SPECTROSCOPIC AND KINETIC STUDIES

OF HIGHLY EXCITED DIATOMIC SPECIES

by

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A thesis presented for the degree of
Doctor of Philosophy in the
Faculty of Science at the
University of Edinburgh, 1986
DECLARATION

I hereby declare that this thesis has been composed by me, and that the work described in it is my own and was carried out at the University of Edinburgh, except where due acknowledgement is made. The thesis has not been submitted previously for any other degree.

Signed

Date 27th November 1986.
ACKNOWLEDGEMENTS

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ABSTRACT

There are at least two ion-pair states of IBr which are accessible by single photon absorption in the region 160-200nm. The lowest of these, the DO state, gives rise to two bound-free fluorescence systems in the UV/visible. This state is efficiently collisionally transferred by CF$_4$, SF$_6$ and N$_2$ to the D'2 state which lies ca. 640cm$^{-1}$ lower.

The excitation spectrum of I$_2$ in the region 175-215nm shows that a wide range of vibrational levels of the DO$_u$ state fluoresce, and that the state is not predissociated. The reaction of I$_2$(DO$_u$) with Xe to form XeI(B$^2\Sigma^+$) occurs for excitation at $\lambda \leq 190$nm, implying that there is little or no activation barrier.

Values of 27$^\pm$4, 11$^\pm$2, 7.25$^\pm$0.2 and 8.57ns were obtained for the pure radiative lifetimes of IBr(D0$^+$), IBr(D'2), I$_2$(D'2$_g$) and XeI(B$^2\Sigma^+$) respectively. The D and D' states of IBr are removed extremely efficiently by the reactive gases CH$_4$, CH$_3$Cl, C$_2$H$_6$, CH$_3$Cl and O$_2$. The non-reactive gases CF$_4$, SF$_6$ and N$_2$ do not remove IBr(D'2) but do remove IBr(D0$^+$) efficiently through interstate transfer to IBr(D'2). The various processes are rationalised in terms of a curve-crossing mechanism, where an ionic intermediate curve couples the entrance and exit channels.

CH(A$^2\Delta$) was produced from CH$_3$Br, CHBr$_3$, CH$_3$OH, (CH$_3$)$_2$CO, CH$_2$I$_2$ and C$_2$H$_2$ via multiphoton fragmentation processes. The dominant
mechanism for the unsaturated precursor molecules involves secondary photolysis of primary photofragments. Rotationally hot CH(A\textsuperscript{2}\text{\Delta}) radicals are relaxed more efficiently by H\textsubscript{2}, Ar and SF\textsubscript{6} (collision numbers = 3.5, 4 & 5 respectively) than they are by He (collision number = 8). The removal rates determined for CH(A\textsuperscript{2}\text{\Delta}) with CH\textsubscript{4}, H\textsubscript{2}, O\textsubscript{2} and N\textsubscript{2} are all slower than those with ground state CH radicals.
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## CHAPTER 1 - INTRODUCTION

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GENERAL INTRODUCTION

The work presented herein comprises spectroscopic and kinetic observations of processes involving highly excited electronic states of diatomic molecules. The species studied include ion-pair states of halogen molecules, I₂(D0⁺), I₂(D'2g), IBr(D0⁺), IBr(D'2) and the A²Δ state of the CH radical. The unusual chemical and physical properties of the halogen ion-pair states merit attention, particularly with reference to the development of UV lasers, while study of the CH radical is necessary if we are to develop our understanding of such diverse chemical and physical environments as those of flames and comets.

The ion-pair states were produced by single photon absorption in the far ultraviolet. When excited in the presence of a foreign gas, one or more of the following processes resulted:
1. Radiative decay to a (lower) valence state;
2. Physical quenching to the ground state or a lower valence state;
3. Chemical reaction;
4. Collisional transfer to another ion-pair state.

When step 4 was operative, the resultant ion-pair state subsequently underwent some combination of steps 1, 2 and 3.

The CH(A²Δ) radical was produced in the fragmentation of multiphoton excited parent molecules (ie molecules excited by the absorption of two or more photons), and monitored via the A²Δ→X²Π emission band centred at 431nm. Quenching and reactive processes were studied by the addition of foreign gases.

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In the past, limitations imposed by instrumentation have greatly hindered detailed studies of such highly excited species. However, recent technological advances have opened up many new fields of research. The range of molecular states and phenomena under study is expanding, with observations increasingly being made on individual rovibronic levels. Pulsed UV lasers and synchrotron radiation (two major developments from the photochemists point of view) were utilised as excitation sources for most of the work reported here. Both of these have several features which make them ideal tools for spectroscopic and kinetic studies (see Table 1.1).

The excimer laser produces extremely powerful pulses of UV radiation at a fixed wavelength in a narrow bandwidth. The pulse duration is short and the beam divergence is small. As a result of the high intensity, multiphoton processes can compete with single photon absorption, and the production of highly excited states lying in the vacuum UV ($\lambda \leq 200\text{nm}$) by this means eliminates the need to use VUV transmitting optical materials and high vacuum techniques.

Using synchrotron radiation it is possible to tune through wide regions of the electromagnetic spectrum. The light beam is highly polarised, and has a well defined time structure of extremely short pulses. Although the beam is much lower in intensity, a very high repetition rate enables rapid data acquisition in certain types of experiments.
TABLE 1.1: Comparison between some features of a typical excimer laser operating on the ArF transition, and those of the Synchrotron Radiation Source at Daresbury.

<table>
<thead>
<tr>
<th>Feature</th>
<th>ArF Laser</th>
<th>Synchrotron Radiation Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>193</td>
<td>Tunable from X-rays to IR</td>
</tr>
<tr>
<td>Bandwidth (nm)</td>
<td>1</td>
<td>0.004 - 3</td>
</tr>
<tr>
<td>Pulse energy (mJ)</td>
<td>100 - 400</td>
<td>1.2 x 10^{-10}</td>
</tr>
<tr>
<td>Pulse duration (S)</td>
<td>1.5 x 10^{-8}</td>
<td>5 x 10^{8} in multi-bunch mode</td>
</tr>
<tr>
<td>Repetition rate (Hz)</td>
<td>0.25 - 20</td>
<td>3.125 x 10^{6} in single bunch mode</td>
</tr>
</tbody>
</table>
The electronic states of halogen molecules fall into three categories: the valence states, the ion-pair states, and the Rydberg states. The potential energy curves for some of these are represented in Figure 1.1.

The low lying electronically excited states ($E \approx 20000 \text{ cm}^{-1}$ in the case of $I_2$) are of valence character, i.e. in the dissociation limit they give atoms in either their ground state ($^2P_{3/2}$) or spin-orbit excited state ($^2P_{1/2}$). These valence states, and particularly the $B^0u^+_x$ state of $I_2$, have been extensively studied providing a good understanding of their spectroscopic $^1$-6 and collisional quenching $^7$-10 properties.

Over 70 years ago McLennan $^{11,12}$ first identified the $I_2$ absorption in the UV at $\lambda = 180-200\text{nm}$ using various light sources and filters. This absorption has been assigned $^{13}$ to the $D^0u^+_x \leftrightarrow X^0g^+$ transition. Some years later Duschinsky and Pringsheim $^{14}$, while conducting a similar experiment, noted that the addition of He or Ne to the $I_2$ sample gave rise to a strong fluorescence near 340nm. This emission band is known to originate from the $D'2g \rightarrow A'2u$ transition. The D and D' states are examples of ion-pair states, however it is only recently that these and other similar higher lying electronic states have received much attention. Much of the impetus for recent studies has come from rapidly advancing technology, particularly that associated with lasers operating in the UV and visible.
Figure 1.1: Selected electronic states of I₂

(Taken from M A MacDonald, Ph.D. thesis, 1984)
As these states (E ≥ 40000 cm⁻¹) are ion-pair in character¹³ (ie they correlate with X⁺ + X(Y)⁻ in the diabatic dissociation limit), they are expected to exhibit behaviour which differs markedly from their valence-counterparts. An example which bears this out is the efficiency of the reaction of I₂(DO⁺) with CH₄ and CH₃Cl¹⁷,¹⁸, in sharp contrast to I₂(BO⁺). In fact I₂(DO⁺) is so reactive that it can break extremely strong C - F bonds¹⁹ (Bond Energy = 485KJmol⁻¹) to form radicals.

One of the areas of great interest in the ion-pair states stems from the possible development of halogen lasers. A decade ago several groups demonstrated the possibility of an I₂ laser operating on the D'2g → A'2u transition at 342nm using electron beam excitation²⁰-²². Using the same technique the analogous Br₂ laser²₃,²₄ (operating at 291nm) and a range of interhalogen lasers²₅,₂₆ have been investigated. Figure 1.2 shows the potential energy curves for an interhalogen laser. More recently the possibility of an efficient optically pumped I₂ laser has been investigated²⁷,²₈. This 4-level laser system is represented schematically in Figure 1.3. Optical excitation of the DO⁺ state is very efficient for 180nm < λ < 200nm making the ArF excimer laser (operating at 193nm) a suitable pump source. The DO⁺ state is coupled by rapid collisional relaxation to the D'2g state, which is believed to be the lowest of the ion-pair states¹⁵,²₉. Relaxation is efficiently accomplished by the addition of moderate pressures of inert gases. The D'2g state is vibrationally and rotationally relaxed by inert gases, but only very weakly quenched³₀-³₂.
Figure 1.2: Potential curve diagram of an interhalogen laser molecule, XY
Figure 1.3: Optically pumped $I_2$ laser (schematic)
In some cases excitation of halogen ion-pair states in the presence of rare gases can provide an alternative route in the production of rare gas-halide exciplexes, which are important in the development of pulsed UV laser systems. The pathway involving an electronically excited rare gas atom (RG*) and a ground state halogen molecule or halogen containing molecule, eg.

\[
\text{RG}^* + \text{X}_2 \rightarrow \text{RG} - \text{X}^* + \text{X} \quad -(1.1)
\]

has been studied extensively\textsuperscript{33-38} and is the basis of commercially available excimer laser systems. However, the complementary pathway may prove to be a viable alternative for some systems; the reaction

\[
\text{IBr(D)} + \text{Xe} \rightarrow \text{XeBr(B)} + \text{I} \quad -(1.2)
\]

has been shown to produce XeBr* efficiently\textsuperscript{39} (quantum yield = 30%).

The electronic configuration of the ion-pair states correspond to the promotion of one or two electrons in the filled orbitals of the ground state (\(\ldots (5p\sigma_g)^2(5p\pi_u)^4(5p\pi_g)^4\) for I\(_2\)) to a vacant \(\sigma^*\) orbital (the 5p \(\sigma_u^*\) orbital in the case of I\(_2\))\textsuperscript{40}. As previously mentioned, the behaviour of these states differs greatly from that of the lower valence states. This is mainly due to the potentials (see Figure 1.1): the two charges in the
ion-pair attract each other electrostatically and so the attractive part of the potential is of the form \( r^{-1} \left( \frac{e^2}{4 \pi \epsilon_0 r} \right) \), c.f. \( r^{-6} \) for the lower valence states. This results in a deeply bound potential with a gently sloping attractive limb reaching the dissociation limit at a large separation. The vibrational spacings are small, compared with the valence states, and converge very slowly towards the dissociation limit due to the uniformity of the gradient of the potential in the attractive and repulsive limbs. For comparison, typical values of some parameters are given in Table 1.2, taking \( \text{I}_2 \) as an example.

<table>
<thead>
<tr>
<th>( \text{I}_2(\text{XO}^+) )</th>
<th>( \text{I}_2(\text{Ion-pair state}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_e (\text{Å}) )</td>
<td>2.67</td>
</tr>
<tr>
<td>( D_0 (\text{eV}) )</td>
<td>1.542</td>
</tr>
<tr>
<td>( \omega_e (\text{cm}^{-1}) )</td>
<td>214</td>
</tr>
<tr>
<td>( \omega_{e'x} (\text{cm}^{-1}) )</td>
<td>0.614</td>
</tr>
</tbody>
</table>

Table 1.2: Some parameters for \( \text{I}_2(\text{XO}^+) \) compared to typical values for the ion-pair states correlating with \( \text{I}^-(1S) + \text{I}^+(3P_2) \). Data taken from KP Huber and G Herzberg, "Molecular structure and molecular spectra Vol. 4, Constants of diatomic molecules" (Van Nostrand, Princeton, 1979).
As the predominant ionic attraction term, $e^2 / 4\pi \epsilon_0 r$, does not discriminate between the different ion-pair states they all have virtually identical shapes and are nested within one another (the only crossings that need be considered are those with neighbouring Rydberg states). Another consequence of this is that the members of any group of ion-pair states (ie. states correlating in the diabatic dissociation limit with a particular pair of ions such as $X^{-}(1S) + X^+(3P_2)$) will have similar term values. The close (energetic) proximity of the lowest group of $I_2$ ion-pair states coupled with the small vibrational spacings within the states facilitates the extremely efficient collisional transfer process:

$$I_2(D_0 u^+, v^\prime) + M \rightarrow I_2(D'2g, \text{thermalised } v^\prime) + M \quad -(1.3)$$

which creates the necessary population inversion for the $I_2$ laser.

In fact it is reasonable to assume that all the states within the lowest group will be collisionally coupled to each other, but will only be very weakly quenched (ie. transferred to lower valence states). Thus in the presence of a large excess of inert gas the lowest state within the group should be dominantly populated, provided that its term value is lowest by a margin greater than $kT$. This, together with the fact that all of the ion-pair states are expected to have at least one strong transition to the valence states\textsuperscript{13}, supports the assertion that the $D'2g$ state is lowest. This is borne out experimentally and a term value of 40388 cm\textsuperscript{-1} has been determined for the $D'2g$ state\textsuperscript{16,41}, while one of 40821 cm\textsuperscript{-1} has been determined for the next lowest $\beta 1g$ state\textsuperscript{42} of $I_2$. 

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Provided that the selection rules permit single-photon transitions from the ground state, the large equilibrium bond lengths of the ion-pair states dictate that the resultant excited species will be highly vibrationally excited (eg \( v' \approx 140 \) for \( I_2^+(D_0^+) \) excited at 193nm). Single-photon studies have been largely restricted to the \( D_0^+/(D_0^+) \) state (and states collisionally populated therefrom) in the case of \( I_2 \)\(^{17,18,28,32,43-45} \) and \( IBr \)^{39,46}.

Restrictions imposed by the selection rules and Franck-Condon factors can be overcome by probing the states in two-step multiphoton transitions through an intermediate state (usually \( B_0^+/B_0^+ \)). A variety of multiphoton processes have been devised, giving access to many of the other ion-pair states. Thus, for \( I_2 \), gerade states have been accessed via two-photon processes\(^{47-50} \), while the \( F'O_u^+ \) state has been accessed via a three-photon process\(^{51} \). A summary of the spectroscopic investigations of \( I_2 \) ion-pair states has been given by Tellinghuisen\(^{52} \). By comparison the ion-pair states of \( IBr \), excepting the \( D_0^+ \) and \( D'2 \) states, have received little attention\(^{53,54} \).

Finally, the Rydberg states lie above the minima of the ion-pair states (\( E \geq 50000 \text{ cm}^{-1} \) for \( I_2 \)) and are similar to the lower valence states but with an (essentially) non-bonding electron excited into an orbital with a higher principal quantum number. Their interactions with the ion-pair states give rise to complex spectra, but they are not expected to be efficiently collisionally coupled with the ion-pair states due to their different character.
1.3 ELECTRONIC STATES OF HALOGENS: NOMENCLATURE

In diatomic molecules composed of two light atoms, spin-orbit coupling is small and the conventional $(\Lambda, \Sigma)$ notation scheme provides a valid description of the molecular electronic states. Under this scheme a molecule is described by three main quantum numbers in the format $2\Sigma^+\Lambda \Omega$ where $(2\Sigma^\pm)$ is the electron spin multiplicity, $\Lambda$ is the orbital angular momentum, and $\Omega$ is the total electronic angular momentum ($\Omega = |\Lambda + \Sigma|$, $|\Lambda + \Sigma| - 1, \ldots, |\Lambda - \Sigma|$).

A further small splitting occurs between pairs of 'degenerate' $\Omega = 0$ states when symmetry is taken into consideration: reflection in a plane which contains the nuclei will either leave the electronic wave function unchanged (denoted +) or produce a sign inversion (denoted -) giving, for example $\Sigma^+/\Sigma^-, \Pi^+/\Pi^-$ states. For degenerate states with $\Omega > 0$, no such distinction arises. Finally, electronic states of homonuclear diatomics can be further characterised according to whether or not the sign of the wavefunction is changed upon inversion through the centre of symmetry. The electronic wavefunction can be either even (no change of sign, denoted by subscript g) or odd (change of sign, denoted by subscript u) with respect to this operation.

In diatomic molecules composed of heavy atoms (e.g. Br$_2$, I$_2$, IBr), electrons experience a greater magnetic field due to their presence in greater numbers, giving rise to considerable spin-orbit coupling. In these cases $\Omega$ is the only meaningful
quantum number with $\Sigma$ and $\Lambda$ becoming redundant, and the designation of electronic states takes the format $\Omega^+/-_g/u$ (or $\Omega^+/-$ in the case of heteronuclear diatomics).

The ion-pair states of the halogen molecules correlate with $X^+X^-$ ($X^+Y^-$ in the case of interhalogens) in the dissociation limit. By considering the combination of the two ions to form a molecule, the electronic states which arise can be deduced.

1.4 THE ION-PAIR STATES OF I$_2$

The ion-pair states of I$_2$ dissociate to $I^+([\text{Kr}]5s^24d^{10}5p^4)$ plus $I^-([\text{Kr}]5s^24d^{10}5p^6)$. In order of increasing energy, the electronic states of $I^+$ will be $3p_J$, $^1D$ and $^1S$ (cf. Group VI atoms), while $I^-$ will be produced in a $^1S$ state (cf. rare gas atoms). 20 ion-pair states can be formed by taking all the possible combinations of the angular momentum quantum numbers of the ions, i.e. $\Omega = |J_1 + J_2|$. Figure 1.4 illustrates the construction of the various states, which can be roughly divided (energetically) into four groups in accordance with the energies of the various $I^+$ states.

The $3p_J$ state has three spin-orbit components, corresponding to $J=0,1,2$ (in order of decreasing energy). The six states ($0^+u(D)$, $0^+_g(E)$, $1^+_u(\gamma)$, $1^+_g(\beta)$, $2^-u(\delta)$ and $2^-g(D')$) from $I^+(3p_2)$ should be lowest. Tellinghuisen et al$^{15}$ have suggested that this group begins at around 40000 cm$^{-1}$, and this view is supported by
Figure 1.4: Relative energetic ordering of $I_2$ ion-pair states (not to scale)
theoretical calculations\textsuperscript{55} as well as by experimental results\textsuperscript{56}.

The four states ($O_u^-, O_g^-(g), l_u$ and $l_g(G)$) from $I^+ (^{3}P_1)$ and the two ($O_u^+(F)$ and $O_g^+(f)$) from $I^+ (^{3}P_0)$ should be higher by about 7000\,cm\textsuperscript{-1}, and the six states ($O_u^+(F'), O_g^+, l_u, l_g, 2_u$ and $2_g$) from $I^+ (^{1}D_2)$ still higher by about 7000\,cm\textsuperscript{-1}. The two remaining states from $I^+ (^{1}S_0)$ lie at much higher energy (approximately 17500 \,cm\textsuperscript{-1} higher still than the states from $I^+ (^{1}D_2)$).
1.5 THE ION-PAIR STATES OF IBr

The ion-pair states of IBr dissociate to either $I^+([\text{Kr}]5s^24d^{10}5p^4)$ plus $Br^-([\text{Ar}]4s^23d^{10}4p^6)$ or $Br^+([\text{Ar}]4s^23d^{10}4p^4)$ plus $I^-([\text{Kr}]5s^24d^{10}5p^6)$. Of the 20 ion-pair states which can be thus formed, half dissociate to $I^+Br^-$ and half to $Br^+I^-$. The relative energetic orderings within these two groups are determined by the energies of the various $X^+$ states ($^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$ and $^1S_0$), while all states dissociating to $Br^+I^-$ will be displaced to higher energy by approximately 9000 cm$^{-1}$ relative to the states dissociating to $I^+Br^-$. This displacement can be calculated, using equation 1.4, from the ionization potentials and electron affinities of I and Br atoms:

$$-\Delta = \text{I.P.}(I)+\text{E.A.}(Br)-\text{I.P.}(Br)-\text{E.A.}(I) \quad -(1.4)$$

Figure 1.5 illustrates the construction of the various states, which can be roughly divided (in theory) into six groups of three plus two individual states. The lowest group lies in the region 37840 - 49490 cm$^{-1}$ above the ground state (see section 3.1).

The vertical axis on Figure 1.5 is not to scale: Table 1.3 gives approximate, theoretical energy gaps between the term values of the lowest states in each successive group. A gap of 3000 cm$^{-1}$ may not be significant compared with the spread of term values within a group, in which case two or three of the groups may merge.
Figure 1.5: Relative energetic ordering of ion-pair states of IBr (not to scale)
TABLE 1.3: Approximate theoretical energy gaps between successive groups of ion pair states of IBr.

<table>
<thead>
<tr>
<th>Pair of Ions Produced in the Dissociation Limit</th>
<th>No of States in the Group</th>
<th>Approximate Energy Gap (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Br}^+\left( ^1S_0 \right) + \text{I}^-\left( ^1S_0 \right) )</td>
<td>1</td>
<td>10000</td>
</tr>
<tr>
<td>( \text{I}^+\left( ^1S_0 \right) + \text{Br}^-\left( ^1S_0 \right) )</td>
<td>1</td>
<td>11000</td>
</tr>
<tr>
<td>( \text{Br}^+\left( ^1D_2 \right) + \text{I}^-\left( ^1S_0 \right) )</td>
<td>3</td>
<td>8000</td>
</tr>
<tr>
<td>( \text{I}^+\left( ^1D_2 \right) + \text{Br}^-\left( ^1S_0 \right) )</td>
<td>3</td>
<td>3000</td>
</tr>
<tr>
<td>( \text{Br}^+\left( ^3P_{0,1} \right) + \text{I}^-\left( ^1S_0 \right) )</td>
<td>3</td>
<td>3000</td>
</tr>
<tr>
<td>( \text{Br}^+\left( ^3P_2 \right) + \text{I}^-\left( ^1S_0 \right) )</td>
<td>3</td>
<td>3000</td>
</tr>
<tr>
<td>( \text{I}^+\left( ^3P_{0,1} \right) + \text{Br}^-\left( ^1S_0 \right) )</td>
<td>3</td>
<td>6000</td>
</tr>
<tr>
<td>( \text{I}^+\left( ^3P_2 \right) + \text{Br}^-\left( ^1S_0 \right) )</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>
1.6 OSCILLATORY CONTINUUM FLUORESCENCE FROM I₂

I₂ gives rise to oscillatory continuum fluorescence when excited at 170 ≤ λ ≤ 200nm, in the absence of a buffer gas. Figure 1.6 shows a low resolution fluorescence spectrum of I₂ in the region 200-500 nm following 193 nm excitation (taken from M. Martin et al 28). Figure 1.7 shows the potential curves of the X(0⁺) and D(0⁺) states, with the difference potential above the ground state curve (dashed line) representing the locus of points to which transitions can occur (classically) from the high vibrational level of the D(0⁺) state while conserving kinetic energy. Since single photon absorption from the ground state at 170 ≤ λ ≤ 200nm populates very high vibrational levels of the upper state, there is a large range of r from which transitions can occur, and it is evident from Figure 1.7 that a large fraction of such transitions will terminate in unbound levels of the ground state. In addition to intensity maxima corresponding to transitions from the two turning points on the upper potential, there will be a third, long-wavelength maximum corresponding to transitions at intermediate r to the (maximum) turning point on the difference potential. This 'accumulated' intensity (at 322 nm) results from the very flat gradient of the difference potential in the region of its turning point, i.e. isoenergetic transitions can occur over a relatively large range of internuclear separation.
Figure 1.6: Low resolution fluorescence spectrum of I₂(10Nm⁻²), following excitation at 193nm

(Taken from M Martin et al, Nouvo Cimento 63B, 300 (1981))
Figure 1.7: The difference potential ($\Delta$) for fluorescence from $I_2(DO_u^+,V')$ to $I_2(XO_g^+)$.  
Taken from M A MacDonald, Ph.D. Thesis (1984)
On either side of this maximum turning point there are pairs of values of \( r \) with identical vertical transition energies. Depending on the phase of the wavefunctions of these pairs of points, constructive or destructive interference will result. The oscillations in the continuum emission are the manifestation of this interference. At higher resolution, a high frequency interference structure can be observed superimposed upon the low frequency structure. This high frequency structure results from the changing phase difference between the upper and lower state wavefunctions.

Similar considerations apply to the second oscillatory continuum system with maximum intensity at 420 nm. Transitions to a difference potential above the lower state (in this case purely repulsive), with associated constructive and destructive interference, give rise to the intensity oscillations in this long wavelength band.

For a rigorous treatment of this phenomenon, see RS Mulliken\(^{13}\) and J Tellinghuisen\(^{57}\).

1.7 THE CH RADICAL

The CH radical is an important radical in hydrocarbon combustion systems. Its chemiluminescence at \( \lambda = 420-440 \text{ nm} \) (from the \( A^2\Delta \rightarrow X^2\Pi \) transition) has been observed in various high temperature hydrocarbon flames\(^{58-61}\), and in atomic oxygen.
Reactions with hydrocarbons\textsuperscript{62,63} (particularly unsaturated hydrocarbons). CH radicals have also been produced in electron bombardment of organic molecules\textsuperscript{64}, in compression ignition of petrol in combustion engines\textsuperscript{65}, and in ion-molecule reactions of $N^+$, $O^+$, $He^+$ and $Ar^+$ with hydrocarbons.

Figure 1.8 is an energy level diagram showing potential curves for some of the experimentally observed electronic states of the radical: the $A^2\Delta$, $B^2\Sigma^-$ and $C^2\Sigma^+$ states have been observed in emission to the $X^2\Pi$ ground state\textsuperscript{70}. These emission spectra (along with the spectra of other small radicals such as CN, OH, NH, $C_2$ and $C_3$) are observed from many stars and comets\textsuperscript{71-73}, and from interstellar space\textsuperscript{74-78}. These radicals are produced either by the absorption of far-UV solar radiation by certain parent molecules or by chemical reactions, their fluorescence being subsequently excited by sunlight of longer wavelengths.

The CH radical is also important as a precursor to other radicals, for example the $\text{OH}(A^2\Sigma^+ \rightarrow X^2\Pi)$ emission has been observed in many hydrocarbon flames and has been attributed in part to the reaction\textsuperscript{79}:

$$\text{CH}(X^2\Pi) + O_2(X^3\Sigma_g^-) \rightarrow \text{CO}(X^1\Sigma^+) + \text{OH}(A^2\Sigma^+)$$

while electronically excited CH radicals are believed to promote chemi-ionization in flames through their reaction with atomic oxygen\textsuperscript{80,81}, viz:

$$\text{CH}^* + O \rightarrow \text{HCO}^+ + e^-$$
Figure 1.8: Potential curves of the lower electronic states of CH.
Our understanding of the extreme physical/chemical environments of hydrocarbon flames and interstellar space will benefit from any information that we can obtain on small free radicals in the laboratory. However, a reasonable understanding of the kinetics and mechanics of CH formation and reaction has only recently been established. This stems partly from the complexity of hydrocarbon combustion chemistry in general, and partly from the difficulty in the past of producing high enough concentrations of the highly reactive radical, making direct measurements very difficult. The second of these problems has been greatly alleviated by the advent of high-power UV excimer lasers, as a result of which several detailed studies have been carried out in the last few years. These include kinetic studies\textsuperscript{62,82-87}, and studies of photodissociation processes leading to CH formation\textsuperscript{88-96} which yield information on excited state dynamics and fragmentation. In these experiments multiphoton processes are responsible for CH production.

1.8 \textbf{MULTIPHOTON PROCESSES}

The probability, $P$, of the absorption of photons is given by the relation:

$$P \propto \alpha_1 I + \alpha_2 I^2 + \alpha_3 I^3 + \ldots.$$  \hfill -(1.7)
Where $\alpha_n$ is the cross-section for the absorption of $n$ photons and $I$ is the radiation intensity. From equation 1.7 it can be seen that a high radiation intensity favours the higher order terms, i.e., multiphoton processes become more feasible. These processes can be divided into three categories: sequential (resonant) multiphoton excitation (MPE), simultaneous (non-resonant) MPE, and secondary photolysis of photofragments formed in the primary step. The first two are illustrated in Figure 1.9 for a 2-photon process, the same principles being extendable to higher order processes.

In sequential MPE (see figure 1.9a) the first photon excites the parent molecule, $A$, to a real intermediate state, $A^*$, which is further excited by a second photon to a super-excited state, $A^{**}$. The intermediate state is said to resonantly enhance the process. Super-excited states produced by UVMPE usually have energies near or above the ionization potentials of the parent molecules, and can subsequently ionize, dissociate (often producing electronically excited fragments), fluoresce, react with other species present, or undergo collisional quenching. Fluorescence is seldom observed, and if desired the reaction and quenching pathways can be precluded by working with sufficiently low gas pressures.

In simultaneous MPE (see Figure 1.9b) there is no real intermediate state involved: instead the electric field of the first photon interacts with the parent molecule to produce a 'virtual' state with a lifetime of about $10^{-15}$ seconds (the photon...
Figure 1.9: Schematic representation of 2-photon MPE processes -
(a) sequential, (b) simultaneous (non-resonant),
(c) simultaneous (near-resonant)
fly-by time). If a second photon arrives during this time the molecule can simultaneously absorb them both. The presence of a nearby off-resonant state (or states) can increase the probability of absorption of the two photons (see Figure 1.9c).

Secondary excitation of primary photofragments can be represented schematically as follows:

\[
A + (n)h\nu \rightarrow A^* \quad -(1.8a)
\]
\[
A^* \rightarrow B + C \quad -(1.8b)
\]
\[
B \text{ (or } C) + (n)h\nu \rightarrow B^* \text{ (or } C^*) \quad -(1.8c)
\]

After absorption of the first photon(s) the parent molecule fragments. The second photon(s) is then absorbed by one of the photofragments taking it into an excited state. The overall process must occur during a single laser pulse (typically 15ns for an ArF excimer laser).

When a fluorescent species is produced in MPE, a lower limit to the order of the process can be determined from the dependence of the fluorescence intensity upon the laser energy. However, excepting the case of simultaneous MPE, this will be less than the true order if one of the transitions becomes saturated.

For processes involving an odd number of photons the parity selection rule is the same as that for single-photon absorption, ie g→u, g→g, u→u, but the reverse applies to processes involving an even number of photons where the selection rule is g→g, u→u, g→u.
An interesting feature of MPE is that it is possible to form doubly excited states, i.e., states in which two separate electrons are excited. This has been proposed for the ArF laser photolysis of CH₃I:

\[
\text{CH}_3\text{I} + 2h\nu \xrightarrow{\text{SIMULTANEOUS}} \text{CH}_3^*\text{I}^* \quad -(1.9a)
\]

\[
\text{CH}_3^*\text{I}^* \rightarrow \text{CH}^* + \text{H}_2 + \text{I} \quad -(1.9b)
\]

where CH₃$I$* has one electron excited into a C-I antibonding orbital and another into a CH₃ antibonding orbital.

1.9 QUENCHING MECHANISMS

Since much of the work to be reported here involves collisional quenching processes, a résumé of the various models used in the past to explain these processes will now be given. These models evolved initially in order to rationalise processes involving electronically excited atoms, and have since been extended to molecular systems.

Electronic quenching processes have been studies since the 1920's, but it is only recently that a reasonably complete understanding of the mechanisms governing them has been obtained. This is due to the difficulties involved in the theoretical treatment of excited state potentials. Three classes of mechanisms will be considered: (a) near-resonant (long-range) electronic energy transfer, (b) curve-crossing, and (c) collision complex formation.
Near-resonant Electronic Energy Transfer

Electronic relaxation may be strongly influenced by this mechanism where near resonances are involved, and where strongly allowed electric dipole or electric quadrupole transitions are involved. In atom-atom systems this necessitates a small energy mismatch, \( \Delta E \), between the initial and final states involved. In atom-molecule (or molecule-molecule) systems some of the internal energy can be 'soaked up' by the rovibrational degrees of freedom, thus giving more nearly resonant conditions.

An example of an atom-atom system in which this mechanism is operative involves electronic energy transfer between the multiplet levels of alkali metals induced by collisions with rare gas atoms. The experimental results have been reviewed by Krause, and exhibit a logarithmic decrease in transfer probability with increasing \( \Delta E \). This behaviour is characteristic of the near-resonant electronic relaxation mechanism. When the long-range dipole-dipole mechanism is operative (ie when the electronic states involved for both atoms are connected by dipole matrix elements), the resonant energy transfer probability is given by

\[
P_{if} = \sin^2 \left( \frac{2C}{\hbar b^2 v} \right)
\]

assuming a straight line trajectory, where \( b \) is the impact parameter, \( v \) is the relative velocity and \( C \) is given by

\[
C = \mu_{1if} \mu_{2if} \times \text{angular matrix elements}
\]
where the $\mu_{if}$ are the transition moments. Such interactions can give rise to extremely large cross-sections, of the order $10^3 - 10^4 \AA$, and thus resonant electronic energy transfer for dipole-allowed transitions is very efficient.

In atom-molecule (or molecule-molecule) systems the situation is less straightforward as complications arise due to the internal degrees of freedom of the collision partners. Resonant energy transfer usually involves excitation of rovibrational motion in the collision partner, either exclusively ($E \rightarrow V,R$), or in addition to electronic excitation ($E \rightarrow E,V,R$). Expressions for calculating the transfer probabilities for the various types of electrostatic interactions are given by Yardley$^{102}$.

There are several sets of experimental results which provide good tests for this theory. The results of Fink and co-workers$^{103}$ indicate that energy is resonantly transferred in collisions of optically excited Ar* with H$_2$, HD and D$_2$. Observations of the resulting light emission from individual rovibronic levels of the $B^1\Sigma_u^+$ state of H$_2$/HD/D$_2$ show that the largest cross-sections occur for transitions which are electric dipole-allowed and for which $\Delta E < 200 \text{cm}^{-1}$. Relaxation of Ar* is also dipole allowed, and cross-sections calculated on the basis of the long-range dipole-dipole mechanism gave excellent agreement with experiment in the case of $\Delta E \leq 20 \text{cm}^{-1}$. Poor agreement was obtained for larger values of $\Delta E$ as another mechanism(s) becomes predominant.

Examples of dipole-quadrupole$^{104,105}$ and quadrupole-quadrupole$^{106}$
near-resonant energy transfer processes can also be found in the literature.

(b) **Curve-Crossing Mechanism**

In this model quenching proceeds by transfer from the diabatic curve of the initial state $(X^*+Q)$ to one or more diabatic potential surfaces leading to the final state(s) $(X + Q^\pm)_{107-117}$.

When the entrance and exit channels are coupled directly and the collision energy is sufficient to reach the crossing point, $\sigma_Q$ is obtained classically by averaging the Landau-Zener transfer probability over impact parameter and the Boltzmann velocity distribution. A large $\sigma_Q$ results if the entrance channel crosses a large number of exit channels. Reactive quenching, with the entrance channel adiabatically converted to a product channel, may also have a large $\sigma_Q$. For small crossing probabilities, $P_x$, the quenching cross section is given approximately by $^{109,114}$

$$\sigma_Q = 2\pi r_x^2 P_x \exp\left\{-\Delta E/kT\right\}$$

- (1.12)

where $\Delta E$ is the energy defect between the curves.

The entrance and exit channels may be coupled by an intermediate potential, which is frequently an ion-pair curve $^{107}$. Figure 1.10 illustrates this type of coupling, which was first suggested by
Figure 1.10: Potential energy curves illustrating the quenching of an excited species, $A^*$, by a collision partner, $M$, via an ionic intermediate state, $A^+M^-$. 

Initial State: $A^* + M$

Ionic State: $A^+ + M^-$

Final State: $A + M + \text{k.e.}$

Intermolecular Distance, $r$
Laidler in 1942. If the entrance channel is nearly flat up to the crossing point \( r_x \), its value can be estimated from the condition

\[
e^2 / r_x = \text{IP}(A^*) - \text{EA}(M)
\]

where IP is the ionization potential and EA the electron affinity.

If the collision pair transfers to the ionic curve a variety of exit channels may become accessible as the steeply attractive curve crosses them, and the distribution of products will be determined by the relative strength of the couplings between the ionic curve and the various product channels. Ultimately the ion-pair will dissociate either back into the initial elastic channel, or into some other neutral channel due to a crossing of the ionic curve with a lower energy neutral curve. In the special case for which a second strong coupling does not occur, either because the interactions are very weak or because no exit channel exists, the collision pair follows the ionic potential and reactive quenching can result.

The electron transfer model has been successfully applied to E-V transfer in the Na*-N\(_2\) system, however the model is not generally applicable to E-V transfer processes.

c. Collision Complex Theory

In an atom-molecule or molecule-molecule encounter it is
possible for a long-lived collision complex to form provided that there is a sufficiently strong attraction between the species. This entails a partitioning of the available energy between the various degrees of freedom of the complex (i.e. inter- and intra-molecular). When such a complex is formed a curve-crossing point may be crossed several times during its lifetime, thus enhancing the energy transfer rate. Statistical theories can be used to predict the probability of decomposition of the complex.

Collision complex formation has been proposed for a number of systems. Polanyi and co-workers\textsuperscript{122} have suggested that an Hg-CO complex is produced in the interaction of Hg\textsuperscript{*} with CO, while Levine and Bernstein\textsuperscript{123} have argued a similar case in the interaction of Na\textsuperscript{*} with CO. By applying a collision complex model to the quenching of O\textsuperscript{1D} by N\textsubscript{2}, Tully\textsuperscript{124} was able to calculate a rate constant of 7\times10^{-11} \text{cm}^3\text{molec}^{-1}\text{s}^{-1}, which agrees well with the experimental value of (6.9\pm0.6)\times10^{-11} \text{cm}^3\text{molec}^{-1}\text{s}^{-1}.\textsuperscript{125} Tully also calculated that (30\pm10)\% of the available energy will appear as vibrational excitation, c.f. the experimental value of 33\%\textsuperscript{126}. 

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## CHAPTER 2 : EXPERIMENTAL

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2.1 THE SYNCHROTRON RADIATION SOURCE

The synchrotron radiation source (SRS) used is located at the SERC Daresbury Laboratory, and consists of an evacuated \( p = 10^{-8} \text{Nm}^{-2} \) storage ring around which bunches of electrons are accelerated at close to the speed of light. Radiation, covering the entire electromagnetic spectrum, is produced at each of 16 magnets which steer the electrons in a near circular path. Beams of this radiation are collected at several experimental ports where the desired wavelength can be selected by an appropriate means, eg a monochromator when working in the UV.

The SRS can be run in either of two modes. In 'multibunch' mode, 160 discrete bunches of electrons (each 3.6cm in length) are accelerated around the ring. This produces light pulses of \(~120\text{ps}\) duration at 2ns intervals. In 'single-bunch' mode as the name suggests, only one bunch of electrons is accelerated around the ring, producing 120ps pulses at intervals of 320ns. The beam energy was 1.8-2.0 GeV and the current was normally \(\leq 180\text{mA} \) (multibunch) or \(\leq 20\text{mA} \) (single-bunch).

2.2 ABSORPTION SPECTRA (PORT VUV3)

The absorption spectrum of IBr in the region 160-200nm was recorded on port VUV3 of the SRS (operating in multibunch mode). The synchrotron radiation was dispersed using a McPherson 5m monochromator (dispersion 0.16nm/mm), and then directed along the axis of a cylindrical pyrex cell containing the gas sample. The
cell, path length 10cm, was fitted with front and rear LiF windows. The rear (exit) window was coated externally with sodium salicylate to allow monitoring of transmitted light with a conventional photomultiplier detector (EMI 62565). The photomultiplier output was fed via a current integrator to a PDP 11/04 minicomputer, which recorded the wavelength setting simultaneously. The stepping of the monochromator grating was also controlled by the minicomputer. Digitised spectra were then transferred to an AS7000 mainframe computer for plotting.

The monochromator wavelength setting was calibrated before commencement and after completion of the experiments by recording the Schumann-Runge absorption bands of $O_2$.

2.3 **EXCITATION AND ABSORPTION SPECTRA (PORT HA12)**

Excitation and absorption spectra were recorded simultaneously using beam line HA12 of the SRS (operating in multibunch mode). The radiation from the ring was dispersed using a Spex 1500 SP Czerny-Turner monochromator. The beam was then directed along the axis of a 10cm spectrosil fluorescence cell containing the sample, which was mounted in an evacuable box fitted with two photomultiplier detectors (see Figure 2.1). The box could be pumped down to a pressure of $0.5 \text{Nm}^{-2}$. Absorption was monitored using a conventional photomultiplier detector (EMI 62565) which was bolted in position, in direct line with the excitation beam, behind a sodium salicylate coated screen. Undispersed fluorescence was monitored using a quartz windowed photomultiplier.
Figure 2.1: Schematic diagram of experimental set-up employed to record excitation/absorption spectra on SRS port HA12
(Mullard PM2020Q), which was bolted in position, opposite the cell, at right angles to the beam. A concave mirror and focussing lens were utilised to maximise the fluorescence signal, and a filter (cut-off below 280nm) was positioned in front of the photomultiplier to exclude scattered light. Thus fluorescence was detected for $280 \leq \lambda \leq 650$nm.

Outputs from the photomultipliers were sent via current integrators to a PDP 11/04 minicomputer, which also recorded the wavelengths and controlled the stepping motor of the monochromator grating during scans. Digitised spectra were then transferred to an AS7000 mainframe computer for plotting.

The monochromator was calibrated before and after runs using the O$_2$ Schumann-Runge band system, which was recorded in the region 188-200nm with the box full of air.

2.4 FLUORESCENCE SPECTRA RECORDED WITH A SPECTROFLUORIMETER

 Fluorescence spectra were recorded on a Perkin-Elmer 650-40 spectrofluorimeter, using an excitation wavelength of 200nm with various bandpasses. The samples were contained in standard 1cm$^2$ quartz spectrofluorimeter cells. The use of a 280nm cut-off pyrex filter prevented scattered light from the excitation lamp reaching the detection photomultiplier. All spectra were recorded in 'ratio' mode, whereby the fluorescence intensity is automatically scaled to compensate for random fluctuations in the excitation lamp intensity.
2.5 LIFETIME STUDIES (PORT HA12)

Lifetime studies on ion-pair states of IBr and I₂ were carried out on port HA12 of the SRS, operating in single bunch mode. Radiation from the storage ring was dispersed by a Spex 1500 SP Czerny-Turner monochromator, then passed through a 1cm² spectrosil fluorescence cell containing the gas sample. The cell was mounted in a blacked-out chamber to exclude light from the surroundings. Fluorescence at right angles to the excitation beam was passed through a filter (usually LF30, λ >300nm), then detected by a Mullard XP2020Q photomultiplier. Fluorescence lifetimes were determined by measuring successive time intervals between photomultiplier pulses (after constant fraction discrimination) and the zero time reference signal from the storage ring, using a time-to-amplitude converter (TAC). Output pulses from the TAC were accumulated in a multichannel analyser. Lifetime spectra were recorded on a PDP 11/04 minicomputer, from which they were transferred to an AS7000 mainframe computer for data analysis and plotting. This arrangement is represented schematically in Figure 2.2. This time-resolved work was carried out with my colleague, Dr M MacDonald.

2.6 SPECTRALLY RESOLVED CH(A²Δ→X²Π) EMISSION RECORDED AT EDINBURGH

The focussed output of a Lambda Physik EMG500 excimer laser operating at 193nm (ArF laser) was passed axially through a large cross-shaped cell (fitted with specrosil windows) containing the gas samples. Typically the laser energy was ~6mJ, with a pulse...
Figure 2.2: Schematic diagram of experimental set-up employed in lifetime studies on SRS port HA12.
duration of 14ns, a repetition rate of 2Hz, and a bandwidth of 1nm. The resulting focussed output intensity was of the order of 5 MWcm\(^{-2}\). Photofragment fluorescence was observed at right angles to the laser beam. The fluorescence was dispersed by means of a monochromator (McKee-Pederson MP1018B or Jobin-Yvon HRS2) prior to detection by a photomultiplier (EMI 9661B or Hamamatsu R928). The signal from the photomultiplier was processed by a gated integrator (Brookdeal 9415), and the output of the integrator was recorded on a strip chart. The resultant spectra were not corrected for the spectral response of the system.

2.7 SPECTRALLY RESOLVED CH\(\text{A}_2\text{A} \rightarrow \text{X}_\text{II}^2\) EMISSION RECORDED AT THE RUTHERFORD APPLETON LABORATORY

The focussed output of a Lambda Physik EMG201 excimer laser operating at 193nm (ArF laser) was passed through a large cross-shaped cell (fitted with spectrosil windows) containing the gas samples. Laser energies as high at 200mJ were obtained, with a pulse duration of 14ns and \(\Delta \lambda = 0.5\text{nm}\). Photofragment fluorescence was observed at right angles to the laser beam. The fluorescence was dispersed using a Jobin Yvon 0.3m monochromator fitted with a medium-resolution grating (resolution \(\Delta \lambda = 0.35\text{nm}\)). Light was detected at the exit port of the monochromator with an optical multichannel analyser (Princeton Applied Research/EG+G OMA2 with silicon intensified vidicon). In this way fluorescence spectra covering the region 400-460nm were recorded using a single laser pulse.
2.8 KINETIC STUDIES ON CH(A²Δ)

Time-resolved studies of CH(A²Δ → X²Π) emission were carried out at the Rutherford Appleton Laboratory. The focussed output of a Lambda Physik EMG201 excimer laser operating at 193nm was passed through a large cross-shaped cell, fitted with spectrosil windows, containing the gas samples (precursor plus quenching gas). The CH(A²Δ → X²Π) fluorescence at 431.5nm was viewed using a monochromator (Monospek 600) plus photomultiplier (NPAG334) combination. The photomultiplier output signal was taken via a 50Ω termination to a fast storage oscilloscope (Tektronix 466). The oscilloscope trace was photographed for subsequent measurement and least squares analysis.

Helium buffer gas (1.3x10⁻³Nm⁻²) was added to the photolysis mixtures to minimize the rate at which the CH(A²Δ) fragments moved out of the viewing region.

2.9 GAS HANDLING AND CHEMICALS USED

Gas samples were introduced to the cells via a conventional pyrex vacuum line. All of the cells were fitted, by means of black wax, with greasless taps. Ampoules containing solid/liquid substances and bulbs containing gaseous substances were also fitted for the most part with greaseless taps. To facilitate degassing, bulbs with 'cold fingers' were used for condensable gases.

IBr samples were prepared by filling a bulb with a 3:1 mixture of
Br$_2$:I$_2$, in order to completely suppress I$_2$. After degassing, the mixture was left for several days to allow equilibration: I$_2$+Br$_2$ $\rightleftharpoons$ 2IBr.

The reagent pressures used in the experiments were measured with a capacitance manometer (MKS Baratron). The chemicals used were as follows: I$_2$ (BDH, Analar grade, 99.9% purity), Br$_2$ (Fisons, SLR grade, 99% purity), SF$_6$ (Matheson, CP grade), Xe (BOC, Spectroscopic grade), CF$_4$ (BOC), CH$_4$ (BOC, Spectroscopic grade, 99% purity), N$_2$ (BOC, oxygen free), CH$_3$Cl (BDH), C$_2$H$_6$, CF$_3$Cl (Matheson), O$_2$ (BOC, 'Zero' grade), CH$_3$Br, CHBr$_3$, C$_2$H$_2$ (BOC), CH$_3$OH (May + Baker, AR grade), (CH$_3$)$_2$CO (Fisons, AR grade), CH$_2$I$_2$, He (BOC, 'A' grade), Ar (BOC, high purity), H$_2$ (BOC, CP grade).
CHAPTER 3 - SPECTROSCOPIC STUDIES OF IBr

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3.4 The Fluorescence Spectrum of IBr Excited at 200nm 74

3.5 Conclusion 81
3.1 INTRODUCTION

The spectroscopic studies outlined in this chapter were carried out in order to elucidate the ion-pair states of IBr in the region 160-200 nm. Aside from the intrinsic value of such studies, the excitation spectra were useful in the selection of excitation wavelengths for lifetime experiments (see Chapter 5).

Figure 3.1 shows approximate potential energy curves for some electronic states of IBr. Most of the purely repulsive states have been omitted.

Spectroscopic studies of the ion-pair states (three of which are shown in Figure 3.1) have been scarce to date. Diegelmann and co-workers\(^{26}\) observed the D'(2) A'(2) emission following electron bombardment of IBr, and have estimated the spectroscopic constants for the (lowest) D'(2) state (see Table 3.1). Brand and co-workers\(^{54}\) have probed the other two states which dissociate to \(\text{I}^+(3\text{P}_2)+\text{Br}^-(1\text{S})\), the "E" (O\(^+\)) and the 1\((3\text{P}_2)\) state (\(\Omega=1\)), and the f(0\(^+\)) state which dissociates to \(\text{I}^+(3\text{P}_0)+\text{Br}^-(1\text{S})\). A 2-photon pump-probe technique was used, giving access to the lower vibrational levels \((v < 31)\) for these states. The derived spectroscopic constants are given in Table 3.1 where the "E" state is renamed D(O\(^+\)). There are two reasons for renaming it: (1) the "E" designation was adopted in analogy to the E(O\(^{2+}\)) state of I\(_2\) which can only be probed by 2-photon excitation from the ground state, however the parity selection rule is not applicable to IBr.
Figure 3.1: Approximate potential energy curves for selected valence states plus three of the six lowest ion-pair states of IBr.
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<th>DIABATIC DISSOCIATION PRODUCTS</th>
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<th>$r_e/\text{Å}$</th>
<th>$\omega_e/\text{cm}^{-1}$</th>
<th>$\omega_e x_e/\text{cm}^{-1}$</th>
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<td>$D'(2)$</td>
<td>$I^+(3P_2) + Br^- (1S)$</td>
<td>-37840\textsuperscript{a}</td>
<td>-3.105\textsuperscript{a}</td>
<td>154\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>$D(0^+)$</td>
<td>$I^+(3P_2) + Br^- (1S)$</td>
<td>39487\textsuperscript{b}</td>
<td>3.42\textsuperscript{b}</td>
<td>119.5</td>
<td>0.211\textsuperscript{b}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>39491.35\textsuperscript{b}</td>
<td>3.360\textsuperscript{b}</td>
<td>119.818\textsuperscript{b}</td>
<td>0.2063\textsuperscript{b}</td>
</tr>
<tr>
<td>$I(3P_0)$</td>
<td>$I^+(3P_0) + Br^- (1S)$</td>
<td>$\leq 39520$</td>
<td>-3.4</td>
<td>-120</td>
<td></td>
</tr>
<tr>
<td>$f(0^+)$</td>
<td>$I^+(3P_0) + Br^- (1S)$</td>
<td>45383</td>
<td>3.40</td>
<td>128.8</td>
<td>0.363</td>
</tr>
</tbody>
</table>

Data from Brand et al\textsuperscript{54}, except when marked

\textsuperscript{a} : Diegelmann et al\textsuperscript{26}
\textsuperscript{b} : King et al\textsuperscript{53}
(2) the first Rydberg state (energy $= 51200 \text{ cm}^{-1}$) has already been designated "E"$^{127}$ and this could confuse matters. Therefore the lowest $0^+$ state shall be referred to as $D(0^+)$, in analogy to the $D(0^+)$ state of $I_2$. ($I_2 D(0^+)$ lies below $I_2 E(0^+)$ by $-400 \text{ cm}^{-1}$). This $0^+$ state has also been probed by King and co-workers$^{53}$ using a similar 2-photon absorption technique. The spectroscopic constants derived by them are also given in Table 3.1.

3.2 THE IBr ABSORPTION SPECTRUM

RESULTS

The absorption spectrum of IBr, recorded at a resolution of 0.064nm, is shown in the region 160-200nm in Figure 3.2 (for experimental details see section 2.2). The pressure of IBr in the cell was reduced by expansion until the strongest peak gave less than total absorption. Figure 3.3 shows the instrument response which was measured with the cell evacuated. A comparable spectrum of $I_2$ is also presented (Figure 3.4) as it exists in equilibrium with IBr, viz:

$$I_2 + Br_2 \leftrightarrow 2IBr \ , \ K_{eq} \quad -(3.1)$$

for which $K_{eq}$ has been measured as $480^{128}$. None of the $I_2$ absorption features are evident in Figure 3.2, indicating that the 3:1 mixture of $Br_2 : I_2$ is sufficient to reduce $I_2$ absorption below the noise level. As the onset of $Br_2$ absorption in the UV is at $-165$nm, contamination of the spectrum due to the excess $Br_2$ will
Figure 3.2: The absorption spectrum of IBr recorded at 0.064nm resolution. (NB: the scale reads high by 2.8λ)
Figure 3.3: Instrument response of SRS port VUV3, recorded with the cell evacuated. (*: these features are noise spikes)
Figure 3.4: The absorption spectrum of I$_2$ (27 Nm$^{-2}$) recorded at 0.064nm resolution (NB: the scale reads high by 2.8$^\lambda$).
be minimal.

The most prominent features in the spectrum are due to three previously assigned Rydberg systems, i.e. $E \rightarrow X(v_{oo} = 51200\text{cm}^{-1})$, $F \rightarrow X(v_{oo} = 54900\text{cm}^{-1})$ and $G \rightarrow X(v_{oo} = 60900\text{cm}^{-1})$. The spacings between the peaks in the structured region at 166-173nm are $-0.9\text{nm} (\equiv 300\text{cm}^{-1})$, indicating that they also form part of the Rydberg series. Other than this, there is a broad continuous absorption extending from 163-180nm, and possibly another less intense absorption underlying the $E \rightarrow X$ Rydberg system. Higher frequency structure, if found, would be indicative of the ion-pair states, which are expected to have vibrational spacings of $\leq 70\text{cm}^{-1}$ at levels accessible by single photon absorption. Therefore higher resolution spectra were recorded in a search for such structure.

A high resolution (0.016nm) spectrum of the region 190-195nm is presented in Figure 3.5. Although there is possible structure between the Rydberg peaks, it is not clearly resolved and thus gives no information on any underlying state(s). The region 185-190nm is shown under even higher resolution (0.008nm) in Figure 3.6. Very small peaks are barely discernible between the Rydberg peaks, with spacings of $-0.21\text{nm} (\equiv 60\text{cm}^{-1})$. This suggests that they belong to an ion-pair system.

The region 180-185nm was found to be completely devoid of resolvable features. In sharp contrast, the broad absorption at $\lambda < 180\text{nm}$ which underlies the $F \rightarrow X$ Rydberg system clearly shows high frequency structure (see Figure 3.7). A resolved series of
Figure 3.5: The absorption spectrum of IBr in the region 190-195nm, recorded at 0.016nm resolution. (NB: the scale reads high by 2.8Å)
Figure 3.6: Absorption spectrum of IBr in the region 185-190nm, recorded at 0.008nm resolution. The arrows show peaks due to an ion-pair state absorption. (NB: the scale reads high by 0.28nm)
Figure 3.7: Absorption spectrum of IBr in the region 170-180nm, recorded at 0.016nm resolution. (NB: the scale reads high by 2.8Å)
peaks forming a single progression can be seen extending from -171-179nm. The small peak spacings and the very gradual convergence are both symptomatic of an ion-pair state ($\Delta \nu = 45 \pm 5 \text{cm}^{-1}$ at 171nm). As the room temperature population of $\text{IBrX}(v''=0)$ is approximately four times that of $\text{IBrX}(v''=1)$ this progression is likely to be dominantly $v' \leftarrow v''=0$. (If the Franck-Condon factors are favourable, it is possible that this is a $v''=1$ progression).

In the region below 170nm any high frequency structure, if present, is below the noise level.

DISCUSSION

Any ion-pair states observed must have total angular momentum, $\Omega = 0$ or 1. The state detected in the region 185-190nm will almost certainly belong to the lowest grouping of these states (correlating with $\text{Br}^- (1\text{S}) + \text{I}^+(3\text{P}_2)$ in the diabatic dissociation limit), and this being the case it must be either the $D(0^+)$ state or the $1(3\text{P}_2)$ state previously observed using sequential 2-photon absorption. The vibrational spacing of $60 \pm 5 \text{cm}^{-1}$ at 188.5nm (marked with arrows on Figure 3.6) is possibly an extrapolation of the trend in $\Delta \nu$ from $-30 \rightarrow -45 \text{cm}^{-1}$ noted in the progression at shorter wavelengths. If this is the case it is most likely that a single ion-pair state is (at least partially) responsible for the absorption underlying the $E \leftarrow X$ and $F \leftarrow X$ Rydberg systems. (The lack of structure in the intermediate region does not affect this argument: a contribution from a $v' \leftarrow v''=1$ progression or from absorption to another ion-pair state could obscure any structure).
To test this the vibrational quantum numbers and expected vibrational spacings were calculated at the relative wavelengths, using the spectroscopic constants derived for the D(O⁺) state in references 54 and 53 (see Table 3.1). The results of these calculations are set out in Table 3.2. (Insufficient information is available to perform similar calculations for the 1(^3P₂) state which lies < 30 cm⁻¹ above the D(O⁺) state and is believed to have an almost identical potential.) There is good agreement at 188.5 nm between the observed vibrational spacings and those calculated from the constants in reference 53, given that these were derived from the analysis of data for the lowest vibrational levels (ν < 21) of the D(O⁺) state. However, due to the limitations imposed by this (their RKR analysis only extended to r = 3.999 Å in the attractive limb) they did not derive any higher order terms, and this deficiency is illustrated by the rapid convergence of the peaks (the limit being reached at a wavelength longer than 171 nm). The pairs of values obtained for ωₑ and ωₑXₑ are in excellent agreement (see Table 3.1). In addition, Brand and co-workers obtained a value of -2.34 x 10⁻⁴ cm⁻¹ for ωₑνₑ in their analysis which extended to ν' = 30.54 When this term is included in the calculations it overcompensates, slowing down the rate of convergence. (In the absence of higher order terms, i.e. νⁿ(n ≥ 4), the series would start diverging at higher ν', never reaching a convergence limit.) The agreement in the vibrational spacings at 188.5 nm suggests that the ion-pair state observed is in fact the D(O⁺) state. The disagreement at shorter wavelengths results from the inaccuracy of
TABLE 3.2: Calculated values of $v$ and $\Delta \nu$ for IBrD(O$^+$) at selected wavelengths, using the spectroscopic constants from Table 3.1

(Reference 54 gives $\omega_e \gamma_e = 2.34 \times 10^{-4}$ cm$^{-1}$).

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\lambda=188.5$nm</th>
<th>$\lambda=179$nm</th>
<th>$\lambda=171$nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v'$ $ \Delta \nu$/cm$^{-1}$</td>
<td>$v'$ $ \Delta \nu$/cm$^{-1}$</td>
<td>$v'$ $ \Delta \nu$/cm$^{-1}$</td>
</tr>
<tr>
<td>54</td>
<td>145 72.9</td>
<td>185 65.3</td>
<td>227 59.8</td>
</tr>
<tr>
<td>53</td>
<td>156 54.4</td>
<td>227 25.1</td>
<td>--- ---</td>
</tr>
<tr>
<td>Experimental Observation</td>
<td>60</td>
<td>45</td>
<td>30</td>
</tr>
</tbody>
</table>
the value of $\omega_e \gamma_e$ : it can be seen from Table 3.2 that the term in $v^3$ has a marked effect at $v' \geq 150$.

A more accurate value for $\omega_e \gamma_e$ was obtained by imposing the restriction that $v'(170.21 \text{nm})-v'(174.29 \text{nm})=41$ (see Figure 3.8). Using values of $\omega_e=119.518 \text{cm}^{-1}$ and $\omega_e \gamma_e=0.2109 \text{cm}^{-1}$, a value of $\omega_e \gamma_e=-1.13 \times 10^{-4} \text{cm}^{-1}$ was obtained by iteration. This value was then used to calculate the vibrational levels and spacings at various wavelengths (see Table 3.3). These spectroscopic constants provide a good fit to the observations in both spectral regions where high frequency structure was resolved. However, the vibrational levels are predicted to converge at $v'=436$, which corresponds to a well depth of 21384 cm$^{-1}$. The actual well depth of the D(0$^+$) state can be calculated as

$$E = D_e(\text{IBrX} \rightarrow \text{Br}^{-}(1S) + \text{I}^+(3P_2)) - T_e(\text{IBrD})$$  \hspace{1cm} (3.2)

which yields a value of 32557 cm$^{-1}$. This implies that higher order terms ($v^n, n \geq 4$) must dominate at very high $v'$.

There are two other possible explanations for these results : (1) the absorption discussed above may be due to the transition $1(3P_2) \leftrightarrow X(0^+)$ rather than $D(0^+) \leftrightarrow X(0^+)$, or (2) there may be contributions from both of these transitions. The second possibility would provide a feasible explanation for the absence of structure in the region 180-185 nm,
Figure 3.8: Absorption spectrum of IBr recorded at 0.008nm. The peaks referred to in the text are marked ↑.
TABLE 3.3: Values of \( v' \) and \( \Delta \nu ((v'+1)-v') \) of IBrD(0\(^+\)) for selected wavelengths calculated using

\[
\begin{align*}
\omega_e &= 119.518 \text{ cm}^{-1}, \\
\omega_{xe} &= 0.2109 \text{ cm}^{-1}, \\
\omega_{ye} &= -1.13 \times 10^{-4} \text{ cm}^{-1}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>( \lambda / \text{nm} )</th>
<th>( v' )</th>
<th>VIBRATIONAL SPACING/cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>107</td>
<td>-80</td>
</tr>
<tr>
<td>195</td>
<td>124</td>
<td>-72</td>
</tr>
<tr>
<td>190</td>
<td>144</td>
<td>-66</td>
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<td>185</td>
<td>167</td>
<td>-58</td>
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<td>180</td>
<td>194</td>
<td>-50</td>
</tr>
<tr>
<td>175</td>
<td>230</td>
<td>-40</td>
</tr>
<tr>
<td>170</td>
<td>279</td>
<td>-28</td>
</tr>
<tr>
<td>164.43</td>
<td>436</td>
<td>0</td>
</tr>
</tbody>
</table>

NB In reality the \( v' \) levels will not converge as a Coulombic potential contains an infinite number of vibrational levels.
ie it being due to overlap of transitions to the two states (rather than overlap of \( v''=0 \) and \( v''=1 \) progressions). However both of these possibilities are unlikely as they involve a perpendicular transition, \( \Delta \Omega = +1 \), which is expected to be very weak. The loss of ion-pair vibrational structure at \( \lambda \geq 190 \text{nm} \) and \( \lambda \leq 171 \text{nm} \) will be largely due to diminishing Franck-Condon factors for transitions to these vibrational levels (ie \( v' \leq 140 \) and \( v' \geq 280 \)). The possibility of absorption to the higher group of ion-pair states correlating with \( \text{Br}^- (1S) + \text{I}^+(3P_1 \text{ or } 3P_0) \) also exists. For example the \( f(0^+) \) state (correlating with \( \text{Br}^- (1S) + \text{I}^+(3P_0) \)) which lies 5896 cm\(^{-1}\) above the \( D(0^+) \) state has a comparable equilibrium bond length. As the potentials of these two states will be similar it seems reasonable to assume that the Franck-Condon factors will favour transitions to vibrational levels lying -5900 cm\(^{-1}\) above the accessible levels of the \( D(0^+) \) state. This translates to appreciable absorption setting in at 170.9 nm, taking 190 nm as the onset for the \( D(0^+) \) state, which corresponds roughly to the short wavelength limit of the resolved (ion-pair) vibrational progression. Absorption to a higher ion-pair state of \( \text{IBr} \) is therefore a distinct possibility at shorter wavelengths.

### 3.3 Excitation/Absorption Spectrum of IBr

**RESULTS**

The excitation and absorption spectra of \( \text{IBr} \) in the region 155-200 nm were recorded simultaneously on SRS port HA12 (for experimental details see section 2.3). Figure 3.9 shows the variation of the light throughput with wavelength, with the box
Figure 3.9: The light throughput of SRS port HA12 under the conditions employed in experiments as a function of wavelength.
evacuated. The intensity falls off appreciably toward shorter wavelengths, and this will be reflected in the excitation fluorescence spectrum. (The fall in throughput was mainly due to the monochromator grating, which was blazed at 350nm.)

Figure 3.10 shows a superimposition of medium resolution excitation/absorption spectra in the region 169-197nm (bandpass = 0.5nm). The sample contained a large excess of Br\textsubscript{2} (Br\textsubscript{2}/I\textsubscript{2}=5/1) in order to completely suppress I\textsubscript{2} which has a very intense fluorescence spectrum when excited in this wavelength region (see Chapter 4). The total pressure in the cell was 1kNm\textsuperscript{-2}. Although the E\textleftarrow{} X Rydberg system can be clearly seen in the absorption spectrum, there is no sign of the F\textleftarrow{} X system (cf Figure 3.2). The apparent absence of the F\textleftarrow{} X Rydberg bands is due to the poor sensitivity which results from a low beam intensity at shorter wavelengths. The fluorescence excitation spectrum consists of a broad feature extending from \textasciitilde{}175-195nm, with a banded structure superimposed. This structure (spacings \textasciitilde{}1.2nm corresponding to \(\Delta E\approx300\text{cm}^{-1}\)) is due to the high optical density of the sample, ie, absorption to the Rydberg states reduces the beam intensity before it reaches the region of the cell from which fluorescence is observed, and is not related to the fluorescence. This is verified by the exact coincidence of the E\textleftarrow{} X Rydberg absorption peaks with the series of dips in the excitation spectrum at \(\lambda\geq186\text{nm}\).

This structure continues to shorter wavelengths, extending beyond the F\textleftarrow{} X Rydberg system. While the structure in the excitation spectrum at \(173\leq\lambda\leq179\text{nm}\) corresponds to the F\textleftarrow{} X Rydberg absorption spectrum (see Figure 3.2), the origin of the structure
Figure 3.10: Simultaneously recorded absorption (top) and excitation (bottom) spectra of IBr: $P_{\text{IBr}} = 333 \text{nm}^{-2}$, $P_{\text{Br}_2} = 667 \text{nm}^{-2}$, excitation bandpass = 0.5 nm. (NB scale reads high by 7%.)
in the intermediate region and at $\lambda < 173\text{nm}$ is unclear.

Higher resolution excitation spectra of the most intense area near 180nm were recorded. However, due to very low signal levels no fine structure was discernible above the noise.

Medium resolution excitation/absorption spectra extending down to 153nm are shown in Figures 3.11 and 3.12. These were recorded when the SRS was carrying a very large current (-200mA), giving a more intense beam. The improved resolution is a result of the increased signal : noise ratio. The absorption spectrum shows traces of the F$\rightarrow$X Rydberg system in addition to the E$\rightarrow$X system. The excitation fluorescence spectrum shows two new broad features in addition to the one previously noted, with an extensive banded structure imposed throughout. This structure, due to the high optical density of the sample, can be largely accounted for by transitions to the E, F and G Rydberg systems. The onsets of the latter two systems are marked on Figure 3.11. (Comparison of Figure 3.12 with Figure 3.2 illustrates the inferior sensitivity of this experimental set-up at shorter wavelengths.)

DISCUSSION

The broad feature in the excitation fluorescence spectrum at $\lambda > 171\text{nm}$ corresponds to the ion-pair state identified in the high resolution absorption spectrum and provisionally designated D($0^+$). In fact this observation lends support to the assignment, as the
Figure 3.11: Excitation spectrum of IBr. Conditions used: $P_{IBr} = 333\text{Nm}^{-2}$, $P_{Br_2} = 667\text{Nm}^{-2}$, excitation bandpass = 0.5nm. The wavelengths of the 0-0 transitions are marked for the $F \leftarrow X$ and $G \leftarrow X$ Rydberg systems.
Figure 3.12: Absorption spectrum of IBr. Conditions used: $P_{IBr} = 333 \text{ Nm}^{-2}$, $P_{Br_2} = 667 \text{ Nm}^{-2}$, excitation bandpass $= 0.5 \text{nm}$. The F-$\alpha$ Rydberg absorption is discernible in this spectrum.
analogous $I_2D(0_u^+)$ state also fluoresces in the UV/visible when excited in this wavelength region (see Chapter 4).

The broad feature with maximum intensity at -167nm would be increased in height by -50% relative to the maximum at -179nm if a correction was made for the decreased excitation beam intensity at the shorter wavelength. This feature must also be the result of fluorescence from an ion-pair state of IBr, which, taking energetic considerations into account, is likely to be a member of the next ion-pair grouping. The group of states correlating with $Br^-|S^+)+I^+(3P_0,1)$ lies -5400-5900cm$^{-1}$ above the $D(0^+)$ state, while the separation between the maxima (167-179nm) translates to an energy gap of -4000cm$^{-1}$. This discrepancy is tolerable in view of the following facts: (1) the potentials are not identical in shape and may be slightly displaced relative to the lower ion-pair grouping, and (2) the beam intensity falls off markedly toward shorter wavelengths and thus the true maximum of the second system may lie at a higher energy. To date there have been no experimental observations of the $0^-|P_1^+)$ or $1^+(3P_1)$ states which correlate with $Br^-|S^+)+I^+(3P_1)$, so the most logical assignment of the second ion-pair system is to the $f(0^+)$ state. (The analogous $F(0_u^+)$ state of $I_2$, correlating with $I^-|S^+)+I^+(3P_0)$, has previously been observed in single-photon excitation.$^{130}$)

The remaining broad feature, with maximum intensity at 163nm, can be reasonably confidently assigned to fluorescence from the "K" state of $Br_2$. The reasons for this are three-fold. Firstly, $Br_2$
gives rise to intense emission from this state in the region 210-440nm when excited at 157.8nm with a F₂ laser.\textsuperscript{131} Secondly, Br₂ "K"\textarrowleft X(Og+) absorption occurs at λ\lesssim 166nm\textsuperscript{132}. And finally, there was a large excess of Br₂ present in the sample cell. On the basis of this, the feature would be expected to extend to shorter excitation wavelengths then 160nm if it were not for the cut-off of the spectrosil fluorescence cell. (The "K" state of Br₂ has recently been established as the D(Ou+) state, corresponding to the D(Ou+) state of I₂\textsuperscript{133}.)

3.4 THE FLUORESCENCE SPECTRUM OF IBr EXCITED AT 200nm

RESULTS

The dispersed fluorescence from IBr excited at 200nm was recorded on a Perkin-Elmer 650-40 spectrofluorimeter, in the region 280-510nm (see section 2.4 for additional experimental details). The spectrum, recorded with an excitation monochromator slit width of 10nm and a detection monochromator slit width of 2nm, is shown in Figure 3.13. The IBr sample, total pressure 280Nm\textsuperscript{-1}, was composed of equal pressures of IBr and Br₂ (ie [Br]/[I] =3/1). A greater ratio of Br₂/I₂ would be required to completely suppress I₂ fluorescence (see Figure 3.13), but the Br₂ pressure can only be increased at the expense of the fluorescence intensity, which it quenches extremely efficiently (see Chapter 5). As the fluorescence is already weak, a small contamination due to I₂ was tolerated. On scanning the detection monochromator out to 850nm,
Figure 3.13: Fluorescence spectrum of IBr excited at 200nm. The conditions used were as follows: excitation monochromator slit width = 10nm, fluorescence monochromator slit width = 2nm, $P_{IBr} = P_{Br_2} = 140 \text{Nm}^{-2}$. 

$I_2(0)$
no additional fluorescence was found.

The spectrum is seen to consist of two oscillatory continua\textsuperscript{57,134,135} ranging between 300-380 and 390-460nm. The interference structure associated with bound-free emission of this type has been observed previously for diatomic halogen molecules,\textsuperscript{45,131,136} and the two systems in Figure 3.13 have been noted in IBr fluorescence following 193nm laser excitation.\textsuperscript{46} The IBr oscillatory continua are similar to those previously observed from I\textsubscript{2}D(0, +),\textsuperscript{28,45,57} and have therefore been assigned to bound-free emission from IBrD(0\textsuperscript{+}).\textsuperscript{46} (Bound-bound emission, D(0\textsuperscript{+})→X(0\textsuperscript{+}), can only occur at λ≤270nm, which is below the filter cut-off.)

A second fluorescence spectrum of IBr was recorded under similar conditions, except for the addition of a large pressure (14.26KNm\textsuperscript{-2}) of SF\textsubscript{6} to the sample, and is reproduced in Figure 3.14. (The vertical scale is approximately 4x that in Figure 3.13.) The use of alternative inert buffer gases, such as CF\textsubscript{4},N\textsubscript{2} and the lighter noble gases, produced a similar result. This spectrum is virtually entirely composed of new features, and is dominated by two narrow peaks at 342 and 385nm. Two other less intense features at 410 and 490nm are also now present, while the feature at 447nm is greatly diminished. The intensities of the four new features increase in parallel, upon raising the buffer gas pressure, and the peak at 385nm also narrows down and shifts slightly to the red.
Figure 3.14: Fluorescence spectrum of IBr+SF₆ excited at 200nm. The conditions used were as follows: excitation monochromator slit width = 10nm, fluorescence monochromator slit width = 2nm, $P_{IBr}=P_{Br_2}=140\text{Nm}^{-2}, P_{SF_6} = 14.26\text{Nm}^{-2}$.
DISCUSSION
In the absence of buffer gas the IBr fluorescence spectrum originates entirely from the initially populated upper state. Apart from analogy to $I_2 D(0_u^+)$, the assignment to the D($0^+$) state is supported by the fact that the spectrum is very weak compared to $I_2$ excited under similar conditions - this is to be expected as 200nm excitation only accesses the tail of the D-state absorption, populating $v' = 107$ (see preceding sections). In view of this a shorter excitation wavelength would have been desirable (see Figure 3.10), but this was restricted to $\lambda \geq 200$nm by the instrument. The fluorescence in the region 300-380nm results from transitions terminating in unbound levels of the ground state, while the fluorescence at 390-460nm is due to a transition which terminates on an unbound lower state. In analogy to Tellinghuisen's tentative assignment for $I_2$, this repulsive state is probably $0^+$, correlating with two ground state atoms.

In the presence of a large excess of inert buffer gas the oscillatory continuum emission is virtually completely quenched, leaving only a weak peak at 447nm and a shoulder on the short wavelength side of the 385nm peak. The D-state emission at 447nm is relatively narrow, indicating that it has been vibrationally relaxed by the SF$_6$.

The emission at 342nm can be readily assigned to the $I_2 D'(2_g) \rightarrow A'(2_u)$ emission, which results from the residual $I_2$ pressure in the sample cell. The strong peak at 385nm is the IBr analogue, i.e. the $D'(2) \rightarrow A'(2)$ emission, which has
previously been observed following 193nm laser excitation of IBr in the presence of excess Ar buffer gas\textsuperscript{39}. The narrowing and red shift of this peak at high SF\textsubscript{6} pressures indicates efficient vibrational relaxation of the D'-state, however physical quenching of this state is extremely inefficient, corroborating the assertion that it is the lowest of the ion-pair states.

The most likely assignment of the broad feature at 490nm is to a D'(2) $\rightarrow \Omega=2$ transition in which the lower state is repulsive, and correlates with I($^2P_{1/2}$)+Br($^2P_{3/2}$) in the dissociation limit (cf. the 505nm emission peak of I\textsubscript{2} which has been assigned D'(2) $\rightarrow 2_u(3\Delta)^{15}$). Given that the D'(2) state is vibrationally relaxed, the breadth of this feature can only be explained if the lower state is repulsive.

The feature at 410nm in Figure 3.14 is most likely to originate from the D'(2) state also, since it gains intensity in tandem with the 385 and 490nm peaks. It is quite broad so the lower state must again be repulsive. Of the several possible contenders for the lower state (there is no parity selection rule for IBr), the counterpart of the lower state in the 490nm emission is the most obvious choice. This repulsive state, $\Omega=2$, will correlate with I($^2P_{3/2}$)+Br($^2P_{1/2}$) in the dissociation limit, and will lie below the previously mentioned $\Omega=2$ repulsive state since the spin splitting in Br($^2P_{j}$) is less than in I($^2P_{j}$).

However, the possibility of the 410nm peak originating from the \textit{l}($^3P_2$) state of IBr cannot be completely discounted. There are
two reasons for this. Firstly, it is extremely likely that the interstate transfer process involves a cascade down the vibronic levels of all three ion-pair states in the lowest grouping (cf $I_2$ collisional transfer$^{18}$), in which case the $1(3P_2)$ state will at least have a transient population. Secondly, by analogy with $I_2$, all of these states should have at least one allowed transition to a valence state$^{13}$. (As this peak gains in intensity at the expense of the oscillatory continuum emission, the D($O^+$) state can be excluded.)

The effect of adding inert gases is thus to promote collisional transfer between the ion-pair states in this (lowest) grouping, with concomitant vibrational relaxation of the individual states. When a high enough pressure of inert gas is used, this cascading process will terminate in a Boltzmann distribution over the vibronic levels of the states. A general characteristic of the halogen ion-pair states is that they are efficiently transferred collisionally to the lowest state in the manifold$^{15}$, which lends further support to the above assignments. This process is facilitated by the very high density of states within the manifold, and it may well be the case that interstate transfer is more rapid than intrastate vibrational deactivation.

A rough estimate of the difference in the term energies of the D($O^+$) and D'(2) states can be obtained using the Boltzmann relation and the relative peak areas at 385 and 447nm. This can only be very approximate due to several factors: (1) the instrument response varies with the fluorescence wavelength, (2)
the entire emission from a state is not confined to a single wavelength, and (3) the transition probability will be different for each of the states. The ratio of the areas at 447/385nm tends to 0.0234 at high buffer gas pressures. Taking the degeneracies of the two states into account (1 for D(0^+), 2 for D'(2)), this gives \( T_e(D) = T_e(D') + 640 \text{cm}^{-1} \). The term energy of the D(0^+) state is known accurately to be 39457\text{cm}^{-1} (see Table 3.1), and so an absolute value of \( T_e(D') = 38850 \text{cm}^{-1} \) is obtained.

It will be noted that this value differs markedly from that of Diegelmann et al\(^{26}\) who calculated \( T_e(D') = 37840 \text{cm}^{-1} \). However, their value is also subject to a degree of uncertainty, which is introduced in the computation of the D'(2) and A'(2) potential curves. Both curves, and particularly that of the D'(2) state, are poorly characterized. Their model predicts that the D'(2) \( \rightarrow \) A'(2) emission will occur at 395.8nm rather than 385nm. This discrepancy can be rectified by taking \( T_e(D') = 38550 \text{cm}^{-1} \). Given the uncertainties involved in the calculation of \( T_e(D') \) from spectrofluorimeter data, the value of 38850\text{cm}^{-1} is credible.

3.5 CONCLUSION

There are at least two ion-pair states of IBr which are accessible by single photon absorption in the region 160-200nm, as well as three Rydberg systems. The lowest of these ion-pair states is the D(0^+) state which correlates with Br^-\((1S)\)+I^+(3P_2) in the diabatic
dissociation limit. This state is populated by excitation at $170 \leq \lambda \leq 200$ nm, and gives rise to two fluorescence systems in the UV/visible which are of the bound-free type. The vibrational band structure in the absorption spectrum gives a reasonable fit to the equation:

$$v_v = v_{00} + (v+1/2) \omega_e -(v+1/2)^2 \omega_e x_e -(v+1/2)^3 \omega_e y_e$$

using the spectroscopic constants $v_{00} = 39432$ cm$^{-1}$, $\omega_e = 119.518$ cm$^{-1}$, $\omega_e x_e = 0.2109$ cm$^{-1}$ and $\omega_e y_e = -1.13 \times 10^{-4}$ cm$^{-1}$. Maximum fluorescence intensity is obtained for excitation at 179 nm, which corresponds to $v' = 199 \leftarrow v'' = 0$.

The second of the ion-pair states gives rise to fluorescence at $\lambda \geq 280$ nm when excited at $165 \leq \lambda \leq 170$ nm. This is possibly the $f(0^+)$ state which should lie $-5900$ cm$^{-1}$ above the $D(0^+)$ state, and correlates with $\text{Br}^- (1S) + \text{I}^+(3P_0)$ in the diabatic dissociation limit. The possibility of absorption to other ion-pair states cannot be excluded.

Finally, the $D(0^+)$ state undergoes rapid collisional interstate transfer to the $D'(2)$ state in the presence of an inert buffer gas. This state in turn is vibrationally relaxed, but not physically quenched, by excess buffer gas. The overall process probably proceeds in part via levels of all three ion-pair states in the group correlating with $\text{Br}^- (1S) + \text{I}^+(3P_2)$ in the diabatic dissociation limit. The $D'(2)$ state is the lowest ion-pair state of IBr, probably lying $-640$ cm$^{-1}$ below the $D(0^+)$ state. In the
absence of a reactive gas it decays spontaneously, giving rise to a sharp emission band at 385nm.
CHAPTER 4 - SPECTROSCOPIC STUDIES OF $I_2$

4.1 Introduction

4.2 The excitation/absorption spectrum of $I_2$

4.3 Formation of $XeI^*(B)$ from $I_2(D)+Xe$

4.4 Conclusion
4.1 INTRODUCTION

The absorption and fluorescence spectra of I₂ excited at \(180 \leq \lambda \leq 210\text{nm}\) have been extensively studied and are well characterised. The transition responsible for the strong absorption in this region (see Figure 3.4) is \(D(O_u+) \rightarrow X(O_g^+)\). Very high vibrational levels of the upper state \((v' > 100)\) are populated in single photon absorption due to the large difference in the equilibrium bond lengths of the two states \(r_e(X) = 2.67\text{Å}, r_e(D) = 3.60\text{Å}\).

The fluorescence spectrum following excitation in this wavelength range (see for example Figure 1.6) consists of a typical resonance series at short wavelengths, followed by two groups of diffuse bands at longer wavelengths. These diffuse bands, or "oscillatory continua", are the manifestation of transitions from the \(D(O_u+)\) state to unbound lower levels. (For a brief description of this phenomenon, see section 1.6). In the presence of an inert buffer gas the \(D(O_u+)\) state is efficiently transferred collisionally to the \(D'(2_g)\) state, which is the lowest ion-pair state of I₂. This state is not efficiently quenched, and decays spontaneously giving rise to a strong peak at 342nm and a weaker one at 505nm.

In this chapter, the complementary I₂ excitation spectrum
will be reported on. This will substantiate some of the comparisons and analogies drawn between IBr and I\textsubscript{2} in Chapter 3, and serve as a pointer for excitation wavelengths in the lifetime studies that follow (Chapter 5). The possibility of XeI\textsuperscript{*} formation from the reaction:

\[ \text{I}_2(\text{D}_0\text{u}^+) + \text{Xe} \rightarrow \text{XeI}(\text{B}_2\Sigma^+) + \text{I} \quad -(4.1) \]

will also be examined. XeI\textsuperscript{*} exciplex formation has previously been observed in the complementary reaction of metastable Xe atoms with iodine-containing molecules\textsuperscript{138-140}.

4.2 THE EXCITATION/ABSORPTION SPECTRUM OF I\textsubscript{2}

The fluorescence excitation and absorption spectra of I\textsubscript{2} in the region 165-215nm were recorded simultaneously on SRS port HA12 (for experimental details refer to section 2.3). The 10cm spectrosil fluorescence cell contained a few crystals of I\textsubscript{2} which were thoroughly degassed, so an I\textsubscript{2} pressure of \(-30\text{mTorr}\) (ie the vapour pressure at room temperature) was present. Figure 4.1 shows the fluorescence excitation spectrum, recorded with a bandpass of 0.3nm. The corresponding absorption spectrum showed no features (for an absorption spectrum in this region refer to Figure 3.4).

Absorption to the D(0\textsubscript{u}+) state ranges from 175-215nm, with maximum intensity at \(-188\text{nm}\) excitation. The only regular
Figure 4.1: Excitation spectrum of \( I_2 \) (27 Nm\(^{-2}\)). Excitation bandpass = 0.3nm (NB: scale reads high by 6.2Å).
structure occurs at 175-177nm, where there are a few peaks with spacings of \(-0.65\text{nm} (\equiv 210\text{cm}^{-1})\). In fact, this structure is not related to the excitation spectrum, but results from the high optical density of the sample: the dips in this region correspond to the removal of beam intensity through absorption to the Rydberg series of \(I_2\). These bands have previously been analysed\(^{141}\).

Higher resolution spectra were recorded, covering the whole of the above region. Figure 4.2 shows a superimposition of the excitation and absorption spectra in the region 185-195nm, recorded with an excitation bandpass of 0.075nm. Both spectra display high frequency structure (spacings \(\equiv 0.19\text{nm}\)), with exact coincidence between the peaks in the excitation spectrum and the peaks in the absorption spectrum. Thus the fluorescence intensity is increased upon scanning the excitation wavelength through a vibrational peak in the absorption spectrum, and so the structure in the excitation is not simply due to self-absorption by the sample before the excitation beam crosses the region of the cell from which fluorescence is observed (i.e., the structure in both spectra are manifestations of the same physical process). The structure is clearly resolved from 196-189nm, in which interval the peaks converge slowly from separations of \(57^{\pm}5\text{cm}^{-1}\) to \(50^{\pm}5\text{cm}^{-1}\). This corroborates the assignment of both the absorption and excitation spectra to the \(D(O_u^+)^{\text{ion-pair state of}}\) \(I_2\). The lack of resolved structure at \(\lambda < 189\text{nm}\) and \(\lambda > 196\text{nm}\) is most likely due to overlap of
absorption originating from two vibrational levels of the ground state.

4.3 FORMATION OF XeI*(B) FROM I₂*(D) + Xe

The possibility of XeI(B₂Σ⁺) exciplex formation in the reaction of I₂D(O_u⁺) with Xe(1S) was investigated by recording the excitation spectrum of I₂ (175-200nm) in the presence of various pressures of Xe (see previous section for experimental details). A 254nm interference filter (bandpass ≈ 15nm FWHM) was positioned in front of the fluorescence detection photomultiplier. With this arrangement, only the XeI B₂Σ⁺ → X₂Σ⁺ emission at 253nm plus a small fraction of the I₂D(O_u⁺ → X₀g⁺) emission should be observed. Due to low signal levels, incurred through the use of a narrow bandpass filter with a maximum transmission of only ~50%, an excitation bandpass of 1nm had to be employed.

Figure 4.3 shows a superimposition of I₂ + Xe excitation spectra, with Pₓₑ = 0.475, 13.07 and 53.3kNm⁻². Increasing the Xe pressure to ~13kNm⁻² causes a decrease in fluorescence intensity at λ ≥ 190nm, has little effect on the fluorescence intensity for excitation at 184nm ≤ λ ≤ 190nm, and increases the fluorescence intensity to shorter wavelengths. At very high Xe pressure the intensity is
Figure 4.3: Excitation fluorescence spectra of I$_2$(27Nm$^{-2}$) plus Xe, recorded with an excitation bandpass of 1nm. The following Xe pressures were used: (a) 0, (b) 4.76kNm$^{-2}$, (c) 13.07kNm$^{-2}$, (d) 53.3kNm$^{-2}$. (NB: the scale reads high by 6.2%).
reduced over the entire range.

As a check, an excitation spectrum of $I_2$ plus $CF_4$ buffer gas (13kNm$^{-2}$) was recorded. In this case the fluorescence intensity decreased uniformly over the entire excitation range. Therefore the extra emission intensity for excitation at $\lambda \leq 190$nm at intermediate Xe pressures is not the result of emission from another ion-pair state of $I_2$ populated through collisions with Xe. This implies a chemical reaction between Xe and $I_2DO_u^+$, excited at these energies, with $XeI(B^2\Sigma^+)$ responsible for the additional intensity.

At first sight it would appear that the quantum efficiency for $XeI(B)$ production is $=1$ for $I_2$ excitation at $\lambda \leq 190$nm, since the fluorescence intensity remains effectively constant over a range of Xe pressures. However, it must be borne in mind that $I_2DO_u^+$ fluoresces over a very broad spectral range, while $XeI(B)$ emits predominantly at 253nm. The picture is further complicated by several considerations: (1) there is likely to be a contribution from collisional transfer processes involving other ion-pair states of $I_2$, (2) the $I_2$ absorption may be pressure broadened by the added Xe (making the apparent quantum efficiency greater), and (3) $XeI(B)$ itself appears to be quenched by Xe. Therefore dispersed fluorescence spectra would be required to determine the extent of $XeI(B)$ production.

Energetically, the lower limit for $XeI(B)$ production occurs
at 190.9nm. Production appears to set in at 190±1nm, implying that there is little or no activation barrier to reaction 4.1. This is highly plausible, as the reaction of IBr(D) + Xe to produce XeBr(B) has also been found to proceed under close to thermoneutral conditions. The extension of the fluorescence intensity to shorter wavelengths upon increasing the Xe pressure can be explained by a contribution from the C-state of XeI. XeI(C) production becomes energetically possible for excitation at λ≤188.4nm. Although this state does not fluoresce in the correct spectral region, it is very efficiently collisionally transferred to the B-state whence it can emit at 253nm. Thus, an indirect contribution from XeI(B) at shorter wavelengths would increase upon raising the Xe pressure. Ultimately, the XeI(B) fluorescence is quenched by Xe (see bottom trace on Figure 4.3). However, extremely high pressures are required so the process does not appear to be very efficient.

4.4 CONCLUSION

The excitation spectrum of I₂ at 175 ≤ λ ≤ 215nm is complementary to previously recorded absorption and fluorescence spectra in this region, as it shows that a wide
range of vibrational levels of the $D(O_{u^+})$ state fluoresce. In fact, the fluorescence-excitation spectrum matches the absorption spectrum down to 185nm. Thus the $D(O_{u^+})$ state is not predissociated.

The reaction of $I_2D(O_{u^+})$ with $Xe$ to form $XeI \ B(^2\Sigma^+)$ occurs for excitation at $\lambda < 190$nm, implying that there is little or no activation barrier. It is also highly probable that $XeI(C)$ is formed at shorter wavelengths and transferred to $XeI(B)$ by collisions with $Xe$ atoms.
CHAPTER 5 - KINETIC STUDIES OF ION-PAIR STATES OF IBr AND I₂

5.1 Introduction ........................................ 96

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5.3 IBr* Quenching Studies on the Spectrofluorimeter .. 121

5.4 Conclusion ........................................... 154
This chapter is devoted to the kinetics of chemical and physical processes involving ion-pair states of IBr and I₂. Previous studies on the ion-pair states of I₂ have demonstrated that such species have extremely large cross-sections for collisions with a wide range of gases, and that they can cleave strong bonds.

Initially, dispersed fluorescence spectra were obtained (with the spectrofluorimeter) for mixtures of halogen plus various pressures of foreign gases (excited at 200nm), with subsequent Stern-Volmer analysis of the plots, yielding relative removal rate constants. In order to put these data on an absolute basis, experiments were carried out on the SRS at Daresbury to obtain the lifetimes of the ion-pair states under the experimental conditions used. Pure radiative lifetimes for the states under study - IBr(DO⁺), IBr(D'2), I₂(DO_u⁺) and I₂(D'2_g) - were also obtained. These lifetime studies were carried out in collaboration with a colleague, Dr Michael MacDonald.

No ion-pair state lifetimes have been measured previously for
IBr, while for I\textsubscript{2} only three have been measured - DQ\textsuperscript{+}(15.5ns\textsuperscript{142}), D\textsuperscript{2}g(6.7ns\textsuperscript{31}) and E0\textsuperscript{+}(27ns\textsuperscript{143}). As these states have very short lifetimes, the SRS with its well defined, pulsed time profile, proved an ideal tool for such measurements. The experimental details are set out in section 2.5.

RESULTS

(1) IBr: For work on IBr an excitation wavelength of 188nm (\(\Delta\lambda=3\)nm) was exclusively used - this gave the maximum signal attainable without the sample chamber evacuated. (Although higher signal levels could be obtained at shorter wavelengths with the chamber evacuated, the time savings thus afforded were negated by the laborious process of pumping down for each run.) Figure 5.1 shows a typical decay plot, obtained in this case for IBr(DO\textsuperscript{+}) fluorescence at \(\lambda \geq 300\)nm (LF30 filter). Generally the data gave an excellent fit to a single exponential decay over at least two decades, providing very precise lifetimes. The residuals, shown in the lower half of Figure 5.1, illustrate the standard deviation of the experimental points from the curve generated by computer fitting. The main source of error in these experiments therefore arose through uncertainties in the partial pressures of the various constituents of the samples, estimated to be \(\pm 15\%\).

The relative removal rate constants for IBr(DO\textsuperscript{+}) with various
Figure 5.1: Top trace - IBr* fluorescence decay following 188nm excitation ($P_{\text{IBr}} = 133 \text{Nm}^{-2}$, $P_{\text{Br}_2} = 266 \text{Nm}^{-2}$, one channel = 0.1132ns)

The bottom trace shows the residuals (see text).
foreign gases (see next section) were obtained using IBr samples comprising 2:1 of Br$_2$:IBr, in order to suppress I$_2$. The lifetime of IBr(DO$^+$) under these conditions was determined by recording fluorescence decays over a range of total pressures while holding the ratio of Br$_2$:IBr constant at 2:1. An LF30 filter was utilised throughout, to eliminate scattered excitation light. Figure 5.2 shows a plot of the reciprocal of the fluorescence lifetime of IBr against the combined IBr + Br$_2$ pressure. The reciprocal of the intercept gives a value of 27±4ns for the pure radiative lifetime of IBr(DO$^+$), while the gradient gives a removal rate constant, $k_{REM} = (7.3±0.3)\times10^{-10}$ cm$^3$ molec$^{-1}$s$^{-1}$. This rate constant represents contributions to the removal process by IBr and by Br$_2$.

Figure 5.3 shows a plot of the reciprocal of the IBr lifetime in the presence of increasing pressures of Br$_2$, with the IBr pressure held constant at 133Nm$^{-2}$. The slope of this plot yields a value for the rate constant for the removal of IBr(DO$^+$) by Br$_2$, $k_{REM}(Br_2) = (6.4±0.4)\times10^{-10}$ cm$^3$ molec$^{-1}$s$^{-1}$. Combining this with the result from the slope of Figure 5.2 gives a value for self-quenching (ie the removal of IBr(DO$^+$) by IBr), $k_{REM}(IBr) = (9.1±1.4)\times10^{-10}$ cm$^3$ molec$^{-1}$s$^{-1}$. These plus other rate constants are collected for ease of comparison in Table 5.1.

The effect of added buffer gas upon the fluorescence decay time profile was investigated next, using various pressures
Figure 5.2: Plot of the reciprocal of the fluorescence lifetime of IBr against the total pressure of IBr + Br₂ ($P_{Br₂} = 2P_{IBr}$)
Figure 5.3: Plot of the reciprocal of the fluorescence lifetime of IBr in the presence of increasing pressures of Br₂ (P_{IBr} = 133 Nm⁻²).
TABLE 5.1: Total removal rate constants for halogen ion-pair states with various collision partners (M).

<table>
<thead>
<tr>
<th>HALOGEN STATE</th>
<th>M</th>
<th>( k_{\text{REMOVAL}} \text{cm}^3\text{molec}^{-1}\text{s}^{-1} \times 10^{10} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBr(DO(^+))</td>
<td>Br(_2)</td>
<td>6.4±0.4</td>
</tr>
<tr>
<td>IBr(DO(^+))</td>
<td>IBr</td>
<td>9.1±1.4</td>
</tr>
<tr>
<td>IBr(D'2)</td>
<td>IBr+Br(_2)</td>
<td>6.5±0.5</td>
</tr>
<tr>
<td>IBr(DO(^+))</td>
<td>CH(_4)</td>
<td>1.9±0.2</td>
</tr>
<tr>
<td>I(<em>2)(DO(</em>{u+}))</td>
<td>CH(_4)</td>
<td>1.9±0.2</td>
</tr>
</tbody>
</table>
of CF₄. Figure 5.4 shows the decay of IBr fluorescence in the presence of an intermediate pressure of CF₄ (3kNm⁻¹), recorded using two different filters. Using an LF30 filter (top trace), a marked risetime of ~6ns is apparent and the computer fit for a single exponential is extremely poor. This is due to collisional transfer of IBr from the DO⁺ to the D'2 state, which subsequently fluoresces. While the fit is improved in the case of an LF42 filter (λ ≥ 420nm, bottom trace), there is still evidence of a risetime. This is further supporting evidence for the assignment of the IBr emission system at 490nm to a transition from the D'2 state. (see Figure 3.14, section 3.4). Therefore the accuracy of lifetime data obtained at intermediate buffer gas pressures is questionable as there are three processes to be deconvoluted: a risetime plus decays from two different electronic states.

On going to higher buffer gas pressures it was found that the risetime decreased, with concomitant improvement in the computer fit to the data points. For CF₄ pressures ≥ 50kNm⁻² the accuracy of the fit and measured lifetime reach steady values, with a minimum risetime of ~1.5ns. This then is the minimum CF₄ pressure required to bring about complete collisional transfer between the DO⁺ and D'2 state, culminating in a Boltzmann distribution over the two states.
Figure 5.4: IBr* fluorescence decay, following 188nm excitation, in the presence of 3kNm$^{-2}$ of CF$_4$. Top trace - fluorescence at $\lambda \geq 300$nm, bottom trace - fluorescence at $\lambda \geq 420$nm.
(Conditions used: $P_{IBr} = P_{Br_2} = 213$Nm$^{-2}$, 0.0792ns/channel).
The lifetime of IBr(D'2), under conditions used in the spectrofluorimeter experiments (see next section), could now be determined. Figure 5.5 shows a plot of the reciprocal of the IBr(D'2) fluorescence lifetime against the total pressure of IBr+Br₂, in the presence of a large excess of CF₄. The Br₂ : IBr ratio was held constant at 2:1. To ensure a minimum contribution from IBr(DO), 50kNm⁻² of CF₄ was added to each sample and an LF38 filter (λ ≥ 380nm) was employed. (This also excluded any contribution from the residual I₂(D'2) → A'2_u) emission at 342nm : see Figure 3.14). Other experiments demonstrated that quenching of IBr(D'2) by CF₄ is negligible. As with IBr(DO), relative rate constants for IBr(D'2) can be converted to absolute by taking 1/τ from the best fit straight line at the required total pressure. The intercept gives the pure radiative lifetime of IBr(D'2), T_{RAD} = 11±2ns, while the gradient gives a combined (IBr+Br₂) rate constant for the removal of this state, k_{REM} = 6.5±0.5x10⁻¹⁰ cm³ molec⁻¹ s⁻¹.

(2) I₂ : The fluorescence lifetime of I₂ was measured over a range of vapour pressures (temperatures = 0.7 - 27.3°C) and a range of excitation wavelengths (188 - 200nm). The lifetime remained effectively constant over the pressure range studied, while it fluctuated randomly with excitation wavelength at constant temperature giving an average value of ~13ns (see Table 5.2). However, excepting the runs at low temperatures, the decay plots gave very poor single exponential fits (see for example Figure 5.6, top trace), implying that the fluorescence signal originates from more
Figure 5.5 : Plot of the reciprocal of the fluorescence lifetime of IBr, in the presence of 50 kN m\(^{-2}\) of CF\(_4\), against the total pressure of IBr + Br\(_2\) (\(P_{Br_2} = 2P_{IBr}\)).
TABLE 5.2: The fluorescence lifetime of $I_2$ (vapour pressure at 26°C) excited at a range of wavelengths.

<table>
<thead>
<tr>
<th>$\lambda_{\text{EXC./nm}}$</th>
<th>$\tau/\text{ns}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>188</td>
<td>14.3 ± 2.1</td>
</tr>
<tr>
<td>192</td>
<td>11.8 ± 1.7</td>
</tr>
<tr>
<td>194</td>
<td>13.0 ± 1.9</td>
</tr>
<tr>
<td>196</td>
<td>12.4 ± 1.8</td>
</tr>
<tr>
<td>198</td>
<td>12.8 ± 1.9</td>
</tr>
<tr>
<td>200</td>
<td>14.6 ± 2.2</td>
</tr>
</tbody>
</table>
Figure 5.6: $I_2^*$ (27Nm$^{-2}$) fluorescence decay ($\lambda \geq 300$nm) following 196nm excitation. Top trace - fitted to a single exponential decay, bottom trace - fitted to two expotential decays.
than one electronic state. When re-analysed for double exponential decays (see Figure 5.6, bottom trace), the plots gave excellent fits yielding pairs of lifetime values. Unfortunately these values were subject to huge fluctuations, varying by a factor of 2 (cf. -20% for the single exponentials). This is symptomatic of two lifetimes with similar magnitudes (the deconvolution program can only separate out two exponentials reliably if their values differ markedly). However, the ratio of the two lifetimes was virtually constant at ~1.9. Taking 15.5ns for the lifetime of $I_2(D_0^+)$, this implies a lifetime of ~8ns for the other electronic state involved.

The lifetime of $I_2(D'2g)$ was ascertained from a decay plot of $I_2^*$ fluorescence, excited in the presence of 50kNm$^{-1}$ of CF$_4$. Other experiments demonstrated that quenching of $I_2(D'2g)$ by CF$_4$ is negligible. This gave a value of 7.25ns for the radiative lifetime (reproducible to ±0.2ns), which is in good agreement with the previously reported value of 6.7ns$^{31}$.

(3) Removal by CH$_4$ : The rate constants for the removal of IBr(DO$^+$) and $I_2(D_0^+)$ by CH$_4$ were obtained by recording fluorescence decays in the presence of increasing CH$_4$ pressures. The IBr samples comprised 67Nm$^{-2}$ of IBr plus 133Nm$^{-2}$ of Br$_2$, while the $I_2$ samples were at room temperature vapour pressure. The reciprocals of the lifetimes for the two states were plotted against CH$_4$ pressure (Figures 5.7 and 5.8), and total removal rate constants were derived from the gradients. In both cases a
Figure 5.7: Plot of the reciprocal of the fluorescence lifetime of IBr*, excited at 188nm, against added pressure of CH$_4$ ($P_{IBr} = 67$Nm$^{-2}$, $P_{Br_2} = 133$Nm$^{-2}$). The identity of IBr* is discussed in the text and states other than DO$^+$ may be involved.
Figure 5.8: Plot of the reciprocal of the fluorescence lifetime of $I_2^*(27\text{Nm}^{-2})$, following 192nm excitation, against added pressure of CH$_4$. The identity of $I_2^*$ is discussed in the text and states other than DO$_u^+$ may be involved.
value of $k_{REM} = (1.9^{+0.2}_{-0.2}) \times 10^{-10} \text{cm}^3\text{molec}^{-1}\text{s}^{-1}$ was obtained.

(4) XeI* formation: Evidence for the formation of XeI(B) from the reaction of $I_2(D0^+)$ plus Xe was presented in section 4.3, based on excitation fluorescence spectra, with the energetic threshold of formation at $190^{+1}_{-1}\text{nm}$. Lifetime decays were measured for $I_2^*$ excited at 184nm, in the presence of $7.1\text{kNm}^{-1}$ of Xe, using various filters. Figure 5.9 shows two such decay plots, recorded under identical conditions excepting the use of LF40 filter in one case (top trace) and a 254nm interference filter in the other (bottom trace). The top trace gives an extremely poor fit to a single exponential decay and shows a marked risetime of $\sim 2\text{ns}$. Thus the fluorescence being monitored here is largely from a state that has been collisionally populated, most likely the $D'2^g$ state of $I_2$ which has an emission system at $505\text{nm}^{15}$. The lifetime calculated from this decay plot is 5.6ns which, even allowing for error due to the poor fit, is short compared to the pure radiative lifetime of 7.25ns for $I_2(D'2_g)$. It therefore seems likely that $I_2(D'2_g)$ is quenched by Xe with moderate efficiency.

In sharp contrast, the plot recorded using the 254nm interference filter gives a better fit, has a minimal risetime, and yields a fluorescence decay lifetime of $8.57\text{ns}$ (note the different time scales for the two traces in Figure 5.9). A different species, which is formed extremely rapidly, is being monitored here. In view of the excitation
Figure 5.9: Fluorescence decay from a sample of I₂(27Nm⁻²) + Xe(7.1kNm⁻²), following 184nm excitation, observed through different filters. Top trace - LF40 filter (λ≥400nm), 0.0402ns/channel. Bottom trace - 254nm interference filter, 0.0792ns/channel.
spectra (see Figure 4.3, section 4.3) this is most likely to be XeI(B), emitting at 253nm. (NB it cannot be the initially populated I₂(DO_u+) state that is being monitored as other experiments showed that the lifetime of this state is reduced to less than 8.5ns by the addition of Xe at pressures ≥ 3kNm⁻²). Comparison with XeCl(B) lends further support to this assignment; the reaction of the analogous \(^1\Sigma_u^+\) ion-pair state of Cl₂ with Xe to form XeCl(B) has been found to be extremely rapid \(k_{\text{FORMATION}} = (3.0^{+0.5} \times 10^{-10} \text{cm}^3\text{molec}^{-1}\text{s}^{-1})\)\(^{144}\), and the lifetime of XeCl(B), \(\tau_{\text{RAD}} = 11.1^{+0.2}\text{ns}\)\(^{145}\), is of the same order as the decay lifetime derived from the bottom trace.

DISCUSSION

The measured radiative lifetimes for IBr(DO⁺), IBr(D'2) and I₂(D'2_g) are clear cut, with good agreement between the latter and the previously reported literature value of 6.7±0.5ns\(^{31}\). However, the situation is more complicated in the measurement of lifetimes for I₂(DO_u+) excited in the absence of buffer gas. With the exception of decays recorded at low temperatures, and hence low I₂ vapour pressures, the data cannot be satisfactorily fitted to a single exponential decay. Two possible explanations exist: (1) more than one state is populated in the initial excitation process, or (2) the initially populated DO_u+ state is transferred collisionally to one or more other states which subsequently fluoresce.
The emission from excited iodine in the region 430 - 470nm (see Figure 1.6), following 193nm excitation, has not been assigned to the DO\textsubscript{u} state and probably accounts for the additional decay process(es) observed (a contribution from underlying continuum emission cannot be ruled out). There are five peaks in this region: the peak at -430nm (on the shoulder of the system at 420nm) is probably the well known EO\textsubscript{g} \rightarrow BO\textsubscript{u} emission, while the other four peaks presumably originate from at least two of the other ion-pair states in the manifold dissociating to I\textsuperscript{+}(3P\textsubscript{2})+I\textsuperscript{-}(1S). Tellinghuisen and co-workers\textsuperscript{15} have assigned I\textsubscript{2}\textsuperscript{*} emission systems in this region, following excitation by an electrical discharge in the presence of Ar, to at least three of these states.

Other than the DO\textsubscript{u} state, the only ion-pair state in this region to which transitions are allowed is lu(3P\textsubscript{2}), correlating with I\textsuperscript{+}(3P\textsubscript{2})+I\textsuperscript{-}(1S). This perpendicular transition (\Delta\Omega = +1) is expected to be weaker than DO\textsubscript{u} \rightarrow X0\textsubscript{g}, and therefore should only make a minor contribution to the absorption process. Mulliken\textsuperscript{13} has noted the distinct possibility of a small contribution from the lu(3P\textsubscript{2}) \rightarrow X0\textsubscript{g} transition to the absorption spectrum in the region of the D \rightarrow X system, but it has not been positively identified. Viswanathan and Tellinghuisen\textsuperscript{52} have tentatively ascribed the \gamma state of King et al\textsuperscript{49} to the lu(3P\textsubscript{2}) state. However the \gamma state was produced in two-photon excitation: a two-photon transition from the ground state to the lu(3P\textsubscript{2}) state is parity forbidden making
this assignment dubious. The \( ^3P_2 \) state is thus an unknown quantity, and it is highly improbable that a single electronic state could give rise to all five extraneous emission peaks in Figure 1.6.

Therefore the second possibility, that of collisional transfer to other ion-pair states followed by emission therefrom, is the most plausible. At first glance this might seem unlikely, given the low \( I_2 \) vapour pressures and the short lifetime of \( I_2(D_{0u}+) \). However, the cross section for the process:

\[
I_2(D_{0u}+) + I_2 \rightarrow I_2^* + I_2 \tag{5.1}
\]

is expected to be extremely large (cf rate constants in Table 5.1). The emission at \( 430 < \lambda < 470 \) nm is only a small fraction of that from the \( DO_u^+ \) state (the instrument response in Figure 1.6 falls off drastically at shorter wavelengths), so what is witnessed is only the initial phase of a cascade through the vibrational levels of the ion-pair states, which would ultimately populate the (lowest) \( D'2g \) state. This also explains the fact that the \( I_2^* \) fluorescence decay plots recorded at low temperatures give satisfactory fits to a single exponential decay, i.e. at very low vapour pressures the interstate transfer process is negligible. Extra, diffuse \( I_2^* \) emission bands at long wavelengths, which are absent at low temperatures, have previously been observed upon raising the temperature of the
The efficiency of the cascade process can be understood in terms of the very high density of rovibrational levels per cm\(^{-1}\): those of the DO\(_u^+\) state are embedded in a densely packed manifold of levels belonging to the other electronic states in the ion-pair cluster. There is no discernible risetime on the I\(_2^*\) decay plots because emission from these other states only constitutes a small fraction of the total emission intensity. (In their determination of the I\(_2\)(DO\(_u^+\)) lifetime, Callear and co-workers\(^{142}\) used a high frequency detection technique which samples narrow spectral regions, so they only observed a single exponential decay of the fluorescence intensity).

In contrast to I\(_2\)(DO\(_u^+\)), IBr(DO\(^+\)) does not appear to undergo a cascade process of this type through self-collisions or collisions with Br\(_2^+\), even when much higher reagent pressures are employed. This could be partly explained by the lower density of vibrational levels in the lowest IBr ion-pair manifold, due to the fact that there are only half as many states and the vibrational frequencies are slightly higher. However it seems likely that collisional deactivation (ie quenching out of the ion-pair manifold) assumes a greater importance in the case of IBr, relative to interstate transfer. This is borne out by the invariance of the IBr\(^*\) fluorescence spectral profile (ie Figure 3.13) with changing IBr/Br\(_2\) pressure.
It seems reasonable that the removal rate constants of \( \text{I}_2^* \) and \( \text{IBr}^* \) by \( \text{CH}_4 \) should be of the same order of magnitude. However, for \( \text{I}_2^* \) \( k_{\text{REM}} \) is a factor of 4 less than the previously reported value\(^{18} \) of \( 7.9 \times 10^{-10} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1} \). This discrepancy is due to the fact that a large spectral region is being monitored in this work, whereas the previous value was derived from Stern-Volmer analysis of spectrally resolved \( \text{I}_2^* \) fluorescence over a range of \( \text{CH}_4 \) pressures. With the latter method, contributions from other fluorescing states are excluded as areas are measured under a single, isolated peak originating from the \( \text{DO}_u^+ \) state. From Figure 2 of reference \(^{18} \) is it obvious that, in addition to reacting, \( \text{CH}_4 \) promotes significant interstate transfer from \( \text{I}_2(\text{DO}_u^+) \) to other ion-pair states which subsequently fluoresce (or react). Thus the temporally resolved \( \text{I}_2^* \) fluorescence decays (which monitor undispersed fluorescence) will contain contributions from ion-pair states which are collisionally populated and yield lifetime values longer than those of the \( \text{DO}_u^+ \) state itself. This in turn leads to a value of \( k_{\text{REM}} \) which is too small, and implies an approximate value of 0.75 for the quantum yield for interstate transfer from \( \text{I}_2(\text{DO}_u^+) \). It will be seen in the next section that these considerations also apply to the removal rate constant for \( \text{IBr}(\text{DO}^+) \) with \( \text{CH}_4 \).

The results for \( \text{I}_2^* + \text{Xe} \) support the assertion that \( \text{XeI}(\text{B}) \) is formed in the reaction of \( \text{I}_2(\text{DO}_u^+) \) with \( \text{Xe} \). Assuming that quenching of \( \text{XeI}(\text{B}) \) by \( \text{Xe} \) is slow, a radiative lifetime of
- 8.5ns is obtained for XeI(B). This assumption can be justified on the basis of the following comparisons between the halogen ion-pair states and the bound states of XeI.

Table 5.3 compares the spectroscopic constants of the D/D' states of I₂/IBr and the C/B states of XeI. These constants are very similar for all six species. The XeI* exciplexes resemble the halogen ion-pair states in several ways:

(1) they give ions (Xe⁺ + I⁻) is the dissociation limit,
(2) they emit to repulsive lower states giving rise to oscillatory continuum fluorescence (see Figure 2 of reference 139),
(3) interstate transfer from C→B is efficient with a range of collision partners, 139
(4) they generally have extremely large removal cross sections ($k_{REM}$ of the order of $10^{-10} - 10^{-9}$ cm³/molec⁻¹/s⁻¹).

It can therefore be concluded that the C and B states of XeI exhibit behaviour which parallels that of the D and D' states of the halogens. As the D' states of I₂ and IBr are not efficiently removed by inert gases, it seems reasonable to assume that the same applies to XeI(B).

Additionally, in an analogous system, IBr excited at 193nm in the presence of 7.09kNm⁻¹ of Xe gave rise to an intense XeBr B→X emission. 39 Therefore quenching of XeBr(B) by Xe does
TABLE 5.3: Comparison of the spectroscopic constants of the D/D' states of I₂/IBr with those of the C/B states of XeI

<table>
<thead>
<tr>
<th></th>
<th>I₂</th>
<th>IBr</th>
<th>XeI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D₀⁺ₐ</td>
<td>D'₂₉ᵇ</td>
<td>(Δ)</td>
</tr>
<tr>
<td>Tₑ/cm⁻¹</td>
<td>41011</td>
<td>40388</td>
<td>(623)</td>
</tr>
<tr>
<td>Dₑ/cm⁻¹</td>
<td>31150</td>
<td>31773</td>
<td></td>
</tr>
<tr>
<td>ωₑ/cm⁻¹</td>
<td>98.8</td>
<td>104.0</td>
<td></td>
</tr>
<tr>
<td>rₑ/Å</td>
<td>3.56</td>
<td>3.61</td>
<td></td>
</tr>
</tbody>
</table>

a Reference 132
b Reference 41
c Reference 54
d See discussion in section 3.4
e Reference 139
not appear to be very efficient. These considerations vindicate the assumption that the removal of XeI(B) by Xe is slow.

5.3 IBr* QUENCHING STUDIES ON THE SPECTROFLUORIMETER

Experiments were carried out on the Perkin-Elmer 650-40 Spectrofluorimeter to elucidate the kinetics of physical and chemical processes involving the DO⁺ and D'2 states of IBr with a range of foreign gases. (For experimental details see section 2.4) Previous studies of the kinetics of IBr* - rare gas systems are here extended to systems with reactive and inert molecules. These molecules can be divided into three classes according to the effect which they have upon the IBr* fluorescence spectrum.

Class 1 gases, while altering the overall intensity, have no effect upon the fluorescence spectral profile. Br₂ and IBr itself fall into this category. Class 2 gases display similar behaviour to the lighter rare gases in collisions with IBr*, i.e. they bring about D → D' interstate transfer while chemical reaction is insignificant. Included in this category are SF₆, CF₄ and N₂. Class 3 gases are more complicated both reacting with IBr*, and effecting collisional transfer between the ion-pair states.
The reactive gases studied were CH$_4$, CH$_3$Cl, C$_2$H$_6$, CF$_3$Cl and O$_2$. All three classes of molecules bring about some physical quenching to the lower valence states, with the possible exception of SF$_6$. For Class 1 molecules this appears to be the principal deactivation pathway.

The features of the fluorescence spectrum of IBr* excited at 200nm (see Figures 3.13) have already been discussed in section 3.4.

RESULTS

(1) Class 1 molecules: IBr and Br$_2$ have been dealt with in the previous section.

(2) Class 2 molecules: The effect of intermediate added pressures of CF$_4$ are demonstrated in Figure 5.10. The D0$^+$ emission intensity can be seen to diminish with increasing CF$_4$ pressure (witness the main peak in the long-wavelength oscillatory continuum system at 447nm) while peaks at 342, 385, 410 and 505nm assume greater intensity. The intensity of the small peak at 490nm remains practically invariant over the pressure range presented. At high CF$_4$ pressures, a fluorescence spectrum identical to that obtained in the presence of 14.26 kNm$^{-2}$ of SF$_6$ is obtained (see Figure 3.14), with the IBr(D'2 $\rightarrow$ A'2) emission at 385nm dominant. The height of this peak increases, with concurrent narrowing, up to a CF$_4$ pressure of ~50kNm$^{-2}$, and remains virtually
Figure 5.10: The effect of added CF$_4$ upon the fluorescence spectrum of IBr*, excited at 200nm. P$_{IBr}$=P$_{Br_2}$=213Nm$^{-2}$ plus 
(a) P$_{CF_4}$=0, (b) P$_{CF_4}$=733Nm$^{-2}$, (c) P$_{CF_4}$=2.08kNm$^{-2}$. 
constant at higher pressures. The features at 342, 385, 410 and 490nm have been discussed in section 3.4, leaving only the broad emission at 505nm to be accounted for. In fact this is an I₂* emission peak which has been assigned to a bound-free, D'₂ → 2u(3Δ), transition.

Using fluorescence intensities measured at 447nm, a Stern-Volmer plot of ln(I₀/I) vs. CF₄ pressure was constructed and is shown in Figure 5.11. The slope of this plot divided by the lifetime of IBr(DO⁺) under these conditions gives the total removal rate constant (all channels) for IBr(DO⁺) with CF₄, kₐₖₜ = \(4.3 ± 0.2 \times 10^{-10}\) cm³molec⁻¹s⁻¹. This rate constant and others are gathered in Table 5.4.

The effects of added SF₆ and N₂ upon the IBr* fluorescence were similar, except for differences in the rate of disappearance of the 447nm peak. Stern-Volmer plots of the DO⁺ emission intensities at 447nm are shown for these two quenching gases in Figure 5.12. The slopes give total removal rate constants of \((8.2 ± 0.7) \times 10^{-10}\) and \((5.0 ± 1.0) \times 10^{-10}\) cm³molec⁻¹s⁻¹ for SF₆ and N₂ respectively.

(3) Class 3 molecules: The effects of small added pressures of CH₄ are demonstrated in Figure 5.13. The DO⁺ emission intensity is observed to fall off very rapidly with increasing CH₄ pressure, and this is
Figure 5.11: Stern-Volmer plot for the removal of IBr(DO⁺) (intensities measured under the 447nm peak) by CF₄.
TABLE 5.4: Removal rate constants, $k_{\text{REM}}$, for IBr(DO$^+$) and IBr(D'2) with various foreign gases

<table>
<thead>
<tr>
<th>Foreign gas</th>
<th>$k_{\text{REM}}$IBr(D)/cm$^3$molec$^{-1}$s$^{-1}$$\times 10^{10}$</th>
<th>$k_{\text{REM}}$IBr(D$'$)/cm$^3$molec$^{-1}$s$^{-1}$$\times 10^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_4$</td>
<td>4.3$\pm$0.2</td>
<td></td>
</tr>
<tr>
<td>SF$_6$</td>
<td>8.2$\pm$0.7</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>5.0$\pm$1.0</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>9.4$\pm$1.0</td>
<td>7.0$\pm$0.8</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>9.6$\pm$1.4</td>
<td>13.9$\pm$1.7</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>11.0$\pm$1.2</td>
<td>12.3$\pm$1.1</td>
</tr>
<tr>
<td>CF$_3$Cl</td>
<td>8.1$\pm$0.8</td>
<td>2.6$\pm$0.5</td>
</tr>
<tr>
<td>O$_2$</td>
<td>2.1$\pm$0.3</td>
<td>2.9$\pm$0.3</td>
</tr>
</tbody>
</table>
Figure 5.12: Stern-Volmer plot for the removal of IBrDO$^+$ (intensities measured under the 447nm peak) by non-reactive gases SF$_6$ and N$_2$. 
Figure 5.13: Quenching of IBr* (excited at 200nm) by CH₄. $P_{IBr} = P_{Br} = 120\text{Nm}^{-2}$ plus

(a) $P_{CH_4} = 0$, (b) $P_{CH_4} = 280\text{Nm}^{-2}$, (c) $P_{CH_4} = 1.3\text{kNm}^{-2}$, (d) $P_{CH_4} = 6.7\text{kNm}^{-2}$. 
reflected in the large removal rate constant, \( k_{REM} = (9.4^{+1.0}_{-1.0}) \times 10^{-10} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1} \), obtained from a Stern-Volmer analysis of the intensity under the 447nm peak (plotted in Figure 5.14). The \( D'2 \rightarrow A'2 \) emission at 385nm increases in intensity up to a \( CH_4 \) pressure of 1.3kN\( m^{-2} \), then decreases at higher \( CH_4 \) pressure. At a \( CH_4 \) pressure of 6.7kN\( m^{-2} \), where emissions from the D and \( D' \) states of IBr are virtually eliminated, a moderately intense continuum emission remains. This continuum emission is prevalent between 300 and 400nm, and may be due to scattered white light.

The other group 3 molecules exhibited similar behaviour to \( CH_4 \). The overall intensity removal followed the same pattern except for a variation in the relative magnitude of the 385nm emission peak. This variation was small in the case of \( CH_3 Cl \), \( C_2 H_6 \) and \( O_2 \) while an increase in the relative intensity at 385nm was observed with \( CF_3 Cl \) (see Figure 5.15). Stern-Volmer analyses of spectrofluorimeter traces were performed for the removal of IBr(DO\(^+\)) by \( CH_3 Cl \), \( C_2 H_6 \), \( CF_3 Cl \) and \( O_2 \). These are shown graphically in Figures 5.16 - 5.19, and the removal rate constants derived from them are presented in Table 5.4.

(4) IBr(D'2) removal by class 3 molecules : In order to study the removal of IBr(D'2) by class 3 molecules, a series of experiments was carried out in the manner described above but with the addition of large excesses
Figure 5.14: Stern-Volmer plot for the removal of IBr(DO⁺) by CH₄.
Figure 5.15: Effect of added CF$_3$Cl on the fluorescence spectrum of IBr* (excited at 200nm).

\[
P_{\text{IBr}} = P_{\text{Br}_2} = 213 \text{ Nm}^{-2} \text{ plus (a) } P_{\text{CF}_3\text{Cl}} = 0, \text{ (b) } P_{\text{CF}_3\text{Cl}} = 933 \text{ Nm}^{-2}, \text{ (c) } P_{\text{CF}_3\text{Cl}} = 1.48 \text{ kNm}^{-2}.
\]
Figure 5.16: Stern-Volmer plot for the removal of IBr(DO\textsuperscript{+}) by CH\textsubscript{3}Cl.
Figure 5.17: Stern-Volmer plot for the removal of IBr(DO⁺) by C₂H₆.
Figure 5.18: Stern-Volmer plot for the removal of IBr(DO$^+$) by CF$_3$Cl
Figure 5.19: Stern-Volmer plot for the removal of IBr(DO⁺) by O₂.
of SF$_6$ (a non-reactive, class 2 molecule) to the sample cell in addition to various pressures of class 3 molecules. Rapid IBr(D$_0^+$ $\rightarrow$ D'2) interstate transfer is promoted by SF$_6$ (see section 3.4 and Figure 3.14) and the addition of a sufficiently high pressure ensures that virtually all IBr* molecules are transferred to the D'2 state prior to collision with a class 3 molecule.

Figure 5.20 shows the effect of the addition of small pressures of CH$_4$ on the fluorescence spectrum of IBr(D'2) excited at 200nm in the presence of 12.7kNm$^{-2}$ of SF$_6$. The intensities of all the peaks fall off steadily with increasing CH$_4$ pressure. The IBr(D'2 $\rightarrow$ A'2) peak intensity at 385nm was utilised in a Stern-Volmer analysis (see Figure 5.21) which yielded a removal rate constant for IBr(D'2) by CH$_4$, $k_{REM} = (7.0 \pm 0.8) \times 10^{-10}$ cm$^3$ molec$^{-1}$ s$^{-1}$. Figures 5.22-5.25 show the Stern-Volmer plots for the removal of IBr(D'2) by CH$_3$Cl, C$_2$H$_6$, CF$_3$Cl and O$_2$. The removal rate constants thus obtained are included in Table 5.4.

DISCUSSION

The preceding results can be rationalised in terms of the following scheme:
Figure 5.20: Quenching of IBr(D') by CH₄. \( P_{IBr} = P_{Br_2} = 213 \text{Nm}^{-2} \), \( P_{SF_6} = 12.7 \text{kNm}^{-2} \) plus

(a) \( P_{CH_4} = 0 \), (b) \( P_{CH_4} = 133 \text{Nm}^{-2} \), (c) \( P_{CH_4} = 260 \text{Nm}^{-2} \), (d) \( P_{CH_4} = 400 \text{Nm}^{-2} \).
Figure 5.21: Stern-Volmer plot for the removal of IBr(D'2) by CH₄.
(Intensities measured under the 385nm peak.)
Figure 5.22: Stern-Volmer plot for the removal of IBr(D') by CH$_3$Cl
Figure 5.23: Stern-Volmer plot for the removal of IBr(D'2) by C₂H₆
Figure 5.24: Stern-Volmer plot for the removal of IBr(D') by CF$_3$Cl.
Figure 5.25: Stern-Volmer plot for the removal of IBr(D'2) by O₂.
IBr(\(X_0^+\)) + h\nu \xrightarrow{I_a} IBr(\(D_0^+\))

IBr(\(D_0^+\)) \xrightarrow{k_D} \text{SPONTANEOUS DECAY}

IBr(\(D_0^+\)) + M(R) \xrightarrow{k_M} IBr(\(D'2\)) + M(R)

IBr(\(D_0^+\)) + R \xrightarrow{k_1} \text{PRODUCTS}

IBr(\(D'2\)) + R \xrightarrow{k_2} \text{PRODUCTS}

IBr(\(D'2\)) \xrightarrow{k_F} IBr(\(A'2\)) + h\nu

where \(M\) is a class 2 molecule and \(R\) is a class 3 molecule.

(1) Removal mechanism for IBr* (\(D_0^+\)) : The large removal rate constants are not entirely unexpected. A previous study produced comparable values for the removal of I\(_2\)(\(D_0^+\)) by a range of molecules. The fact that the removal rate constants are extremely large and virtually independent of the polarity of the collision partner suggests that a curve-crossing mechanism plays a major part in these processes. Although IBr* has a relatively diffuse electron cloud, it would be impossible to account for the rate constants in Table 5.4 on the basis of a mechanism where the dispersion forces are responsible for the attraction between the collision partners. When long-range permanent dipole-dipole interactions are
involved the 'Golden Rule' quenching mechanism can give rise to rate constants which are greater than gas kinetic. However, with the exception of CH₃Cl and CF₃Cl all of the quenching molecules in the present study are apolar.

Figure 5.26 illustrates the curve-crossing mechanism which is proposed to account for the kinetic data collected in this chapter. The entrance and exit channels for the quenching processes are coupled by a steep ionic potential which dissociates to IBr⁻ + Q(R)⁺ in the diabatic dissociation limit. In the quenching of IBr(DO⁺) the initial entrance channel corresponds to IBr(DO⁺,v' = 107) + Q(R) : 200 nm excitation populates v' = 107 (see section 3.2). In addition there may be subsequent re-entry from other vibrational levels following inelastic collisions: although only one potential curve is shown to represent each of the neutral channels and the ionic state, in reality each would comprise a nested series of curves representing the various vibrational levels. Crossings will occur at the intersections of the ionic state with the various channels with probability $P_X$, so the initial crossing onto the ionic curve will occur with probability $P_{1a}$. Once an ionic intermediate (ion-pair) has been formed, it can exit the ionic state via various routes, with the following possible outcomes: (a) elastic recoil (exit channel = entrance channel) (b) inelastic recoil with
Figure 5.26: Schematic of the curve-crossing mechanism operative in the removal of IBr ion-pair states by various foreign gases (not to scale). The ionic intermediate is formed by partial donation of an electron from Q(R) into the vacancy in an inner orbital of IBr*.
the production of IBr(DO⁺, v' < 107) + Q(R)⁺, (c) interstate transfer with the production of IBr(D'2,v) + Q(R)⁺, or (d) chemical reaction with the formation of some other products. The extent of vibrational relaxation within the D-state (ie route (b)) is indeterminate in these experiments since the spectral profile of the oscillatory continuum fluorescence is virtually unaltered (at the resolution of these experiments) for small changes in the upper vibrational level, v', from which the transition occurs. The fourth possibility only exists for reactive gases, R.

The situation is simplified in the case of IBr(D'2) removal as studied here, since a large excess of buffer gas ensures thermalisation of the vibrational levels prior to collision. The entrance channel corresponds to IBr(D'2, low v) + Q(R) and crossing to the ionic curve occurs with probability P₂. Only elastic collisions are possible with inert gases, which have no product channel available. However, elastic and reactive processes are possible with some gases.

Large quenching cross-sections are possible with this model as the ionic curve will extend to very large separations (attractive potential, \( V \propto 1/r \)), and there will be a high density of neutral exit channels available
to the ionic intermediate as a result of the high density of rovibrational levels.

In view of this mechanistic proposal the results for the removal of IBr(D0⁺) and IBr(D'2) are similar to each other: they correspond to different entrance channels but the exit channels in the case of IBr(D'2) are a subset of those available in quenching from IBr(D0⁺). In both cases the branching between the available exit channels will be determined by the various P_x. A similar situation will exist for each of the collision partners (Q,R) except for displacements in the position of the ionic curve due to the different ionization potentials of these species.

In the quenching of IBr(D0⁺) by class 2 molecules exit channels (1) and (2) dominate with little (if any) chemical reaction. This is not surprising in the case of N₂ as excitation at 200nm corresponds to an energy of 598 kJmol⁻¹ which is insufficient to break the extremely strong triple bond (N ≡ N bond energy = 946 kJmol⁻¹). Although there is sufficient energy to break an S-F bond (bond energy = 326 kJmol⁻¹), SF₆ is known to be extremely inert. This is attributed to a combination of factors: (1) the S-F bond is strong, (2) the S-atom is coordinately saturated, (3) the S-atom is sterically
hindered, and (4) the molecule is apolar. Similar considerations apply to CF$_4$ which, like SF$_6$, is extremely inert (C-F bond energy = 485 kJmol$^{-1}$). The relative magnitudes of the rate constants for the removal of IBr(DO$^+$) by these gases is thus determined by the density of entrance and exit channels and the magnitudes of the crossing probabilities for these channels.

In the quenching of IBr(DO$^+$) by class 3 molecules, all 3 exit channels are available. The removal rates for CH$_4$, CH$_3$Cl, C$_2$H$_6$ and CF$_3$Cl are very similar, which implies that the crossing points ($r_x$) and probabilities ($P_{1a}$) have similar magnitudes. However, removal by O$_2$ is appreciably slower implying smaller magnitudes in this case. Previous studies$^{18,34}$ indicate that a similar situation exists for the removal of I$_2$(DO$_{u+}$) by class 3 molecules, ie removal by O$_2$ is also appreciably slower (see Table 5.5).

Qualitative observations can be made on the relative contributions of exit channels (2) and (3) for the various reactive gases, on the basis of spectra such as those shown in Figures 5.13 and 5.15.
**TABLE 5.5**: Removal rate constants, $k_{REM}$, for I$_2$(DO$_4$) with various foreign gases.

<table>
<thead>
<tr>
<th>Foreign gas</th>
<th>$k_{REM}$/cm$^3$molec$^{-1}$s$^{-1} \times 10^{10}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>7.9$\pm$0.2</td>
<td>18</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>21.0$\pm$1.0</td>
<td>18</td>
</tr>
<tr>
<td>CF$_3$Cl</td>
<td>7.1$\pm$0.4</td>
<td>18</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.96</td>
<td>43</td>
</tr>
</tbody>
</table>
The intensity of the peak at 385nm reflects the extent of the contribution from exit channel (2), but the picture is complicated by subsequent reaction of IBr(D'2) with these gases. For CH₄, CH₃Cl, C₂H₆ and O₂ exit channel (3) appears to dominate over exit channel (2), while for CF₃Cl exit channel (2) assumes a greater importance (see Figure 5.15). In fact CF₃Cl would be better classified as being intermediate between classes (2) and (3). In a study of the reactions of I₂(D0⁺) with methane and various halomethanes, Willard and Glasgow found a marked decrease in the quantum yield for reaction (exit channel (3)) upon increasing the number of F atoms, n, in the serious CFₙH₄₋ₙ, and an increase upon including a Cl atom (see Table 5.6). Therefore an intermediate classification for CF₃Cl fits in with previously observed behaviour in the removal of the analogous D₀⁺ state of I₂.

Collisions between thermalised IBr(D'2) and class 3 molecules (entrance channel 2) can result in either elastic recoil (exit channel 2) or reaction (exit channel 3). Again the variations in the removal rates can be explained by the following factors: (1) differences in the curve-crossing positions and probabilities, and (2) differences in the relative contributions of the two exit channels. Since the intermediate ionic curve (or nest of curves) is common to the removal of IBr(D0⁺) and IBr(D'2) for a particular collision partner, it seems most plausible that the relatively small
TABLE 5.6: Quantum yields for the reactive removal of $I_2(2 DO_u^+)$ by methane and various halomethanes (100 torr). From reference 17.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Phi_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_4$</td>
<td>0.002</td>
</tr>
<tr>
<td>CF$_3$H</td>
<td>0.07</td>
</tr>
<tr>
<td>CFH$_3$</td>
<td>0.20</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.30</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>0.40</td>
</tr>
</tbody>
</table>
removal rate constant for IBr(D'2) with O₂ is a result of a small crossing probability, P₂, to form the intermediate ionic species. Taking the ionization potentials of the class 3 molecules in the present study into account, the intersection of the neutral and ionic curves should occur at a relatively large separation for R=O₂ - see Table 5.7. The relatively small removal rate found for IBr(D'2) with CF₃C1 is a result of the predominance of exit channel (2) over exit channel (3), as previously discussed for IBr( DO⁺).

The extremely large removal rate constant for IBr(D'2) with CH₃C1 and C₂H₆, in relation to CH₄, will be due primarily to the lower ionization potentials of these molecules which will result in larger values of rₓ. In addition to this it is likely that IBr(D'2) has a greater reactivity towards C-Cl and C-C bonds, both of which are weaker than C-H bonds. This would correspond to a higher probability for crossing onto the reactive exit channel (P₃) with these molecules.

(2) Discrepancy between the removal rates for IBr(DO⁺) with CH₄ as measured on SRS port HAl2 (time resolved) and on the spectrofluorimeter: the temporally resolved studies reported in section 5.2 yielded a value of 1.9 x 10⁻¹⁰ cm³molec⁻¹s⁻¹ for the removal of IBr(DO⁺) by CH₄. This is a factor of 5 less than the value derived from Stern-Volmer analysis of spectrofluorimeter traces. As discussed for I₂(DO⁺) in section 5.2, this discrepancy is due to the fact that a large spectral region was monitored in the time
TABLE 5.7: Ionization potentials for the class 3 molecules discussed in this chapter. (Taken from "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions", US Department of Commerce, National Bureau of Standards, NSRDS-NBS 26 (1969).

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>IONIZATION POTENTIAL (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>13.21</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>11.93</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>11.60</td>
</tr>
<tr>
<td>CF₃Cl</td>
<td>12.90</td>
</tr>
<tr>
<td>O₂</td>
<td>12.20</td>
</tr>
</tbody>
</table>
resolved work on port HA12 and so contributions from the underlying continuum emission and possibly from other ion-pair states cannot be precluded. In the Stern-Volmer analysis of the spectrofluorimeter traces data were derived from a single IBr(DO$^+$) emission peak, and thus result in an accurate removal rate constant.

5.4 CONCLUSION

The values obtained for pure radiative lifetimes of halogen ion-pair states are summarised in Table 5.8. The value obtained for I$_2$(D'2 9g) agrees well with a previously reported value of 6.7ns$^{31}$. It was not possible to determine the radiative lifetime of I$_2$(DO$_u^+$) as it was found that more than one electronic state of I$_2$ was responsible for the signal detected following excitation. It is postulated that the additional state(s) is populated as a result of collisional transfer from I$_2$(DO$_u^+$) rather than by direct excitation.

The lowest bound state of XeI*, the B-state, which resembles the D'-states of IBr and I$_2$ in its physical behaviour, has a radiative lifetime of 8.57ns.

The principal deactivation pathway in the removal of
The following conclusions can be drawn for the reactive gases studied: (1) IBr(D'2) is removed more rapidly by CH₃Cl and C₂H₆, in comparison to CH₄, as a result of the lower ionization potentials of these molecules which result in larger values for rₓ (see Figure 5.26). In the removal of IBr(DO⁺), where the picture is complicated by additional exit channels, only C₂H₆ shows a marked increase relative to CH₄. (2) As expected on the basis of its ionization potential, CF₃Cl removes IBr(DO⁺) at a rate comparable to CH₄. However it is less reactive than CH₄ in that interstate transfer (i.e. D0⁺ → D'2, exit channel 2) plays a more dominant role in the removal process. The assertion is supported by the relatively small removal rate found for IBr(D'2) with CF₃Cl: as the intermediate ionic curve is common to both removal processes it can be concluded that crossing onto the reactive exit channel is not very efficient (i.e. P₃ is low). (3) O₂, which has an ionization potential ca. 1 eV lower than CH₄, provides an intriguing exception to the behaviour observed for the other class 3 molecules. The results indicate that removal of IBr(D/D') by O₂ is relatively inefficient due to inefficiency in crossing onto the ionic intermediate curve (i.e. P₁a and P₂ are low).

While the curve-crossing model provides a good basis for explaining these results, the true picture is more complicated. This is to be expected since the model, which was developed to rationalise a range of atomic collisional
processes, takes no account of the internal degrees of freedom of the colliding molecules.
CHAPTER 6 - STUDIES OF CH(A^2\Delta) FORMATION IN PHOTOFRAGMENTATION PROCESSES

6.1 Introduction 159

6.2 Results 160

6.3 Discussion 175

6.4 Conclusion 181
In this chapter photofragmentation processes leading to the production of the first excited state of the methylidyne radical, CH(A^2Δ), will be examined. Several small organic molecules which give rise to CH(A^2Δ → X^2Π) emission following multiphoton absorption at 193nm (ArF laser) will be dealt with.

There are three categories of excitation mechanisms which could be involved in the dissociation processes: (1) sequential excitation of the parent molecule via real intermediate state(s), (2) simultaneous excitation of the parent molecule via virtual state(s), and (3) stepwise dissociative excitation via intermediate fragment(s). These are described more fully in section 1.8. The objectives of the investigations were two-fold: firstly, to address the crucial question as to which of the excitation mechanisms dominates, and secondly, to give guidance in the selection of a suitable precursor for the study of collisional processes involving CH(A^2Δ) (see next chapter).

Various other excited species were observed in emission, but will not be dealt with here.
With the exception of CH$_2$I$_2$, all of the investigations were carried out at Edinburgh using the experimental set-up described in section 2.6. CH$_2$I$_2$ was investigated at the laser facility of the Rutherford Appleton Laboratory using the experimental set-up described in section 2.7.

(a) CH$_3$Br

Absorption by CH$_3$Br in the UV sets in at 285nm and results primarily in dissociation to CH$_3$+Br. At 193nm the molar extinction coefficient is $\varepsilon = 100$ l/mole cm$^{-1}$. Figure 6.1a shows the CH(A$^2 \Delta \rightarrow X^2 \Pi$) fluorescence that results from 193nm laser photolysis of CH$_3$Br, at a resolution of 0.13nm. The CH$_3$Br pressure employed was 14.7Nm$^{-2}$. The effective rotational 'temperature' of CH(A$^2 \Delta$)thus produced was determined from the relative intensities of the R-branch rotational lines (v'=0) using a method previously detailed in the literature$^{149,150}$. The graphical determination (see Figure 6.2) yielded the value $T_{rot} = 2900^{+150}_{-150}$K. This value and several others are collected in Table 6.1. The extent of vibrational excitation is not so easily quantified due to the high degree of overlap, particularly at the Q(0,0) band-head, of the various transitions from the three bound upper vibrational levels. However a simulated spectrum (Figure 6.1b) with $T_{rot} = 3000$K and the vibrational populations in
Figure 6.1: (a) CH(A^2Δ → x^2Π) photofragment fluorescence following ArF laser photolysis of CH₃Br (p = 13.3Nm⁻²); (b) computer simulation of spectrum (a).
Figure 6.2: Relative rotational populations of CH(A^2 \Delta, v' = 0), produced in the 193nm laser photolysis of CH_3 Br, as a function of rotational quantum number, J (J + 1). The error quoted for T_{rot} is 2\sigma. (Relative population, P_J = \ln(I/S \nu^3) where I = measured intensity, S = linestrength and \nu is the transition frequency.)

T_{rot} = 2900 \pm 150 K
TABLE 6.1: Rotational temperatures of CH($A^2\Delta$) radicals produced in 193nm laser photolysis of various precursors.

<table>
<thead>
<tr>
<th>PRECURSOR</th>
<th>$T_{\text{rot}}(A^2\Delta)/K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$Br</td>
<td>2900±150</td>
</tr>
<tr>
<td>CHBr$_3$</td>
<td>2600±100</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>2250±300</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CO</td>
<td>2250±200</td>
</tr>
<tr>
<td>CH$_2$I$_2$</td>
<td>-3000</td>
</tr>
<tr>
<td>CH$_3$NH$_2$</td>
<td>2200±250 a</td>
</tr>
<tr>
<td>C$_2$H$_3$CHO</td>
<td>4700±200 b</td>
</tr>
</tbody>
</table>

a Calculated from Figure 1 of reference 94

b reference 91
v=0, 1 and 2 corresponding to a Boltzmann temperature of 2000K, gives a good fit to the experimentally observed spectrum. The computer program used for the simulation was based on one described by Baas and Beenakker\textsuperscript{151}, and an annotated copy is presented in Appendix 1.

Figure 6.3 illustrates the effect of increased vibrational excitation on the CH(A\textsuperscript{2}∆ → X\textsuperscript{2}Π) emission spectrum, with a fixed amount of rotational excitation (T\textsubscript{rot} = 3000K). These simulations were used to estimate the vibrational temperatures in other spectra through comparison of the intensities at the Q(0,0) and Q(2,2) band-heads.

(b) CHBr\textsubscript{3}
Bromoform absorbs strongly from 285nm to shorter wavelengths, with excitation at 193nm corresponding to absorption in the highest of the four bands predicted by symmetry considerations\textsuperscript{152}. In the flash photolysis of CHBr\textsubscript{3} at \( \lambda \geq 165\text{nm} \), CH(X\textsuperscript{2}Π) is believed to be generated by a successive photodetachment process\textsuperscript{82}

\[
\text{CHBr}_3 + h\nu (\lambda \geq 165\text{nm}) \rightarrow \rightarrow \text{CH(X}^2\text{Π}) + 3\text{Br} \quad -(6.1)
\]

Figure 6.4 shows part of the CH(A\textsuperscript{2}∆ → X\textsuperscript{2}Π) photofragment fluorescence which follows 193nm laser photolysis of CHBr\textsubscript{3}. The R-branch rotational lines of the v=0 level are identified. A CH(A\textsuperscript{2}∆) rotational temperature of 2600 ± 100K was determined graphically from the relative intensities of
Figure 6.3: Simulated CH($A^2\Delta \rightarrow X^2\Pi$) emission spectra illustrating the manifestation of increased vibrational excitation ($T_{\text{rot}} = 3000K$).
Figure 6.4: R-branch of $\text{CH}(\text{A}^2\Delta \rightarrow \text{X}^2\Pi)$ photofragment fluorescence following ArF laser excitation of CHBr$_3$ ($p = 13.3 \text{Nm}^{-2}$, resolution = 0.13nm). The $v=0$ rotational levels are identified.
c) $\text{C}_2\text{H}_2$

Acetylene is the simplest molecule from which CH radicals can be produced. The absorption spectrum is highly structured between 237 nm (the onset of the $\tilde{A}^1\text{A}_u \rightarrow \tilde{X}^1\Sigma^+$ transition) and the ionization limit near 110 nm. In the 237-150 nm region it consists of many weak, diffuse bands corresponding to the forbidden $\tilde{A}^1\text{A}_u \rightarrow \tilde{X}^1\Sigma^+$ and $\tilde{B}^1\text{B}_u \rightarrow \tilde{X}^1\Sigma^+$ transitions, with the $\tilde{B}^1\text{B}_u \rightarrow \tilde{X}^1\Sigma^+$ origin occurring near 185 nm. Absorption of a single 193 nm photon corresponds to excitation of a very high vibrational level of the $\tilde{A}^1\text{A}_u$ state and the resultant fluorescence is weak.

The weak $\text{CH}(A^2\Delta \rightarrow X^2\Pi)$ fluorescence which results from 193 nm laser photolysis of $\text{C}_2\text{H}_2$ is shown in Figure 6.6. The $\text{CH}(A^2\Delta)$ emission is confined to the region 427-433 nm, with the 'structure' to shorter wavelengths illustrating the noise level. Thus it can be concluded that $\text{CH}(A^2\Delta)$ is produced with very little internal excitation. It is noteworthy that, unlike the other precursors studied, $\text{C}_2\text{H}_2$ did not give rise to $\text{CH}(C^2\Sigma^- \rightarrow X^2\Pi)$ or $\text{CH}(C^2\Sigma^+ \rightarrow X^2\Pi)$ emissions. The anomalously high 'P-branch' intensity in Figure 6.6 at $\lambda = 433-440$ nm is in fact assignable to the $\Delta v = -2$ progression of the $\text{C}_2(d^3\Pi_g \rightarrow a^3\Pi_u)$ Swan bands.
Figure 6.5: Relative rotational populations of CH(A2Δ, v'=0), produced in the 193nm laser photolysis of (a) CHBr3, (b) CH3OH, (c) (CH3)2CO, and (d) CH3NH2, as a function of rotational quantum number, J(J+1).
Figure 6.6: CH($A^2\Delta \rightarrow X^2\Pi$) photofragment fluorescence following ArF laser photolysis of $C_2H_2$ ($p = 26.7 \text{Nm}^{-2}$). The intensity in the region 440-433nm is attributed to the $C_2(d^3\Pi_g \rightarrow a^3\Pi_u, \Delta \nu = -2)$ emission band.
(d) CH₃OH
Methanol shows only continuous absorption in the UV/vacuum UV region. It absorbs weakly at 193nm (ε = 125)\(^{159}\). Figure 6.7 shows the CH(A\(^2\Delta \rightarrow \chi^2\Pi\)) fluorescence that results from 193nm laser photolysis of CH₃OH. The CH(A\(^2\Delta\)) rotational temperature was determined to be 2250±300K (see Figure 6.5b), while an estimate of 1500-2000K can be made for the vibrational temperature.

(e) (CH₃)₂CO
Acetone has a moderately strong absorption in the near UV extending from 330-220nm which corresponds to the A ← X electronic transition. To shorter wavelengths there are three or four strong band groups. The ArF laser transition coincides with the first of these, the B ← X transition, which comprises sharp bands and extends from 194.5-179nm (log ε = 3.5 at 193nm).\(^{160}\) Figure 6.8 shows the CH(A\(^2\Delta \rightarrow \chi^2\Pi\)) fluorescence that results from 193nm laser photofragmentation of (CH₃)₂CO. The intensity distribution of the rotational lines corresponds to a rotational temperature of 2250±200K (see Figure 6.5c), while an estimate of ~1500K can be made for the vibrational temperature.

(f) CH₂I₂
Methylene iodide absorbs strongly from ~350nm to shorter wavelengths,\(^{152}\) and has four absorption bands extending through the UV. 193nm excitation coincides with the highest of these bands, and absorption is very strong (ε = 12000
Figure 6.7: \( \text{CH}(A^2\Delta \rightarrow X^2\Pi) \) photofragment fluorescence following ArF laser excitation of \( \text{CH}_3\text{OH} \) (\( p=13.3\text{Nm}^{-2} \)).
Figure 6.8: \( \text{CH}(A^2\Delta \rightarrow X^2\Pi) \) photofragment fluorescence following ArF laser excitation of \((\text{CH}_3)_2\text{CO} \) (p = 16N\text{m}^{-2}, resolution = 0.2nm)
Figure 6.9 shows the $\text{CH}(A^2\Delta \rightarrow X^2\Pi)$ photofragment fluorescence which follows 193nm laser excitation of $\text{CH}_2\text{I}_2$. The spectrum was recorded in a single laser shot on an OMA (see section 2.7). It was necessary to record the spectrum in this way as $I_2$ is a product in the UV photolysis of $\text{CH}_2\text{I}_2$ at this wavelength, and itself gives rise to strong fluorescence when excited at 193nm (see Figure 1.6).

Although the resolution is insufficient for a graphical determination of the $\text{CH}(A^2\Delta)$ rotational temperature, the profile of the R-branch indicates that $T_{\text{rot}} \approx 3000$K. The relative intensity of the Q(2,2) band-head indicates a vibrational temperature of about 2000K.

(g) $\text{CH}_3\text{NH}_2$

Nishi and co-workers\textsuperscript{94} have published a rotationally resolved $\text{CH}(A^2\Delta \rightarrow X^2\Pi)$ emission spectrum, produced in the 193nm laser photolysis of $\text{CH}_3\text{NH}_2$. From this a $\text{CH}(A^2\Delta)$ rotational temperature of $2200\pm250$K was ascertained; see Figure 6.5d.

(h) Other Precursors

All of the precursors discussed so far absorb to some degree at 193nm. Two molecules which are completely transparent at 193nm, but which are potential sources of CH radicals, were photolysed with an ArF laser. Of these, acetaldehyde gave an extremely weak fluorescence signal at 431nm, while acetonitrile did not yield $\text{CH}(A)$. Therefore it appears that

1 mol$^{-1}$cm$^{-1}$)\textsuperscript{161}
Figure 6.9: CH($A^2\Delta \rightarrow \chi^2\Pi$) photofragment fluorescence following ArF laser excitation of CH$_2$I$_2$

($p=13.3$ mN$^{-2}$). Resolution $= 0.35$ nm.
purely simultaneous absorption processes are insignificant at the laser energies employed in these experiments.

6.3 DISCUSSION

The two most striking aspects of the CH(A^2Δ) internal energy distributions in these studies are: (1) with the possible exception of C_2H_2 the rotational level populations always correspond to Boltzmann distributions (in the temperature range 2000-3000K), and (2) invariably there is more energy partitioned into the rotational degrees of freedom than into the vibrational degree of freedom. C_2H_2, which gives rise to CH(A^2Δ) with very little internal excitation, will be dealt with later.

The fact that the rotational distributions appear Boltzmann, and may be assigned 'temperatures', implies statistical behavior of the internal energy of the precursor species. (Note that if CH(A^2Δ) production involves secondary photolysis of primary photofragments the precursor and parent molecule will be different species). Such distributions can be computed using formalisms such as Phase-space theory (PST)\textsuperscript{162-167} or statistical adiabatic-channel theory (SACT)\textsuperscript{168,169}. Both of these models assume statistical behavior of internal energy in the precursor while they contain different assumptions
concerning the dynamical constraints associated with the fragmentation. In PST angular-momentum coupling together with the form of the radial potential describing the separating fragments are included. Due to lack of constraints on the range of the angular potential between separating fragments PST tends to predict similar values of $T_{\text{rot}}$ and $T_{\text{vib}}$, sometimes in contrast to experimental observations (as is the case here). However SACT does contain a parameter which describes the range of the angular potential, and Beresford and co-workers have used it successfully to reproduce their experimentally observed 'temperatures' ($T_{\text{rot}} = T_{\text{vib}}$) for CN($X^2\Sigma^+$) produced in the IR multiple-photon dissociation of CF$_3$CN. Therefore it is possible, using theories such as SACT, to account for internal energy distributions in photofragments such as have been observed in these experiments.

The similarity of the values of $T_{\text{rot}}$ for a range of molecules, together with the consistent finding of $T_{\text{rot}} > T_{\text{vib}}$, suggests that a common route may be operative in the production of CH($A^2\Delta$) and that to some extent the internal energy distribution is independent of the parent molecule. A number of mechanistic proposals have been put forward for the production of CH* in the 193nm laser photolysis of molecules of the type CH$_3$X ($X=$halogen, OH, NH$_2$, etc.).

Fotakis and co-workers$^{88}$ favour a simultaneous two-photon
absorption into a doubly excited CH$_3^*$ state (see equation 1.9) which subsequently fragments to yield CH$^*$ and other products. The CH(A$^2 \Delta \rightarrow x^2 \Pi$) fluorescence intensity was found to depend quadratically upon the laser energy. Jackson and co-workers have also suggested a two-photon mechanism but with the precursor produced via sequential absorption$^{171}$, while another group$^{94}$ opt for a doubly excited precursor to CH$^*$ without specifying the absorption mechanism.

Although CH$_3$ is transparent to 193nm radiation$^{172}$, Baronavski and co-workers$^{89}$ suggest that secondary photolysis of an intermediate methyl radical is the route to CH$^*$, viz:

\[
\text{CH}_3 \text{X} + h\nu (\lambda = 193\text{nm}) \rightarrow \text{CH}_3 + \text{X} \quad -(6.2a)
\]

\[
\text{CH}_3 + h\nu (\lambda = 193\text{nm}) \rightarrow \text{CH}^* + \text{H}_2 \quad -(6.2b)
\]

Nagata and co-workers$^{92}$ have managed to resolve the $\Lambda$-doublet components of the higher rotational levels of the R-branch in the CH(A$^2 \Delta \rightarrow x^2 \Pi$) emission spectrum following 193nm laser excitation of three methyl-containing molecules. On the basis of the unequal $\Lambda$-doublet intensities and the cubic power dependence of the emission intensity they have proposed that CH(A$^2 \Delta$) is produced through multiple processes where either CH$_3$, or CH$_2$, or both, are the precursors, viz:
\[
\text{CH}_3\text{X} + h\nu \rightarrow \text{CH}_3 + X
\] 
-(6.3a)

\[
\text{CH}_3 + 2h\nu \rightarrow \text{CH}(A^2\Delta) + 2\text{H} \text{ (or H}_2\text{)}
\] 
-(6.3b)

\[
\text{CH}_3 + h\nu \rightarrow \text{CH}_2 + \text{H}
\] 
-(6.3c)

\[
\text{CH}_2 + h\nu \rightarrow \text{CH}(A^2\Delta) + \text{H}
\] 
-(6.3d)

This last mechanism is most likely to be prevalent as it best explains the similarities in the internal energy disposals in \(\text{CH}(A^2\Delta)\) produced from a range of methyl containing molecules, ie once the C-X bond has been broken the processes are identical except for the extent of internal excitation of the precursor fragment. The following arguments give additional support to this proposal.

Firstly, the differences in the \(\text{CH}(A^2\Delta)\) rotational temperatures can be explained primarily by differences in the C-X bond strengths : if the C-X bond is weak (eg C-I, C-Br) there is a greater excess of energy available for disposal in the various degrees of freedom of the departing fragments. This excess energy will subsequently be transmitted to the secondary photofragments.

Secondly, it has been demonstrated in the photodissociation of \(\text{CH}_3\text{I}\) at 248 and 266nm :\textsuperscript{173,174
\[
\text{CH}_3\text{I} + h\nu (\lambda = 248 \text{ or } 266\text{nm}) \rightarrow \text{CH}_3^+ + I
\] 

that internal excitation of the recoiling \text{CH}_3\ group is exclusive to the \nu_2 \text{ out-of-plane ('umbrella')} bending mode. As repulsive excited states are accessed in the 193nm excitation of the other molecules studied here, it seems likely that they will also produce \text{CH}_3^+ as a primary photofragment. \text{CH}(A^2\Delta) could then be produced by some combination of processes 6.3b-d. Changes in the H-C-H bond angle upon going from parent molecule to \text{CH}_3 and/or \text{CH}_2 precursor fragments, coupled with excitation of bending modes such as the \nu_2 'umbrella' mode of \text{CH}_3 or the \nu_2 'scissors' mode of \text{CH}_2, will provide the torque necessary to excite rotation of \text{CH}(A^2\Delta) as the fragments dissociate on a repulsive surface. Additionally, any change(s) in the equilibrium C-H bond length en route will favour vibrational excitation of \text{CH}(A^2\Delta).

Thirdly, the phenomenon of unequal \Lambda\-doublet populations, reported by Nagata and co-workers in the production of \text{CH}(A^2\Delta) from \text{CH}_3X type molecules,\textsuperscript{92} has also been observed in the production of \text{NH}(c^1\Pi) following the VUV photodissociation of \text{NH}_3.\textsuperscript{175} This is strong supporting evidence for the involvement of \text{CH}_3^+ in these photodissociation processes.

Fourthly, the parent species with the strongest (continuous) absorptions at 193nm gave rise to the greatest
CH\(A^2\Delta \rightarrow x^2\Pi\) emission intensities. Thus it is unlikely that simultaneous multiphoton absorption by the parent species plays a significant role in the production of CH\(A^2\Delta\). The quadratic power dependence reported for the CD\(A^2\Delta \rightarrow x^2\Pi\) fluorescence intensity following 193nm laser photolysis of CD\(_3\)I\(^{88}\) is probably the result of saturation of the primary absorption:

\[
\text{CD}_3\text{I} + \text{hv} (\lambda = 193\text{nm}) \rightarrow \text{CD}_3^+ + \text{I} \quad \text{-(6.5)}
\]

in a 3-photon process (it is unlikely that a simultaneous mechanism is dominant as CD\(_3\)I absorbs strongly at 193nm).

Finally, this mechanistic proposal can be extended to cover CH\(A^2\Delta\) production from all saturated parent species (ie of the type CH\(_2\)X\(_2\) and CHX\(_3\)), which absorb to repulsive electronic states at 193nm, by invoking intermediate precursor fragments of the type CH\(_n\)X\(_{3-n}\) (pseudo-methyl) and CH\(_n\)X\(_{2-n}\) (pseudo-methylenic). The results for CH\(_2\)I\(_2\) and CHBr\(_3\) indicate that this is the case, and it has previously been suggested that this type of mechanism is operative in the flash photolysis of CHBr\(_3\)\(^{82}\) (see equation 6.1).

Results for unsaturated parent species are limited to C\(_2\)H\(_3\)CHO\(^{91}\) and C\(_2\)H\(_2\), neither of which fit the pattern observed for their saturated counterparts. McDonald and co-workers\(^{93}\) have examined the production of CH\(A^2\Delta\) from C\(_2\)H\(_2\) in detail and concluded that a sequential 2-photon
mechanism, with a high vibrational level of the $A^1\Lambda_u$ state functioning as the resonant intermediate state, is most likely.

6.4 CONCLUSION

The dominant mechanism involved in the production of $\text{CH}(A^2\Delta)$ from parent species of the type $\text{CH}_nX_{4-n}$ $(n=1,2,3)$ is a 3-photon mechanism involving the secondary photolysis of $\text{CH}_3(\text{CH}_nX_{3-n})$ and/or $\text{CH}_2(\text{CH}_nX_{2-n})$ primary photofragments.

Parent species which absorb strongly at 193nm, such as $(\text{CH}_3)_2\text{CO}$ and $\text{CH}_2\text{I}_2$, are most suitable for kinetic studies on $\text{CH}(A^2\Delta)$ as they give rise to the greatest $\text{CH}(A^2\Delta \rightarrow X^2\Pi)$ fluorescence intensities.
CHAPTER 7 - COLLISIONAL PROCESSES INVOLVING CH(A²Δ )

7.1 Introduction 183

7.2 Rotational relaxation of CH(A²Δ ) 184

7.3 Kinetics of CH(A²Δ ) removal processes 194

7.4 Conclusion 204
This chapter is devoted to collisional processes involving 
\( \text{CH}(A^2\Delta) \), subsequent to its production in the multiphoton 
dissociation of \((\text{CH}_3)_2\text{CO}\) and \(\text{CH}_2\text{I}_2\). These processes fall 
into two categories; inelastic and reactive.

Firstly, the rotational relaxation of \( \text{CH}(A^2\Delta) \) by a range of 
molecules was studied. The experiments were carried out at 
the Rutherford Appleton Laboratory (RAL). Spectrally 
resolved \( \text{CH}(A^2\Delta \rightarrow \chi^2\Pi) \) emission was recorded on an OMA, as 
detailed in section 2.7, following the 193nm laser photolysis 
of \(\text{CH}_2\text{I}_2\) or \((\text{CH}_3)_2\text{CO}\) in the presence of increasing partial 
pressures of foreign gases. Changes in the rotational 
temperature of \( \text{CH}(A^2\Delta) \) could be deduced from changes in the 
emission band contour. In this way, approximate collision 
numbers for the rotational deactivation of \( \text{CH}(A^2\Delta) \) by \( \text{He}, \) 
\( \text{Ar}, \) \( \text{SF}_6 \) and \( \text{H}_2 \) were determined. The considerable convenience 
of being able to record entire fluorescence spectra from a 
single laser shot allowed a wide range of conditions to be 
explored efficiently and this compensated for the partial 
loss of resolution.

Following this, the removal of \( \text{CH}(A^2\Delta) \) by a range of 
molecules was studied. These experiments were also carried 
out at RAL, and the experimental details are given in section 
2.8.
7.2 ROTATIONAL RELAXATION OF CH(A^2Δ)

RESULTS
Semi-quantitative investigations of the rotational relaxation of CH(A^2Δ) were made by adding increasing partial pressures of He, Ar, SF₆ and H₂ to the mixtures with CH₂I₂ undergoing photolysis. With the exception of H₂, none of these gases are efficient with regard to electronic quenching of CH(A^2Δ), with He being totally ineffective (see section 7.3). Increasing the CH₂I₂ pressure caused a decrease in the overall emission intensity without effecting any change in the band contour.

Figure 7.1 illustrates the effect of an added excess of He upon the CH(A^2Δ → X^2Π) emission band contour. The nascent rotational distribution (dashed curve) corresponds to a rotational temperature of ca. 3000K while the distribution in the presence of 99kNm⁻² of He (solid curve) corresponds to a rotational temperature of ca. 300K (ie thermalised). A gradual decrease in the rotational temperature was noted at intermediate He pressures, ie as the average number of collisions suffered by the CH(A^2Δ) radical during its effective lifetime increased (the effective lifetime takes account of removal by CH₂I₂, the rate constant for which was determined - see section 7.3). The rotational relaxation is manifest as a decrease in intensity in the high rotational levels of the P- and R-branches coupled with a red shift and sharpening of the Q-branch. As the distribution approaches...
Figure 7.1: CH($A^2 \Delta \rightarrow X^2 \Pi$) photofragment fluorescence following ArF laser excitation of CH$_2$I$_2$ ($p = 46.7$Nm$^{-2}$), resolution $\approx 0.35$nm. Dashed curve: no added gas. Solid curve: with $99$kNm$^{-2}$ of added He.
room temperature the extent of overlap between the Q- and R-branches decreases, and eventually a gap appears between the branches at $\lambda = 430.5\text{nm}$. The R-branch in the solid curve of Figure 7.1 peaks at $J = 2$, which is predicted for a rotational temperature of 300K.

No evidence was seen for a bimodal rotational distribution at intermediate pressures, however this may be due to the limited resolution available with the equipment. The total area under the curve remained constant within experimental error, reflecting the inefficient electronic quenching.

The results indicate that 99kNm$^{-2}$ of He is necessary to transform the rotationally hot spectrum ($T_{\text{ROT}} = 3000\text{K}$, $J_{\text{MAX}} = 8$) to the 'room temperature' spectrum ($T_{\text{ROT}} = 300\text{K}$, $J_{\text{MAX}} = 2$) under the conditions employed. The average number of collisions suffered by a CH$^\Delta (A^2\Delta)$ radical at this pressure (during its effective radiative lifetime) was calculated to be approximately 47 176. If this is considered as an average change in $J$ after 47 collisions, bearing in mind that higher $J$ states will relax less efficiently than lower ones due to the larger energy spacings involved, it can be deduced that ca. 8 collisions (since $J_{\text{MAX}}$ changes from 8 to 2) are required for the loss of one rotational quantum from CH$^\Delta (A^2\Delta, v' = 0, J' = 8)$. The relative rotational relaxation efficiencies of He and the other gases studied are given in Table 7.1 in terms of collision numbers, $Z_R$.
TABLE 7.1: Collison numbers for the rotational relaxation of CH(A^2Δ, v'=0, J'= 8) by various foreign gases.

<table>
<thead>
<tr>
<th>COLLISION PARTNER</th>
<th>Z_R</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>8</td>
</tr>
<tr>
<td>Ar</td>
<td>4</td>
</tr>
<tr>
<td>SF_6</td>
<td>5.5</td>
</tr>
<tr>
<td>H_2</td>
<td>3.5</td>
</tr>
</tbody>
</table>
The results obtained for rotational deactivation of CH(A^2\Delta) by Ar and SF_6 were similar to those obtained with He. In both cases, however, lower pressures were necessary to promote a thermal distribution and some reduction in the overall emission intensity was observed at higher pressures, indicating that electronic quenching, although inefficient, is operative with these collision partners. Figure 7.2 illustrates this for SF_6 as the added gas. Collision numbers, \(Z_R\), for the rotational relaxation of CH(A^2\Delta) by these gases can be found in Table 7.1.

Figure 7.3 shows the effect of increasing partial pressures of H_2 upon the CH(A^2\Delta \rightarrow X^2\Pi) emission. It is clear that the removal of CH(A^2\Delta) either by reaction or electronic quenching competes efficiently with rotational relaxation as the intensity of emission is greatly reduced before a significant change in the rotational distribution is observed. A value of \(Z_R=3.5\) was obtained for the rotational relaxation of CH(A^2\Delta) by H_2.

**DISCUSSION**

These data provide an interesting view of the rotational cascading that occurs as the initially hot rotational distribution relaxes towards the much cooler distribution associated with the translational degrees of freedom of the bulk sample. It should be borne in mind, however, that the results only reflect the net dissipation of rotational energy, and there will be contributions from collisions which
Figure 7.2: Effect of added SF$_6$ on CH($A^2\Delta \rightarrow X^2\Pi$) photofragment fluorescence following ArF laser excitation of CH$_2$I$_2$ ($p = 13.3$ Nm$^{-2}$). Dashed curve: no added SF$_6$. Full curve: with 13.3 kNm$^{-2}$ of SF$_6$ added.
Figure 7.3: Effect of added H₂ on CH(A²∆ → X²Π) photofragment fluorescence following ArF laser excitation of CH₂I₂ (p = 13.3Nm⁻²). H₂ pressure: (a) 0, (b) 550Nm⁻², (c) 2.02kNm⁻², (d) 4.81 kNm⁻², (e) 8.25kNm⁻².
increase J. It is also likely that collisions giving rise to jumps of $|\Delta J| > 1$ will contribute, especially in collisions at low impact parameters. (Although multiple quantum transitions occur most readily in heavier diatomics\textsuperscript{9,177-179}, transitions of $|\Delta J| \leq 3$ have been observed in collisions of BH(A\textsuperscript{1} \Pi, v' = 0) with He, Ar and H\textsubscript{2}.\textsuperscript{180})

Two reports on the rotational relaxation of CH(A\textsuperscript{2} \Delta) by ranges of molecules, including He and Ar, have previously been published.\textsuperscript{181,182} Brennen and Carrington\textsuperscript{181} interpreted their spectra as the superposition of two Boltzmann distributions with the fraction of molecules in the low-temperature rotational distribution giving a measure of the extent of relaxation. However, their results have since been shown to be erroneous due to their misinterpretation of the A\textsuperscript{2} \Delta \rightarrow X\textsuperscript{2} \Pi emission spectrum\textsuperscript{149}, the apparent low temperature distribution being due to strong contamination of the R-branch by the Q-branch at wavelengths near 430nm.

Clerc and Schmidt\textsuperscript{182}, studying the rotational relaxation of CH(A\textsuperscript{2} \Delta) produced in the pulsed radiolysis of C\textsubscript{2}H\textsubscript{2} and CH\textsubscript{4}, also mistakenly interpreted the 'hot' rotational distribution ($T_{\text{ROT}} \geq 4600$K) observed when C\textsubscript{2}H\textsubscript{2} was used as the precursor as the superposition of two Boltzmann distributions. However, when CH\textsubscript{4} was used as the precursor, CH(A\textsuperscript{2} \Delta) was produced at a much lower rotational temperature ($T_{\text{ROT}} = 550$K), in which case there is negligible overlap between the Q- and R-
branches. They estimated that 70 binary collisions with He are required, on average, to lower the rotational temperature of CH(A^2\Delta) from 550K (J_{\text{MAX}} = 3) to room temperature (J_{\text{MAX}} = 2). This is an order of magnitude greater than the collision number obtained in this work.

The results presented herein indicate that Ar, SF\textsubscript{6} and \textsubscript{2}H all bring about rotational relaxation of CH(A^2\Delta) very efficiently, while He is about half as efficient. This is somewhat surprising as high rotational transfer efficiencies are expected for He, relative to Ar and SF\textsubscript{6}, on classical mechanical grounds. An improved efficiency is expected for \textsubscript{2}H in comparison to He due to the improved momentum matching, and this could account for the decrease in ZR. In order to explain the observed behaviour more fully, factors other than the masses of the collision partners must be invoked. The most likely factors to consider are the range and anisotropy of the long-range interaction potentials, and the possibility of rotation-rotation or rotation-vibration energy transfer.

Perhaps the most surprising result is that for Ar. The high efficiency observed suggests that strong torques are experience by CH(A^2\Delta) in the vicinity of Ar atoms and that the interaction potential is strongly anisotropic. This may be connected with the open shell structure of CH(A^2\Delta) and the nature of the interaction between the carbon-end of the
radical and the collision partner. As well as interacting over a longer range than He atoms the larger Ar atoms are much more polarisable, making dipole-induced dipole interactions with the polar CH(A^2 Δ) species possible contributors to the overall relaxation process.

The high efficiency with which SF\textsubscript{6} rotationally relaxes CH(A^2 Δ) is almost certainly due to contributions from rotation-vibration energy transfer processes. This will result from the extremely high density of states of the SF\textsubscript{6} molecule.\textsuperscript{183}

Three factors are likely to contribute to the improved efficiency observed for H\textsubscript{2} in comparison with He: (1) the (previously mentioned) improved momentum matching, (2) the strongly anisotropic interaction potential, and (3) the possibility of rotation-rotation energy transfer. From the observation of a cool 300K rotational distribution in the presence of 8kNm\textsuperscript{-2} of H\textsubscript{2} it can be concluded that either the high J levels are removed by electronic quenching more rapidly than lower J levels (thus removing the emission from the high rotational component) or that rotational relaxation from high J into low J levels occurs at a rate which is at least comparable to the rate for total removal of CH(A^2 Δ) with a rotational temperature of 300K. The rate constant for the removal of CH(A^2 Δ) has been determined as 8.8 x 10\textsuperscript{-12} cm\textsuperscript{3}molec\textsuperscript{-1}s\textsuperscript{-1} (see section 7.3). Therefore, the second proposal implies an average collision number, Z_R ≤ 20, for
rotational relaxation by H$_2$. The value obtained, $Z_R = 3.5$, is compatible with this, more likely proposal.

Generally, the observed pattern of relaxation can be accounted for by assuming that deactivation occurs predominantly by small changes in $J$ ($|\Delta J|=1$), and that the probability of energy transfer decreases with increasing $J$ according to a law such as Polanyi's Exponential Law$^{184}$ which states that the transfer probability is proportional to $\exp(-\Delta E)$, $\Delta E$ being the energy deficit. The absence of sharp peaking at intermediate $J$ in the course of relaxation by this mechanism is due to the fact that the rate of transfer into the intermediate levels is slower than the rate of transfer out of them. Consequently, the populations in intermediate $J$ levels cannot accumulate.

7.3 KINETICS OF CH(A$^2\Delta$) REMOVAL PROCESSES

RESULTS

Figure 7.4 shows a typical CH(A$^2\Delta$)$\rightarrow$X$^2\Pi$ photofragment fluorescence decay. The fluorescence intensity ($I_f$) is sufficient to allow single-shot observations with a good signal-to-noise ratio. The decay of CH(A$^2\Delta$), which is formed during the laser pulse, is a smooth exponential and is
Figure 7.4: Decay of CH(A^2\Delta), produced by ArF laser excitation of (CH_3)_2CO \((p(CH_3)_2CO = 21\;\text{Nm}^{-2},\quad p_{H_2} = 62\;\text{Nm}^{-2})\).
dominated by radiative removal in the absence of added quenching gas. The effect of added reactive or quenching gas is to shorten the decay, as illustrated by the first-order plots in Figure 7.5 for increasing pressures of CH$_4$. The first-order rate constants thus derived are plotted against CH$_4$ pressure in Figure 7.6, the gradient of which yields a value of $(2.0^{+0.1}) \times 10^{-11}$ cm$^3$molec$^{-1}$s$^{-1}$ for the absolute rate constant for the total removal of CH($A^2\Delta$). The rate constants determined in this work, together with rate constants for the removal of ground state CH, are summarised in Table 7.2.

The first-order rate constants used to construct Figure 7.7 were determined in an identical manner to that described above, excepting the use of CH$_2$I$_2$ rather than (CH$_3$)$_2$CO as the precursor to CH($A^2\Delta$). A value of $(1.9^{+0.1}) \times 10^{-11}$ cm$^3$molec$^{-1}$s$^{-1}$ was obtained for the removal rate constant with CH$_4$. The agreement between the two values is excellent, indicating that the kinetics are independent of the precursor used.

Figure 7.8 illustrates the graphical determination of the rate constant for the removal of CH($A^2\Delta$) by CH$_2$I$_2$. The effective lifetimes of CH($A^2\Delta$) at the CH$_2$I$_2$ pressures used in the rotational relaxation studies (previous section) were obtained from the best fit straight line through the data points. The intercept corresponds to a pure radiative lifetime of $435^{+98}$ns ($2\sigma$ error). Given the large uncertainty, this is in reasonable agreement with the most
Figure 7.5: First-order plots (log $I_f$ vs. time) for the decay of $\text{CH}(A^2\Delta)$ in the presence of increasing pressures of $\text{CH}_4$. 

- $P_{\text{CH}_4} = 200 \text{ N m}^{-2}$
- $P_{\text{CH}_4} = 1.12 \text{ kN m}^{-2}$
- $P_{\text{CH}_4} = 3.09 \text{ kN m}^{-2}$
- $P_{\text{CH}_4} = 8.29 \text{ kN m}^{-2}$
- $P_{(\text{CH}_3)_2\text{CO}} = 25 \text{ N m}^{-2}$
Figure 7.6: Plot of first-order rate coefficients for quenching of CH($A^2\Delta$) against pressure of added CH$_4$. (Acetone as CH($A^2\Delta$) precursor).
TABLE 7.2: Second-order rate constants for the removal of CH(A^2Δ) and CH(X^2Π) by various reactant/quenching gases.

<table>
<thead>
<tr>
<th>REACTANT/QUENCHING GAS</th>
<th>CH(A^2Δ) k/cm^3 molec^-1 s^-1</th>
<th>CH(X^2Π) k/cm^3 molec^-1 s^-1</th>
<th>SOURCE OF CH(X) DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH2I2</td>
<td>7.9±0.6x10^-10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH4</td>
<td>1.9±0.1x10^-11 a</td>
<td>3.0±1.0x10^-10</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>2.0±0.1x10^-11 b</td>
<td>1.0±0.3x10^-10</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.02±0.04x10^-10</td>
<td>84</td>
</tr>
<tr>
<td>H2</td>
<td>8.8±1.7x10^-12 a</td>
<td>2.3±0.5x10^-11</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>8.5±0.4x10^-12 a</td>
<td>2.63±0.5x10^-11</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4±0.1x10^-11</td>
<td>85</td>
</tr>
<tr>
<td>O2</td>
<td>1.10±0.04x10^-11 b</td>
<td>5.9±0.8x10^-11</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.3±0.4x10^-11</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8±3x10^-11</td>
<td>186</td>
</tr>
<tr>
<td>N2</td>
<td>4.1±0.5x10^-13 a</td>
<td>7.7±2.0x10^-13</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.9±0.3x10^-13</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.3±1.3x10^-13</td>
<td>83</td>
</tr>
<tr>
<td>He</td>
<td>0 a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>1.6±0.7x10^-13 a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF6</td>
<td>5.9±1.1x10^-13 a</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a This work - CH2I2 as parent species
b This work - (CH3)2CO as parent species
Figure 7.7: Plot of first-order rate coefficients for quenching of CH(A2Δ) against pressure of added CH4. (CH2I2 as CH(A2Δ) precursor)

\[ k_{REM} = 1.9 \pm 0.1 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}. \]
Figure 7.8: Plot of first-order rate coefficients for quenching of CH(A^2Δ) against pressure of CH₂I₂

\[ k_{REM} = 7.9 \pm 0.6 \times 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \]
reliable values reported in the literature (for the \( v' = 0 \) level) of 534±5ns\(^{172}\) and 537.5±5ns\(^{185}\).

**DISCUSSION**

A more detailed study of the temperature and pressure dependencies of the reactions of CH(A\(^2\Delta\)) would be necessary in order to establish the nature of the reactive/quenching interaction. However, the data do provide an interesting comparison with CH(X\(^2\Pi\)) kinetic data which is relatively abundant in the literature.

The data on CH(X\(^2\Pi\)) represent the rates of reaction with the molecules in question. However, the data on CH(A\(^2\Delta\)) removal represent contributions from both physical quenching and reactive processes, and thus only give upper limits for the chemical reaction rates. It is apparent from Table 7.2 that the reactions of CH(A\(^2\Delta\)) with CH\(_4\), H\(_2\) and O\(_2\) are significantly slower than those of CH(X\(^2\Pi\)). As the internal energy content of CH(A\(^2\Delta\)) is greater than that of CH(X\(^2\Pi\)) by ca. 2.9eV, the explanation for this behaviour must lie in the electronic configurations of the two states:

\[ (1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi) \text{ for the ground state,} \]
\[ (1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2 \text{ for the A-state.} \]

This means that the shapes of the potential surfaces are the controlling factors in these reactions. It is well established for atomic reactions that the symmetry of the collision intermediate is of paramount importance in determining the reactivity of individual electronic states, while the total
energy content is of secondary importance. Although there are relatively large numbers of degrees of freedom associated with the collision intermediates in the reactions under study (cf atomic systems), symmetry considerations are still prevalent.

The data for the less/non reactive gases \((N_2, \text{He, Ar and SF}_6)\) indicate that \(\text{CH}(A^2\Delta)\) is relatively stable to physical quenching. The removal rates for both electronic states with \(N_2\) are similar in magnitude and this again must relate to the potential energy surfaces. Nokes and Donovan have noted a broadly parallel kinetic behaviour for \(\text{CH}(A^2\Delta), \text{CH}(X^2\Pi)\) and the equivalent united atom state, \(N(2D)\), with the order of reactivity \(\text{CH}(X^2\Pi) > \text{CH}(A^2\Delta) > N(2D)\).

The mechanistic possibilities which could be considered for these reactions include insertion into bonds, addition across unsaturated bonds, and direct abstraction. The mechanism proposed by Berman and Lin for the reaction of \(\text{CH}(X^2\Pi)\) with saturated hydrocarbons and \(H_2\) involves the formation of a chemically activated, radical intermediate by insertion through a loose transition state. In the case of hydrocarbons this is followed by fragmentation of the adduct to form more stable reaction products. Wagal and co-workers have proposed that the removal of \(\text{CH}(X^2\Pi)\) by \(N_2\) is due to collisional stabilization of an intermediate \(\text{HCN}_2\) complex, most likely of \(C_{2v}\) symmetry. This corresponds to
addition across the unsaturated N = N bond. If these proposals are correct the implication is that symmetry considerations favour CH(X^2 \Pi) over CH(A^2 \Delta) for insertion into \sigma bonds, while there is little discrimination between the two states for addition across the N≡N bond.

7.4 CONCLUSION

Rotationally hot CH(A^2 \Delta) radicals are relaxed more efficiently by H_2, Ar and SF_6 than by He. Therefore classical collision theory (i.e. momentum matching) is not applicable to these inelastic processes. The observed pattern of relaxation can be interpreted by assuming that deactivation occurs by small changes in J, and that the probability of energy transfer decreases with increasing J.

In general, CH(A^2 \Delta) is not efficiently removed by reactive or non-reactive (quenching) gases. With the exception of CH_2I_2, for each reactive gas studied the rate constant for removal of CH(A^2 \Delta) is less than that for the ground electronic state, CH(X^2 \Pi). This indicates that the reactivities of the species are determined principally by the symmetry of the collision intermediate, rather than the internal energy content.

The resilient nature of CH(A^2 \Delta), to both chemical and physical quenching processes, provides at least a partial
explanation for the wide ranging observations of fluorescence from this state under what would generally be regarded as chemically hostile conditions.
APPENDIX 1: ANNOTATED COPY OF COMPUTER PROGRAM

USED TO SIMULATE CH($A^2\Delta \rightarrow X^2\Pi$) SPECTRA.
SIMULATION OF CH(A-X) EMISSION SPECTRUM

This program computes the spectrum of the CH(A-X) electronic transition. The first section calculates the Rotational Term Values (RTV) in the ground (A:ST=1) and 1st excited (A:ST=2) electronic states.

**Variables used are:**
- \( k \): Total angular momentum apart from spin.
- \( V \): Vibrational number.
- \( L \): Component of electronic angular momentum along internuclear axis.
- \( Y \): Measure of strength of the spin-orbital coupling.
- \( G \): Rotational constants dependent on \( V \).
- \( S \): Measure of strength of spin splitting.
- \( LA \): Measure of strength of Lambda-type doubling.
- \( ST \): Electronic state.
- \( SI \): Sign (+/-) upper and lower levels from spin-orbital coupling.
- \( P \): (Relative) Population of vibrational level.
- \( T \): Rotational temperature.
- \( h \): Planck's constant.
- \( c \): Speed of Light (cm/s).
- \( KB \): Boltzmann constant.

**Details of implementation:**

```c
C The Rotational Term Values array is dimensioned thus : RTV(F,K,V,ST)
C K = Rotational Quantum Number
C V = Vibrational Quantum Number
C ST = Electronic State
C F = 1. The P1c sublevel
C F = 2. The P1d sublevel
C F = 3. The F2c sublevel
C F = 4. The F2d sublevel

DO 80 ST=1,2
DO 40 V=0,2
DO 80 K=1,35
W=EV(V,ST)тип*(K*(K+1)-L(ST)**2)-DV(V,ST)тип*(K+0.5)**4
X1=1.0+Y(V,ST)*тип*(Y(V,ST)-4.0)*L(ST)**2/(4.0*(K+1)**2)
X2=1.0+Y(V,ST)*тип*(Y(V,ST)-4.0)*L(ST)**2/(4.0*K**2)
Y1=G(ST)*K/2.0
Y2=G(ST)*K+1.0)/2.0
Z=0.5*LA(ST)*тип*(K+1.0)
IF(X1.LT.1.OD-9) THEN RTV(1.K.V.ST)=0.0
ELSE RTV(1.K.V.ST)=YV*Z
END
```

The Quantum Numbers / Constants /
30 IF (X2.LT. I:OD-9) THEN
   RTV(3,K,V,ST) = 0.0
   RTV(4,K,V,ST) = 0.0
   900 40
   END IF
40 XX = SQRT(X2)
X2 = BV(V,ST) * K *(1.0-XX)
YY = X2 - Y2
RTV(3,K,V,ST) = YY + Z
RTV(4,K,V,ST) = YY - Z
40 CONTINUE
60 CONTINUE
80 CONTINUE

The next section calculates the wavelengths of the individual transitions.
The wavelength array is dimensioned thus: WL(BR,K,V)

C BR = Rotational Branch
C BR = 1: Pled Branch
C BR = 2: P2dc Branch
C BR = 3: P2dd Branch
C BR = 4: P2dc Branch
C BR = 5: Glic Branch
C BR = 6: G1d Branch
C BR = 7: G2c Branch
C BR = 8: G2d Branch
C BR = 9: R1cd Branch
C BR = 10: R1dc Branch
C BR = 11: R2cd Branch
C BR = 12: R2dc Branch
C BR = 13: P1lc2d Branch
C BR = 14: P11c2d Branch
C BR = 15: GP2clc Branch
C BR = 16: GP2dllu Branch
C BR = 17: GR1c2c Branch
C BR = 18: GR1d2d Branch
C BR = 19: R2d2d Branch
C BR = 20: R22dl Branch

Wavelengths are converted from vacuum to air using the conversion factor (CF).
Subroutines WAVLNI-2 calculate the wavelengths of transitions in particular branches.

C BR = 1: The Pled—branch.
C  CALL WAVLNI(BR,A,B)
C BR = 2: The P2dc—branch.
C  CALL WAVLNI(BR,A,B)
C BR = 3: The P2dd—branch.
C  CALL WAVLNI(BR,A,B)
C BR = 4: The P2dc—branch.
C  CALL WAVLNI(BR,A,B)
C BR = 5: The Glic—branch.
C  CALL WAVLNI(BR,A,B)
C BR = 6: The G1d—branch.
C  CALL WAVLNI(BR,A,B)
C BR = 7: The G2c—branch.
C  CALL WAVLNI(BR,A,B)
C BR = 8: The G2d—branch.
C  CALL WAVLNI(BR,A,B)
CALL WAVLN2(BR, A, B)

BR = 9 : The R1c3d-branch.

BR = 9
A = 1
B = 2
CALL WAVLN1(BR, A, B)

BR = 10 : The R1d3c-branch.

BR = 10
A = 2
B = 1
CALL WAVLN2(BR, A, B)

BR = 11 : The R2c3d-branch.

BR = 11
A = 3
B = 4
CALL WAVLN3(BR, A, B)

BR = 12 : The R2d3c-branch.

BR = 12
A = 4
B = 0

BR = 13 : The PQ1c2d-branch.

BR = 13
A = 1
B = 4
CALL WAVLN1(BR, A, B)

BR = 14 : The PQ1d2c-branch.

BR = 14
A = 2
B = 3
CALL WAVLN1(BR, A, B)

BR = 15 : The GP2c1d-branch.

BR = 15
A = 3
B = 1
CALL WAVLN2(BR, A, B)

BR = 16 : The GP2d1d-branch.

BR = 16
A = 4
B = 2
CALL WAVLN2(BR, A, B)

BR = 17 : The GR1c2c-branch.

BR = 17
A = 1
B = 3
CALL WAVLN2(BR, A, B)

BR = 18 : The GR1d2c-branch.

BR = 18
A = 2
B = 4
CALL WAVLN2(BR, A, B)

BR = 19 : The RQ2c1d-branch.

BR = 19
A = 3
B = 2
CALL WAVLN3(BR, A, B)

BR = 20 : The RQ2d1c-branch.

BR = 20
A = 4
B = 1
CALL WAVLN3(BR, A, B)

The next section of program the linestrengths for all the rovibronic transitions.

Initially the 'U-Factors' and 'C-Factors' are calculated.

DO 100 ST = 1, 2

100 V = 0.2

DO 120 K = 1, 35

2 = (Y(V, ST) * (Y(V, ST) - 4.0) * L(ST)**2 * 4.0 * K**2)

IF (I.LT.ID-6) THEN

DO 120 SI = 1, 2

U(SI, K, V, ST) = 0.0

C(SI, K, V, ST) = 0.0

120 CONTINUE
END IF
YY=SQRT(Z)
Y=V(ST)*(Y(V,ST)-2.0)
Wd=0.08*(k+2-L(ST)**2)
U(1,K,V,ST)=YY*X
U(2,K,V,ST)=YY*X
DO 160 SI=1,2
C(SI,K,V,ST)=0.9*(U(SI,K,V,ST)**2+W)
160 CONTINUE
140 CONTINUE
120 CONTINUE
100 CONTINUE

C The following section of program calculates the linestrengths for the rovibronic transitions in the following branches:

BR=1 : P1
BR=2 : P2
BR=3 : Q1
BR=4 : Q2
BR=5 : R1
BR=6 : R2
BR=7 : P012
BR=8 : GP21
BR=9 : OR12
BR=10 : RG21

C The P1-Branch : BR = 1
BR=1
SI=2
DO 200 V=0,2
200 CONTINUE

DO 220 K=1,3
Y=8.0*(V+0.5)*C(I,K,V,2)*C(E1,K1,V,1)
IF(ABS(Y).LT.1D-6)THEN
S(BR,K,V)=0.0
END IF
ZZ=4.0*14.0+2.0>
Z=(U(I,K,V,2)*U(SI,K1,V,1)+ZZ)**2
S(SR,K,V)=(K*Z)/YY
220 CONTINUE

DO 205 V=0,2
205 CONTINUE

DO 225 V=0,2
225 CONTINUE

DO 220 K=1,3
S(SR,K,V)=0.0
220 CONTINUE

The P2-Branch : BR = 2
BR=2
SI=1
DO 225 V=0,2
225 CONTINUE

DO 200 K=4,35
Y=8.0*(K-0.5)*C(SI,K0,V,2)*C(SI,K1,V,1)
IF(ABS(Y).LT.1D-6)GOTO 260
X=(K-L(1)-1.0)*(K-L(1))
ZZ=4.0*K*(K+2.0)
Z=U(SI,K,V,2)*U(SI,K1,V,1)+ZZ)**2
S(SR,K,V)=(K*Z)/YY
260 CONTINUE

DO 240 V=0,2
240 CONTINUE

DO 260 K=4,35
S(SR,K,V)=0.0
260 CONTINUE

DO 240 V=0,2
240 CONTINUE

C The following calculations give a value of zero for S(P2,K=3,V=0-2).
C However these 3 lines are observed in the spectrum, so a linestrength value of 0.236 is assigned to them:

DO 225 V=0,2
225 CONTINUE

DO 235 V=0,2
235 CONTINUE

S(SR,K,V)=0.236
235 CONTINUE

C The Q1-Branch : BR = 3
BR=3
SI=2
DO 270 V=0,2
270 CONTINUE

S(SR,K,V)=0.0
270 CONTINUE

C Values of 1.766 assigned to S(Q1,K=2,V=0-2) - (see P2 above)

DO 275 V=0,2
275 CONTINUE

S(SR,K,V)=1.766
275 CONTINUE
DO 280 V=0, 2
DO 300 K=2, 3.34
   DO 280 V=0, 2
      K1=K+1
   DO 280 V=0, 2
      YY=4.0*(K+0.5)*(K+1.5)*C(SI, K1, V, 2)*C(SI, K1, V, 1)
   IF(ABS(YY).LT.1D-6)GOTO 300
   YY=(K-L(1)+2.0)*(K-L(1)+2.0)
   IF(ABS(YY).LT.1D-6)GOTO 300
   Z=(U(SI, K1, V, 2)+U(SI, K1, V, 1))*ZZ**2
   S(BR, K, V)=(X*Z)/YY
280 CONTINUE
290 CONTINUE
300 CONTINUE
310 DO 290 V=0, 2
320 CONTINUE
330 CONTINUE
340 C The G2-Branch : BR = 4
345 BR=4
346 SI=1
350 DO 320 V=0, 2
360 CONTINUE
370 DO 340 V=0, 2
380 CONTINUE
390 CONTINUE
400 CONTINUE
410 CONTINUE
420 CONTINUE
430 CONTINUE
440 CONTINUE
450 C The R1-Branch : BR = 5
455 BR=5
460 SI=2
470 DO 330 V=0, 2
480 CONTINUE
490 CONTINUE
500 CONTINUE
510 CONTINUE
520 CONTINUE
530 CONTINUE
540 C The R2-Branch : BR = 6
545 BR=6
550 SI=1
560 C Values of 1.07 assigned to S(G2, K=2, V=0-2) - (see P2 above)
570 DO 400 V=0, 2
580 CONTINUE
590 CONTINUE
600 CONTINUE
610 CONTINUE
620 CONTINUE
630 CONTINUE
640 CONTINUE
650 CONTINUE
660 CONTINUE
670 CONTINUE
680 CONTINUE
690 CONTINUE
700 CONTINUE
710 CONTINUE
720 CONTINUE
730 CONTINUE
740 CONTINUE
750 CONTINUE
760 CONTINUE
770 CONTINUE
780 CONTINUE
790 CONTINUE
800 CONTINUE
810 CONTINUE
820 CONTINUE
830 CONTINUE
840 CONTINUE
850 CONTINUE
860 CONTINUE
870 CONTINUE
880 CONTINUE
890 CONTINUE
900 CONTINUE
910 CONTINUE
920 CONTINUE
930 CONTINUE
940 CONTINUE
950 CONTINUE
960 CONTINUE
970 CONTINUE
980 CONTINUE
990 CONTINUE
402 CONTINUE
403 DO 500 V=0.2
404 DO 520 =3.
35
404 Vy=4.0*(K_O.5)*'0.5)*C(2 , K , V , 2)*C(l , R , V , I>
405 IF(ABS(YY),LT.1D-)6OTO 
520
406
407 Z=U(2,K,V,2)*U(1,K,V,1)-ZI)**2
408 S(R.,K, V)=(X*Z)/YY
409 520 CONTINUE
410 500 CONTINUE
411 C The &P2-Branch : BR = A
412 BR=8
413 DO 540 V=0.2
414 DO 560 K=1.2
415 S(BR, K, V)=0.0
416 540 CONTINUE
417 540 CONTINUE
418 DO 560 V=0.2
419 DO 580 K=3.34
420 K userManager
421 YY=4.0*(K+0.5)*C(1,K.V, 2)*C(2,K.V, 1)
422 IF(ABS(YY),LT.1D-)GOTO 500
423 X=(K-L(1)-1.0)*K*(K-L(1))
424 Z=4.0*K*(K-2.0)
425 Z=U(1.K, V, 2)*U(2.K, V, 1)-ZZ)**2
426 S(BR, K, V)=(X*Z)/YY
427 500 CONTINUE
428 530 CONTINUE
429 DO 590 V=0.2
430 S(BR, 33, V)=0.029
431 590 CONTINUE
432 C The GP12-Branch : BR = 9
433 BR=9
434 DO 620 V=0.2
435 DO 640 K=2.34
436 K userManager
437 YY=4.0*(K+0.5)*C(1,K.V, 2)*C(2,K.V, 1)
438 IF(ABS(YY),LT.1D-)GOTO 600
439 X=(K-L(1)+1.0)+K*(K-L(1)+2.0)
440 Z=4.0*K*(K-2.0)
441 Z=U(2,K, V, 2)*U(1,K, V, 1)-ZZ)**2
442 S(BR, K, V)=(X*Z)/YY
443 600 CONTINUE
444 640 CONTINUE
445 DO 650 V=0.2
446 S(BR, 33, V)=0.0314
447 650 CONTINUE
448 C The GP12-Branch : BR = 10
449 BR=10
450 DO 680 V=0.2
451 DO 700 K=2.34
452 K userManager
453 YY=4.0*(K+0.5)*C(1,K.V, 2)*C(2,K.V, 1)
454 IF(ABS(YY),LT.1D-)GOTO 720
455 X=(K-L(1)+1.0)+K*(K-L(1)+2.0)
456 Z=4.0*K*(K-2.0)
457 Z=U(1,K, V, 2)*U(2,K, V, 1)-ZZ)**2
458 S(BR, K, V)=(X*Z)/YY
459 720 CONTINUE
460 700 CONTINUE
461 DO 710 V=0.2
462 S(BR, 33, V)=0.0295
463 710 CONTINUE
464 C The next section of program calculates the intensity of each individual
465 C vibronic transition
466 C Three subroutines - [INTEN1-3] are used.
467 C E=(H+SDL)/N
468 IMAX=0.0
469 CALL INTENI(BR, RB, F)
470 C The Plcd-Branch : BR = 1
471 BR=1
472 R5=1
473 F=1
474 C The Plcd-Branch : BR = 2
475 BR=2
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RB=1
F=2
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 3
BR=3
RB=2
F=3.
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 4
BR=4
RB=2
F=4
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 5
BR=5
RB=3
F=5
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 6
BR=6
RB=3
F=6
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 7
BR=7
RB=4
F=7
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 8
BR=8
RB=4
F=8
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 9
BR=9
RB=5
F=9
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 10
BR=10
RB=5
F=10
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 11
BR=11
RB=6
F=11
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 12
BR=12
RB=6
F=12
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 13
BR=13
RB=7
F=13
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 14
BR=14
RB=7
F=14
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 15
BR=15
RB=8
F=15
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 16
BR=16
RB=8
F=16
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 17
BR=17
RB=9
F=17
CALL INTEN1(BR, RB, F)
The P2cd-Branch : BR = 18
BR=18
RB=9
F=18
CALL INTEN2(BR, RB, F)

The RG2c1d-Branch : BR = 19
BR = 19
RB = 10
F = 3
CALL INTEN2(BR, RB, F)

The RG2c1d-Branch : BR = 20
BR = 20
RB = 10
F = 4
CALL INTEN2(BR, RB, F)

The next section takes account of "dummy" points (zero intensity) then
arranges the real points in order of increasing wavelength.

IF(WL(BR, K, V) .LT. 400.0) THEN
   IEROS = IEROS + 1
END IF

DO 1050 BR = 19, 20
DO 1070 K = 1, 35
IF(WL(BR, K, V) .LT. WLMIN) THEN
   TEMPBR = BR
   TEMPK = K
   TEMPV = V
   WL(BR, K, V) = 1000.0
END IF

DO 1090 CONTINUE

OPEN 1, FILE=OUTPUT, FMT='CHARACTER'
WRITE(1, 10) POINTS
WRITE(1, 10) POINTS
DO 1070 BR = 19, 20
DO 1090 K = 1, 35
IF(WL(BR, K, V) .LT. WLMIN) THEN
   TEMPBR = BR
   TEMPK = K
   TEMPV = V
   WL(BR, K, V) = 1000.0
END IF

END

SUBROUTINE WAVLN1(BR, A, 0)

DOUBLE PRECISION WL, RTV, CF, VO
INTEGER BR, A, K, V
COMMON/BLOCK1/WL(20, 35, 0:2), RTV(4, 25, 0:2)
COMMON/BLOCK2/CF, VO(0:2)
DO 8005 VO = 0, 2
DO 8020 K = 1, 2
DO 8005 VO = 0, 2
DO 8020 K = 1, 2
WL(BR, K, V) = CF*10**7/(VO(V) + RTV(A, K, V, 2) - RTV(A, K, V, 1))

END

SUBROUTINE WAVLN2(BR, A, D)

DOUBLE PRECISION WL, RTV, CF, VO
INTEGER BR, A, K, V
COMMON/BLOCK1/WL(20, 35, 0:2), RTV(4, 25, 0:2)
COMMON/BLOCK2/CF, VO(0:2)
DO 8005 VO = 0, 2
WL(BR, 1, V) = 0.0

RETURN

END
910 CONTINUE
    DO 8100 V=0,2
    DO 8120 K=2,35
      IF (ABS(RTV(A,K,V,2)) .LT. 1D-6 .OR. ABS(RTV(B,K,V,1)) .LT. 1D-6) THEN
        WL(BR,K,V)=0.0
      END IF
      DO 8210 W=0,1
      WL(BR,K,V)=CF*10**7/(VO(V)+RTV(A,K,V)-RTV(B,K,V))
    END DO
  END DO
  CONTINUE
  RETURN
END

SUBROUTINE WAVLNR(BR,A,B)
DOUBLE PRECISION WL,RTV,A,B,F,G
INTEGER BR,A,B,K,L,V
COMMON/BLOCK1/WL(20,35,0:2),RTV(4,35,0:2)
COMMON/BLOCK2/WF(10,35,0:2),I(20,35,0:2),P(0:2),T(0:2),E,IMAX
DO 8500 V=0,2
  DO 8520 K=1,35
  DO 8540 W=0,1
  WL(BR,K,V)=CF*10**7/(VO(V)+RTV(A,K,V)-RTV(B,K,V))
  END DO
  CONTINUE
  RETURN
END

SUBROUTINE INTEN1(BR,RE,F)
DOUBLE PRECISION WL,RTV,A,B,F,G
INTEGER BR,A,B,K,L,V
COMMON/BLOCK1/WL(20,35,0:2),RTV(4,35,0:2)
COMMON/BLOCK2/I(10,35,0:2),I(20,35,0:2),P(0:2),T(0:2),E,IMAX
DO 8500 V=0,2
  DO 8520 K=1,35
  DO 8540 W=0,1
  WL(BR,K,V)=CF*10**7/(VO(V)+RTV(A,K,V)-RTV(B,K,V))
  END DO
  CONTINUE
  RETURN
END

SUBROUTINE INTEN2(BR,RE,F)
DOUBLE PRECISION WL,RTV,A,B,F,G
INTEGER BR,A,B,K,L,V
COMMON/BLOCK1/WL(20,35,0:2),RTV(4,35,0:2)
COMMON/BLOCK2/I(10,35,0:2),I(20,35,0:2),P(0:2),T(0:2),E,IMAX
DO 8500 V=0,2
  DO 8520 K=1,35
  DO 8540 W=0,1
  WL(BR,K,V)=CF*10**7/(VO(V)+RTV(A,K,V)-RTV(B,K,V))
  END DO
  CONTINUE
  RETURN
END
SUBROUTINE INTEN3(BR, R, F)
DOUBLE PRECISION WL, RTV, S, I, P, E, IMAX, X, V3
INTEGER V, K1, BR, R, F
COMMON/BLOCK1/WL(20, 35, 0: 2), RTV(4, 35, 0: 2), I(20, 35, 0: 2), P(0: 2), T(0: 2), E, IMAX
DO 8700 V=0: 2
I(BR, 35, V) = 0.0
8700 CONTINUE
DO 8720 V=0.2
DO 8740 K=1, 34
K1=K+1
X=E*RTV(F, K1, V, 2)/T(V)
V2=(1-2*7/WL(BR, X, V))**3
I(BR, K, V) = V3*3(RE, K, V)*DEXP(X)*P(V)
IF(I(BR, K, V) GT IMAX) IMAX=I(BR, K, V)
8740 CONTINUE
8720 CONTINUE
RETURN
END
LECTURE COURSES ATTENDED

In accordance with the regulations of the University of Edinburgh (Department of Chemistry) the following lecture courses were attended.

1. Fortran 77 Computing
2. Microcomputers
3. Quantum Optics - Lasers
4. Lasers in Chemistry
5. History of the Department of Chemistry
6. The Chemistry of Photographic Processes
7. Case Studies in Molecular Reaction Dynamics

Additionally, many of the regular departmental seminars and all research group meetings were attended.
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102. J T Yardley, "Introduction to Molecular Energy Transfer" (Academic Press, 1980, New York) page 221, equations 8.3-1 - 8.3-6


133. D Austin, private communication.


