the other hand exhibits the lowest dark current of all tubes (for the near U.V. and visible) as well as the highest efficiency in the blue. In addition to this, the high work function of the photocathode means that cooling is relatively ineffective in reducing dark count. Thus since cooling requires elaborate precautions to guard against icing the window and the base, this tube can be used effectively uncooled and exposed to the atmosphere.

Ideally, P.M.T.'s for S.P.C. should exhibit high gain, low transit time and jitter and be interfaced to fast (10 - 100 MHz) electronics. In the present case there was no emphasis on timing and low gain electronics could be used if a suitably large load resistor was used. Since the P.M.T. anode amounts to an ideal current generator, its noise current is given by

\[ i_N = \left( 2e G I_A \Delta f + \frac{4kT \Delta f}{R_L} \right)^{1/2} \]  \hspace{1cm} (3.27)

where \( G = \) P.M.T. gain, \( I_A = \) mean anode current, \( \Delta f = \) amplifier bandwidth, \( R = \) load resistor. The respective terms in (3.27) are due to shot (photon) noise and Johnson (thermal) noise respectively. The condition for "noise-in-signal" operation is

\[ \frac{R_L}{e} \gg \frac{4kT}{2G I_A} \]  \hspace{1cm} (3.28)
Thus, for $T = 300 \text{ K}$, $G = 10^6$, $I_A = 5 \times 10^{-12} \text{ A}$, equation (3.28) requires $R_L >> 10^4 \Omega$ and a value of $120 \text{ k} \Omega$ was consequently chosen. The circuit used is shown in Figure 3.15(a) and the tube used was an EMI 9824B. Here, the values of the final stage capacitances were as recommended for pulse counting\(^{88}\) and for S.P.C. this is admittedly a gross overkill. In fact the stray capacitance in the dynamode chain is probably sufficient to boost the final stages with the exception of the d - A stage where a $10 - 20 \text{ pF}$ capacitor would suffice for signal rates up to $\sim 10^5 \text{ Hz}$.

The low observed dark count rate ($\sim 20 \text{ Hz}$) through the discriminator window was further reduced by gating\(^{83}\) to $\sim 10^{-2} \text{ Hz}$, a negligibly low figure justifying operation without cooling. However, laser scatter ($\sim 200 \text{ Hz}$) was high enough to produce after pulsing\(^{83}\) and operation of the tube at low gain was necessary to minimise this. The penalty for this is low detective quantum efficiency\(^{76}\) (D.Q.E.)

\[
\text{D.Q.E.} = \text{Q.E.} \times \text{C.E.} \quad \ldots\ldots\ldots\ldots \quad (3.29)
\]

Q.E. = quantum efficiency of photocathode
C.E. = collection efficiency of anode

which can be as low as $3\%$. 

Figure 3.15 - (a) P.M.T. output circuit
(b) P.M.T. output pre-amplifier equivalent circuit

R1 = 200 kΩ
R = 100 kΩ
C1 = C2 = 0.001 μF
C3 = 0.01 μF; C4 = 0.05 μF
R_L = 120 kΩ

R_{in} = 100 MΩ
R_{out} = 100 Ω
C_s \sim 30 \text{ pF}
C_{in} \sim 20 \text{ pF}
(b) Amplification: counting: This is outlined in Figure 3.1. The output from the detector P.M.T. is fed into a preamplifier (Nuclear Enterprises NE 5281) as close to the P.M.T. as possible to reduce pickup and signal degradation through impedance mismatch. The equivalent circuit for this is given in Figure 3.15(b). This pre-amp is a simple emitter follower of unity gain whose function is to match the load to the driving line (50 Ω) by impedance transformation. The output time constant, \( \tau \), seen by the P.M.T. is \( \sim 10^{-6} \) s and the voltage at the pre-amp input

\[
V(t) \sim \frac{G}{C_{\text{eff}}} \left\{ \exp \left( -\frac{t}{\tau_s} \right) - \exp \left( -\frac{t}{\tau} \right) \right\} \quad \ldots \ldots \quad (3.30)
\]

\( \tau_s = \text{anode pulse FWHM} = 50 \text{ ns for EMI 9824B} \)

peaks at around 15 mV. This signal was then fed to an amplifier (Nuclear Enterprises NE 5259), discriminator (NE 5159) and scaler (NE 5079) along a co-axial cable of some 3 m length. The electronic bandwidth was 1 MHz. Counting could be done either manually or automatically by a minicomputer interfaced to the scaler.

A beam monitor situated at the output window of the vacuum chamber recorded the intensity of the laser. This consisted of an identical P.M.T. to the detector whose pulsed output was mechanically smoothed by a sensitive electrometer (Keithley) and a proportional voltage sent along co-axial cable to the input of a fast A/D converter in the minicomputer. The digitised signal was read under software control and used to normalise the L.I.F. intensity.
The implementation of the computer controlled detection system was due to Glen and is described in his thesis. Although the author was unable to investigate the performance of the detection system it soon was apparent that it was wholly unsuitable for the job. The very low single photoelectron signals from the pre-amp were completely immersed in pick-up radiated by the \( \text{N}_2 \) laser and its associated pulse circuitry. This amounted to up to 5V whereas the signal was over two orders of magnitude less. A better arrangement would have been to have the amplifier and discriminator close to the pre-amp and shielded from the R.F.I. and to send only standard pulses (5V) along the line to the scaler. However, the modular operation of the equipment and limitations of space precluded this. Indeed, had it even been possible, the effects of noise might not have been overcome - the basic fault of the electronics is that it was originally designed for scintillation counting in nuclear physics, certainly not for low level signal detection in high noise environments.

To ensure maximum overall detection efficiency at the anticipated light levels of this experiment the use of a photon-counting P.M.T. with high gain and low rise time in conjunction with fast (\( \sim 100 \text{ MHz} \)), high gain electronics is mandatory, the whole system having only 50 \( \Omega \) terminations and lines. An added advantage in such a case is the ability to accurately measure radiative lifetimes.
APPENDIX  ELECTRICAL DETAILS OF $N_2$ LASER

A: CHARGING PROCESS

The equivalent circuit and charging waveforms are shown in Figure 3.16. The input voltage, $V_S$, is

\[ V_S = V_0 \sin \omega t \quad 0 < \omega t < \pi \]  \hspace{1cm} (3.31)

and the circuit equation is

\[ V_S = V_R + V_C \]  \hspace{1cm} (3.32a)

i.e. \[ V_0 \sin \omega t = R \frac{dq}{dt} + \frac{q}{C} \] \hspace{1cm} (3.32b)

This is linear and first order with solution

\[ V_C = \frac{V_0}{1 + Q^2} \left[ \sin \alpha - Q \cos \alpha + Q \exp (-\alpha/Q) \right] \]  \hspace{1cm} (3.33)

where $Q = \omega R C$ and $\alpha = \omega t$. The charging voltage, $V_C^{\text{max}}$, is obtained from

\[ V_C = V_0 \sin \omega t^* \]  \hspace{1cm} (3.34a)

i.e. \[ \cos \alpha^* + Q \sin \alpha^* = \exp (-\alpha^*/Q) \] \hspace{1cm} (3.34b)
(a) - Laser charging circuit

(b) - Voltage waveforms from circuit in (a)

Figure 3.16
and solutions to (3.34) are given graphically in Figure 3.16 as a function of $Q$.

The choice of $R$ is governed by the need to protect the supply from overloading. Thus since the maximum ratings of the supply are 30 kV/300 mA, then $R > 10^5 \, \Omega$. The value of $C$ was 27 nF and for $R = 200 \, k \, \Omega$, the laser operated according to $Q = 1.7$.

The voltmeter on the supply measured the mean d.c. voltage across the rectifier. When operating at 100 Hz, the charging of $C$ reverse biases the H.V. diodes above $V_{C}^{\text{max}}$ such that for $Q = 1.7$ the mean voltage $\sim 0.7 \, V_{o}$. Thus, since $V_{C}^{\text{max}} \sim 0.6 \, V_{o}$ and hence

$$V_{C}^{\text{max}} = 0.86 \, V_{\text{meter}} \quad \ldots \ldots \ldots (3.35)$$

B: DISCHARGE CHARACTERISTICS OF $N_2$ LASER

The circuit relevant to the discharge through the thyratron is given below. This is formally identical to the Blumlein circuit of Fitzsimmons et al.\textsuperscript{54}.

Here, lumped circuit elements only have been used since the discharge rise time, $\tau_D$, is significantly greater than the transit time of the strip-line ($\sim 5 \, \text{ns}$). The former is given by

$$\tau_D \sim \frac{L}{R} \quad ; \quad L = L_T + L_C \quad \ldots \ldots \ldots (3.36)$$

$$R = \frac{R_T}{R}$$
R = 200kΩ

C₁ = C₂ = 13.5 nF

Rₜ = 1kΩ

L.C. = Laser Cavity

Th. = Thyatron

**Figure 3.17 - Thyatron discharge circuit**

For the strip-line of Figure 3.8

\[ L_{C₁} = \frac{\mu_0 \cdot d \cdot L}{W} \text{ Henry} \]  

(3.37)

and substituting the appropriate values \( L_{C₁} \sim 2 \text{ nH} \). This is much smaller than the thyatron inductance which is usually 10 - 20 nH although this is seldom quoted in the technical literature. For the thyatron resistance a value of 0.1 - 1 Ω is appropriate although again seldom specified. This figure accords with spark gaps. Substitution in (3.36) yields \( 10 < \tau_D < 100 \text{ ns} \) and the distributed circuit approximation which requires \( \tau_D << 5 \text{ ns} \) fails.
The equivalent circuit for the thyatron discharge is

![Electrical Circuit Diagram]

where \( R \) is 0.1 - 1 \( \Omega \) and \( L = L_T + L_{C1} + L_{C2} \) is 20 - 40 nH.

The equation for this circuit is

\[
V^0 = L \frac{d^2q}{dt^2} + R \frac{dq}{dt} + \frac{q}{C} \quad \text{............... (3.38)}
\]

where \( q = \) charge on \( C_2 \) and whose initial conditions are \( q (t = 0) = 0; \frac{dq}{dt} (t = 0) = 0 \). The solution is then

\[
V_{C2} = V^0 \left\{ (1 - \exp\left( -\frac{Rt}{2L} \right) (\cos \Omega t + \frac{R}{2L} \sin \Omega t) \right\} \quad \text{...... (3.39)}
\]

where \( \Omega^2 = \left( \frac{1}{LC} - \frac{R^2}{4L^2} \right) \)

\( C_2 \) therefore reaches a peak pulse-charging voltage at \( \Omega t = \pi \) given by

\[
V_{C2}^* = V^0 \left( 1 + \exp\left( -\frac{R\pi}{2\Omega L} \right) \right) \quad \text{............... (3.40)}
\]
which for the values quoted lies in the range $1.2 V^0 < V_{C2}^* < 1.9 V^0$.

The relationship between the voltage read on the power supply, $V_{\text{meter}}$, and the effective charging voltage on $C_2$ is

$$1.0 < \frac{V_{C2}^*}{V_{\text{meter}}} < 1.6 \quad \text{.............. \hspace{1cm} (3.41)}$$

using (3.35).

For the discharge across the laser gap, conditions differ from the above case in that the strip-line can no longer be considered as "lumped". The equivalent circuit for this is

![Equivalent Circuit Diagram]

where $Z_0$ is the characteristic impedance of $C_2$ above, now considered as a distributed component charged initially to a voltage $V^*$ given by $V_{C2}^*$ above. The equation for this is then

$$V^* = L_g \frac{di}{dt} + i (R_g(t) + Z_0) \quad \text{.............. \hspace{1cm} (3.42)}$$
Typical values of $\frac{di}{dt}$ range from $10^{11} - 10^{12}$ A/s and $L_g$ for the laser discharge is 4 nH. Thus, the first term in (3.42) is 0.4 - 4 kV and is substantially less than $V^*$ (10 - 16 kV) such that the approximations

$$V^* \sim i \left( R_g(t) + Z_0 \right) \quad \text{............... (3.43a)}$$

i.e.

$$i \sim \frac{V^*}{(R_g(t) + Z_0)} \quad \text{............... (3.43b)}$$

are valid. Typical values for $R_g(t)$ are similar to those for thyratrons and spark gaps i.e. 0.1 - 1 $\Omega$. The characteristic impedance, $Z_0$, of a Blumlein pulse-forming line is

$$Z_0 = \frac{L_g^{\frac{1}{2}}}{C}$$

$$= \frac{377d}{2 \sqrt{K} W} \quad \text{............... (3.44)}$$

and substituting $d = 6.35$ mm, $W = 1$ m, $K = 2.3$ yields $Z_0 = 0.79 \Omega$. Peak currents of $\sim 10^4$ A are therefore to be expected for this laser.
C: TRIGGERING THE MAIN THYRATRON

This was accomplished using the line-type pulser arrangement suggested by the manufacturers. It appears that this approach gives best accuracy in these applications. In particular, use of a d.c. resonant charging circuit in conjunction with a thyatron switched line-type pulser allows highly reproducible pulse generation with low timing jitter which is necessary when triggering the main thyatron in order to avoid jitter and drift in the anode pulses. The relevant portion of Figure 3.9 is shown below.
The P.F.N. is resonantly charged through the 30 H choke and clamped at the peak voltage by D1 (IS 107), this being almost twice the d.c. voltage across the 8 μF smoothing capacitor (~ 200 V). Discharge of the P.F.N. occurs when the 12 V pulse is delivered from the logic circuitry and this sets up a positive-going pulse (360 V) to grid 2 of the main thyatron via the 1 : 1 pulse transformer (hand-wound). Negative going pulses in the line which arise from impedance mismatch are shorted to ground through D2 (IS 107). A principal feature of resonant charging is that recovery of the trigger thyatron (EN 91) is assisted by the charging choke which resists current surges.

The shape of the trigger pulse is determined by the P.F.N. and the amplitude by the charging voltage and both of these must be reproducible for satisfactory laser operation. Ideally, the P.F.N. should be constructed of low loss co-axial cable to provide a clean, fast rising edge. However, for 1 μs pulses this would require ca. 200 m of 50 Ω cable! A lumped constant P.F.N. can be made with capacitors and inductors which can be tailored to requirements. For the present case, the P.F.N. was
with \( L = 4.2 \, \mu H \) and \( C = 1500 \, pF \). The inductors were wound on a perspex rod using enamelled copper wire and the capacitors were high voltage (8 kV) polyesters. The whole P.F.N. was mounted in a separately shielded compartment to reduce R.F.I.

Choice of P.F.N. components centred round

(a) characteristic impedance, \( Z_0 \)
(b) pulse width, \( t_p \) (70%)
(c) pulse rise time, \( t_r \) (10-80%).

The relevant equations are

\[
Z_0 = (L/C)^{\frac{1}{2}} \quad \text{................. (3.45a)}
\]

\[
t_p = \frac{2N}{\sqrt{LC}} \quad \text{................. (3.45b)}
\]

\[
t_r = \sqrt{LC} \quad \text{................. (3.45c)}
\]

\( Z_0 \) was chosen as 50 \( \Omega \); \( t_p \) as 1 \( \mu s \) and \( t_r < 0.1 \, \mu s \). For \( N = 6 \) (\( N \) is the number of \( L - C \) meshes in the P.F.N.) \( t_r = 80 \, ns \) was obtained. Both \( t_r \) and \( t_p \) were found to equal their estimates from (3.45) very accurately.

Having chosen the P.F.N. values, the choke, \( L_c \), in the resonant charging circuit is governed by the charging frequency, \( f_r \).

\[
f_r = \frac{1}{\pi \sqrt{L_c C_N}} \quad \text{................. (3.46)}
\]
for d.c. resonant charging where \( C_N \) is the net P.F.N. capacitance. For 100 Hz P.R.F. and \( C_N = 9000 \text{ pF} \), \( L_C = 0.1125 \text{ H} \) is necessary - a wholly unreasonable value. Reduction of \( L_C \) is permissible by use of a charging diode which clamps the P.F.N. and in practice, the minimum value of \( L_C \) is determined by the circuit Q factor

\[
Q = \frac{\omega L}{R}
\]

which must exceed \( 10^{89} \). For the present case \( Q \sim 75 \) and satisfactory operation obtained.

D: MAIN THYRATRON BIAS/EXCITATION CIRCUITRY

The appropriate circuit for this, reproduced below, was taken direct from the manufacturer's data. However, some tailoring to the exact needs of the laser was necessary.

The Cockcroft-Walton doubler stage (enclosed) permits bipolar d.c. from the same rectifier. The +ve output primes the thyatron with a constant cathode-grid 1 ionisation current of \( \sim 125 \text{ mA} \) through the 1.1 k resistor (W/W 20 W). Grid 2 is held -ve to bias the cathode-anode gap off. The trigger pulse to grid 2 (360 V +ve going) matched to the P.F.N. by \( R_1 (R_1 = Z_0 (P.F.N.) = 50 \text{ \Omega}) \) whilst \( R_2 \) is present to dampen capacitative pickup from the anode to grid 2 (C \( \sim 20 \text{ pF} \)). It was found necessary to vary this for best performance, a value of 2 k being used. The inclusion of \( C_s \), a high voltage ceramic capacitor (10,000 pF/30 kV) was necessary to eliminate arcing between the thyatron base grid-1 pin and earth. The source of this was presumably stray capacitance between the anode or grid 2
and grid 1 and once shorted via $C_s$ its effect was not evident in the long
and short term performance of the thyratron.

At a running voltage of 10 kV (meter) the mean discharge current
through the thyratron during pulsing exceeds 1000 A if a 50 ns pulsewidth
is assumed. Similarly, the rate of rise of current, assuming a 100 ns rise
time exceeds $10^{10}$ A/s. In both cases, the rated maximum specified performance is well exceeded. The fact that the thyratrons lasted over $10^7$ shots
and more is a tribute to their excellent engineering.
CHAPTER 3

REFERENCES

   (b) Also J. Chem. Phys. (in press).
16. J.C. Whitehead, Private communication.
    This reviews covers the period 1963 - 1973.
73. I. Hutchinson, Univ. of Edinburgh, unpublished work.
CHAPTER 4

CLASSICAL TRAJECTORY STUDY

OF THE REACTIVE SYSTEM:

\[ \text{O} + \text{I}_2 \rightarrow \text{OI} + \text{I} \]
4.1 GENERAL INTRODUCTION

There are now essentially two independent methods in common use for modelling collision systems, namely dynamical and statistical. Within each, however, there is a large number of differing approaches necessitated by the diversity of nature. For example, dynamical techniques may require a fully quantum mechanical description on one hand or a purely classical description on the other. In between these extremes, an increasing arsenal of semi-classical techniques exists which permits approximate solution of the wave equation by imposition of certain classical constraints.

Traditionally, reaction kinetics has drawn on statistical methods such as the transition state theory (activated rate) of Eyring or the RRKM theory both of which are based on equilibrium statistical thermodynamics. The advent of molecular beam techniques with their ability to velocity and internal-state select in both reactant and product channels has meant that preference in modelling has shifted from the above statistical/dynamical methods to purely dynamical ones to match the non-equilibrium conditions encountered. However, this is again changing direction as better techniques open up new areas of interest. Currently, reactions of oxygen atoms which tend to proceed via complex dynamics are being studied in beams by the Harvard, Berkeley and Manchester groups. Interpretation of the dynamics of these systems is invariably in terms of revised versions of the old theories although some hope for dynamical treatment of these inherently more difficult systems has recently arisen.
The criteria by which an appropriate method can be chosen are dependent on the required objectives as well as the suitability of the method. Thus, interactions between electrons and atoms or molecules which are characterised by short partial wave expansions require purely quantum mechanical descriptions whatever the objective of the investigation. Collisions between heavy molecules are generally treated by classical mechanics unless quantum effects are explicitly sought. Thus, reactive scattering of most atomic and molecular systems lends itself to a classical description in the majority of cases whereas elastic and inelastic scattering is best described by quantum mechanics unless low resolution is sufficient when classical mechanics may suffice. More recently, a method for predicting reaction rate constants using a combination of phase space theory and classical trajectories has emerged. This approach was designed to overcome the basic deficiency of classical trajectories - that the majority of trajectories led to non-reactive scattering. However, it has been heavily criticised as being less efficient in certain cases for a given accuracy and generally inapplicable where equilibrium conditions do not apply. Nevertheless, cases do exist where this technique is attractive and these are currently being examined.

Gordon has proposed an algorithm by which the most appropriate choice of dynamical theory can be made. Here, it is argued that, where possible, statistical methods should be used if detailed dynamical information is not required. Although the full quantum treatment is universally applicable, it is prejudiced by limitations in its implementation at present. Trajectory calculations which solve the wave equation rather than Hamilton's or Lagrange's equations have seldom been done for
other than colinear geometries. This is extremely restrictive where angular momentum effects or rotational energy transfer are important factors. Fortunately, these phenomena lend themselves to quantitative analysis via classical trajectories in many cases.\textsuperscript{12, 17}

The method of classical trajectories is presently the most widely adopted dynamical technique. Where the classical approximations fail, quantum effects can be mimicked by the imposition of ad hoc constraints. Thus, tunnelling effects at low energy can be reproduced by permitting complex valued trajectories\textsuperscript{18} and diffraction effects in elastic scattering by permitting complex angular momenta\textsuperscript{19}. However, in reactive scattering, neither of the above effects have been seen to be of major consequence due to the low contribution of the former and the washout of the latter by ensemble averaging.

A sufficient condition for the application of classical methods is that for a given potential characterised by a range parameter, $\rho$

$$\lambda_{\text{de B}} \ll \rho \quad \text{................. (4.1)}$$

where $\lambda_{\text{de B}}$ is the Broglie wavelength for the system. Table 4.1 lists $\lambda_{\text{de B}}$ (Å) for the systems $H + AB$ and $O + I_2$.

In general, the $H + AB$ systems will be most likely to exhibit quantum effects although the form of the potential is particularly important in deciding this. Thus, potentials with thin barriers around the incident energy will support tunnelling much more readily than gradual, high barriers. For the $O + I_2$ system under study, the range of the potential is around 1 Å which satisfies equation 4.1 at the lowest energy used (0.57 k. cal. mol\textsuperscript{-1}) and justifies the use of the classical method.
TABLE 4.1

<table>
<thead>
<tr>
<th>E/k. cal. mol⁻¹</th>
<th>H + AB</th>
<th>O + I₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.207</td>
<td>.053</td>
</tr>
<tr>
<td>3</td>
<td>.120</td>
<td>.031</td>
</tr>
<tr>
<td>10</td>
<td>.065</td>
<td>.017</td>
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<td>30</td>
<td>.038</td>
<td>.010</td>
</tr>
<tr>
<td>100</td>
<td>.021</td>
<td>.005</td>
</tr>
</tbody>
</table>

Since general details of the classical trajectory method have been well documented elsewhere, they will not be presented here. Rather, the details of specific aspects of this work are given in Sections 6-8 and in the relevant appendices.

4.2 CLASSICAL TRAJECTORY STUDIES OF LONG-LIVED-COMPLEX SYSTEMS

A long-lived complex (LLC) is defined as a species containing three or more atoms which is temporarily unable to dissociate due to

(a) insufficient energy to surmount a centrifugal barrier or

(b) insufficient energy in the mode which leads to reaction.

Implicit in the above is that the LLC is quasi-bound only and that stabilisation via collisional or radiative energy loss does not occur.
Except for the pioneering work of Bunker on unimolecular decay of activated molecules, most classical trajectory work has been concerned with the simple exchange exchange reaction \( A + BC \rightarrow AB + C \). The majority of these studies has revolved round systems exhibiting activation energies and have been carried out in the region near threshold where dynamical effects are greatest. From these studies, much information has been derived which has permitted classification of reactive systems according to the mass combination employed and the dynamic and static properties of the potential surfaces.

These classifications cannot be readily applied to systems which react via LLC formation and decay since the effect of multiple encounters causes the system to lose "memory" of its past history, bringing about a random character to the trajectory outcomes. The ability to correlate initial and final states which was important in formulating the above classifications is therefore lost. Despite this, no attempt has yet been successful in classifying the properties of LLC systems, the only attempt having recently been heavily criticised on account of the failure of the integration technique used. Of the studies reported, the salient features are as follows:

A: COMPLEX LIFETIMES

Where these have been explicitly studied, they have been shown to follow an exponential (decay) distribution. This is to be expected from the RRKM theory of unimolecular decay in which the energy required to dissociate the complex migrates at random between the sites in the complex. An exception to this has been reported for the
ion-molecule reaction \( C^+ + H_2 \rightarrow CH^+ + H \) in which two distinct regimes have emerged: that of direct encounter and that of osculating/long-lived complex. Whereas it is not entirely unreasonable to expect a bimodal time distribution in analogy with bimodal angular and energy distributions, insufficient information on the details of the trajectories in Ref. 36 precludes further comment.

A practical criterion for the existence of LLC dynamics is that the LLC lifetime exceeds the complex rotational period. The latter is given by

\[
\tau_R \sim 2\pi (I/L) \tag{4.2}
\]

and the former by

\[
\tau_C \sim \tau_{\text{stat}} \sim \tau_0 \left( \frac{E}{E_E} \right)^3 \tag{4.3a}
\]

which, when corrected for centrifugal effects, yields

\[
\tau_C \sim \tau_0 \left( \frac{E - (I^+I^-) <B'>}{E - E_0 - <B'>} \right)^3 \tag{4.3b}
\]

Here, \( E = E_t + E_{\text{int}} + \Delta D_0 + E_0 \) is the total energy available to the complex where \( E_0 \) is its binding energy relative to the products \(<B'>\) is the mean centrifugal energy given by

\[
<B'> = \frac{2}{5} \frac{B'}{m} \tag{4.3c}
\]
\[ B_m' = (\mu/\mu')^{3/2} \left( \frac{C}{C'} \right)^{1/2} E_t \]  \hspace{1cm} (4.3d)

assuming entrance (exit) potentials of the form

\[ V(V') = - \frac{C}{R^6} \left( C'/R'^6 \right) \] \hspace{1cm} (4.4)

\( I^+ / I^- \) is the ratio of moments of inertia for the transition state (+) and complex (-). \( \tau_0 \) is a representative vibrational period of the complex. The exponent \( n = 3 \) applies to a "loose" complex; for a "tight" complex \( n = 5/2 \) would apply.

**B: DIFFERENTIAL CROSS SECTIONS (ANGULAR DISTRIBUTIONS)**

If the reaction is dominated by LLC formation and decay, then, providing that the entrance angular momenta are not polarised, the angular distributions are governed solely by conservation of angular momentum. The forms of these distributions have been established by Herschbach et al. by direct analogy with the compound nucleus theory of nuclear reactions.

The total (vector) angular momentum \( \vec{\Theta} \) is given by

\[ \vec{\Theta} = \vec{L} + \vec{J} = \vec{L}' + \vec{J}' \] \hspace{1cm} (4.5)

where \( J, L \) are rotational, orbital angular momenta; the primes referring to the exit channel. Since \( \vec{\Theta} \) is fixed in space, its projections on space-fixed axes must also be fixed. In particular, its projection along the line of the initial relative \( \vec{v} \) is fixed and equal to the projection of \( \vec{J} \) on \( \vec{v} \). This constant, \( M \), takes values in the range \( (+J, -J) \) with equal weight ascribed to each.
Figure 4.1 - Constructions for generating angular distributions in Fig. 4.2. Limiting cases correspond to those of Herschbach et al (ref. 44). M and M' are projections of 3 on v and v'. Conical surfaces represent precessions of v' about 3.

Equally, the projection of 3 along an arbitrary space-fixed vector v' is fixed. If, however, v' corresponds to the final relative velocity, the projection M' can only take integral values from a set (-K, +K) if v' is parallel to the principal axis of a well defined symmetric top molecule. Such a situation obtains if the intermediate complex is, long-lived. The distribution of M' in this case is given by
\[ P(M') = \exp \left( \pm \frac{K^2}{2K^2} \right); \quad M' = K \] ................. (4.6a)

\[ K^* = \sqrt{k_T R IR^2} \] ................. (4.6b)

\[ I_R = I_{\perp} I_{\parallel} / (I_{\perp} - I_{\parallel}) \] ................. (4.6c)

where \( T_R \) is the rotational temperature and the moments of inertia are defined with respect to the above principal axis.

The resulting angular distributions can be obtained by precessions of \( v' \) about \( \varphi \) and \( \vartheta \) about \( \psi \) in Figure 4.1. If averages over \( \varphi, M \) and \( M' \) are included, the general expression for the angular distribution is

\[ I(\theta) = \sum_{\varphi} \sum_{M} \sum_{M'} P(\varphi, M, M') \cdot D_{MM'}^{\varphi} (\cos \theta) \] ^2 ................. (4.7)

where \( D_{MM'}^{\varphi} \) is a Wigner function \(^{45}\). These are depicted in Figure 4.2 on the next page.

It is seen \(^{46}\) that these distributions can be completely characterised by the parameter \( X \), where

\[ X = \frac{L_{\text{max}}}{K^*} \] ................. (4.8a)

and further, that in the case of a prolate intermediate, \( X \) is given by the experimental anisotropy ratio in the centre of mass (CM) angular distribution \(^{45}\)

i.e. \[ X = \frac{T(0^\circ)}{T(90^\circ)} \] ................. (4.8b)
Symmetric peaking of the angular distribution at or near the poles has been reported in numerous experiments\textsuperscript{46, 47} and has been reproduced in classical trajectory studies\textsuperscript{34, 35, 37, 40, 41}. The approximations inherent in the statistical complex model\textsuperscript{44} are likely to be manifest by unequal peaking around the poles if the complex lifetime is reduced by (for example) increased reactant translational energy. This situation represents the extreme osculating complex region and has been observed in complex
reactions using supersonic seeded beams to increase the translational energy. The same observations have been made by Kwei et al. and Whitehead in trajectory calculations. In all cases, a gradual transition from equal forward-backward peaking at low energy to increased forward scattering at higher incident energies has occurred. This is at variance with the observations and conclusions of Clough et al. who argue that osculating complexes can result in backward peaking in the C.M. if the (arbitrary) time origin is shifted.

More recent work by the Harvard School on vector correlations has resulted in revision of the earlier work for the case where \( L, L' \gg J, J' \). It transpires from these studies that for the case in question the symmetry about \( \theta = 90^\circ \) in the C.M. need not hold. What occurs in its place is not yet fully evident (at least to the author!)

C: ENERGY DISTRIBUTIONS

If the complex lives sufficiently long to permit equipartition of the total energy available amongst all its modes of motion, Boltzmann-like distributions for each degree of freedom would be expected. For small complexes however, the classical limit is not reached and departures from exponential decay arise.

Safron has formulated expressions for these distributions based on RRKM theory. Thus, for the translational energy, \( E_t' \)

\[
P(E_t') = A(E_t') (E' - E_t')^6 + r/2 - 2J \quad \text{\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.9a)}
\]
where

\[ A(E'_t) = \left( \frac{E'_t}{B'_m} \right)^{2/3} \] \quad \text{for} \quad E'_t < B'_m \]
\[ = 1 \quad \text{for} \quad E'_t > B'_m \] \hspace{1cm} (4.9b)

\[ E' = E - E'_0 \] is the energy available for distribution amongst products. 's' and 'r' are the numbers of active vibrations and rotations in the complex at the transition state. For a three atom "loose" complex, \( s = r = 2 \) yielding

\[ P(E'_t) = A(E'_t) (E' - E'_t) \] \hspace{1cm} (4.9c)

The peak occurs at \( B'_m \) in this case and the decay is linear rather than exponential.

Similarly, the expressions for the internal energy are given by\(^{51, 53}\)

\[ P(E'_{R,V}) = (E' - E'_{RV} - 2/5 \cdot B'_m) \left( B'_m \right)^{2/3} \quad E'_{RV} < E' - B'_m \]
\[ = \frac{3}{5} (E' - E'_{RV})^{5/3} \quad E'_{RV} > E' - B'_m \] \hspace{1cm} (4.10)

where \( E'_{RV} \) is either the rotational or the vibrational energy.

Generally, \( B'_m \ll E' \) which means that all the distributions exhibit a monotonic linear decay with approximately equal fractions \( (E'/3) \) of the available energy partitioned into each.
Since the total energy released on reaction is constant, the distribution of internal energy, the sum of the rotational and vibrational contributions, can be obtained from the translational energy distribution (Equation 4.9). Thus since

\[ P(E_t' = X) = P(E_{\text{int}}' = E' - X) \] ........................ (4.11)

then the distributions \( P(E_t') \) and \( P(E_{\text{int}}') \) are images of each other under reflection in \( X = E'/2 \). For the limiting case \( B_m' \ll E' \) which applies to the \( 0 + I_2 \) reaction (\( B_m' \approx 0.1 E_t' \)) typical distributions are given in Figure 4.3 below.

![Figure 4.3](image_url)
The significance of this result lies in the similarity of $P(E_{int}^{'})$ (or $P(E_t^{'})$) to that found from reactions with 'early-downhill' energy release which do not necessarily proceed via LLC formation. Given the large errors inherent in the best molecular beam work ($\sim 10\%$ in velocity; $\sim 20\%$ in translational energy) it is evident that velocity distributions alone are insufficient to identify LLC dynamics. Simultaneous measurement of the differential cross-section, $\sigma(\theta)$, by inversion of the laboratory angular distribution aids definition of the dynamics but cases are known where symmetric $\sigma(\theta)$ occur for non-complex dynamics. The most definitive test lies in the rotational or vibrational energy distributions: the statistical model weighs heavily against population inversions especially at high quantum numbers and where dynamical uncertainty arises recourse to internal state distributions must be taken.

The classical trajectory calculations which have reported detailed energy distributions for each degree of freedom$^{35, 39, 40}$ have not encountered such population inversions, the internal distributions being monotonic decreasing to a greater or lesser extent. In the four centre work of Brumer and Karplus$^{34}$ energy equilibration in the four stretching modes was observed although high angular momenta reduced the excitation in one mode by forcing the complex to take up a linear configuration, the most stable configuration being rhombic.
4.3 DESCRIPTION OF THE REACTIVE SYSTEM \( \text{O} + \text{I}_2 \rightarrow \text{OI} + \text{I} \)

This system has been studied in molecular beam experiments by two groups \(^{47, 49, 55, 56}\) at the collision energies 0.78 \(^{47, 55, 2.9\text{ }56}\) and 7.1 k. cal. mol\(^{-1}\) \(^{49}\). The most extensive studies are at low energy (0.78 k. cal. mol\(^{-1}\)) and these have indicated the reactive scattering occurs via LLC formation primarily having an anisotropy ratio of almost two (see Section 4.2 B) and disposing some 20\% of the exoergicity into product translation. The reaction cross-section has been proposed as less than \(10\) \(\text{Å}^2\) by analogy with the corresponding reaction with \(\text{Br}_2\) which has a cross-section of some \(2\) \(\text{Å}^2\) at thermal energies \(^{57}\). (Direct estimation of the \(\text{O} + \text{I}_2\) cross-section and activation energy have proved fruitless by discharge flow studies due to interference from higher iodine oxides \(^{57}\)).

At a slightly higher energy of 2.9 k. cal. mol\(^{-1}\), Brown \(^{56}\) has shown that the (laboratory) angular distribution and (centroid) velocity distribution both resemble those of the earlier studies \(^{17, 55}\). However, the interpretation of the results was less clear since signal limitations precluded measurement of the full velocity distribution. In addition, difficulties in characterising the O-atom source (which was derived from ozone pyrolysis) prevented accurate determination of an effective temperature. The end result was that accurate backfits to the data were not possible: no combination of parameters when inserted into the stochastic analysis procedure \(^{58}\) could reproduce both the angular and velocity distributions. The former could be reasonably fitted but the insensitivity of the model to the adopted form of the C.M. angular distribution weighed against reliable conclusions. The velocity distributions could not be fitted for any appropriate range of parameters in the RRKM-AM model \(^{52, 59}\).
Work by the Belfast group\textsuperscript{49} was carried out at two collision energies: 7.1 and \textasciitilde 0.8 k. cal. mol\textsuperscript{-1}. The latter was used to check their system against the results of the Cambridge group\textsuperscript{47, 55} and acceptable agreement was found\textsuperscript{49, 60}. The results at 7.1 k. cal. mol\textsuperscript{-1} were consistent with a backward peaked differential cross-section, a result unexpected in terms of conventional models for reactions on potential surfaces with wells, and at variance with recent work. The reaction \( \text{O} + \text{Cl}_2 \rightarrow \text{OCI} + \text{Cl} \) has been studied at C.M. collision energies of 3.1 and 7.4 k. cal. mol\textsuperscript{-1}\textsuperscript{48} and the dynamics were seen to change from LLC to osculating complex/stripping as the energy was raised. At the higher energies, the extra orbital angular momentum prevents sampling the full depth of the potential well resulting in weaker interactions and concomitant forward scattering.

The velocity distributions measured by Clough \emph{et al}\textsuperscript{49} were angle independent indicating separable angle and velocity functions in the C.M. However, as in Ref. 56, the velocity distributions were not carried out over the whole angular range accessible and the conclusions regarding the C.M. angular distribution were therefore little more than tentative. Nevertheless, irrespective of the velocity distribution adopted in the back-fit, the observed (lab) angular distribution could only be reproduced by adopting a backward peaked C.M. angular distribution.

In addition to angular and velocity data, the ratio of reaction cross-sections at 0.8 and 7.1 k. cal. mol\textsuperscript{-1} was found to be

\[
\frac{\sigma_R (0.8)}{\sigma_R (7.1)} = 1.16 \pm 0.3 \quad \cdots \quad (4.12)
\]
which was normalised to the reaction \(0 + \text{CS}_2 \rightarrow \text{SO} + \text{CS}\) to be less than 5 Å\(^2\). The large uncertainty in the ratio did not permit confident conclusion on the energy dependence of the cross-section. (If the \(E^{-1/3}\) dependence expected for reactions on attractive surfaces without activation barriers (see eqn. 4.4) held, the ratio in eqn. 4.12 would have been 2.0).

### 4.4 REQUIREMENTS FOR THE \(\text{O}_2\) POTENTIAL SURFACE

To establish a potential for the \(\text{O}_2\) system it is necessary to draw on the available spectroscopic, kinetic and dynamical information and then to choose an algorithm to generate the potential. In this particular case, it is not expected that a single adiabatic surface will reproduce all the observed dynamical features; evidence for distinct two-channel effects in this and other systems being available. However, at low energy, agreement does exist on the dynamics and this must be reproduced by dynamical calculations if the derived potential is accurate. If, then, the same potential is applied and found to be successful at higher energies, it is unlikely that the success is fortuitous since the inevitable accessibility of other surfaces and concomitant non-adiabatic effects weighs heavily against continued use of a single surface.

In many respects the systems \(0 + \text{I}_2\) and \(\text{Hg} + \text{I}_2\) present similar challenges when seeking a potential. Both are characterised by a lack of specific information. The approach used by Bernstein and co-workers has been detailed for \(\text{Hg} + \text{I}_2\) and the approach presented here for \(0 + \text{I}_2\) is largely similar.

\(^{†}\)The \(\text{Ba} + \text{SO}_2\) reaction (see Chap. 1) is complex at low collision energies changing to complex + rebound as higher-lying states of the complex become accessible. For \(0 + \text{Br}_2\), the effect is similar but more marked (R. Grice et al, work in progress). The transition is from long-lived-complex to osculating complex to rebound + osculating complex with increasing collision energy.
A: DYNAMICAL AND SPECTROSCOPIC INFORMATION

Molecular beam studies have been made on the related systems:

\[ \text{Ref.} \]

\[ \begin{align*}
R1 & : \quad 0 + I_2 \rightarrow OI + I \quad 47, 49, 55, 56 \\
R2 & : \quad 0 + ICl \rightarrow OI + Cl \quad 47, 55 \\
R3 & : \quad 0 + IBr \rightarrow OI + Br \quad 62, 63 \\
R4 & : \quad 0 + Br_2 \rightarrow OBr + Br \quad 47, 55, 62, 63 \\
R5 & : \quad 0 + Cl_2 \rightarrow OCl + Cl \quad 48, 62, 63
\end{align*} \]

A key feature common to all the above reactions is that they proceed via LLC formation and decay. In R2 and R3 no detectable amounts of OCl or OBr could be resolved by the electron-bombardment mass filter detector used. The comparatively high signal levels of OI implied that these effects were not solely due to the reduced detection efficiency at the lower masses but principally to the nature of the complex intermediate thought to be of the form \( O-I-X (X = Cl, Br, I) \). If the complex was of the \( O-X-I \) or \( X-O-I \) types, then reaction to \( OX \) would have been expected since, due to its higher exoergicity, it would 'see' a far larger volume in phase-space.

The preference for the OI product has a profound bearing on the electronic nature of the complex since the reactants \( O(3p_g) + XY (12^+ \) approach on a triplet potential surface. The species \( F_2O, 64 Cl_2O, 65-67 \) and \( Br_2O, 64, 68, 69 \) are known to exist as chemically stable singlets and the LLC behaviour of the \( O + Br_2, Cl_2 \) reactions could be explained in terms of this providing some mechanism existed to permit the necessary triplet to singlet surface crossing. However, these singlets are of the symmetrical
(X-O-X) form based on spectroscopic evidence and Walsh's rules\textsuperscript{70} with the inter-bond angle being close to $90^\circ$ (F-O-F $\sim 103^\circ$ and Cl-O-Cl $\sim 110^\circ$\textsuperscript{64}). If then the series of reactions R1 - R5 proceeded \textit{via} oxygen insertion, the products of R2 and R3 would be predominantly OC1 and OBr since these have stronger bonds\textsuperscript{71} than OI\textsuperscript{72}. This is not the case and it is concluded that these reactions all proceed on the lowest triplet surface at low energy.

There is now sound evidence to support the existence of quasi-bound triplet intermediates of the form X-Y-0 where Y is the least electronegative of the halogen atoms X and Y. Rochkind and Pimentel\textsuperscript{73} have observed the species Cl-Cl-0 subsequent to the photolysis of matrix isolated Cl-O-Cl and concluded that the Cl-Cl-0 bond angle is $120^\circ$ with an extended Cl-Cl bond (2.267 Å cf 1.988 Å for isolated Cl\textsubscript{2}). Although no conclusive spectroscopic evidence exists to call this species a triplet the molecular beams evidence\textsuperscript{48, 62, 63} along with Walsh's rules\textsuperscript{70} are consistent with this assignment. Subsequent evidence supporting the analysis of Ref. 73 has recently appeared but with a less conclusive bond angle\textsuperscript{65} statement: $120^\circ < \theta < 180^\circ$. The chemically similar species F-Cl-0 has also been reported\textsuperscript{74} further substantiating the above argument. Here, the bond angle is $\sim 120^\circ$ and the FCl-0 bond is stronger than in isolated ClO presumably due to charge transfer from the ClO antibonding orbitals to the electronegative F-atom.
For the species OBr₂ and OI₂ much less decisive information is available. OBr₂ has been known for many years⁶⁴, ⁶⁸ but little detail is known despite measurement of its UV-visible absorption spectrum⁷⁵, ⁷⁶. This has been due to the context in which it has been used, namely as a source of Br radicals for organic synthesis using the reactions:⁷⁷, ⁷⁸

\[ \text{R6 : } \text{HgO} + 2\text{Br}_2 \rightarrow \text{HgOBr}_2 + \text{Br}_2 + \text{HgBr}_2 + \text{Br}_2\text{O} \]

\[ \text{R7 : } \text{Br}_2\text{O} \rightarrow \text{Br} + \text{BrO} \]

The existence of symmetrical Br-O-Br has been reported⁶⁴, ⁶⁹ along with vibrational frequencies and bond angles (113° and 87° respectively). The latter data are without empirical proof and the former disagree significantly. Unsymmetrical O-Br-Br has been reputedly observed by Tevault et al⁶⁹ but its assignment was by comparison with Cl-Cl-O and F-Cl-O and is therefore subject to some uncertainty. If Ref. 69 is correct then both forms of Br₂O exist, a result which is eminently reasonable in the light of Walsh's rules⁷⁰ due to the comparable electronegativity of Br and O (see Section C).

Even less information regarding OI₂ exists. The only report on this species concerns its production in situ as a reactive intermediate for organic iodination⁷⁹ using the reaction R6. The effect of the irradiation of the HgO-I₂ reagent mixture by a 150 W tungsten lamp was to enhance the formation of the iodinating species according to R7, this being the rate determining step. Since the system was more light sensitive than heat sensitive it is possible that photodissociation of OI₂ was brought about by direct absorption of radiation from the W-lamp.
If this was true then a value of the OI-I dissociation energy would be $\sim 30$ k. cal. mol$^{-1}$ since the lamp output peaks at $\sim 1 \mu$m, the reaction vessels (borosilicate?) transmitting only in the region 0.35 - 1.3 $\mu$m. The author concedes the speculative nature of the above argument, it being more probable that other sensitization processes occur.

It is thus entirely possible that OI$_2$ and OBr$_2$ exist as reported, but since these reports concern the solid and liquid phases, it is less reasonable to extrapolate to the gas phase since solvent interactions may well stabilise these intermediates. It has indeed been reported that OBr$_2$ is only stable at low temperatures in the gas phase, the I.R. spectrum vanishing above liquid nitrogen temperatures$^{64}$.

B: KINETIC INFORMATION

For the primary reactions:

$$R8: \quad O + X_2 \rightarrow OX + X \quad X = F, Cl, Br$$

the following activation energies have been measured.

<table>
<thead>
<tr>
<th>$X$</th>
<th>$E_a$ (k. cal. mol$^{-1}$)</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>F</td>
<td>$10.36 \pm 1.51$</td>
<td>80</td>
</tr>
<tr>
<td>Cl</td>
<td>$3.33 \pm .24$</td>
<td>81, 82</td>
</tr>
<tr>
<td>Br</td>
<td>$\sim 1$</td>
<td>83</td>
</tr>
<tr>
<td>I</td>
<td>$&lt; 0$</td>
<td>See text.</td>
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</tbody>
</table>

The values for $X = Cl, Br, I$ have been substantiated by molecular beams work$^{47, 48}$. 
The trend in \( E_a \) suggests that a similar mechanism governs the kinetics and it has been suggested variously\(^{80}\) that this is due to the polarisability of the halogen molecule governing the degree of attractiveness of the entrance channel potential. The long range interaction is largely due to dispersion forces\(^{84}\):

\[
V(\text{disp.}) = \frac{\text{const.} \, \alpha(X_2) \cdot \alpha(0)}{R^6} \quad \cdots \quad (4.13)
\]

where \( \alpha = \) polarisability; \( R = X_2-O \) distance. The polarisabilities are as follows\(^{85}\)

\[
X_2 : \quad F_2 \quad Cl_2 \quad Br_2 \quad I_2
\]

\[
\alpha(Å^3) : \quad 1.21 \quad 4.61 \quad 6.99 \quad 12.4
\]

and these, when used in the relation

\[
E_a = \frac{\text{const.}}{\alpha} \quad \cdots \quad (4.14)
\]

predict the observed activation energies to less than 1 k. cal. mol\(^{-1}\).

However, equation 4.13 does not predict an activation energy at all, rather, a monotonic decrease in \( V \) with decreasing \( X_2-O \) separation. This is due in part to the breakdown of the (London) equation for dispersion forces in the close interaction region although no detailed information on the position of the activation barriers is known.
Finally, values of the pre-exponential factors, \( A \), for R8 (\( X = \text{Cl, Br} \)) are known at thermal temperatures. These are listed below along with the corresponding cross-sections evaluated from the approximate expression:

\[
A = \langle v \rangle \sigma_{\text{calc}}. \quad \text{(4.15)}
\]

with \( \langle v \rangle = \text{mean velocity} \).

<table>
<thead>
<tr>
<th>( X )</th>
<th>( F )</th>
<th>( \text{Cl} )</th>
<th>( \text{Br} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log_{10}(A/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) )</td>
<td>12.99 ± 68</td>
<td>12.78 ± .02</td>
<td>12.72 ± .18</td>
</tr>
<tr>
<td>( \sigma_{\text{calc}}(\text{A}^2) )</td>
<td>~0.0</td>
<td>1.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Ref</td>
<td>80</td>
<td>48</td>
<td>86</td>
</tr>
</tbody>
</table>

The low value for \( X = F \) is due to the extremely large activation energy. From the data of Refs. 47 and 49 a value of \( \sigma_R \) for \( X = I \) in the range \( 2 - 5 \text{ A}^2 \) seems appropriate.

C: THEORETICAL INFORMATION

A simple valence bond picture of the approach of \( O(3P_g) \) to \( X_2 (1\Sigma_g^+) \) is as follows:

**COLLINEAR:** \( +O^+ +XX^+ \rightarrow +O^+XX^+ \)

**BROADSIDE:** \( +O^+ +XX^+ \rightarrow +X^++O^++X^+ \)

for \( O:XX \)

The colinear case is not altered if \( O(1D_g) \) approaches \( X_2 \) but the broadside case becomes
An identical picture arises for the approach of \( O(3P_g \text{ and } 1D_g) \) to \( H_2(1\Sigma_g^+) \).
In this latter case it is well known experimentally that triplet oxygen cannot readily insert into ground state hydrogen and that reactions are necessarily by direct abstraction. For the case of excited oxygen, \( O(1D_g) \), insertion is the norm, abstraction being possible but less commonly observed. Both cases can be rationalised in terms of spin polarisation in the \( H_2 \) (or \( X_2 \)), as discussed by Bader and Gangi\(^{87} \). Thus, it is seen that the \( C_{2v} \) approach of ground state reactants is repulsive due effectively to the tendency to violate the exclusion principle.

The above ideas are complemented by molecular orbital theory. In particular orbital correlations derived from Walsh's rules\(^{70} \) predict a near linear geometry for the triplet \( OX_2 \) (or \( OXY \)) intermediate with the least electronegative atom occupying the central position. This latter condition, the so-called "electro-negativity ordering rule" arises from the requirement on atom A in BAC systems to freely share its charge with B and C and hence facilitate bonding. However, from the electronegativities given below

\[
\begin{align*}
O & \quad F & \quad Cl & \quad Br & \quad I \\
3.5 & \quad 4.0 & \quad 3.0 & \quad 2.8 & \quad 2.5
\end{align*}
\]

it appears that this rule is not inflexible since Cl-O-Cl and Br-O-Br are known to exist.
Walsh diagrams relevant to the 0-I-I species are given in Figure 4.4. Case (A) applies when the $a'^* - \sigma^*$ orbital lies above the $a'' - \pi^*$ and $a'_s - \pi^*$ orbitals at all angles whilst case (B) applies when the $\sigma^*$ and $\pi^*$ orbitals exchange positions. (Note that the $a'^* - \pi^*$ and $a' - \sigma^*$ orbitals have an avoided intersection in case (B). Depending on the extent of this, a minimum in the $a'^* - \pi^*$ orbital may occur at an angle $< 180^\circ$). The uncertainty in the ordering of these orbitals was first raised by Walsh in his original papers and has since been invoked by Herschbach et al. to demonstrate the plausibility of a triplet ground state for near colinear approach of $O(3P_g)$ to $Br_2(1\Sigma^+_g)$. In both cases (A) and (B), the lowest triplet state in highly bent configurations, $a'(1) a''(1)$, is seen to be strongly repulsive whilst the lowest singlet state is most strongly bound at around $90^\circ$. In the near-linear configurations Walsh's rules fail to predict clearly which multiplicity lies lowest as does the valence bond model. However, since the non-repulsive singlet states correlate with excited state products (see below), access to these states must be via a triplet-singlet crossing induced by spin-orbit mixing of the two states.

There are three possible lowest-lying states in the linear or near-linear configuration:

\[ (\pi^*)^4 \quad \text{or} \quad (a'_s)^2(a'')^2 \quad 1\Sigma^+ \quad \text{or} \quad 1A' \quad \text{case (A)} \]

\[ (\pi^*)^3(\sigma^*)^1 \quad \text{or} \quad (a'_s)^2(a'')^1(a'^*)^1 \quad 3\Pi \quad \text{or} \quad 3A'' \]

and \[ (\sigma^*)^2(\pi^*)^2 \quad \text{or} \quad (a'_s)^2(a'')^1(a'^*)^1 \quad 3\Sigma^- \quad \text{or} \quad 3A'' \quad \text{case (B)} \]
Whilst in the strongly bent configuration one lowest-lying state occurs, in both cases (A) and (B) viz: \((a'')^2 \sim 1A'\).

Whether or not these states can take part in the overall reaction depends on the electronic correlations which span reactants and products. In general, if a given intermediate state can take part, it must connect with both reactants and products when the respective states are resolved into \(C_s\) symmetry\(^{89}\). However, it is more instructive to consider the entrance channel in two limiting symmetries, colinear \((C_{\text{ov}})\) and broadside \((C_{2v})\), since this description permits more meaningful identification of the strictly \(C_s\) states involved. Figures 4.5 and 4.6 show these correlations with the appropriate states derived from the Walsh diagrams (Figure 4.4) marked.

It is evident that reaction on a purely triplet surface requires considerable energy to overcome the repulsion in the states \(3A_2, 3B_2\) and \(3B_1\) upon broadside approach. There is the possibility of a surface crossing between the \(3B_2\) and \(1A_1\) states (both \(A'\) in \(C_s\) symmetry) when \(I-O-I\) is non-symmetric, this being brought about by spin-orbit mixing. However, as previously discussed, this is quite unlikely and the broad-side approach is expected to exhibit substantial repulsion.

Colinear \((C_{\text{ov}})\) approach is seen to be unrestricted in both cases (A) and (B). The lowest surface is either \(3\Sigma - (\pi)^3(\sigma)^1\) (case (A)) or \(3\Sigma^- - (\sigma^*)^2(\pi^*)^2\) (case (B)). The other states correlating with the reactants \(3\Sigma^- - (\pi^*)^2(\sigma^*)^2\) and \(3\Pi - (\sigma^*)^1(\pi^*)^3\) respectively) are shown as mildly repulsive although this is quite arbitrary. The former may well lie below \(1\Sigma^+ - (\pi^*)^4\) and \(1\Pi - (\pi^*)^3(\sigma^*)^1\) states which correlate with
Figures 4.4 - 4.6

4.4 - Walsh diagrams for 0-I-I: Case A is the original for B-A-C systems as proposed by Walsh (J.Chem.Soc. 1953 p.2288) whilst case B allows the $\sigma^*$ orbital to lie below the $\pi^*$ orbital in the spirit of the findings of Herschbach et al (Faraday Discussions Chem. Soc. 55,385,1973).

4.5 - 4.6 - Electronic orbital correlations for broad-side($C_{2v}$) and colinear($C_{oo}$),cases A and B, are presented. The full spin-orbit species are not included since they add greatly to the complexity. In addition, it has not yet been demonstrated that spin-orbit effects are important. A list of the symmetry species correlating with low-lying reactants and products is given in Table 4.13 overleaf.

Due to the lack of information specific to the 0-I-I intermediate states, these have been placed roughly according to the considerations given in the text.

There is a large number of states correlating with low-lying excited reactants which may contribute to the reaction mechanism(s). These have not been included for the sake of simplicity. The origins of the low-lying intermediate singlets are uncertain and have been marked as originating from any of the excited reactants states.

The dashed lines $E_1, E_2$ and $E_3$ correspond to C.M. collision energies 0.025, 0.25 and 2.5 eV resp..
Figure 4.4 - Walsh Orbital Diagram for O-I-I

Case A

Case B
Figure 4.5 Electronic Correlation Diagram for Broadside (C_{2v}) Approach of reactants
Figure 4.6a - Electronic Correlation Diagram for Colinear Approach of Reactants (Walsh Case A)
Figure 4.6b - Electronic Correlation Diagram for Colinear Approach of Reactants (Walsh Case B)
### REACTANTS

<table>
<thead>
<tr>
<th>0</th>
<th>I₂</th>
<th>(C_{2v}/C_s)</th>
<th>(C_{\text{cov}}/C_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3p_g)</td>
<td>(1\Sigma^+)</td>
<td>(3\Sigma^+ 3\Pi^+)(^a)</td>
<td>(3\Sigma^- 3\Pi^+)(^b)</td>
</tr>
<tr>
<td>(3p_g)</td>
<td>(3\Pi_u)</td>
<td>(5,3,1(2A_1/\Xi))(^a)</td>
<td>(5,3,1(\Delta/A + A))(^a)</td>
</tr>
<tr>
<td>(1D_g)</td>
<td>(1\Sigma^+)</td>
<td>(2^1A_1/2^1A')(^a)</td>
<td>(1^1\Delta/1^1\Delta)(^a)</td>
</tr>
</tbody>
</table>

### PRODUCTS

<table>
<thead>
<tr>
<th>OI</th>
<th>I</th>
<th>(C_{\text{cov}})</th>
<th>(C_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2\Pi)</td>
<td>(2p_u)</td>
<td>(1,3\Delta)(^a)</td>
<td>(1,3(A + A))(^a)</td>
</tr>
<tr>
<td>(1\Sigma)</td>
<td>(1,3\Pi)</td>
<td>(1,3\Sigma)(^a)</td>
<td>(1,3\Sigma)(^a)</td>
</tr>
</tbody>
</table>

Table 4.13 - Symmetry Species for Low-lying Reactants & Products
excited reactants in case (A) whilst the latter may only be slightly above the lowest $^3\Sigma^-$ state, both depending on the orbital spacing and on its relation to exchange energy.

At low initial relative energy ($E_1 = 0.57 \text{ k. cal. mol}^{-1}$) it seems reasonable that reaction proceeds predominantly via a single adiabatic triplet surface. At the intermediate energy ($E_2 = 5.7 \text{ k. cal. mol}^{-1}$), the accessibility of non-adiabatic pathways to quasi-bound intermediate singlet states increases. This however has not been shown to occur to any great extent\textsuperscript{49, 56} and motion on a single adiabatic triplet surface is again expected to occur albeit with diminished confidence.

The situation at the highest energy used in the calculations ($E_3 = 57 \text{ k. cal. mol}^{-1}$) is much less clear. There are clearly many pathways all capable in principle of reactive, elastic, inelastic and dissociative scattering. The probability of a non-adiabatic transition, $P_{ab}$, between the general adiabatic states (a) and (b) is given approximately by the Landau-Zener-Stueckelberg expression:\textsuperscript{90}

\begin{equation}
P_{ab} = \exp (- \frac{v^*}{v_R}) \tag{4.16a}
\end{equation}

where

\begin{equation}
\frac{v^*}{v_R} = \exp (- \frac{v^*}{v_R}) \tag{4.16b}
\end{equation}

\begin{align*}
\text{and} & \\
& v_R = \text{radial velocity} \\
& H_{12} = \text{interaction energy between diabatic states} \\
& \frac{\partial}{\partial R} |H_{11} - H_{22}|_{R_c} = \text{diabatic state potential derivatives at cross-over point, } R_c.
\end{align*}
\( P_{ab} \) is evidently enhanced by high radial velocities and low interaction energies and, in the light of this, many potential surfaces are likely to be accessible especially from crossings on the repulsive walls. However, the total lack of information on other surfaces precludes a multi-channel analysis and the information derived from these high energy trajectories will reflect the properties of the single adiabatic surface used rather than the physical characteristics of the \( O + I_2 \) system.

In summary, the requirements placed on the lowest triplet surface are:

1. It should have no activation barriers, passing smoothly from reactants to products via a quasi-bound, near-linear intermediate whose binding energy is sufficient to maintain it for some rotational periods. The maximum binding energy is given by the \( I_2 \) dissociation energy\(^{47} \).

2. It should present a substantial barrier to insertion of the oxygen atom.

3. It should take account of the reactive symmetry of \( I_2 \) by permitting the reactions \( A + BC \rightarrow AB + C \) and \( AC + B \) where \( A = O \) and \( B = C = I \).

4. It should display a substantial barrier to migration of the O-atom from one I-atom to the other since this involves passing through the isosceles configuration which is repulsive according to Walsh's rules\(^{70} \).
4.5 CHOICE OF POTENTIAL SURFACE

The field of potential energy surfaces for use in dynamical calculations has been examined by Karplus and, more recently, by Balint-Kurti and Kuntz. Less extensive but highly practical considerations for surfaces in classical trajectory calculations have been put forward by Bunker and by Poianyi and Schreiber.

Four categories of surface have been defined:

1. ab-initio
2. semi-theoretical
3. semi-empirical
4. purely-empirical

It has only been comparatively recently that ab-initio surfaces have been used in trajectory calculations. This has been due to the prohibitive amount of computational effort required to generate sufficient data points to characterise the surface. Up till now, mostly one-dimensional (colinear) surface have been calculated and these have necessarily been for systems with low total numbers of electrons eg. H$_3$, H + F$_2$, and Be + HF. In addition to calculating the surface at discrete points, an analytic (functional) fit must be made to the data set to permit interpolation and derivative evaluation. This process itself is approximate as well as computationally expensive and, it has been pointed out that it is far from trivial.
The best success of the \textit{ab-initio} method has been in predicting electronic properties of stable polyatomic molecules in their ground states and in their most symmetrical configurations (which aids integral evaluations). Serious departures from these conditions (e.g. into the asymptotes) are not easily treated by these methods and in particular, by the common Hartree-Fock (S.C.F.) method. In this event, recourse must be taken to means by which exact or near-exact asymptotic surfaces can be computed and smoothly joined to the \textit{ab-initio} surface\textsuperscript{97}.

With the introduction of faster computer systems, it is anticipated that \textit{ab-initio} methods will become more popular in trajectory calculations with the possibility of three-dimensional surfaces becoming more available. However, for dynamical systems containing heavy atoms, (i.e. beyond 1\textsuperscript{st} row elements) corrections due to configuration interaction and electron correlation become extremely difficult to apply, particularly in the latter case\textsuperscript{98}. For the reactive system $\text{O}_2 + \text{I}_2$ there is faint hope, if any, of \textit{ab-initio} surface computation in the foreseeable future.

For systems which are too large to be treated by \textit{ab-initio} methods, physically reasonable approximations can often be made to render tractable the computation whilst not departing seriously from the exact approach. One of the more popular of these semi-theoretical methods is the pseudo-potential method. Here, a system containing $N$ core electrons and $Z$ valence electrons is reduced to a $Z$-electron problem by considering the core electrons as a single unit of charge which exhibits the necessary orthogonality properties with respect to the valence electrons\textsuperscript{99}. The potential is then calculated \textit{ab-initio}. 
One of the most notable successes of this method has been the application of the Roach/Child surface\textsuperscript{100} in a classical trajectory study of the system:\textsuperscript{35}

\[ \text{R9 : } K + \text{NaCl} \rightarrow \text{KCl} + \text{Na} \]

This study reproduced experimental trends seen previously (in molecular beams experiments) with the exception of the branching ratio for decomposition of the complex. This failure was attributed to the weakness of the long range attraction of K to Na. It was not a limitation of the pseudo-potential method \textit{per se} but rather of the fitted potential \textit{sic} which traded accuracy in some configurations for accuracy in the more physically dominant configurations.

The success above can be contrasted with the notable failure of the pseudo-potential method applied to alkali clusters by Pickup and Byers Brown\textsuperscript{101}. Here, Na\textsubscript{3} and K\textsubscript{3} clusters were found to be unstable with respect to the isolated atom and molecule whereas subsequent calculations\textsuperscript{102-104} found exactly the opposite in keeping with the experimental observation of stable trimers for all the alkalis\textsuperscript{105}. Evidently, for (AB)\textsuperscript{+}X\textsuperscript{−} systems (A, B = alkali, X = halogen), the approximation to a single electron moving in an ionic framework of A\textsuperscript{+}, B\textsuperscript{+} and X\textsuperscript{−} is extremely realistic on a variety of grounds\textsuperscript{106}, whilst for alkali trimers with three valence electrons, the simple approximation is not so valid and an extended basis set is necessary\textsuperscript{101}. The state of development of pseudo-potential methods in more complex molecules is low and variants of the technique which invoke configuration interaction \textit{inter alia} are being developed. Nonetheless, substantial effort is required to generate such surfaces and,
further, to fit them to parameterised forms suitable for trajectory calculations. To have applied this method to the $O + I_2$ system would have been pointless since the two oxygen valencies would add to the complexity of the description which is brought about by the lack of information on the bonding character in the $OI_2$ species.

The third category of surface is presently the most promising since the methods it contains are based on well-founded quantum-mechanical formalisms to which approximate methods are applied to reduce computational effort and ensure physical reality for configurations (e.g. asymptotic regions) which are well described experimentally. Some of these methods permit calculation of ground- and excited-state potentials which are of considerable importance when non-adiabatic pathways arise such as in the $H^+ + D_2$ collision system$^{107}$.

The most widely applicable method in this category is the Diatomics-in-Molecules (DIM) method first reported by Ellison$^{108}$. Here, the potential is expressed in terms of all possible combinations of smaller molecular units and atoms which comprise the polyatomic under study. Depending on the excited state information required, the extent of the atomic basis set is varied. This results in the potential for a triatomic $ABC$ being expressed as

$$V_{ABC} = H_{AB} + H_{BC} + H_{AC} - H_A - H_B - H_C \quad \ldots \ldots \quad (4.17)$$

where the R.H.S. is composed of one and two centre integrals of atomic basis functions. The freedom from three centre integrals rests upon the
basic assumption of the method: that equation (4.17) is exact and its components expressible in terms of experimental energies. However, without a means of simply evaluating the diatomic energies (the atomic energies are read from tables), the method is not easily applied. To overcome this limitation it is usual to introduce approximate functional forms for the diatomic potentials which fit the experimental energies and permit ready evaluation of the potential and its derivatives. For a triatomic composed of three hydrogen-like atoms (i.e. \( ^2 \text{S} \)), the DIM expression reduces to

\[
V = Q_1 + Q_2 + Q_3 - \frac{1}{\sqrt{2}} (J_1^2 + J_2^2 + J_3^2 - J_1J_2 - J_2J_3 - J_1J_3) ^{\frac{3}{2}} \quad (4.18)
\]

which is identical to the London equation for \( H_3 \), the Q's and J's being Coulomb and exchange integrals for each atom pair.

The limitations of the DIM method as proposed by Ellison have been discussed critically by Tully. Principal among these is its innately approximate nature which does not guarantee a solution which converges to the true potential (it is not variationally based) and its inability to handle directional bonds. The latter was corrected by Tully in a more general formulation of the method and shown to yield accurate results. The former was reduced by choosing sufficiently large basis sets and accurate diatomic potentials. Although no serious departures from a reasonable solution have been reported, the method is not sufficiently accurate to predict barrier heights or well depths to better than a few k. cal. mol\(^{-1}\).
For ground state surfaces, Kuntz\textsuperscript{109, 110} has proposed using the DIM method with accurate ground state diatomic functions but allowing the excited state parametric flexibility in order to match the DIM surface either to experimental data or \textit{ab-initio} computations. In this way, he has constructed a three dimensional DIM surface for HeH\textsubscript{2}\textsuperscript{+} which has been fitted to a colinear \textit{ab-initio} surface by altering the excited diatomic states. In this particular case, the DIM expression for the potential energy was

\begin{equation}
V(\text{HeH}_2^+) = Q_1 + Q_2 + Q_3 - ((J_1 - J_3)^2 + J_2^2)^{\frac{1}{2}} \tag{4.19}
\end{equation}

The Q's and J's being evaluated by approximating the diatomic potentials to Morse-type functions.

The important points emerging from Kuntz' studies were:

(1) the DIM method permits \textit{ab-initio} accuracy with minimal effort.

(2) that one-dimensional (colinear) surfaces can be extended to two- or three dimensions using DIM as the fitting procedure.

Since there are a large number of colinear \textit{ab-initio} surfaces already computed the possibility of using DIM to extend the range and dimensionality of these surfaces is within reach. In the asymptotes where \textit{ab-initio} methods are inaccurate, the DIM method is at its best and the two can be combined to yield a physically reasonable potential which is computationally tractable.
Since DIM is a method of considerable predictive power whose accuracy depends on the accuracy of the information drawn on, its application to the system OI$_2$ is severely hampered by the lack of detailed information on IO. The presently available data on IO are subject to considerable uncertainty (see Chapter 2) and, if fed into a DIM program, are not likely to lead to a potential more realistic than purely empirical ones. At the outset of this project even less was known on IO and I$_2$O (particularly by the author!) and it was considered poor economy to attempt to find a DIM surface.

A more restrictive but well used semi-empirical treatment is the valence-bond formalism of London which is strictly applicable to molecules composed of hydrogen only. However, derivatives of this method have been used to treat systems of $^2S$ and $^2P$ atoms such as HF$_2$, H$_2$F, Li$_3$ etc. The expressions for the Coulomb (Q) and exchange (J) integrals are, in their most general form

\[
Q = \frac{1}{2} [(1 + S^2) ^1E + (1 - S^2) ^3E] \quad \text{(4.20a)}
\]

\[
J = \frac{1}{2} [(1 + S^2) ^1E - (1 - S^2) ^3E] \quad \text{(4.20b)}
\]

where $S$ = overlap integral

$^1E$ = diatomic singlet potential function

$^3E$ = first excited triplet potential function.

With all $S = 0$, Cashion and Herschbach have used the $^1\Sigma^+_g (^1E)$ and $^3\Sigma^+_u (^3E)$ curves for H$_2$ to compute the H$_3$ potential surface with surprising accuracy. Apparently, neglect of overlap (which is equivalent to assuming
an orthogonal atomic basis set) does not lead to serious error. This has also been seen in the DIM method from which the above can be derived\textsuperscript{112}.

A valuable test of the applicability of this method has been made by Whitehead\textsuperscript{39, 40, 103, 113} in a series of reports concerning alkali trimers. Surfaces for trimers containing Na and Li were calculated\textsuperscript{103} according to equation (4.20), the diatomic potentials being derived from reliable experimental data. The overlaps, $S$, were calculated by assuming Slater-type atomic orbitals or otherwise set to zero. The effects of the non-zero overlaps were not marked but it did yield slightly more attractive surfaces with smaller bond lengths in the most stable configuration. When classical trajectory calculations were made for the corresponding systems\textsuperscript{39, 40} results were seen to agree with the experimental data\textsuperscript{113} in respect of total cross-sections, energy distributions and differential cross-sections\textsuperscript{114}. More recent calculations on Li\textsubscript{3} by DIM\textsuperscript{104} and \textit{ab-initio} methods\textsuperscript{115} have not departed seriously from Whitehead's earlier work.

Some general properties of London-type surfaces are highlighted in the elegant study of Gorry\textsuperscript{114, 116}. Prominent among these is the existence of a conical intersection between the ground- and first excited states of LiNa\textsubscript{2} in the $C\textsubscript{2v}$ approach. Such intersections occur in all hydrogen-like triatomic clusters irrespective of symmetry\textsuperscript{117} and result in a closure of the reactive channel for certain approaches of reactants. This behaviour is not expected for the system OI\textsubscript{2} which should exhibit purely repulsive characteristics as the O-atom approaches I\textsubscript{2} in $C\textsubscript{2v}$ symmetry. Furthermore, the facile insertion process permitted by Whitehead's surface for Li-Na-Na (C\textsubscript{ov}) $\rightarrow$ Na-Li-Na (D\textsubscript{coh}) has been shown to be inconsistent
with molecular beams results on $O(^3P_g) + XY (^1Σ^+)$. The development of classical trajectory studies has paralleled developments in computer technology and one consequence of this has been that the potential surfaces used in earlier work have necessarily been simple to reduce the time devoted to potential and force evaluations. The functions have invariably been purely empirical being principally:

(a) LEP, LEPS or extended LEPS
(b) BEBO or extended BEBO
(c) HMF
(d) Switching functions

for non-ionic systems.

The most widely used have been those based on the London equation. Originally, Eyring and Polanyi modified this equation by using a Morse function to represent the diatomic ground states and eliminated the need to evaluate the exchange contribution by assuming a constant Coulomb ratio:

$$Q(R) = \text{const.} \ J(R) \ \\
\text{...............} \ \\
(4.21)$$

This LEP method was seen to be extremely unreasonable since it predicted the colinear $H_3$ system to be bound contrary to sound evidence for a substantial barrier.
Sato\textsuperscript{119} modified the LEP form to include an analytic representation for the triplet state based solely on the corresponding singlet. This LEPS equation took the form:

\begin{equation}
V = \frac{1}{1 + S^2} \left[ Q_1 + Q_2 + Q_3 - (J_1^2 + J_2^2 + J_3^2 - J_1 J_2 - J_2 J_3 - J_1 J_3)^{\frac{1}{2}} \right]
\end{equation}

\text{.......................... (4.22a)}

where \( \frac{Q_i + J_i}{1 + S^2} = D_i \exp (-\beta_i \Delta r_i) \left\{ \exp (-\beta_i \Delta r_i) - 2 \right\} \) \text{ ............ (4.22b)}

and \( \frac{Q_i - J_i}{1 - S^2} = \frac{D_i}{2} \exp (-\beta_i \Delta r_i) \left\{ \exp (-\beta_i \Delta r_i) + 2 \right\} \) \text{ ............ (4.22c)}

The \( S^2 \) term bears formal resemblance to the overlap terms in the London equation but is in fact a simple parameter. This expression predicted a barrier to colinear exchange of H with \( \text{H}_2 \) as observed and in general produces potential surfaces free from secondary basins (but not wells\textsuperscript{118, 120, 121}).

A further modification to Sato's formulation was made by Kuntz \textit{et al}\textsuperscript{122} in which the single \( S^2 \) parameter was replaced by three adjustable parameters corresponding to each diatom in the ABC system. The Coulomb and exchange terms were evaluated according to Sato. This simple modification resulted in a vastly more flexible form which permitted key topological features to be varied in a systematic manner thus allowing dynamical characterisation of the surfaces. The HX chemical laser systems (\( X = \text{F, Cl, Br} \)) have been extensively modelled with great success using
these extended LEPS surfaces to the point that kinetic information can be reliably predicted for these systems by classical trajectories\textsuperscript{123}. The LEPS method has however been criticised for permitting excessive tunnelling through barriers narrower than observed\textsuperscript{120} and more recently for seriously disagreeing with trajectory results from an \textit{ab-initio} surface to which it had been fitted\textsuperscript{96}.

Despite the flexibility of the extended LEPS procedure, it is not appropriate to systems containing non-hydrogen-like atoms by virtue of its memory of the London equation. Nonetheless, species containing both group 1 and group 7 elements ($^2S$ and $^2P$ respectively) are frequently modelled using LEPS with considerable success. For the system $O(^3P_g) + I_2 ({}^1\Sigma^+_g)$ it is wholly inappropriate - the $I_0$ product not possessing the simple $H_2$-like potential curves and the existence of a conical intersection (which is another consequence of its origin) being expressly undesirable. It is however conceivable that the singlet - triplet intersections expected in the $OI_2$ system (see Figures 4.5 and 4.6) can be mimicked using LEPS but this would be fortuitous at the very least! For ABB systems, LEPS has been criticised for its inability to handle isosceles configuration where cusps in the potential arise (resulting in force discontinuities)\textsuperscript{25}. In view of this and the fact that similar problems have been overcome using non-LEPS surfaces\textsuperscript{124} it was decided not to apply it to $O + I_2$. The recent application of LEPS to the $O(^3P_g) + H_2 ({}^1\Sigma^+_g)$ system seems (to the author) a curious choice in view of the work of Bader and Gangi\textsuperscript{87}. Due to the considerable difficulty in making molecular beam measurements on this system little, as yet, can be said on the $O + H_2$ results.
The bond energy bond order (BEBO) method\textsuperscript{126} is an entirely empirical method originally used to obtain reaction co-ordinates. It draws on three basic assumptions:

(a) that throughout a colinear reaction the extent of bonding (bond order) is constant.
(b) that the potential for a three atom system is the sum of three pair-potentials.
(c) that rules of thumb based on empirical observation (e.g. Badgers rule) can be used to predict bond energies as a function of bond length.

Extension of the method to cases where multiple bonds are broken has been made by Mayer\textsuperscript{127} including the case for four centre quasi-bound intermediates. Also, a more recent advance which permits calculation of the full three dimensional surface using an iterative scheme to establish bond order has been reported\textsuperscript{128}. However, very little trajectory work has been done with these systems, the majority of work using BEBO having been directed towards A + HB systems and in particular to establishing barrier properties\textsuperscript{129}. For trajectory calculations, a potential which is evaluated iteratively is to be avoided if possible especially if complex trajectories occur.
The most highly parameterised and possibly the most flexible empirical surface is the hyperbolic map function (HMF) due to Bunker, Blais\textsuperscript{130} and Parr\textsuperscript{131}. In its most general form\textsuperscript{132} the HMF permits independent adjustment of each channel in A + BC systems to suit requirements by providing a means by which barrier height (or well depth), approach angle and reaction co-ordinate can be controllably varied. This is effected by defining the reaction co-ordinate as one of an infinite family of rectangular hyperbolas

\[ xy = u ; \quad x = r_1 - r_1^0 \text{ or } r_3 - r_3^0 \]

\[ y = r_2 - r_2^0 \quad \text{.................(4.22)} \]

Such a choice provides control over the sharpness of the 'corner' in the fixed angle contour plot of the surface.

Variation of the potential profile along the reaction co-ordinate is then brought about by defining the infinite family of hyperbolas conjugate to it:

\[ y^2 - x^2 = v \quad \text{.................... (4.23)} \]

A parameterised Morse function along each hyperbola defined by equation (4.23) then provides the required surface topology.

\[ i.e. \quad V = F(\alpha) D(v) \left[ \exp(-2\beta(v)s) - 2 \exp(-\beta(v)s) \right] \quad \text{.......... (4.24)} \]

where \( F(\alpha) \) controls the variation of surface properties with approach angle,
\(\alpha\) and \(D(v), B(v)\) control the barrier height (well depth) and attractiveness (repulsiveness) of the potential.

To account for two reactive pathways the potential is written as

\[
V = f(\alpha) V(\text{ABC}) + (1 - f(\alpha)) V(\text{ACB}) \quad \cdots \cdots \cdots \cdots \quad (4.25)
\]

where the reaction product for each channel is underlined. In the case where \(B = C\), \(f(\alpha)\) should be chosen such that derivative discontinuities at isosceles configurations are smoothed out such that the equations of motion under such a potential can be integrated by the particular algorithm chosen.

Clearly, the HMF is eminently suited to metathetical studies of reactions as a function of surface features and to specific, well-known systems to which the HMF could be fitted. However, it has been criticised implicitly by the Polanyi school\(^{133}\) who found that they could not fit such a function to the \textit{ab-initio} \(\text{FH}_2\) potential whilst a good fit was possible using LEPS. Unfortunately, no details were given by the authors regarding the cause of this failure. Despite this, two general studies using HMF have appeared\(^{130, 27}\), one of them\(^{27}\) dealing with quasi bound triatomic intermediates. This latter publication has since been discredited by Brumer\(^{28}\) who showed that the HMF originally used was insufficiently smoothed at isosceles configurations to permit integration through them. A suitably smoothed potential was then used in conjunction with a stiffly-stable integration algorithm (see Section 4.8) and Bunker's original work repeated with the result that many of the distributions previously described\(^{27}\) were considerably altered. The most important outcome of this re-analysis\(^{28}\) was that the conclusions of Borne and Bunker...
regarding the effect of wells in the potential were reversed and a
restoration in existing qualitative concepts brought about.

Since the OI₂ system is not well defined both asymptotically and
at close interaction and since the aim of this project was to study the
above system dynamically rather than topologically it was decided that
the heavy parameterisation of the HMF method was not appropriate to our
requirements. This view was strengthened by the author's failure to
accept the findings of Ref. 27. which, at that time (1976), had not been
challenged.

The remaining category of empirical surface and indeed the one
used in this study is the switching function of Bunker and Blais¹³⁴.
This takes the following form for the A + BC → AB + C system:

\[
V_{ABC} = D_{AB} \exp (-\beta_{AB} \Delta r_{AB}) \left( \exp (-\beta_{AB} \Delta r_{AB}) - 2 \right)
+ D_{BC} \exp (-\beta_{BC} \Delta r_{BC}) \left( \exp (-\beta_{BC} \Delta r_{BC}) - 1 - \tanh \left( \Delta r_{AB} + b \right) \right)
+ D_{AC} \exp (-\beta_{AC} \Delta r_{AC}) \quad \ldots \ldots \ldots \quad (4.26)
\]

where \[D = \text{diatomic dissociation energy}\]
\[
\Delta r = r - r_e \quad ; \quad r_e = \text{equilibrium separation}\]
\[
\beta = \text{Morse \(\beta\) parameter.}\]

Application of this surface to the K + CH₃I reaction has been
made on three occasions¹³⁴, ⁵⁴. In Ref. 134, the potential was as written
in equation (4.26) with each Morse function using spectroscopic values
as parameters. This resulted in a total cross-section of ca. 400 Å²,
whereas the experimental value was 7 Å². To obviate this, two methods
were employed to reduce the long range K-I attraction. The first of these increased the $\beta$-value for the K-I pair and the effect of this was to reduce the cross-section to 25 $\text{Å}^2$. The second approach kept the parameters to their observed values but added a second switch term of the form

$$D_{AB} \exp (-\beta_{AB} \Delta r_{AB}) \left\{ \exp (-\beta_{AB} \Delta r_{AB}) - 1 - \tanh (c r_{BC} + d) \right\} \quad (4.27)$$

to counteract the K-I attraction. This also reduced the total cross-section (to 36 $\text{Å}^2$) but in a more physically acceptable fashion than above. Both modifications also resulted in a change in the differential cross-section from sideways to the observed backwards scattering.

Using the same potential, a systematic study of the effect of particle masses was made. Included in this was an 'M + HH' case (M \approx 16 amu; H = 128 amu) which almost exactly corresponds to $O + I_2$. The results obtained by Bunker and Blais were similar to those to be reported in Section 4.9 in some respects and will be discussed below.

In order to take account of the reactive symmetry of the $O + I_2$ system, two parametrically identical functions were used, one permitting reaction to $AB + C(V_{ABC})$ and the other to $AC + B (V_{ACB})$. The potential initially used was

$$V = f V_{ABC} + (1 - f) V_{ACB} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (4.28a)$$

where $f = \exp (\alpha \Delta V) / \left\{ 1 + \exp (\alpha \Delta V) \right\} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (4.28b)$

and $\Delta V = V_{ACB} - V_{ABC} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (4.28c)$
The parameter $\alpha$ was chosen to be \(100 \text{ eV}^{-1}\) in accord with Godfrey and Karplus\textsuperscript{136} and this resulted in a rapid transition from $V_{\text{ABC}}$ to $V_{\text{ACB}}$ near the isosceles configuration. A simpler version of this surface was also used:

$$V = \text{MINIMUM} (V_{\text{ABC}}, V_{\text{ACB}})$$ \hspace{1cm} (4.29)

which corresponds to the limit $\alpha \to \infty$.

The differences between the two surfaces were negligible in terms of trajectory outcomes but considerable in terms of computer time due to the complex expression for the derivatives of equation (4.28). It was therefore decided to adopt the latter version (equation (4.29)) in the hope that trajectories sampling isosceles configurations would be handled by the automatic-step-length-halving routine used\textsuperscript{54}.

The parameters used were the following:

<table>
<thead>
<tr>
<th></th>
<th>(D. (\text{k cal. mol}^{-1}))</th>
<th>(\beta(\text{au}^{-1}))</th>
<th>(r_e(\text{au}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>OI</td>
<td>53.0</td>
<td>1.269</td>
<td>3.530</td>
</tr>
<tr>
<td>(Ref.)</td>
<td>(72)</td>
<td>(\footnote{\textastern})</td>
<td>(138)</td>
</tr>
<tr>
<td>I\textsubscript{2}</td>
<td>35.5</td>
<td>1.232</td>
<td>5.047</td>
</tr>
<tr>
<td>(Ref.)</td>
<td>(137)</td>
<td>(\footnote{\textastern})</td>
<td>(137)</td>
</tr>
</tbody>
</table>

\footnote{\textastern}: See Chapter 2.
Three trial surfaces were used with different values of the parameter B.

<table>
<thead>
<tr>
<th>SURFACE</th>
<th>A (au⁻¹)</th>
<th>B</th>
<th>WELL DEPTH (w.r.t. PRODUCTS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.S.1</td>
<td>1.00</td>
<td>-4.00</td>
<td>3.0 k. cal. mol⁻¹</td>
</tr>
<tr>
<td>P.S.2</td>
<td>1.00</td>
<td>-3.50</td>
<td>10.0 &quot;</td>
</tr>
<tr>
<td>P.S.3</td>
<td>1.00</td>
<td>-3.00</td>
<td>21.0 &quot;</td>
</tr>
</tbody>
</table>

Detailed features of these surfaces are presented in figures 4.7 - 4.9.

The contour maps in Figure 4.7 (for A + BC → AB + C) reflect a lack of angular specificity in the surfaces: for A-B-C angles of 90° - 180° the surface features change little. This is not too unreasonable since the considerations already made imply the existence of a relatively stable triplet state over a wide angular range. For angles below 90°, a barrier to formation of AB occurs since this requires crossing the isosceles configuration at low separations. Minimum potential paths corresponding to Figure 4.7 and to other approach angles are shown in Figure 4.8. It can be readily seen that the steric factor of 0.1 proposed by Radlein et al. cannot be met by these surfaces on a purely static basis. It is possible that it can be met dynamically but its extent cannot be predicted a priori.

The barrier to insertion of O (³P₉) into I₂ (¹Σ⁺) is indicated in Figure 4.9b. For translational energies below 20 k. cal. mol⁻¹ insertion is forbidden. The existence of small wells in the C₂ᵥ approach is not expected to have much effect on the dynamics since the motion of BC is likely to destabilise the isosceles configuration to a more bound scalene one as shown in Figure 4.9a. The potential energy profiles shown
Figures 4.7, 4.8 & 4.9a,b

4.7 - Contour plots of potential surfaces P.S.1, P.S.2 and P.S.3. Each contour separation is 5 kcal/mol. Reactants enter at bottom right and products leave at top left.

4.8 - Potential profiles along reaction co-ordinate. These have been generated by constructing the contour map array and scanning this along a line, from a point corresponding to A+B+C, at various angles from 0° (products) to 90° (reactants) and noting the minimum at each angle.

4.9 (a) - Minimum potential profile for migration of atom A around BC. Curves have been constructed by finding minimum value of V for given Θ by variation of r(BC) and r(A-BC). Note that in all three cases the barrier maximum falls short of the lowest total energy used (0.025 eV) in the calculations. The application of models for a 'loose' complex are therefore appropriate.

4.9 (b) - Minimum potential profiles for broadside approach of atom A to BC obtained by variation of r(BC) for a given value of R(A-BC). The insertion of A into BC is energetically forbidden for collision energies below ≈ 21 kcal/mol. In keeping with Walsh's rules, spin-polarisation repulsion and the observations for A=O(3P) and BC = I2(X 1Σg⁺)
Figure 4.7 - Fixed Angle Contour Maps for $\angle ABC = 180^\circ$ & $45^\circ$

Contours in k.cal.mol$^{-1}$; Separations in au
Figure 4.8 - Reaction Co-ordinates (reaction proceeds from top right to middle left of each box)
Figure 4.9 - Potential Profiles (ink.cal/mol)

(a) Potential Profiles

(b) Potential Profiles with energy levels:
- $E_t = 0.025$ eV
- $E_t = 0.25$ eV
- $E_t = 0.025$ eV
in Figure 4.9 correspond to minimum paths; thus in (a) although migration of the O-atom is possible, it only arises in a minority of cases (at low translational energy) and approaching the isosceles configuration is most likely to result in the O-atom retracing its path after reflection at the boundary. Thus, some 'tight' character is endowed upon the complex but the lack of angular specificity in the potential must endow more 'loose' character.

4.6 EQUATIONS OF MOTION AND CO-ORDINATE SYSTEMS

The co-ordinate systems are shown in Figures 4.10 and 4.11 for both 2-D and 3-D. The origin of the co-ordinate system is chosen as the centroid of BC to simplify the choice of starting conditions. The generalised position co-ordinates $Q_i$ are given by:

**3-D**

\[
\begin{align*}
Q_1 &= R \sin \theta \cos \phi \\
Q_2 &= R \sin \theta \sin \phi \\
Q_3 &= R \cos \theta \\
Q_4 &= R_{BC} \sin \beta \cos \alpha \\
Q_5 &= R_{BC} \sin \beta \sin \alpha \\
Q_6 &= R_{BC} \cos \beta
\end{align*}
\]

\[\text{......................... (4.30)}\]
Origin is B-C centroid
A is \((Q_1, Q_2, Q_3)\)
B is \((Q_4, Q_3, Q_6)\) w.r.t. C

Figure 4.10 - 2-D & 3-D Co-ordinate Systems
Figure 4.11 - Linear and Angular Momenta in 3-D Constructional Aid
2-D

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

\[ (4.31) \]

Since \( P_\mu = \mu \dot{q}_\mu \) (see Appendix A) the conjugate momenta \( P_\mu \) are given by

3-D

\[ P_1 = -\mu_{A, BC} v_{rel} \{ \cos \delta \sin \theta \cos \phi - \sin \delta \cos \chi \cos \theta \cos \phi + \sin \delta \sin \chi \sin \phi \} \]

\[ P_2 = -\mu_{A, BC} v_{rel} \{ \cos \delta \sin \theta \sin \phi - \sin \delta \cos \chi \cos \theta \sin \phi - \sin \delta \sin \chi \cos \phi \} \]

\[ P_3 = -\mu_{A, BC} v_{rel} \{ \cos \delta \cos \theta + \sin \delta \cos \chi \sin \theta \} \]

\[ P_4 = \mu_{BC} \{ \dot{R}_{BC} \sin \beta \cos \alpha + \omega_{R_{BC}} (\sin \eta \sin \phi + \cos \eta \cos \beta \cos \phi) \} \]

\[ P_5 = \mu_{BC} \{ \dot{R}_{BC} \sin \beta \sin \alpha + \omega_{R_{BC}} (-\sin \eta \cos \phi + \cos \eta \cos \beta \sin \phi) \} \]

\[ P_6 = \mu_{BC} \{ \dot{R}_{BC} \cos \beta + \omega_{R_{BC}} \cos \eta \sin \beta \} \]

\[ (4.32) \]
\[
P_1 = -\mu_{A, BC} \cdot v_{\text{rel}} \cdot \cos (\pi/2 - \theta + \alpha)
\]
\[
P_2 = -\mu_{A, BC} \cdot v_{\text{rel}} \cdot \sin (\pi/2 - \theta + \alpha)
\]
\[
P_3 = \pm \mu_{BC} \cdot R_{BC}
\]
\[
P_4 = \pm \mu_{BC} \cdot \omega \cdot R_{BC}
\]

where \(\mu_{A, BC}\) and \(\mu_{BC}\) are the reduced masses of \(A + BC\) and \(BC\). The rotational velocity of \(BC\) is given by \(\omega \cdot R_{BC}\).

4.7 STARTING CONDITIONS

\(\theta\):

Fixed at 17.5 au (9.3 Å). This choice ensured effectively zero change in potential over first few integration steps.

\(\theta\):

This has a distribution weighted by its sine as explained in Reference 139 (Appendix C).

i.e. \(\theta = \cos^{-1} (1 - 2 \cdot \text{RN}) \) ................. (4.34)

where RN is a random number taken from a uniform distribution in the range (0, 1).
\[ \phi = 2\pi \cdot \text{RN} \]  

Since azimuthal symmetry is present.

\( \alpha \):

The same remarks apply for \( \alpha \) as for \( \phi \). However, variation of both in a uniform manner is equivalent to variation of one only and \( \alpha \) is therefore set to \( \pi/2 \).

\( \beta \):

It is not clear what sampling method is appropriate here. A similar co-ordinate system fixes it at an arbitrary value\(^{140} \) using the \((\theta, \phi)\) variation to account for its orientation. However, this is not in accord with the definitive work of Karplus, Porter and Sharma\(^{139} \) who orient the BC molecule with respect to the initial relative velocity vector (taken along the \( z \)-axis). To test this, distributions of the angle between the relative velocity vector and the B-C axis were constructed for \( \beta \) fixed and \( \beta \) varying uniformly and randomly in \((0, 2\pi)\).

These distributions are shown in Figure 4.12 with the sine distribution shown for comparison. None of the distributions show serious departure from the ideal one and this is reflected in chi-squared goodness-of-fit tests. The worst (visually) distribution for \( \beta = 30^\circ \) has a chi-squared value of 13.35 which for 18 classes \((10^\circ \text{ intervals})\) indicates a high confidence level for the null hypothesis of a sine distribution.
Figure 4.12 - Distributions of angle between relative velocity vector and B-C axis. $\theta$ is either fixed or varied uniformly and randomly in $(0, 2\pi).$
The distribution of $\beta$ was originally chosen according to equation (4.35) although it could equally well have been fixed.

For BC in the zero point state this is selected from a Gaussian distribution. The simple harmonic wave function is given by

$$\Psi_V = 0 \Psi = \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} \exp\left(-\beta x^2\right) \quad \text{................. (4.36)}$$

which, when making the substitution

$$\beta x^2 = \frac{1}{2} t^2 \quad \text{................. (4.37)}$$

defines a standard normal distribution. Values of $t$ are taken from a random number generator with a Gaussian distribution. The displacement, $x$, is then calculated from equation (4.37) and $R_{BC}$ obtained by addition of $R_e$, the equilibrium separation.

If $R_{BC}$ exceeds the classical limit the process is repeated until a satisfactory result is obtained.

This is preset to correspond to a given CM collision energy. Sampling from a thermal (or other) distribution seldom yields significantly different results.
δ: This angle is set by the impact parameter, b, according to

\[ \delta = \sin^{-1} \frac{b}{R} \] ................. (4.39)

b: The impact parameter dependence of the trajectory outcomes is a smooth function and has no discontinuities. This permits sampling b at fixed values which represent the mean of a range of b. In these calculations, b was stepped from zero to \( b_{\text{max}} \) in steps of 1 or \( \frac{1}{2} \) au.

X: This is sampled according to equation (4.35).

η: The allowed orientations of the rotational angular momentum are contained in the plane \( \pi \) of Figure 4.11 (b) which is perpendicular to BC. If there are no constraints on the rotational motion of BC (such as those caused by alignment) then \( \eta \) is obtained according to equation (4.35). In these calculations, the effect of different orientations of the rotational angular momentum were considered and details of the choice of \( M_\eta \) states are given in Appendix B.

The vibrational phase which is not explicitly indicated in the figures is obtained from the Gaussian random number generator. This generates positive or negative parity with equal probability. To obtain the vibrational velocity, the simple harmonic approximation is used. Thus

\[ R_{BC} = s \cdot \Omega \cdot (x_{\text{max}}^2 - x^2)^{\frac{1}{2}} \] ................. (4.40)
where \( S = \text{sign} \), \( \Omega = \text{vibrational frequency} \) and \( x = \text{displacement from equilibrium} \).

In the 2-D case, the starting conditions are much simpler. The orientation angle, \( \theta \), is no longer weighted by its sine and is given by equation (4.35). \( \alpha \) is likewise given by equation (4.39). The initial orientation of BC is taken as the positive x-axis without loss of generality. Lastly, the vibrational phase, displacement and velocity are given by the same procedure as for the 3-D case above. However, for \( v > 0 \) the harmonic assumption is still made but rather than mimic these wave functions, fixed displacements which correspond to peaks in \( |\psi_v|^2 \) are used. The probability of a given displacement is set equal to the area under its corresponding hump in \( |\psi_v|^2 \).

4.7.1 BEHAVIOUR OF RANDOM NUMBER GENERATORS

The requirement to observe this stems from the publication of Holmlid and Rynefors\textsuperscript{141} which commented critically on this behaviour. At the outset and in a previous report\textsuperscript{142} the IBM-supported generator RANDU was used for the uniform distribution. On advice from the Regional Computing Centre, this was removed and generators from the NAG\textsuperscript{143} library were adopted. In particular, the generators G05AAF (uniform) and G05ADF (Gaussian) were used.
Each single batch of trajectories (one surface, one energy) typically required roughly 1000 random numbers. To test the quality of the distributions, these were binned into 20 classes of equal width, this number being the resolution of the outcomes approximately (e.g. 18 bins of $10^0$ for the angular distribution). GØ5AAF and GØ5ADF were then tested against null hypotheses of uniformity and Gaussian shape using the simple chi-squared test with 19 degrees of freedom. For 100 tests using 1000 random numbers per test, the results were:

$$\chi^2 (\text{GØ5AAF}) = 18.5 \pm 6.7$$

$$\chi^2 (\text{GØ5ADF}) = 18.3 \pm 6.1$$

where the error represents one standard deviation in the $\chi^2$ results. The corresponding significant levels exceed 30% which lends strong support for the null hypotheses and indicates good behaviour in the random number generators.

4.8 INTEGRATING THE EQUATIONS OF MOTION

Most classical trajectory calculations thus far reported have been concerned with direct reactions using potential surfaces with barriers. These typically require integration over less than $10^{-12}$ s. at thermal energies to completely define a trajectory. However, on attractive surfaces and/or surfaces containing wells, certain ranges of initial conditions lead to the system being bound within centrifugal barriers, the binding persisting for $10^{-12} - 10^{-11}$ s typically. These LLC's present
considerable difficulty in their numerical integration since the large number of steps required per trajectory creates inaccuracies due to round-off error build-up and unbounded propagation of the truncation error. The former can be minimised using multiple precision arithmetic (usually double on IBM and ICL machines) but this increases the storage requirement and the execution time concomitantly. The latter is generally more serious since it builds up in a fashion which is neither linear nor predictable. If this occurs, the system of equations and/or the integration algorithm h has become unstable.

Three relevant definitions of stability arise in molecular scattering problems:

(1) Absolute stability
(2) Relative stability
(3) Dynamic stability.

(1) and (2) refer to the integration procedure whilst (3) refers to the system of differential equations, assumed linear. For absolute stability the truncation error is bounded whereas for relative stability it is unbounded but takes a value acceptably less in magnitude than the final solution. Systems of equations displaying dynamic instability should have solutions which are relatively stable, absolute stability being appropriate to dynamically stable systems. Since integration algorithms have well defined regions of absolute and relative stability, the choice of one for a given system of equations can often be pre-judged according to the dynamic stability of the system.
4.8.1 NUMERICAL INSTABILITY

Casting Hamilton's equations (4.76) in the form

\[ \frac{dy}{dt} = f(y, t) \]  \hspace{1cm} (4.41)

where \( y \) is the column vector of the generalised co-ordinates

i.e. \[ y = (y_1, y_2, y_3, \ldots, y_k)^T \]  \hspace{1cm} (4.42)

with \( k = 8 \) for planar calculations and 12 in the full 3-D case.

If at any time \( t_n \) during the integration, the computed solution is \( z_n \) whilst the true solution is \( y_n \), then the error \( e_n \) is given by

\[ e_n = y_n - z_n \]  \hspace{1cm} (4.43)

Differentiating and applying (4.43)

\[ \frac{de_n}{dt} = \frac{dy_n}{dt} - \frac{dz_n}{dt} = f(e_n + z_n) - f(z_n) \]  \hspace{1cm} (4.44)

Expanding (4.44) as a Taylor series about \( z_n \) yields

\[ \frac{de_n}{dt} = (f(z_n) + e_n f'(z_n) + \text{higher order terms}) - f(z_n) \]

\[ = e_n f'(z_n) \]  \hspace{1cm} (4.45)

to first order.
The propagation of the error $e_n$ is described in (4.45). In matrix notation, this becomes

$$\frac{d}{dt} (e_1, e_2, ..., e_t)^T = S (e_1, e_2, e_3 ..., e_t)^T \quad (4.46)$$

with $S$ given by

$$S = \begin{bmatrix}
\frac{\partial f_1}{\partial z_1} & \frac{\partial f_1}{\partial z_2} & \cdots & \frac{\partial f_1}{\partial z_k} \\
\frac{\partial f_2}{\partial z_1} & \frac{\partial f_2}{\partial z_2} & \cdots & \frac{\partial f_2}{\partial z_k} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial f_k}{\partial z_1} & \frac{\partial f_k}{\partial z_2} & \cdots & \frac{\partial f_k}{\partial z_k}
\end{bmatrix} \quad (4.47)$$

The matrix, $S$, is known as the stability matrix and its eigenvalues $\lambda_i$ determine the position of the algorithm, at a given point in the integration, on the stability diagram. If the product $h \lambda_i$, where $h$ is the integration step-size, lies outside the stability region of the algorithm, the integration procedure becomes unstable and variation of $h$ is necessary to regain stability. It is therefore possible to maintain a watchful eye over the stability behaviour of the algorithm as the integration proceeds. However, even for modest systems of equations (e.g. $k = 12$) the process of evaluating the functional derivatives for $S$ and determining its
eigenvalues is a time consuming procedure which should be minimised if not avoided.

Since direct trajectories do not suffer from instabilities to the same extent as those proceeding via LLC's, it is seldom that stability-conscious methods are used in their solution. An extreme example of the reverse of this situation is the alkali-halide, alkali-halide exchange system studied by Brumer and Karplus

The potential for this system exhibited a number of wells and the interaction times of the order of $10^{-11}$ s reflected this as did the (real) processor time of up to fifteen minutes per trajectory. It is extremely unlikely that hitherto conventional methods would have yielded an accurate solution in cases and the cost of using an algorithm which did is manifest in the excessive execution time, much of which was devoted to the supervisory aspects of the algorithm mentioned above.

4.8.2 CHOICE OF INTEGRATION ALGORITHM

There are three classes in common use

(1) single step methods
(2) multiple step methods
(3) hybrid methods

The first category were almost exclusively used in classical trajectory calculations prior to 1971. The basic equation here is:

$$y_n = y_{n-1} + h g (y_{n-1}; h) \cdots \cdots \cdots \cdots \cdots \cdots \cdots \ (4.48)$$
g is commonly a truncated Taylor series. For first order truncation, Euler's method obtains whilst higher order truncation gives rise to a family of Runge-Kutta methods of which the fourth order variant dominated early trajectory work. Their great advantages are that they are self-starting, requiring one initial condition vector, and that they are simple to code. However, for extended calculations they suffer from inefficiency brought about by multiple function evaluations at each step and instability. Since the local truncation error cannot readily be evaluated, their instability cannot be corrected. Their unsuitability in complex trajectory integration and in inelastic, direct trajectories has been noted.

During the '70's, the use of multi-step methods has become widespread. These offer the advantages of higher inefficiency, and controllability with low (and estimable) truncation error generation. The basic equation in this category is

\[ a_o y_n = \sum_{i=1}^{j} a_i y_{n-i} + h \sum_{i=0}^{j} b_i f(y_{n-i}) \]  \hspace{1cm} (4.49)

where \( b_0 = 0 \) for explicit methods and is non-zero for implicit methods. In general, implicit methods are more applicable than explicit ones since they permit easy truncation error estimation and have associated regions of stability wider than those of explicit methods. However, since \( y_n \) must be well approximated in the RHS of (4.49) before final solution, a convergent iterative procedure for predicting \( y_n \) must be used. Such implicit methods are known as predictor-corrector methods and are dominated by the accuracy of the corrector. The scheme is
with (4.50) an explicit predictor and (4.51) an implicit corrector.

Evidently two function evaluations are required per step and in order to
minimise computational effort only one iteration step should be used to
obtain the necessary tolerance. Schemes for effecting this have been
devised \[145, 149\] which either modify the corrector directly or include an
extra modifier step. The local truncation error can be estimated from the
difference between the predictor and corrector and the integration step
size can be modified to maintain stability.

The cause of the increased efficiency in multistep methods in
general is that a table of past values can be constructed which permits
forward integration with fewer function evaluations than a single step
method of the same order. However, if stability considerations dictate
altering $h$ mid-course some efficiency is lost since smaller step-lengths
require interpolation to restart the algorithm. Usually, $h$ is either
doubled or halved. The former presents no problems requiring only a
sufficiently large store of past values. The latter requires interpolation
which introduces further error. Alternative approaches to this involve
variable-mesh methods \[146, 148\] which permit arbitrary step size changes
and consequently obviate the overkill of halving and doubling.
The commonest predictor-corrector method is the Adams-Moulton type with the fourth order version being particularly popular. More recently, higher order methods having 5th and 10th order predictors with 6th and 11th order correctors\textsuperscript{150, 151} have been used. Generally, the higher the order, the less flexible the algorithm is with respect to step-size changes since more interpolated points are required for the re-start. Also, the range of stability decreases with increasing order which restricts their application to dynamically stable systems.

A less common predictor-corrector algorithm is that due to Hamming\textsuperscript{145}. This is a modified version of the well-established method due to Milne which does not suffer from instability. It was used with success by Whitehead\textsuperscript{39, 40} in his studies on long-lived tri-alkali systems and by Fluendy et al\textsuperscript{142} in the superthermal K + I\textsubscript{2} studies. In addition to this, the author has applied it to laser kinetics simulation\textsuperscript{152} and found it to be acceptable under the stiff conditions of such rate processes. The results of the following section were obtained using this method after a protracted effort to obtain acceptable stability.

The last category, hybrid methods, are derived from the other two types. These methods are variable in both order and step-size and generally permit solution to stiff systems of equations which the others cannot handle\textsuperscript{147}. The most common source of stiff equations (i.e. equations with widely differing frequency domains) is in chemical kinetics where a given system, e.g. the atmosphere, has reactions occurring with vastly different rate constants. They are less common in trajectory calculations since historically, these have been concerned with direct reactions. However, an interest in complex reactions is now growing with the refinement and expansion of beams experiments towards polyatomic systems.
 Basically, the hybrid method is a variable order, variable step-size methods which makes use of the stability matrix (equation 4.47) whose eigenvalues it calculates when necessary. The algorithm computes the maximum stepsize allowable at orders one greater and one less than the instant order and then decides whether a change in the order to maintain stability is necessary. In this fashion, an optimum compromise between step-size and order can be achieved with minimal computational effort. In 4.8.3 it will be shown that this method can be more time consuming than straightforward predictor-corrector methods due to the extra processor time devoted to its supervision.

There are currently two variants of the method generally available: the original (DIFSUB in Gear's book 147 and a modified version due to Craigie, DIVDIF 153. The latter has been shown to be superior to DIFSUB for large systems of equations (k > 10). There are, in addition, two routines available from the NAG library, D02AEF and D02AJF, the latter being modelled on Craigie's work.

4.8.3 DESCRIPTION AND PERFORMANCE ON INTEGRATION ALGORITHM

In the purely attractive potentials used in these computations, both entrance and exit channels can be described by a multipolar expansion in $R^{-1}$ where $R$ is the atom-diatomic separation

$$V \sim \sum_{i>1} \frac{C_i}{R^i} \quad \text{...............} \quad (4.5)$$
Brumer has shown that such a form gives rise to dynamic instability as the particles approach, the stability matrix taking real, positive eigenvalues. The effect of this is minimised by using suitably small step-sizes and a condition of relative stability can be reached. With closer approach of the particles, the system crosses into a region of absolute stability providing the step length is considerably shorter than the lowest characteristic time constant of the quasi-bound species ($\sim 5 \times 10^{-14}$ s for $\text{O}_2$).

Since long-lived complexes take up random positions and momenta between centrifugal barriers it is expected that the system will exhibit considerable instability both absolute and dynamic as the eigenvalues change. It is therefore difficult to predict a priori how a given algorithm will perform; the best approach is to test all options.

The two algorithms tested in this study were

1. Hamming's predictor-corrector method and
2. Subroutine DØ2AEF from NAG based on Gear's DIFSUB.

The details of (1) were:

Predictor: $p_{n+1} = y_{n-3} + \frac{4h}{3}(2f_{n-2} - f_{n-1} + 2f_{n-2}) \quad (4.52)$

Modifier: $m_{n+1} = p_{n+1} - \frac{112}{121}(p_n - c_n) \quad (4.53)$

Corrector: $c_{n+1} = \frac{1}{8}(9y_n - y_{n-2} + 3h m_{n+1} + 2f_n - f_{n-1}) \quad (4.55)$
Final value \( y_{n+1} = c_{n+1} + \frac{9}{121}(p_{n+1} - c_{n+1}) \) ................ (4.56)

To start the algorithm, a table of values was constructed using a fourth order Runge-Kutta procedure.

\[
y_{n+1} = y_n + 0.17476028226269037 k_1 - 0.55148066287873294 k_2 + 1.205535993965235 k_3 - 0.17118478121951903 k_4
\]

where \( k_1 = hf(y_n) \)
\( k_2 = hf(y_n + 0.4 k_1) \)
\( k_3 = hf(y_n + 0.29697760924775360 k_1 + 0.15875964497103583 k_2) \)
\( k_4 = hf(y_n + 0.21810038822592047 k_1 - 3.0509651486929308 k_2 + 3.8328647604670103 k_3) \) ............. (4.57)

The algorithm described in equation (4.57) although unstable is extremely accurate having a truncation error about half that of the more popular Runge-Kutta methods. Since it is only used three times to generate a starting table of values for Hamming's method, its instability is unimportant.
Method (2) is detailed by Gear\textsuperscript{147}. It is variable in order from one to six being self starting in first order. The stepsize can be varied by doubling or halving as in Hamming's method but the interpolation procedure used is different for halving. Here, a Nordsieck (variable mesh)\textsuperscript{153} vector of derivatives obtained from previous steps is used to obtain interpolated values using a Taylor expansion. By contrast, the Hamming's method uses

\begin{align*}
y_{n-\frac{1}{2}} &= \frac{1}{256} (80y_n + 135y_{n-1} + 40y_{n-2} + y_{n-3}) \\
&\quad + \frac{h}{256} (-15f_n + 90f_{n-1} + 15f_{n-2}) \quad (4.58)
\end{align*}

and

\begin{align*}
y_{n-\frac{3}{2}} &= \frac{1}{256} (12y_n + 135y_{n-1} + 108y_{n-2} + y_{n-3}) \\
&\quad + \frac{h}{256} (-3f_n - 54f_{n-1} + 27f_{n-2}) \quad (4.59)
\end{align*}

There are a number of complementary ways of evaluating the performance of an integration routine. These are:

1. conservation of total energy (Hamiltonian)
2. conservation of total angular momentum
3. re-attainment of initial conditions by backward integration
4. insensitivity to initial step-size
5. stability with respect to small changes in initial conditions
6. insensitivity to processor arithmetic precision.

Whereas (1), (2) and (6) are mainly related to round-off error, (3), (4) and (5) are determined by the stability of the equations and/or the algorithm. Satisfaction of conditions (1), (2) and (6) is necessary for...
reliable integration although not sufficient\textsuperscript{35} whilst (3), (4) and (5) alone are invariably sufficient.

For the Hamming routine, Hamiltonian (H) conservation to better than 2 in 1,000 obtained for the lowest energy, snarled trajectories in 3-D. The 2-D case was expectedly better with at least 5 in 10,000 precision. The optimum values of the local truncation error and initial step length (PRMT (4) and PRMT (3) in programs listed in Appendix C) were

<table>
<thead>
<tr>
<th>$E_{\text{rel}}$ (eV)</th>
<th>PRMT (4)</th>
<th>PRMT (3)/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-15}$</td>
</tr>
<tr>
<td>0.100</td>
<td>&quot;</td>
<td>$5.0 \times 10^{-16}$</td>
</tr>
<tr>
<td>0.250</td>
<td>&quot;</td>
<td>$4.0 \times 10^{-16}$</td>
</tr>
<tr>
<td>1.000</td>
<td>&quot;</td>
<td>$2.0 \times 10^{-16}$</td>
</tr>
<tr>
<td>2.500</td>
<td>&quot;</td>
<td>$1.0 \times 10^{-16}$</td>
</tr>
</tbody>
</table>

The truncation error tolerance had a marked affect on trajectory outcomes - too low a value resulted in an error flag due to too many bisections of the initial step-size and gave rise to instability whilst returning high precision in H. Too high a value caused serious non-conservation of H irrespective of initial step-size and in some cases caused ill-conditioning with respect to initial conditions.

Conservation of angular momentum was seen to be a poorer guide than H conservation. At low energy, a total swing in angular momentum of 2 in 10,000 represented worst case conditions, a typical value being 7 in 100,000. For the high energy trajectories (2.5 eV) this figure rose to better than 1 in $10^7$ whilst that for H fell between 1 and 100 in $10^7$. 

\textsuperscript{35}
In general, better dynamical behaviour is expected at high energies due to the relatively lower interactions involved.

It has been pointed out by various authors that conservation of constants of the motion are an unreliable guide to integrator performance.\^{35, 15} A better test is given by (3) or (4) mentioned previously. In special cases where analytic solutions are available, an absolute measure of their performance is possible.\^{31}

For Hamming's method, backward integration could be achieved for most trajectories tested at 0.025 and 0.25 eV collision energy. Long-lived trajectories of 5 ps or more particularly on P.S.3 could never be integrated backwards. To selectively remove these from consideration, a device was incorporated in the programs by which trajectories snarling for longer than a preset time were output graphically for visual inspection. This enabled immediate acceptance/rejection according to Brumer's notion of "completeness".\^{34} It also indicated a source of systematic error in that a few "long-lived" trajectories were in fact direct ones with low final translational energy. This is clearly indicated in Figure 4.13(a).

At high energy (2.5 eV) backward integration was only successful for those trajectories which did not cross the isosceles configuration at close range. The form of the potential gave rise to force discontinuities at these configurations which increased with decreasing impact parameter giving rise to dynamic instability. Where the $C_{2v}$ configuration was not sampled and in test trajectories on a single surface, backward integration to five significant figures was routinely achieved.
Figure 4.13 (a) - Direct trajectory appearing as complex on basis of integration time. The product AC is highly excited both vibrationally and rotationally.
The performance of Hamming's method with respect to halving the initial step length depended on the choice of local truncation error tolerance. At the optimum value of $1.0 \times 10^{-4}$, the trajectories were stable in all but two cases where, although conservation was above average, the final P's and Q's diverged completely, resulting in different product formation! Since this occurred only once in the test period lasting some twelve months prior to final batch running, this was considered spurious and disregarded.

The behaviour of Hamming's algorithm is indicated in Figure 4.13(b). Two criteria for abortive outcomes arose

1. Number of initial step length halvings (IHLF in program) exceeded 10.
2. Trajectory would not complete in allotted time.

Whereas (1) was exclusive to high energy trajectories, (2) related to low energy ones particularly at 0.025 eV on P.S.3. For (1), the fall off with increasing impact parameter reflects the discontinuous nature of the potential derivatives at low separation as well as the high forces involved in hard-sphere interactions. The low energy behaviour stems from the high binding energy of OI$_2$ on P.S.3. The variation of stability matrix eigenvalues is likely to be higher for this surface due to the larger interactions involved. The dynamic instability resulting from this causes unbounded error growth such that these could never be integrated backwards.
Figure 4.3b - Probability of Abortive Trajectory vs. Impact Parameter
The NAG routine D02AEF was compared with the Hamming's one under identical conditions. In general results for the former were ultimately identical to the latter but at considerable extra cost in CPU time. Agreement up to 4 significant figures could be obtained. The major differences between the two were:

(1) D02AEF required substantially more function evaluations than Hamming's.

(2) the CPU time for D02AEF exceeded that for Hamming's method by a factor significantly greater than the ratio of function calls.

As an example, the following results for a specific trajectory were obtained.

<table>
<thead>
<tr>
<th></th>
<th>HAMMING'S</th>
<th>NAG/D02AEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>FUNCTION CALLS</td>
<td>9801</td>
<td>14971</td>
</tr>
<tr>
<td>CPU TIME (s)</td>
<td>375</td>
<td>701</td>
</tr>
<tr>
<td>E(t) (ARB)</td>
<td>58.6</td>
<td>59.9</td>
</tr>
<tr>
<td>H, J CONSERVATION</td>
<td>Better than 1 in 10^3 and 10^4 resp.</td>
<td></td>
</tr>
</tbody>
</table>

The extra inefficiency in the NAG routine arises from the innate requirement to monitor the stability by evaluating the $S$ matrix eigenvalues (see Ref. 147 p. 158) which requires a $12 \times 12$ matrix inversion. The extra function evaluations must stem from the lower order of integration required when the stability is poor.
Evidently, the Hamming's method was superior in this instance although the most recent implementations of the NAG libraries (Mk.'s 6 and 7) have phased out D02AEF in favour of D02AJF which is not restricted to only halving and doubling the step-size. In hindsight, the author now feels that the 'stiffly-stable' hybrid methods are much easier to use in cases of stiff equations since other predictor-corrector methods although acceptable need to be tuned into the appropriate region of stability by a time-consuming trial and error procedure.

The batch running of the trajectories was done on two processors, an ICL 4-75 for 2.5/0.25 eV and an ICL 2980 for 0.025 eV. For identical trajectories on each machine, the latter was about ten times faster. Low energy trajectories thus took typically 10-60 s on the 2980. At high energy on the 4-75, trajectories ran in 1-5 s. The effect of processor speed is clearly a major factor and it is not envisaged that these low energy trajectories would lend themselves to dedicated mini-computer integration as has been done for $\mathrm{H} + \mathrm{F}_2 ^{156}$.

4.9 RESULTS

A total of over 16,000 planar and 3-D trajectories were run on three potential surfaces P.S.1, P.S.2 and P.S.3 at three energies 0.025, 0.25 and 2.5 eV (0.57, 5.7 and 57 k. cal. mol$^{-1}$). In addition, some planar trajectories were run at 1.0 eV (23 k. cal. mol$^{-1}$). The distribution of outcomes was as follows:
The inclusion of planar trajectories was to compare the dimensionalities (2-D and 3-D) in the long-lived complex (LLC) régime. The use of 2-D calculations had previously fallen out of favour due to the effect of out of plane scattering on the angular distributions. If these were found to be successful for LLC's then much of the effort would be removed from such calculations.

The effect of rotational angular momentum polarisation, $M_\pi$, was also studied to determine where, if at all, this constrains the collisions. Also, for the 2-D low energy trajectories, the effect of vibrational excitation of the reactant molecule was studied since this had not previously been done in a parametric fashion. Lastly, the choice of collision energies spanning three decades was made to investigate the potentials and the fate of the LLC. Scanning energy over less than 1 eV as in the papers of Whitehead and Kwei et al was considered inappropriate since, unlike the present study, the authors above started from reliable and accurate potentials.
4.9.1 LIFETIMES

Histograms of total integration times are presented in Figures 4.14 and 4.15 for the 3-D and 2-D cases respectively. The end-point was determined as the smallest separation for which the potential changed by one unit in the fourth significant figure, a value of 17.9 au (9.5 Å).

Visual inspection of the outcomes of certain long-lived trajectories showed that direct encounters which left the products highly internally excited contributed anomalously high values for the total integration time by virtue of their low exit velocity. The procedure adopted in previous work* of defining the complex lifetime as the time the system remained within a circle of given radius is subject to error when the translational energy is low. Consequently, very long-lived trajectories were output graphically and their integration times were assigned by visual inspection.

At collision energies of 1.0 eV (23 k. cal. mol⁻¹) or less, the lifetime distributions take on a familiar exponential type decay on P.S.1 and P.S.2. This is not so evident on P.S.3 due to the poorer statistics but at 0.025 and 0.25 eV there are indications here of a long-lifetime decay. The results for complex lifetimes are listed in table 4.2 together with the predictions of RRKM theory for loose/tight complexes given in parentheses.

* Kwei et al., hereinafter called KBS.
Whitehead, " " JCW.
Figure 4.14 - Distributions of Integration Times for Reactive (and Dissociative) Collisions

Abscissae in units of $10^{-14}$ s.
Figure 4.15 - Total Integration Time Distributions

0.025 eV

0.250 eV

1.000 eV

2.500 eV
<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>0.025</th>
<th>0.25</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS1</td>
<td>.67 ± .03</td>
<td>.43 ± .02</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>.63 ± .04</td>
<td>.33 ± .01</td>
<td>.29 ± .02</td>
</tr>
<tr>
<td></td>
<td>(.26/.24)</td>
<td>(.23/.22)</td>
<td>(.20/.20)</td>
</tr>
<tr>
<td>PS2</td>
<td>1.01 ± .05</td>
<td>.73 ± .04</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.00 ± .06</td>
<td>.75 ± .05*</td>
<td>.5 ± .07</td>
</tr>
<tr>
<td></td>
<td>(.61/.49)</td>
<td>(.47/.40)</td>
<td>(.31/.29)</td>
</tr>
<tr>
<td>PS3</td>
<td>2.5 ± .3*</td>
<td>.8 ± .09*</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2.5 ± .2*</td>
<td>.9 ± .17*</td>
<td>.4 ± .1*</td>
</tr>
<tr>
<td></td>
<td>(1.61/1.10)</td>
<td>(1.12/.81)</td>
<td>(.57/.47)</td>
</tr>
</tbody>
</table>

* → Not possible to fit to $e^{-t/\tau}$ and mean value consequently taken.

**Table 4.2** Complex Lifetimes (p.s.)
There is evidently close agreement the 2-D and 3-D cases in each category shown. In addition, the RRKM predictions are consistently lower than the trajectory results especially for the tight, complex case. The only exception (P.S.3/1 eV/2-D) suffers from very poor statistics.

This type of behaviour has been reported previously for the exothermic reaction of Li + Na₂ and contrasts with similar work for Li + Li₂ and Na + Li₂ which are thermoneutral and endoergic respectively in that the RRKM predictions are always smaller than observed. This effect is due to the effective reduction of the well-depth by the exoergicity of the reaction. There is otherwise good agreement between predicted and observed lifetimes which differ by a factor of two at most but maintain a consistent trend. These results along with the (visual) observation of snarled trajectories displaying non-rigid, non-linear (i.e. "loose") complexes lend support to a predominantly long-lived-complex mechanism for reaction at collision energies less than and around 1.0 eV.

At 2.5 eV collision energy the reactive channel has virtually closed entirely but for a few low impact parameter trajectories. In its place, inelastic and dissociative processes occur and time distributions for the latter are also given in Figures 4.14 and 4.15. Due to a logical error in the programming which characterised dissociation solely on the basis of the three inter-atom distances, only one dissociation mechanism was observed which resembled a direct, 'clouting' mechanism. However, re-analysis (see Appendix D) revealed a 'clutching' component characterised by a strikingly different time distribution. The longer time distribution of the clutching mechanism/marked 'R/D') implies osculating rather than direct interaction. It is reasonable to assume that this is analogous to
reactive scattering at low energies which, being complex, disposes most of
the available energy into internal modes. When more than sufficient
energy to dissociate the complex into its constituent atoms is disposed into
the relevant exit co-ordinates, dissociation occurs with a long time constant.
The fly-by time at this energy is ca. 0.25 ps which leaves the complex
lifetime for the R/D case as ca. 0.25 ps which is above the RRKM value of
0.16 ps in keeping with the trends for reactive scattering. The results for
3-D and 2-D are similar at least for 'clouting' dissociation. For 2-D, the
correction required on re-analysis of the reactive scattering was consi-
derably less than in 3-D, the behaviour with respect to reaction and
dissociation in 2-D being significantly less as evidenced by their respective
cross-sections:

\[
\begin{array}{ccc}
 & 3-D/2-D & 3-D/2-D \\
\text{P.S.1} & .68/.24 & 6.5/4.2 \\
\text{P.S.2} & .14/.00 & .64/.60 \\
\text{P.S.3} & .00/.00 & .38/.00 \\
\end{array}
\]

However, the counts in the 45/55 \( \times 10^{-14} \) s bin arose entirely from
R \( \rightarrow \) R/D corrections, none of which contributed to shorter time bins.
4.9.2 PROBABILITIES AND CROSS-SECTIONS FOR REACTION AND DISSOCIATION

The opacity functions for reaction and dissociation are shown in Figure 4.16 (3-D) and Figure 4.17 (2-D). In both cases reactive symmetry was observed on all surfaces and under all conditions (i.e. \( A + BC \rightarrow AB + C \) and \( AC + B \) with equal probability) within statistical error. This provided an assurance as to the combined behaviour of the potential and Monte-Carlo sampling procedure. In addition it was seen that no significant angular momentum constraints to reaction or dissociation could be obtained by variation of \( M_j \) (see Section 4.9.5). Consequently, the opacity functions given in the figures draw on the totality of the reactive scattering.

For all surfaces at collision energies less than 2.5 eV, the opacity function \( P_R(b) \) takes on the general form:

\[
P_R(b) = \begin{cases} 
\text{constant}, & b < b_{\text{max}} \\
0, & b > b_{\text{max}} 
\end{cases}
\]

This is just what would be expected of a reaction proceeding, without activation energy, via a LLC defined between centrifugal barriers. At the lowest energy all surfaces indicate a \( b_{\text{max}} \) of 12 au. For a spherically symmetric, attractive potential without activation barriers, the probability of reaction is governed solely by the decomposition of the intermediate complex providing its pathway to reactive decomposition is not dynamically blocked by a high exit centrifugal barrier (see equation (4.3d)). This probability for a sufficiently exoergic reaction will be close to unity.
Figure 4.1b - Probability of Reaction vs. Impact Parameter for Various Collision Energies (3-D). Also included is Dissociation Probability for $E=2.500 \text{ eV}$. 
Figure 4.17 - Probability of reaction and dissociation as function of impact parameter.

x---x-P.S.1; o---o-P.S.2; - - - - P.S.3
Clearly, this behaviour is exhibited by P.S.1 and, to a lesser extent, P.S.2. The absence of static steric effects has been shown in Figure 4.8 where the reaction co-ordinate changes little over 120° from colinear approach. Thus, at low energy the surfaces P.S.1 and P.S.2 are effectively spherically symmetric and a sharp cut-off in the opacity function is expected due to the $\delta$-function nature of the initial translational energy distribution. For P.S.3 at 0.025 eV the reaction probability is significantly lower and this reflects its highly attractive nature (Figures 4.7 and 4.8) which accelerates the incoming reactants towards each other with subsequent scaling of the repulsive wall and backward 'reflection' into the entrance channel.

The mass combination of the $0 + 1_2$ system approximates to LHH in Polanyi's classifications\textsuperscript{25} which corresponds to a skew angle of $\sim 14^0$ and a scale factor of $\sim 2$ in the mass weighted co-ordinate representation\textsuperscript{2}. This means that in the absence of directional intermolecular forces there is little inertial coupling between the entrance and exit co-ordinates since the axes are inclined at nearly 90° in the mass weighted contour map. The high scaling factor means that, for an identical potential in both entrance and exit channels, the collision duration (for a direct interaction) is relatively small which works against efficient momentum transfer to the product co-ordinates. Both these effects combine constructively with the deep well exhibited by P.S.3 which is only marginally displaced into the product valley. This latter property does not readily permit momentum coupling between the entrance and exit channels. However, from the contour plots of Figure 4.7 the well is progressively displaced into the exit channel as P.S.3 - P.S.1 is traversed bringing about a smoother connection between reactant to product valley.
Therefore, whereas a rectangular opacity function with $P(b) < 1$ is often symptomatic of a complex mechanism with a substantial orientation dependence for LLC formation (i.e. steric factor)\(^{157}\) it can also result from the nature of the potential surface for the mass combination LHH irrespective of the nature of the interaction\(^{156}\).

At higher collision energies two effects are evident in both 2-D and 3-D: a reduction in the maximum impact parameter for reaction ($b_{\text{max}}$) occurs and the height of the rectangular opacity function decreases according to the potential surface. The former is expected in both direct and complex collisions because of the larger centrifugal energy which results in a wholly repulsive potential for progressively lower $b_{\text{max}}$. The latter observation is in keeping with the above discussion on momentum coupling. Thus, P.S.1 is reduced to a lesser extent than P.S.2 than P.S.3 such that at 1.0 eV (2-D) appreciable reaction only occurs on P.S.1.

The situation at 2.5 eV is totally different than those at lower energies since all barriers posed by the potentials (see Figure 4.9) can be overcome as well as the dissociation threshold of 1.545 eV (35.5 k. cal. mol\(^{-1}\)). The results show that the most likely collision outcome is non-reactive for all surfaces with dissociation and reaction occurring to a progressively lesser extent as P.S.1 - P.S.3 is traversed, dissociation having a substantially higher cross-section than reaction. As previously observed by JCW and KBS, the reaction opacity function loses its rectangular shape in favour of a monotonic decreasing of impact parameter. This is characteristic of direct reaction\(^{139, 158}\) and is supported by the low collision durations for reactive scattering at 2.5 eV discussed previously. The explanation for this is twofold: firstly, at large impact parameters the centrifugal term in the effective potential given by
\[ V_{\text{eff}} = V + V_{\text{centrifugal}} \]  
\[ V_{\text{centrifugal}} = \frac{E_b^2}{2\mu r^2} \]

results in \( V_{\text{eff}} \) being repulsive for all values of \( V \) in the entrance channel; secondly, as \( E \) is increased, repulsive regions of the potential not accessible at lower energies are more likely to be sampled. Thus, an energy dependent steric effect occurs in conjunction with an impact parameter dependent repulsion giving rise to the characteristic, direct opacity function.

The impact parameter dependence of dissociation shown most clearly for P.S.1 is, as previously discussed, composed of two parts. At low impact parameters a "knock-on" or "clouting" mechanism occurs which changes to a "clutching" mechanism at higher impact parameters. As for reaction, the dissociation opacity function drops off at higher impact parameters due to centrifugal effects.

Both dissociation mechanisms have analogues in reactive scattering. The "clutching" mode most resembles reaction at low energies via LLC formation. Beyond the threshold for dissociation, trajectories which at slightly lower energy would have resulted in reaction are no longer able to transfer momentum to the departing products with the result that the 0-atom departs from the attracted I-atom and the other I-atom does likewise in a near "spectator" fashion. These explanations are supported by the reaction and dissociation cross-section dependence on potential coupling which decreases markedly from P.S.1 to P.S.3 as noted above.
The values of the total cross-sections (in A^2) for reaction and dissociation are given in Table 4.3.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>P.S.1</th>
<th>P.S.2</th>
<th>P.S.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>99.7/112 (± 3)</td>
<td>86.3/95 (± 3)</td>
<td>26.3/29.6 (± 3)</td>
</tr>
<tr>
<td>0.250*</td>
<td>46/54</td>
<td>25/40</td>
<td>2.5/6.3</td>
</tr>
<tr>
<td>1.0**</td>
<td>23.9 ± 0.8</td>
<td>4.9 ± 0.6</td>
<td>1.3 ± 0.3</td>
</tr>
<tr>
<td>2.5 (R)</td>
<td>0.7/0.5 (± .1)</td>
<td>0.1/0.0</td>
<td>0.0/0.0</td>
</tr>
<tr>
<td>2.5 (D)</td>
<td>4.2/6.5</td>
<td>0.24/.68</td>
<td>0.00/.37</td>
</tr>
</tbody>
</table>

*Lower bound
**2-D only.

Table 4.3 - Reaction and Dissociation Cross Sections (2-D/3-D)

The energy dependence of these cross-sections are displayed in Figures 4.18 (3.D) and 4.19 (2-D). In both dimensionalities, the reaction cross-sections exhibit roughly the expected E^{-1/3} dependence for a LLC (formed in a potential having R^{-6} dependence) and the closeness of each result agrees well with the results of Raff and Karplus 54. The departure from the E^{-1/3} line at 1.0 eV (2-D) is progressively greater from P.S.1 to P.S.3 since the probability of complex formation is being increasingly hindered by the nature of the potentials. The extent of elastic scattering below the dissociation threshold is a manifestation of the failure of the
Figure 4.8 - Variation of Reactive, Dissociative and Elastic Cross Section with Collision Energy (3-D)
Figure 4.9 - Variation of Reactive and Dissociative Cross Section with Collision Energy (2-D) (Dashed line has $E^{-1/3}$ dependence)
surface to promote reaction. This increases with collision energy and as P.S.1 to P.S.3 is traversed. Beyond the dissociation threshold, inelastic scattering is dominant especially on P.S.1 whose momentum coupling ability can transfer energy from reactants' translation to reactants' internal energy to a greater extent than P.S.2 or P.S.3.

4.9.3 ANGULAR DISTRIBUTIONS

Histograms of $N(\theta)^*$ vs. $\theta$ where $\theta$ is the angle between the C.M. velocities of the atomic fragments are shown in Figures 4.20 (3-D) and 4.21 (2-D). The results in 3-D are significantly different from those in corresponding 2-D cases. Symmetry about $\theta = 90^\circ$ is evident in 3-D for all surfaces below 2.5 eV whilst this only occurs at 0.25 eV in 2-D. The LLC model\(^{44}\) predicts such 3-D distributions when the potential is spherically symmetric and the entrance and exit angular momenta are comparable in magnitude. The trajectory work of KBS reproduces such a distribution at 0.5 k. cal. mol\(^{-1}\) collision energy, the angular momenta having the required relationship. This same study indicates deviations from this behaviour as the energy is raised unlike the present study. In 2-D, no angular momentum considerations apply and isotropy obtains providing the complex lives long enough.

*The relationship between the angular distribution and the differential cross-section $\sigma(\theta)$ is as follows:

2-D $\sim N(\theta) \alpha \sigma(\theta)$; 3-D $\sim N(\theta) \alpha \sigma(\theta) \sin(\theta)$. 
Figure 4.20 - Angular Distributions of Reactive Scattering (3-D) (Distributions for 2.500 eV are for non-reactive scattering)

- 0.025 eV
- 0.250 eV
- 2.500 eV

P.S.1

P.S.2

P.S.3

0 180 0 180 0 180
For the $0 + I_2$ system, the angular momenta are:

$$E = \begin{array}{ccc}
0.025 \text{ eV} & 0.25 \text{ eV} & 1.0 \text{ eV} \\
L_{\text{max}}/\hbar & 85 & 225 & 400 \\
J/\hbar & 55 & 55 & 55
\end{array}$$

Thus, only at 0.025 (3-D) would this system be expected to yield a sine-shaped $N(\theta)$ on the basis of the LLC model, a progression to an isotropic $N(\theta)$ being expected above this. At 0.025 and 1.0 eV in 2-D the results show a significant departure from the expected isotropy. This is clearly indicative of the presence of other reaction pathways or indeed of a mechanism not involving a LLC as it is usually envisaged. Bunker's angle anomalies cannot be the cause of this since the angular momentum available and the mass combination do not support this. A search was therefore made for a meaningful correlation between scattering angle, impact parameter and collision lifetime. This showed that at 0.025 eV low duration rebound scattering occurred for $b < 6 \text{ au}$. For $b > 10 \text{ au}$ the angular distribution was isotropic and the corresponding trajectories had long complex lifetimes $(> 1 \text{ ps})$. At 1.0 eV, this was reversed: isotropic scattering occurred for $b < 2.5 \text{ au}$ and correlated with long lifetimes whereas at higher impact parameters the collision lifetime decreased with a very pronounced shift towards forward scattering of the molecular product.
These observations can be rationalised in terms of an effectively direct interaction between reactants. Since the O-atom is comparatively light, it will experience considerable attraction towards the nearest I-atom. At low impact parameters at 0.025 eV, scattering of the OI product in the backward direction is likely since the O-atom has insufficient momentum to carry it beyond the I₂ centroid to be subsequently forward scattered. The potential is least affected by centrifugal motion at low impact parameters which makes for fairly rapid departure of the I-atoms and the attendant backward (molecular) scattering. Raising the impact parameter gives rise to higher centrifugal barriers and a tendency towards more long-lived complex interactions with consequent isotropic scattering.

At 1.0 eV, the O-atom has sufficient momentum to ensure that scattering into the forward and backward directions occurs at low impact parameters. As b is raised, the propensity of the system to form products (the O-I₂ attraction is unaffected by I-I separation) results in an I-atom being attracted towards the O-atom in a spectator-stripping interaction. The relative weighting of high impact parameters alters the shape of the angular distribution to one displaying predominant forward scattering of the product molecule.

Using a very similar surface both Bunker and Blais²⁴, ¹³⁰ and Karplus and Raff⁵⁴ have obtained strikingly similar angular distributions in both 2-D and 3-D to those presented here for the K + CH₃I system. The most significant contrast between the two systems is that the O + I₂ one exhibits pronounced complex dynamics, the K + CH₃I system being predominantly 'direct'. This suggests that the observed isotropy (2-D/0.25 eV) and symmetry about 90° (3-D) do not arise from the LLC nature of the interaction. Indeed, since the O-atom is comparatively light, the
rotational period of the \( \text{O}_2 \) complex, however arranged, will be largely that of the \( \text{I}_2 \) molecule for which the period \( (J = 55) \) is \( \approx 8 \) ps. The maximum observed complex lifetime is \( \approx 1 \) ps (except for P.S.3). Thus it is unlikely that the angular symmetry originates from "memory" loss from a sticky collision since it would have to snarl for a duration of some 10-20 ps! For the great majority of trajectories run complex lifetimes were individually less than \( \approx 2 \) ps. The time regime observed here is of the near osculating domain, the complex lifetimes being less than one (complex) rotational period.

A more likely explanation of the observations is that the \( \text{I}_2 \) molecule is effectively frozen along a line through the nuclei on the time scale of the interaction. The \( \text{O} \)-atom, being light, is attracted towards one end of the molecule and then proceeds to vibrate and migrate about it (this is well illustrated in the time evolution diagram, Figure 4.22). Ultimately the complex breaks up and the final relative velocity corresponds to the I-I orientation at point of break-up which itself is not far removed from the initial I-I orientation. As already noted in Figure 4.12 the latter takes up an approximately sine-shaped distribution of angle between itself and the initial relative velocity. Also, the form of the angular distributions in 3-D is essentially sine-shaped which suggests that the angular distributions are a reflection of the initial conditions, in this case the I orientation angle. Similar considerations apply in 2-D.
Figure 4.22 - Non-reactive trajectory exhibiting multiple interactions ("clouting"). Atom A is effectively interacting with BC in a two-body fashion.
It should be stressed that such a line-of-centres model as proposed previously is not at variance with the LLC model based on RRKM theory. This theory predicts a time constant for energy equilibration rather than for kinematic effects and the existence of separate time constants for both effects seems reasonable although the present results reverse the traditional view that the time constant for energy equilibration exceeds that of spatial randomisation\(^159\). The observations on the K + CH\(_3\)I (trajectory) reaction\(^24\), \(^54\) of a backward tendency in 2-D can be explained in terms of the less facile reaction when the I-atom points away from the attacking K-atom, a line-of-centres model being appropriate here as well.

Further support for this model is given by the re-orientation angles of the orbital and rotational angular momenta (Figures 4.23 and 4.24 respectively). Since the potential here is largely independent of approach angle the final rotational angular momentum vector reflects the available reactant orientations which peak at 90° to the I-I line (see Figure 4.12) and constrain the product rotational angular momentum (RAM) vector principally to directions perpendicular to the initial RAM vector. Again, since the I\(_2\) molecule is effectively frozen, break-up of the complex will result in a uniform distribution of orbital angular momentum (OAM) vectors in a plane perpendicular to the initial I\(_2\) line in the limit of zero entrance angular momentum. Taking all possible planes into account it can be seen that the most probable OAM re-orientation angle is 90°. However, due to the finite OAM, the momentum of the attacking O-atom is partially transferred to the OI product and a shift towards lower angles comes about which increases with increasing collision energy. At still

* The co-ordinate system of Ref. 139 is eminently suited to this.
Figure 4.24 - Re-orientation Angle of Rotational Angular Momentum

P.S. 1

P.S. 2

P.S. 3

- 0.025 eV
- 0.250 eV
- 2.500 eV
(Non-Reactive)
higher collision energies this memory effect increases and a tendency towards planar scattering occurs.

In summary, it appears that the 2-D treatment, in addition to its computational ease, offers a more sensitive test of the potential properties for this mass combination, the 3-D case tending to wash out the finer details. Although there is slight evidence in 3-D for backward scattering at 0.025 eV and forward scattering at 0.25 eV the 2-D angular distributions are quite unambiguous in these respects. Thus, although this departure from isotropy is not expected from truly LLC's in 2-D, it seems that this approach, which traditionally fails for direct interactions due to the unpredictable effects of out of plane scattering, is acceptable in the limit LHH or MHH\textsuperscript{130} on attractive surfaces. The extension to 3-D can be effected by the transformation Jacobian.

4.9.4 ENERGY DISTRIBUTIONS

A: TRANSLATIONAL ENERGY

The distributions of product translational energy are shown in Figures 4.25 (3-D) and 4.26 (2-D). A common feature in all cases is the gradual reduction in the probability with increasing translational energy which resembles those distributions expected for a "loose" three-atom complex on the basis of the RRKM theory (see Section 4.2). The fractions of the available energy disposed in translation are given in Table 4.4.
Figure 4.26 - Translational Energy Distributions of Reactively Scattered Species

- 0.025 eV
- 0.250 eV
- 1.000 eV
- 2.500 eV
Table 4.4: Fractions of available energy in translation. First figure in each column is the 2-D result.

There is however marked disagreement between the results and the RRKM-AM predictions on three counts. Firstly, the position of the peak given by $E_t' = B_m' (= B_m/10$ for $0 + I_2$) in the RRKM-AM theory is

<table>
<thead>
<tr>
<th>(eV)</th>
<th>$E_t$</th>
<th>$B_m'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025 eV</td>
<td>0.025</td>
<td>0.003</td>
</tr>
<tr>
<td>0.25 eV</td>
<td>0.25</td>
<td>0.025</td>
</tr>
<tr>
<td>1.0 eV</td>
<td>1.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

whereas the observed peak positions are:

<table>
<thead>
<tr>
<th>P.S.1</th>
<th>P.S.2</th>
<th>P.S.3</th>
<th>BIN SIZE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025 eV</td>
<td>0.15/.23</td>
<td>0.15/.08</td>
<td>0.05/.08</td>
</tr>
<tr>
<td>0.25 eV</td>
<td>0.25/.25</td>
<td>0.30/.15</td>
<td>0.25/.05</td>
</tr>
<tr>
<td>1.0 eV</td>
<td>0.4 ± .1/-</td>
<td>0.7 ± .1/-</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 4.5: Observed peak positions in translational energy distributions. First entry is 2-D result.

and despite the uncertainties invoked by the binning procedure ($± 1$ bin)
and poor statistics, there is sound evidence that the peak of the distribution extends beyond the RRKM-AM predictions.

Secondly, the RRKM-AM formula predicts equipartition of the available exoergicity in the limit $B'_m << E'$. Thus 33% is expected to be channelled into translation with 67% into internal modes. For P.S.1 and P.S.2, where best statistics prevail, there is significantly higher translational energy than predicted above, especially at 1.0 eV.

The behaviour of the non-reactive scattering provides the most convincing evidence against the statistical interpretation of the reactive scattering results. $E'_t$ distributions for non-reactive scattering are also shown in Figure 4.25 for 2.5 eV collision energy. The results for 1.0 and 0.25 eV although not shown have nearly identical forms for each surface. If the non-reactive scattering occurred predominantly via complex decay then the RRKM-AM treatment would yield similar distributions to the reactive ones, but modified for zero exoergicity. This has been observed by JCW at energies < 1 eV with a definite transition towards elastic scattering above this energy. In the present case however, the two scattering outcomes exhibit different characteristics at all energies indicating different mechanisms for each neither of which merits interpretation in terms of the RRKM-AM theory.

B: INTERNAL ENERGY

The partitioning of rotational and vibrational energy for a LLC is given by equation (4.10). For $B'_m << E'$ monotonic (linear) decreasing distributions are anticipated. Strictly against the spirit of the RRKM-AM
model under these conditions is the existence of a population inversion.

Vibrational energy distributions are presented in Figures 4.27 (3-D) and 4.28 (2-D). The most striking characteristic of these is in fact a population inversion over all the energetically accessible levels at low collision energy and on all surfaces. At 0.25 eV, only the 2-D case shows appreciable inversion whilst at 1.0 eV a Boltzmann-like form is regained. The fractions of the available energy channelled into vibration are given in Table 4.5.

<table>
<thead>
<tr>
<th></th>
<th>0.025 eV</th>
<th>0.25 eV</th>
<th>1.0 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.S.1</td>
<td>.60/.57</td>
<td>.44/.37</td>
<td>.36/-</td>
</tr>
<tr>
<td>P.S.2</td>
<td>.52/.52</td>
<td>.45/.33</td>
<td>.22/-</td>
</tr>
<tr>
<td>P.S.3</td>
<td>.49/.49</td>
<td>.46/.36</td>
<td>.14/-</td>
</tr>
</tbody>
</table>

Table 4.5: Fractions of available energy into vibration
First figure is for 2-D case.

For rotation, energy distributions are given in Figures 4.29 (3-D) and 4.30 (2-D) and the fractions disposed into it given in Table 4.6.

<table>
<thead>
<tr>
<th></th>
<th>0.025 ev</th>
<th>0.25 ev</th>
<th>1.0 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.S.1</td>
<td>.07/.07</td>
<td>.15/.32</td>
<td>.23/-</td>
</tr>
<tr>
<td>P.S.2</td>
<td>.07/.08</td>
<td>.13/.33</td>
<td>.28/-</td>
</tr>
</tbody>
</table>

Table 4.6: Fractions of available energy disposed into rotation. First entry is for 2-D case.
Figure 4.27 - Vibrational Energy Distributions for Reactive Scattering
(For 2.500 eV, distributions are for non-reactive scattering)
Figure 4.28 - Vibrational Energy Distribution of Reactively Scattered Species

- P.S.1
- P.S.2
- P.S.3

Energy Levels:
- 0.025 eV
- 0.250 eV
- 1.000 eV
- 2.500 eV

Energy Levels Chart:

- 0.0
- 1.0
- 2.0
- 3.0
- 4.0
- 5.0
- 6.0
- 7.0
- 8.0
- 9.0
- 10.0

Energy Levels: 0.025 eV, 0.250 eV, 1.000 eV, 2.500 eV
Figure 4.29 - Rotational Energy Distributions for Reactive Scattering
(For 2.500 eV, distributions are for non-reactive scattering.)
Figure 4.30 - Rotational Energy Distribution of Reactively Scattered Species

- P.S.1
- P.S.2
- P.S.3

Energy Levels:
- 0.025 eV
- 0.250 eV
- 1.000 eV
- 2.500 eV
For $E < 0.25 \text{ eV}$, only the $0.25 \text{ eV}/3$-D case exhibits distributions resembling those expected statistically with fractional partitioning of ca. $1/3$ into each mode. However, the 2-D results corresponding to these show significant differences particularly in rotation which appears restricted. The general form of the rotational distributions are monotonic decreasing but the early cut-off ($E' \sim 0.8 \text{ eV}$) in the tail of the distribution is not characteristic of the statistical model.

Since the vibrational distribution is markedly similar to that of Blais and Bunker$^{24, 130, 135}$ particularly for the $M + \text{HH}$ combination ($M = 16, H = 128$) the explanation of the vibrational inversions at $0.025 \text{ eV}$ is probably on the basis of an "early-downhill" surface which releases the exoergicity in reactant approach. As the translational energy increases there is more energy placed in product rotation as a consequence of the increased initial OAM. Since the 0-atom is light and the products velocity and reduced mass exceeds that of the reactants the departure of the products along the $I_2$ line-of-centres results in low exit impact parameters and correspondingly low exit OAM. The probability distribution for entrance OAM, $L$, is given by

$$P(L) = \frac{2L}{L_{\text{max}}}$$

with the result that

$$\bar{L} = \frac{2}{3} L_{\text{max}}$$

$\bar{L}$ being the mean entrance OAM listed below.
Figure 4.31 shows the distribution of final OAM in 3-D. For 0.025 eV there is only a slight increase in the mean from reactants to products and this is not appreciably shifted at the higher energy. Thus, an increasing amount of entrance OAM ends up in product rotation which is evident in Figure 4.32.

The restriction in rotational energy seen in 2-D can be explained in terms of the potential surfaces which forbid insertion of the O-atom into the \( \text{I}_2 \) molecule. The attractiveness of the surface causes a rapid spiralling in of the light O-atom. On orbiting a given I-atom, a configuration close to the isosceles one will arise which restricts further rotation converting the energy released into translation and vibration instead, the former taking up the available angular momentum. The likelihood of reaching such repulsive configurations is considerably reduced in 3-D explaining the sharp rise in product rotational energy from 0.025 to 0.25 eV. At 1.0 eV, the repulsion encountered in \( C_{2v} \) configurations can be cleared for a larger sample of trajectories and this results in larger fractions of \( E' \) disposed into rotation.

C  TOTAL INTERNAL ENERGY

A common property of attractive potentials displaying early release of energy is that the distribution of internal energy peaks at high values. For the \( O + \text{I}_2 \) system, these distributions are shown in Figures 4.33 (3-D) and 4.34 (2-D) and it is seen that they all exhibit the above property. However, the constituent \( (E'_{\text{rot}}, E'_{\text{vib}}) \) distributions are lost in this representation.
Figure 4.31 - Final Orbital Angular Momentum Distributions for Reactive Scattering (Abscissae in units of h)
Figure 4.32- Distribution of Final Rotational Angular Momentum for Reactive Scattering (Abscissa unit, h)
Figure 4.33 - Distributions of Relative Internal Energy for Reactive Scattering (--- Non-Reactive)
Figure 4.34 - Fraction of available energy channelled into internal modes.
P.S.1; ----- P.S.2; ----- P.S.3

- 0.025 eV
- 0.250 eV
- 1.000 eV
- 2.500 eV
Since these histograms are nominally identical to those for product translational energy, the same comments apply as in sub-section A. Their qualitative similarity to both the RRKM-AM distributions and those for attractive surfaces with a mass combination L(M) + HH serves to highlight the point that if such a range of potentials operated in reality for O + I\textsubscript{2} then, given that the experimental and computed data yielded symmetric angular distributions and RRKM-AM-like translation energy distributions, the absence of internal state distributions would lead almost certainly to the conclusion of long-lived dynamics in the spirit of the above theory. Clearly, the vibrational distributions at low collision energy hold the key to the behaviour in such cases.

4.9.5 ROTATIONAL ANGULAR MOMENTUM POLARISATION EFFECTS

In the 2-D computer code listed in Appendix C, the direction of the RAM vector could take two orientations, parallel and antiparallel to the initial orbital angular momentum. In the 3-D code also listed, the RAM vector was allowed to take up two specific orientations depending on the relative velocity vector (see Appendix B for details). Batches of trajectories were run for each of these M\textsubscript{J} states with initial variables not involving M\textsubscript{J} dependence kept identical to eliminate as much as possible the effects of non-random sampling.

Since the RAM and OAM are comparable in magnitude at 0.025 eV collision energy (J = 55, L\textsubscript{max} = 85) the effects of their relative orientation are expected to be most pronounced here. The distributions of scattering angle and product energy are shown in Figure 4.35 for each M\textsubscript{J} state (3-D). Evidently there is no significant difference between the
Figure 4.35 - Comparison of energy and angular distributions for each $M_J$ state. (3-D; 0.025 eV)
energy distributions for each polarisation but there appears to be a slight tendency for greater rebound scattering for $M_J \sim 1$ ($J$ perpendicular to $V_{rel}$). A similar situation exists at 0.25 eV collision energy, the results of which are summarised as mean values in Table 4.7.

<table>
<thead>
<tr>
<th>M state</th>
<th>$\bar{\theta}$ (molecule)</th>
<th>$E_{\text{trans}}$ (eV)</th>
<th>$E_{\text{rot}}$ (eV)</th>
<th>$E_{\text{vib}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-D ) P.S.1</td>
<td>100/81</td>
<td>.41/.43</td>
<td>.16/.16</td>
<td>.46/.46</td>
</tr>
<tr>
<td>3-D )</td>
<td>84/80</td>
<td>.32/.34</td>
<td>.33/.33</td>
<td>.40/.36</td>
</tr>
<tr>
<td>2-D ) P.S.2</td>
<td>104/83</td>
<td>.42/.44</td>
<td>.14/.12</td>
<td>.47/.47</td>
</tr>
<tr>
<td>3-D )</td>
<td>85/77</td>
<td>.37/.37</td>
<td>.34/.34</td>
<td>.33/.35</td>
</tr>
<tr>
<td>2-D ) P.S.3</td>
<td>105/98</td>
<td>.32/.38</td>
<td>.20/.22</td>
<td>.51/.44</td>
</tr>
<tr>
<td>3-D )</td>
<td>94/81</td>
<td>.24/.28</td>
<td>.39/.43</td>
<td>.41/.33</td>
</tr>
</tbody>
</table>

Table 4.7: Mean values of scattering outcomes for each $M_J$ state. (2-D entries are $M_J = -1/M_J = +1$; 3-D entries are $M_J \sim 1/M_J \sim 2$).

The 2-D case can be readily explained in terms of the rotational motion of the $I_2$ molecule which, if infinitely slow, would result in a mean scattering angle nearer $90^\circ$ for both $M_J$ states. However, the finite period ($\sim 8$ ps) means that the initial orientations which largely determine the angular
distributions are perturbed unequally: the high impact parameter collisions which weight all distributions to the greatest extent will, on account of their longer interaction time, follow the $I_2$ motion which will either be towards ($M_j = -1$) or away from ($M_j = +1$) the attacking 0-atom leading to increased backward ($M_j = -1$) and forward ($M_j = +1$) scattering of the product molecules.

For the angular distributions in the 3-D case, the general trend is towards more forward than backward scattering but at a much reduced confidence level. Where good statistics prevail (P.S.1 and P.S.2) the difference in mean values is less than the bin size ($10^0$). However, since the 3-D case contains fewer trajectories and more initial variables than in 2-D the observed differences probably arise from "noise" in the calculations.

The observation that the energy disposal is universally unaffected by angular momentum polarisation lends added confidence to the earlier assertion (Section 4.9.3) that the potential is the major controlling factor here.

4.9.6 EFFECT OF REAGENT VIBRATION

To date, no general reports concerning the effects of excited reactants on the outcomes of trajectories run on surfaces with wells have appeared. One specific report concerns the thermoneutral reaction $M + M_2 \rightarrow M_2 + M$ proceeding on a surface with a short range 7 k. cal. mol$^{-1}$ well$^{160}$. With the well in the entrance channel (- I) the preferred mode for reaction is vibration whilst for a well in the exit channel (- II) the preferred mode is translation although only marginally so over vibration. These findings are the reverse of the case with barriers in place of wells.
In contrast to the latter, Whitehead\textsuperscript{39} has studied the endoergic reaction of \( \text{Na} + \text{Li}_2 \rightarrow \text{NaLi} + \text{Li} \) and the exoergic reaction of \( \text{Li} + \text{Na}_2 \rightarrow \text{LiNa} + \text{Na} \) for two vibrational states of reactants (\( v'' = 0, 4 \)). For the former, the vibrational excitation was seen to extend the attractiveness of the potential thus increasing the reaction cross-section but not to significantly alter the energy distributions when compared to \( v'' = 0 \). The vibrational "adiabaticity" reported by Polanyi \textit{et al}\textsuperscript{161} evidently does not occur here. The exoergic reaction is most likely to resemble the \( 0 + \text{I}_2 \) system. (\( \Delta D_0 = 17.4 \text{ k. cal. mol}^{-1} \)). Here, the cross-section increases for \( v'' = 4 \) at high collision energies due to the effective increase in the attractiveness of the potential as in the endoergic case. Again, however, there is no indication of vibrational adiabaticity. For both the above reactions neither potential surface can be distinctly categorised as - I or - II thereby making comparison with Nomura's work difficult.

The (colinear) surfaces of the present work can be seen from Figure 4.7 to correspond to the - II type, the extent of this character decreasing from P.S.1 to P.S.3. The small displacement of the well into the exit valley for P.S.3 is amplified by the co-ordinate scaling factor of \( \sim 2 \) removing any uncertainty about its designation. Batches of 390 2-D trajectories were run on each surface at 0.025 eV collision energy for the \( \text{I}_2 \) vibrational levels \( v'' = 0, 1, 2, 3 \). Distributions of reaction probability, integration time, atomic scattering angle and internal energy are shown in Figures 4.36 - 4.39 respectively.
Figure 436 - Probability of Reaction vs. Impact Parameter (a.u.)
For the opacity functions (Figure 4.36) the only significant difference is for P.S.2 whose total cross section (Figure 4.40) decreases by 30% from $v'' = 0$ to $v'' = 1, 2, 3$. The extent of the opacity functions are invariant with vibrational excitation in contrast to Whitehead's observations where $b_{\text{max}}$ becomes extended; the forms of $P_R(b)$ are invariant with $v'' (I_2)$ in agreement with the latter.

The integration time distributions shown in Figure 4.37 display a slight tendency to narrow as $v'' (I_2)$ is increased. Fitting these distributions to an exponential form is prone to considerable error and no attempt has been made in this case since the differences are small. However, listed below in Table 4.8 are the mean integration times estimated from the above distribution.

<table>
<thead>
<tr>
<th></th>
<th>$v'' = 0$</th>
<th>$v'' = 1$</th>
<th>$v'' = 2$</th>
<th>$v'' = 3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.S.1</td>
<td>235</td>
<td>218</td>
<td>216</td>
<td>213</td>
</tr>
<tr>
<td>P.S.2</td>
<td>290</td>
<td>277</td>
<td>260</td>
<td>254</td>
</tr>
<tr>
<td>P.S.3</td>
<td>422</td>
<td>392</td>
<td>383</td>
<td>378</td>
</tr>
</tbody>
</table>

Table 4.8: Mean Integration Times for $v'' = 0 - 3$ (2-D).

Values are in units of $10^{-14}$ s.

Since the maximum swing in these results is less than the bin size ($50 \times 10^{-14}$ s) it is reasonable to conclude that the drift in the integration time is not significant.
Figure 4.37 - Total Integration Time Distributions for Reactive Scattering at 0.025 eV Collision Energy Abscissa: $10^{-14}$s.
The angular distributions \( \langle N(\theta) \rangle \) or \( \sigma(\theta) \) for P.S.1 and P.S.2 all exhibit the tendency to backward scatter the product molecule and no discernible trend can be seen with changing \( v''(I_2) \). The mean atomic scattering angles are given in Table 4.9.

<table>
<thead>
<tr>
<th></th>
<th>( v'' = 0 )</th>
<th>( v'' = 1 )</th>
<th>( v'' = 2 )</th>
<th>( v'' = 3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.S.1</td>
<td>71</td>
<td>71</td>
<td>69</td>
<td>71</td>
</tr>
<tr>
<td>P.S.2</td>
<td>75</td>
<td>73</td>
<td>68</td>
<td>68</td>
</tr>
<tr>
<td>P.S.3</td>
<td>84</td>
<td>73</td>
<td>73</td>
<td>79</td>
</tr>
</tbody>
</table>

Table 4.9: Mean atomic scattering angles (degrees) for \( v'' = 0 - 3 \) and \( M_J = -1 \).

The partitioning of the exoergicity into internal modes shown in Figure 4.39 again shows little variation with \( v''(I_2) \) although P.S.1/\( v'' \) = 0 shows substantially greater excitation than \( v'' = 1, 2, 3 \). The mean fractions of E' disposed into internal modes are
Figure 4.38 - Angular Distribution of Reactive Scattering for Collision Energy of 0.023 ev
Figure 4.39 - Fraction of available energy deposited in internal modes as a function of surface/reactant vibrational quantum number.

- 0.025 eV / P.S.1
- 0.025 eV / P.S.2
- 0.025 eV / P.S.3

V = 0, 1, 2, 3
The swing for P.S.1 is 11% which is greater than the 10% bin sizes used. Break-up into constituent components reveals that some degree of vibrational adiabaticity occurs for P.S.2 and P.S.3 whilst P.S.1 channels the reactant excitation into translation (see Figure 4.40 (b)).

Table 4.9: Fraction of available Energy into Internal Modes for \( v'' = 0 - 3 \).

<table>
<thead>
<tr>
<th></th>
<th>( v'' = 0 )</th>
<th>( v'' = 1 )</th>
<th>( v'' = 2 )</th>
<th>( v'' = 3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.S.1</td>
<td>0.67</td>
<td>0.59</td>
<td>0.57</td>
<td>0.56</td>
</tr>
<tr>
<td>P.S.2</td>
<td>0.57</td>
<td>0.59</td>
<td>0.60</td>
<td>0.63</td>
</tr>
<tr>
<td>P.S.3</td>
<td>0.72</td>
<td>0.74</td>
<td>0.70</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Table 4.10: Mean Translational/Vibrational Energy for \( v'' = 0-3 \) (in eV).

<table>
<thead>
<tr>
<th></th>
<th>P.S.1</th>
<th>P.S.2</th>
<th>P.S.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v'' = 0 )</td>
<td>.27/.50</td>
<td>.34/.43</td>
<td>.23/.49</td>
</tr>
<tr>
<td>( v'' = 1 )</td>
<td>.36/.47</td>
<td>.37/.46</td>
<td>.22/.55</td>
</tr>
<tr>
<td>( v'' = 2 )</td>
<td>.39/.48</td>
<td>.38/.50</td>
<td>.28/.56</td>
</tr>
<tr>
<td>( v'' = 3 )</td>
<td>.45/.50</td>
<td>.37/.59</td>
<td>.23/.68</td>
</tr>
</tbody>
</table>
Figure 4.40 - (a) Effect of Initial Vibrational Energy on Reaction Cross Section
(b) Mean Vibrational Energy of Product vs. Reactant Vibrational Excitation (2-D)
The following very tentative conclusions can be drawn from the previous results:

(1) The more the - II character, the less the vibrational adiabaticity.

(2) The attractiveness of the potential is not extended by increased reactant vibration. Thus, cross-sections and collision lifetimes are approximately invariant with v" (I₂).

(3) Angular distributions are insensitive to reactant vibration.

(4) Vibrational to translational (v" \rightarrow T') energy transfer occurs for highly - II type surfaces.

The observations leading to (1) and (4) may well be due to the gentle curvature of the surface in going from reactants to products which efficiently channels both vibration and translation of the reactants to product translation. The detailed nature of the potential accounts for point (2); here, fixed molecule contour diagrams²⁵ for various I - I separations are superimposable for the range of v" (I₂) studied indicating no variation in attractiveness with increasing v" (I₂). Lastly, the line-of-centres model for the angular distributions discussed in 4.9.3 is supported by the observations leading to point (3).
4.9.7 NON-REACTIVE SCATTERING

A previous study\(^{142}\) has shown the usefulness of high energy non-reactive scattering in elucidating features of the potential surface(s) accessible to laboratory experiments. At lower energies, where reactive scattering is important, the differences and similarities between the two types of scattering can help to identify the mechanism(s) operating. Thus, in Whitehead's study\(^{39}\) the non-reactive scattering was seen to follow the same statistical model as the reactive type at low energies, both tending towards a direct mechanism at higher energies in excess of the well depth.

It has already been noted (Section 4.9.4) that the distributions of \(E_i\) for non-reactive scattering are widely different to those for reactive scattering at all energies. The same is true of the angular distributions which exhibit a very dominant forward peak at all energies with integration times considerably below those for reactive scattering under the same conditions. These observations are totally at variance with the RRKM theory and statistical complex model. The direct nature of the non-reactive scattering observed therefore permits investigation of the dynamical effects of the potential surfaces used since freedom from multiple encounters minimises the "scrambling" brought about by the complex. The variation of the cross-sections for elastic scattering\(^*\), vibrational excitation\(^{**}\) and rotational excitation\(^{***}\) is shown in Figure 4.41 for 3-D and a progressive variation from surface to surface is evident. Elastic scattering varies as P.S.3 \(\gg\) P.S.2 \(\approx\) P.S.1 which is exactly the

\[
\begin{align*}
* & \quad \text{Elastic is defined as } |E'_t - E_t| < 0.025 \text{ eV} \\
** & \quad \text{Vibrational excitation occurs if } E'_{\text{vib}} > E_{\text{vib}} + 0.027 \text{ eV} \\
*** & \quad \text{Rotational excitation occurs if } E'_{\text{rot}} > 0.015 \text{ eV}
\end{align*}
\]
Figure 4.41 - Variation of Elastic, Rotation Excitation and Vibration Excitation Cross Section with Collision Energy (3-D)
reverse of the reactive scattering trend. However, although the total scattering at 0.025 eV is either reactive or elastic, raising the collision energy brings about inelastic processes to a progressively greater extent from P.S.1 to P.S.3. With the exception of P.S.1 which allows significant dissociation at 2.5 eV, the cross-sections for all the processes are dominated by inelastic events.

<table>
<thead>
<tr>
<th></th>
<th>P.S.1</th>
<th>P.S.2</th>
<th>P.S.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotational Excitation</td>
<td>16.2/4.3</td>
<td>20.2/15.3</td>
<td>19.2/27.3</td>
</tr>
<tr>
<td>Vibrational Excitation</td>
<td>18.3/2.9</td>
<td>21.3/17.1</td>
<td>17.7/24.3</td>
</tr>
<tr>
<td>Elastic</td>
<td>1.0/5.4</td>
<td>0.9/6.1</td>
<td>2.9/17.1</td>
</tr>
<tr>
<td>Reaction</td>
<td>0.7/53.7</td>
<td>0.1/39.7</td>
<td>0.0/6.3</td>
</tr>
<tr>
<td>Dissociation</td>
<td>6.5/-</td>
<td>0.7/-</td>
<td>0.4/-</td>
</tr>
</tbody>
</table>

Table 4.11: Cross-sections ($\text{A}^2$) for processes at 2.5/0.25 eV.
At 0.25 eV reactive trajectories are swallowed up by inelastic ones on P.S.1 and P.S.2 whilst P.S.3 shows considerable elastic scattering. Since reaction involves the capture of the O-atom by an I₂ molecule which is already breaking up (the extent of which decreases from P.S.1 to P.S.3) it is clear that those which fail to react by this mechanism will result in vibrational excitation of the I₂ molecule which is reformed from an extended intermediate state. Rotational excitation arises from torques on the I₂ molecules caused by the attacking O-atoms which change the relative orientations of the angular momenta.

The energy dependence of the inelastic cross sections suggests that the extent of internal excitation decreases from P.S.1 to P.S.3 since (on P.S.1 and 2) a tradeoff between reactive and inelastic cross-section occurs. Those inelastic events on P.S.1 have more reactive character than on the other surfaces leading to higher vibrational excitation.

This view is reinforced by the energy distributions in Figure 4.42 for non-reactive scattering at 2.5 eV. The similarity between the translational and vibrational distributions implies that loss of collision energy results in vibrational excitation predominantly with rotational excitation becoming more important for P.S.3 at the expense of vibration.

The relevant mean values for each excitation are given next in Table 4.12. Notable is the fraction of the mean energy loss into vibration: for P.S.1 this is ~100%; for P.S.2 ~80%; and P.S.3 ~60%.
Figure 4.42 - Non-Reactive Scattering at 2.500eV—Energy Distributions

- E' (trans)
- E' (rot)
- E' (vib)

Dissociation Limit (1.545 eV)
Table 4.12: Mean energies into each mode from non-reactive scattering at 2.5 eV. $\langle \Delta E \rangle$ is the mean energy loss.

These data reflect the ability of the potential surface to transform motion in the approach co-ordinate to that in the exit (product) co-ordinate. The ability of each surface to bring about chemical reaction varies qualitatively in the same manner. The $E'_{\text{trans}}$ distribution in Figure 4.42 for P.S.3 is very similar to that reported by Whitehead\textsuperscript{39} for Na $+$ Li\textsubscript{2} at 0.9 eV collision energy, the potential well in both cases being in a similar position.

Angular distributions for inelastic scattering are shown together with the distribution for the O.A.M. re-orientation angles in Figure 4.43. In both cases the distributions broaden from P.S.1 to P.S.3 with the former also exhibiting a marked change in peak position characteristic of rainbow scattering under different potentials. The out-of-plane forces are expected to increase from P.S.1 to P.S.3 since the potential derivatives are everywhere larger for P.S.3. This qualitatively explains the small but significant trend towards greater out-of-plane scattering for the latter. The approximate peak positions in the angular distributions are
P.S.1 \(\sim 20^0\); P.S.2 \(\sim 30^0\) and P.S.3 \(\sim 40^0\). When these are divided by the respective well depths (21, 28 and 39 k. cal. mol\(^{-1}\) respectively) yields a roughly constant number thereby substantiating the view that the form of \(N(\theta)\) is governed by rainbow scattering in the same manner expected for purely elastic scattering. In this respect the results are similar to Fluendy et al.\(^{142}\).

Finally, distributions of mean rotational and vibrational excitation for non-reactive scattering at 2.5 eV are plotted against impact parameter in Figure 4.44. The form taken for each is approximately invariant with potential surface although the extent of energy transfer is highly dependent on this. The hump in the \(\left\langle E'_{\text{vib}} \right\rangle\) distributions at impact parameters less than ca. 3 au indicates the presence of hard-sphere interactions (the 'radius' of the \(I_2\) molecule is 2.5 au) softened by the ability of the potential to follow the motion of the attacking O-atom. It is expected that trajectories at higher energies still would exhibit a more pronounced effect as previously observed\(^{142}\) since then the momentum of the approaching O-atom will require a force larger than the potential can supply outside the hard-sphere region to bring about any effect. It is particularly noteworthy that P.S.3 whose topology least favours vibrational excitation shows a much more pronounced top-hat-like excitation function with a cut-off at the hard sphere radius. The rapid reduction in vibrational excitation below \(\sim 1\) au is a consequence of the improbability of near colinear collisions. On P.S.1 where this is most evident, inelastic collisions are replaced by reactive ones. The rotational excitation does not differ appreciably in form than that for vibration indicating a similar mechanism is responsible for both. There is no clear evidence of selective internal excitation at low and high impact parameters as for
Figure 4.4.4 - Mean Rotational (b) and Vibrational (a) Excitation (3-D, 2-5000 eV) vs. Impact Parameter (au)
K + I₂¹⁴² and this is most likely due to the form of the potential which, being almost spherically symmetric has insufficient anisotropy to bring about rotational excitation.

4.10 SUMMARY AND CONCLUSIONS

Classical trajectory calculations have been performed for the mass combination corresponding to O + I₂ on three "double-ended" potential surfaces with OI₂ binding energies of 4, 10 and 21 k. cal. mol⁻¹ with respect to products. Four collision energies, 0.025, 0.25, 1.0 and 2.5 eV have been used and the calculations have been compared in both 2-D and 3-D.

Results indicate the presence of a complex intermediate living longer than predicted by the RRKM formulae but considerably shorter than one rotational period of I₂ or of the complex (~ 8 ps). Angular distributions are similar to those expected from random decomposition of a complex having appreciable angular momentum in rotational and orbital in both entrance and exit channels. These distributions have also been obtained by other workers modelling LLC systems. However, the similarity of the angular distribution in both 2-D and 3-D, to those obtained for the direct reaction of K + CH₃I²⁴, ⁵⁴ coupled with the observation of vibrational inversions at low energy provide a strong case against the statistical model favouring a dynamical interpretation. This is further strengthened by the decidedly non-statistical forms assumed by the non-reactive scattering.
The observed rectangular opacity functions are interpreted in terms of the surface topology rather than the traditional statistical and dynamical interpretations. The unfavourable mass combination, $M + HH$, means that the extent of chemical reaction is determined by the ability of potential surface to couple to entrance and exit channel momenta. This latter property is manifest in the extent of vibrational excitation in the non-reactive scattering at high energy. Thus for this mass combination, motion on an attractive surface results in apparently statistical behaviour and it is necessary to know the internal state distributions before an unambiguous statement about the dynamics can be made.

The observed total cross-sections for reaction are estimated from the calculations to be one to two orders of magnitude above the experimental results. This is most likely due to the unrealistic tendency of the potential to permit reaction in the presence of a nearby third atom which does not decrease the attraction between the other two as would be intuitively expected. The correction made to the potential in Reference 54 when applied here was found to give potentials with much shallower wells or even barriers and to change the position of the extrema into the entrance channel. Since the emphasis at the outset of this project lay in determining the effect of the well depth *inter alia*, the potentials were chosen on the assumption that the fine details of their topology would be lost by the complex nature of the interaction. This is evidently not a valid assumption.
There appears to be little selectivity with respect to RAM polarisation and $I_2$ vibrational quantum number (for $v'' \leq 3$). The former is due to the slow rotational velocity of the $I_2$ molecule in conjunction with the light $O$-atom mass which results in facile re-arrangement of the angular momentum vectors by the potential. The latter is a consequence of the low vibrational quantum for $I_2$ which resulted in little change in the 3-atom potential with $v'' (I_2)$. Also, the inability of the potential surface to transform this mode into product modes contributes to this.

Since the work of Raff and Karplus$^{54}$ it has been usual to carry out trajectory studies in 3-D where possible. However, the present results indicate that 2-D calculations are acceptable for projection into 3-D even in the case of angular distributions. For a better measure of the effect of angular momentum polarisation and of the potential itself, the 2-D treatment is to be recommended since it is more specific and less prone to integration error. These remarks do not apply to truly long-lived-complexes$^{35, 39, 40}$ since angular momentum coupling in these cases has a critical effect on the trajectory outcomes.

For a system as poorly characterised as $O + I_2$ it is not expected that the present study would add to its understanding mainly due to the potentials used. The exercise must therefore be regarded as purely tutorial as much of the early work by Bunker's and Polanyi's schools was. This is in contrast to KBS and JCW where the potentials were fairly well defined. More recent work on the aerodynamically important reaction of ClO + $O$ $^{162}$ which has predicted acceptable rate constants highlights an eminently practical approach to potential surfaces evaluation by piecewise construction from reasonably well established
regions. This is similar in approach but more empirical than the elegant method of Sorbie and Murrell. However, since both rely heavily on accurate input, neither is applicable to the OI\textsubscript{2} system yet.

As regards the trajectory method per se the future looks extremely bright. The many problems inherent in Monte Carlo sampling are being critically re-examined and more efficient sampling procedures suited to the information required are being constructed. The use of information theory to project from 2-D into 3-D is a notable refinement which will relieve computational effort where dedicated processors are not available. Unfortunately, the predictive power of the information theoretic transformations is much reduced for 1-D \rightarrow 2-D, 3-D projections which means that non-colinear quantum calculations are still a long way off.

However, despite the advances above, there is still an urgent need for systematic studies of reactions proceeding via long-lived-complexes following the discrediting by Fitz and Brumer of Borne and Bunker's earlier work. This arises from recent molecular beams work and the revision and detailed classification of the statistical theory in terms of vector correlations by Herschbach et al. An eminently reasonable starting point would be tri-halogen and/or tri-alkali systems since these seem to be well described by the LEPS formalism and are experimentally fairly well defined. The F + I\textsubscript{2} system in particular is of interest subsequent to the recent observation of a vibrational inversion in a laser-induced-fluorescence study. If the entrance channel is attractive in this system (a reasonable assumption based on other tri-halogen systems) then the similarity of the masses to the present
system would predict an inversion though not necessarily a long-lived-complex mechanism.

Note added in proof:

The H + ICl system studied by Polanyi et al\textsuperscript{170} using a LEPS surface with a 20 k. cal. mol\textsuperscript{-1} well for H - I - Cl approach and a barrier for H - Cl - I approach yields differential cross-sections in good agreement with those obtained here. The translational and vibrational distributions for the HI product are also similar with the latter exhibiting the same trend in the vibrational distribution with increasing energy. It is also comforting to note that similar difficulties in integrating the equations of motion occurred here. In particular the ill-conditioning of the problem with respect to initial step-size was one of the problems encountered here.
APPENDIX A  CO-ORDINATE TRANSFORMATIONS

This is intended to show the relationship between the Cartesian co-ordinates in a three particle system to the generalised co-ordinates required in Hamiltonian dynamics. It is based on Bunker's description with some of the missing steps filled in.

The three particles A, B and C have co-ordinates \((q_1-3, p_{1-3})\), \((q_{4-6}, p_{4-6})\) and \((q_{7-9}, p_{7-9})\) and masses \(m_A, m_B\) and \(m_C\) where the momenta are given by

\[
p_i = m_i q_i \quad ; \quad m_i = m_A, \quad i = 1, 2, 3
\]
\[
= m_B, \quad i = 4, 5, 6
\]
\[
= m_C, \quad i = 7, 8, 9 \quad \ldots \ldots \ldots \ldots (4.63)
\]

and the total energy \(H\) is given by

\[
H(p, q) = T(p, q) + V(q)
\]
\[
= \frac{1}{2} \sum_{i=1}^{q} m_i q_i^2 + V(q_i) \quad \ldots \ldots \ldots \ldots (4.64)
\]

The time evolution of such a system is given by Hamilton's equations

\[
q_i = \frac{\partial H}{\partial p_i} = \frac{\partial T}{\partial p_i} \quad \ldots \ldots \ldots \ldots (4.65a)
\]
\[
p_i = - \frac{\partial H}{\partial q_i} \quad \ldots \ldots \ldots \ldots (4.65b)
\]
The most convenient co-ordinate system to tackle such an integration in is one which eliminates unnecessary integration. The most obvious choice is one in which the CM is stationary since the potential is a function of inter-particle distances only. Also, recourse to conservation laws (H, AM) can be made to link variables and reduce the dimensionality of the problem. However, this in practice adds effort. The use of these conservation laws lies in monitoring the course of the integration.

The transformation is made to a set of internal co-ordinates $Q_i (q_i)$ and $P_j (p_j)$, $i, j = 1, \ldots, 9$ with $(Q_7, Q_8, Q_9)$ and $(P_7, P_8, P_9)$ being the CM co-ordinates. The latter can be assumed without loss of generality to be zero (i.e. conservation of linear momentum assumed since no external forces act). In the new representation the Hamiltonian becomes

$$H = \frac{1}{2} \sum_{i,j=1}^{6} \mu_{ij} Q_i Q_j + V(Q_i) \quad \cdots \cdots \cdots \quad (4.66)$$

The simplest form of $H$ and the one most amenable to computation is a simple sum of squares. This places a requirement on the transformed masses $\mu_{ij}$ that

$$\mu_{ij} = a_{ij} \delta_{ij}; \quad \delta_{ij} = \text{Kronecker delta} \quad \cdots \quad (4.67)$$

or in matrix terminology, $\mu$ is diagonal.
Denoting the sets of co-ordinates by column matrices \( q_i(q_i) \), \( p_i(p_i) \), \( Q_j(q_j) \), \( P_j(p_j) \) and choosing \( Q \) at liberty in terms of \( Q_j(q_j) \) (these \( Q_j \)'s normally represent 'sensible' vectors e.g. atom to diatom centroid and atom-atom in diatom) a set of momenta can be chosen such that \( P \) and \( Q \) are a conjugate pair in the Lagrangian spirit. Thus

\[
T = \frac{1}{2} \sum_i P_i \dot{q}_i \quad \text{where} \quad P_i = \mu_{ii} \dot{q}_i \quad \text{............ (4.68)}
\]

If now \( Q \) is related to \( q \) by a contact transformation

i.e. if \( Q = A q \)

then \( \dot{Q} = A \dot{q} \) and \( \dot{q} = A^{-1} \dot{Q} \) \quad \text{............ (4.69)}

Thus, the kinetic energy \( (T) \) in the Cartesian representation:

\[
T = \frac{1}{2} Q^T \bar{M} Q \quad \text{............ (4.70)}
\]

where \( \bar{M} \) is a diagonal matrix containing the particle masses \( m_A, m_B, m_C \) only becomes:

\[
T = \frac{1}{2} (A^{-1} \dot{Q})^T \bar{M} A^{-1} \dot{Q} = \frac{1}{2} \dot{Q}^T (A^{-1})^T \bar{M} A^{-1} \dot{Q} = \frac{1}{2} \dot{Q}^T \mu \dot{Q} \quad \text{............ (4.71)}
\]
where

\[ \mathcal{H} = (A_c^{-1})^T \mathcal{M} A_c^{-1} \] ........................ (4.72)

\( A_c \) is a 9 x 9 matrix which is tedious to invert. However, since \( \mathcal{M} \) and \( \mathcal{M} \) are both diagonal, their inverses are trivial to construct. Thus

\[ A_c^{-1} = ((A_c^{-1})^T \mathcal{M} A_c^{-1})^{-1} \]

\[ = A_c^{-1} \mathcal{M}^{-1} ((A_c^{-1})^T)^{-1} \]

\[ = A_c^{-1} \mathcal{M}^{-1} A_c^T \] ........................ (4.73)

since for any non-singular matrix \( A_c \),

\[ (A_c^T)^{-1} = (A_c^{-1})^T \] ........................ (4.74)

Thus, using equation (4.71)

\[ H = \frac{1}{2} \sum_{i=1}^{6} \mu_{ii} \dot{Q}_i^2 + V \{Q\} \] ........................ (4.75a)

\[ = \frac{1}{2} \sum_{i=1}^{6} p_i^2/\mu_{ii} + V \{Q\} \] ........................ (4.75b)

and the Hamiltonian equations become
\[
\begin{align*}
Q_i &= \frac{\partial T}{\partial p_i} = \frac{p_i}{\mu_{ii}} \quad \cdots \quad (4.76a) \\
\text{and} \quad \dot{p}_i &= -\frac{\partial \mathcal{H}}{\partial q_i} = -\frac{\partial V}{\partial q_i} \quad \cdots \quad (4.76b)
\end{align*}
\]

**APPENDIX B : CHOICE OF M\_J STATES**

2-D

The \( P \) and \( Q \) matrices are given in equations (4.31) and (4.33). Referring to Figure 4.10 it can be seen that the angular momentum contributions are given by:

\[
\begin{align*}
L (\text{orbital}) &= Q_1 P_2 - P_1 Q_2 \\
L (\text{rotational}) &= Q_3 P_4 - P_3 Q_4
\end{align*}
\]

\text{in } k \text{ direction} \quad \cdots \quad (4.77)

\( Q_4 \) is set to zero and \( Q_3 \) is negative by definition, thus for

\( M_J = +1 \) (Parallel angular momenta):

If \( Q_1 P_2 - P_1 Q_2 > 0 \) (or \( < 0 \)) then

\[
\begin{align*}
P_4 &< 0 \quad \text{(or} \quad > 0) \quad \cdots \quad (4.78)
\end{align*}
\]
\[ M_J = -1 \]

If \( Q_1 P_2 - P_1 Q_2 > 0 \) (or \(< 0\) ) then

\[ P_4 > 0 \] (or \(< 0\) ) .................. (4.79)

The sign of \( P_4 \) is then altered by the program if necessary for a specified \( M_J \).

3-D

The simple assignment in 2-D is not possible in 3-D without constraining BC to rotate in a plane parallel to the relative velocity vector. Two arbitrary choices of \( M_J \) state were made:

\( M_J \sim 1 \): Initial RAM vector is perpendicular to the initial relative velocity vector.

\( M_J \sim 2 \): Initial RAM vector perpendicular to that for \( M_J \sim 1 \).

Referring to Figure 4.11:

(a) \( V_{rel} \) is the vector \((P_1, P_2, P_3)\)

(b) \( L \) is the vector \((\ell_1, \ell_2, \ell_3)\) for the rotational angular momentum.

Since \( L \) is constrained to plane \( \pi \) formed from \( R_{BC} = (Q_4, Q_5, Q_6) \) then

\[ \ell_1 Q_4 + \ell_2 Q_5 + \ell_3 Q_6 = 0 \] .................. (4.80)
and since \( L \) is perpendicular to \( \mathbf{v}_{\text{rel}} \) for \( M_j \sim 1 \) then:

\[
\ell_1 p_1 + \ell_2 p_2 + \ell_3 p_3 = 0 \quad \cdots \quad (4.81)
\]

Solving (4.80) and (4.81) yields for \( L \):

\[
L = \left\{ \ell_2 \frac{p_2 - q_5}{p_3 - q_6}, \ell_2, \ell_2 + q_5 \left[ \frac{p_2 - q_5}{p_3 - q_6} \right] \right\}
\]

\cdots \quad (4.82)

The angle \( \eta \) is defined with respect to the unit vector \( \hat{e} \):

\[
\hat{e} = \frac{RBC \times \hat{k}}{RBC} ; \quad \hat{k} = (0, 0, 1)
\]

\[
= \left[ \frac{q_5}{(q_4^2 + q_5^2)^{1/2}}, \frac{-q_4}{(q_4^2 + q_5^2)^{1/2}}, 0 \right] \quad (4.83)
\]

Now, \( \eta = \cos^{-1} \frac{L \cdot \hat{e}}{L} = \cos^{-1} (N/D) \)

with

\[
N = \left[ \frac{p_2 - q_5}{p_3 - q_6}, \frac{q_5}{(q_4^2 + q_5^2)^{1/2}}, \frac{q_4}{(q_4^2 + q_5^2)^{1/2}} \right]
\]

and
\[ D^2 = 1 + \left( \frac{Q_5 - Q_6}{P_3 - P_2} \right)^2 + \left[ \frac{Q_5}{Q_6} + \frac{Q_4}{Q_6} \right]^2 + \left[ \frac{P_2 - Q_5}{P_3 - Q_6} \right]^2 \]  

In the special case \( Q_4 = 0 \) (\( \alpha = \pi/2 \))

\[ \eta = \cos^{-1} \left( \frac{1}{\frac{Q_5 - P_2}{P_3}} \right) \]

where

\[ D^2 = 1 + \left( \frac{Q_5 - P_2}{Q_6} \right)^2 \cdot \frac{1}{P_1^2} + \frac{Q_5^2}{Q_6^2} \]  

For \( M_j \sim 2 \), \( \eta \) is set at \( \eta(M_j \sim 1) + \pi/2 \).
APPENDIX C: DETAILS OF TRAJECTORY PROGRAMS

Listings of the 2-D and 3-D programs are given below with a flow diagram of the 2-D program. The 3-D version differs in that the analysis program is separate. Both programs share the same logical sequence although some of the subroutines have different names. For the 2-D program the order of events is:

MAIN PROGRAM - Input data for batch running is read here and the subroutines START (which sets up the integration) and SOLVE (which integrates the equations) are called. Stratified sampling of impact parameter is done here and when preset number of trajectories are run, the program is terminated.

START - This subroutine sets up the initial variables and parameters including control parameters for the integration (error weights and tolerance as well as step size). It then calls on CHOOSE to generate some random numbers to enable the starting values for P and Q to be calculated. The reduced units are as follows:

TIME - in units of $10^{-14}$ s (= TRED)

$Q'$s - atomic units ($= 0.529 \times 10^{-10}$ m)

$P'$s - in units of amu. au. s$^{-1}$. This is further reduced by division by TRED in subroutine SOLVE to yield small numbers for computational ease.
Figure 4.45 - Flow Diagram of 2-D Trajectory Program
IF (LOUP .GT. 55) BB=11.0
IF (LOUP .GT. 66) BB=12.0

CALL START (P, O, PRMT, CDOT, LOOP, E, IV, MJ)
WHITE (4) LOOP, BB
WHITE (6, 600) LOOP, BB
CALL SOLVE (P, O, PRMT, CDOT)

CONTINUE

C FORMATS ...
609 FORMAT ('11,3F5.2', 'TRAJECTORY NO.,', 'I4', 'U5', 'SNX', 'IMPACT PARAM.,', 'F5.1')
602 FORMAT ('11,10(/)'), '**********
*R, 2D_TRAJETORIES=-(L.*F6.3,*,EV.*).*
* * BATCH NO.,', 'I3', '15X', '*'*
* * POTENTIAL PARAMETERS..: ****
* * I1X*A1=1.0U, 4X, '*'*
* * I1X*B1=**F9.2, 7X, '*'*
* * VIBIL. LEVEL.,', 'I2', '14X', '*'*
* * MJ STATE.,', 'I2', '17X', '*'*
* STOP

END

C SUB-R.: OPT. T.E.C. = CONTRL (T, C, CDOT, IHLF, NDim, PRMT)

C ********************
C  PURPOSE -
C  CONTROLS INTEGRATION AND DETERMINES FINISHING POINT
C  ********************

C DOUBLE PRECISION PRMT, C, CDOT, T, HAM, DELHAM, POTNOT, FINH, TF
C DOUBLE PRECISION DELAM, AMNOT, S, SSAM, RAB, RAC, HBC, PROD,
C DIMENSION PRMT(9), C(6), CDOT(8), STORE(7, 101)
C DIMENSION P(4), O(4), PF1(4), QF1(4)
C COMMON/ELK11/TF
C COMMON/BLK14/S, SS
C COMMON/BLK40/IFlag

Iflag=0
CALL HAMPOT (C, HAM, PUT, AN, 2)
Iflag=1
RCB=DSRT (C(3)*C(3)+C(4)*C(4))
RAB=DSRT ((C(1)+S*C(3))*2+(C(2)+S*C(4))*2)
RAC=DSRT ((C(1)-S*C(3))*2+(C(2)-S*C(4))*2)
IF (T, GT, 0.000) GOTO 1
IHM=1
IAM=0
HAMNOT=HAM
AMNOT=AM
PUTNOT=PUT
RCBNOT=SHGL (RCB)
RABNOT=SHGL (RAB)
RACNOT=SHGL (RAC)
IF=PRMT (2)/100
L=1
UU 2 K=1, 101
STORE (3+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
CONTINUE
2 CONTINUE
IF (T, LT, (L-1)*TF) GOTO 3
STORE (1, L) = T
STORE (2, L) = HAM.
DETERMINE HISTORY OF TRAJECTORY & COMPUTE CONSERVATION OF ENERGY & ANGULAR MOMENTUM

IF (DELTA(I) .GT. 4) PRINT(5) PRN(1) = 3.0F0

IF (PRN(1) .GT. 1.0F0) IFRAC = 2

IF (PRN(1) .GT. 1.0F0) PRINT(5) = 1.0F0

IF (R(3) .LT. 1.0F0) PRINT(5) = 0.0F0

CONTINUE

RETURN

CALL TB (S, T)

WRITE (69602) 

.....

CALL STRU (1)

WRITE (69602)

.....

CALL TB (S, T)

RETURN

CALL TB (S, T)

RETURN
END
SUBROUTINE GRAPH
C
C ******************************************************************************
C
C PURPOSE -
C  GRAPH R,R1,R2,R3 AGAINST TIME
C
C******************************************************************************
C
DOUBLE PRECISION TF,TRED
COMMON BLK11, TF
COMMON BLK35, TRED
LOGICAL *1 A(115), MIN/1, EYE/1, PLUS/1, BLA/1, 1/
LOGICAL *1 DIGIT(10)/1, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10/1
LOGICAL *1 SYMBOL(5)/'G', 'C', 'B', 'A', 'F'/
DIMENSION TIME(5)
GO TO 4
ENTRY AXES
UO.1, J=1, 115
UO. 1, J=1, 55
1. A(I,J)=BLA
GO. 2, I=1, 115
2. A(I,51)=MIN
3. A(I,51)=EYE
DO. 7, I=6, 31, 15
A(I+1, J)=PLUS
DO. 8, I=10, 110, 20
A(I+1, J)=PLUS
A(7+1)=DIGIT(1)
A(9+4)=DIGIT(5)
A(7+21)=DIGIT(1)
A(3+1)=DIGIT(10)
A(3+36)=DIGIT(5)
A(3+3)=DIGIT(10)
RETURN
ENTRY PLOT(IC, Y+JX)
IX=JX+9
IY=51-INT(3.0+Y+U.5)
IF (IC.LT.1.0 OR IC.GT.5) IC=5
IF (IX.LE.0. OR IX.GE.116. OR IY.LE.0. OR IY.GE.56) RETURN
A(IX+JY)=SYMBOL(IC)
RETURN!
WRITE (6, 5) ((A(I,J), I=1, 115), J=1, 52)
5 FORMAT ('1', '5', 115A1/IX), 115A1)
DO. 6, J=1, 5
TIME(J)=TF*J+20.0E14/TRED
6 CONTINUE
WRITE (6, 9) TIME.
9 FORMAT (8X, '0 I', 115X+G11.4, 4, 9X+G11.4))
WRITE (6, 10) ((A(I,J), I=1, 115), J=54, 55)
10 FORMAT (1X, 115A1/IX), 115A1)
WRITE (6, 11)
11 FORMAT ('1Y-VALUES IN ATOMIC UNITS. X-VALUES IN SECONDS. 10**14'.
1'/W(1AB)=C R(AC)=B R(BC)=A**0')
RETURN!
END
C
******************************************************************************
C
C******************************************************************************
C
C INTEGRATION ROUTINE -
C THIS IS AN EARLY VERSION OF THE IBM
C SSP111 SUBROUTINE UNPCG 5 DETAILS OF IT CAN BE FOUND IN
C THAT AUGUST PUBLICATION.
DIMENSION PRMT(5), Y(6), DERY(6), AUX(16, 8)
DOUBLE PRECISION Y, DERY, AUX, PRMT, X, H, Z, DELT, DBAS

NDIM = 8
HLF = 0

X = PRMT(1)
N = PRMT(2)
PRMT(5) = 0, 0, 0
UO, I = 1, HUI
AUX(I + 1) = 0, 0
AUX(I + 1) = DERY(I)
1. AUX(I + 1) = Y(I)
2. H(1)(PPMT(2) - X)) = 3, 2, 4,
3. HLF = 12
GOTO 4

4. CALL FCT(X, Y, DERY)
5. CALL OUTP(X, Y, DERY, IHLF, NDIM, PRMT)
6. IF (PRMT(5)) = 5, 6,
7. IF (IHLF) = 7, 7, 6
8. RETURN
9. UO, I = 1, NDIM
10. AUX(2, I) = Y(I)
11. IHLF = IHLF + 1
12. X = X + H
13. UO, I = 1, NDIM
14. AUX(4, I) = AUX(2, I)
15. N = 1
16. ISW = 6
17. GOTO 100
18. CALL FCT(X, Y, DERY)
19. N = 2
20. UO, I = 1, NDIM
21. AUX(2, I) = Y(I)
22. AUX(9, I) = DERY(I)
23. ISW = 3
24. GOTO 100
25. UO, I = 1, NDIM
26. N = 3
27. UO, I = 1, NDIM
28. N = 4
29. UO, I = 1, NDIM
30. N = 5
31. UO, I = 1, NDIM
32. N = 6
33. UO, I = 1, NDIM
34. N = 7
35. UO, I = 1, NDIM
36. N = 8
37. UO, I = 1, NDIM
38. N = 9
39. UO, I = 1, NDIM
40. N = 10
41. UO, I = 1, NDIM
42. N = 11
43. UO, I = 1, NDIM
44. N = 12
45. UO, I = 1, NDIM
46. N = 13
47. UO, I = 1, NDIM
48. N = 14
49. UO, I = 1, NDIM
50. N = 15
51. UO, I = 1, NDIM
52. N = 16
53. UO, I = 1, NDIM
54. N = 17
55. UO, I = 1, NDIM
56. N = 18
57. UO, I = 1, NDIM
58. N = 19
59. UO, I = 1, NDIM
60. N = 20
61. UO, I = 1, NDIM
62. N = 21
63. UO, I = 1, NDIM
64. N = 22
65. UO, I = 1, NDIM
66. N = 23
67. UO, I = 1, NDIM
68. N = 24
69. UO, I = 1, NDIM
70. N = 25
71. UO, I = 1, NDIM
72. N = 26
73. UO, I = 1, NDIM
74. N = 27
75. UO, I = 1, NDIM
76. N = 28
77. UO, I = 1, NDIM
78. N = 29
79. UO, I = 1, NDIM
80. N = 30
81. UO, I = 1, NDIM
82. N = 31
83. UO, I = 1, NDIM
84. N = 32
85. UO, I = 1, NDIM
86. N = 33
87. UO, I = 1, NDIM
88. N = 34
89. UO, I = 1, NDIM
90. N = 35
91. UO, I = 1, NDIM
92. N = 36
93. UO, I = 1, NDIM
94. N = 37
95. UO, I = 1, NDIM
96. N = 38
97. UO, I = 1, NDIM
98. N = 39
99. UO, I = 1, NDIM
100. N = 40
$I(i+5,1)+AUX(H+4,1)+AUX(H+5,1)$

$Y(i)=\text{DEL}T+0.2561903710743800*AUX(16,1)$

207  $AUX(16,1)=\text{DEL}T$

208  CALL FCT($X,Y,\text{DER}Y$)

209  DO 208 $I=1,\text{NDIM}$

210  $\text{DEL}T=.12500*$(9.0$*AUX(N-1,1)-AUX(N-3,1))3.0$*$H*(\text{DER}Y(I)+AUX(N+6,1))

211  $AUX(16,1)=AUX(16,1)-\text{DEL}T$

212  $Y(i)=\text{DEL}T+.0743801652892562000*AUX(16,1)$

213  $\text{DEL}T=0.0$

214  DO 209 $I=1,\text{NDIM}$

215  IF(DEL$T$=DEL$T$+2$AUX(15,1)$*DA$BS(AUX(16,1))$

216  CALL FCT($X,Y,\text{DER}Y$)

217  CALL OUTP($X,Y,\text{DER}Y,\text{IHLF},\text{NDIM},\text{PRMT}$)

218  IF(DEL$T$=DEL$T$+2$AUX(16,1)$*DA$BS(AUX(16,1))$

219  I$\text{MOD}=\text{ISTEP}/2$

220  H$=H+H$

221  I$\text{HLF}=I\text{HLF}-1$

222  $\text{ISTEP}=\text{ISTEP}+1$

223  IF($\text{ISTEP}=10$)223,223,210

224  H$=500*H$

225  $\text{ISTEP}=\text{ISTEP}+1$

226  DO 225 $I=1,\text{NDIM}$

227  UX($i-1,1)=AUX($i-2,1)$

228  UX($i-2,1)=AUX($i-4,1)$

229  UX($i+5,1)=AUX($i-6,1)$

230  AUX($i+i,1)=AUX($i+5,1)$

231  UX($i+i,1)=AUX($i+3,1)$

232  UX($i+i,1)=AUX($i+4,1)$

233  $\text{DEL}T=AUX((i+6,1)+AUX(N+5,1))$

234  $\text{DEL}T=\text{DEL}T+\text{DEL}T$

235  $UUX(16,1)=3.96279296296296300*(Y(i)-AUX(N-3,1))$

236  $=3.15611111111111111111000*H*(\text{DER}Y(I)+\text{DEL}T+AUX(N+4,1))$

237  $$.GOT0201$

238  IF($\text{ISTEP}=10$)223,223,210

239  H$=500*H$

240  $\text{ISTEP}=\text{ISTEP}+1$

241  DO 240 $I=1,\text{NDIM}$

242  $Y(i)=\text{DEL}T-\text{DEL}T$

243  $\text{DEL}T=\text{DEL}T+\text{DEL}T$

244  $\text{DEL}T=(H+H)$

245  CALL FCT($\text{DEL}T,Y,\text{DER}Y$)

246  DO 245 $I=1,\text{NDIM}$

247  $AUX(i-2,1)=Y(I)$

248  $AUX(H+5,1)=\text{DEL}T$+DER$Y(I)$

249  $Y(I)=AUX(i-4,1)$

250  $\text{DEL}T=\text{DEL}T+(H+H)$

251  CALL FCT($\text{DEL}T,Y,\text{DER}Y$)

252  DO 252 $I=1,\text{NDIM}$

253  $\text{DEL}T=AUX(i+5,1)+AUX(H+4,1)$

254  $\text{DEL}T=\text{DEL}T+\text{DEL}T$

255  UUX(16,1)=3.96279296296296300*(AUX(N+1,1)-Y(I))
1 -3.3611111111111111D0*H*(AUX(I+6, I)+DELT+DERY(I))
226 AUX(I+3, I) = DERY(I)
GOTO 206

END

SUBROUTINE H, E = POTFUN(T, C, CDOT)

******************************************************************************

* PURPOSE -
* EVALUATES DH/DQ(I) AND DH/UP(I) DURING INTEGRATION

******************************************************************************

IMPLICIT REAL*8 (A-H, L, M, O-Z)

COAH0=BLK0/BLK01/HAM+H4, MC

COAH0=BLK0/BLK02/HOL, H'R, HRO, H'U, H'MU2, H'MU1, H'R2, H'R1

COAM=BLK0/BLK05/BETAAB, BETAAC, BETABC, UAB, UAC, UBC, R01, R02, R03

CUMU=PUTPAR/A, B

CUMU0=BLK14/S, SS

CUMU0=BLK35/TKCO

CUMU0=BLK40/IFLAG

T1=SENS/0U C(3), C(DOT(8), DR1DQ(4), DR2DQ(4), DR3DQ(4), PDOT(4), QDOT(4))

Z1=C(1)*S*C(3)

Z2=C(2)*S*C(4)

K1=USNRT(Z1*Z1+Z2*Z2)

Z1=C(1)*S*C(3)

Z2=C(2)*S*C(4)

K2=USNRT(Z1*Z1+Z2*Z2)

K3=USNRT(C(3)*C(3)+C(4)*C(4))

K1=1/K1

K2=1/K2

K3=1/K3

RURSAB=EXP(-BETAAB*(R1-R01))

RURSAC=EXP(-BETAAB*(R3-R03))

RURSBC=EXP(-BETAAB*(R2-R02))

HYPTAB=UTAMH(A*K1+B)

HYPTAC=UTAMH(A*K3+B)

ENTRY_HAM=POT(C+HAM+POT+AN, Z)

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-

MOL, Z IS ALSO CALCULATED.

POTABC=DAB*MORSAB*(MURSAB-2)+DAB*HORSAB

L=1*H+MORSAB*(MURSAB-1)-HYPTAB

POTABC=DAB*MORSAC*(MURSAC-2)+DAB*HORSAC

POTABC=POTABC/U.344560629

POTACB=POTACB/U.344560629

Z=POTABC-POTACB

IF((Z, LE, 0.0000000000)-GOTO 13

POT=POTACB

GOTO 12

13. MU1=POTABC

12. CONTINUE

S1=0.0

S2=0.0

DO 21 J=1, 2

S1=S1+C(J+4)*THED*U.5291770-8)**2

S2=S2+C(J+6)*THED*U.5291770-8)**2

21 CONTINUE

S1=S1+U.1036410-11

S2=S2+U.1036410-11

HAM=POT+(0.5*MU1*S1+0.5*MU2*S2)
Agi

IF(IFLAG9EQ01) (70T07

-----

7 CONTINUE

IF (Z,LI,0,000000000000000D0) GO TO 9

DUVR3=2.D0*DA*BETAAC*(1.DO-MORSAC)*MORSAC

1-UBC*UCKSEC*A*(1.DO-M01TAC*HYPTAC)

DUVR2=UBC*MORSAC*BETAAC*(1.DO-2.DO*MORSAC+HYPTAC)

8 DUVR1= BETAAC*DA*BORSAC

GO TO 8

9 CONTINUE

DUVR1=2.DO*DA*BETAAC*(1.DO-MORSAC)*MORSAC

1-UBC*UCKSEC*A*(1.DO-M01TAC*HYPTAC)

DUVR2=UBC*MORSAC*BETAAC*(1.DO-2.DO*MORSAC+HYPTAC)

14 UR1DN(1)=SRR1*Z1

UR1DG(2)=SRR1*Z2

SPR1=S*HR1

UR1DG(3)=Z1*SR1

UR1DN(4)=Z2*SR1

UR3UG(1)=RR3*X1

UR3UG(2)=RR3*X2

SR3R3=SS*HR3

UR3UG(4)=SSR3*X1

UR3UG(5)=SSR3*X2

DO 1 J=1,2

1 DRUG(J)=0.DO0

DO 2 J=3,4

2 DRUG(J)=C(J)*RHK2

DO 3 J=5,4

PDOT(J)=DUR1*UK1DG(J)-DVUK2*UK2DG(J)-DVUK2*UK3DG(J)

DU 4 J=1,2

4 QUOT(J)=RHK1*C(J+4)

DO 5 J=3,4

5 QUOT(J)=RHK2*C(J+4)

DO 6 J=1,4

CDOT(J)=CDOT(J)/TRED**2

6 CDOT(J+4)=PDOT(J)/TRED**2

RETURN

SUBROUTINE SOLVE(P,G,PRMT,CDOT).

C ******************************************************************************
C * PURPOSE: 
C * PREPARES VALUES FOR INTEGRATION BY LIBRARY SUBROUTINE
C ******************************************************************************
C EXTERNAL POTFUN,CONTRL
D01,4 DIMENSION P(4),P(4),C(8),PFI(4),QFI(4),PRMT(5),CDOT(8)
WRITE(4),P,Q
DO 1 J=1,4
1 C(J)=0(J)
C(J+4)=P(J)/TRED
C CONTINUE
CALL SW09(C,POTFUN,CONTRL,PRMT,CDOT)
DO 2 J=1,4
2 QFJ(J)=SNGL(C(J))
PFI(J)=SNGL(C(J+4)*TRED)
CONTINUE
WRITE(4),PFI,QFI
CALL TRANSF(IPROD,SHAM)
NAME=DFRE(SHAM)
C * PURPOSE -
CALCULATES STARTING VALUES OF G(1) ... C(4), P(1) ... P(4)
C *.............................................................................
C REAL* 4 P-MIN:
DOUBLE PRECISION MAM,M,C,MMOL,M,RMOL,MU1,MU2,MRU1,MRU2,PRMT
DOUBLE PRECISION CDOT,CUV1,BETAAB,BETAC,BETABC
DOUBLE PRECISION RMA,RA,RC,MRRA,MRRA,MRRA,RMRA,RCRA,RMRA
COMM/BLK01/MA,MC,MRMA,MRMA,MRMA,MRMA,MRMA,MRMA,MRMA,MRMA,MRMA
COMM/BLK02/MMOL,M,RMOL,MU1,MU2,MRU1,MRU2
COMM/BLK05/BETAAB,BETAC,BETABC,LAB,DBC,K01,K02,K03
COMM/PUTPAR/AB
COMM/BLK09/BB
COMM/BLK14/S,SS
COMM/BLK35/TRKD
COMM/BLK40/IFLAG
DIMENSION P(4),U(4),PRMT(5),CDOT(8)
IFLAG=1
DATA CUV/0.344560326/,CUV1/0.344560329/
IF (LOOP.GT.1) GOTO 13
C TOTAL INTEGRATION TIMES ARE OBTAINED BY MULTIPLYING FLY-BY
C TIM BY CA, 2
ISTASK=5000
PRMT(1)=4.000
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 (PRMT(2).GE.600.000) ISTASK=6000
IF (PRMT(2).GE.500.000) ISTASK=7000
PRMT(3)=PRMT(2)/ISTASK
PRMT(4)=1.000
MMOL=MB+MC
MU=MA+MMOL
MU2=MB+MC+RMOL
MU1=1.0/MU1
MU2=1.0/MU2
RMA=1.*A+1./MB
RMAC=1.*A+1./MC
MRUC=1.*A+1./MC
MAB=MA+MB
MAC=MA+MC
MBC=MB+MC
MTOT=MA+MB+MC
S=-MC*MMOL
SS=MB*MMOL
HKLKE=T*CONV
UAB=UAB*CONV1
UAC=UAC*CONV1
UBC=UBC*CONV1
VK=SQRT(SINGL(2.0*RELKE/MU1))
PI=3.14159
BCMAX0=.142
BCMAX1=.237
BCMAX2=.293
BCMAX3=.350
AMPU=BCMAX0-R02
AMP1=BCMAX1-R02
AMP2=BCMAX2-R02
AMP3=BCMAX3-R02
R=17.5
FK=2*DBC*BTABC*BTABC
ANFEQ=SQRT(FK/SINGL(MU2))
HS=9.62196E-34
ISH/1.RC=19
HBAR=H*CONV/(2*PI)
BTABC=M2*ANFREQ/HBAR
BCMAX(I) & AMP(I) ARE THE MAX. SEPARATION & THE MAX. HARMONIC
C AMPLITUDE RESP. CLASSICALLY ALLOWED FOR VIBR. LEVEL 'N'

E-KUT FOR 1-9 ROTOR IS L*L/(2*1) WHERE L=JAY*HBAR
C BUT L=I*OMEGA & IF JAY IS KNOWN OMEGA CAN BE OBTAINED

JAY IS SET AT JAY(HMP) FOR 12 AT 333K.=-IE JAY=55
JAY=55

C DIM IN UNITS OF AMP AU*AU

1 CONTINUE
UD 14 1=1,3
1* COOT(I)=1.000/8.000
PRAT(5)=0.000
Y=605AUF(XX)

YFL=SINGL(Y)
THETA=2.0*PI*YFL

G(1)=R*SIN(THETA)
G(2)=R*COS(THETA)

LABEL=IV+1
GOTO (10,20,30,40)*LABELV

10 Y=605AUF(XX)
C PERTINENT TO V=0
AMPNOT=Y*SQT(2*BETA)
IF (AMPHOT.GT.AMPJ) GOTO 10
U(3)=-K02*AMPNOT
U300T=ANFREG*SQRT(AMP0*AMPJ-AMPJ*AMPNOT)
GOTO 50

20 Y=605AUF(XX)
C PERTINENT TO V=1
RBC=2.130
IF (Y.LE.0.000) RBC=4.96
U(3)=-RBC
AMPNOT=R02-RBC
U300T=ANFREG*SQRT(AMP1*AMPJ-AMPJ*AMPNOT)
GOTO 50

30 Y=605AUF(XX)
C PERTINENT TO V=2
RBC=R02
IF (Y.LE.0.3900) RBC=4.92
IF (Y.GE.0.6100) RBC=5.18
U(3)=-RBC
AMPNOT=R02-RBC
U300T=ANFREG*SQRT(AMP2*AMPJ-AMPJ*AMPNOT)
GOTO 50


DIMENSION PIN(4), QIN(4), PFI(4), QFI(4)
COMMON/BLK01/MAC, MBC, MAC, MBC, TOT, MAC, MAC, MBC
COMMON/BLK35/TRLU

WRITE(5,200).

200 FORMAT('O',50X,'*REACTION* AB+C FORMED*)

C TO EVALUATE TRANSLATIONAL ENERGY & SCATTERING ANGLE
C
ETRANS=0.
CHINU=0.
CHDE1=0.
CHDE2=0.
Q1=J+1/2.
TERM=PI(J)/MBC+PFI(J+2)/MC.
ETRANS=TRANS+0.5*MTOT*MC/MAB*TERM*TERM.
CHINU=CHINU+PIN(J)*TERM.
CHDE1=CHDE1+TRNA*ELMA.
CHDE2=CHDE2+PIN(J)*PIN(J)

1 CONTINUE
ETRANS=ETRANS/0.344560E29.

C CARLSON (CHINU/SK/1+CHDE1*CHDE2))

C ETRANS IN EV; CHI IN DEGREES
C
UAM=M+T*MC/MAB+M+D*QFI(1)/MTOT+MAC*QFI(3)/MAB.
& PFI(2)/MBC+PFI(4)/MAB*(MAC*QFI(2)/MTOT+MAC*QFI(4)/MBC).
& PFI(1)+MBC+PFI(3)/MAB/TRLU.

LAMBDA=QAM/TRLU.
K=QIN(3)*PIN(J+4)-QIN(4)*PIN(3)

KAM=LAM/I*TRLU.
TAM=LAM+KAM/RA.
TAM=OAMF+RA.

UAM=2.501.

READ=2.50.
EROT=RAMF*RAPM*RAUAB/(2.2*ream*ream).
EROT=EROT/0.344560E29.

DELTAM=OAMF-QAM)/0.227.

BI=2.23E+5.

SOJ=EROT/SQJ.

LAM=EROT+KAM+EROT.
PE=ETOT-ETRANS/ETOT.

WHITE(6,100). ET2=SK/TRLU.
WHITE(6,101). QAM1=QAM1+TRAMF+TAM.
WHITE(6,102). IELT=JAYFE.

RETURN.

101 FORMAT('O',50X,'*ORB,ANG,MOM,*'). X, F8.4, 4X, F8.4/

SUBTOTAL(ANG,MOM), 5X,F6.4, 4X, F8.4.

& IOR, TOTAL ANG, MOM, X, F8.4, 4X, F8.4.

LAM=0.100. GETRANS=1. F7.4/DEVI8=1. F7.4/DEVI8=1. F7.4/

& VSCAT(6, ANGLE, F6.1).

102 FORMAT('O',50X,'*TRANSF OF ORB, AM (HBAR) *'). IN/

& ROTATIONAL QUANTUM NUMBER, T4/.

& FRACTION OF LAMBDA INTO INTERNAL MODES, F6.3.

END

SUBROUTINE ACAHUB(PIN, QIN, PFI, QFI, HAM)

C Computes final state properties of *

C

END
* AC+B SYSTEM

* ************************************************************

DOUBLE PRECISION MA, MB, MC, RMAU, RMVAB, RMVAC, RMVBC, TOT, MAB, MAC, MBC

DOUBLE PRECISION TRED, HAM

DIMENSION PIN(4), Q1N(4), PFI(4), OFI(4)

COMMON/BLK01/MA, MB, MC, RMAU, RMVAB, RMVAC, RMVBC, TOT, MAB, MAC, MBC

COMMON/BLK35/TRED

WRITE(6,300)

300 FORMAT('0',50X,'*REACTION* AC+B FORMED')

C TO EVALUATE TRANSLATIONAL ENERGY & SCATTERING ANGLE

C ETRANS=0.
C CHN=0.
C CHN=0.
C CHN=0.
D0 1 J=1,2
   TERM=-PFI(J)/MBC+PFI(J-2)/NB
   ETRANS=ETRAN+J*5*MB+TOT/MAC*TERM*TERM
   CHN=CHN+TERM*PIN(J)
   CHN=CHN+TERM*PIN(J)
   CHN=CHN+TERM*PIN(J)
   CHN=CHN+TERM*PIN(J)
1 CONTINUE

C FINAL ORBITAL & ROTATIONAL ANGULAR MOMENTUM COMPTS

UAMF=TOT*MB/MBC*([-MA*QFI(1)/TOT+MC*QFI(3)/MBC]*
&-PFI(2)/MBC+PFI(4)/MBC)
&(-MA*QFI(1)/TOT+MC*QFI(3)/MBC)*
&(-PFI(1)/MBC+PFI(3)/MBC)/TRED

RANF=MA*MC/MBC*([-MA*QFI(3)/MBC+QFI(1)))*(PFI(4)/MC
&+PFI(2)*TOT/MBC)+(MB+QFI(4)/MBC
&+QFI(2)*TOT/MBC+MA*PFI(1)/MBC))/TRED

OAMF=Q1N(1)*PIN(2)-Q1N(2)*PIN(1)

RAMF=Q1N(3)*PIN(4)-Q1N(4)*PIN(3)

TAMF=Q1N(1)+RAMF

C ROTATIONAL ENERGY APPROXIMATED TO THAT OF RIGID ROTOR

C AT EQUILIBRIUM SEPARATION IN POTENTIAL WELL

DEAC=2.301

HEAC=3.230

ETOT=HOT+RANF*RMVAB/2.0*REAC*REAC

ETOT=HOT+TRED*ETOT/0.34569229

ELIB=CLAC+HAM-ETRAN-EROT

DELTAM=(OAMF-OAMF)/0.2271

IDELT=INT(DELTAM)

B10=4.23L.5

SQD=EROT/B10

JAY=INT(SQRT(SQD))

ETF=ETRAN+ELIB+ETOT

FE=ETF-ETRAN/ETF

WRITE(6,100) ETF,OFI,ETF,ETRAN,ETF,ETF,ETF

100 FORMAT(6X,106E13.5)

WRITE(6,101) OAMF,RAMF,TAMF,TAMF,TAMF

101 FORMAT(6X,106E13.5)

RETURN
SUBROUTINE M0EPAC(PIN,QIN,PFI,OFI,HAM,JMARK)

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

C DOUBLE PRECISION MA, MB, MC, RMAB, RMUC, RMUB
C DOUBLE PRECISION RTOT, HAB, MAC, MBC, HAH, TRED
C DIMENSION PIN(4),QIN(4),PFI(4),OFI(4)
C COMPO/BLK01/MA, MB, MC, RMAB, RMUC, RMUB, RTOT, HAB, MAC, MBC
C COMPO/BLK35/TRED
C IF (JMARK.EQ.3) WRITE(6,400)
C IF (JMARK.EQ.4) WRITE(6,401)
C 400 FORMAT('UNION-REACTION')
C 401 FORMAT('DISSOCIATION')
C TO EVALUATE TRANSLATIONAL ENERGY & SCATTERING ANGLE

C ETRANS=0.
C CHINM=0.
C CHIDEN=0.
DO 1 J=1,2
  ETRANS=ETRANS+PFI(J)*PFI(J)
  CHINM=CHINM+PIN(J)*PIN(J)
  CHIDEN=CHIDEN+PIN(J)*PIN(J)
       CONTINUE
C CHI=APLO(S(ChINM/SORT(ChIDEN*ETRANS))
C CHI=CHI*180./3.14159.
C ETRANS=ETRANS/HAB*(MAC*MBC)*0.5
C ETRANS=ETRANS/0.34456029
C FINAL ORBITAL & ROTATIONAL ANGULAR MOMENTUM COMPONENTS

C UAMF=GFI(1)*PFI(2)-QFI(2)*PFI(1).
C UAMF=UAMF*TRED
C RAMF=GFI(3)*PFI(4)-QFI(4)*PFI(3).
C RAMF=RAMF*TRED
C UAM1=GIN(1)*PIN(2)-QIN(2)*PIN(1).
C UAM1=UAM1*TRED
C RAM1=GIN(3)*PIN(4)-QIN(4)*PIN(3).
C RAM1=RAM1*TRED
C TAF1=OAM1+RAM1
C TAMF=OAMF+RAMF
C SEPARATE ACCORDING TO WHETHER SCATTERING IS DISSOCIATIVE OR NOT
C IF (JMARK.EQ.3) OCTO_3
C ECTOR=RMUBG*(PFI(3)*PFI(3)*PFI(4)*PFI(4))/2.0
C POTCHK=UAMF=ETRANS-ECTR
C WRITE(6,102) TAF1,TAMF,ETRANS,ECTR,CHI,POTCHK
C 102 FORMAT('ORBITAL MOMENTUM, EXP, F1.4, F1.4, F1.4, F1.4, F1.4, F1.4, F1.4')
C IF (JMARK.EQ.4) OCTO_4
C ECTOR=RMUBG*(PFI(3)*PFI(3)*PFI(4)*PFI(4))/2.0
C POTCHK=UAMF=ETRANS-ECTR
C WRITE(6,102) TAF1,TAMF,ETRANS,ECTR,CHI,POTCHK
C 102 FORMAT('ORBITAL MOMENTUM, EXP, F1.4, F1.4, F1.4, F1.4, F1.4, F1.4')
C
C APPROXIMATE ROTATIONAL ENERGY
C
3 KEBE=5.047
ULBE=1.545

2 EKOT=RAMF*RAMF*KMGC/(2.0*REDC*REBC)
EKOT=TRKD*TRKD*ETOT/0.34560E29
EVIB=REBC+RAHF*TRANS-EROT
DELTA=(GAMF-GAMI)/U.2271

5 IDLT=INT(DELTA)
UJ=INT(RAFM/U.2271)
JU=INT(RAMF/U.2271)
JU=JF-JU

10 ETF=TRANS*ETOT+EVIB.
FE=ETOT-TRANS/ETOT

12 WRITE(6,100)GAMF,GAMI,RAHF,RAHF,TAMI,TAMI

14 IF (GAMF) GT GAMI*4.0*4.0*4.0*4.0

16 IF (TOTAL ANG.*6.0*4.0*4.0*4.0)

18 WRITE(6,100)ETF,ETOT+EVIB
WRITE(6,103)IDLT+JF+JUEL+FE

20 FORMAT(14/14/14/14/14/15/F6.3)

22 FORMAT(14/14/14/15/F6.3)

24 CONTINUE

28 CONTINUE

C

30 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TCPF

32 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

34 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

36 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

38 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

40 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

42 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

44 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

46 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

48 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

50 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

52 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

54 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

56 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

58 COMMON/BLK35/BLKC,TRKD,TRKD,TCPF,TCPF,TCPF,TRKD

60 **ERCC=4-75-EMAS**** EGHP64
**ERCC=4-75-EMAS**** EGHP64
**ERCC=4-75-EMAS**** EGHP64
**ERCC=4-75-EMAS**** EGHP64
**ERCC=4-75-EMAS**** EGHP64
**ERCC=4-75-EMAS**** EGHP64
**ERCC=4-75-EMAS**** EGHP64
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**ERCC=4-75-EMAS**** EGHP64
**ERCC=4-75-EMAS**** EGHP64
**ERCC=4-75-EMAS**** EGHP64
**ERCC=4-75-EMAS**** EGHP64
**ERCC=4-75-EMAS**** EGHP64
**ERCC=4-75-EMAS**** EGHP64
**ERCC=4-75-EMAS**** EGHP64
FILE=POTBATCH

PURPOSE IS TO RUN IN BATCH MODE 3-D TRAJECTORIES, OUTPUTTING RESULTS TO TAPE OR DISK (SEG.FILE ONLY) AND ANALYSING THEM IMMEDIATELY AFTER CODING IS OPTIMISED TO REDUCE CPU TIME SPENT IN EVALUATING DERIVATIVES. INTEGRATION IS BY HAMMING'S STABLE MODIFICATION OF MILNE'S PREDICTOR-CORRECTOR METHOD & THIS REQUIRES 2 CALLS TO DERIVATIVE SUBROUTINE PER INTEGRATION STEP. A SERIES OF DIAGNOSTICS IS O/P FROM INTCHK ACCORDING TO VARIOUS CODES. DATA O/P TO TAPE IS UNFORMATTED TO SAVE SPACE.

DOUBLE PRECISION A,B,PRMT(5),CDOT(12),Y,XX,G05AAF,G05ADF

COMMON/POTPAR/A,B
COMMON/BLK09/BB
COMMON/BLK18/ISUM3
COMMON/BLK99/ISUM1
DIMENSION P(6),O(6)
ISUM3=0
REWIND 4
READ(5,*) IBATCH,B,MJ
IF. (IBATCH.LE.5) MHEG=1
SUBROUTINE CHOOSE(ATHETA, APHI, X, JAY, ABETA)

**Purpose -**
*Selects suitable values of seven starting parameters*
*COORD SYSTEM FULLY DOCUMENTED IN DPF'S THESIS*

DOUBLE PRECISION XX, Y, GO5AAF
PI = 3.14159
Y = GO5AAF(XX)
YFL = SHNGL(Y)
ATHETA = ARCOS(YFL*2.0-1.0)
Y = GO5AAF(XX)
YFL = SHNGL(Y)
APHI = YFL*2.0*PI
Y = GO5AAF(XX)
YFL = SHNGL(Y)
X = YFL*2.0*PI
Y = GO5AAF(XX)
YFL = SHNGL(Y)
ABETA = YFL*2.0*PI
JAY = 55
RETURN

SUBROUTINE CONTRL(T, CDGT, INFL, NDIM, PRMT)
* PURPOSE *
* CONTROLS INTEGRATION AND DETERMINES FINISHING POINT *

REAL *8 PRMT, T, C, CDOT, HAM, DELHAM, HAMNOT, S, SS
DIMENSION PRMT(5), C(12), CDOT(12)
COMMON /BLK14/ S, SS
COMMON /BLK40/ IFLAG

IFLAG = 0

* ABOVE MEANS THAT ONLY HAMPOT PART OF POTFUN IS COMPUTED *
CALL HAMPOT(HAM)
IFLAG = 1

* ABOVE MEANS THAT WHEN POTFUN IS NEXT CALLED BOTH PARTS WILL BE *
* COMPUTED UNLESS IFLAG IS ALTERED MID-COURSE *
IF (T .GT. 0.000) GOTO 1
IHFTOT = 0
IMARK = 0
HAMNOT = HAM
1
CONTINUE
DELHAM = DABS(HAM - HAMNOT)
IF (DELHAM .GT. 1.0D-4) IMARK = 1
IF (DELHAM .GT. 1.0D-3) IMARK = 2
IF (IMARK .EQ. 2) PRMT(5) = 1.000
IHFTOT = IHFTOT + IHLF

* FOLLOWING STOPS INTEGRATION IF ANY INTER-PARTICLE DISTANCE *
* IS >17 AU. SQUARES ARE USED TO AVOID TIME-CONSUMING DSORT'S *
RABSQ = (C(1) + S*C(4))**2 + (C(2) + S*C(5))**2 + (C(3) + S*C(6))**2
RACSQ = (C(1) - SS*C(4))**2 + (C(2) - SS*C(5))**2 + (C(3) - SS*C(6))**2
RBCSQ = (C(4)*C(4) + C(5)*C(5) + C(6)*C(6))**2
IF (T LT 75.000) GOTO 2
IF (RABSQ .GT. 320.000) PRMT(5) = 2.000
IF (RACSQ .GT. 320.000) PRMT(5) = 3.000
IF (RBCSQ .GT. 320.000) PRMT(5) = 4.000
2
CONTINUE
RETURN
ENTRY INTCNK
WRITE(4) IHFTOT, IMARK, T, PRMT(5), IHLF
RETURN
END

SUBROUTINE INTEGR(Y, FCT, OUTP, PRMT, DERY)
DIMENSION PRMT(5), Y(12), DERY(12), AUX(16, 12)
DOUBLE PRECISION Y, DERY, AUX, PRMT, X, H, Z, DELT, DABS
N = 1
NDIM = 12
IHLF = 0
X = PRMT(1)
H = PRMT(3)
PRMT(5) = 0.000
DO 1 I = 1, NDIM
AUX(16, I) = 0.000
AUX(15, I) = DERY(I)
1
AUX(1, I) = Y(I)
IF (H*(PRMT(2) = X))3, 2, 4
3
IHLF = 12
GOTO 4
4
CALL FCT(X, Y, DERY)
CALL OUTP(X, Y, DERY, IHLF, NDIM, PRMT)
IF (PRMT(5))6,5, 6
5
IF (IHLF)7, 7, 6
7
RETURN
8
END
22 6 RETURN
23 7 DO & I=1,NDIM
24 8 AUX(8,1)=DERY(I)
25 9 ISW=1
26 GOTO 100
27 10 AUX(2,1)=Y(1)
28 11 IHFL=IHFL+1
29 X=X+H
30 DO 10 I=1,NDIM
31 12 AUX(4,1)=AUX(2,1)
32 H=.5D0*H
33 N=1
34 ISW=2
35 GOTO 100
36 13 X=X+H
37 CALL FCT(X,Y,DERY)
38 N=2
39 DO 14 I=1,NDIM
40 10 AUX(2,1)=Y(I)
41 11 AUX(9,1)=DERY(I)
42 ISW=3
43 GOTO 100
44 15 DELT=0.0 D0
45 16 DELT=DELT+AUX(15,1)*DBYS(Y(I)-AUX(4,1))
46 17 IF(IHFL=10)11,18,18
47 18 IHFL=11
48 19 X=X+H
49 CALL FCT(X,Y,DERY)
50 DO 20 I=1,NDIM
51 20 AUX(3,1)=Y(I)
52 21 AUX(10,1)=DERY(I)
53 N=3
54 ISW=4
55 GOTO 100
56 22 Y(I)=AUX(1,1)+H*(.375D0*AUX(8,1)+.7916666666666667DC*AUX(9,1))
57 23 X=X+H
58 N=N+1
59 CALL FCT(X,Y,DERY)
60 X=PRMT(I)
61 DO 22 I=1,NDIM
62 22 AUX(11,1)=DERY(I)
63 23 Y(I)=AUX(1,1)+.3333333333333333D0*H*(AUX(8,1)+DELT+DELT(9,1))
64 CALL OUTP(X,Y,DERY,IHFL,NDIM,PRMT)
65 IF(PRMT(5))6,24,6
66 10 DO 26 I=1,NDIM
67 26 AUX(N+7,1)=DERY(I)
68 IF(N=3)27,29,200
69 27 DO 28 I=1,NDIM
70 28 DELT=AUX(9,1)+AUX(10,1)
71 29 X=X+H
72 N=N+1
73 CALL FCT(X,Y,DERY)
74 CALL OUTP(X,Y,DERY,IHFL,NDIM,PRMT)
75 IF(PRMT(5))6,24,6
76 24 DO (N=4)25,260,200
77 25 DO 26 I=1,NDIM
78 26 AUX(N+7,1)=DERY(I)
79 IF(N=3)27,29,200
80 27 DO 28 I=1,NDIM
81 28 DELT=AUX(9,1)+AUX(10,1)
82 29 X=X+H
83 CALL FCT(X,Y,DERY)
84 30 DO (N=3)27,29,200
85 29 CALL OUTP(X,Y,DERY,IHFL,NDIM,PRMT)
86 30 DO 28 I=1,NDIM
87 28 DELT=AUX(9,1)+AUX(10,1)
DELTAUX(9,1) + pdiX(10.1) + DELTYELT + DELTYELT

Y(1) = AUX(1,1) + 3.75000 * H * (AUX(3,1) + DELT + AUX(11,1))

DO 23 I = 1, NDIM

Z = H * AUX(N+7,1)
AUX(5,1) = Z

DO 101 I = 1, NDIM

Z = x + 4.00 * H
CALL FCT(Z, Y, DERY)
DO 102 I = 1, NDIM
Z = H * DER(1)
AUX(6,1) = Z

DO 102 Y(1) = AUX(N,1) + 0.29697769247753600 * AUX(5,1) + 0.15875964497103593
Z = x + 4.55737254218789430 * H
CALL FCT(Z, Y, DER)
DO 103 I = 1, NDIM
Z = H * DER(1)
AUX(7,1) = Z

DO 103 Y(1) = AUX(N,1) + 2181603082259204700 * AUX(5,1) - 0.0509651486929308
AUX(6,1) = 0.83264766467013000 * Z
Z = x + H
CALL FCT(Z, Y, DER)
DO 104 I = 1, NDIM
Z = 1.747602322626903700 * AUX(5,1) - 0.55148066287873294
AUX(6,1) + 1.2055359393523500 * AUX(7,1) + 1.711347812195190300
Z = x + 40.00000000000000000
CALL FCT(Z, Y, DER)
DO 105 I = 1, NDIM
Z = H * DER(1)
AUX(8,1) = Z

DO 105 Y(1) = AUX(N,1) + 0.17476023?2626903700 * AUX(5,1) - 0.5514 806628773 294
AUX(6,1) + 1.2055359393523500 * AUX(7,1) + 0.17113473l2195190300
Z = x + H...
154 218 IF(ISTEP=4)201,219,219
155 219 I=STEP/2
156 219 IF(ISTEP=MOD=MOD)201,220,201
157 220 H=H+H
158 220 IHLF=IHLF+1
159 220 ISTEP=0
160 DO 221 I=1,NDIM
161 AUX(N-1.I)=AUX(N-2.I)
162 AUX(N-2.I)=AUX(N-4.I)
163 AUX(N-3.I)=AUX(N-6.I)
164 AUX(N-6.I)=AUX(N-5.I)
165 AUX(N+5.I)=AUX(N+3.I)
166 AUX(N+4.I)=AUX(N+1.I)
167 DELT=AUX(N+6.I)+AUX(N+5.I)
168 DELT=DELT+DELT+DELT
169 221 AUX(16.I)=8.96296296262629663DO*(Y(I)=AUX(N-3.I))
170 1-3.3611111111111111D0*H*(DERY(I)+DELT+AUX(N+4.I))
171 GOTO 201
172 222 IHLF=IHLF+1
173 IF(IHLF=10)223,223,210
174 223 H=.5D0*H
175 ISTEP=0
176 DO 224 I=1,NDIM
177 DY(I)=3.39025D0-2*(8.D1*AUX(N-1,I)+135.D0*AUX(N-2,I)+4.D1*AUX(N-4,I)+15.D0*AUX(N-6,I)+17.D0*AUX(N-5,I)-AUX(N+1.I))
178 1108.DO*AUX(N+4.I)+AUX(N+5.I))=-.023375D0*(AUX(N+6,I)+
179 224 DO*AUX(N+5.I)+AUX(N+4.I))
180 CALL FCT(DELT,Y,DERY)
181 DO 225 I=1,NDIM
182 AUX(N-3,I)=AUX(N-2,I)
183 AUX(N+4,I)=AUX(N+5,I)
184 DELT=X-(H+H)
185 CALL FCT(DELT,Y,DERY)
186 DO 225 I=1,NDIM
187 AUX(N-2,I)=Y(I)
188 AUX(N+5,I)=DERY(I)
190 225 Y(I)=AUX(N-4,I)
191 DELT=DELT-(H+H)
192 CALL FCT(DELT,Y,DERY)
193 DO 226 I=1,NDIM
194 DELT=AUX(N+5,I)+AUX(N+4,I)
195 DELT=DELT+DELT+DELT
196 226 DO*AUX(16,I)=8.96296296262629663DO*(AUX(N-1.I)=Y(I))
197 1-3.3611111111111111D0*H*(AUX(N+6,I)+DELT+DERY(I))
199 GOTO 206
200 END

SUBROUTINE POTFUN(T,C,CDOT)

******************************************************************************

* PURPOSE -
* EVALUATES DH/RO(I) AND DH/JP(I) DURING INTEGRATION

******************************************************************************

IMPLICIT REAL*8(A-H,L,N,O-Z)
COMMON/ELK01/HA,MB,MH
COMMON/ELK02/RMOL,M1,RMOL,LU1,LU2,LMU1,LMU2
COMMON/POTPAR.A,B
COMMON/ELK05/BETAAB,BETABC,BETABC,DAB,DAC,DBC,R01,R02,R03
COMMON/ELK14/S,SS
COMMON/ELK35/TRED
COMMON/BLK40/IFLAG
COMMON/BLK99/ISUM1
DIMENSION C(12),CDOT(12),PDOT(6),QDOT(6)
DIMENSION DR1DO(6),DR2DO(6),DR3DO(6)
ISUM1=ISUM1+1
Z1=C(1)+S*C(4)
Z2=C(2)+S*C(5)
Z3=C(3)+S*C(6)
R1=DSQRT(Z1*Z1+Z2*Z2+Z3*Z3)
X1=C(1)-S*S*C(4)
X2=C(2)-S*S*C(5)
X3=C(3)-S*S*C(6)
R2=DSQRT(C(4)*C(4)+C(5)*C(5)+C(6)*C(6))
R3=DSQRT((X1*X1+X2*X2+X3*X3)
RR1=1/R1
RR2=1/R2
RR3=1/R3
MORSAB=DEXP(-BETAAB*(R1-R01))
MORSAC=DEXP(-BETAAC*(R3-R03))
MORSBC=DEXP(-BETABC*(R2-R02))
HYPTAB=DTAH(A*A+1+B)
HYPTAC=DTAH(A*A+3+B)
ENTRY 14AMPOT (H:AM)
MORSBC=EXP(_BETA5C*(R2-R02))
MORSAB=EXP(_BETAAB*(R1-R01))
MORSAC=EXP(_BETAAC*(R3-R03))
MORSBC=EXP(_BETA5C*(R2-R02))
4 HYPTAB=DTAH(A*A+1+B)
5 HYPTAC=DTAH(A*A+3+B)
6 ENTRY HAMPO T (H:HM)
7 POTABC=AB*MORSAB*(MORSBC=2.000)+DAC*MORSAC
8 1+DBC*MORSBC*(MORSBC=1.000)*HYPTAB
9 POTABC=AB*MORSAB*(MORSBC=2.000)+DAC*MORSAC
10 1+DBC*MORSBC*(MORSBC=1.000)*HYPTAC
11 POTABC=POTABC/0.344560029
12 POTABC=POTABC/0.344560029
13 C V NOW IN UNITS OF EV
14 Z=POTABC-POTABC
15 IF (Z.LE.0.0DO) GOTO 11
16 POT=POTABC
17 GOTO 22
18 22 CONTINUE
19 S1=0
20 S2=0
21 DO 21 J=1,3
22 S1=(C(J+6)*TRED*0.529177D-8)**2
23 S2=(C(J+9)*TRED*0.529177D-8)**2
24 21 CONTINUE
25 S1=S1*0.103641D11
26 S2=S2*0.103641D11
27 IF (IFLAG.E(4.1) GOTO 7
28 RETURN
29 7 CONTINUE
30 IF (Z ..LE .0 • 0 DO) GOTO 10
31 D VDR3=4.0*DAC*BETAAC*(1.0D0-MORSAC)*MORSAC
32 1+DBC*MORSBC*A*(1.0D0-HYPTAB)*HYPTAC
33 D VDR2=DBC*MORSBC+BETABC*(1.0D0-Z.DO*MORSBC+HYPTAC)
34 D VDR1=BETABC*DAB*MORSAB
35 GO TO 8
36 8 CONTINUE
37 D VDR1=2.0DO*DAB*BETABC*(1.0D0-MORSAB)*MORSAB
38 1+DBC*MORSBC*A*(1.0D0-HYPTAB)*HYPTAB
39 D VDR2=DBC*MORSBC+BETABC*(1.0D0-Z.DO*MORSBC+HYPTAB)
40 D VDR3=BETABC*DAB*MORSAC
41 9 CONTINUE
42 D R10Q(1)=RR1*Z1
43 D R1DO(Z)=RR1*Z2
44 D R1DO(3)=RR1*Z3
45 SRR1=S*RR1
46 D R10Q(4)=Z1*SRR1
47 D R1DO(5)=Z2*SRR1
48 D R1DO(6)=Z3*SRR1
**SUBROUTINE SOLVE(P,Q,PRMT,CDOT)**

* PURPOSE -

* PREPARES VALUES FOR INTEGRATION BY LIBRARY SUBROUTINE

*-----------------------------------------------*

EXTERNAL POTFUN,CONTRL
DOUBLE PRECISION TRED,PRMT,CDOT
DIMENSION P(6),Q(6),C(12),PRMT(5),CDOT(12)
COMMON/BLK35/TRED
WRITE(4) P,Q
DO 1 J=1,6
 C(J)=Q(J)
 C(J+6)=P(J)/TRED
 1 CONTINUE
 CALL INTEGR(C,POTFUN,CONTRL,PRMT,CDOT)
DO 2 J=1,6
 Q(J)=C(J)
 P(J)=C(J+6)*TRED
 2 CONTINUE
 WRITE(4) P,Q
 CALL INTCHEK
RETURN
END

**SUBROUTINE START(P,Q,PRMT,CDOT,LOOP,IK,MJ)**

* PURPOSE -

* CALCULATES STARTING VALUES OF Q(1) ... Q(6), P(1) ... P(6)

*-----------------------------------------------*

REAL MOMIN
DOUBLE PRECISION MA,MB,MC,MMOH,MA,MMOH,NU1,NU2,NU1,NU2,PR
DOUBLE PRECISION CDOT,CMOH,BETAAB,BETACD,BETABC
DOUBLE PRECISION DAB, DAC, DBC, A, B, R01, R02, R03
DOBLE PRECISION TRED, S, SS
COMMON/BLK01/HA, HB, MC
COMMON/BLK02/MMOL, MMOL, NU1, MU2, RMU1, RMU2
COMMON/POTPAR/A, B
COMMON/BLK05/BETAAB, BETAAC, BETABC, DAB, DAC, DBC, R01, R02, R03
COMMON/BLK09/B8
COMMON/BLK14/S, SS
COMMON/BLK16/SUM3
COMMON/BLK35/TRED
COMMON/BLK40/IFLAG
DIMENSION P(6), Q(6), PRNT(5), CDOT(12)
DATA CONV/0.3445663297, CONV1/0.3445663297/
DO 14 I=1, 12
14 CDOT(I)=1.000/12.000
PRNT(5)=0.000
C INITIALISE DATA FOR COMMON BLOCKS AND FOR SUBSEQUENT CALLS
C TO 'START'.
IF (LOOP.GT.1) GOTO 13
RELE0=.025
ISTASK=3000
PRNT(1)=0.000
PRNT(2)=300.00
PRNT(3)=PRNT(2)/ISTASK
PRNT(4)=1.00-4
MUOL=MB+MC
M=HA+MMOL
RMOL=1.0/MMOL
MU1=HA+MMOL/M
MU2=MB+MC/MMOL
RMU1=1.0/MU1
RMU2=1.0/MU2
S=HC*RMOL
SS=HB*RMOL
RELKE=RELKE*CON
DAB=DAB*CONV
DAC=DAC*CONV
DBC=DBC*CONV
BONDBC=5.137
PI=3.14159
R=17.5
H=6.626196E-34
H=H/1.6E-19
HBAR=H*CONV/(2.*PI)
AMP=BONDBC-R02
FK=2.0*DAB*BETABC*BETA3C
BETA=SQRT(FK*SGL(MU2))/HBAR
C VARIABLES SET:
(1) R=INITIAL RADIAL SEPN. OF A BT BC
(2) HBAR=K UNITS OF AMU.AU**2.5**-1
(3) AMP=SIMPLE HARMONIC VIBN. AMPLITUDE OF B-C
(4) VIBNU=ANGR. FREQ. OF ZERO-PT. MOTION
(5) BETA-GAUSSIAN DISTN. TRANSFORMATION
C PARAMETER FOR ZERO PT. WAVE FN.*SEE L.F.PHILLIPS*
(6) FK=FORCE CONSTANT FOR BC,OBTAINED FROM
C SMALL DISPLACEMENT APPROX. TO MORSE POTENTIAL.
VR=SQRT(SNL(G2.0*RELKE/MU1))
13 CONTINUE
IFLAG=1
CALL CHOOSE (ATHETA, APHI, X, JAY, ABETA)
Q(1)=R*SIN(ATHETA)*SIN(APHI)
Q(2)=R*SIN(ATHETA)*COS(APHI)
Q(3)=R*COS(ATHETA)
Q(4)=0.0
Y=G05ADF(XX)
ISUM=ISUM3+1
SQRTX=X/SQRT(BETA)
IF (ABS(AMPNOT).GT.AMP) GO TO 19
RBCDOT=R2+AMPNOT
Q(5)=-RBCNOT* SIN(ABETA)
Q(6)=+RBCNOT*COS(ABETA)
C ISUM IS COUNTER ON CALLS TO GO5ADF-FOR RERUN
C PURPOSES.
ADELTA=ARSIN(BB/R)
MUHIN=MU2*RBCNOT*RBCNOT
OME=SQRT(JAY*(JAY+1.)) *HBAR/MOMIN
VBPERP=OMEGA*RBCNOT
P(1)=-VR+H12*(COS(ADELTA)*SIN(ATHETA)*COS(APHI)=
* SIN(ADELTA)*COS(ATHETA)*COS(APHI)*SIN(X)=SIN(ADELTA)*SIN(APHI)*
+ COS(X))
P(2)=-VR+H12*(COS(ADELTA)*SIN(ATHETA)*SIN(APHI)=
* SIN(ADELTA)*COS(ATHETA)*SIN(APHI)*SIN(X)=SIN(ADELTA)*
+ COS(APHI)*S(X))
P(3)=-VR+H12*(COS(ADELTA)*COS(ATHETA) + SIN(ADELTA)*SIN(ATHETA) *
+ SIN(X))
C THIS DETERMINES WHETHER TRAJECTORY WILL BE RUN -IF IOK=0
C TRAJ. RUNS; IF IOK=1 NO GO.PURPOSE IS TO AVOID EXCESSIVELY
C LARGE VALUES IN FOLLOWING LINES
IF (ABS(P(1)).LT.1.0E12) IOK=1
IF (ABS(Q(6)).LT.1.0E-3) IOK=1
ARG=Q(5)+P(3)/Q(6)-P(2)/P(1)
DENOM=SQRT(ARG*ARG+1+Q(5)*Q(5)/(Q(6)*Q(6)))
ANGMA=ARCOS(ARG/DENOM)
IF (MJ.EQ.1) ETA=ANGMA+PI/2.0
IF (MJ.EQ.2) ETA=ANGMA
RBCDOT=SQRT(FK/SNGL(MU2)) *SQRT(AMP*AMP-AMPNOT*AMPNOT)
ISIGN=1
Y=GO5ADF(XX)
ISUM=ISUM+1
IF (Y.GT.0.0D0) ISIGN=-1
RBCDOT=ISIGN*RBCDOT
PPAR=MU2*RBCDOT
C VELOC. OF B ALONG BC IS OBTAINED FROM SIMPLE HARMONIC FORMULA
C SENSE OF VELOC. IS OBTAINED FROM RANDOM NO. GENERATOR (GAUSSIAN)
C PPAR IS MOMENTUM OF B WRT C.
P(4)=+MU2*VBPERP*COS(AETA)
P(5)=MU2*VBPERP*SIN(AETA)*COS(ABETA)+PPAR*SIN(ABETA)
P(6)= MU2*VBPERP*SIN(AETA)*SIN(ABETA)+PPAR*COS(ABETA)
RETURN
END

BLOCK DATA
DOUBLE PRECISION MA, MB, MC, DAB, DAC, DBC, R01, R02,
* A, B, BETAAB, BETAAC, BETAAB, R03
COMMON/BLK01/MA, MB, MC
COMMON/BLK04/PRNT, CDOT
COMMON/POTPAR/A, B
COMMON/BLK05/BETAAB, BETAAC, BETAAC, DAB, DAC, DBC, R01, R02, R03
COMMON/BLK35/TRED
DATA TRED/1.0D14/
DATA MA, MB, MC, *
*/ 16.0000, 126.9000, 126.9000,
DATA BETAAB, BETAAC, BETAAC, *
+ 1.269000, 1.269000, 1.269000,
DATA DAB, DAC, DBC,
+ 2.301000, 2.301000, 1.545000,
DATA A, B/1.0000, -3.5000,
DATA R01, R02, R03,
+ 3.530000, 5.047000, 3.530000,
C IMPLICIT REAL(L,M)
REAL*8 TEND,EOCE,A,B
DIMENSION PIN(6),QIN(6),PFI(6),GFI(6)
COMMON/BLK01/PIN,QIN,PFI,GFI
COMMON/BLK02/HA,MB,MC,RMUAB,RMUAC,RMUBC,MTOT,MAB,MAC,MBC
COMMON/BLK03/LIORTX,LIORBY,LIORBZ,LIORR
COMMON/BLK04/LIOTX,LIOTY,LIOTZ,LIOT
COMMON/BLK05/HAM,LIN
COMMON/ENDTIM/TEND
COMMON/POTPAR/A,B
DATA CONV/0.344560E29/

C READ IN POTENTIAL PARAMETER B

C RE WIND 4
READ(4,ERR=10,END=20) IBATCH,B,IMJ
WRITE(6,601) IBATCH,B,IMJ
601 FORMAT('1',//,///,/',0',
2'***********************************************************************/
8' * ANALYSIS OF BATCH ',13,5X,'*/
&' * A = 1.0000
&' * B = 'N 5.2, 2.0X, '*/'
&' * MJ STATE 'N 12, 15X, '*/'
&' * **********************************')

A = 1.0000
MA = 16.000
MB = 126.910
MC = 126.910
MAC = MA + MB
MAB = MA + MB
MBC = MB + MC
RMUAB = 1.0/MA + 1.0/MB
RMUBC = 1.0/MB + 1.0/MB
MTOT = MA + MB + MC
RMUABC = 1.0/MA + 1.0/MB + 1.0/MBC

C NOW READ IN INFORMATION FROM DISK

1 READ(4, ERR=10, END=20) ILOOP, B6, IOK
IF (I0K .EQ. 1) GOTO 1
READ(4, ERR=10, END=20) PIN, QIN
READ(4, ERR=10, END=20) PFI, OFI
READ(4, ERR=10, END=20) IHFTOT, IMARK, TEND, ECODE, IHLF
READ(4, ERR=10, END=20) SUM1, SUM2
WRITE(6, 600) B6, ILOOP, IHFTOT, IHLF, ECODE, IMARK

600 FORMAT('1', 'IMPACT PARAMETER', F6.1/
&'0', 'TRAJECTORY NO.', I4/
&'OTOTAL BISECTIONS', I5/'FINAL HALVING STATE', I4/
&'END CODE', F6.1/'ENERGY CONSERVATION', I3)
IF (IHLF .GE. 11) WRITE(6, 107) IHLF.
IF (IHLF .GE. 11) GOTO 1

C ECODE=1,000 => BAD H CONSERVATION (<1 IN 1000)

IF (ECODE .EQ. 1,000) WRITE(6, 118) ILOOP, ECODE
IF (ECODE .EQ. 1,000) GOTO 1

C INITIAL ORBITAL & ROTATIONAL Angular Momentum Compt.

LIORBX = QIN(2) * PIN(3) - QIN(3) * PIN(2)
LIORY = QIN(3) * PIN(1) - QIN(1) * PIN(3)
LIORZ = QIN(1) * PIN(2) - QIN(2) * PIN(1)
LIORX = QIN(5) * PIN(6) - QIN(6) * PIN(5)
LIOTX = QIN(6) * PIN(4) - QIN(4) * PIN(6)
LIOTZ = QIN(4) * PIN(5) - QIN(5) * PIN(4)
LIOR = SQRT(LIORBX**2 + LIORBY**2 + LIORZ**2)
LIROT = SQRT(LIOTX**2 + LIOTY**2 + LIOTZ**2)
LIN = (LIORBX * LIOTX)**2 + (LIORBY * LIOTY)**2 + (LIORZ * LIOTZ)**2
LIN = SQRT(LIN)

C INTER-PARTICLE DISTANCES CALCULATED PRODUCT OF COLLISION
C TAKEN AS THAT PARTICLE-PAIR WITH SMALLEST SEPARATION.
C THIS MAY BE INVALID IF TRAJECTORY IS STILL SNARLING
C AT T='INFINITY' OR IF DISSOCIATIVE SCATTERING RESULTS!

A5 = 0.
AC = 0.
BC = 0.
ABNOT = 0.0
ACNOT = 0.0
BNOT = 0.0
DO 2 J = 1, 3
A5 = A5 + (MC * OFI(J+3) / MB = OFI(J))**2
AC = AC + (MB * OFI(J+3) / MB = OFI(J))**2

2 A5 = A5 + (MC * OFI(J+3) / MB = OFI(J))**2
AC = AC + (MB * OFI(J+3) / MB = OFI(J))**2
C C HAMILTONIAN EVALUATION AT T=0 AND T=END
103 C
104 HNOT=0.0
105 DO 5 1=1,3
106 HNOT=HNOT+0.5*RMUABC*PIN(I)*PIN(I)+0.5*RMUBC*PIN(I)*PIN(I+1)
107 5 CONTINUE
108 HNOT=HNOT/CONV
109 POTNOT=PQT(ABNOT,ACNOT,BCNOT)
110 HAM=HNOT+POTNOT
111 H=0.0
112 DO 4 J=1,3
113 H=H+0.5*RMUABC*PFJ(J)*PFJ(J)+0.5*RMUBC*PFJ(J)*PFJ(J+1)
114 4 CONTINUE
115 H=H/CONV
116 POTEND=POT(AB,AC,BC)
117 HAMEND=H+POTEND
118 WRITE(6,104) HAM,POTNOT,HAMEND,POTEND
119 C C TO DETERMINE NATURE OF SCATTERING PROCESS....
120 C
121 PROD=RMIN(AB,AC,BC)
122 JMARK=0
123 IF (HAM.LE.0.0) GOTO 3
124 IF (AB.GT.10.0.AND.AC.GT.10.0.AND.BC.GT.10.0) JMARK=1
125 C
126 C JMARK=0<==> NON-DISSOCIATIVE.....JMARK=1<==>DISSOCIATIVE
127 C
128 3 CONTINUE
129 IF (PROD.EQ.AB) CALL ABANDC
130 IF (PROD.EQ.AC) CALL ACANDB
131 IF (PROD.EQ.BC) CALL NUREAC(JMARK)
132 GOTO 1
133 C C FORMATS...LABELS...
134 C
135 103 FORMAT('O',12X,'(R(A)',12X,'(R(B)',12X,'(R(C)',12X,'(R(D)'/
138 104 FORMAT('INITIAL HAMILTONIAN',2X,E13.6,7X,'...POTENTIAL',2X,E13.6)
139 &'FINAL HAMILTONIAN',2X,E13.6,7X,'...POTENTIAL',2X,E13.6)
140 105 FORMAT(209.D2)
141 106 FORMAT('TOTAL INTEGRATION TIME',F6.1)
142 107 FORMAT('TRAJECTORY NOT ANALYSED...BSECTIONS=',I3)
143 108 FORMAT('TRAJECTORY NO.',13,' NOT ANALYSED BAD II CONS',
144 &' END CODE=',F4.1)
145 109 FORMAT('ERROR IN READING INPUT FILE')
146 110 FORMAT('END OF SO FILE REACHED')
147 C C CONTINUE
148 C
149 C
150 C
151 C
152 C
REAL FUNCTION POT(RAB, RAC, RBC)

IMPLICIT REAL*8 (M)
REAL*8 DRAB, DRAC, DRBC, A, B, BETAB, BETAAC, BETA3C
REAL*8 DAB, DAC, DBC, RAB, RAC, RBC, HYPTAB, HYPTAC
REAL*8 VABC, VACB, DPOT
COMMON/POTPAK/A, B
DATA BETAB, BETAAC, BETA3C/1.26900, 1.26900, 1.23200/
DATA DAE, DAC, DBE/2.30100, 2.30100, 1.54500/
DATA ROAB, ROAC, ROBC/3.53000, 3.53000, 5.04700/
DRAB=DBLE(RAB)
DRAC=DBLE(RAC)
DRBC=DBLE(RBC)
MORSAB=DEXP(-BETAB*(DRAB-ROAB))
MORSAC=DEXP(-BETAAC*(DRAC-ROAC))
MORSBC=DEXP(-BETA3C*(DRBC-ROBC))
HYPTAB=HYPTA(HA*DRAB+B)
HYPTAC=HYPTA(HA*DRAC+B)
VABC=DAB*MORSAB*(MORSAB-2.0)+DAC*MORSAC
S+DBC*MORSBC*(MORSBC-1.0-HYPTAB)
VACB=DAC*MORSAC*(MORSAC-2.0)+DAB*MORSAB
S+DBC*MORSBC*(MORSBC-1.0-HYPTAC)
IF (VABC.LE.VACB) DPOT=VABC
IF (VACB.LT.VABC) DPOT=VACB
POT=SNGL(DPOT)
RETURN
END

REAL FUNCTION RMIN(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

********************************************************************************
* COMPUTES FINAL STATE PARAMETERS FOR * 
* AB+C SYSTEM. EQUATIONS WRITTEN IN * 
* FULL IN DPF'S THESIS * 
********************************************************************************
IMPLICIT REAL (L, H)
REAL*8 TEND
DIMENSION PIN(6), QIN(6), PFI(6), GFI(6)
COMMON/BLKO1/PIN, QIN, PFI, GFI
COMMON/BLKO3/MA, MB, MC, RHUB, RHUBA, RHUBC, MTOT, MAB, MAC, NBC
COMMON/BLKOS/LIOA, LIOB, LIOC, LIORX, LIORY, LIORZ, LIORT
COMMON/BLKOS/HAM, LIN
COMMON/ENDTIM/TEND
WRITE(6, 200)
200 FORMAT(0', 'AB+C FORCED')

C TO EVALUATE TRANSLATIONAL ENERGY & SCATTERING ANGLE

ETRANS=0.

CHINUM=0.

CHDEN1=0.

CHDEN2=0.

DO 1 J=1,3

TERM=PF1(J)/HBC+PF(J+3)/HC

ETRANS=ETRANS+C.5*MTOT*MC/HAB*TERM

CHINUM=CHINUM+PIN(J)*TERM

CHDEN1=CHDEN1+TERM

CHDEN2=CHDEN2+PIN(J)*PIN(J)

1 CONTINUE

ETRANS=ETRANS/0.344565E29

CHI=ARCS(CHINUM/SQRT(CHDEN1*CHDEN2))

CHI=CHI*180./3.14159

C ETRANS IN EV; CHI IN DEGREES

C LFORB(X,Y,Z) IS FINAL ORBITAL ANGULAR MOMENTUM

C LFROTX(X,Y,Z) IS FINAL ROTATIONAL ANGULAR MOMENTUM

C LFORB=X=MTOT*MC/HAB*(M1*QFI(2)/MTOT*MB*QFI(5)/HBC)*

C&(PF1(3)/HBC+PF(6)/HBC)-(M1*QFI(3)/MTOT*MB*QFI(4)/HBC)*

C&&PF1(2)/HBC+PF(5)/HBC)

C LFORBY=MTOT*MC/HAB*(M1*QFI(3)/MTOT*MB*QFI(6)/HBC)*

C&(PF1(1)/HBC+PF(4)/HBC)-(M1*QFI(1)/MTOT*MB*QFI(4)/HBC)*

C&&PF1(3)/HBC+PF(6)/HBC)

C LFORBZ=MTOT*MC/HAB*(M1*QFI(1)/MTOT*MB*QFI(4)/HBC)*

C&(PF1(2)/HBC+PF(5)/HBC)-(M1*QFI(2)/MTOT*MB*QFI(5)/HBC)*

C&&PF1(3)/HBC+PF(4)/HBC)

C LFORO=SQRT(LFORBX**2+LFORBY**2+LFORBZ**2)

C LFORO=SQRT(LFOROX**2+LFROTY**2+LFROTZ**2)

C LF=SQR(LFORB)

C TO COMPUTE THE RE-ORIENTATION ANGLE OF THE FINAL ROTATIONAL ANGULAR MOMENTUM VECTOR WRT INITIAL AM VECTOR

C ANGLE1=ARCOS((LIROT*X+LFROTX)**2+(LIROT+LFROTX)**2)

C ANGLE1=180./3.14159

C TO COMPUTE THE RE-ORIENTATION ANGLE OF THE ORBITAL ANGULAR MOMENTUM VECTOR WRT INITIAL AM VECTOR

C ANGLE2=ARCOS((LIORB*X+LFORBX)**2+(LIORB+LFORBX)**2)

C ANGLE2=180./3.14159

C ROTATIONAL ENERGY APPROXIMATED TO THAT CORRESPONDING TO A RIGID ROTOR AT THE EQUILIBRIUM SEPARATION IN POTENTIAL WELL.
SUBROUTINE ACANDB

* COMPUTES FINAL STATE PROPERTIES OF * * *

* AC+B SYSTEM *

* ************************* *

IMPLICIT REAL (L,M)

REAL*8 TEND

DIMENSION PIN(6),CIN(6),PFI(6),GFI(6)

COMMON/BLK01/PIN,QN,PFI,GFI

COMMON/BLK02/MA,MB,MC,RHUB,RHUA,RHUBC,HTOT,MA3,MAC,MBC

COMMON/BLK03/LIORDX,LIOFBY,LIORBY,LIORBZ,LIRBB

COMMON/BLK04/LIOTX,LIOITY,LIOOTZ,LIOIT

COMMON/BLK05/HAM,LIN

COMMON/EINT,TEND

WRITE(6,300)

300 FORMAT('AC+B FORMED')

TO EVALUATE TRANSLATIONAL ENERGY & SCATTERING ANGLE

ETRAN=0.

CHINU=0.

CHDEN1=0.

CHDEN2=0.

DO 1 J=1,3

TERM=-PFI(J)/MB+PFI(J+3)/MB

ETRAN=ETRAN+0.5*MB*HTOT/MAC+TERM+TERM

CHINU=CHINU+TERM*PIN(J)

CHDEN1=CHDEN1+TERM+TERM

CHDEN2=CHDEN2+PIN(J)*PIN(J)

1 CONTINUE

CHI=ARCOS(CHINU/SORT(CHDEN1+CHDEN2))

CHI=CHI*180./3.14159

ETRAN=ETRAN/0.34456E29

FINAL ORBITAL & ROTATIONAL ANGULAR MOMENTUM COMPTS

LFORBX=HTOT*MB/MAC*(-MA*GFI(2)/HTOT+MC*GFI(5)/MBC)*
>&(-PFI(3)/MB+PFI(6)/MB)*(-MA*GFI(3)/HTOT+MC*GFI(6)/MBC)*
>&(-PFI(2)/MB+PFI(5)/MB))

LFORBY=HTOT*MB/MAC*(-MA*GFI(3)/HTOT+MC*GFI(6)/MBC)*
>&(-PFI(1)/MB+PFI(4)/MB)*(-MA*GFI(1)/HTOT+MC*GFI(4)/MBC)*
>&(-PFI(3)/MB+PFI(6)/MB))

LFORBZ=HTOT*MB/MAC*(-MA*GFI(1)/HTOT+MC*GFI(4)/MBC)*
>&(-PFI(2)/MB+PFI(5)/MB))

END
**Subroutine NOREAC(JMARK)**

**Computes Final State Properties**

For Case of Elastic/Inelastic or Dissociative Scattering

**Rotational Energy Approximated to that of Rigid Rotor**

At Equilibrium Separation in Potential Well

---

```
1 48 LFORBZ=MTOT+MB/MAC*(-MA*QFI(1)/MTOT+MC*QFI(4)/MBC)*
  &(-PF1(2)/MBC+PF1(5)/MB)=(-MA*QFI(2)/MTOT+MC*PF1(5)/MBC)*
  &(-PF1(1)/MBC+PF1(4)/MB))
2 49 C
3 50 C LFOROTX=MA+MC/MAC*((MB+QFI(5)/MBC+QFI(2))*(PF1(6)/MC
4 51 C &MTOT/MA+PF1(3)/MBC)-(MB+QFI(6)/MBC+QFI(3))*(PF1(5)/MC
5 52 C &MTOT/MA+PF1(2)/MBC))
6 53 C LFROTY=MA+MC/MAC*((MB+QFI(6)/MBC+QFI(3))*(PF1(4)/MC
7 54 C &MTOT/MA+PF1(1)/MBC)-(MB+QFI(4)/MBC+QFI(1))*(PF1(6)/MC
8 55 C &MTOT/MA+PF1(3)/MBC))
9 56 C LFROTZ=MA+MC/MAC*((MB+QFI(4)/MBC+QFI(1))*(PF1(5)/MC
10 57 C &MTOT/MA+PF1(2)/MBC)-(MB+QFI(5)/MBC+QFI(2))*(PF1(4)/MC
11 58 C &MTOT/MA+PF1(1)/MBC))
12 59 C LFORB=SQR(LFORBX**2+LFORBY**2+LFORBZ**2)
13 60 C LFOROT=SQR(LFOROTX**2+LFOROTY**2+LFROTY**2)
14 61 C LFO=LFORB+LFOROT+LFROTY**2+LFROTY**2+LFROTZ**2
15 62 C LF=SQR(L)
16 63 C TO COMPUTE RE-ORIENTATION ANGLE OF ANGULAR (ROTATIONAL)
17 C VECTORS BY DOT PRODUCT
18 C ANGLE1=ARCOS((LFOROTX*LFROTX+LFOROTY+LFOROTZ)
19 64 C */(LFOROT*LFROT))
20 65 C ANGLE1=ANGLE1*180/3.14159
21 66 C TO COMPUTE RE-ORIENTATION ANGLE OF ORBITAL ANGULAR MOMENTA
22 C ANGLE2=ARCOS((LORBX*LFORB+LORBY+LORBY+LORBY+LORBY+LFORBZ)
23 67 C */(LORB*LFORB))
24 68 C ANGLE2=ANGLE2*180/3.14159
25 69 C ROTATIONAL ENERGY APPROXIMATED TO THAT OF RIGID ROTOR
26 C AT EQUILIBRIUM SEPARATION IN POTENTIAL WELL
27 C DEAC=2.301
28 60 REAC=3.530
29 70 EROT=LFROT*LFROT*RHUAC/(2.0*REAC*REAC)
30 71 EROT=EROT/0.345656029
31 72 EIVB=DEAC-HAM-ETRANS-EROT
32 73 WRITE(6,100) ETRANS,EROT,EIVB,CHI,ANGLE1,ANGLE2
34 100 FORMAT('ETRANS=',F7.4,'EROT=',F7.4,'EIVB=',
35 75  &F7.4,'OESCATG.ANGLE=',F6.1,'OROTNL. AM RE-ORIEMTN.AN',E12.5,
36  76  &'OINITIAL AM RE-ORIENTN.AN',F6.1)
37 77 WRITE(6,101) LIN,LX,LORB,LFORB,LIROT,LFROT
38 101 FORMAT('OINITIAL TOTAL AM',E12.5,'OFINAL TOTAL AM',E12.5,
39 102 &OINITIAL ORBITAL AM',E12.5,'OFINAL ORBITAL AM',E12.5,
40 103 &OINITIAL ROTNL AM',E12.5,'OFINAL ROTNL AM',E12.5)
41 78 RETURN
42 END
```

---

The above code snippet is a part of a subroutine in a computational chemistry program. It calculates various properties and angles related to the final state of a reaction, such as the rotational energy, re-orientation angles of angular and orbital momenta, and their initial and final states. The subroutine also prints out these values in a formatted manner. The code is written in Fortran and includes various mathematical operations and formulas to compute these properties.
REAL*8 TEND
DIMENSION PIN(6), QI(6), PFI(6), QFI(6)
COMMON/BLK01/PIN, QI, PFI, QFI
COMMON/BLK02/MA, MB, IC, RMUA, RMUB, MTOT, MA, MB, MC
COMMON/BLK03/LIFEX, LIFBY, LIFRZ, LIOT
COMMON/BLK04/LIOTX, LIOTY, LIROTZ, LIROT
COMMON/BLK05/HAH, LIN
COMMON/ENDTIM/TEND
IF (JMARK.EQ.0) WRITE(6, 400)
IF (JMARK.EQ.1) WRITE(6, 401)

400 FORMAT('CONJ-REACTIVE')
401 FORMAT('ODISSOCIATION')

TO EVALUATE TRANSLATIONAL ENERGY & SCATTERING ANGLE

ETRANS=0.
CHINUM=0.
CHIDEN=0.
DO 1 J=1, 3
ETRANS=ETRANS+PFI(J)*PFI(J)
CHINUM=CHINUM+PIN(J)*PFI(J)
CHIDEN=CHIDEN+PIN(J)*PFI(J)
1 CONTINUE
CHI=ARCCOS(CHINUM/SQRT(CHIDEN*ETRANS))
CHI=CHI*180./3.14159
ETRANS=ETRANS+LIOT/(MA*MB)*0.5
ETRANS=ETRANS/0.344560E29

FINAL ORBITAL & ROTATIONAL ANGULAR MOMENTUM COMPONENTS

LFORBX=QFI(2)*PFI(3)-QFI(3)*PFI(2)
LFORBY=QFI(3)*PFI(1)-QFI(1)*PFI(3)
LFORBZ=QFI(1)*PFI(2)-QFI(2)*PFI(1)
LFORTX=QFI(5)*PFI(6)-QFI(6)*PFI(5)
LFORTY=QFI(6)*PFI(4)-QFI(4)*PFI(6)
LFORTZ=QFI(4)*PFI(5)-QFI(5)*PFI(4)
LFORB=SQR(T(LFORBX**2+LFORBY**2+LFORBZ**2)
LFOROT=SQRT(LFORTX**2+LFORTY**2+LFORTZ**2)
LF=(LFORBX+LFORTX)**2+(LFORBY+LFORTY)**2+(LFOREZ+LFORTZ)**2
LF=SQR(T(LF)

RE-ORIENTATIONAL ANGLE OF ROTATIONAL ANGULAR MOMENTUM

ANGLE1=ARCCOS((LIOTX*LFROTX+LIOTY*LFROTY+LIROTZ*LFROTZ)/LIROT*LFROT)
ANGLE1=ANGLE1*180./3.14159

TO COMPUTE THE RE-ORIENTATIONAL ANGLE OF ORBITAL ANGULAR MOMENTA

ANGLE2=ARCCOS((LIORBX*LFORBX+LIORBY*LFORBY+LIORDZ*LFORBZ)/LIORB*LFORB)
ANGLE2=ANGLE2*180./3.14159

SEPARATE ACCORDING TO WHETHER SCATTERING IS DISSOCIATIVE OR NOT

IF (JMARK.EQ.0) GOTO 3

TO PREERVE TAPE FORMAT DUMMY RECORDS WILL BE WRITTEN
WRITE(6,102) ETRANS, CHI, ANGLE1, ANGLE2
GOTO 2

APPROXIMATE ROTATIONAL ENERGY

3 RESC=5.047
DEBC=1.545
EROT=LFROT+LFROT+RNUBC/(2.0*REBC*REBC)
EROT=EROT/0.344560E29
EVIB=DEBC+HAB-TRANS-EROT
WRITE(6,100) ETRANS, EROT, EVIB, CHI, ANGLE1, ANGLE2
100 FORMAT( 'OETRANS=', 'F7.4/'OEROT=', 'F7.4/'OEVIB=',
 & 'USCATTO,ANGLE=', 'F6.1/''OROTHN,AM RE-ORIENTN,ANGLE=',
 & 'F6.1/''ORBITAL AM RE-ORIENTN,ANGLE=', 'F6.1')
2 WRITE(6,101) LIN, LF, LIORB, LFORB, LIROT, LFROT
101 FORMAT('OINITIAL TOTAL AM', 'E12.5/'OFINAL TOTAL AM', 'E12.5/
 &'OINITIAL ORBITAL AM', 'E12.5/'OFINAL ORBITAL AM', 'E12.5/
 &'OINITIAL ROTN,AM', 'E12.5/'OFINAL ROTN,AM', 'E12.5)
102 FORMAT('OETRANS=', 'F7.4/'OCHI=', 'F6.1/''ORANGLES=', 'F6.1/
 &'ORANGLES2=', 'F6.1')
RETURN
END

1 BLOCK DATA
2 IMPLICIT REAL (L, I)
3 REAL*8 TEND
4 DIMENSION PIN(6), QIN(6), PF1(6), QF1(6)
5 COMMON/BLK01/PIN, QIN, PF1, QF1
6 COMMON/BLK02/MA, MB, MC, RNUAB, RNUAC, RNUBC, MTOT, MAB, MAC, MBC
7 COMMON/BLK03/LIORB, LIORBY, LITORB, LITORB
8 COMMON/BLK04/LROTOX, LROTOY, LROTOZ, LROT
9 COMMON/BLK05/HAB, LIN
10 COMMON/ENDTIM/TEND
11 COMMON/POTPAR/A, B
12 DATA PIN/1.0,2.0,3.0,4.0,5.0,6.0/
13 DATA QIN/1.0,2.0,3.0,4.0,5.0,6.0/
14 DATA PF1/1.0,2.0,3.0,4.0,5.0,6.0/
15 DATA QF1/1.0,2.0,3.0,4.0,5.0,6.0/
16 DATA HAB/1.0,2.0,3.0,4.0,5.0,6.0/
17 DATA MAC, MBC/1.0,2.0,3.0,4.0,5.0,6.0,7.0,8.0,9.0,10.0/
18 DATA LIORB, LITORB, LITORB/1.0,2.0,3.0,4.0/
19 DATA LITORX, LITORY, LITORZ, LITOR/1.0,2.0,3.0,4.0/
20 DATA LIN, TEND/1.0,0.0/
21 DATA A, B/1.0,2.0/
22 END

CODE  6678 BYTES   PLT+DATA  5232 BYTES   DIAG TABLES  228 BYTES
TOTAL 11538 BYTES
COMPILATION SUCCESSFUL

MODULE NAME IS ICL9CEMAINM
TRAJECTORY NO. 23

IMPACT PARAM. 7.0

TIME AT END 557.0

FINAL HALVING STATE 0

H CONS MARKER 0

AM CONS MARKER 1

END CODE 4.0

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* NON - REACTIVE *

ORB. ANG. MOM.    | -11.2719       |
|                  | -1.7134        |
| ROTNL. ANG. MOM. | 12.4909        |
|                  | 2.9322         |
| TOTAL ANG. MOM.  | 1.2189         |
|                  | 1.2188         |
| ETRANS = 0.0015  |               |
| EROT = 0.0008    |               |
| EVIB = 0.1240    |               |
| SCATTG. ANGLE = 39.9 |          |

TRANSFER OF ORB. A.M. = 42

ROTATIONAL QUANTUM NUMBER = 12  RAM TRANSFER = -43

FRACTION OF E(TOT) INTO INTERNAL MODES 0.988

Figure 4.46 - Typical output from 2-D program without graphics
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Figure 4.47b - Time history graph accompanying Fig. 4.47a
Figure 4.48 - Elastic collision at 1.0 eV (C.M.) relative energy

Y-VALUES IN ATOMIC UNITS  X-VALUES IN SECONDS 10**14

R(AB)=C  R(AC)=B  R(HC)=A
Figure 449 - Non-reactive collision displaying short-range crossing of isosceles configuration ("X").

Y-values in atomic units, X-values in seconds, 10^14.

R(AB) = C, R(AC) = B, R(DC) = A.
Figure 4.50 - Inelastic collision following short-lived-complex interaction. The apparent complex lifetime is again increased by the low $E_t$ value.
Figure 4.51 - Highly snarled reactive trajectory. Note that isosceles crossings ("X") occur only at fairly long range.
SOLVE - This subroutine prepares the P' and Q' for integration and integrates them subject to the potential contained in subroutine POTFUN. The integration subroutine STWOD is based on the (no longer supported) IBM subroutine DHPCG. The initial and final P' and Q' are written to tape or disk in unformatted fashion. The progress of the integration is monitored by CONTRL which is regularly called by STWOD. CONTRL contains an entry TRANSF which determines the nature of the collision (reactive, dissociative etc.) The entry OPTION is called finally and this outputs a graphical time history if the collision is long-lived.

Typical output from the programs is given in Figures 4.46 - 4.51. Although crossing of the C2v configuration occurs it is never below VAC = VAB = 8 au. The diagrams convey the overall impression of the 0-atom vibrating about an I-atom in a near colinear fashion. This is best displayed in Figure 4.22.

APPENDIX D: FINAL STATE PROPERTIES

The formulae quoted in this appendix refer explicitly to the 3-D case. For the 2-D case, straightforward reduction of the 3-D formulae is necessary.

1) Interparticle separations

\[ R_{AB}^2 = \left[ Q_1 - \frac{m_C}{m_{BC}} Q_4 \right]^2 + \left[ Q_2 - \frac{m_C}{m_{BC}} Q_5 \right]^2 + \left[ Q_3 - \frac{m_C}{m_{RC}} Q_6 \right]^2 \]

\[ R_{AC}^2 = \left[ Q_1 + \frac{m_B}{m_{BC}} Q_4 \right]^2 + \left[ Q_2 + \frac{m_B}{m_{BC}} Q_5 \right]^2 + \left[ Q_3 + \frac{m_B}{m_{BC}} Q_6 \right]^2 \]

\[ R_{BC}^2 = Q_4^2 + Q_5^2 + Q_6^2 \]

............... (4.86)
(2) Angular momenta

The total angular momentum \( = \mathbf{L} + \mathbf{J} \) is given by

\[
\mathbf{L}_{\text{tot}} = \sum_{i=A,B,C} \left[ \mathbf{r}_i \times \mathbf{P}_i \right]
\]

which in the generalised co-ordinate system simplifies to

\[
\mathbf{L}_{\text{tot}} = (Q_1, Q_2, Q_3) \times (P_1, P_2, P_3) + (Q_4, Q_5, Q_6) \times (P_4, P_5, P_6)
\]

\[
\text{................. (4.87)}
\]

The Cartesian components of \( \mathbf{L}_{\text{tot}} \) are:

\[
L_x = (Q_2 P_3 - Q_3 P_2) + (Q_5 P_6 - Q_6 P_5)
\]

\[
L_y = (Q_3 P_1 - Q_1 P_3) + (Q_6 P_4 - Q_4 P_6)
\]

\[
L_z = (Q_1 P_2 - Q_2 P_1) + (Q_4 P_5 - Q_5 P_4)
\]

\[
\text{................. (4.88)}
\]

The total angular momentum is then

\[
\mathbf{L}_{\text{tot}}^2 = L_x^2 + L_y^2 + L_z^2
\]

\[
\text{................. (4.89)}
\]

Each separate term in braces in (4.88) corresponds to the orbital and rotational components respectively.
(3) **Scattering Angle**

This is defined for the atomic product of the collision as the angle between the initial and final relative velocity vectors (i.e. the relative velocity of the atom w.r.t. the molecule). It is therefore obtained from the scalar product of these two vectors.

(4) **Re-orientation Angles**

These are calculated from the initial and final RAM and OAM as for the scattering angle.

(5) **Translational Energy**

This is generally given by

\[
E_t' = \mu'/2 \cdot (v_{rel}')^2 \quad \text{............... (4.90)}
\]

where \(\mu'\) and \(v_{rel}'\) depend on the nature of the products.

(6) **Rotational/Vibrational Energy**

These are not strictly separable in classical mechanics and each varies according to the vibrational phase. As a first approximation, the rotational energy is obtained from

\[
E_{rot}' = \frac{(L_{rot}')^2}{2\mu'(r_e')^2} \quad \text{............... (4.91)}
\]

where \(L_{rot}'\) is the final RAM and \(r_e'\) is the product diatomic's equilibrium separation. The vibrational energy is then obtained from
where
\[ E'_{\text{int}} = D' + H - E'_{\text{trans}} \] .... (4.93)

with \( D' \) being the product diatomic's dissociation energy and \( H \), the Hamiltonian.

Expressions for each of the former categories (3) - (6) are given for each type of scattering: non-reactive \( (A + BC \rightarrow A + BC) \); reactive \( (A + BC \rightarrow AB + C) \) and reactive \( (A + BC \rightarrow AC + B) \). The final state characteristics have little meaning if the scattering is dissociative and this is treated separately.

A: Non-reactive scattering (subroutine NOREAC)

Scattering Angle

The initial relative velocity vector is
\[ v_R^i = \frac{1}{\mu_{A, BC}} (p_1^i, p_2^i, p_3^i) \] .... (4.94)

and the final is the same expression with the superscript 'i' replaced by 'f'. The atomic scattering angle is then given by
\[ \theta = \cos^{-1} \left[ \frac{v_R^i \cdot v_R^f}{v_R^i \cdot v_R^f} \right] \]
Using equation (4.90)

\[ E'_{\text{trans}} = \frac{1}{2} \nu_A, BC \sum_{j=1}^{3} (p_j^f)^2 \]  \hspace{1cm} \text{........... (4.96)}

Vibrational/Rotational Energy

\[ E'_{\text{vib}} = D_{BC} + H - E'_{\text{trans}} - E'_{\text{rot}} \]  \hspace{1cm} \text{...................... (4.97)}

OAM re-orientation angle (\( \Delta \phi \) (OAM))

The components of the OAM are given by the first terms in (4.88) for both reactants and products. \( \Delta \phi \) (OAM) is given by:

\[ (\text{OAM}) = \cos^{-1} \left[ \frac{(L_i^i L_x^f + L_i^i L_y^f + L_i^i L_z^f)}{L_i^i \cdot L_f^f} \right] \]  \hspace{1cm} \text{................. (4.98)}

where \( L_i^i \) and \( L_f^f \) are obtained from equation (4.89).
**RAM re-orientation angle** ($\Delta \phi \text{ (RAM)}$)

This is identical to (4.98) but with the rotational components substituted.

**B : Reaction to AB + C** (Subroutine ABANDC)

The vector from the AB centroid to C is given by

$$
Q_{AB, C}^f = -\frac{M}{m_{AB}} \left[ \frac{m_A}{M} (Q_1^f, Q_2^f, Q_3^f) + \frac{m_B}{m_{BC}} (Q_4^f, Q_5^f, Q_6^f) \right]
$$

and the corresponding momentum vector is

$$
P_{AB, C}^f = -m_C \left[ \frac{(P_1^f, P_2^f, P_3^f)}{m_{BC}} + \frac{(P_4^f, P_5^f, P_6^f)}{m_C} \right] \quad \ldots \ldots \ldots (4.99)
$$

The vector from mass B to mass A is

$$
Q_{BA}^f = -\frac{m_C}{m_{BC}} \cdot (Q_4^f, Q_5^f, Q_6^f) + (Q_1^f, Q_2^f, Q_3^f)
$$

and the corresponding momentum vector is

$$
P_{BA}^f = \frac{m_A m_B}{m_{AB}} \left[ -\frac{(P_4^f, P_5^f, P_6^f)}{m_B} + \frac{M}{m_A m_{BC}} (P_1^f, P_2^f, P_3^f) \right] \quad \ldots \ldots \ldots \ldots (4.100)
$$
Angular Momentum

\[ L^f_x = \frac{Mm_C}{m_{AB}} \left[ \frac{m_A Q_2^f}{M} + \frac{m_B Q_5^f}{m_{BC}} \right] \left[ \frac{p_3^f}{m_{BC}} + \frac{p_6^f}{m_C} \right] - \left[ \frac{m_A Q_3^f}{M} + \frac{m_B Q_6^f}{m_{BC}} \right] \left[ \frac{p_2^f}{m_{BC}} + \frac{p_5^f}{m_C} \right] \]

\[ L^f_y = \frac{Mm_C}{m_{AB}} \left[ \frac{m_A Q_3^f}{M} + \frac{m_B Q_6^f}{m_{BC}} \right] \left[ \frac{p_2^f}{m_{BC}} + \frac{p_5^f}{m_C} \right] - \left[ \frac{m_A Q_1^f}{M} + \frac{m_B Q_4^f}{m_{BC}} \right] \left[ \frac{p_3^f}{m_{BC}} + \frac{p_6^f}{m_C} \right] \]

\[ L^f_z = \frac{Mm_C}{m_{AB}} \left[ \frac{m_A Q_1^f}{M} + \frac{m_B Q_4^f}{m_{BC}} \right] \left[ \frac{p_2^f}{m_{BC}} + \frac{p_5^f}{m_C} \right] - \left[ \frac{m_A Q_2^f}{M} + \frac{m_B Q_5^f}{m_{BC}} \right] \left[ \frac{p_1^f}{m_{BC}} + \frac{p_4^f}{m_C} \right] \]

.......................... (4.101)
\[
\text{RAM: } L_f = Q_{BA}^f \times p_{BA}^f
\]

\[
L_x^f = \mu_{AB} \left[ \begin{bmatrix}
- \frac{m_c \cdot Q_5^f}{m_{BC}} + Q_2^f \\
- \frac{m_c \cdot Q_6^f}{m_{BC}} + Q_3^f
\end{bmatrix} \cdot \begin{bmatrix}
- \frac{p_6^f}{m_B} + \frac{M \cdot P_3^f}{m_A m_{BC}} \\
- \frac{p_5^f}{m_B} + \frac{M}{m_A} \cdot \frac{P_2^f}{m_{BC}}
\end{bmatrix}
\right]
\]

\[
L_y^f = \mu_{AB} \left[ \begin{bmatrix}
- \frac{m_c \cdot Q_6^f}{m_{BC}} + Q_3^f \\
- \frac{m_c \cdot Q_4^f}{m_{BC}} + Q_1^f
\end{bmatrix} \cdot \begin{bmatrix}
- \frac{p_4^f}{m_B} + \frac{M \cdot P_3^f}{m_A m_{BC}} \\
- \frac{p_5^f}{m_B} + \frac{M}{m_A} \cdot \frac{P_2^f}{m_{BC}}
\end{bmatrix}
\right]
\]

\[
L_z^f = \mu_{AB} \left[ \begin{bmatrix}
- \frac{m_c \cdot Q_4^f}{m_{BC}} + Q_1^f \\
- \frac{m_c \cdot Q_5^f}{m_{BC}} + Q_2^f
\end{bmatrix} \cdot \begin{bmatrix}
- \frac{p_4^f}{m_B} + \frac{M \cdot P_3^f}{m_A m_{BC}} \\
- \frac{p_5^f}{m_B} + \frac{M}{m_A} \cdot \frac{P_2^f}{m_{BC}}
\end{bmatrix}
\right]
\]

\[
\text{Scattering Angle}
\]

\[
\theta = \cos^{-1} \left[ \frac{p_f^i \cdot \frac{p_{AB, C} \cdot p_i}{P_{AB, C} \cdot P_{i, A, BC}}}{p_f^i \cdot \frac{p_{AB, C} \cdot p_i}{P_{AB, C} \cdot P_{i, A, BC}}} \right]
\]

Thus,

\[
\theta = \cos^{-1} \left[ \frac{- \sum_{j=1}^{3} \frac{p_j^f}{m_{BC}} \cdot \frac{p_{j+3}^f}{m_c}}{\sum_{j=1}^{3} \frac{p_j^f}{m_{BC}} + \frac{p_{j+3}^f}{m_c}} \right]^{\frac{1}{2}} \cdot \left[ \frac{3}{\sum_{j=1}^{3} (P_j^i)^2} \right]^{\frac{1}{2}}
\]

\[
\text{................. (4.102)}
\]

\[
\text{................. (4.103)}
\]
Translational Energy

\[ E'_{\text{trans}} = \frac{1}{2} \left[ \frac{P_{AB, C}^f}{m_{AB}} \right]^2 \]

\[ = \frac{1}{2} \cdot \frac{M \cdot m_C}{m_{AB}} \cdot \frac{3}{3} \sum_{\sigma=1} \left[ \frac{p_j^f}{m_{BC}} + \frac{p_{j+3}^f}{m_C} \right]^2 \]

\[ \text{......................... (4.104)} \]

Vibrational/Rotational Energy

Formed from equations (4.91) - (4.93) using Cartesian components from (4.102).

\[ \Delta \phi \text{ (OAM) and } \Delta \phi \text{ (RAM)} \]

Formed from equation (4.98) with initial components from (4.89) and final components from (4.101) and (4.102) respectively.

C: Reaction to AC + B (Subroutine ACANDB)

The relevant displacement vectors are:

\[ Q_{AC, B}^f = \frac{M}{m_{AC}} \left[ -\frac{m_A}{M} (Q_1^f, Q_2^f, Q_3^f) + \frac{m_C}{m_{BC}} (Q_4^f, Q_5^f, Q_6^f) \right] \]

\[ P_{AC, B}^f = m_B \left[ -\frac{(P_1^f, P_2^f, P_3^f)}{m_{BC}} + \frac{(P_4^f, P_5^f, P_6^f)}{m_B} \right] \]

\[ \text{......................... (4.105)} \]
\[
Q^{f}_{CA} = \frac{m_B}{m_{BC}} (Q^f_4, Q^f_5, Q^f_6) + (Q^f_1, Q^f_2, Q^f_3)
\]

\[
P^{f}_{CA} = \frac{m_A \cdot m_C}{m_{AC}} \left[ \frac{(P^f_4, P^f_5, P^f_6)}{m_C} + \frac{M}{m_A \cdot m_{BC}} (P^f_1, P^f_2, P^f_3) \right]
\]

............... (4.106)

Angular Momentum

\[
OAM: \quad L^f = Q^{f}_{AC, B} \times P^{f}_{AC, B}
\]

\[
L^f_x = \frac{Mm_B}{m_{AC}} \left[ \frac{-m_A \cdot Q^f_2 + \frac{m_C}{m_{BC}} Q^f_5}{M} \right] \left[ \frac{-p^f_3}{m_{BC}} + \frac{p^f_6}{m_B} \right] - \\
\left[ \frac{-m_A \cdot Q^f_3 + \frac{m_C}{m_{BC}} Q^f_6}{M} \right] \left[ \frac{-p^f_2}{m_{BC}} + \frac{p^f_5}{m_B} \right]
\]

\[
L^f_y = \frac{Mm_B}{m_{AC}} \left[ \frac{-m_A \cdot Q^f_3 + \frac{m_C}{m_{BC}} Q^f_6}{M} \right] \left[ \frac{-p^f_1}{m_{BC}} + \frac{p^f_4}{m_B} \right] - \\
\left[ \frac{-m_A \cdot Q^f_1 + \frac{m_C}{m_{BC}} Q^f_4}{M} \right] \left[ \frac{-p^f_3}{m_{BC}} + \frac{p^f_6}{m_B} \right]
\]

\[
L^f_z = \frac{Mm_B}{m_{AC}} \left[ \frac{-m_A \cdot Q^f_1 + \frac{m_C}{m_{BC}} Q^f_4}{M} \right] \left[ \frac{-p^f_2}{m_{BC}} + \frac{p^f_5}{m_B} \right] - \\
\left[ \frac{-m_A \cdot Q^f_2 + \frac{m_C}{m_{BC}} Q^f_5}{M} \right] \left[ \frac{-p^f_1}{m_{BC}} + \frac{p^f_4}{m_B} \right]
\]

............... (4.107)
\[ L_x^f = \mu_{AC} \left[ \left( \frac{m_B}{m_{BC}} \cdot Q_5^f + Q_2^f \right) \cdot \left( \frac{P_6^f}{m_C} + \frac{M_A}{m_A} \cdot \frac{P_3^f}{m_{BC}} \right) \right] - \left[ \left( \frac{m_B}{m_{BC}} \cdot Q_6^f + Q_3^f \right) \cdot \left( \frac{P_5^f}{m_C} + \frac{M_A}{m_A} \cdot \frac{P_2^f}{m_{BC}} \right) \right] \]

\[ L_y^f = \mu_{AC} \left[ \left( \frac{m_B}{m_{BC}} \cdot Q_6^f + Q_3^f \right) \cdot \left( \frac{P_4^f}{m_C} + \frac{M_A}{m_A} \cdot \frac{P_1^f}{m_{BC}} \right) \right] - \left[ \left( \frac{m_B}{m_{BC}} \cdot Q_4^f + Q_1^f \right) \cdot \left( \frac{P_6^f}{m_C} + \frac{M_A}{m_A} \cdot \frac{P_3^f}{m_{BC}} \right) \right] \]

\[ L_z^f = \mu_{AC} \left[ \left( \frac{m_B}{m_{BC}} \cdot Q_4^f + Q_1^f \right) \cdot \left( \frac{P_5^f}{m_C} + \frac{M_A}{m_A} \cdot \frac{P_2^f}{m_{BC}} \right) \right] - \left[ \left( \frac{m_B}{m_{BC}} \cdot Q_5^f + Q_2^f \right) \cdot \left( \frac{P_4^f}{m_C} + \frac{M_A}{m_A} \cdot \frac{P_1^f}{m_{BC}} \right) \right] \]

\[ \theta = \cos^{-1} \left( \frac{P_{AC, B}^f \cdot P_{A, BC}^i}{P_{AC, B}^f} \right) \]
\[ = \cos^{-1} \left[ \frac{\sum_{j=1}^{3} p_j^i \left( \frac{p_j}{m_{BC}} + \frac{p_{j+3}}{m_B} \right)}{\left( \frac{\sum_{j=1}^{3} (p_j^i)^2}{2} \right)^{\frac{1}{2}}} \right] \]

\[ = \cos^{-1} \left[ \frac{\sum_{j=1}^{3} p_j^i \left( \frac{p_j}{m_{BC}} + \frac{p_{j+3}}{m_B} \right)}{\left( \frac{\sum_{j=1}^{3} (p_j^i)^2}{2} \right)^{\frac{1}{2}}} \right] \]

\[ \text{Translational Energy} \]

\[ E_{\text{trans}} = \frac{1}{2} \Psi_{AC, B} \left| \frac{p_{AC, B}}{m_{AC}} \right|^2 \]

\[ = \frac{1}{2} \frac{m_B \cdot M}{m_{AC}} \sum_{j=1}^{3} \left[ -\frac{p_j^f}{m_{BC}} + \frac{p_{j+3}^f}{m_B} \right]^2 \]

\[ \text{Vibrational/Rotational Energy} \]

Formed from equations (4.91) - (4.93) using equations (4.108) for components.

\[ \Delta \phi \text{ (OAM) and } \Delta \phi \text{ (RAM)} \]

Equations (4.107) and (4.108) supply the final Cartesian components for (4.98) with the initial components from (4.89).
D : Dissociative Scattering

A test based on inter-particle distances suffices to identify the nature of the collision outcome, \( A + BC \) or \( AB + C \) or \( AC + B \).

If the Hamiltonian, \( H \), exceeds a value given by the potential of the 3-atom system with all separations infinite, then the further possibility of dissociation arises.

In the listed programs, the dissociation potential was chosen as zero. The condition for dissociation is then

\[
H > 0 \quad \text{.................. (4.111)}
\]

But

\[
H = T' + V'
\]

\[
= E'_\text{trans} + E'_\text{int} - D'
\]

i.e.

\[
E'_\text{int} = (H - E'_\text{trans}) + D' \quad \text{............. (4.112)}
\]

Two cases arise in (4.112)

(i) \( E'_\text{trans} > H \) \( \sim \) product molecule is bound.

(ii) \( E'_\text{trans} < H \) \( \sim \) product molecule is dissociated.

Thus, for any of the scattering outcomes given in sub-sections A, B and C the tests for dissociation are:
(a) Is $H > V_D$ ($R_{AB} = R_{BC} = R_{AC} = \infty$) ?

(b) If (a) is true is $E_{\text{trans}}' < (H - V_D)$ ?

Success in both (a) and (b) determine dissociation unambiguously.

Presently, the tests for dissociation in the analysis programs are based on the 3 separations exceeding a certain limit. This is obviously insufficient as remarked in 4.9.1.
CHAPTER 4. REFERENCES


11. Ref. 4, p. 176.


25. P.J. Kuntz, Chapter 2 in Ref. 22. and Chap. 3 in Ref. 23.


57. M.A.A. Clyne - personal communication to R. Grice.


59. The model of Ref. 52 has been revised by L. Holmlid and K. Rynefors, Chem. Phys., 19, 261, (1977) to allow for more than one complex dissociation channel. For a "loose" triatomic complex both versions agree.


   Note: The evidence for designating the intermediate as OI₂ is cited as Ref. 2 in the above paper. However, no trace of this reference could be found and no other citations by the cited authors could be found which related to this. Further, no report of I₂O could be found on reviewing the C.A. formula index.


118. H. Eyring and S.M. Lin, Ref. 26, Chap. 2.
129. D.G. Truhlar, P.C. Olson and C.A. Parr, J. Chem. Phys., 57, 4479, (1972). In this paper X-H-X colinear surfaces are calculated (X = Cl, Br, I) and it is seen that for the BEBO parameter 'p' < 1, bound X-H-X species are formed.
140. L.M. Raff, J. Chem. Phys., 44, 1202, (1966). The 4-body co-ordinate system for A + BCD described here appears to be the origin of the 3-body system described in the text.
143. NAG - Numerical Algorithms Group, 7, Banbury Road, Oxford, OX2 6NN.

This author has contributed a classical trajectory code "CLASTR" to Q.C.P.E., Indiana University which uses an 11th order predictor and corrector. The program number is "# 229."


L.M. Raff and R.N. Porter, Ref. 1, Chap. 1.


Note: Although reference by Polanyi has been made to a forthcoming publication co-authored by Nomura, none as yet has appeared. I am indebted to Dr. J.C. Whitehead for informing me on (b).


R. Grice, Specialist Periodical Reports of the Chemical Society - to be published.


