REACTIVE AND INELASTIC PROCESSES
INVOLVING SULPHUR AND IODINE ATOMS.

by

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1980
DECLARATION

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

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To my mother

Mary Trainer
ABSTRACT

The reactions of ground state sulphur atoms, $S(3^3P_J)$, with various molecular species have been examined. These molecules included halogens, aromatics, nitrogen oxides, halomethanes, ozone and ammonia. The kinetics of these reactions were compared with those for similar reactions involving $O(2^3P_J)$ atoms.

The $S(3^3P_J)$ atom reactions were studied using the technique of time-resolved atomic absorption spectrophotometry. The source of the $S(3^3P_J)$ atoms was carbonyl sulphide. Photolysis of OCS in the U.V. yielded excited state $S(^1D_2)$ atoms which were subsequently quenched to the ground state with nitrogen.

Reactions and energy transfer processes involving electronically excited iodine atoms, $I(5^2P_1)$, were investigated using time-resolved resonance fluorescence spectrophotometry. The reaction of $I(5^2P_1)$ with ozone was examined and compared with that for the ground state iodine atom, $I(5^2P_3)$, and other halogen atoms.

Quenching of $I(5^2P_1)$ by a wide range of gases (NH$_3$, HCN, sulphur containing triatomics, aromatics and halocarbons) was investigated and emphasis was placed on systems where resonant electronic vibrational + rotational energy transfer is thought to be important.

Using the FORTRAN IV computer language a number of computer programs were written to process data and generate potential energy curves.
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CHAPTER ONE
CHAPTER 1

INTRODUCTION

1.1 Gas kinetic research on atom-molecule systems has often had practical applications and has contributed to the development of the fundamental theory of reaction dynamics. Accurate kinetic data arising from research has given a clear understanding of the role of atomic reactions in atmospheric, combustion and explosion processes. The rapid progress that has taken place in the development of gas phase discharge and chemical lasers in recent years has primarily been due to an understanding of the kinetics involved in these systems. These lasers in turn have provided tools for kinetic experiments.

This thesis is primarily concerned with the kinetics of reactive and inelastic processes involving ground state sulphur atoms, \( S(3P_J) \), and excited state iodine atoms, \( I(5^2P_{\frac{3}{2}}) \) or \( I^* \), with molecular species. The technique used to study the \( S(3P_J) \) atom reactions was time-resolved atomic absorption spectrophotometry which is fully discussed in chapter 2. For the \( I(5^2P_{\frac{3}{2}}) \) processes the technique utilized was time-resolved resonance fluorescence spectrophotometry which is also described in chapter 2.

The chemistry of \( S(3P_J) \) atoms has not been thoroughly studied so the reactions of this species with various classes of molecules have been examined to help rectify this situation. Also since it is believed that \( S(3P_J) \) atoms can be generated in the stratosphere by the photolysis of OCS then it is important to study their reaction with important atmospheric molecules such as \( O_3 \) and \( NO_2 \). Energy transfer from \( I(5^2P_{\frac{3}{2}}) \) to molecules should also be
carefully studied as processes such as these are important in laser chemistry.

This chapter serves as an introduction to ground state and excited state chemistry. Some consideration will be given to the characteristics of the sulphur and iodine atoms and their reactions. The various techniques used to study the kinetics of reactions will be discussed.

1.2 CHEMISTRY OF GROUP VI ATOMS

This group of elements includes O, S, Se, Te and Po. The chemistry of these elements is very similar, however there are differences in reactivity of these elements towards specific molecules. The ground and excited states of these atoms can take part in reaction processes such as abstraction, insertion and addition. Many of the reactions studied have been confined to those for the oxygen atom since both the excited and ground states of this atom are important in the chemistry of the atmosphere. Some of the reactions of the above atoms have been reviewed.\(^2\)\(^3\)

Oxygen and sulphur atoms can take part in simple reactions of the type

\[ A + BC \rightarrow AB + C \]  

Modern theory of bimolecular reactions\(^4\) classifies gas phase reactions of this type into reactions involving an intermediate complex or direct reactions. In reactions involving an intermediate complex the primary stage of the mechanism is formation of a complex \(ABC^*\) and the second stage is breakdown of this complex along all possible channels. The direct reactions can be subdivided into three groups according to the mechanism involved.
These are the rebound mechanism, the direct dislodgement mechanism and the stripping mechanism. Molecular beam studies have shown that these direct reactions do not involve the formation of a long-lived complex and the time of interaction between A and one of the atoms in BC is short in comparison with the period of rotation of AB or BC.

1.3 REACTIONS OF SULPHUR ATOMS

Figure 1.1 shows the energy level diagram for some of the metastable states of the sulphur atom. Present day kinetic studies have concentrated on the lowest lying electronic states, $^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$ and $^1S_0$. In this work only the reactions of the ground triplet states are considered.

The $S(^1S_0)$ state has been directly observed and was found to be less reactive and less easily quenched than the $S(^1D_2)$ state. The $S(^1D_2)$ state has also been directly observed and rate constants for its quenching by inert gases have been evaluated. Studies have shown that the $S(^1D_2)$ state is more reactive than the ground state. For example whereas $S(^1D_2)$ can undergo insertion reactions with paraffins, $S(^3P_1)$ cannot.

The reactions of $S(^3P_1)$ atoms with olefins such as ethylene and propene have been extensively studied. This is considered to be the first observation of a stereospecific triplet state addition. Generally electrophilic species such as triplet oxygen atoms and triplet carbenes add in a non-stereospecific manner whereas the singlet states were found to add stereospecifically. The stereochemistry of such an addition is a two step mechanism. The triplet species adds to the C=C bond forming
Figure 1.1 Energy level diagram for the sulphur atom.

Figure 1.2 Energy level diagram for the iodine atom.
a triplet diradical which then, after spin inversion to a singlet state, closes to a 3-membered cyclic product (thiirane). For the normal triplet species rotation about the C-C bond must occur at a faster rate than spin inversion and this gives non-stereospecific products. In the case of \( S(3P_J) \) it is believed that in the intermediate diradical, C-C bond rotation is slowed down by the heavy sulphur atom and interactions between orbitals, leading to a stereospecific product.

The reaction of \( S(3P_J) \) with \( O_2 \) has been studied in depth.\(^3,8\) The reactions of \( S(3P_J) \) atoms with halogens, ozone and nitrogen dioxide have also been investigated and essentially the abstraction of a halogen or oxygen atom is involved. These will be discussed in detail in chapter 3.

The most useful photolytic source of \( S(3P_J) \) atoms is OCS, the relevant primary processes being

\[
\text{OCS}(\tilde{X}^1Σ) + hν \rightarrow \text{CO}(1Σ) + S(1D) \quad \lambda < 283 \text{ nm} \quad (1.2)
\]

\[
\rightarrow \text{CO}(1Σ) + S(1S) \quad \lambda < 207 \text{ nm} \quad (1.3)
\]

\( (\lambda > 200 \text{ nm}) \)

At least 74% of the photolysis proceeds according to process (1.2).\(^7\) In the event of a large pressure of a quenching gas (\( N_2, \text{OCS}, \text{etc.} \)) being present the excited state sulphur atoms formed can undergo deactivation by collision to form \( S(3P_J) \) atoms,

\[
S(1D) + N_2 \rightarrow S(3P_{2,1,0}) + N_2 \quad (1.4)
\]

\[
k_4 = 5 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}.10\]

Donovan\(^11\) observed that the three ground states \( S(3P_{2,1,0}) \) are formed in a non-Boltzmann distribution however the \( 3P_0 \) and \( 3P_1 \) states are rapidly deactivated by collision with inert gas and OCS to give an equilibrium distribution.
Subsequently the $S(\text{3}_P\text{j})$ atoms formed can react with a reactant or OCS,
\[ S(\text{3}_P\text{j}) + \text{OCS} \rightarrow \text{CO} + \text{S}_2 \]  
\( k_5 = 3.5 \times 10^{-15} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \).

Other possible sources of $S(\text{3}_P\text{j})$ atoms are SO\(_2\) and CS\(_2\) however these have been found to be unsatisfactory.

1.4 REACTION AND QUENCHING OF $I(\text{5}_P\text{j})$

Figure 1.2 shows an energy level diagram for atomic iodine transitions of relevance in this study. The first excited state $I(5p^5(2P_3))$ or $I^*$ is 7603 cm\(^{-1}\) above the ground state $I(5p^5(2P_3))$. Husain and Donovan\(^{12}\) have shown that the excited state iodine atom is more reactive towards halogens and interhalogens than the ground state atom.

The excited halogen atom can take part in dissociative, abstraction and insertion reactions and a number of physical processes are available for removal of the electronic excitation energy.\(^{13}\) For example emission processes or energy transfer. Quenching of the electronic excitation of the $I^*$ atom via electronic $\rightarrow$ vibration + rotation ($E \rightarrow \text{VR}$) energy transfer is an important process
\[ I^* + Q \rightarrow I + Q^\dagger + \Delta E \]  
(1.6)
where $Q^\dagger$ indicates vibrational and rotational excitation of the quenching molecule and $\Delta E$ is the energy mismatch. This process can be resonant or non-resonant. In the resonant case the energy transfer is believed to occur via specific and near resonant channels and results in selective vibrational excitation of the
quenching molecule. This process is of particular importance in energy transfer lasers. In non-resonant transfer a range of vibrational levels are excited. The energy mismatch is channeled into translational energy of the products.

The reactions and inelastic processes of $I(5^2P_3^2)$ have been thoroughly studied and extensive reviews are available. Polyatomic halides such as $\text{CH}_3\text{I}$, $\text{CF}_3\text{I}$ and $\text{i-C}_3\text{F}_7\text{I}$ are good sources of $I^*$ atoms since population inversions of $I(5^2P_3^2)$ over $I(5^2P_3)$ have been observed following their photolysis. The perfluoro-alkyl halide, $\text{i-C}_3\text{F}_7\text{I}$ was exclusively used as the source of $I^*$ in this study and proved to be excellent.

1.5 EXPERIMENTAL TECHNIQUES

Reactive and inelastic processes of gas-phase atom-molecule systems can be studied using bulk or beam methods. Bulk methods are concerned with the overall kinetics of a reaction and fairly high pressures of reagents are used to maximize the absorption or fluorescence signal to be detected. Fluorescence can be due to electronic or vibrational transitions. Some commonly used bulk methods will be described, followed by some beam methods.

Flash Photolysis and Kinetic Spectroscopy

This important technique was devised by Norrish and Porter. Reaction in a gas mixture is induced by photolysis of one of the components to produce atoms or free radicals. The reaction products are monitored by kinetic absorption spectroscopy, i.e. a beam of light from a spectroflash lamp passes along the reaction vessel and is focused onto a slit of a spectrograph. Hence an absorption spectrum of the reaction products can be recorded on...
a photographic plate. By varying the delay between photolysis and triggering of the spectroflash lamp a picture can be built up which shows the unstable intermediates and the rise of the final products. Product vibrational distributions can be obtained using this method.

The time-resolved resonance absorption spectrophotometric technique used in this study to measure the bulk rate constants for the reactions of $S(^3P)$ atoms evolved from Norrish and Porters' apparatus. The apparatus is described in chapter 2. Basically, the OCS in a gas mixture was photolyzed to produce $S(^1D)$ atoms which were rapidly quenched by nitrogen to produce $S(^3P)$ atoms. The $S(^3P)$ atom concentration was monitored by absorption of a resonance line from an atomic lamp. This was either the 182.63, 182.04 or 180.73 nm line (see figure 1.1 for transitions). However with this technique it is only possible to speculate on the type of mechanism occurring from the kinetics observed.

The absorption technique can be used in conjunction with a stationary or flow system.

**Time-Resolved Resonance Fluorescence Spectroscopy**

This technique was used to determine the $I(5^2P_{\frac{1}{2}})$ reaction and quenching rate constants, and the apparatus is described in chapter 2. The $I(5^2P_{\frac{1}{2}})$ atoms, produced by photolysis of $i$-$C_3F_7$I, were monitored by exciting them to a higher level using the resonance line (206.2 nm) from an atomic lamp, and observing the fluorescence (178.3 nm) resulting from the transition from this state to the ground state. This technique is based on the observation that the fluorescence intensity is proportional to the concentration of the excited iodine atoms.
The technique has also been used in conjunction with stationary and discharge flow systems for the study of $S(^3P_J)$ atom reactions.

**Chemiluminescent Flow**

In this technique reactants are mixed in a fast flow apparatus and the chemiluminescence resulting from the reaction products is observed at a point close to the mixing zone. Measurement of infra-red luminescence arising from vibrationally excited molecules can therefore be undertaken. Ultra-violet emissions have also been observed in reactions of metastable rare gas atoms

$$
\text{Xe}(^3P_2) + \text{Cl}_2 \rightarrow \text{XeCl}^* + \text{Cl} \quad (1.7)
$$

$$
\text{XeCl}^* \rightarrow \text{Xe}(^1S) + \text{Cl}(^2P) + h\nu \quad (1.8)
$$

**Chemical Lasers**

The reaction to be studied is initiated by flash photolysis and a vibrationally excited product is formed. For example, the reaction

$$
\text{F} + \text{H}_2 \rightarrow \text{HF}^+ + \text{H} \quad (1.9)
$$

I.R. Fluorescence

The reaction cell can be incorporated into a laser cavity where the infra-red chemiluminescence is amplified and appears as laser action on a few lines. Methods have been developed to determine the relative vibrational populations.

The main disadvantages of the bulk methods are that there is often uncertainty about the reactions involved, competing reactions may be present and significant vibrational and rotational relaxation of the products often occurs.

**Beam Methods**

Beam methods require a high vacuum as single collision conditions
are required. Some of the techniques are described.

Angular Scattering Measurements

The crossed beam method can yield information on the energy disposal and provide an angular distribution of the scattered products of a reaction. The shape of the angular distribution can provide a great deal of information on the dynamics of a reaction. For example in the reaction

\[ \text{K} + \text{I}_2 \rightarrow \text{KI} + \text{I} \]  

(1.10)

the KI product is scattered predominantly in the forward direction (stripping mode behaviour).\(^5\) Preferential scattering such as this indicates that the reaction is over before any number of rotational periods can take place. This is a direct reaction mechanism. In the situation where a complex is formed, that has a lifetime of a number of rotational periods, scattering of the reaction product would tend towards a backward-forward symmetric configuration.

Collimated beams of atoms, ions or molecules are usually crossed at 90° and a mass spectrometer detects the products. This can be rotated at various angles with respect to the beam system and thus the angular distribution of the various scattered species can be measured. The velocity distribution of the products can be measured. Translational energies of reactants can be varied by using accelerated beams. Beams of high intensity with high collision energies can be obtained by seeding the atoms or molecules in a diluent gas such as helium and employing high pressures behind the nozzle. This is useful for studying endothermic reactions.

Arrested Relaxation (A.R.) Infra-red Chemiluminescence

In this technique, infra-red chemiluminescence from a vibrationally excited reaction product is monitored. For example the
reaction

\[ H + Cl_2 \rightarrow HCl^+ + Cl \]  \hspace{1cm} (1.11)

I.R. Chemiluminescence

Gas-phase vibrational and rotational relaxations are arrested by the rapid removal of the excited products at a liquid nitrogen cooled surface. Intersecting beams in the reaction chamber are uncollimated. The beams are usually produced by microwave discharge or thermal dissociation, hence the translational energy of the reagents can be varied. The rotational and vibrational populations can be calculated from the infra-red spectra obtained using a spectrometer. Complete energy partitioning is obtained using this technique.

U.V. / Visible Chemiluminescence

This technique monitors the electronic emission spectrum of electronically excited reaction products. The atomic and molecular beams are normally oven or nozzle source and a crossed beam configuration is used. The emission spectrum can be analyzed to yield the relative populations of the different excited states and the populations within them. Also the angular distribution of emission can be measured and provides information concerning translational excitation of the products. Reactants can also be excited prior to reaction by a laser or by electron bombardment. For example the reaction

\[ Xe\left( ^3P_{0,2}\right) + F_2 \rightarrow XeF^* + F \]  \hspace{1cm} (1.12)

U.V. Chemiluminescence

Laser Induced Fluorescence (L.I.F.)

In a crossed beam set-up a tunable laser can be directed at
the reaction zone and scanned across the electronic absorption spectrum of a product molecule. Molecules in the ground state will thus be excited to upper state levels and will subsequently fluoresce. The monitored fluorescence can be related to the populations of the molecules in specific rotational and vibrational levels in the ground state, since the electronic spectrum has resolvable vibrational and rotational bands. An example of a reaction studied by this technique is

\[
\text{Ba} + \text{HF} \rightarrow \text{BaF}_{v,J} + \text{H} \\
\downarrow \text{laser excitation} \\
\text{BaF}^* \downarrow \text{fluorescence} \\
\text{BaF} \text{ (ground state)}
\]
REFERENCES

10. M.C. Addison, private communication.
CHAPTER TWO
CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 INTRODUCTION

In this chapter the techniques used to study the kinetics of ground state sulphur and excited state iodine atoms are described. Time-resolved absorption photometry was used to study the reactions of sulphur atoms, while the more sensitive technique of time-resolved resonance fluorescence was used to study iodine atoms.

2.2 TIME-RESOLVED RESONANCE FLUORESCENCE

Atomic fluorescence is a result of the emission of light associated with the return of an atom from an excited electronic state to a lower state or to the ground state. The longest wavelength capable of exciting this type of emission is called the resonance line and therefore the resulting emission is known as resonance fluorescence. When relatively intense sources of atomic emission became available then their combination with the conventional flash photolysis technique led to the technique of atomic resonance fluorescence which could be utilized to study elementary gas-phase atom-molecule reactions. The principles on which this technique are based have been described in chapter 1.

At the onset of the work a relatively simple apparatus was used\(^1,2\) which naturally evolved to a more sophisticated system as the work progressed. The main features of the modified apparatus are shown in figure 2.1, and the various components are described individually in the following pages.
Figure 2.1 Modified apparatus for time-resolved resonance fluorescence.
Flash Lamp

In the early stages of experimental work a conventional quartz capillary type flash lamp (i.d. 2 mm) was used which was filled with research grade krypton to a pressure of 500 Nm\(^{-2}\). Much research has been done on the principles, characteristics and design of flash lamps.\(^3\) The maximum flash energy emitted from the lamp is determined by the formula

\[ E = \frac{1}{2} CV^2 \]  

(2.1)

where \( E \) = energy (Joules)
\( C \) = capacitance (farads)
\( V \) = voltage (V).

The circuit for firing the spectroflash lamp has previously been described.\(^4\) With a 1.5 \( \mu \)F capacitor charged to 8 kV, typical flash energies were 48 J.

The modifications to the original apparatus involved the use of a Xe-pulsed flash lamp (Oriel Scientific Ltd., 3021 pulsed light source) which has several advantages over the conventional quartz capillary flash lamp:

1. The output peaks in the UV region (200 - 400 nm)
2. It is a compact light source which is more easily focused
3. Higher flash repetition rates makes signal averaging of a number of signals possible
4. Less electrical noise
5. It is more reproducible from flash to flash.

The output radiation consists of a continuum overlapped with emission lines from the Xenon and is shown in figure 2.2. The lamp is very small (figure 2.2) and is housed in a head unit.
Figure 2.2 Xe-pulsed flash lamp characteristics.
Figure 2.3 Xe-pulsed flash lamp electronic circuits.
which also contains a storage capacitor and firing circuit (see figure 2.3). The control unit is remote from the head unit and contains a 500 V power supply, trigger oscillator and connection for external triggering. The pulse rate can be adjusted from single shot to 40 pulses per second, and either high (0.25 J) or low (0.03 J) energy can be chosen; the output characteristics of these alternatives are shown in figure 2.2. In this study the low energy output was sufficient to produce photolysis of the i-C$_3$F$_7$I.

Figure 2.1 shows the optics used to focus light pulses to the centre of the cell and consists of the Xe-pulsed flash lamp, a lens of focal length 10 cm (75 mm diam.) to gather the emitted light and an iris diaphragm adjusted to give an even circular distribution of light which falls on another lens of focal length 9 cm (40 mm diam.) to focus the light to the centre of the cell. A piece of black card with a 10 mm diameter hole was placed in front of the window. The purpose of this was to give an even distribution of light falling on the cell window. The apparatus was mounted on an optical bench and was carefully aligned. Black cloth was placed over the optics to prevent any scattered light reaching the photomultiplier.

**Reaction Cell**

This is used to contain the reactants. In a previous study of resonance fluorescence from excited iodine atoms a glass reaction cell had been used but gave too much scattered light, however a robust metal cell which could be easily dismantled was used for all the excited iodine atom work in this study. Figure 2.4 shows
Figure 2.4 Reaction cell construction.

Cube face showing insert for O-ring

left side

face

base

right side

Plate with window

Section through cell

O-ring, lightly greased.

Brass screws, not tightly screwed (2 mm diam.)

Plates with Wood's horn

Plates with Wood's horn with connection to gas line

Construction

(1) Face: - LiF window
(2) Top: - MgF$_2$ window
(3) Leftside: - Spectosil window
(4) Rear: - Wood's horn (facing down)
(5) Base: - Wood's horn
(6) Rightside: - Wood's horn plus connection to gas line.
details of the cell, plates and various attachments with dimensions (designed by H.M. Gillespie). The body of the cell was constructed from a 6 cm cube of aluminium alloy, through which three 4 cm diameter holes had been drilled to form a roughly spherical reaction volume. Inserts were also machined on the cell walls into which 5 cm diameter Viton O-ring seals could be inserted. To seal off the reaction cell and gain access to it, six aluminium plates of 6 cm diameter were constructed with holes drilled in the centre. To these plates either Wood's horns or specific windows had been connected using Araldite epoxy resin as adhesive. These plates can be screwed on to the sides of the cell body using four brass screws with a lightly greased Viton O-ring seal in between. By this means a good vacuum was obtained in the cell ($<10^{-2}$ Nm$^{-2}$).

The cell was designed such that diffusion of excited atoms to the cell walls and hence deactivation would be kept to a minimum. Experiments carried out with another cell showed that the level of scattered light increased dramatically when flat plates with metallic surfaces were used instead of Wood's horns, particularly if the plate was on the side facing the entrance window of the flash. So Wood's horns were used on three sides to keep scattered light to a minimum. The outside of the Wood's horns were painted black.

Atomic Resonance Lamp

Two types of emission lamp were used, sealed lamps and flow lamps.

The sealed lamp consisted of a 26 cm length of quartz tubing (10 mm o.d.) bent to form an L-shape, with a spectrosil window
fused on at one end, the other end being sealed. This lamp contained a few small crystals of pure iodine (the tube was evacuated and the iodine degassed before it was sealed).

A continuous microwave discharge was excited in the lamp by using a 25 mm X 50 mm cylindrical Evenson-Broida cavity coupled to a microwave generator (Microton 200, M.P.G. Mark 3, Electro-Medical Supplies). In operation the microwave generator was maintained at 60 W, i.e. 30% of maximum output of the generator. The cavity was tuned to give a visible discharge of about 6 cm in length. The distance of the centre of the reaction cell to the discharge zone was 18 cm. The discharge was initiated by means of a Tesla coil. To prevent ozone formation in the proximity of the atomic lamp, the lamp was surrounded by a pyrex glass sleeve, the lamp being cooled by a continuous flow of air. This type of lamp gave a clean intense output consisting of a number of lines corresponding to specific atomic transitions.

Figure 2.5 shows the construction of the flow lamp. The design is similar to that used by Davis and Braun. An iodine flow lamp has also been described by Harteeck et al. The lamp consists of a 24/29 quickfit cone fused to a length of pyrex tubing (12 mm o.d.) and has two 10 mm o.d. inlet and outlet tubes. The socket end of the lamp allows a convenient method of connecting the lamp to a reaction cell or monochromator. The apparatus necessary for operation of the lamp is shown in figure 2.6. The lamp was pumped from the outlet side with a rotary pump, with a liquid nitrogen cold trap in between to prevent pump oil from diffusing back into the lamp and coating the window. The liquid nitrogen trap could be isolated from the line by closing
position of microwave cavity

spectrosil window (black wax adhesive).

inlet

Jubilee clip used to connect tubing to arm of lamp.

Figure 2.5 Iodine flow lamp.

Key
A Atomic lamp
I Iodine reservoir
M Manometer
MW Microwave generator
N Needle valve

Figure 2.6 Apparatus for operation of iodine flow lamp.
a stopcock. The gas pressure was monitored at the outlet side of the lamp by using a manometer containing silicone oil. The inlet side of the lamp was connected with polyethylene tubing to a reservoir containing a few crystals of iodine. Flexible tubing from this vessel connected it to a needle valve and finally to a 2 litre bulb containing argon. To operate the lamp, the line was first evacuated, the iodine crystals being kept cold by means of liquid nitrogen. Then a flow of argon was allowed to pass through the lamp carrying the iodine vapour with it. The gas flow was adjusted to a pressure of $133 \text{ Nm}^{-2}$ for best results, with the iodine at room temperature. This flow lamp gave a very intense atomic emission, however the window of the lamp rapidly became coated with iodine deposits so that the window had to be cleaned regularly. The sealed lamp thus proved to be superior, mainly because of its simplicity and ease of use.

Since the fluorescence is induced by the 206.2 nm line from the iodine lamp then ideally this is the only line that should reach the cell. The configuration of the lamp ensures that atomic lines of wavelengths shorter than 206.2 nm are absorbed by the oxygen in the air gap between the lamp and the cell. However an interference filter with maximum transmission at $\sim 205 \text{ nm}$ was placed between the lamp and cell. This reduced the level of scattered light from the lamp and also helped to reduce photolysis of the $\text{1-C}_3\text{F}_7\text{I}$ by the lamp. A shutter was also placed in front of the filter which helped reduce iodide photolysis further since the shutter was only opened for a brief period while the experiment was carried out. The phenomenon of self-reversal is important in atomic lamps of the above design and is outlined
Photodetection Unit

This consisted of an E.M.I. type EXP5241, eleven stage solar blind photomultiplier housed in a brass casing for protection and to minimize interference; the casing was earthed. Between the photomultiplier and the cell was a collimating tube of length 40 mm and 60 mm i.d. The tube was painted black inside and just fitted loosely around the circular plate on the face of the resonance cell. It was necessary to flush the photomultiplier housing with a flow of nitrogen, as oxygen in the tube would absorb the 178.3 nm fluorescence line. The nitrogen flow was turned on a half-hour before commencing experiments. The cathode of the photomultiplier was held at a voltage of -870 V using a Brandenburg Model 475R power supply.

The signal from the photomultiplier was fed to a Datalab DL905 transient recorder and could be viewed on an oscilloscope coupled to the transient recorder. The output from the transient recorder was interfaced to an X-Y chart recorder so that permanent records of the signal could be obtained. A certain proportion of the transient recorder memory can be chosen to record signals preceding the firing of the flash lamp, so that a base line is obtained. In this work sweep times of 5 - 50 ms were used.

Signal Averager

In the apparatus which used a repetively pulsed flash lamp a Datalab DL4000 signal averager was interfaced with the transient recorder and a specific number of traces could be averaged giving a high signal-to-noise ratio. With this system excellent I*
fluorescence decay traces were obtained by using the low intensity output of the pulsed light source and taking an average of 64 - 128 signals.

**General Experimental Method**

The preparation of the i-C$_3$F$_7$I plus quencher/reactant in diluent gas was carried out by the following method. Using a spiral gauge for all pressure measurements, 213 Nm$^{-2}$ of i-C$_3$F$_7$I was put into four bulbs. Into three of the bulbs a specific quantity of quencher/reactant was measured: this quencher/reactant in most cases was diluted with helium according to its efficiency. To the alkyl iodide plus quencher/reactant mixture a diluent gas (helium) was added to make the total pressure 6.65 kNm$^{-2}$. The fourth bulb contained only C$_3$F$_7$I plus helium and this gave the signal for the decay of I$^*$ when no quencher except helium was present. All mixtures were left for not less than 2 hours to ensure thorough mixing by diffusion.

About 30 minutes before the start of an experiment a continuous flow of nitrogen was flushed through the photomultiplier housing and all the apparatus was made ready. Approximately 10 minutes before starting a kinetic experiment the atomic resonance lamp was switched on and allowed to stabilize.

The experiments were then carried out as follows. First the flash profile was recorded with the cell empty. Then the required pressure of mixture was measured into the cell (2.9 - 3.3 kNm$^{-2}$). The shutter between the atomic lamp and cell was locked open and then in the case of the conventional quartz capillary flash lamp the capacitor was charged up to 8 kV.
and the lamp triggered by means of a trigger unit connected to a thyratron. A decay trace was observed on the CR0 and this was then transferred to the X-Y chart recorder. In the case of the Xe-pulsed flash lamp and signal averager, the required number of sweeps was chosen on the signal averager and the flash lamp switched on. After the specified number of sweeps had been reached the stored signal could be transferred to chart paper for processing.

2.3 TIME-RESOLVED RESONANCE ABSORPTION SPECTROPHOTOMETRY

The second experimental technique used was time-resolved resonance absorption spectrophotometry. This was employed to measure the rate constants for \( S(3^3P_J) \) reactions. A diagram of the apparatus is shown in figure 2.7. The apparatus was constructed by M.C. Addison. A more detailed description of the apparatus follows.

Reaction Vessel

This consisted of a cylindrical tube of vitreosil grade quartz of length 50 cm and 22 mm o.d. The reaction vessel was constructed of this material to limit photolysis to wavelengths of greater than 200 nm. One end of the cell had a LiF window attached by means of epoxy resin and this end was joined to the monochromator. The other end of the cell had the flow lamp attached to it.

Flash Lamp

The flash lamp used in the system was a conventional linear flash lamp ~50 cm in length and 14 mm o.d., constructed of quartz with mild steel electrodes at either end. A high vacuum tap at
Figure 2.7  Apparatus for time-resolved resonance absorption spectrophotometry.
one end allowed filling of the lamp with $\sim 500 \text{ Nm}^{-2}$ of krypton: this would give several hundred flashes before it needed refilling. The flash lamp was mounted parallel to the reaction vessel, the distance between centres being $\sim 30 \text{ mm}$. Aluminium foil was wrapped around the flash lamp and reaction vessel to obtain the maximum amount of light from the flash lamp. During an experiment flash energies of 320, 180 or 80 J were obtained by using a plunger to discharge a 10 $\mu\text{F}$ capacitor charged to 8, 6 or 4 kV respectively, by means of a high voltage power supply (Hipotronics Model 820-20).

**Atomic Resonance Lamp**

The atomic lamp used to obtain sulphur resonance lines was the same type as that described for the iodine flow lamp. The apparatus for operation of the flow lamp is shown in figure 2.8. In operation it was only necessary to let $\text{H}_2\text{S}$ into the system occasionally as the inside of the lamp became coated with sulphur and this was sufficient to provide intense enough emission of the required sulphur lines. The pressure of helium in the line was held at 300 - 400 Nm$^{-2}$ and this could be altered to give maximum emission. Keeping a low concentration of sulphur atoms in the atomic lamp kept self-reversal of the atomic line to a minimum. A microwave discharge was obtained in the lamp by means of an Evenson-Broida cavity fed by an E.M.I. microwave power generator (Type T.1001). The output from the microwave generator was $\sim 50 \text{ W}$ and the cavity was tuned to give minimum reflected power. The cavity was cooled by means of a compressed air supply. Figure 2.9 shows the emission lines obtained from the lamp and table 2.1.
Figure 2.8 Apparatus for operation of sulphur flow lamp.

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>182.63</td>
<td>( 4s^3S^o \rightarrow 3p^3P^2 )</td>
</tr>
<tr>
<td>182.04</td>
<td>( 4s^3S^o \rightarrow 3p^3P^1 )</td>
</tr>
<tr>
<td>180.73</td>
<td>( 4s^3S^o \rightarrow 3p^3P^1 )</td>
</tr>
</tbody>
</table>

Table 2.1 Assignments.

Figure 2.9 Output from sulphur flow lamp.
gives the assignments. For most of the \( S(3P) \) experiments the 182.63 nm line was used. The lines were isolated using a Hilger and Watts Vacuum Monochromator (Model E766). This was evacuated to a pressure of \( \approx 10^{-4} \text{ Nm}^{-2} \) by using a rotary pump and oil diffusion pump. Pressures in the line and body of monochromator were monitored by means of a pirani gauge and penning (ionization) gauge. Slit widths were kept constant at 0.153 mm. A shutter between the monochromator and reaction vessel was only opened when carrying out an experiment.

**Light Detection System**

Light from the monochromator was detected by means of a photomultiplier housed in a brass casing and coupled to the monochromator. The photomultiplier was an E.M.I. 9616 QB, employing a thirteen dynode chain. A photomultiplier power supply (Brandenburg Model 475R) held the cathode at -1000 V. The signal from the photomultiplier was fed to a Datalab DL905 transient recorder, set to sweep times of 5 - 50 ms. The transient recorder was coupled to an oscilloscope for visual display of the absorption signals and also to an X-Y chart recorder.

**General Experimental Method**

All gas mixtures were prepared on a gas line and pressures were accurately measured using two Baratron heads coupled to an MKS Instruments Baratron digital readout (pressure ranges: 0 - 1.33 kNm\(^{-2}\) and 0 - atmospheric pressure). A mixture was made up as follows. Into the mixing vessel 133 Nm\(^{-2}\) of OCS was measured then a specific quantity of reactant was added: this reactant in most cases was diluted with nitrogen according to its efficiency
as a reactant with $S(^3P_J)$. The total pressure in the mixing vessel was then made up to 7.98 kNm$^{-2}$ using nitrogen as a diluent. This mixture was then thoroughly mixed for about 1½ minutes using a paddle mixer powered by an electric motor.

The experiments were carried out in the following manner. First the signal with the shutter at the monochromator closed was recorded using the X-Y chart recorder. The 1.33 kNm$^2$ of the mixture was measured into the reaction vessel. The shutter of the monochromator was then opened, the capacitor charged up to 6 or 8 kV and discharged by means of a plunger. The $S(^3P)$ absorption signal was observed on the CRO and transferred to the X-Y chart recorder. Mixtures were made up containing various partial pressures of a specific reactant and a set of absorption traces were thus obtained which were processed as described in the next section.

2.4 DATA PROCESSING

Time-resolved Resonance Fluorescence Spectroscopy

Figure 2.10 shows an $I(^2P_J)$ fluorescence decay signal obtained by photolyzing 93.1 Nm$^{-2}$ of $i$-C$_3$F$_7$I using a quartz capillary flash lamp with a flash energy of 49 J. The profile of the curve shows the variation of fluorescence intensity with time. In comparison figure 2.11 is an $I(^5P_J)$ fluorescence decay obtained by photolyzing the same pressure of $i$-C$_3$F$_7$I using a Xe-pulsed flash lamp (0.03 J). The signal is an average of 128 flashes and clearly has a much better signal-to-noise ratio.

Since molecular iodine is formed in the photolysis of $i$-C$_3$F$_7$I it was necessary to carry out experiments to determine the variation of the first order rate coefficient (i.e. the rate of fluorescence decay) with repeated photolysis using the pulsed
Use a quartz capillary flash lamp.

Figure 2.10 I (2F-h) Fluorescence decay signal.

Fluorescence Intensity

931 Nm⁻² s⁻¹ F⁻¹
50 ms full sweep time
1 flash
Flash energy = 4.9 J

-33-
Figure 2.11. Fluorescence decay signal (Xe-pulsed flash lamp).

Fluorescence Intensity

Time

-934 µm. 2 µs,

50 ms full sweep time

Average 128 flashes

Xe-pulsed flash lamp ‘Low’ intensity.
light source. Figure 2.12 shows the variation of the first order rate coefficient according to the number of flashes used for photolysis. This graph indicates that the \( i-C_3F_7I \) can be photolyzed a considerable number of times without serious deterioration. Figure 2.13 compares the results obtained by using a quartz capillary flash lamp with those obtained from the use of a Xe-pulsed flash lamp. Clearly deterioration of the first order rate coefficient is much more rapid when the quartz capillary flash lamp is used.

To obtain the first order rate coefficient from the signal in figure 2.11 the following procedure was carried out. A baseline was drawn on the trace using the pre-trigger delay signal as a guide. A smooth curve was drawn through the decay part of the trace. Taking the point at which the flash occurs as \( t = 0 \), the curve was divided into 1 or 0.5 cm sections. Each of these was equivalent to a specific time interval depending on the full sweep time of the signal. At each interval the distance from the baseline to the curve was measured in mm. Normally measurements were started at a point equivalent to \( \sim 2 \) ms from \( t = 0 \) and 10 - 20 measurements were taken. So these values gave a measure of the fluorescence intensity at known times after the flash. The natural logarithm of these intensity values were taken and plotted against their corresponding time value. The gradient of this plot gave the first order rate coefficient. Data was usually processed using a computer program incorporating a least mean square technique.

This procedure was carried out for various pressures of reactant/quencher and a set of first order rate coefficients was obtained. These first order rate coefficients were plotted
Figure 2.12 Variation of first order rate coefficient with repeated photolysis of the 1-C$_3$F$_7$I.

Figure 2.13 Comparison of first order rate coefficients obtained from use of different types of flash lamp.
against their corresponding partial pressure of reactant/quencher and the gradient of the plot was equivalent to the second order rate constant. This is a measure of the rate of reaction or quenching of I* with a specific molecule.

Two computer programs were written to process the data (see Appendix II). LGRAPH and LGR calculate the second order rate constant using the least mean square technique and give graphical output. LGR also draws the error bars on the plot whereas LGRAPH incorporates automatic scaling of the points to fit a 25 cm X 12.5 cm plot. Plots obtained using these programs are illustrated in chapter 4.

Now considering the kinetics of the system

\[ I^* + R \rightarrow \text{Products} \quad (2.2) \]

This process is second order but the kinetics can be treated as pseudo-first order because of the following conditions. The fluorescence intensity is proportional to the concentration of excited iodine atoms. The concentration of the reactant or quencher is greatly in excess over I*, so that the I* atom concentration changes with time yet [R] remains constant.

The differential rate equation is

\[ -\frac{dI_f}{dt} \propto -\frac{d[I^*]}{dt} = k[I^*] \quad (2.3) \]

where k is a pseudo-first order rate coefficient containing a number of terms

\[ k = k_q[Q] + \beta + A_{nm} + \rho A_{nm} \quad (2.4) \]

\[ k_q = \text{second order rate constant for quenching/reaction of I* by Q} \]

\[ \beta = \text{rate coefficient for diffusion of I* out of the reaction zone} \]
A_{nm} = \text{Einstein coefficient for spontaneous emission}
\rho A_{nm} = \text{a term for decay by stimulated emission of radiation.}

k_q is the rate constant of interest in expression (2.4) and all the other terms can be minimized or kept constant. For example, diffusion of \( I^* \) atoms out of the reaction zone was kept constant by keeping the total pressure in the reaction cell constant for each experiment. Also the pressure was kept above a certain minimum value which has been determined, since the rate of diffusion is inversely proportional to the pressure. Diffusion of atoms in an inert gas in a cylindrical reaction vessel of radius \( r \) and length \( L \) has been discussed and the diffusion equation derived for diffusion to the walls was

\[ [I^*]_t = [I^*]_{t=0} \exp(-\beta t) \]

where

\[ \beta = D \left( \frac{\pi^2}{L^2} + \frac{5.81}{r^2} \right) \]

\( D = \text{diffusion coefficient at a given pressure.} \)

Expression (2.3) can be integrated to give

\[ -\ln[I^*]_t = kt + \text{constant} \]

Evaluating the integration constant from initial conditions of

\[ [I^*]_{t=0} \text{ at } t = 0 \text{ gives} \]

\[ \ln[I^*]_t = -kt + \ln[I^*]_{t=0} \]

where \( \ln[I^*]_t \) is equal to the concentration of excited atoms at time \( t \) after the flash which occurs at \( t = 0 \). So a plot of the logarithm of concentration versus time yields a straight line of gradient \( (-k) \). Equation (2.8) may be rearranged to give equation (2.9) which clearly emphasizes that the decay of \([I^*]\) is exponential

\[ [I^*]_t = [I^*]_{t=0} e^{-kt} \]
**Time-resolved Resonance Absorption Spectroscopy**

A typical absorption signal for \( S(3P) \) is shown in figure 2.14. This was obtained by photolyzing 22.17 \( \text{Nm}^{-2} \) of OCS in nitrogen. The total pressure was 1.33 \( \text{kNm}^{-2} \) and the flash energy 320 J. The trace shows the absorption of the 182.63 line emission from the atomic lamp by the \( S(3P) \) atoms present in the cell.

The pre-trigger delay mode of the transient recorder was used and this gave a base line on the trace from which measurements were taken. \( I_0 \) in figure 2.14 is the intensity of the atomic lamp emission in the absence of absorption. The absorption trace was divided into a number of 1 cm sections each representing an increment of time. The point at which the flash occurred is \( t = 0 \). After drawing a smooth curve through the decay part of the trace, intensity values \( I_t \) were measured for each increment of time by taking the distance from the curve to the \( I = 0 \) line. This line represents the signal when the emission from the atomic lamp was attenuated by closing the shutter on the monochromator. A plot of \( \ln \ln(I_0 / I_t) \) versus time gave a gradient equal to the first order rate coefficient. By varying the partial pressure of the reactant a set of first order rate coefficients was obtained. These were plotted against their corresponding pressure of reactant and a second order rate constant was obtained from the gradient of the plot. However this was not the true rate constant and had to be corrected using a correction factor which is discussed below.

The Beer-Lambert law describes the rate at which quanta of light are absorbed in a system. If the light emitted by the atomic S-lamp passes through a reaction vessel (length \( L \)) containing a substance (concentration \( c \)) and the incident light has intensity
2217 Nm\(^{-2}\) OCS
20 ms full sweep time
320 J flash energy.
Total pressure = 1.33 kNm\(^{-2}\)
Diluent gas – N\(_2\)
I_o, then the intensity of light transmitted I_t is given by
\[ \ln \left( \frac{I_o}{I_t} \right) = \varepsilon \lambda cL \] (2.10)

where \( \varepsilon \lambda \) = extinction coefficient which determines how strongly the substance absorbs at wavelength \( \lambda \).

However depending on the experimental set-up this Beer-Lambert relationship has to be modified to the form:
\[ \ln \left( \frac{I_o}{I_t} \right) = \varepsilon cL \gamma \] (2.11)

\( \gamma \) is a correction factor called the Beer-Lambert exponent which must be determined. This modification is linked to the phenomenon of self-reversal of line emissions. The relationship between the absorption and the atomic concentration is very complex. However if the concentration of the absorbing atoms is kept within a certain range the relationship is linear and \( \gamma \) can be determined.

Experiments were carried out with various concentrations of OCS diluted with nitrogen to a total pressure 1.33 kNm\(^{-2}\). By extrapolating the plot of \( \ln \ln \left( \frac{I_o}{I_t} \right) \) versus time back to \( t = 0 \) an intercept on the y-axis was obtained. By plotting the intercept values against their corresponding \( \ln(\text{OCS pressure}) \) values a straight line was obtained of gradient \( \gamma \). For the 182.53 nm line \( \gamma = 0.67 \pm 0.09 \) and for the 182.04 nm line \( \gamma = 0.74 \pm 0.1 \).

From the kinetics previously described the form of expression (2.9) for the absorption technique is
\[ \ln \left( \frac{I_o}{I_t} \right) = \ln \left( \frac{I_o}{I_t=0} \right) e^{-kt} \] (2.12)

Therefore from expression (2.11)
\[ \varepsilon (Lc_t)^\gamma = \varepsilon (Lc_{t=0})^\gamma e^{-kt} \] (2.13)

where \( k' \) = experimentally determined first order rate coefficient.
Cancelling out the $E$ and $L$ the following equation is obtained:

$$c_t = c_{t=0} \exp\left(-\frac{kt}{\gamma}\right)$$

(2.14)

So the measured rate coefficient $k'$ must be divided by $\gamma$ to obtain the correct value $k$. In practice the correction factor $\gamma$ was applied to the experimentally measured second order rate constant to give the true value.
REFERENCES  Chapter 2


CHAPTER THREE
CHAPTER 3

REACTIONS OF ATOMIC SULPHUR, \( S(3P) \)

3.1 INTRODUCTION

This chapter deals with reactions of ground state sulphur atoms, \( S(3P) \), and presents rate constant values for a range of reactant molecules. As stated in chapter 1, the ground triplet state for sulphur atoms has three components, \( 3P_2 \), \( 3P_1 \) and \( 3P_0 \). However, since the energy span for these components is only 6.7 kJmole\(^{-1}\), one might expect that it would be very difficult to discriminate between their individual reactivities, although differences may occur. So in this study the ground state has been considered, for simplicity, as a degenerate state. Only in one case was any attempt made to discriminate between the reactivities of different states of \( S(3P) \) and details are to be found in the section dealing with the \( S(3P) + Cl_2 \) reaction.

Although the reaction of \( S(3P) \) with olefins has been extensively studied there is still very little known about the reaction of ground state atomic sulphur with other categories of molecular species. In this study the molecules chosen have been segregated into six groups, namely halogens, aromatics, nitrogen oxides, halocarbons, ozone and ammonia.

Some of the rate constants for these reactions have previously been measured by other techniques and will be discussed in the relevant section.

3.2 THE REACTIONS OF \( S(3P) \) + HALOGENS

Recently Clyne and Townsend\(^1\) have measured the rate constants for the reaction of \( S(3P) \) with \( Cl_2 \), \( Br_2 \) and \( F_2 \) using the atomic
resonance fluorescence technique in conjunction with a discharge flow system. The Cl\textsubscript{2} and Br\textsubscript{2} reactions have been repeated in this section and the I\textsubscript{2} reaction rate constant has been determined for the first time.

Experiments and Results

The technique used to measure the rate constant for these reactions was kinetic absorption spectrophotometry (described in chapter 2). After some preliminary experiments it was found that difficulties were encountered in the determination of these rate constants due to adsorption and reaction of the halogens on the walls of the reaction vessel, mixer and mixture bulbs. To counteract this effect a relatively high pressure of the halogen was put into the line for a number of hours and then pumped for several hours to remove any excess halogen. So any hydrocarbon present on the glassware walls reacted with the halogen preventing any further removal during the experiments. After this treatment it was found that more consistent results were obtained. Also it was found that the conventional diffusion method of making up reaction mixtures was unsatisfactory. Two alternative methods were used to prepare the halogen/nitrogen mixtures:–

(1) Hot spot method: the required pressures were put into a bulb and the bulb heated directly underneath by means of a hot air blower for 5 minutes. Hence a convection current was created which mixed the gases.

(2) Mixer method: the halogen and nitrogen was thoroughly mixed for 5 minutes using a paddle mixer rotated by an electric motor. This mixer method proved to give the best results.

The total pressure of mixture used in the reaction vessel was
1.33 kN.m\(^{-2}\) and consisted of 22 Nm\(^{-2}\) of OCS, a partial pressure of halogen as noted in the table and nitrogen as diluent gas. Two traces at each specific partial pressure of halogen were recorded and processed using the method described in chapter 2, to give the first order rate coefficients. A critical evaluation of the errors in the rate coefficients was carried out by displacing the estimated base line by ± 2 or ± 3 mm depending on the extent of noise on the trace. Therefore the upper and lower limits of the coefficients could be determined and these were used for location of error bars on the plots.

Plots of the first order rate coefficients against partial pressure of Br\(_2\), Cl\(_2\) and I\(_2\) are given in figure 3.1. The gradients obtained from these plots are not the true second order rate constants and must be modified by applying the \(\gamma\)-factor for the modified Beer-Lambert relationship (see chapter 2). For the 182.63 nm sulphur line, \(\gamma = 0.67 \pm 0.09\). This corresponds to the S(\(^3P_0\)) state. For the 182.04 nm sulphur line, \(\gamma = 0.74 \pm 0.1\) and this corresponds to the S(\(^3P_1\)) state.

It can be seen from figure 3.1 that at the lowest partial pressures of halogen the first order rate coefficients do not fit a straight line as well as the other points. This is probably due to two effects, photolysis of the halogen and adsorption onto the walls of the glassware.

The results obtained are shown in table 3.1. The rate constants shown in this table were determined at a temperature of 296 K and the monochromator was set on the 182.63 nm line.

To determine whether there was any difference in the reactivity of the S(\(^3P_0\)) and S(\(^3P_1\)) components of the S(\(^3P_0\)) state the mono-
Figure 3.1 Plots of first order rate coefficients against partial pressure of halogen.

Figure 3.2 Energy profile along reaction path for an exothermic reaction.
chromator was also set on the 182.04 nm line. For the $S(3P_1) + Cl_2$ the gradient was $(1.89 \pm 0.14) \times 10^{-11}$ cm$^3$/molecule$^{-1}$s$^{-1}$ which gave a rate constant at 320 J flash energy of

$$k_{Cl_2} = (2.6 \pm 0.4) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}.$$ 

Table 3.1 Second order rate constants for the $S(3P_3)$ + Halogen reactions.

<table>
<thead>
<tr>
<th>Halogen</th>
<th>Partial Pressures (Nm$^{-2}$)</th>
<th>Gradient (cm$^3$/molecule$^{-1}$s$^{-1}$)</th>
<th>Rate Constant (cm$^3$/molecule$^{-1}$s$^{-1}$)</th>
<th>Flash Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br$_2$</td>
<td>0.024 - 0.109</td>
<td>(4.8 ± 0.3) $\times 10^{-11}$</td>
<td>(7.2 ± 0.6) $\times 10^{-11}$</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(4.9 ± 0.4) $\times 10^{-11}$</td>
<td>(7.4 ± 0.7) $\times 10^{-11}$</td>
<td>180</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>0.055 - 0.275</td>
<td>(1.7 ± 0.1) $\times 10^{-11}$</td>
<td>(2.5 ± 0.4) $\times 10^{-11}$</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.7 ± 0.1) $\times 10^{-11}$</td>
<td>(2.5 ± 0.4) $\times 10^{-11}$</td>
<td>180</td>
</tr>
<tr>
<td>I$_2$</td>
<td>0.044 - 0.225</td>
<td>(2.9 ± 0.2) $\times 10^{-11}$</td>
<td>(4.3 ± 0.4) $\times 10^{-11}$</td>
<td>180</td>
</tr>
</tbody>
</table>

Discussion

The overall reaction for $S(3P_3)$ with halogens is halogen atom abstraction,

$$S(3P_3) + X_2(X^1\Sigma^+_g) \rightarrow SX(X^2\Pi) + X(2P_{1/2})$$

(3.1)

($X_2 = Br_2, Cl_2$ or $I_2$)
Molecular beam experiments have demonstrated that the oxygen atom reactions equivalent to (3.1) proceed via a 'sticky' collision complex\(^2\) which persists for many vibrational periods and at least a few rotational periods, or typically \(\sim 5 \times 10^{-12}\) seconds. In these systems the intermediate complex is considered to be a bound molecular species which correlates with the ground state reactants and products. Figure 3.2 shows the energy profile along the reaction path for an exo-ergic reaction proceeding via a long-lived complex. This is for the general case and shows a barrier, \(E_0\), leading from reactants to the complex. A barrier may also exist between the complex and the products.

Crossed beam experiments\(^3\) on the reaction

\[
O(^3P_J) + Br_2 \rightarrow BrO + Br \quad \Delta H_{298}^0 = -41 \text{ kJ mole}^{-1} \quad (3.2)
\]

\[
k_2 = (1.4 \pm 0.2) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \text{ at } 298 \text{ K} \quad (4)
\]

have shown that it proceeds via a persistent collision complex, with a large reaction cross-section and no activation energy. The velocity distribution of the product BrO was measured at various scattering angles and the properties of the distribution were characteristic of a persistent complex (i.e. forward-backward symmetry). The known stable molecule, \(\text{Br}_2\text{O}\), seemed the obvious choice for the complex but this is unlikely since it does not correlate with the reactants. \(\text{Br}_2\text{O}\) has a symmetric bent structure and in analogy to molecules of the form \(\text{AE}_2\) should have a singlet ground state.\(^5\) From the selection rules\(^6\) determining the multiplicity of the complex arising from the reactants a triplet intermediate is required,

\[
\text{Singlet} + \text{Triplet} \rightarrow \text{Triplet} \rightarrow \text{Doublet} + \text{Doublet} \quad (3.3)
\]

An asymmetric \(\text{O-Br-Br}\) structure has therefore been suggested for
the complex and this may well have a triplet ground state. This structure is also consistent with the electronegativity ordering rule which predicts that the preferred geometry of an XYZ complex has the least electronegative atom in the middle. An examination of the electronegativity values for O and Br clearly shows that Br should be central for the most stable configuration of the complex.

If the symmetric Br₂O was involved as the intermediate complex then a transition from the initial triplet surface would be required.

Having examined the O + Br₂ reaction it is now possible to consider the S(3P) + Br₂ reaction. By analogy with the O + Br₂ system it may proceed via a complex with the structure S-Br-Br which is expected to have a triplet ground state however this configuration is expected to be less stable than the alternative complex Br-S-Br according to the electronegativity rules. If this latter structure is the intermediate then a triplet-singlet transition would be required on the potential surface as the ground state is expected to be singlet. Molecular beam experiments involving S atoms and Br₂ would be required to determine the form of the potential.

The value obtained for k₁ for Br₂ in this study is less than that obtained by Clyne and Townsend, i.e. $k_1 = (9.5 \pm 1.7) \times 10^{-11}$ cm³molecule⁻¹s⁻¹. In their determination however they experienced difficulty due to significant removal of Br₂ by the impurity species O(3P) and SO(X2Σ⁻) from the dissociation of SO₂ (their S(3P) source). Also it was possible that S(3P) was being removed by BrO formed in the reaction of O(3P) with Br₂. So Clyne et al
had three fast reactions competing with the $S(^3P_J) + Br_2$ reaction

\[ O(^3P_J) + BrO \rightarrow Br + O_2 \quad (3.4) \]

\[ k_4 = (5.0 \pm 2.5) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \]

\[ S(^3P_J) + BrO \rightarrow SO + Br \quad (3.5) \]

\[ k_5 < 5.0 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \]

and reaction (3.2).

The determination of $k_1$ therefore had to be carried out by computer modelling, with these competing reactions being taken into consideration. It is believed that the absolute value measured by atomic absorption spectroscopy is likely to be more accurate since no competing reactions are present.

Applying collision theory to the reaction, the gas kinetic collision frequency is

\[ Z_{AB} = \frac{2n_A n_B (\delta_A + \delta_B)^2}{\sqrt{\pi}} \left( \frac{\Sigma \sigma_T (M_A + M_B)}{M_A M_B} \right)^{3/2} \quad (3.6) \]

where $n_A$ and $n_B$ are the number of molecules per unit volume of A and B,

$M_A$ and $M_B$ are the molecular weights,

$\delta_A$ and $\delta_B$ are the collision diameters,

$(\delta_S = 0.208 \text{ nm and } \delta_{Br_2} = 0.36 \text{ nm}).$

At 296 K for $S(^3P_J) + Br_2$, $Z_{AB} \sim 3 \times 10^{-10} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}.$

So this gave a collision efficiency of 0.25 (c.f. Clyne et al value of 0.3) where collision efficiency = $k / Z_{AB}$. A high efficiency for a simple reaction such as this suggests that $k_1$ is very nearly independent of temperature for Br$_2$.

The mechanism of the $S(^3P_J) + Cl_2$ reaction should be similar to that for $S(^3P_J) + Br_2$

\[ S(^3P_J) + Cl_2 \rightarrow SCl + Cl \quad \Delta H_{298}^0 \leq 0 \text{ kJmole}^{-1} \quad (3.7) \]
The analogous $O(3P_j)$ reaction:\(^4\)

$$O(3P_j) + Cl_2 \rightarrow ClO + Cl \quad (3.8)$$

$$k_8 = (4.8 \pm 0.5) \times 10^{-14} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

has been studied using a neon seeded $O$ atom beam\(^9\) and was shown to proceed via a short-lived collision complex (i.e. predominantly forward scattering of the ClO product). In matrix isolation studies\(^10\) the molecule $O$-Cl-Cl has been found and has a bent configuration with a weak Cl-Cl bond.

Both the $Cl(2P_{3/2})$ and $Cl(2P_{1/2})$ states are known to be formed in reaction (3.8). However rapid spin orbit relaxation by collision occurs producing equilibrium concentrations. The equilibrium concentration of $Cl(2P_{3/2})$ is given by

$$\left[\frac{Cl(2P_{3/2})}{Cl(2P_{1/2})}\right]_{eq} = \exp \left[\frac{-10.5 \text{ kJ/mole}}{RT}\right] \quad (3.9)$$

At 300 K the equilibrium concentration of $Cl(2P_{3/2})$ is 0.8% that of $Cl(2P_{1/2})$.

Niki and Weinstock\(^11\) found that in $Cl_2$-rich systems the overall rate constant for (3.8) and the secondary reaction

$$O(3P) + ClO \rightarrow O_2 + Cl \quad (3.10)$$

is twice that for systems containing less $Cl_2$ indicating that reaction (3.10) is faster than (3.8) with an estimate of $k_{10} > 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

Nearly all of the $O_2$ produced in (3.10) is vibrationally excited\(^12\) and accounts for over 50% of the heat of formation. This supports the generalization of McGrath and Norrish\(^13\) that in exothermic reactions of this type most of the energy could be accumulated in the newly formed bond.

From these findings on the $O(3P)$ reaction with $Cl_2$ it is
possible to draw some conclusions concerning the \( S(3P) \) reaction. Figure 3.3 shows a correlation diagram for the \( S(3P) + Cl_2 \) reaction.

Clyne et al.\(^1\) obtained a rate constant for \( 3.7 \) of about half that obtained in this study i.e. \( k_7 = (1.1 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 298 K. In this case they had no problems with impurity species as they react very slowly with \( Cl_2 \). An Arrhenius expression for \( 3.7 \) was also obtained by Clyne et al., with a pre-exponential factor \( A = (2.8 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and an activation energy of \( (2.4 \pm 0.5) \text{ kJ mole}^{-1} \). \( A \) is close to \( 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) which is the value predicted by 'Transition-State Theory'\(^{14} \) for a non-linear \( S-Cl-Cl \) complex. Ground state \( Cl(2P_1) \) atoms were also observed by monitoring their resonance fluorescence.

The rate constants for the reaction of \( S(3P_0) \) and \( S(3P_1) \) with \( Cl_2 \) show an insignificant difference indicating that the three spin orbit states are in equilibrium on the time scale of the experiment.

The reaction mechanism for \( S(3P) \) with \( I_2 \) is believed to be similar to that proposed for \( Br_2 \) and \( Cl_2 \),

\[
S(3P_j) + I_2 \rightarrow SI + I \quad (3.11)
\]

In the analogous reaction

\[
O(3P_j) + I_2 \rightarrow IO + I \quad (3.12)
\]

angular and velocity distribution measurements of IO reactive scattering\(^{15} \) suggested a long-lived triplet \( O-I-I \) complex which has a lifetime estimated from

\[
\tau = \nu^{-1} \left[ \frac{E_{\text{tot}}}{(E_{\text{tot}} - E_x)} \right]^3
\]

where \( E_x \) = \( X-X \) bond energy in the \( O-X-X \) complex, \( \nu^{-1} \) = vibrational period of the complex,
Figure 3.3 Correlation diagram for $S(^3P) + Cl_2$ reaction.

Figure 3.4 Potential surfaces for $S(^3P) + I_2$ reaction.
\[ E_{\text{tot}} = \text{total energy (trans. + vib., etc).} \]

For \( E_x \approx D_0(I_2) = 148 \text{ kJ mole}^{-1} \) and \( E_{\text{tot}} = 75 \text{ kJ mole}^{-1} \) then \( \gamma \approx 30 \) vibrational periods for O-I-I. The activation energy for (3.12) was about zero.

In figure 3.4 it is seen that the reactants \( O(3\text{P}) + I_2 \) approach on a triplet surface. The lowest potential energy surface however corresponds to a bound singlet bent symmetrical structure I-O-I. The diagram illustrates a crossing of a triplet surface with a singlet surface and this is the point where a triplet-singlet transition can occur. Exit from the complex to products involves a transition state and this is expected to have a tight linear configuration I...I-0 correlating with the geometry of the X-X-O type complex.

It is believed that the potential surfaces represented in figure 3.4 will be similar for \( S(3\text{P}_J) + I_2 \). Also by Walsh's electronegativity ordering rule an S-I-I configuration for the complex is possible since the electronegativity value of S is equal to that for I.

**Trends in Group Chemistry**

It is useful to look at the trends of reactivity within group VI. Table 3.2 shows the rate constants for reaction of ground state group VI atoms with halogens. In group VI the order of reactivity with halogen molecules is

\[ [S(3\text{P}_J)] > [O(3\text{P}_J)] \]

Also for \( S(3\text{P}_J) \) the order of reactivities is

and for $O(3^3P_J)$ it is

$$[Br_2] > [Cl_2] > [F_2]$$

Table 3.2 Rate constants for reactions of group VI ground state atoms with halogens.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\Delta H^0_{298}$ (kJ mole$^{-1}$)</th>
<th>$k$ (cm$^3$ mole$^{-1}$ s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2$</td>
<td>-61</td>
<td>$&lt;1.0 \times 10^{-14}$</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$&lt;3.3 \times 10^{-15}$</td>
<td>17</td>
</tr>
<tr>
<td>$Cl_2$</td>
<td>-27</td>
<td>$4.2 \times 10^{-14}$</td>
<td>4</td>
</tr>
<tr>
<td>$BrCl$</td>
<td>-16</td>
<td>$2.1 \times 10^{-11}$</td>
<td>4</td>
</tr>
<tr>
<td>$Br_2$</td>
<td>-41</td>
<td>$1.4 \times 10^{-11}$</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S(3$^3P_J$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2$</td>
</tr>
<tr>
<td>$Cl_2$</td>
</tr>
<tr>
<td>$Br_2$</td>
</tr>
<tr>
<td>$I_2$</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

There may also be a trend in the geometry of the complex in the $S(3^3P_J) +$ Halogen reaction. McDonald et al. believed that in the $H + X_2$ reaction the geometry of the complex changes according to the halogen. $H-Cl-Cl$ is roughly collinear, $H-Br-Br$ is moderately bent whereas $H-I-I$ is strongly bent. This trend is due to the
decrease in relative electronegativity of the central atom (Cl = 3.0, Br = 2.8, I = 2.5). It is possible that this may be occurring in the S-X-X complex. As the central atom changes from Cl to Br to I, the preferred geometry may indeed change from a slightly bent to a strongly bent configuration.

3.3 THE REACTIONS OF S(3P_J) + AROMATICS

This is the first work carried out on the rate of reaction of S(3P_J) with aromatics and is essentially confined to the simpler aromatic molecules, benzene, toluene, aniline, benzaldehyde and C_6F_6. However the rate and mechanism of reactions of these compounds with O(3P_J) have been extensively studied and provide an interesting comparison.

Experiments and Results

The rate constants for these reactions were measured using the technique of atomic absorption spectroscopy (see chapter 2). The aromatics were diluted with nitrogen and allowed to mix by diffusion for at least two hours. The monochromator was set on the 182.63 nm line. Figure 3.5 shows a plot of first order rate coefficients versus partial pressure of the aromatic. The η-factor was 0.67 ± 0.09. Table 3.3 shows the results obtained at 295 K. C_6F_6 strongly absorbed the atomic resonance line and determination of the rate constant therefore proved to be difficult. The value obtained should therefore be considered as approximate.

Discussion

Each reaction has been considered in the subsections in the following pages.
Figure 3.5 Plots of first order rate coefficients against partial pressure of aromatics.

Figure 3.6 Correlation diagram for the $S(3P) + C_6H_6$ reaction.
Table 3.3  Second order rate constants for the $S(3\text{P}_J) + \text{Aromatics}$ reactions.

<table>
<thead>
<tr>
<th>Aromatic</th>
<th>Partial Pressures (Nm$^{-2}$)</th>
<th>Partial Gradient (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Rate Constant</th>
<th>Flash Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_6$</td>
<td>0.226 - 1.303</td>
<td>$(2.2 \pm 0.2)$ x $10^{-12}$</td>
<td>$(3.3 \pm 0.3)$ x $10^{-12}$</td>
<td>320</td>
</tr>
<tr>
<td>$C_6H_5CH_3$</td>
<td>0.133 - 0.505</td>
<td>$(6.6 \pm 0.2)$ x $10^{-12}$</td>
<td>$(9.9 \pm 0.5)$ x $10^{-12}$</td>
<td>320</td>
</tr>
<tr>
<td>$C_6F_6$</td>
<td>1.796 - 14.018</td>
<td>$(0.9 \pm 0.1)$ x $10^{-13}$</td>
<td>$(1.3 \pm 0.3)$ x $10^{-13}$</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(0.9 \pm 0.1)$ x $10^{-13}$</td>
<td>$(1.3 \pm 0.3)$ x $10^{-13}$</td>
<td>180</td>
</tr>
<tr>
<td>$C_6H_5NH_2$</td>
<td>0.443 - 1.109</td>
<td>$(5.5 \pm 0.3)$ x $10^{-12}$</td>
<td>$(8.2 \pm 0.8)$ x $10^{-12}$</td>
<td>320</td>
</tr>
<tr>
<td>$C_6H_5CHO$</td>
<td>0.028 - 0.180</td>
<td>$(2.8 \pm 0.2)$ x $10^{-11}$</td>
<td>$(3.4 \pm 0.4)$ x $10^{-11}$</td>
<td>320</td>
</tr>
</tbody>
</table>
The addition of \( O(3P) \) and \( S(3P) \) atoms to \( \text{C} = \text{C} \) bonds has been widely studied. While in \( O(3P) \) studies this has included olefins and aromatics,\(^{19}\) for \( S(3P) \) work this has been confined to olefins.\(^{20}\) In an attempt to speculate on the \( S(3P) + \text{C}_6\text{H}_6 \) mechanism this study has drawn from the analogous \( O(3P) + \text{C}_6\text{H}_6 \) reaction. Two modes of attack of \( O(3P) \) on \( \text{C}_6\text{H}_6 \) have been considered:\(^{21}\)

1. Abstraction of an \( \text{H} \) atom which leads to a hydroxyl and a phenyl radical. This however is thought to be unfavourable.

2. Addition of the \( O(3P) \) atom to the aromatic nucleus to produce a biradical, followed by rearrangement to form phenolic products or ring cleavage to form highly reactive conjugated oxygenates which readily undergo further reactions to form polymers. Carbon monoxide was also detected as a product. The following mechanism has been suggested,

\[
\begin{align*}
\text{H} \quad &\quad (3.14) \\
\text{CHO} \quad &\quad \text{polymers} \\
\end{align*}
\]

\[ k_{14} = 1.5 - 5.98 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.} \] \(^{22}\)

The \( O(3P) \) atoms behave as distinctly electrophilic reagents in their reaction with aromatics and the electrophilic characteristics have been well studied.\(^ {23}\)

A crossed molecular beam study of the \( O(3P) + \text{C}_6\text{H}_6 \) reaction\(^ {24}\) monitored the reaction products with a mass spectrometer and
detected a polymeric hydrocarbon (probably based on HCC=CH=CHCH₂) with CO, and C₆H₆O (probably phenol). The polymer and CO were formed in their ground state and are believed to be the products of the decomposition of a vibrationally excited phenol adduct. However the ground state of a phenol intermediate is a singlet and this does not correlate with the reactants (i.e. triplet + singlet). According to spin conservation rules these should give a triplet intermediate, so it is likely that a triplet-singlet transition occurs sometime during the course of the reaction. This can be explained by curve crossing and is determined by the lifetime of the reaction complex and the accessibility of the crossing region. So the transition has been considered to be between the lowest triplet state and the ground state of phenol.

Assuming that the above mechanism may well apply to the S(3P) + C₆H₆ reaction, a semi-quantitative electronic state correlation diagram was constructed (see figure 3.6). The electrophilic S(3P) adds to the double bond of the benzene ring and an addition complex is formed which becomes partially stabilized as a compound analogous to phenol, or ring cleavage may occur leading to polymer formation.

\[ \Delta H^\circ = -248.3 \text{ kJ mole}^{-1} \]  

After the formation of the thiol the reaction pathway is uncertain and product analysis would be required. C₅H₆ and CS may be formed as indicated in figure 3.6, however any CS formed will take part in further reactions.
It is expected that the \( S(3P) + C_6H_5CH_3 \) reaction will follow a reaction path similar to that for \( C_6H_6 \).

The \( O(3P) + C_6H_5CH_3 \) reaction has been studied in depth and it is necessary to draw conclusions concerning the \( S(3P) \) reaction from this.

Gaffrey et al. thoroughly studied the \( O(3P) \) with toluene reaction and using gas chromatography identified the reaction products as phenol, o-cresol, m-cresol, p-cresol, CO and tar. In addition small amounts of \( CH_4 \) and \( C_2H_6 \) were found. The latter two products suggest the presence of \( CH_3 \) radicals which can abstract a \( H \) atom to form \( CH_4 \) or recombine to form \( C_2H_6 \). The major initial reaction is addition of an electrophilic \( O(3P) \) atom to the aromatic ring, predominantly at the ortho position, followed by isomerization of the phenol compounds. Ring cleavage or contraction may occur to form a number of highly reactive compounds that can form polymers. Since phenol is also a major product of the reaction, it is expected that it is formed by addition of the \( O(3P) \) to the 1 position followed by an intermolecular methyl migration and then \( H \) atom abstraction by the phenoxy radical.

\[
O(3P_J) + \text{toluene} \rightarrow \text{products} \quad (3.16)
\]

\[
O(3P_J) + \begin{array}{c}
\text{O} \\
\text{OH}
\end{array} + \begin{array}{c}
CH_3 \\
\text{from toluene}
\end{array} \rightarrow \begin{array}{c}
\text{O} \\
\text{OH}
\end{array} + \begin{array}{c}
\text{CH}_4
\end{array}
\]
The rate constants measured for the $O(^3P) + \text{toluene}$ reaction were in the range $k_{\text{toluene}} = 5.68 - 23.2 \times 10^{-14} \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, at room temperature. The $O(^3P)$ reaction is much slower than the $S(^3P)$ reaction.

So the reaction mechanism possible for the $S(^3P)$ reaction is

$$S(^3P) + \text{toluene} \rightarrow \begin{array}{c}
\text{POLYMERS} \\
\text{(thiol)}
\end{array}$$

The electrophilic $S(^3P)$ atom adds to the ring primarily at the ortho position, although other sites of addition are possible but account for minor products. This is followed by isomerization of the thiolic intermediate. Ring cleavage or contraction may occur to form a variety of olefinic species. The thiols are well known compounds and have been extensively studied. In thiols the S-H(C-S) bond energy is less than that of the corresponding O-H(C-O) bond so free-radical H atom abstraction from S-H is much easier than in O-H. A product analysis study however would be required to determine if the proposed mechanism is correct.

$$S(^3P) + C_6\text{F}_6$$

It has been shown that with fluorobenzene the $O(^3P)$ atom can add to the position of the F group with subsequent migration of the F atom. However this minor reaction has been found to be very slow in comparison to addition to the other sites of the benzene ring.

The mechanism suggested for the $S(^3P) + C_6\text{F}_6$ reaction is therefore
As expected the rate constant measured has shown this to be a slow reaction in comparison to that for benzene and toluene.

**Trends of Reactivity in S(^3P) + Aromatic Reactions**

The $S(^3P) + \text{toluene}$ reaction has been observed to be faster than that for benzene and it therefore would be of interest to determine the rate constants for $S(^3P)$ reactions with other substituted benzenes and their isomers.

This study has already been carried out for $O(^3P)$ and shows some interesting results that may help to predict the outcome of a similar $S(^3P)$ study. Grovenstein et al. studied the reactions of $O(^3P)$ with thirteen aromatic compounds and found that in most cases phenolic products accounted for 95% of the volatile products and also varying amounts of tar was formed. However one important feature of their work was the calculation of partial rate factors relative to benzene (i.e. calculated from relative reactivities and product distribution determined by vapour phase chromatography) for the formation of phenols from the various aromatics. Table 3.4 shows the molecules and the partial rate factors associated with the possible sites of $O(^3P)$ addition. Addition to benzene has been given the value 1.00 and the other values determine the reactivity of the different sites in the other molecules relative to this value. Some conclusions can be drawn from this table:

(a) the ortho positions are more reactive than the para,

(b) increasing the number of methyl groups on the benzene ring renders some sites of addition more desirable to the $O$ atom.
Table 3.4  Partial rate factors for formation of phenols with O(3Pγ), temperature 303 K.
(The chemical symbols were constructed using a computer program).
The electron donating character of the C=C bond is enhanced by increased methyl substitution and this enhancement thus makes the bond more susceptible to attack by the electrophilic O(3P). So steric hinderance has no role to play in these reactions. O(3P) is evidently a reagent of low steric requirements. However this may not be the case for the more massive sulphur atom.

These trends were also shown in a further study\(^{19}\) of the reactions of O(3P) with methylated aromatics. Table 3.5 shows the relative overall rate constants for these and also the S(3P) reactions studied.

Table 3.5 Relative rate constants for reactions of aromatics with O(3P) and S(3P).

<table>
<thead>
<tr>
<th>Aromatic Molecule</th>
<th>Relative rate constant O(3P)(^{19})</th>
<th>S(3P) This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Toluene</td>
<td>3.1 ± 0.6</td>
<td>3.00</td>
</tr>
<tr>
<td>1,2 - Dimethylbenzene</td>
<td>7.3 ± 1.2</td>
<td></td>
</tr>
<tr>
<td>1,3 - Dimethylbenzene</td>
<td>14.7 ± 2.5</td>
<td></td>
</tr>
<tr>
<td>1,4 - Dimethylbenzene</td>
<td>7.6 ± 1.3</td>
<td></td>
</tr>
<tr>
<td>1,2,3 - Trimethylbenzene</td>
<td>48 ± 8</td>
<td>available</td>
</tr>
<tr>
<td>1,2,4 - Trimethylbenzene</td>
<td>42 ± 7</td>
<td></td>
</tr>
<tr>
<td>1,3,5 - Trimethylbenzene</td>
<td>117 ± 22</td>
<td></td>
</tr>
</tbody>
</table>

It is believed that the analogous S(3P) reactions will show the same trends since the benzene and toluene reactions seem to suggest this. However further work is required to confirm this.
To understand the mechanism of this reaction it is useful to examine similar reactions. The rate constant for the $O(^3P) +$ aniline reaction has been determined as
\[ k_{\text{aniline}} = 2.4 \times 10^{-13} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \] at room temperature. This is more than an order of magnitude slower than the $S(^3P)$ reaction.

Atkinson and Pitts have suggested the likely reaction pathway for $O(^3P)$ with the amines $\text{CH}_3\text{NH}_2$ and $\text{C}_2\text{H}_5\text{NH}_2$. These are
1. H atom abstraction from the C-H bonds.
2. H atom abstraction from the N-H bond and this is considered to be a minor reaction.
3. Formation of an addition adduct which can undergo collisional stabilization or decomposition. The latter has the following mechanism

\[
O(^3P) + \text{CH}_3\text{NH}_2 \longrightarrow [\text{CH}_3\text{NH}_2O]^* \longrightarrow [\text{CH}_3\text{NHOH}]^* \quad (3.19)
\]
\[
[\text{CH}_3\text{NHOH}]^* + \text{M} \longrightarrow \text{CH}_3\text{NHOH} + \text{M} \quad (3.20)
\]
\[
[\text{CH}_3\text{NHOH}]^* \longrightarrow \text{fragmentation products} \quad (3.21)
\]

So with this background some pathways can be suggested for the $S(^3P) +$ aniline reaction.

**Scheme I**

This is a reaction pathway similar to that for toluene, in which the amine group has enhanced the nucleophilic character of the C=C bond, making it more susceptible to attack by the electrophilic $S(^3P)$, particularly at the ortho position.

**Scheme II**

\[
S(^3P) + \quad \text{NH}_2 \quad \longrightarrow \quad \text{SH} + \quad \text{NH} \quad (3.22)
\]
Abstraction of a H atom by the sulphur atom after which further reaction is possible.

In the similar OH + aniline reaction

\[ \text{C}_6\text{H}_5\text{NH}_2 + \text{OH} \rightarrow \text{C}_6\text{H}_5\text{NH} + \text{H}_2\text{O} \] (3.23)

the resulting radical has an N-H linkage. However this radical undergoes resonance stabilization,

\[ \text{NH} \rightarrow \text{NH} \] (3.24)

so that the radical is stabilized towards further H atom abstraction.

**Scheme III**

\[
\begin{align*}
\text{S}^{(3P_j)} &+ \text{NH}_2 &\rightarrow &\left[ \text{NH}_2\text{S} \right]^* &\rightarrow &\left[ \text{NHSH} \right]^* \\
\text{NHSH} &+ M &\rightarrow &\text{NHSH} &+ M &\quad (M = \text{N}_2, \text{etc})
\end{align*}
\] (3.25, 3.26)

This reaction proceeds via an addition adduct which rapidly isomerizes to a more stable form that can subsequently be collisionally stabilized or decompose.

It is necessary to have a study of the products of reaction to determine the importance of each of these schemes.

\[
\text{S}^{(3P_j)} + \text{C}_6\text{H}_5\text{CHO}
\]

It is useful to study the reactions of aldehydes as they are important species in atmospheric pollution and combustion chemistry.
The rate constant for the $O(3P) + C_6H_5CHO$ reaction has been determined at room temperature as

$$k_{\text{benzaldehyde}} = 4.8 \times 10^{-13} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1},$$

and is $\sim 2$ orders of magnitude slower than the $S(3P)$ reaction.

The reaction of $O(3P)$ + formaldehyde has been studied using a flow system attached to a mass spectrometer and the products detected were $CO_2$, $H_2$, $H_2O$ and $CO$. The rate constant was determined as $1.5 \times 10^{-13} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at 300 K, and the following primary step was postulated

$$O(3P_J) + CH_2O \rightarrow OH + CHO$$

i.e. abstraction of an H atom by the $O(3P)$.  

The reaction of another aldehyde, acetaldehyde, with $O(3P_J)$ has also been examined and the main products were $(CH_3CO)_2$, $H_2O$ and $CH_3COCH_3$. The major step was considered to be

$$O(3P_J) + CH_3CHO \rightarrow CH_3CO + OH$$

The aldehyde of interest in this study, benzaldehyde has been considered as a free radical scavenger because of its easily extractable H atom. For example consider the reaction of OH and benzaldehyde,

$$\cdot OH + C_6H_5CHO \rightarrow H_2O + C_6H_5CO.$$  

This occurs by a simple abstraction of the H atom from the aldehydic group.

So all the evidence from the O chemistry suggests that the analogous S reaction proceeds by a simple primary step of H atom abstraction

$$S(3P_J) + \rightarrow \text{SH}$$
These radicals can take part in further reactions. So possible secondary reactions are

\[
\begin{align*}
C_6H_5CO & + SH \rightarrow C_6H_5CO + H_2S \\
C_6H_5CO & + C_6H_5CO \rightarrow C_6H_5CO.COC_6H_5
\end{align*}
\] (3.32) (3.33)

Only a study of the products by analysis will confirm if this proposed mechanism is correct.

3.4 THE REACTIONS OF $S(^3P_J) +$ NITROGEN OXIDES

Using the technique of atomic absorption spectrophotometry (described in chapter 2), the reaction rate constants for $S(^3P_J)$ with nitrogen dioxide and nitrous oxide were determined. It is useful to examine these reactions as nitrogen oxides and sulphur containing compounds are important species in the atmosphere.

Experiments and Results

The NO$_2$ was prepared as described in Appendix I. NO$_2$ was diluted with nitrogen before use; this being carried out in a mixer. The resulting mixture was transferred to a storage bulb and used immediately. With the monochromator set at 182.63 nm and a temperature of 295 K the results obtained are shown in table 3.6 and figure 3.7. The $\gamma$-factor = 0.67 ± 0.09. An 80 J flash energy was used to keep photolysis of NO$_2$ to a minimum.
Figure 3.7 Plot of first order rate coefficients against NO$_2$ pressure.

Reaction of S($^3$P) + NO$_2$

\[ k = (3.76 \pm 0.22) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \]

Temp. = 295 K  Flash Energy = 80 J
Total Pressure = 1.33 kNm$^{-2}$
OCS Press. = 22 Nm$^{-1}$
N$_2$ Diluent
Table 3.6 Second order rate constants for the $S(^3P_J) +$ Nitrogen Oxide reactions.

<table>
<thead>
<tr>
<th>Nitrogen Oxide</th>
<th>Partial Pressures (Nm$^{-2}$)</th>
<th>Gradient Rate Constant (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Flash Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>0.058 - 0.134</td>
<td>(2.5 ± 0.1) x 10$^{-11}$</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3.8 ± 0.6) x 10$^{-11}$</td>
<td></td>
</tr>
<tr>
<td>N$_2$O</td>
<td>22.6 - 1103.9</td>
<td>-</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;1 x 10$^{-16}$</td>
<td></td>
</tr>
</tbody>
</table>

The N$_2$O rate constant is an approximate since additions of these pressures of N$_2$O appeared to make no difference to the rate of decay of the $S(^3P)$ atoms.

Discussion

The primary reaction in the $S(^3P_J)$ with NO$_2$ system is

$$ S(^3P_J) + NO_2 \rightarrow SO + NO \ \Delta H_{298}^0 = -215 \text{kJmole}^{-1} $$ (3.34)

Clyne and Townsend$^1$ using an atomic resonance fluorescence - discharge flow system determined $k_{34}$ as

$$ k_{34} = (6.24 \pm 1.37) \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} $$

at room temperature and this is ~1.6 times faster than that measured in this study. However the presence of appreciable concentrations of impurity species ($[^3P_J] < 1.7 \times 10^{13}$ atoms cm$^{-3}$ and $[^3S] < 9.0 \times 10^{11}$ molecules cm$^{-3}$) meant that competing reactions were occuring in their system

$$ O(^3P_J) + NO_2 \rightarrow NO + O \ \Delta H_{298}^0 = -192 \text{kJmole}^{-1} $$ (3.35)

$$ k_{35} = 0.93 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} $$ 35
So their value for $k_{34}$ was determined using computer modelling, taking these competing reactions into consideration. Clyne et al.\textsuperscript{37} also determined the Arrhenius expression for reaction (3.34) within the 296 - 410 K temperature range

$$k_{34} = (4.9 \pm 1.0) \times 10^{-11} \exp\left(\frac{84 \pm 60}{T}\right) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

and concluded that the reaction was virtually independent of temperature within this range. The value of the rate constant at 298 K, i.e. $k_{34} = 6.5 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$, agreed well with their previous result.

Although it is believed that a direct measurement of $k_{34}$ is likely to be more accurate than that arising from a system containing impurity species and competing reactions it is essential to look for any source of error in the evaluation using the absorption spectrophotometry technique. The dimerization equilibrium

$$N_2O_4 \rightleftharpoons 2\text{NO}_2 \quad (3.37)$$

and the 3-body recombination

$$\text{NO}_2 + \text{NO}_2 + \text{M} \rightleftharpoons N_2O_4 + \text{M} \quad (M = N_2) \quad (3.38)$$

should be considered as they may effect the NO\textsubscript{2} concentration. Bemand et al.\textsuperscript{35} using a value $K_{eq} = 41.18$ atm at 300 K determined the factor by which the NO\textsubscript{2} concentration should be corrected to account for the presence of N\textsubscript{2}O\textsubscript{4}. This factor varied between 1.05 and 1.15. Applying this factor to the concentrations of NO\textsubscript{2} used in this study made very little difference to the rate constant (i.e. the value is within the experimental error given).

It is useful to consider reaction (3.35) as this may give
further information concerning the $S(3^3P)$ reaction. Measurements of the rate constants for $k_{35}$ within the temperature range $298 - 1055$ K indicated a small negative temperature dependence of the form $k_{35} \propto T^{-0.5}$. From the general principles of Transition State Theory this reaction is predicted to proceed via a non-linear complex. Basco and Norrish$^{40}$ have shown that the ground state $O_2$ molecule formed can have up to 11 quanta of vibrational energy, the energy of the 11th vibrational level being equal to the exothermicity of the reaction.

A model proposed by Simons$^{41}$ accounts for the ready production of $O_2^*$ in the $O + NO_2$ reaction. In this model

$$A + BCD \rightarrow AB^* + CD$$

$^{(3.39)}$

he visualized that atom A approaches B with such a velocity that when A comes to rest, the internuclear distance of A-B is very short compared with the equilibrium distance, so that on separation the molecule AB is vibrationally 'hot'. However some conditions must be adhered to in order for the model to be viable:-

1. the B-C bond is weak relative to A-B so that dissociation of the ABCD complex occurs easily,
2. little of the impact of A and B is transmitted to the C-D bond,
3. there must be an attractive force between A and B to overcome the normal repulsion of non-interacting particles.

Applying this model to the $S(3^3P) + NO_2$ system it is believed that most of the exothermicity will be channeled into vibrational excitation of the newly formed SO molecule. To determine the extent of vibrational excitation, the energy of a number of vibrational levels was calculated using a simple computer program, VIB1 (see Appendix II). The program utilizes the expression for allowed vibrational levels for an anharmonic oscillator.$^{42}$
Table 3.7 shows some results from the program.

Table 3.7  Vibrational energy of SO.

<table>
<thead>
<tr>
<th>Vibrational quantum number</th>
<th>Energy above ( v = 0 )</th>
<th>% of Exothermicity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm(^{-1})</td>
<td>kJmole(^{-1})</td>
</tr>
<tr>
<td>( v = 18 )</td>
<td>18140</td>
<td>217.3</td>
</tr>
<tr>
<td>17</td>
<td>17236</td>
<td>206.4</td>
</tr>
<tr>
<td>16</td>
<td>15391</td>
<td>195.5</td>
</tr>
<tr>
<td>13</td>
<td>13498</td>
<td>161.6</td>
</tr>
</tbody>
</table>

\[ \text{SO}(X^3\Sigma^-) \quad \omega_e = 1123.7 \text{ cm}^{-1} \quad \omega_{e\nu} = 6.116 \text{ cm}^{-1} \]

As can be seen from the table, SO can be excited up to \( v = 18 \) if all of the heat of formation goes into vibrational excitation. The SO formed can take place in further reaction and it has been observed that the reactivity of a species is enhanced when vibrationally excited.

\[ \text{S}(^3P_{\text{J}}) + \text{N}_2\text{O} \]

Two bimolecular reactions have been considered for the \( \text{S}(^3P) + \text{N}_2\text{O} \) system,

\[ \text{S}(^3P_{\text{J}}) + \text{N}_2\text{O} \rightarrow \text{SO} + \text{N}_2 \quad \Delta H_{298}^\circ = -354.6 \text{ kJmole}^{-1} \quad (3.40) \]

\[ \text{S}(^3P_{\text{J}}) + \text{N}_2\text{O} \rightarrow \text{SN} + \text{NO} \quad \Delta H_{298}^\circ = -17.6 \text{ kJmole}^{-1} \quad (3.41) \]

Both of these reactions are thermodynamically favourable but since a very slow rate constant was obtained then a high activation energy may be required for their occurrence.

However some other mechanism may be involved and some clues
can be obtained from a study of the $S(^3P) + NO$ reaction.\textsuperscript{45} $S(^3P)$ atoms resulting from the photolysis of OCS in CO\textsubscript{2} were monitored by kinetic absorption spectroscopy at 180.7 nm; spectra were recorded on film. A bimolecular rate constant for the total pressure range, 6.7 - 80.0 kNm\textsuperscript{-2} was obtained with a high pressure limit of $(1.5 \pm 0.4) \times 10^{-11}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}. Below 1.3 kNm\textsuperscript{-2} total pressure a termolecular rate constant of $5 \times 10^{-31}$ cm\textsuperscript{6} molecule\textsuperscript{-2} s\textsuperscript{-1} was obtained. This suggested a mechanism with the primary step being a termolecular combination,

$$S + NO + CO_2 \rightarrow SNO + CO_2$$ (3.42)

This was interpreted in terms of an energy transfer (ET) mechanism

$$S + NO \rightarrow SNO^*$$ (3.43)

$$SNO^* + M \rightarrow SNO + M \quad (M = CO_2)$$ (3.44)

Formation of the stable SNO molecule by the combination of S and NO requires collision of these mutually approaching species with a third body (CO\textsubscript{2}).\textsuperscript{46} The CO\textsubscript{2} absorbs the excess energy of the molecule just formed thus enabling it to be stabilized. Transfer of excess energy from the excited molecule to the third body may depend on the structure of the latter, particularly the presence of resonating levels that can accept the excitation energy (vibrational or electronic).

Alternatively an atom-molecule complex mechanism (AMC) may be involved

$$S + M \rightarrow SM^* \quad (M = CO_2)$$ (3.45)

$$SM^* + NO \rightarrow SNO + M$$ (3.46)

The efficiency of a third body on its ability to form a complex reversibly with the S atom. The complex, having excess energy can now react with the NO to form SNO and the chemically unchanged
third body ($CO_2$).

The ET mechanism is believed to be consistent with the observation of a change to second order behaviour with increasing chaperon pressure. Also SNO has been identified by infra-red spectroscopy as a product of HNSO photolysis in an Ar matrix. The major secondary reactions are believed to be slow disproportionation of the SNO,

$$2\text{SNO} \rightarrow S_2(\tilde{X}^3\Sigma^-) + 2\text{NO} \quad (3.47)$$

$$\rightarrow S_2(a^1\Delta_g) + 2\text{NO} \quad (3.48)$$

Also the analogous $O(3P) + N_2O$ reaction

$$O + O + N_2O \rightarrow O_2 + N_2O \quad (3.49)$$

$$k_{49} = 3.9 \times 10^{-33} \text{ cm}^6\text{molecule}^{-1}\text{s}^{-1}, \quad 46$$

suggests that the reaction of $S(3P) + N_2O$ may well be a termolecular combination.

In terms of the ET mechanism this is

$$S(3P) + N_2O \leftrightarrow SN_2O^* \quad (3.50)$$

$$SN_2O + M \rightarrow SN_2O + M \quad (M = N_2) \quad (3.51)$$

An excited complex would be formed from the collision of $S$ and $N_2O$. The $N_2$ accepts the excess energy of this complex and stabilizes it. However it is not known whether a molecule such as $SN_2O$ exists.

Reactions such as these are generally of the order of $10^{-33}$ cm$^6$ molecule$^{-2}$s$^{-1}$ at room temperature and have low negative activation energies in the range $0 - 20.9$ kJ mole$^{-1}$. In the secondary reactions the hypothetical $SN_2O$ could disproportionate to $S_2$ and $N_2O$ and the $N_2O$ may well take place in polymerization reactions with the production of $S_3$ and $S_4$.

It is impossible at this stage to state conclusively what type of reaction is occurring however the termolecular reactions appears likely.
3.5 S(3P) + HALOCARBON REACTIONS

Reactions are presented here that may help fill some of the gaps in S(3P) chemistry, since the only reactions that have previously been studied in this area are S(3P) + CF₃I and CF₃I. The S(3P) + HCl reaction has also been included in this section.

Experiments and Results

The technique used was kinetic atomic absorption spectrophotometry. The halocarbons strongly absorbed the sulphur lamp emission so at the higher partial pressures the signals tended to have more superimposed noise. A critical evaluation of the errors in the rate coefficients was essential. The monochromator was set on the 182.63 nm line and \( \chi = 0.67 \pm 0.09 \). The temperature of the determination was 294 K and the results are shown in table 3.8. Figure 3.8 shows plots of the first order rate coefficients against reactant partial pressure for some halocarbons.

Discussion

The halocarbons will be discussed in groups of molecules of similar structure.

S(3P) + CH₃Br, CF₃Br and CF₂ClBr

These reactions are believed to proceed by Br atom abstraction,

\[
\begin{align*}
S(3P) + CH₃Br & \rightarrow CH₃ + SBr \\
S(3P) + CF₃Br & \rightarrow CF₃ + SBr \\
S(3P) + CF₂ClBr & \rightarrow CF₂Cl + SBr
\end{align*}
\]

Support for this mechanism arises from the similar reaction,
Table 3.8  Second order rate constants for $S(^3P_J) +$ Halocarbons reactions (and HCl reaction).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Partial Pressure (Nm$^{-2}$)</th>
<th>Gradient (cm$^3$molecule$^{-1}$s$^{-1}$)</th>
<th>Rate Constant</th>
<th>Flash Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$Br</td>
<td>2.500 - 56.219</td>
<td>(7.4 ± 0.3) x 10$^{-14}$ (6.8 ± 0.4) x 10$^{-14}$</td>
<td>(1.1 ± 0.2) x 10$^{-13}$ (1.0 ± 0.3) x 10$^{-13}$</td>
<td>320 180</td>
</tr>
<tr>
<td>CF$_2$ClBr</td>
<td>2.633 - 26.733</td>
<td>(1.2 ± 0.1) x 10$^{-13}$ (1.1 ± 0.1) x 10$^{-13}$</td>
<td>(1.7 ± 0.2) x 10$^{-13}$ (1.7 ± 0.2) x 10$^{-13}$</td>
<td>320 180</td>
</tr>
<tr>
<td>CFCl$_3$</td>
<td>1.828 - 10.823</td>
<td>(1.2 ± 0.1) x 10$^{-13}$ (1.2 ± 0.2) x 10$^{-13}$</td>
<td>(1.8 ± 0.2) x 10$^{-13}$ (1.8 ± 0.3) x 10$^{-13}$</td>
<td>320 180</td>
</tr>
<tr>
<td>CF$_2$Cl$_2$</td>
<td>11.348 - 44.382</td>
<td>(3.1 ± 0.5) x 10$^{-14}$</td>
<td>(4.7 ± 0.7) x 10$^{-14}$</td>
<td>320</td>
</tr>
<tr>
<td>CF$_3$Cl</td>
<td>100.0 - 516.0</td>
<td>(1.8 ± 0.2) x 10$^{-15}$</td>
<td>&lt;(2.3 ± 0.5) x 10$^{-15}$</td>
<td>320</td>
</tr>
<tr>
<td>CH$_3$Br</td>
<td>5.546 - 16.386</td>
<td>(2.4 ± 0.2) x 10$^{-13}$ (2.4 ± 0.3) x 10$^{-13}$</td>
<td>(3.5 ± 0.5) x 10$^{-13}$ (3.6 ± 0.5) x 10$^{-13}$</td>
<td>320 180</td>
</tr>
<tr>
<td>HCl</td>
<td>45.22 - 248.44</td>
<td>(3.2 ± 0.3) x 10$^{-15}$</td>
<td>&lt;(4.8 ± 0.5) x 10$^{-15}$</td>
<td>320</td>
</tr>
</tbody>
</table>
\[ O(3P_J) + CF_3I \rightarrow CF_3 + IO \]  
\[ k_{55} = (1.1 \pm 0.3) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \text{ at 300 K.}^{49} \]

Molecular beam studies\(^50\) on reaction (3.55) showed that it proceeded by I atom abstraction. Backward reactive scattering of the product IO was observed at low translational energy of a neon seeded O atom beam which suggests the existence of a collision complex of the form OICF\(_3\). At higher translational energies with a helium seeded O atom beam the angular distribution of the IO was almost isotropic. So at low collisional energy the lifetime of the complex is shorter than its rotational period, whereas at higher collision energies a compressed configuration of the complex is obtained which rapidly springs apart to give the products. This latter effect is known as 'induced repulsive energy release' and also results in a reduction of the rotational period and lifetime of the OICF\(_3\) complex. Addison et al\(^49\) have suggested that the reaction may involve a triplet-singlet surface crossing on the potential surfaces associated with \(O(3P_J)\) and \(O(1D_2)\) and the iodide.

Also the rate constants for \(O(3P_J)\) with CF\(_3\)Br\(^51\) have been measured in the temperature range 800 - 1200 K giving an Arrhenius plot with \(A = (1.5 \pm 0.5) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\) and an activation energy of 56 kJmole\(^{-1}\). Extrapolation of the Arrhenius plot gave a rate constant at 298 K of \(k \approx 10^{-16} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\). This is considerably slower than the \(S(3P) + CF_3Br\) reaction. The primary reaction was considered to be abstraction of a Br atom

\[ O(3P_J) + CF_3Br \rightarrow CF_3 + BrO \]  
\[ (3.56) \]

Although the above mentioned mechanism seems to be likely, two alternative reaction pathways can be considered,
(a) \[ S(3P_J) + CH_3Br \rightarrow CH_3S + Br \] (3.57)

This involves production of Br atoms by a displacement reaction. However since it is 22.6 kJ/mole endothermic it is unlikely.

(b) \[ S(3P_J) + CH_3Br \rightarrow [CH_3SBr]^* \rightarrow CH_3 + SBr \] (3.58)

This reaction involves insertion of the S(3P) atom into the C-Br bond followed by decomposition of the vibrationally excited complex to form SBr. An analogous molecule, CH_3SCl, to this complex is known.\(^{52}\)

\[ S(3P_J) + CFCl_3, CF_2Cl_2 \text{ and } CF_3Cl \]

The reaction pathway postulated is believed to involve Cl atom abstraction,

\[ S(3P_J) + CFCl_3 \rightarrow CFCl_2 + SCl \] (3.59)
\[ S(3P_J) + CF_2Cl_2 \rightarrow CF_2Cl + SCl \] (3.60)
\[ S(3P_J) + CF_3Cl \rightarrow CF_3 + SCl \] (3.61)

Now considering the thermodynamics of these reactions. For these to be exothermic the following limiting values would be required for the heat of formation of SCl,

Reaction (3.59) \( \Delta H^0_{f \ 298 \ SCl} \leq 79.5 \text{ kJ/mole}^{-1} \)

(3.60) \( \leq 58.6 \) "

(3.61) \( \leq 46.0 \) "

Since a very slow rate constant was obtained for reaction (3.61) it is believed that this reaction does not occur or is extremely slow and is therefore probably endothermic. This suggests a value of heat of formation of SCl with limits

\[ 46 < \Delta H^0_{f \ 298 \ SCl} \leq 58.6 \text{ kJ/mole}^{-1} \]

This is in reasonable agreement with the value of \( \Delta H^0_{f \ 298 \ SCl} \) given.
by Okabe,\textsuperscript{53} i.e. 62.8 kJ\textit{mole}^{-1} and is in disagreement with Benson's estimated value\textsuperscript{52} of (152.8 \pm 8.4) kJ\textit{mole}^{-1}.

One obvious feature of reactions (3.59), (3.60) and (3.61) is the order of reactivity towards $S(3\, P_J)$

\[ \text{CFCl}_3 \rightarrow \text{CF}_2\text{Cl}_2 \rightarrow \text{CF}_3\text{Cl} \]

This suggests that the greater the number of Cl atoms on the C atom, the more easily is a Cl atom abstracted. This is rationalised in the C-Cl bond strengths for these molecules at 298 K given in table 3.9.

Table 3.9 C-Cl bond strengths of halomethanes.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>C-Cl bond strength\textsuperscript{54} (kJ\textit{mole}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl\textsubscript{4}</td>
<td>305.6</td>
</tr>
<tr>
<td>CFCl\textsubscript{3}</td>
<td>305.6 \pm 8.4</td>
</tr>
<tr>
<td>CF\textsubscript{2}Cl\textsubscript{2}</td>
<td>337.8 \pm 8.4</td>
</tr>
<tr>
<td>CF\textsubscript{3}Cl</td>
<td>360.4 \pm 3.3</td>
</tr>
</tbody>
</table>

If this trend is correct then the $S(3\, P_J)$ with CCl\textsubscript{4} reaction should be faster than reaction (3.59) since there are four Cl atoms on the C atom.

The analogous O($3\, P_J$) + CCl\textsubscript{4} reaction\textsuperscript{55} is known to occur with a rate constant of $(1.88 \pm 0.1) \times 10^{-17}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} at 292 K. From the product analysis it was believed that abstraction of a Cl atom

\[ O(3\, P_J) + \text{CCl}_4 \rightarrow \text{CCl}_3 + \text{ClO} \]  

(3.62)
was not the only primary step and another pathway was suggested which involved the formation of a bound collision complex with two alternative decomposition modes,

\[
\text{O}^3P_J + \text{CCl}_4 \rightarrow [\text{OCCl}_4] \rightarrow \text{COCl}_2 + \text{Cl}_2 \tag{3.63}
\]

\[
\rightarrow \text{CO} + 2\text{Cl}_2 \tag{3.64}
\]

A product study of reactions (3.59) and (3.60) would be required to determine whether this type of mechanism is occurring.

\[\text{S}^3P_J + \text{HCl}\]

The value for this rate constant indicated that reaction is very slow or not occurring at all. Two possible reaction pathways are

\[\text{S}^3P_J + \text{HCl} \rightarrow \text{SH} + \text{Cl} \tag{3.65}\]

\[\text{S}^3P_J + \text{HCl} \rightarrow \text{H} + \text{SCl} \tag{3.66}\]

Considering the thermodynamics, (3.65) is endothermic by 79.5 kJ mole\(^{-1}\) and (3.66) by 92.1 kJ mole\(^{-1}\). So these reaction pathways are unlikely.

However, the similar \[\text{O}^3P_J + \text{HCl}\] reaction should be examined to determine whether any other thermodynamically favourable mechanisms are available. The reaction is believed to proceed by H atom abstraction

\[\text{O}^3P_J + \text{HCl} \rightarrow \text{OH} + \text{Cl} \tag{3.67}\]

with a rate constant of \((1.2 \pm 0.2) \times 10^{-16} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\) at 298 K\(^{56}\) although endothermic by 3.8 kJ mole\(^{-1}\).

So no alternative pathways seem possible and reaction between \[\text{S}^3P\] and HCl is therefore unlikely.
Figure 3.8 Plots of first order rate coefficients against partial pressure of halocarbon.

Figure 3.9 Plots of first order rate coefficient against partial pressure of reactant.
3.6 THE REACTION OF $S(3P) + O_3$

This reaction has been considered because $S(3P)$ atoms resulting from the photolysis of OCS in the stratosphere may take place in reactions involving ozone. In this section comparisons have been made with the much slower $O(3P) + O_3$ reaction. The latter reaction is very important in the atmosphere, being one of the main sinks for $O_3$ in the stratosphere and mesosphere.

Experiments and Results

The ozone was prepared as noted in Appendix I and 66.5 kNm$^{-2}$ of this was diluted with helium to a total pressure of 13.3 kNm$^{-2}$. The mixture bulb had been aged with 500 Nm$^{-2}$ of $O_3$ for 2 days to minimize decomposition of the ozone at the bulb walls. The purity of the ozone in the mixture was determined by U.V. spectroscopy before and after the experiments and proved to be 72 ± 7% pure with 28 ± 7% oxygen. The first order rate coefficients obtained were those due to $O_3$ plus $O_2$ and so had to be corrected,

$$c = c' - k_{O_2}[O_2]$$

(3.68)

where $c$ = true coefficient for $O_3$

$c'$ = coefficient for $O_3 + O_2$

$k_{O_2}$ = rate constant for $S(3P) + O_2$

$(2.2 \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1})^{20}$

$[O_2]$ = concentration of $O_2$.

Table 3.10 shows the results obtained at 294 K. The monochromator was set on the 182.63 nm line and $\gamma = 0.67 \pm 0.09$.

Figure 3.9 shows a plot of the first order rate coefficients against ozone pressure.
Table 3.10 Second order rate constant for $S(^3P_J) + O_3$.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Partial Pressure (Nm$^{-2}$)</th>
<th>Gradient (cm$^3$ molecule$^{-1}$s$^{-1}$)</th>
<th>Rate Constant ($\times 10^{-11}$)</th>
<th>Flash Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_3$</td>
<td>0.057 - 0.160</td>
<td>(1.5 ± 0.2)</td>
<td>(2.2 ± 0.6)</td>
<td>180</td>
</tr>
</tbody>
</table>

Discussion

The primary reaction is believed to be $O$ atom abstraction

$S(^3P_J) + O_3(\tilde{X}^1A_1) \rightarrow SO(\tilde{X}^2\Sigma^-) + O_2(\tilde{X}^3\Sigma_g^-)$  \hspace{1cm} (3.69)

$\Delta H_{298}^0 = -415.3$ kJmole$^{-1}$

This reaction pathway is similar to that for the $O(^3P)$ with $O_3$ reaction,

$O(^3P_J) + O_3 \rightarrow O_2 + O_2 \hspace{1cm} \Delta H_{298}^0 = -390.1$ kJmole$^{-1}$  \hspace{1cm} (3.70)

$k_70 = 7.2 \times 10^{-15}$ cm$^3$ molecule$^{-1}$s$^{-1}$ at 298 K.  \hspace{1cm} 57

It is useful to consider the energy distribution among the products of reaction (3.70). Benson et al\textsuperscript{58} suggested that 415.2 kJmole$^{-1}$ of energy was available for channeling into electronic, vibrational, rotational and translational energy (i.e. 390.1 kJmole$^{-1}$ exothermicity + 25.1 kJmole$^{-1}$ activation energy).

Examining some of the electronic states of the $O_2$ molecule (table 3.11) it is seen that the lowest electronic states $^1\Delta_g$ and $^1\Sigma_g^+$ are accessible. Since by selection rules, at least one triplet $O_2$ should be present in the products then according to Benson the following product distributions are possible

$O(^3P_J) + O_3(\tilde{X}^1A_1) \rightarrow O_2(\tilde{X}^3\Sigma_g^-) + O_2(\tilde{1}^1\Sigma_g^+) \hspace{1cm} (3.71)$

$+ 258.2$ kJmole$^{-1}$
However Basco and Norrish observed that most of the exothermic energy goes into vibrational excitation of the newly formed O-O bond, with up to 19 quanta of vibrational energy (78.5% of the available energy).

Now applying these same principles to the $S^3P + O_3$ reaction. First according to Benson's scheme, the electronic states of SO must be considered (see table 3.12). Since the exothermicity of the $S^3P + O_3$ reaction is 415.2 kJ mole$^{-1}$ then the electronically excited SO($B^3Σ^+$) state is inaccessible; the $b^1Σ^+$, $a^1Δ$ or $X^3Σ^-$ states may be formed. If Basco and Norrish's scheme is correct then most of the excess energy must be channeled into vibrational excitation of the newly formed SO bond. Table 3.13 shows some of the vibrational energy levels for SO($X^3Σ^-$) calculated using computer program VIB1 (see Appendix II). The $v = 39$ vibrational level is accessible if all of the excess energy is channeled into vibrational excitation. However with 74% of the exothermicity going into vibrational excitation of SO, then the $v = 27$ vibrational level would be accessible leaving enough energy to possibly vibrationally excite the $O_2$ ground state molecule or maybe even produce a $^1Δ_g$ state molecule.

Clyne and Townsend using an atomic resonance fluorescence discharge flow system determined the rate constant for (3.69) as $k_{69} = (1.25 \pm 0.26) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ at 298 K. This is slightly less than that obtained in this study. Also they calculated a collision efficiency of 0.03 for this reaction.
Table 3.11  Electronic states of $O_2$.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>Energy above the ground state $^4$</th>
<th>cm$^{-1}$</th>
<th>kJmole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$ $B^3\Sigma_u^-$</td>
<td>49802.1</td>
<td>604.5</td>
<td></td>
</tr>
<tr>
<td>$A^3\Sigma_u^+$</td>
<td>36096.0</td>
<td>431.2</td>
<td></td>
</tr>
<tr>
<td>$b^1\Sigma_g^+$</td>
<td>13195.2</td>
<td>157.0</td>
<td></td>
</tr>
<tr>
<td>$a^1\Delta_g$</td>
<td>7918.1</td>
<td>94.2</td>
<td></td>
</tr>
<tr>
<td>$X^3\Sigma_g^-$</td>
<td>0</td>
<td>ground state</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.12  Electronic states of $SO$.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>Energy above the ground state $^6$</th>
<th>cm$^{-1}$</th>
<th>kJmole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SO$ $B^3\Sigma_u^-$</td>
<td>41629.0</td>
<td>499.5</td>
<td></td>
</tr>
<tr>
<td>$b^1\Sigma_g^+$</td>
<td>10510.0</td>
<td>126.1</td>
<td></td>
</tr>
<tr>
<td>$a^1\Delta$</td>
<td>6350.0</td>
<td>76.2</td>
<td></td>
</tr>
<tr>
<td>$X^3\Sigma_g^+$</td>
<td>0</td>
<td>ground state</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.13  Vibrational energy of $SO$.

<table>
<thead>
<tr>
<th>Vibrational quantum number</th>
<th>Energy above $v = 0$</th>
<th>% of exothermicity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^{-1}$</td>
<td>kJmole$^{-1}$</td>
</tr>
<tr>
<td>$v = 40$</td>
<td>34944.0</td>
<td>418.2</td>
</tr>
<tr>
<td>39</td>
<td>34308.3</td>
<td>410.6</td>
</tr>
<tr>
<td>38</td>
<td>33660.4</td>
<td>403.1</td>
</tr>
<tr>
<td>27</td>
<td>25728.0</td>
<td>308.1</td>
</tr>
</tbody>
</table>
3.7 **THE S(3P) + NH$_3$ REACTION**

In this section an unusual reaction pathway has been suggested for the S(3P) + NH$_3$ reaction and is analogous to a mechanism for the S(3P) + Amine reaction presented in section 3.3.

**Experiments and Results**

Pressures of 2.101 - 8.020 Nm$^{-2}$ of NH$_3$ were used in the experiments. This determination was fairly difficult since absorption of the 182.63 nm resonance line by the NH$_3$ reduced the signal. A flash energy of 320 J was used and some experiments at 180 J indicated that no significant photolysis of NH$_3$ was occurring. A plot of the first order rate coefficients against NH$_3$ pressure (see figure 3.9) yielded a straight line of gradient (3.7 ± 0.2) x $10^{-13}$ cm$^3$ molecule$^{-1}$s$^{-1}$. Applying the correction factor, $\gamma = 0.67 \pm 0.09$ gave

$$ k_{NH_3} = (5.5 \pm 0.6) \times 10^{-13} \text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1} \text{ at } 294 \text{ K}. $$

**Discussion**

The H atom abstraction reaction

$$ S(3P) + NH_3 \rightarrow SH + NH_2 \quad (3.73) $$

was considered but is endothermic by 79.5 kJ mole$^{-1}$. This is analogous to the O(3P) reaction,

$$ O(3P) + NH_3 \rightarrow OH + NH_2 \quad (3.74) $$

$$ k_{74} = 9.9 \times 10^{-17} \text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1} \text{ at } 298 \text{ K}, \quad 59 $$

which is also endothermic but by 1.67 kJ mole$^{-1}$.

Since the H atom abstraction is unlikely for S(3P) then the following addition reaction pathway has been postulated,
The $S(^3P)$ atom adds to the N atom resulting in the production of an unstable addition adduct. This complex rapidly isomerizes to a stable molecule $HS-NH_2$ by means of migration of a H atom from the N to the S atom. The ultimate fate of the $HS-NH_2$ would be decomposition to products. Evidence for this complex comes from a nuclear magnetic resonance spectroscopy study of sulphur-nitrogen compounds.\textsuperscript{60} This includes compounds called sulphenamides ($R_2N-SR$) which have the group $-S-N<$.

However the reaction pathway cannot be established until a product analysis study is carried out.

If photolysis of the $NH_3$ was occurring, resulting in the production of $NH_2$ and H atoms then it is possible that the reaction

$$S(^3P) + H + M \rightarrow SH + M \quad \Delta H_{298}^0 = -346.6 \text{ kJ mole}^{-1}(3.77)$$

for $M = N_2$, etc. could take place. However the results indicated that $NH_3$ photolysis was insignificant.
3.8 SUMMARY

Overall the ground state sulphur atom was found to be more reactive than the ground state oxygen atom towards specific molecules.

The reaction of $S^{(3P_J)}$ atoms with halogens is believed to proceed by halogen atom abstraction via an intermediate complex. The order of reactivities of the halogens was

$$\text{Br}_2 > \text{I}_2 > \text{Cl}_2 > \text{F}_2$$

Reactions of the $S^{(3P_0)}$ and $S^{(3P_1)}$ components of the ground state with $\text{Cl}_2$ showed insignificant difference.

In its reaction with aromatics the $S^{(3P_J)}$ atom is believed to add to the aromatic ring to form thiols. The presence of side groups such as $-\text{CH}_3$ on the aromatic ring make some $\text{C}=$C bonds more susceptible to attack by the $S^{(3P_J)}$ atom. However the kinetic data suggested that more complex mechanisms were involved for the aromatic amine and aldehyde.

The $S^{(3P_J)}$ atom abstracts an oxygen atom from NO$_2$ with the formation of a vibrationally hot SO molecule. However the reaction with N$_2$O is believed to be a termolecular combination and not bimolecular.

In the $S^{(3P_J)} + \text{Halomethane}$ reactions the pathway is believed to involve the abstraction of a halogen atom. Also the greater the number of Cl atoms on the C atom the more easily is a Cl atom abstracted due to the weakening effect on the C-Cl bond.

Reaction of the ground state sulphur atom with ozone involves expected to be abstraction of an O atom and the SO formed is vibrationally excited.

Finally for the $S^{(3P_J)} + \text{NH}_3$ reaction, an insertion mechanism was postulated resulting in the formation of a sulphenamide.
REFERENCES

48. M.C. Addison, private communication.
CHAPTER FOUR
CHAPTER 4

ATOMIC IODINE, I(5^2P_2)

4.1 INTRODUCTION

This chapter deals with reactive and inelastic processes involving the first excited state of the iodine atom, I(5p^5(2P_2)), hereafter referred to as I^+. The first section deals with the reaction between I^+ and ozone, and the remainder of the chapter concentrates on the quenching of I^+ and energy transfer. Although quenching of I^+ has been extensively studied a number of new rate constants are presented.

4.2 THE REACTION OF I(5^2P_2) + O_3

Experiments and Results

The technique used to determine the rate constant for this reaction was time-resolved resonance fluorescence spectrophotometry (see chapter 2). The ozone was prepared as noted in Appendix I and a 412.3 Nm^-2 pressure of this was diluted (to a total pressure of 14.4 kNm^-2) with Helium and left for 2 hours to mix by diffusion. The mixture bulb had been aged with O_3 for 2 days before use. Using U.V. spectroscopy the purity of the O_3 was determined before and after the experiments as 83 ± 7%, the remaining 17 ± 7% being O_2. Reaction mixtures were prepared as described in chapter 2. Photolysis of the i-C_3F_7I was carried out using a conventional quartz capillary flash lamp dissipating 49 J flash energy. Two I^+ decay curve signals were recorded from each mixture and processed as described in chapter 2. The first order rate coefficients obtained had to be corrected (see section 3.6) using the rate constant for I^+ + O_2,
Reaction of $I(^3P_1) + O_3$

\[ k = (7.38 \pm 0.57) \times 10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \]

Temp. = 285 K  Flash Energy = 49 J

\[ P(\text{total}) = 2.9 \text{ kN m}^{-2} \]

931 Nm$^{-2}$ C$_3$F$_7$I

He Diluent

Figure 4.1 Plot of first order rate coefficients against ozone partial pressure.
Partial pressures of O₃ + O₂ used were in the range 0.043 - 0.406 Nm⁻² which on correction gave O₃ pressures of 0.036 - 0.336 Nm⁻². The experimentally determined second order rate constant for O₃ + O₂ was \((1.1 \pm 0.1) \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\) and the corrected value for O₃ was

\[ k_{O_3} = (7.4 \pm 0.6) \times 10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\] at 285 K.

Figure 4.1 shows a plot of the first order rate coefficients against O₃ partial pressure.

**Discussion**

The primary step in the reaction is believed to involve abstraction of an O atom

\[ \text{I}(^2P_{\frac{3}{2}}) + O_3 \rightarrow IO + O_2 \quad \Delta H_{298}^0 = -160.8 \text{kJ mole}^{-1} \quad (4.1) \]

This pathway is the same as that suggested by Clyne and Cruse⁸ for the ground state iodine atom

\[ \text{I}(^2P_{\frac{1}{2}}) + O_3 \rightarrow IO(X^2Π) + O_2 \quad \Delta H_{298}^0 = -70 \text{kJ mole}^{-1} \quad (4.2) \]

Clyne and Cruse used a discharge flow system with time-resolved electronic absorption spectrophotometry. Iodine atoms were formed from the reaction of HI with Cl or Br, and O₃ was added to the I atom stream. The O₃ concentration was monitored via the centre (250 nm) of the O₃ absorption continuum and IO by means of bands observed between 418 and 470 nm.

The \(I^* + O_3\) reaction is \(~4\) times faster than the ground state reaction so any alternative reaction pathways should be considered,

\[ \text{I}(^2P_{\frac{3}{2}}) + O_3 \rightarrow \text{I}(^2P_{\frac{1}{2}}) + O_3^{\cdot \cdot} \quad (4.3) \]
Quenching, followed by reaction of the ground state atom with $O_3$ has been considered, however this seems unlikely since it has been observed that excited atoms tend to be more reactive than their ground state.\(^3\)

Dissociative excitation has also been considered, however this has been discarded

$$I(^2P_3) + O_3 \rightarrow I(^2P_{3/2}) + O + O_2 \quad (4.4)$$

since $D(O_2-O) = 100.3 \text{ kJ mole}^{-1}$ and the energy available from the electronic excitation of the iodine atom (90.8 kJ mole\(^{-1}\)) would not be sufficient to dissociate the $O_3$ molecule.

In the reaction

$$Cl(^2P_{3/2}) + O_3 \rightarrow ClO + O_2 \quad \Delta H_{298}^0 = -167.4 \text{ kJ mole}^{-1} \quad (4.5)$$

$$k_5 = (1.33 \pm 0.26) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \quad \text{at} \ 298 \text{ K} \quad 4$$

the most favourable reaction path was considered to be via a planar configuration\(^5\) to give a transition state $ClO000$ with $Cl-O-O = 180^\circ$ and $O-O$ approximately equal to the $O_3$ bond angle. So the transition state would have the configuration

$$Cl-O-O\cdots0$$

So reaction (4.1) may involve a transition state analogous to $ClO_3$.

Having speculated on the reaction mechanism involved for (4.1) it is interesting to consider the partitioning of energy into the products. An insight can be gained from a consideration of similar reactions. Some general statements can be made about reactions of the type

$$A + BCD \rightarrow AB + CD \quad (4.6)$$

(1) The primary location of vibrational excitation is in the product molecule in which a new bond is formed.
(2) Rotational excitation accompanies the vibrational excitation. The extent of rotational excitation is dependent on the conservation of angular momentum.

(3) In some cases excitation of the molecules occurs to the maximum extent permitted by the energetics of the reaction.

(4) Electronic excitation can occur in atom transfer reactions.

Examples of similar reactions leading to vibrationally excited products are

$$\text{Br}^{(2P_3^1)} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \quad \Delta H_{298}^0 = -79.5 \text{ kJ mole}^{-1} \quad (4.7)$$

$$k_7 = (1.2 \pm 0.1) \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1},$$

$$\text{F}^{(2P_3^1)} + \text{O}_3 \rightarrow \text{FO} + \text{O}_2 \quad \Delta H_{298}^0 = -58.6 \text{ kJ mole}^{-1} \quad (4.8)$$

$$k_8 = 1.3 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1},$$

and reaction (4.5). McGrath and Norrish observed vibrational excitation of ClO up to $v = 5$ and BrO up to $v = 4$. However in the case of FO no vibrational excitation was observed. The vibrationally excited ClO and BrO molecules were chiefly in the level $v = 1$ and the populations of levels with $v \geqslant 1$ were small. However in reaction (4.2) at least one third of the IO($X^2\Pi$) molecules formed were initially in the $v \geqslant 1$ levels.

Since with $I^*$ an extra quantity of energy (90.8 kJ mole$^{-1}$) is available in excess of the 70 kJ mole$^{-1}$ exothermicity of the ground state reaction, then a total of 160.8 kJ mole$^{-1}$ is available for distribution amongst the products.

First considering the electronic states of the IO molecule (see table 4.1). Figure 4.2 shows the potential curves for the IO ground and the $A^2\Pi_2^+$ excited state. These were accurately generated by a computer program. Appendix IV describes the method
Figure 4.2 Potential curves for the IO molecule.
of construction in detail.

Table 4.1 Electronic states of IO.

<table>
<thead>
<tr>
<th>Electronic State $^9$</th>
<th>Energy above the ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>$IO \ A^2\Pi_{\frac{3}{2}}$</td>
<td>21565</td>
</tr>
<tr>
<td>$X^2\Pi_{\frac{3}{2}}$</td>
<td>0</td>
</tr>
</tbody>
</table>

From table 4.1 it is seen that the $A^2\Pi_{\frac{3}{2}}$ excited state of IO is not accessible in this reaction.

Now considering the generalization stating that the primary location of vibrational excitation is in the product molecule IO. Table 4.2 shows the energy of vibrational levels of IO calculated using computer program VIB1 (see Appendix II).

Table 4.2 Vibrational energy of IO.

<table>
<thead>
<tr>
<th>Vibrational Quantum Number</th>
<th>Energy above $v = 0$</th>
<th>% of Exothermicity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^{-1}$</td>
<td>kJ/mole$^{-1}$</td>
</tr>
<tr>
<td>$v = 24$</td>
<td>13488</td>
<td>160.7</td>
</tr>
<tr>
<td>23</td>
<td>13041</td>
<td>155.7</td>
</tr>
<tr>
<td>22</td>
<td>12584</td>
<td>150.3</td>
</tr>
<tr>
<td>13</td>
<td>8021</td>
<td>95.9</td>
</tr>
<tr>
<td>12</td>
<td>7464</td>
<td>89.2</td>
</tr>
<tr>
<td>11</td>
<td>6897</td>
<td>82.5</td>
</tr>
</tbody>
</table>

$IO(2\Pi_{\frac{3}{2}})$ $\omega_e = 687$ cm$^{-1}$, $\omega_e\kappa_e = 5$ cm$^{-1}$.
If the total energy available was channeled into vibration of the ground state IO then the \( v = 24 \) level would be populated. Since many of the IO molecules in the ground state I atom reaction were formed in the \( v = 1 \) level, then the excess energy of \( I^* \) could produce molecules excited to a considerably higher vibrational level.

Now considering the possible extent of rotational excitation of the \( IO(2\Pi_g) \) molecule. This will be dependent on the conservation of angular momentum. Table 4.3 shows the rotational energy for various quantum numbers. These values were calculated using a computer program (see Appendix II). Also the effects of rotational energy on the potential energy curve has been discussed in Appendix IV.

Table 4.3 Rotational energy levels of \( IO(2\Pi_g) \).

<table>
<thead>
<tr>
<th>Rotational Quantum Number</th>
<th>Rotational energy</th>
<th>% of Exothermicity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm(^{-1})</td>
<td>kJmole(^{-1})</td>
</tr>
<tr>
<td>( J = 5 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>20</td>
<td>37</td>
<td>0.4</td>
</tr>
<tr>
<td>40</td>
<td>142</td>
<td>1.7</td>
</tr>
<tr>
<td>60</td>
<td>554</td>
<td>6.7</td>
</tr>
<tr>
<td>80</td>
<td>1236</td>
<td>14.7</td>
</tr>
<tr>
<td>100</td>
<td>2188</td>
<td>26.0</td>
</tr>
<tr>
<td>160</td>
<td>3410</td>
<td>40.6</td>
</tr>
<tr>
<td>200</td>
<td>8697</td>
<td>103.8</td>
</tr>
<tr>
<td>300</td>
<td>13573</td>
<td>162.0</td>
</tr>
<tr>
<td></td>
<td>30488</td>
<td>363.8</td>
</tr>
</tbody>
</table>
As can be seen from the results quite high rotational excitation is possible with only a fraction of the available energy going into rotation. The extent of rotational excitation can be calculated from the laws associated with the conservation of angular momentum.

Now consideration can be given to the possibility of electronic excitation of the O₂ molecule formed in reaction (4.1). The \(^1\Delta_g\) state of O₂ lies at 94.2 kJ mole\(^{-1}\) above the ground state and there certainly is enough energy available to produce this state. In the reaction

\[
\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 \quad \Delta H_{298}^0 = -326.5 \text{ kJ mole}^{-1}
\]  

(4.9)

vibrationally excited OH was formed up to \(v = 9\) (the highest level possible) however there is some evidence for the formation of \(\text{O}_2(\text{a}^1\Delta_g)^3\) and if this an accurate observation then electronic excitation of the O₂ formed in (4.1) may be possible. Alternatively the O₂ could be vibrationally excited to some extent.

From this section some trends of the halogen atom reactivity have been observed. In the ground state halogen + O₃ reaction the order of reactivity is

\[
\text{F}(^2\text{P}_1) \approx \text{Cl}(^2\text{P}_1) > \text{I}(^2\text{P}_1) > \text{Br}(^2\text{P}_1)
\]

Although the excited iodine atom was found to be more reactive towards O₃ than the ground state atom there is little evidence of this for the other halogen atoms. For example an estimate has been given for

\[
\text{Cl}(^2\text{P}_1) + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \quad (4.10)
\]

\[
k_{10} \approx 1 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1},
\]

and this is approximately the same as that for the ground state atom.
Also the trend in the extent of vibration of the XO molecule in the reaction \( X + O_3 \) was
\[
\text{IO} > \text{BrO} > \text{ClO} > \text{FO}.
\]

4.3 \(^{2}P_2 \) + \( \text{NH}_3 \) and HCN

The work presented in this section has been published\(^{10}\) and is concerned with the transfer of electronic energy from the \( I^* \) atom to the molecules \( \text{NH}_3 \) and HCN. The possibility of using these systems in I.R. lasers is discussed.

**Experiments and Results**

The technique used to determine the rate constants for quenching of \( I^* \) was time-resolved resonance fluorescence spectroscopy (see chapter 2). A conventional quartz capillary flash lamp was used, dissipating 49 J. Other flash energies were also utilized to determine whether photolysis of the quenching molecule was occurring. The signal averager was used in conjunction with the transient recorder and averages of 4 to 8 flashes were recorded which improved the signal-to-noise ratio of the \( I^* \) atom fluorescence decay signals. Table 4.4 shows the results obtained at 295 K.

**Table 4.4 Second order rate constants for \( I^* \) quenching.**

<table>
<thead>
<tr>
<th>Quenching Molecule</th>
<th>Partial Pressure (Nm(^{-2}))</th>
<th>Rate Constant (cm(^3)molecule(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_3 )</td>
<td>7.98 - 22.61</td>
<td>((2.1 \pm 0.2) \times 10^{-13})</td>
</tr>
<tr>
<td>( \text{HCN} )</td>
<td>7.91 - 21.28</td>
<td>((6.8 \pm 0.7) \times 10^{-14})</td>
</tr>
</tbody>
</table>
Figure 4.3 shows a plot of the first order rate coefficients against partial pressure of NH₃.

Discussion

Petersen et al. studied the interaction of the first excited state of the bromine atom, Br(4²P₁/₂), with a number of molecular species and produced I.R. lasers pumped by electronic → vibration + rotation (E → VR) energy transfer. For the case of

\[
\text{Br}^* + \text{HCN} \rightarrow \text{Br} + \text{HCN}^+ + \Delta E = 374 \text{ cm}^{-1} \quad (4.11)
\]

\[
k_{11} = (2.0 \pm 0.2) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \text{ at } 295 \text{ K} \quad (4.12)
\]

(\( \dagger \) indicates vibrational excitation and \( \Delta E \) is the energy mismatch).

The kinetic data indicated that efficiency and specificity of the transfer process was high. It has been shown that where quenching is rapid then E→VR energy transfer is efficient. Process (4.11) generated considerable population inversions of vibrationally hot HCN and stimulated emission was observed in the wavelength regions 3.85, 7.25 and 8.48 μm. These correspond to the vibrational transitions (001)→(010), (100)→(010) and (001)→(100) respectively. Since the rate of transfer of the energy of the Br* to the HCN is more rapid than the intermolecular transfer between the HCN molecules,

\[
\text{HCN (001)} + \text{HCN (000)} \rightarrow \text{HCN (mnO)} + \text{HCN (pqO)} \quad (4.12)
\]

\[
k_{12} = (1.7 \pm 0.2) \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}
\]

then the conditions for an efficient E→VR transfer laser are satisfied.

The Br* atom has an energy of 3685 cm⁻¹ and this is close to the 3311 cm⁻¹ energy of the (001) vibrational level of HCN and so
Figure 4.3 Plots of first order rate coefficients against pressure of quencher.
energy transfer is favourable via this specific channel. Figure 4.4 is an energy level diagram for HCN showing the transitions observed.

From this study on Br⁺ it may be expected that quenching of I⁺ by HCN may also favour resonant E→VR transfer. However a much slower quenching rate constant was obtained for the I⁺ + HCN interaction and this suggests that E→VR energy transfer is inefficient in this case. Examination of the HCN energy level diagram (see figure 4.4) shows that the closest transition of HCN to the I⁺ energy level (7603 cm⁻¹) is at 7490 cm⁻¹. This gives an energy mismatch of ΔE = 113 cm⁻¹ however since excitation of three vibrational quanta is required and the (201) combination band is very weak in the infra-red spectrum then E→VR transfer is unfavourable. It has been shown that when only one or two vibrational quanta are involved the transfer process can be efficient and highly mode specific.¹⁴

In the I⁺ + HCl system three quanta of excitation are also required and the quenching rate constant observed is approximately equal to that for I⁺ + HCN. A quenching mechanism for I⁺ + HCl involving the crossing of potential energy surfaces has been proposed¹⁵ and the HCN case may be similar to this. It is unlikely that the I⁺ + HCN system could be used as a basis for a laser system.

The kinetic data for the process

\[ I⁺ + \text{NH}_3 \rightarrow I + \text{NH}_3^+ \ (\text{all states}) + \Delta E \]  \hspace{1cm} (4.13)

suggested that efficient E→VR transfer is involved. To consider the possible channels for the energy transfer the energy level diagram for NH₃ based on the fundamentals, overtones and combination
Figure 4.4 Energy level diagrams for HCN, OCS and NH$_3$. 
bands observed in the infra-red \(^{16}\) can be examined. From figure 4.4 the vibrational levels closest to the \(I^*\) energy (7603 cm\(^{-1}\)) are \(2v_3 + v_2\) and \(2v_1\) (or \(2v_3\)). The \(2v_1\) band involves a large energy mismatch, so the most likely channel appears to be that associated with the \(2v_3 + v_2\) energy level. However three quanta are involved. A medium resolution study of the I.R. spectrum of \(\text{NH}_3\) in the 1.3 \(\mu m\) wavelength region has been carried out \(^{17}\) and revealed a considerable structure involving a number of transitions. Those most appropriate for near resonant energy transfer channels are:

\[
\begin{align*}
7652.3 &\ (49.2) \\
7631.8 &\ (29) \\
7616.7 &\ (13.6) \\
7602.8 &\ (0.3) \\
7592.2 &\ (10.9) \\
7578.5 &\ (24.6) \\
7571.2 &\ (31.9) \\
7554.6 &\ (48.5)
\end{align*}
\]

Units are cm\(^{-1}\) and the \(\Delta E\) values are in brackets.

In particular the 7602.8 cm\(^{-1}\) transition is the most likely channel for \(E \rightarrow VR\) transfer since it is almost exactly resonant with the iodine atom transition with a \(\Delta E = 0.3\) cm\(^{-1}\). The energy mismatch values for all those other lines mentioned suggest that they would also be favourable channels for energy transfer. With such favourable channels for transfer it is surprising that the quenching efficiency is not considerably greater than that observed.

However the quanta requirements may be the limiting factor here or other more complex factors may be involved. In a molecule such as \(\text{NH}_3\) which has more vibrational modes than a diatomic or triatomic the orientation of the collision partners may be of importance.

So the postulated mechanism is

\[I(5^2P_{3/2}) + \text{NH}_3(0000) \rightarrow I(5^2P_{3/2}) + \text{NH}_3(0120) + \Delta E \ (4.14)\]

It would be useful to determine the rates of \(V \rightarrow V\) energy transfer
between the NH₃ molecules and deactivation by helium since these processes reduce the efficiency of E→VR laser systems. Further studies of the fluorescence observed from vibrationally hot NH₃ will indicate if the mechanism in (4.14) is correct. This process may be of use in E→VR energy transfer lasers.

4.4 \( \text{I}(5^2P_1) + \text{OCS, H}_2\text{S, CS}_2 \text{ and SO}_2 \)

Sulphur containing molecules such as OCS and SO₂ are important atmospheric species. Therefore it is essential to examine their reactive and inelastic processes involving halogen atoms. These processes may be occurring in the stratosphere where halogen atoms are generated by photolysis of freons. Also the I* quenching efficiencies of these molecules should be considered to determine whether they would be of use in E→VR laser systems.

Experiments and Results

The technique used was time-resolved resonance fluorescence spectroscopy as described in chapter 2. In the I* + OCS and H₂S experiments a conventional quartz capillary flash lamp was used for photolysis of the i-C₃F₇I. In the CS₂ and SO₂ experiments the Xe-pulsed flash lamp was used in conjunction with a signal averager. The I* fluorescence decay signals obtained for the latter two were averages of 32 and 64 flashes using the low intensity output (0.03 J) of the flash lamp. Table 4.5 shows the results obtained and figure 4.3 shows a plot of the first order rate coefficients against OCS partial pressure. Figure 4.5 shows a computer drawn plot for H₂S (computer program LGRAPH, see Appendix II) and figure 4.6 for SO₂ (computer program LGR).
Flash Energy = 49 J  
Temp. = 298 K  
P(total) = 2.9 kNm⁻²  
93.1 Nm⁻² C₆F₇I  
He Diluent

Figure 4.5  Plot of first order rate coefficients against H₂S partial pressure.
Figure 4.6 Plot of first order rate coefficients against SO$_2$ partial pressure.
Table 4.5 Second order rate constants for I* + Quenching molecule.

<table>
<thead>
<tr>
<th>Quenching Molecule</th>
<th>Partial Pressure (Nm⁻²)</th>
<th>Rate Constant (cm³ molecule⁻¹ s⁻¹)</th>
<th>Flash Energy (J)</th>
<th>Number of flashes</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>12.901 - 61.18</td>
<td>(2.8 ± 0.1) x 10⁻¹⁴</td>
<td>49</td>
<td>1</td>
</tr>
<tr>
<td>CS₂</td>
<td>1.995 - 18.052</td>
<td>(3.85 ± 0.2) x 10⁻¹⁴</td>
<td>0.03</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(4.09 ± 0.2) x 10⁻¹⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>8.778 - 260.68</td>
<td>(1.1 ± 0.1) x 10⁻¹⁵</td>
<td>0.03</td>
<td>32</td>
</tr>
<tr>
<td>OCS</td>
<td>42.56 - 226.1</td>
<td>(1.6 ± 0.1) x 10⁻¹⁴</td>
<td>49</td>
<td>8</td>
</tr>
</tbody>
</table>

Discussion

Hariri and Wittig¹⁴ studied the system

\[ \text{Br}^* + \text{OCS} \rightarrow \text{Br} + \text{OCS}^+ \text{ (all states)} \] \hspace{1cm} (4.15)

\[ k_{15} = (1.4 ± 0.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \text{ K}, \]

and the kinetic data indicated that efficient E→VR energy transfer was occurring. Figure 4.4 shows an energy level diagram for OCS. The channels of energy transfer are unknown for process (4.15) but the closest vibrational levels to the Br* energy are (111) and (031). However these involve excitation of three or four quanta.
The molecular fluorescence observed arises from the (001)→(000) transition but E→VR transfer directly into the (001) vibrational level would involve a very large ΔE value. So the conclusions drawn from this study were that for OCS, E→VR transfer from Br* must involve more than two quanta for a resonant process or alternatively involve a large energy mismatch if one or two quanta are involved.

Now considering the system

\[ \text{I}(5^2P_{3/2}) + \text{OCS} \rightarrow \text{I}(5^2P_{3/2}) + \text{OCS} + \Delta E \] (4.16)

The quenching rate constant measured for this was two orders of magnitude slower than the similar Br* process. As can be seen from the energy level diagram of OCS (see figure 4.4) at least four quanta would have to be excited for near resonant E→VR transfer in (4.16).

Baughcum et al.\(^{18}\) using a tunable laser, infra-red fluorescence technique when studying the quenching of Br* by H\(_2\)S

\[ \text{Br}^* + \text{H}_2\text{S} \rightarrow \text{Br} + \text{H}_2\text{S}^+ \] (4.17)

\[ k_{17} = (2.6 \pm 0.1) \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \]

showed that reactive channels accounted for \(~10\%\) of the total deactivation of Br*

\[ \text{Br}^* + \text{H}_2\text{S} \rightarrow \text{HBr} + \text{HS} \] (4.18)

Product vibrational chemiluminescence from HBr (v = 1) was observed. So in this situation reactive channels are competing effectively with E→VR transfer.

Using the same technique the similar reactions of F and Cl have been studied\(^{19}\)
No attempt was made to discriminate between the reactivities of the excited and ground states of the atoms. However the reactions were found to be rapid. The vibrational and rotational energy disposal and the mean fraction of energy going into each type of energy are shown in table 4.6.

Table 4.6 Energy disposal in X + H₂S reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Total Energy (kJmole⁻¹)</th>
<th>Mean Relative Vibrational Population</th>
<th>Mean Fraction of Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Nᵥ = 1</td>
<td>Nᵥ = 2</td>
</tr>
<tr>
<td>F + H₂S</td>
<td>188</td>
<td>0.26</td>
<td>0.33</td>
</tr>
<tr>
<td>Cl + H₂S</td>
<td>50</td>
<td>0.63</td>
<td>-</td>
</tr>
</tbody>
</table>

Chemical lasers have been constructed based on the Cl and F + H₂S reactions, although they are severely limited by collisional deactivation of HCl and HF by H₂S.

Now examining the I⁺ + H₂S system. The rate constant value suggests that the reaction

I⁺ + H₂S → HI + HS \( \Delta H^0_{298} = -4.2 \text{ kJmole}^{-1} \) (4.20)

is very slow or is not taking place. It would seem likely that quenching is the dominant removal process for I⁺. The corresponding ground state I atom reaction is endothermic and it seems that
the electronic excitation energy cannot be used efficiently for reaction in this case. In order for reaction to occur a non-adiabatic transition from the surface associated with the I* to the ground state surface would be required before HI can be formed in the ground electronic state (from adiabatic correlation rules\textsuperscript{20}).

The closest vibrational levels of H\textsubscript{2}S to the I* energy are at 5154 cm\textsuperscript{-1} (\nu\textsubscript{1} + \nu\textsubscript{3}) and 9911 cm\textsuperscript{-1} (3\nu\textsubscript{1} + \nu\textsubscript{3}). These are well off resonance and efficient E\rightarrow VR transfer is unlikely.

The order of reactivity of halogen atoms towards H\textsubscript{2}S was therefore found to be

\[ \text{F} > \text{Cl} > \text{Br} > \text{I}. \]

The system analogous to I* + CS\textsubscript{2},

\[ \text{Br}^* + \text{CS}_2 \rightarrow \text{Br} + \text{CS}_2^+ \text{ (all states)} \text{ (4.21)} \]

\[ k_{21} = (1.1 \pm 0.1) \times 10^{-12} \text{ cm}^3\text{molecules}^{-1}\text{s}^{-1}, \text{14} \]

has been studied and E\rightarrow VR transfer is efficient. The (102) vibrational energy level of CS\textsubscript{2} is almost resonant with the Br* energy level and three quanta of excitation are involved. Three quanta appears to be close to the limiting value for efficient E\rightarrow VR energy transfer. Molecular fluorescence was observed from the CS\textsubscript{2} (001) state. It is likely that some V\rightarrow V transfer between CS\textsubscript{2} molecules is occurring.

Quenching of I* by CS\textsubscript{2} however was very inefficient reflecting the fact that any near resonant channels would involve at least five quanta. Herzberg\textsuperscript{16} gives the fundamentals of CS\textsubscript{2} at \nu\textsubscript{1} = 656.5 cm\textsuperscript{-1}, \nu\textsubscript{2} = 396.7 cm\textsuperscript{-1} and \nu\textsubscript{3} = 1523 cm\textsuperscript{-1}. Therefore transfer into 5\nu\textsubscript{3} would be required for a near-resonant channel.

The I* + SO\textsubscript{2} interaction resulted in a slow rate constant,
suggesting that efficient $E \rightarrow V_R$ transfer is improbable. Fundamental vibration bands at $v_1 = 1151 \text{ cm}^{-1}$, $v_2 = 519 \text{ cm}^{-1}$ and $v_3 = 1361 \text{ cm}^{-1}$ require that a number of vibrational quanta ($\sim 6$) would have to be excited.

An interesting series of reactions involving Cl and $SO_2$ have been put forward. The reaction

$$Cl + SO_2 + M \rightarrow ClSO_2 + M \quad (M = N_2)$$

(4.22)

$$k_{22} = (2.3 \pm 0.5) \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1}$$

has been studied in a fast flow reactor with mass spectrometric monitoring of Cl atoms and product $Cl_2SO_2$. Reaction (4.22) is followed by the rapid reactions

$$ClSO_2 + Cl \rightarrow Cl_2SO_2^+$$

(4.23)

$$Cl_2SO_2^+ \rightarrow SO_2 + Cl_2$$

(4.24)

$$Cl_2SO_2^+ + M \rightarrow Cl_2SO_2 + M$$

(4.25)

$Cl_2SO_2^+$ represents a molecule with vibrational energy. It has been suggested that reaction (4.22) could be of importance as a sink for stratospheric chlorine, if the predominant subsequent reactions in the stratosphere are

$$ClSO_2 + O_2 \rightarrow ClSO_4$$

(4.26)

$$ClSO_4 + NO \rightarrow ClSO_3 + NO_2$$

(4.27)

$$ClSO_3 + H-R \rightarrow ClSO_3H + R$$

(4.28)

The chlorosulphuric acid ($ClSO_3H$) is believed to be photolytically stable in the stratosphere and would be incorporated into aerosol particles. Therefore the Cl atoms could not be regenerated.

Reactions analogous to these may also be occurring for $I^* + SO_2$. 


Indeed in the flash photolysis of I₂ in the presence of SO₂, it has been shown that SO₂ takes part in the recombination of iodine atoms. It may therefore be of interest to have further studies on the ISO₂ molecule and its reaction with other molecules.

This section has shown that the I⁺ + sulphur containing molecule processes discussed are likely to have little value in E→VR laser systems.

4.5 I(5²P₂) + CH₃CHO, CH₃CN, CH₃Cl, CF₃Br and CF₃Cl.

The I⁺ atom quenching efficiencies of these molecules have been compared with that for CH₄ and also the possibility of reaction has been considered.

Experiments and Results

The technique used was time-resolved resonance fluorescence spectroscopy (see chapter 2). For the CH₃CHO and CH₃CN experiments the Xe-pulsed flash lamp was used in conjunction with the signal averager. The signals obtained were an average of 64 flashes. The other experiments involved the use of a conventional quartz capillary flash lamp. Also an iodine flow lamp was used to provide the resonance line for the experiments involving CH₃Cl, CF₃Br and CF₃Cl. The experiments were carried out at 293 K and table 4.7 shows the results obtained. Figure 4.7 shows a computer drawn plot of the first order rate coefficients against CH₃CN partial pressure.
Table 4.7 Second order rate constants for I$^*$ + Quenching molecule.

<table>
<thead>
<tr>
<th>Quenching Molecule</th>
<th>Partial Pressure (Nm$^{-2}$)</th>
<th>Rate Constant (cm$^3$ molecule$^{-1}$s$^{-1}$)</th>
<th>Flash Energy (J)</th>
<th>Number of flashes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CHO</td>
<td>1.224 - 7.182</td>
<td>(3.3 ± 0.3) x 10$^{-13}$</td>
<td>0.03</td>
<td>64</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>1.596 - 18.354</td>
<td>(1.2 ± 0.4) x 10$^{-13}$</td>
<td>0.03</td>
<td>64</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>4.123 - 20.748</td>
<td>(1.8 ± 0.1) x 10$^{-13}$</td>
<td>49</td>
<td>1</td>
</tr>
<tr>
<td>CF$_3$Br</td>
<td>279.3 - 1792.0</td>
<td>(2.1 ± 0.1) x 10$^{-16}$</td>
<td>49</td>
<td>1</td>
</tr>
<tr>
<td>CF$_3$Cl</td>
<td>292.6 - 1662.5</td>
<td>(4.3 ± 0.6) x 10$^{-16}$</td>
<td>49</td>
<td>1</td>
</tr>
</tbody>
</table>

Discussion

The postulated reaction between I$^*$ and CH$_3$Cl involving the abstraction of an H atom with the subsequent formation of HI is endothermic by 33.1 kJmole$^{-1}$, so there is little chance of reaction here. The dominant removal process for I$^*$ must involve inelastic collisions. The molecule CH$_3$Cl has six fundamental vibrations$^{16}$ Combination bands involving $\nu_1$ (2966.2 cm$^{-1}$) and $\nu_4$ (3041.8 cm$^{-1}$) could give values close to the I$^*$ electronic energy. This is not
Figure 4.7 Plot of first order rate coefficients against CH$_3$CN partial pressure.
suprising since in the process

\[ I(5^2P_2) + CH_4 (0000) \rightarrow I(5^2P_2) + CH_4 (0120) + \Delta E = 89 \text{ cm}^{-1} \quad (4.29) \]

\[ k_{29} = (9.4 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}, \quad 23 \]

involving the similar molecule CH$_4$, the electronic excitation energy of I$^*$ is removed by quenching. There is strong evidence for $E \rightarrow VR$ energy transfer in this situation. Also the CH$_3$Cl quenching rate constant compares favourably with that for CH$_3$I i.e. \((2.6 \pm 0.6) \times 10^{-13} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}.\) It has been shown that in molecules such as these the presence of C-H bonds has a marked effect on the quenching efficiency. For example CD$_4$ is fifty times less efficient at quenching I$^*$ than CH$_4$. Also if the quenching rate constant for CF$_3$Br and CF$_3$Cl are compared with that for CH$_3$Cl it is observed that they are about three orders of magnitude less efficient. This arises from the higher stretching frequencies of C-H compared with C-F or C-D bonds. C-F stretching frequencies are within the range 900 - 1400 cm$^{-1}$ therefore more than five quanta of vibrational excitation would be involved in an $E \rightarrow VR$ energy transfer channel.

The situation seems to be similar for CH$_3$CHO and CH$_3$CN where C-H bonds are present. The reaction

\[ I^* + CH_3CHO \rightarrow HI + CH_3CO \quad \Delta H_{298}^0 = -27.6 \text{ kJ mole}^{-1} \quad (4.30) \]

is thermodynamically favourable, however the ground state I atom reaction is endothermic. Comparison of the CH$_3$CHO kinetic data with that for CH$_4$ and CH$_3$Cl and consideration of the C-H bond strength in CH$_3$CHO suggests that quenching is the dominant removal process for the electronic energy of I$^*$. It would seem that the energy of excitation cannot be used for reaction in this case.
The relative efficiency of the quenching process suggests the possibility of near resonant channels for E → VR energy transfer. Fourteen fundamental frequencies\(^2^4\) have been listed, ranging from \(\nu_1 = 520 \text{ cm}^{-1}\) to \(\nu_{14} = 3004 \text{ cm}^{-1}\) and a large number of combination bands and overtones can arise from these. The vibrational levels closest to the \(I^*\) energy are at 6330 and 7840 \(\text{cm}^{-1}\) and involve three quanta. These give \(\Delta E\) values of over 200 \(\text{cm}^{-1}\). A more detailed study of the I.R. spectrum in the 7000 to 8000 \(\text{cm}^{-1}\) region is necessary to determine the possible E → VR channels.

The postulated reaction

\[ I^* + \text{CH}_3\text{CN} \rightarrow HI + \text{CH}_2\text{CN} \quad (4.31) \]

is exothermic by \(-178.6 \text{ kJmole}^{-1}\) and the I atom ground state reaction is also exothermic by \(-87.8 \text{ kJmole}^{-1}\), according to Benson's\(^2^5\) thermodynamic data. These high exothermicities suggest that in this situation a reactive channel may exist, however the rate constant measured suggests that it is relatively slow. The alternative pathway is physical quenching of the \(I^*\) by \(\text{CH}_3\text{CN}\). Herzberg\(^1^6\) has listed eight fundamental frequencies for \(\text{CH}_3\text{CN}\). A number of the fundamental frequencies are well over 2000 \(\text{cm}^{-1}\). For example \(\nu_1 = 2942 \text{ cm}^{-1}\) and \(\nu_5 = 2999 \text{ cm}^{-1}\). No bands have been listed in the 7600 \(\text{cm}^{-1}\) region but combinations involving about three quanta could very well provide an E → VR channel for energy transfer.

This section has clearly shown that quanta requirements are important in efficiency of E → VR energy transfer and the presence of C-H bonds contributes considerably to quenching efficiency. Also the excitation energy of the \(I^*\) atom cannot be used efficiently for reaction in these cases.
4.6 \text{I}(^5\!\!\!\!\!\!\!\!~_2^2P_1) + AROMATICS

In this section the mechanism of quenching has been considered and charge transfer complexes have been discussed.


Experiments and Results

Two aromatics have been considered in this section, C\textsubscript{6}F\textsubscript{6} and C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}. The technique used was time-resolved resonance fluorescence spectroscopy. Table 4.8 shows the results obtained at 295 K. The Xe-pulsed flash lamp and the signal averager were used for the toluene experiments.

Table 4.8 Second order rate constants for I* + Quenching molecule.

<table>
<thead>
<tr>
<th>Quenching Molecule</th>
<th>Partial Pressure (Nm\textsuperscript{-2})</th>
<th>Rate Constant (\text{cm}^3\text{molecule}^{-1}\text{s}^{-1})</th>
<th>Flash Energy (J)</th>
<th>Number of flashes</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{6}F\textsubscript{6}</td>
<td>3.99 - 19.95</td>
<td>((2.5 \pm 0.1) \times 10^{-14})</td>
<td>49</td>
<td>1</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}</td>
<td>2.128 - 5.054</td>
<td>((5.4 \pm 0.3) \times 10^{-13})</td>
<td>0.03</td>
<td>64</td>
</tr>
</tbody>
</table>

Discussion

Donovan and Gillespie\textsuperscript{26} studied the spin orbit relaxation of \text{I}(^5\!\!\!\!\!\!\!\!~_2^2P_1) by the aromatics C\textsubscript{6}H\textsubscript{6} and C\textsubscript{6}D\textsubscript{6} and observed a large isotope effect,

\[
k_{C_6H_6} = (4.6 \pm 0.7) \times 10^{-13} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}
\]

297 K

\[
k_{C_6D_6} = (9.9 \pm 1.0) \times 10^{-15} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}
\]
Deuterium substitution in the benzene changes the vibration-rotation energy levels thereby altering the near resonant channels.

The mechanism postulated for quenching of $I^*$ is believed to proceed via a charge-transfer (C-T) complex formed between the $I^*$ atom and the aromatic.

$$I(5^2P_2) + \text{Aromatic} \rightarrow \text{C-T complex} \rightarrow I(5^2P_2) + \text{Aromatic} \quad (4.32)$$

For mechanisms such as this a good correlation has been found between the logarithm of the rate constant and the ionization potential. For example in the $I^* + \text{Olefin}$ processes.\textsuperscript{27} So the purpose of this section has been to extend this study to aromatic compounds. Table 4.9 shows the relevant values and figure 4.8 the plot of $-\log_{10}(k_q)$ against ionization potential.

### Table 4.9 Ionization potentials and $\log_{10}(k_q)$ values for aromatics

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\log_{10}(k_q)$</th>
<th>Ionization Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6F_6$</td>
<td>-13.60</td>
<td>9.97</td>
</tr>
<tr>
<td>$C_6H_6$</td>
<td>-12.34</td>
<td>9.24</td>
</tr>
<tr>
<td>$C_6H_5CH_3$</td>
<td>-12.27</td>
<td>8.82</td>
</tr>
</tbody>
</table>

In figure 4.8 the values plotted suggest that there may be a straight line correlation here and the slope of the estimated line drawn on the figure is compatible to that observed for $I^* + \text{Olefin}$. Evidence for the existence of C-T complexes comes from the spectral observation of transient absorbing species in the vapour phase following the flash photodissociation of $I_2$ in the presence
Figure 4.8 Plot of Ionization Potential against $\log_{10}(k_q)$ for Aromatics.

Figure 4.9 Plot of Ionization Potential against $\log_{10}(k_q)$. 
of benzene or toluene. Transient absorption spectra were recorded in the U.V. and visible spectral regions. The band which arises is neither characteristic of the aromatic nor the iodine molecule alone but is attributed to a partial intermolecular transfer of charge between an electron-donor (aromatic) and an electron-acceptor (iodine) species.

The possibility of reaction of I with toluene has been considered via abstraction of an H atom in the methyl group.

\[ \text{This is unfavourable as the C-H bond strength is } 357 \text{ kJ mole}^{-1} \]

in comparison to 300 kJ mole\(^{-1}\) for HI but is exothermic for the I\(^{2P_1}\) reaction.

4.7 I\(^{2P_1}\) + HALOMETHANES

The theme of quenching mechanisms involving charge transfer complexes has been continued in this section with relevance to halomethanes.

**Experiments and Results**

The molecules considered in this section are CDCl\(_3\), CHCl\(_3\), CCl\(_4\), CF\(_2\)ClBr, CF\(_2\)HCl and CCl\(_2\)HF. The technique used was time-resolved resonance fluorescence spectrophotometry. A quartz capillary flash lamp was used for i-C\(_3\)F\(_7\)I photolysis. No averaging of the I\(^*\) fluorescence decay signals was carried out. Table 4.10 shows the second order rate constants obtained for quenching of I\(^*\) by these molecules at 296 K.

**Discussion**

The interaction of I\(^*\) with CDCl\(_3\), CHCl\(_3\) and CCl\(_4\) has already been studied by time-resolved atomic absorption spectrophotometry.
Table 4.10 Second order rate constants for quenching of I* by Halomethanes.

<table>
<thead>
<tr>
<th>Quenching Molecule</th>
<th>Partial Pressure (N m^-2)</th>
<th>k for I* quenching (cm^3 molecule^-1 s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl_3</td>
<td>25.308 - 99.9</td>
<td>(6.6 ± 0.4) x 10^{-14}</td>
</tr>
<tr>
<td>CCl_4</td>
<td>27.972 - 109.224</td>
<td>(2.0 ± 0.2) x 10^{-14}</td>
</tr>
<tr>
<td>CF_2ClBr</td>
<td>11.722 - 50.616</td>
<td>(5.2 ± 0.7) x 10^{-14}</td>
</tr>
<tr>
<td>CF_2HCl</td>
<td>11.988 - 97.236</td>
<td>(1.4 ± 0.1) x 10^{-14}</td>
</tr>
<tr>
<td>CCl_2HF</td>
<td>15.984 - 89.244</td>
<td>(2.5 ± 0.1) x 10^{-14}</td>
</tr>
</tbody>
</table>

The rate constants obtained were

\[ k_{\text{CHCl}_3} = (3.9 \pm 0.5) \times 10^{-14} \text{ cm}^3\text{molecule}^-1\text{s}^-1 \]
\[ k_{\text{CCl}_4} = (1.5 \pm 0.3) \times 10^{-13} \text{ cm}^3\text{molecule}^-1\text{s}^-1 \]

As can be seen the rate constants measured by the time-resolved absorption technique are faster than those obtained from the time-resolved resonance fluorescence technique, particularly that for CCl_4. There is a possibility that in the absorption technique the quenching molecule is photolyzed by the higher flash energies used. In the resonance fluorescence technique much lower flash energies are used for photolysis of the C_3F_7I so the quenching molecule is less likely to be photolyzed.

Table 4.11 shows the log k_q and ionization potential values
for a number of halogen derivatives of methane that have been studied in I* systems. Figure 4.9 shows a plot of the logarithm of the I* quenching rate constant against the ionization potential and as can be seen there seems to be a straight line correlation between log k_q and the ionization potential, the only serious deviation being CF_3Br. This graph is similar to that for I* + olefins and has already been discussed in section 4.6 this is suggestive of a mechanism involving a charge-transfer (C-T) complex. Indeed transient absorptions have been observed from the flash photolysis of I_2 in the presence of CH_3I, CH_3Br and CH_3Cl. The absorption bands are believed to be due to the C-T complexes formed between ground state I and the donor molecule and it is believed that this can occur for I* also. These complexes are

<table>
<thead>
<tr>
<th>Molecule</th>
<th>log_{10}(k_q)</th>
<th>Ionization Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl_3</td>
<td>-13.18</td>
<td>11.5</td>
</tr>
<tr>
<td>CCl_4</td>
<td>-13.70</td>
<td>11.7</td>
</tr>
<tr>
<td>CF_2ClBr</td>
<td>-13.28</td>
<td>11.8</td>
</tr>
<tr>
<td>CF_2HCl</td>
<td>-13.86</td>
<td>12.6</td>
</tr>
<tr>
<td>CCl_2HF</td>
<td>-13.61</td>
<td>12.0</td>
</tr>
<tr>
<td>CF_3Cl</td>
<td>-15.37</td>
<td>13.0</td>
</tr>
<tr>
<td>CF_3Br</td>
<td>-15.68</td>
<td>12.0</td>
</tr>
<tr>
<td>CH_3Cl</td>
<td>-12.74</td>
<td>11.5</td>
</tr>
</tbody>
</table>
assumed to be intermediates in general mechanisms for I atom-gas phase recombination processes, and are believed to play a role in the transfer of energy from I \(^*\) to the quenching molecule.

4.8 \( \text{I}(^2P_1) + \text{CH}_2\text{I}_2 \text{ and (CF}_3)_2\text{CO.1H}_2\text{O} \)

The molecule (CF\(_3\)_2CO is important in some laser systems therefore it was of interest to study the hydrated molecule (CF\(_3\)_2CO.1H\(_2\)O and its interaction with I \(^*\). Also the molecule CH\(_2\)I\(_2\) has been studied in laser systems and the kinetic data obtained in this study can be compared with that from a previous study.

Experiments and Results

The two molecules were studied by the time-resolved resonance fluorescence technique (see chapter 2), and a Xe-pulsed flash lamp was used. Signals were an average of 32 and 64 flashes. Table 4.12 shows the results obtained at 295 K.

<table>
<thead>
<tr>
<th>Quenching Molecule</th>
<th>Partial Pressure (Nm(^{-2}))</th>
<th>Rate Constant (cm(^3)molecule(^{-1})s(^{-1}))</th>
<th>Flash Energy (J)</th>
<th>Number of flashes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)I(_2)</td>
<td>2.527 - 9.177</td>
<td>(5.9 ± 0.3) (\times 10^{-13})</td>
<td>0.03</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(6.0 ± 0.3) (\times 10^{-13})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CF(_3)_2CO.1H(_2)O</td>
<td>1.064 - 5.187</td>
<td>(1.6 ± 0.1) (\times 10^{-12})</td>
<td>0.03</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.6 ± 0.1) (\times 10^{-12})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.10 Plot of first order rate coefficients against Hexafluoroacetone pressure (Hydrate)

Flash Energy = 0.03 J
Temp. = 295 K
P (total) = 2.9 kNm$^{-2}$
93.1 Nm$^{-2}$ C$_2$F$_4$I
He Diluent
Figure 4.11 Plot of first order rate coefficients against CH$_2$I$_2$ pressure.
Figure 4.10 shows a plot of the first order rate coefficients against \((\text{CF}_3)_2\text{CO} \cdot \text{H}_2\text{O}\) partial pressure and figure 4.11 shows the plot for \(\text{CH}_2\text{I}_2\).

Attempts were made to dehydrate the \((\text{CF}_3)_2\text{CO} \cdot \text{H}_2\text{O}\) using phosphoric anhydride \((\text{P}_2\text{O}_5)\) however this proved to be unsuccessful as the distilled substance was identical to the hydrate (by comparison of U.V and I.R. spectra).

Also attempts were made to use \(\text{CH}_2\text{I}_2\) as the source of the \(\text{I}^*\) but this was unsuccessful.

**Discussion**

It is of interest to measure the rate constant for the \(\text{I}^* + (\text{CF}_3)_2\text{CO} \cdot \text{H}_2\text{O}\) interaction because hexafluoroacetone can be used in the regeneration of the iodide laser medium. In a system where an iodide is being repeatedly photolyzed molecular iodine is formed which can lead to deterioration of the system. However regeneration of the parent iodide can occur by reaction of a radical with molecular iodine

\[
R^+ + \text{I}_2 \rightarrow \text{RI} + \text{I} \quad (4.33)
\]

More \(\text{RI}\) should be regenerated if additional radicals are formed in the reaction cell. This has been shown to occur by the addition of hexafluoroacetone as a photolytic source of \(\text{CF}_3\)

\[
(\text{CF}_3)_2\text{CO} \rightarrow 2\text{CF}_3 + \text{CO} \quad (4.34)
\]

Since attempts to dehydrate the \((\text{CF}_3)_2\text{CO} \cdot \text{H}_2\text{O}\) were unsuccessful the hydrate was used in the experiments. However there was no evidence from the experiments that the \((\text{CF}_3)_2\text{CO} \cdot \text{H}_2\text{O}\) was being photolyzed.

The very efficient rate constant obtained for the quenching
of I* by \((\text{CF}_3)_2\text{CO},_1^2\text{H}_2\text{O}\) suggests that it is probably due to the bound \(\text{H}_2\text{O}\) rather than the \((\text{CF}_3)_2\text{CO}\)

c.f. \(k_{\text{H}_2\text{O}} = 2 \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\).

So here a potentially interesting situation is observed in which the \((\text{CF}_3)_2\text{CO},_1^2\text{H}_2\text{O}\) molecules have physical and chemical properties very different from \(\text{H}_2\text{O}\) and yet in the E → VR transfer situation the vibrational characteristics of the \(\text{H}_2\text{O}\) molecule dominate over the \((\text{CF}_3)_2\text{CO}\).

It was of interest to study the \(\text{CH}_2\text{I}_2\) because photodissociation of this molecule with a laser beam leads to vibrational excitation of the \(\text{CH}_2\text{I}\) radical.\(^{33}\) Fluorescence from the \(I(5^2P_{3/2} → 5^2P_{1/2})\) transition was also observed upon photolysis of \(\text{CH}_2\text{I}_2\) at 248 nm and 308 nm with a laser system. However the I* is deactivated by \(\text{CH}_2\text{I}_2\) twice as fast as for \(\text{CH}_3\text{I}\) and over two orders of magnitude faster than \(\text{i-C}_3\text{F}_7\text{I}\).

\[\begin{align*}
I^* + \text{CH}_2\text{I}_2 & \quad k = 6.6 \times 10^{-13} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \quad 33 \\
I^* + \text{CH}_3\text{I} & \quad k = 3.5 \times 10^{-13} \quad " \quad 33 \\
I^* + \text{i-C}_3\text{F}_7\text{I} & \quad k = 1.9 \times 10^{-15} \quad " \quad 29
\end{align*}\]

As can be seen the \(I^* + \text{CH}_2\text{I}_2\) rate constant measured in this study compares well with that of the laser study.\(^{33}\) I* atom fluorescence decay was not observed from the photolysis of \(\text{CH}_2\text{I}_2\) in the resonance fluorescence technique because the I* atoms were rapidly quenched.
4.9 **SUMMARY**

The reaction of the excited iodine atom, \( \text{I}(^{5}P_{\frac{1}{2}}) \), with \( \text{O}_3 \) is believed to proceed by O atom abstraction with the production of vibrationally hot I\( \text{O} \). The excited iodine atom was found to be more reactive towards \( \text{O}_3 \) than the ground state atom.

The excited iodine atom quenching efficiencies of a number of molecules were investigated and the possibility of \( \text{E} \rightarrow \text{VR} \) energy transfer was considered. Some conclusions were drawn from this study. When one or two quanta are involved, then the \( \text{E} \rightarrow \text{VR} \) energy transfer process is efficient. Also energy transfer can be relatively efficient when three quanta are involved but other factors must be of considerable importance in this situation such as the energy mismatch value. However, the involvement of three quanta must be close to the limiting conditions for efficient \( \text{E} \rightarrow \text{VR} \) transfer. For in many cases the transfer process is inefficient. When four or five quanta are involved, the process is inefficient. The presence of C-H bonds has a marked effect on the quenching efficiency of the molecule. For example, when comparing \( \text{CH}_3\text{Cl} \) with \( \text{CF}_3\text{Cl} \).

Also the quenching efficiency of hydrates was found to be determined by the bound \( \text{H}_2\text{O} \).

It has also been observed that in some cases the electronic excitation energy cannot be used efficiently for reaction. For example, the \( \text{I}(^{5}P_{\frac{1}{2}}) + \text{H}_2\text{S} \) system.

Finally, analysis of the kinetic data from the \( \text{I}(^{5}P_{\frac{1}{2}}) + \) Aromatic and Halomethane systems suggest that charge-transfer complexes play a role in the quenching mechanism.
REFERENCES Chapter 4

APPENDICES
APPENDIX I

MATERIALS

Ar : B.O.C. ordinary cylinder grade.
Br₂ : Fisons (99% pure minimum)
Cl₂ : B.O.C. cylinder grade.
C₆H₆ : Fisons analar grade.
C₆H₅CH₃ : Fisons analar grade.
C₆F₆ : Fluorochem lab. reagent.
C₆H₅NH₂ : Analar grade (B.D.H. Chemicals Ltd.).
C₆H₅CHO : Analar grade (B.D.H. Chemicals Ltd.).
CH₃Br : Fisons lab. reagent.
CF₃Br : cylinder grade (Matheson Gas Product).
CF₂ClBr : I.C.I. Arcton, aerosol can grade.
CFC₁₃ : I.C.I. Arcton, aerosol can grade.
CF₂Cl₂ : I.C.I. Arcton, aerosol can grade.
CF₃Cl : cylinder grade (Matheson Gas Products).
i-C₃F₇I : Pierce Chemical Co.
CS₂ : Fisons analar grade.
CH₂CHO : Fisons analar grade.
CH₂CN : B.D.H. lab. reagent (special for spectroscopy).
CH₂Cl : McFarlane-Robson Ltd., cylinder grade.
CH₂I₂ : B.D.H. lab. reagent.
(CF₃)₂CO·¹H₂O : Sigma Chemical Co.
CDCl₃ : Aldrich Chemical Co.
CHCl₃ : Fisons analar grade.
CCl₄ : Fisons analar grade.
CF₂HCl : I.C.I. Arcton, cylinder grade.
CCl₂HF : I.C.I. Arcton, cylinder grade.
HCl : cylinder grade (Matheson Gas Products).
He : B.O.C. ordinary cylinder grade; any water present was trapped out using liquid nitrogen.
HCN : prepared sample.
H₂S : B.O.C. cylinder grade.
I₂ : Fisons (99.5% pure minimum).
Kr : (B.O.C., 99.99% pure) from a sealed bulb, grade 'X'.
NO₂ : prepared from O₂ (B.O.C. cylinder grade) and NO (Matheson cylinder grade). About 17 kNm⁻² of NO was mixed with an excess of O₂ to give a total pressure of 52 kNm⁻² in a bulb. This was left for 2 days to allow the reaction to go to completion and then the unreacted O₂ and NO were pumped away while the NO₂ was freeze-deposited with liquid nitrogen. The NO₂ was thoroughly purified by repeated trapping with a dry ice - isopropyl alcohol slush bath and pumping on the sample. An infra-red spectrum taken of a sample of the NO₂ showed that the nitrogen dioxide was pure and free of NO, although the dimer N₂O₄ is expected to be present.
N₂O : B.O.C. Medical (99% pure).
NH₃ : B.O.C. anhydrous.
N₂ : B.O.C. 'white spot' grade (99.9%).
OCS : cylinder grade (Matheson Gas Products).
O₃ : prepared by a method as described in reference, (P.N. Clough and B.A. Thrush, Chem. and Ind., 1971, (1966)).
SO₂ : B.D.H. cylinder grade.

All the reagents were thoroughly degassed and purified before use in experiments. Where appropriate infra-red spectra were taken and in some cases ultra-violet and mass spectra were also obtained.
APPENDIX II

COMPUTER PROGRAMS

VIB1

PROGRAM TO EVALUATE ENERGY OF VIB. TRANS. OF DIATOMIC

READ(5,1) WE, WEX
READ(5,3) VM
V=1.0
EVO=0.5*WE-0.5**2*WEX
WRITE(6,5) EVO
4 EV=(V+0.5)**2*WE-(V+0.5)**2*WEX
ET=EV-EVO
WRITE(6,2) V, ET
IF(V.GE.VM) STOP
V=V+1.0
GO TO 4
1 FORMAT(F6.1, F4.1)
2 FORMAT(F6.1, F10.1)
3 FORMAT(F4.1)
5 FORMAT (F8.1)
STOP
END

MORSE1

PROGRAM TO EVALUATE POTENTIAL ENERGY VALUES
FOR POTENTIAL ENERGY CURVES.

READ(5,6) A, B
READ(5,1) AN, BN
ABN=SQRT(AN*BN)
READ(5,3) DE, TE
READ(5,2) REQ, DELTAR, DELTAF
5 R=REQ+DELTAH
CALCULATION OF POTENTIAL VALUES
A=DE*(1.0-EXP(-(ABN*DELTAH**2/(2.0*R))))
YA*6SQRT(B**2*ABN/(2.0*H))*DELTAH<
=EXP(-CSQkT(8**2*A8N/(2.0*REQ))*DELTA<))
VRTE+X*(1.0-Y*Z)
TEST FOR RANGE
IF(R.GE.DELTAF) GO TO 7
WRITE(6,4) DELTAR,VR
DELTAH=DELTAH+0.1
GO TO 5
7 WRITE(6,6)
STOP
1 FORMAT(2F6.2)
2 FORMAT(2F6.4, F7.4)
3 FORMAT(F6.4, F7.4)
4 FORMAT(3F10.5)
6 FORMAT(4, 'DELTAH', 'T14', 'K', 'T24', 'VR')
8 FORMAT(2F6.3)
END
MORSE2

PROGRAM TO EVALUATE POTENTIAL ENERGY VALUES FOR A DIATOMIC WITH ROTATIONAL ENERGY.
READ(5,10) A,B
READ(5,1) AN, BN
ABN=SQRT(AN*BN)
READ(5,3) DE,TE
READ(5,2) KEQ,DELTAK,DELTAF
READ(5,8) RUT
READ(5,9) U
5 R=KEQ+DELTAK
CALCULATION OF RJ=0 POTENTIAL VALUES
X=DE*((1.0-EXP(-(ABN*DELTAK**2/(2.0*K)))))
Y=A*SQRT(B**2*ABN/(2.0*K))
Z=EXP(-(SQRT(B**2*ABN/(2.0*K)))*DELTAK)
VR=TE+X*(1.0-Y*Z)
VRC=VR*K**8065.7
VRDT=VRC+(1.674E-15*ROT*(ROT+1))/(U*(K**1.0E-8)**2)
VRDT=VRDT/K**8065.7
TEST FOR RANGE
IF(R.GE.DELTAF) STOP
WRITE(6,4) R, VR, VRC, VRDT, DELTAK
DELTAK=DELTAK+0.1
GO TO 5
1 FORMAT(2F6.2)
2 FORMAT(2F6.4,F7.4)
3 FORMAT(F6.4,F7.4)
4 FORMAT(2F10.5,F10.1,F10.5,F10.1)
8 FORMAT(F5.1)
9 FORMAT(F8.5)
10 FORMAT(2F6.3)
END

LINE

PROGRAM TO EVALUATE ATOMIC LINE PROFILES WITH SELF-REVERSAL.
REAL INT, I
READ(5,1) IO, P
DELTA=1.0
U=-7.0
PV0=(DELTA/3.142)/(DELTA**2)
3 X=U/DELTA
PV=((DELTA/3.142)/(U**2+DELTA**2))
INT=U*PV*EXP(-P*PV/PV0)
WRITE(6,2) X, INT
U=U+0.5
IF(U.GT.-8.0) STOP
GO TO 3
1 FORMAT(2F4.1)
2 FORMAT(2F10.2)
END
PROGRAM TO EVALUATE INTERMOLECULAR POTENTIALS.

WRITE(6,4)
READ(5,5) J
WRITE(6,26)
WRITE(6,27)
WRITE(6,1)
READ(5,5) I
IF(I.EQ.1) GO TO 2
IF(I.EQ.2) GO TO 3
C LENNARD JONES POTENTIAL
IF(J.EQ.1) GO TO 6
READ(5,7) EPSIL1, EPSIL2, DELTA1, DELTA2
EPSIL=SQRT(EPSIL1*EPSIL2)
DELTA=(DELTA1+DELTA2)/2.0
WRITE(6,50) EPSIL, DELTA
GO TO 28
6 READ(5,5) EPSIL, DELTA
28 READ(5,9) K, KMAX
10 V=4.0*EPSIL*((DELTA/K)**12-(DELTA/K)**6)
V1=V*6.62E-5
WRITE(6,11) K, V, V1
K=K+1.*I
IF(K.GE.KMAX) STOP
GO TO 10
C MODIFIED BUCKINGHAM POTENTIAL
2 IF(J.EQ.1) GO TO 12
READ(5,13) EPSIL1, EPSIL2, K1, K2, ALPHA1, ALPHA2
EPSIL=SQRT(EPSIL1*EPSIL2)
K=(K1+K2)/2.0
ALPHA=SQRT(ALPHA1*ALPHA2)
GO TO 29
12 READ(5,14) EPSIL, KM, ALPHA
29 READ(5,15) K, KMAX
16 IF(K.GE.KMAX) GO TO 17
WRITE(6,18)
STOP
17 V2=(EPSIL/(1.0-(6.0/KM*ALPHA)))
V2*6.0/ALPHA*EXP(ALPHA*(1.0-K/KM))-(KM/K)**6)
V1=V*6.62E-5
WRITE(6,11) K, V, V1
K=K+1.*1
GO TO 16
C BUCKINGHAM-CURKNER POTENTIAL
3 IF(J.EQ.1) GO TO 19
READ(5,20) EPSIL, EPSIL2, K1, K2, ALPHA1, ALPHA2, BETA1, BETA2
EPSIL=SQRT(EPSIL1*EPSIL2)
K=(K1+K2)/2.0
ALPHA=SQRT(ALPHA1*ALPHA2)
BETA=SQRT(BETA1*BETA2)
GO TO 30
19 READ(5,21) EPSIL, KM, ALPHA, BETA
30 READ(5,22) K, KMAX
23 C=(EPSIL*ALPHA*KM**6)/(ALPHA*(1.0+BETA)-6.0-6.0*BETA)
B1=(EPSIL*(1.0+BETA)*C*1.0/KM**6)*EXP(ALPHA)
C1=BETA*KM**2+C
IF(K.LE.KM) GO TO 24
COUNT/
CONT.

\[ V = B \times e^{(-\alpha \cdot (k/m))} - (c/k^6 + c1/k^8) \]

GO TO 25

24 \[ V = B \times e^{(-\alpha \cdot (k/m))} - (c/k^6 + c1/k^8) \times e^{(-4 \cdot (k/m - 1.0))^3} \]

25 \[ V1 = V \times 8.62 \times 10^{-5} \]

GO TO 6,11

K = R + U + 1

IF (K GE KMAX) STOP

GO TO 23

1 FORMAT(1H 'LENNARD-JONES POTENTIAL(3)')

26 FORMAT(1H 'MODIFIED-BUCKINGHAM POTENTIAL(1)')

27 FORMAT(1H 'BUCKINGHAM-CUKNER POTENTIAL(2)')

4 FORMAT(1H 'MOLECULES LIKE(1) OR UNLIKE(3)')

5 FORMAT(11)

7 FORMAT(2F6.1,2F6.3)

8 FORMAT(6F5.2)

9 FORMAT(2F6.3)

11 FORMAT(2F16.3,E14.3)

13 FORMAT(6F5.2)

14 FORMAT(3F5.2)

15 FORMAT(2F6.3)

16 FORMAT(1H 'INFINITY')

20 FORMAT(6F5.2)

21 FORMAT(4F5.2)

22 FORMAT(2F6.3)

50 FORMAT(2F12.3)

END

C

PROGRAM TO EVALUATE REDUCED POTENTIAL CURVES USING HULBETT AND HIRSCHFELDER POTENTIAL CURVES.

READ (5,1) D,B,C,BETA

READ (5,2) KEW,KMIN,KMAX

READ (5,5) K,UMEGA,PI

K = KMIN

FK = K*UMEGA**2

4 EPSILON = (K-KEW)/KEW

A = BETA*EPSILON

V = D*(1.0-EXP(-A))**2+C*A**3*(1.0+A)*EXP(-3.0-B)*A

U = V/D

P = (K-(1.0-EXP(-K/PI))*PI)/(KEW-(1.0-EXP(-K/PI))*PI)

WRITE (6,3) K, V, P, U

K = K + U + 0.3

IF (K GE KMAX) STOP

GO TO 4

1 FORMAT(4F7.4)

2 FORMAT(3F6.3)

3 FORMAT(4F14.3)

5 FORMAT(2F9.4,F7.4)

END
PROGRAM TO EVALUATE POTENTIAL ENERGY VALUES OF THE INTERACTION BETWEEN AN ATOM AND A DIATOMIC MOLECULE.

READ(5,1) X,Y
READ(5,1) AMAX,YMAX
READ(5,3) K3
DE=0.5444
B=0.969878
KE=5.7284
F=93.7*8.62E-5
ALPHA=13.75
RM=3.8/0.52917

C CALCULATION OF MOLECULAR POTENTIAL
VM=DE*(1.0-EXP(-B*(K3-RK)))**2
WRITE(6,4) VM

C CALCULATION OF BUCKINGHAM POTENTIAL PARAMETERS
A=(6*EXP(ALPHA))/ALPHA**6
C=ALPHA**6(ALPHA**6)/ALPHA**6
A1=ALPHA/RM
WRITE(6,9) A,C,A1

C CALCULATION OF DISTANCES OF ATOM FROM ATOMS IN MOLECULE
R1=SQR((X-Y)**2+(Y-YMAX)**2)
R2=SQR((X+Y)**2+(Y+YMAX)**2)

C CALCULATION OF POTENTIAL BETWEEN ATOM AND MOLECULE

IF(Y.GT.YMAX) 3070 6
GO TO 7
6 A=1.0
IF(A.GT.AMAX) STOP
GO TO 8

FORMAT(2F5.2)
3 FORMAT(F6.4)
4 FORMAT(E14.3)
9 FORMAT(2F9.2,E14.3)
END

FOR INTERACTION OF ATOM WITH TRIATOMIC WITH A BENT CONFIGURATION K1 AND K2 ARE REPLACED WITH:

K1=SQR((X-K3*COS(ANG)**2+(Y-K3*SIN(ANG)**2)
K2=SQR((X**2+Y**2)
K4=SQR((X-K3*COS(ANG)**2+(Y+K3*SIN(ANG)**2)

THE APPROPRIATE VALUES FOR THE VARIOUS PARAMETERS ARE EDITED INTO THE PROGRAM AND VI IS REPLACED BY:

V2=*(1.0/K1**6+1.0/K2**6+1.0/K4**6)
VI=VI1-V2+VM
GRAPH2

C PROGRAM TO DRAW POTENTIAL CURVES FOR DIATOMICS.

INTEGER*4 PI,NLINE,CH(5)
REAL*8 PA,PY,X(26),Y(26)

DATA CH/'-',' ','3','5','7'/,NLINE/10/,PI/176/

C OPEN PLOTTER FILE AND ADD JOB I.D. INFORMATION
CALL OPENGR(50)
CALL DRSLGR('M,TRAINE1, CHEMISTRY',20)

C WINDOW AND COORDINATE SYSTEM SPECIFICATIONS
CALL GRAREA(0.D0,0.D0,35.D0,35.D0,'CMS')
CALL SCALGR(2.D0,2.D0,4.D0,5.D0,0.D0)

C DRAW X-AXIS, ADD TITLE AND NUMBER IT
CALL AXISGR(U.D6,0.D0,'x',0.5D0.4)
CALL ANNOGR(0.D0,2.100,0.050,0.DO)
CALL DRSLGR('X-AXIS',6)

1 PI=2.DO
DO 1 I=1,5
    PA=-0.4DO
    CALL ANNOGR(PA,PY-0.05D0,0.00DO,0.DO)
    CALL DRSLGR(PA,1.2)
1    PA=PY-0.5D0
C NUMBER X-AXIS, ADD TITLES AND DRAW
PA=0.DO
DO 2 I=1,8
    CALL ANNOGR(PA,-0.1DO,0.05D0,0.DO)
    CALL DRSLGR(PA,1.2)
2    PA=PA+1.DO
    CALL ANNOGR(3.5DO,-0.3DO,0.05DO,0.DO)
    CALL DRSLGR('X-AXIS',6)
    CALL AXISGR(7.DO,0.DO,'-X',1.DO,8)
C READ DATA VALUES
READ(5,10),(X(I),Y(I),I=1,26)

10 FORMAT(208,2)

C DRAW CURVE
CALL CURVGR(X(1),Y(1),26,2.30DO,4.77DO,0.DO2DO,0.DO2DO,
            *1.DO,0.DO,0.DO)
C ADD TITLE OF GRAPH
CALL ANNOGR(2.DO,2.DO,0.06DO,0.DO)
CALL DRSLGR(224)
CALL DRSLGR('POTENTIAL CURVE, IODINE',23)

C COMPLETION OF FILE
CALL CLSGR
STOP
END
PROGRAM TO EVALUATE 2ND ORDER RATE CONSTANTS AND TO DRAW PLOTS WITH ERROR BARS.

INTEGER*4 PI,NLINE,CH(5)
REAL*8 X(30),Y(30),DX(30),DY(30),SP,SC,PMAX
REAL*8 CI,PR,PX,PY,CMAA,GB,A,CY,PMAX,CMIN

DATA CH/'-'.
WRITE(6,8)
WRITE(6,9)
READ(5,6) FMIN,PMAX
WRITE(6,10)
READ(5,7) CMIN,CMAA
WRITE(6,14)
READ(5,15) M
IF(M.EQ.1) GO TO 16
PMAX=PMAX*133.32D0
PMAX=PMAX*133.32D0
PR=(PMAX-FMIN)*0.1D0
CI=(CMAA-CMIN)/5.0D0
SP=1.0D0/PR
SC=1.0D0/CI

CALL OPENGR(50)
CALL DRSTRG('TRAINEX, CHEMISTRY',17)
CALL GRANEA(0.0,0.0,15.0,15.0,'INS')
CALL SCLGR(2.0,2.0,SP,SC,0.0)
CALL AXISGR(PMIN,PMAX,'+',PR,10)
CALL ANUGR(PMIN,PMAX,CMIN-CI,PR/10.0,0.0)
IF(M.EQ.1) GO TO 16
CALL DRSTRG('PRESS.(N.M-2)'',14)
GO TO 26
16 CALL DRSTRG('PRESS.(TORR)'',12)
26 PX=PMAX
DO 2 I=1,11
CALL ANUGR(PX,CMIN-0.4D0*CI,PR/13D0,0.0)
CALL DRNUMG(PX,1.3)
2 PX=PX-PR
CALL AXISGR(PMIN,CMIN,'Y',CI,5)
CALL ANUGR(PMIN-PR,CMIN,PR/10.0,90.0)
CALL DRSTRG('1ST ORDER COEFFS.(1/S)'',22)
PY=CMAA
DO 3 I=1,6
CALL ANUGR(PMIN-PR/1.2D0,PY,PR/13D0,0.0)
CALL DRNUMG(PY,4.0)
3 PY=PY-CI
CALL ANUGR(PR,CMAA,PR/10.0,0.0)
CALL DRSTRG(224)
CALL DRSTRG('2ND ORDER RATE CONSTANT',23)
WRITE(6,11)
READ(5,4) N
WRITE(6,12)
READ(5,1) (X(I),Y(I),I=1,N)
WRITE(6,13)
READ(5,5) (DY(I),I=1,N)
8 FORMAT(1H 'ALL INPUT IN DOUBLE PRECISION')
14 FORMAT(1H 'PRESS. IN TORR(1) OR N.M-2(2)')
15 FORMAT(11)
9 FORMAT(1H 'MINIMUM AND MAXIMUM PRESS. VALUES(TORR)')
CONT.
10 FORMAT(1H 'MIN. AND MAX. 1ST ORDER RATE GUEFF. VALUES')
11 FORMAT(1H 'NO. OF POINTS')
12 FORMAT(1H 'RATE GUEFF. ERRORS')
13 FORMAT(1I2)
14 FORMAT(D9.3,1D11.1)
15 FORMAT(D9.1)
16 FORMAT(2D10.3)
17 FORMAT(D9.1,1D11.1)
18 IF(M.EQ.1) GOTO 18
DO 19 I=1,N
19 Z(I)=X(I)*133.3200
CALL LINESG(Z,Y,1,N,0.D0,0.D0,1,P/13.D0)
GOTO 22
16 CALL LINESG(X,Y,1,N,0.D0,0.D0,1,P/13.D0)
22 CALL LTMS(X,Y,DY,N,N,N,N,A,GB)
CALL DRNUMG(GB,0,2)
CY=GB*3.2D16+A
CALL PLUTGR(1,0.D0,A,0.D0,0.D0)
IF(M.EQ.1) GOTO 24
24 CALL PLUTGR(2,Z(N),CY,0.D0,0.D0)
I=1
25 CALL PLUTGR(1,Z(I),Y(I)-DY(I),0.D0,0.D0)
CALL PLUTGR(2,Z(I),Y(I)+DY(I),0.D0,0.D0)
I=I+1
IF(I.GT.N) GOTO 20
GO TO 25
21 CALL PLUTGR(1,X(I),Y(I)-DY(I),0.D0,0.D0)
CALL PLUTGR(2,X(I),Y(I)+DY(I),0.D0,0.D0)
I=I+1
IF(I.GT.N) GOTO 20
GOTO 21
20 CALL CLOSEG
STOP
END

SUBROUTINE LTMS(X,Y,DY,I,J,L,N,A,GB)
REAL*8 X(I),Y(J),DY(L)
SA=0
SY=0
SAY=0
SA2=0
SDY=0
K=1
WRITE(6,6)
READ(5,4) TEMP
10 SA=SA+A(K)
SY=SY+Y(K)
SAY=SAY+A(K)*Y(K)
SA2=SA2+A(K)**2
SDY=SDY+DY(K)**2
K=K+1
CLOSE.
CONT.

IF(K.LE.N) GO TO 10
AN=N
B=(XN*SA-Y-SY)/(AN*SA-SA**2)
A=(SY-B*SA)/AN
S=SRT(SD/(AN-2.0))
SA=SRT(SA2/(AN*SA2-SA**2))
SB=SB*22400.0D0*760.0D0*TEMP)/(6.023023*273.0D0)
GSB=(SB*22400.0D0*760.0D0*TEMP)/(6.023023*273.0D0)
WRITE(6,8)
WRITE(6,3) GB
WRITE(6,9)
WRITE(6,3) GSB
WRITE(6,12)
WRITE(6,5) A
WRITE(6,11)
WRITE(6,5) SA
4 FORMAT(D9.1)
3 FORMAT(E13.3)
5 FORMAT(F13.1)
6 FORMAT(1H 'TEMP. AT WHICH EAPTS. WERE CARRIED OUT')
8 FORMAT(1H '2ND ORDER RATE CONSTANT(CC.1/MOLECULE.1/S)')
9 FORMAT(1H 'ERROR IN CONSTANT(+ OR -)')
12 FORMAT(1H 'ERROR IN INTERCEPT(+ OR -)')
RETURN
END

LGRAPH

C PROGRAM TO EVALUATE SECOND ORDER RATE CONSTANTS
C AND TO DRAW PLOTS (SCALING OF PLOT INCORPORATED).
DIMENSION X(30), Y(30)
DATA ICODE/244/
WRITE(6,3)
READ(5,2) N
WRITE(6,4)
2 FORMAT(12)
READ(5,1) (A(I),Y(I),I=1,N)
1 FORMAT(F5.3,F7.1)
3 FORMAT(1H 'NO OF POINTS')
4 FORMAT(1H 'INPUT PRESS. AND 1ST ORDER COEFF. VALUES')
WRITE(6,5)
5 FORMAT(1H 'PRESS. IN TURK(1) UN N*M -2(2)')
6 FORMAT(11)
READ(5,6) M
IF(M.EQ.1) GO TO 7
DO 8 I=1,N
8 X(I)=A(I)*133.32
7 CALL PLOTS('TRAINERS CHEMISTRY',17,50)
CALL PLOT(2,2,3)
CALL SCALE(X,10,N,1)
CALL SCALE(Y,5,N,1)
IF(M.EQ.1) GO TO 9
CALL AXIS(0,0,'PRESS. (N*M -2)',-14,10,0,A(N+1),A(N+2))
GO TO 10
9 CALL AXIS(0,0,'PRESS. (TURK)',-12,10,0,A(N+1),A(N+2))
CONT.

10 CALL AXIS(0,0,1ST ORDER COEFFS.(1/S),22,
*5,90.,Y(N+1),Y(N+2))
CALL LINE(X,Y,N,1,-1,244)
CALL PLOT(15.*0.,999)
IF(M.EQ.1) GO TO 10
DU 12 I=1,N
12 X(I)=X(I)/133.32
11 CALL LMS(X,Y,N,NsN,N)
STOP
END

SUBROUTINE LMS(X,Y,I,J,N)
DIMENSION D(30),X(I),Y(I)
SA=0
SY=0
SXY=0
SX2=0
SDY=0
K=1
WRITE(6,6)
READ(5,4) TEMP
WRITE(6,7)
READ(5,2) (D(I),I=1,N)
10 SAS?c+A(K)
S(=SY+Y(K))
SXY=SXY+X(K)*Y(K)
SX2=SX2+X(K)**2
SDY=SDY+D(K)**2
K=K+1
IF(K.LE.N) GO TO 10
XN=N
B=(XN*SXY-SX*SY)/(XN*SX2-SX**2)
A=(SY-B*SX)/XN
S=SQRT(SDY/(XN-2.0))
SA=SQRT(SX2/(XN*SX2-SX**2))
SB=S/SQRT(SX2/XN)*SA)
GB=(B*22400.0*760.0*TEMP)/(6.023E23*273.0)
GSB=(SB*22400.0*760.0*TEMP)/(6.023E23*273.0)
WRITE(6,6)
WRITE(6,3) GB
WRITE(6,9)
WRITE(6,3) GSB
WRITE(6,12)
WRITE(6,5) A
WRITE(6,11)
WRITE(6,5) SA
2 FORMAT(F5.1)
4 FORMAT(F5.1)
3 FORMAT(E13.3)
5 FORMAT(F13.1)
6 FORMAT(1H "TEMP. AT WHICH EXPPTS. WERE CARRIED OUT")
7 FORMAT(1H "INPUT 1ST ORDER COEFF. ERRORS")
8 FORMAT(1H "2ND ORDER RATE CONSTANT(CC. 1/MOLECULE, 1/S)")
9 FORMAT(1H "ERROR IN CONSTANT(+ UK -)")
12 FORMAT(1H "INTERCEPT(1/S)")
11 FORMAT(1H "ERROR IN INTERCEPT(+ UK -)")
RETURN
END
APPENDIX III

SELF-REVERSAL OF LINE EMISSION FROM ATOMIC LAMPS

The phenomenon of self-reversal is important in atomic lamps and has been studied extensively. When light is emitted from the discharge zone in the lamp it has to travel to the reaction cell. During this passage it is subject to absorption as there are in its path atoms of the same kind which cause emission. Thus the light observed outside the lamp is weakened. Different spectral lines may be weakened to a different extent and within a single spectrum line the absorption varies markedly as a function of the wavelength. This phenomenon in the light source itself is known as self-absorption. Self-reversal is an extreme case of self-absorption where the absorption at the centre of the spectrum line is much stronger than on the sides. This can greatly reduce the efficiency of the resonance absorption system.

An intensive theoretical study of self-reversal is beyond the scope of this study however some attempt has been made to simulate the behaviour of a spectral line under different conditions. A computer program, LINE (see Appendix II) was used to generate profiles of lines in different states of self-absorption.

For a spectral line with frequency $\nu_0$ at the centre, which travels with velocity $c$ in the $x$-direction the intensity of the line at a specific wavelength $\nu$ is determined by the expression

$$I(\nu) = I_oP(\nu) \exp\left[\frac{-\rho(\nu)}{P(\nu)}\right]$$

where $I_o$ is the total intensity of the spectral line for no
absorption and the quantity $\phi$ is regarded as a function of the total amount of absorbing vapour that the light traverses and therefore increases with vapour density. $P(\nu)$ is a function giving the frequency distribution of the emitted energy. Two functions are important in the study of self-absorption:—

(a) The natural resonance form which can be expressed as

$$P(\nu) = \left( \frac{b}{\pi} \right) / \left[ (\nu - \nu_0)^2 + b^2 \right]$$  \hspace{1cm} (A3.2)

where $b$ = natural half-width of the spectral line and is a constant.

(b) The Doppler distribution, expressed as

$$P(\nu) = \left( \frac{1}{\tau b^2} \right)^{\frac{1}{2}} \exp \left[ -\frac{\ln 2}{b^2} (\nu - \nu_0)^2 \right]$$  \hspace{1cm} (A3.3)

where with thermal equilibrium the half-width at half the maximum amplitude is

$$b = \left[ \ln 2 \left( \frac{2kT}{mc^2} \right) \right]^{\frac{1}{2}}$$  \hspace{1cm} (A3.4)

where $k$ = Boltzmann constant

$T$ = temperature

$m$ = mass of atom

$c$ = speed of light.

Using the resonance distribution in equation (A3.1) a series of line profiles were generated by varying the parameter and the results are shown in figure A3.1. The shape of a line without absorption occurs at $\phi = 0$. For $\phi > 1.0$ a dip in the centre is clearly seen and this no doubt indicates self-reversal.

Mathematical models of self-reversal systems have been presented by Kaufmann and Parkes\(^2\) and by Braun and Carrington.\(^3\)
Natural Resonance Form.

\[ I(\nu) = I_0 P(\nu) \exp\{-\rho P(\nu) / P(\nu)\} \]

\[ P(\nu) = \left( \frac{\delta}{\pi} \right) / \left[ (\nu - \nu_0)^2 + \delta^2 \right] \]

\[ P(\nu_0) = \text{value of } P(\nu) \text{ when } \nu = \nu_0. \]

**Figure A3.1** Profiles of spectrum line with varying degrees of self-reversal.
REFERENCES

APPENDIX IV
CONSTRUCTION OF 10 POTENTIAL CURVES

The potential curves shown in section 4.2 were accurately constructed using a method presented by Steele and Lippincott. It is essential to have accurate potential curves as they are of considerable value for the understanding of kinetic mechanisms, spectral phenomena, etc.

The potential energy is defined by the expression

\[ V(r) = D_e \left( 1 - \exp\left[-(n\Delta r^2 / 2r)\right]\right) \cdot \left( 1 - a(b^2r / 2r)^{1/2} \Delta r \exp\left[-(b^2r / 2re)^{1/2}\Delta r\right]\right) \]  

(A4.1)

The second term describes the Van der Waal's energies of interaction at large values of \( r \).

- \( D_e \) = dissociation energy
- \( r_e \) = equilibrium value of the interatomic distance
- \( \Delta r = r_e - r \)
- \( b = 1.065 \pm 0.03 \) and is constant for all states of all molecules except \( H_2 \) which has the value of 1.16.

It has been shown that the term \( a \) is periodic within the periodic table for homonuclear diatomics (see table A4.1) and can be determined from the expression

\[ a = \left( \omega_e / 6B_e^2 \right) / \left( 1 + \frac{5}{4} \left( \omega_e / 6B_e^2 \right) \right) \]  

(A4.2)

where the rotational and vibrational constants are as defined by Herzberg.

For heteronuclear diatomics the \( a \) value can be calculated by taking the mean value of \( a \) for each constituent atom (except for hydrides were \( a(H) = 0.376 \)),

\[ a(IO) = \frac{a(I_2) + a(O_2)}{2} = 0.615 \]  

(A4.3)
Table A4.1 Values for the a parameter for homonuclear diatomics in the periodic table.

<table>
<thead>
<tr>
<th></th>
<th>H₂</th>
<th>Li₂</th>
<th>Na₂</th>
<th>K₂</th>
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<tbody>
<tr>
<td></td>
<td>0.344</td>
<td>0.475</td>
<td>0.495</td>
<td>0.515</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>B₂</th>
<th>C₂</th>
<th>N₂</th>
<th>O₂</th>
<th>F₂</th>
</tr>
</thead>
<tbody>
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<td>0.515</td>
<td>0.535</td>
<td>0.555</td>
<td>0.575</td>
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<tr>
<td></td>
<td>Si₂</td>
<td>P₂</td>
<td>S₂</td>
<td>Cl₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.555</td>
<td>0.575</td>
<td>0.595</td>
<td>0.615</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Se₂</td>
<td>Br₂</td>
<td>Te₂</td>
<td>I₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.605</td>
<td>0.635</td>
<td>0.615</td>
<td>0.655</td>
<td></td>
</tr>
</tbody>
</table>

To determine a values for excited states the expression

\[
a^* = \frac{4}{3} \left( 1 - \frac{\omega^*}{\omega(x)} \frac{r^*}{r(x)} \right) \left[ 1 - \frac{5}{4} a(x) \right]
\]

(A4.4)

where \( \omega^* \), \( r^* \) are \( \omega_e \), \( r_e \) of the excited state and \( \omega(x) \), \( r(x) \) and \( a(x) \) are \( \omega_e \), \( r_e \) and a values of the ground state. For the excited state of I0, \( a = 0.656 \).

The term n in expression (A4.1) is defined by

\[
n = \frac{k_e r_e}{D_e}
\]

(A4.5)

where \( k_e \) = force constant.

Table A4.2 shows a periodic table of n values and these are considered as a characteristic property of each homonuclear diatomic containing a specific element.3
Table A4.2 Values for the parameter n for homonuclear diatomics of specific elements in the periodic table.

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>5.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>12.8</td>
<td>N</td>
<td>15.9</td>
<td>O</td>
</tr>
<tr>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td></td>
</tr>
<tr>
<td>9.0</td>
<td>13.0</td>
<td>13.3</td>
<td>16.3</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>9.5</td>
<td>13.5</td>
<td>13.6</td>
<td>17.6</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>15.7</td>
<td>16.0</td>
<td>18.4</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>10.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The n value for a heteronuclear molecule can be determined from the square root of the product of the n values of the atoms in the diatomic,

\[ n_{10} = (n_1 n_0)^{\frac{1}{2}} = 17.8 \]  

(A4.6)

A computer program, MORSEL (see Appendix II) was written incorporating expression (A4.1) for calculation of potential energy values. The output data was shown graphically using computer program GRAPH1.

To check that the program was accurate, potential energy values were calculated for \( I_2(XX^+ \text{g}) \) and compared against observed values. Agreement was good (0.2% discrepancy for large values of \( r \) in the
attractive region and up to 3% discrepancy for small values of \( r \) in the repulsive region). Hence 10 potential curves were constructed using the parameter values given in table A4.3.

Table A4.3  Parameter values for IO potential curve construction.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>( D_e ) (eV)</th>
<th>( r_e ) (Å)</th>
<th>( a )</th>
<th>( b )</th>
<th>( n_I )</th>
<th>( n_0 )</th>
<th>( T_e ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IO(( X^2\Pi_\frac{1}{2} ))</td>
<td>1.9</td>
<td>1.868</td>
<td>0.615</td>
<td>1.065</td>
<td>18.4</td>
<td>17.3</td>
<td>0</td>
</tr>
<tr>
<td>IO(( A^2\Pi_\frac{1}{2} ))</td>
<td>1.2</td>
<td>2.072</td>
<td>0.656</td>
<td>1.065</td>
<td>18.4</td>
<td>17.3</td>
<td>2.6</td>
</tr>
</tbody>
</table>

THE EFFECTS OF ROTATION ON THE POTENTIAL ENERGY CURVE

For the rotating IO molecule the potential energy is increased by a quantity equal to the kinetic energy of the rotation

\[
\text{K.E. of rotation} = \frac{\hbar}{2\pi^2 c \nu r^2} J(J+1) \tag{A4.7}
\]

where \( \hbar \) = Planck's constant
\( c \) = velocity of light
\( \nu \) = reduced mass (\( \nu_{IO} = 14.209 \))
\( J \) = rotational quantum number.

If \( V_0(r) \) is the potential energy of the non-rotating molecule, then the potential energy of the rotating molecule is

\[
V(r) = V_0(r) + \frac{\hbar J(J+1)}{2\pi^2 c \nu r^2} \tag{A4.8}
\]

The potential curves showing rotational effects (figure A4.1) were generated using a computer program, MORSE2 (see Appendix II)
Figure A4.1 Potential curves of the ground state IO molecule showing rotational effects.
which used the Lippincott function and incorporated expression (A4.8) to account for the rotation.

**Reduced Potential Curves**

Since it was desirable to compare the potential energy curves for I, BrO and ClO the concept of the Reduced Potential Curve (RPC) was considered. This makes possible a comparative study of the potential curves of various diatomics in a single scheme. The method adopted here to construct RPCs was that presented by Jenč and Pliva.\(^5\) The reduced potential energy is defined as

\[
u = \frac{V_0(r)}{D_e} \tag{A4.9}
\]

and the reduced internuclear distance by

\[
n = \frac{r - \left[1 - \exp\left(-\frac{r}{\rho_{ij}}\right)\right] \rho_{ij}}{r_e - \left[1 - \exp\left(-\frac{r}{\rho_{ij}}\right)\right] \rho_{ij}} \tag{A4.10}
\]

\[
\rho_{ij} = \frac{r_e - (\kappa D_e/\kappa_e)^{\frac{1}{2}}}{1 - \exp\left(r_e/\rho_{ij}\right)} \tag{A4.11}
\]

\(\kappa = 3.96\) for all molecules and \(\kappa_e = \nu \omega_e^2\). The reduced quantities are dimensionless and for each diatomic the minimum occurs at \(\rho = 1\) and the dissociation limit at \(u = 1\). The parameter \(\rho_{ij}\) takes account of the repulsive effect of the electrons and must be evaluated for each diatomic.

The Hulbert-Hirschfelder function\(^6\) was chosen as a basis for the reduced potential curves

\[
V_0(r) = D_e \left[1 - \exp(-x)\right]^2 + c x^3 (1 + x) \exp(-3 - b) x \tag{A4.12}
\]

where

\[
x = \frac{\omega_e}{2(B_e D_e)^{\frac{1}{2}}} \cdot \frac{r - r_e}{r_e} = 2 \beta \epsilon \tag{A4.13}
\]

\[c = 1 + a_1 (D_e/a_0)^{\frac{1}{2}} \tag{A4.14}\]
Expression (A4.12) was combined with (A4.9) and (A4.10) in a computer program, RED (see Appendix II) which evaluated the RPCs for chosen diatomics. To check the accuracy of the program the RPCs for I₂, Cl₂, Br₂ and H₂ were determined and compared against those evaluated from Rydberg - Klein curves. The latter are calculated directly from experimental data. Good agreement was obtained (0.6% discrepancy in the repulsive region at small reduced interatomic distance values and up to 1.4% discrepancy at large reduced interatomic distance values).

Figure A4.2 shows the RPCs for IO, BrO, ClO and SO. Figures A4.3 and A4.4 show these curves in the expanded regions \( \phi = 0.5 - 0.7 \) and \( \phi = 2.0 - 3.0 \) respectively. Table A4.4 gives the spectroscopic data used to evaluate these RPCs. The \( \phi_{ij} \) values were calculated from equation (A4.11) using an iterative method.

From figure A4.2 it is seen that the RPCs for IO, BrO and ClO are very similar and this is in agreement with the observation that groups of closely related diatomic molecules have similar RPCs. However if IO (group VII for I) is compared with SO (group VI for S) there is a very great difference in the shape of the RPC at higher values of \( \phi \). Presumably SO would be similar to O₂ and SeO. Comparison of IO with I₂ shows a very close similarity of RPCs as does I₂ with Cl₂ and Br₂. So the halogen atom seems to dominate and determine the characteristics of the IO,
Figure A4.2 Reduced potential curves for diatomics.
Figure A4.4 Reduced potential curves in the attractive region.

Figure A4.5 Reduced potential curves in the repulsive region.
Table A4.4 Spectroscopic parameters for reduced potential curve evaluation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>IO(^a)</th>
<th>ClO(^b)</th>
<th>ClO(^d)</th>
<th>BrO(^c)</th>
<th>So(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_e) (eV)</td>
<td>1.9</td>
<td>1.9</td>
<td>2.75</td>
<td>2.2</td>
<td>5.22</td>
</tr>
<tr>
<td>(\nu)</td>
<td>14.209</td>
<td>11.026</td>
<td>10.975</td>
<td>13.332</td>
<td>10.665</td>
</tr>
<tr>
<td>(\omega_e) (cm(^{-1}))</td>
<td>687</td>
<td>780</td>
<td>854</td>
<td>713</td>
<td>1124</td>
</tr>
<tr>
<td>(\omega_e \chi_e) (cm(^{-1}))</td>
<td>5</td>
<td>9.92</td>
<td>5.5</td>
<td>7</td>
<td>6.12</td>
</tr>
<tr>
<td>(B_e) (cm(^{-1}))</td>
<td>0.3389</td>
<td>0.622</td>
<td>0.6234</td>
<td>0.4282</td>
<td>0.7089</td>
</tr>
<tr>
<td>(\alpha_e) (cm(^{-1}))</td>
<td>0.00271</td>
<td>0.00891</td>
<td>0.00364</td>
<td>0.00469</td>
<td>0.00562</td>
</tr>
<tr>
<td>(r_e) (Å)</td>
<td>1.8679</td>
<td>1.571</td>
<td>1.7172</td>
<td>1.72</td>
<td>1.4933</td>
</tr>
<tr>
<td>(\rho_{ij})</td>
<td>2.3374</td>
<td>1.6132</td>
<td>1.422</td>
<td>1.8131</td>
<td>1.152</td>
</tr>
</tbody>
</table>

(References for table A4.4, \(a\) : 2, 4, 7 ; \(b\) : 2, 4, 8 ; \(c\) : 2, 4, 9 ; \(d\) : 10).

ClO and BrO molecules' potential curves. The similarity of the RPCs of a group of molecules is equivalent to the conclusion that the bonding is essentially the same for all these molecules.

When comparing the SO reduced potential curve with those for IO, BrO and ClO, it is seen that in the halogen oxides the curves show a decrease in reduced potential energy in the attractive region. This effect has previously been observed\(^7\) for other groups of diatomics and is due to the higher atomic number of the group VII atoms in the halogen oxides. For the greater atomic number of the halogen atoms in the halogen oxides, the reduced attractive force decreases for \(r > r_e\) (see figure A4.4) and the reduced repulsive force increases for \(r < r_e\) (see figure A4.3).
Within the halogen oxide group it is seen that for IO and BrO the RPCs are very close and a discrepancy was observed in the RPC for ClO in the attractive region. The curve lay too far to the right. Discrepancies have also been observed for the ground state Cl₂ reduced potential curve\(^{11}\) and errors in spectroscopic parameters have been suggested for this effect. However new spectroscopic data became available for ClO\(^{10}\) and was used to construct a new RPC which was found to lie in the predicted region, suggesting that this spectroscopic data is correct.

The reduced potential curves have therefore been useful in showing differences between diatomic groups and in detecting errors in spectroscopic data.

**INTERMOLECULAR POTENTIALS**

In the formation of a complex in an interaction, binding energies are important. Lennard-Jones potentials have been used to calculate binding energies due to dispersion forces for complexes involved in atom and radical recombination reactions.\(^{12}\) Also a correlation has been established between the intermolecular potential well depth and the probability for quenching of excited molecules.\(^{13}\)

To investigate the intermolecular potentials a computer program INPOT (see Appendix II) was written and gives a choice of a Lennard-Jones, a Buckingham-Corner or a Modified Buckingham potential.\(^{14}\)

In a study involving a neon atom and an excited iodine molecule, \(I₂(B³Π\text{ou+})\), the interatomic \(I₂⁺\) potential was represented by a Morse potential and the potential between each of the iodine atoms in the \(I₂\) and the Ne atom was given by a Modified Buckingham potential.\(^{15}\) A computer program POTEN2 (see Appendix II) was written to model this system and may be modified for I atom - quenching molecule systems.
REFERENCES

LECTURES ATTENDED

In accordance with the regulations of the University of Edinburgh, Department of Chemistry, the post-graduate lecture courses etc. attended during the period of study were as follows:

(1) Atomic and molecular collision processes;
(2) The gaseous environment;
(3) Quantum theory and spectroscopy;
(4) Chemistry of the atmosphere;
(5) Chemistry of the aqueous environment;
(6) Colloids and the environment;
(7) Fortran IV computing course;
(8) German translation, including a written examination.

Also many of the seminars in the chemistry department were attended. The kinetic and molecular beam groups discussions were also regularly attended.

In addition, two conferences were attended:
University of Cambridge (August 1978)
University of Keele (September 1979).
TIME-RESOLVED RESONANCE FLUORESCENCE STUDY OF ELECTRONICALLY EXCITED IODINE ATOMS: QUENCHING OF I(5^2P_{1/2}) BY HCN, NH_3 AND OCS

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(Received July 3, 1978)

Summary

Quenching of electronically excited iodine atoms I(5^2P_{1/2}) by HCN, NH_3 and OCS has been studied at 295 K using time-resolved resonance fluorescence. The quenching efficiency for NH_3 is shown to be relatively high \( k(\text{NH}_3) = (2.1 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and it is suggested that quenching occurs via near-resonant electronic to vibration-rotation (E-VR) energy transfer. Quenching by OCS and HCN is less efficient owing to the absence of near-resonant E-VR channels \( k(\text{HCN}) = (6.8 \pm 0.7) \times 10^{-14}, \ k(\text{OCS}) = (1.6 \pm 0.1) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). The use of NH_3, HCN and OCS in E-VR transfer lasers is discussed briefly.

1. Introduction

Recent reports that electronic to vibration-rotation (E-VR) energy transfer can be utilized to pump semi-tunable IR lasers has aroused considerable interest in this area of energy transfer. Petersen et al. [1] have shown that the quenching of electronically excited bromine atoms Br(4^2P_{1/2}) by a number of molecules, including CO_2, HCN, H_2O, N_2O and C_2H_2, leads to mode-selective excitation and provides a method for down conversion of laser frequencies in the IR region. E-VR transfer is also known to be efficient [2-4] for I(5^2P_{1/2}) and it has been shown that quenching by H_2O leads to selective excitation of two stretching quanta with high (near 100%) efficiency [4]. Although quenching efficiencies for I(5^2P_{1/2}) are generally lower than for Br(4^2P_{1/2}), and thus the possibility of intermolecular energy transfer between the quenching molecules higher, it is still expected that E-VR transfer from I(5^2P_{1/2}) will provide a further means of pumping IR molecular lasers [4]. It is therefore of interest to study quenching of I(5^2P_{1/2}) by molecules such as NH_3, HCN and OCS which have large IR transition dipoles; HCN and OCS were thought to
be of interest as they are known to give laser action following E-VR transfer from Br($4^2P_{1/2}$).

In the present work we use time-resolved resonance fluorescence [5] to determine total quenching cross sections. We have shown elsewhere [5] that this is a sensitive and precise technique for studying total cross sections, and that the results can provide considerable insight into quenching mechanisms.

2. Experimental

The experimental arrangement for time-resolved resonance fluorescence has been described in detail previously [5]. It is a relatively simple technique but provides data of higher precision and greater reliability than most other techniques. Flash energies of typically 50 J can be used to produce the excited atoms, which in the present study were derived from the photolysis of C$_3$F$_7$I. Resonance fluorescence was produced following excitation ($\lambda = 206.2$ nm) of I($5^2P_{1/2}$) to the 5p$^4$6s($^2P_{3/2}$) level by means of a microwave-powered atomic lamp. A solar-blind photomultiplier was used to monitor the fluorescence as a function of time after the photolysis pulse. We have previously used a conventional photomultiplier, sensitive in the visible and UV regions, to monitor the resonance fluorescence but find that the use of a solar-blind photomultiplier helps to reduce the initial disturbance due to scattered light from the photolysis flash. The output from the photomultiplier was fed to a fast analogue-to-digital converter (Datalab DL905) which was interfaced to a signal averager (Datalab DL4000).

Signal averaging of four to eight shots was used to improve the signal-to-noise ratio which was slightly degraded owing to absorption of the atomic resonance radiation by the quenching molecules, but was not strictly necessary. The contents of the memory of the signal averager could be inspected on a visual display and transferred to punched tape for computer processing.

2.1. Reagents

C$_3$F$_7$I (Pierce Chemical Company) and OCS (Matheson) were thoroughly degassed and distilled under vacuum; NH$_3$ (BOC anhydrous) was dried over sodium and thoroughly degassed; HCN was prepared by standard methods and distilled under vacuum. The purity of all the reagents was checked by IR and mass spectrometric analysis; no significant level of impurity was found.

3. Results

The quenching of I($5^2P_{1/2}$) was studied under pseudo first order kinetic conditions, the partial pressure of quenching gas being several orders of
magnitude greater than that of the excited atom. Simple exponential decays were observed in all experimental runs in accordance with the expected first order kinetics. First order decay coefficients $k'$ derived from such experiments, which were conducted over a range of quenching gas pressures, are shown in Fig. 1 for OCS and NH$_3$. The second order rate constants derived from such plots are given in Table 1.

An earlier result for OCS determined by time-resolved absorption techniques is also given. It can be seen that the result from time-resolved absorption is significantly larger than that determined here using resonance fluorescence. We have previously compared a range of data obtained by the two techniques [6] and have shown that, where the quenching molecule absorbs in the UV and is photolysed, care is needed in deriving data with the absorption technique. It appears that some atomic and free radical
species produced by the flash have high quenching efficiencies and can thus influence the decay kinetics of the excited atom. Such effects are minimized with the resonance fluorescence technique owing to the lower degree of photolysis employed. In the present work we have demonstrated that the effects of photolysis products are entirely negligible by repeating fluorescence decay measurements over a range of flash energies (typically 40 - 100 J). No significant change in the decay kinetics could be detected for any of the gases studied. It was also found that using the time-resolved fluorescence technique a given mixture could be flashed ten or more times without any significant change in the decay kinetics. This is seldom the case when absorption techniques are used.

4. Discussion

Of the quenching molecules studied here, NH$_3$ is potentially the most interesting. The relatively high quenching efficiency for this molecule suggests that it may prove useful in E$\rightarrow$VR transfer laser systems pumped by iodine atoms. Development of efficient E$\rightarrow$VR transfer lasers requires in general that the rate of transfer to the quenching molecule be more rapid than the rate of intermolecular transfer between quenching molecules. While exceptions to this principle can be envisaged (e.g. where a particular vibrational level acts as a "bottleneck" and possesses an appropriate optical transition), it is generally expected that intermolecular or intramolecular relaxation will reduce the efficiency of E$\rightarrow$VR laser systems. The low quenching efficiencies for OCS and HCN thus render them less likely candidates for laser use.

We next consider each quenching molecule in turn and try to identify the most likely energy transfer channels involved for the quenching of I(5$^2$P$_{1/2}$) atoms.

4.1. Quenching by NH$_3$

There are several near-resonant channels available, involving the excitation of $2\nu_3 + \nu_2$, for quenching of I(5$^2$P$_{1/2}$) by NH$_3$, namely

$$I(5^2P_{1/2}) + NH_3(0000) \rightarrow I(5^2P_{3/2}) + NH_3(0120)$$

The IR spectrum of NH$_3$ in the 1.3 $\mu$m region has been studied under medium resolution [7] and it is clear that the $2\nu_3 + \nu_2$ band possesses an appreciable transition moment. A high resolution study and analysis of the 1.3 $\mu$m band would allow a more detailed discussion of the energy transfer channels involved; however, at the present time we simply note that there are three transitions which lie within 30 cm$^{-1}$ for resonance with the iodine atom transition (7603.15 cm$^{-1}$). One line in the NH$_3$ spectrum lies at almost

---

*Only a small fraction of the light output from the flash is actually absorbed by the reagents in the fluorescence cell as the flash lamp is spaced about 30 cm from the cell.*
exact resonance (7602.8 cm\(^{-1}\)) with the iodine transition. We would therefore expect fairly efficient E-VR transfer to occur via coupling between the quadrupole transition moment of the iodine atom and the electric dipole transition moment of NH\(_3\).

4.2. Quenching by HCN

There are no near-resonant channels available for quenching of \(1(5^2\text{P}_{1/2})\) by HCN; the closest transition would involve the excitation of the combination \(2\nu_1 + \nu_3\) which is about 200 cm\(^{-1}\) off resonance and appears to be very weak as it is not listed by Herzberg [8]. Similar considerations apply to the excitation of the combination \(2\nu_3 + \nu_2\) which is about 370 cm\(^{-1}\) off resonance. The next higher transitions, involving three quanta, are the combinations \(2\nu_3 + \nu_1\) (8586 cm\(^{-1}\)) and \(3\nu_2\) (9627 cm\(^{-1}\)); both of these transitions have been observed in absorption but are endothermic and well off resonance.

Combinations involving four or more quanta can be found [8] which provide resonant E-VR transfer channels but they will have very low transition moments and will therefore be inefficient.

Quenching by HCN can be compared with HCl where again the excitation of three quanta is required and the absence of near-resonant channels leads to a low quenching rate constant [3] \((k(\text{HCl}) = 1.5 \times 10^{-14} \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1})\). The quenching mechanism proposed for HCl involves the crossing of potential energy surfaces and it seems likely that quenching by HCN proceeds by the same mechanism.

4.3. Quenching by OCS

Quenching of \(1(5^2\text{P}_{1/2})\) via an E-VR mechanism would require the excitation of four or more vibrational quanta. We would therefore expect the quenching efficiency to be significantly lower than for the other molecules considered here, as is indeed observed. An even lower efficiency is observed [9] for quenching of \(1(5^2\text{P}_{1/2})\) by CO\(_2\) \((k(\text{CO}_2) = 1.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})\). This contrasts with the situation for Br\((4^2\text{P}_{1/2})\) with CO\(_2\) where the presence of near-resonant E-VR channels involving excitation of two quanta leads to a high quenching efficiency [10]:

\[
\text{Br}(4^2\text{P}_{1/2}) + \text{CO}_2(000) \rightarrow \text{Br}(4^2\text{P}_{3/2}) + \text{CO}_2(101) - 30 \text{ cm}^{-1}
\]

\[
k = (1.6 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

These data clearly reveal the rapid decline in efficiency for resonant E-VR transfer with increasing number of quanta excited in the exchange process.

Acknowledgments

We thank Professor C. Kemball for encouragement and laboratory facilities, and the S.R.C. for an equipment grant. We also thank Professor W. H.
Breckenridge for helpful discussion and the N.A.T.O. Research Grants Committee for support of collaborative research on fluorescence techniques.

References

to give information on the collision dynamics. In the case of triatomic molecules, in particular, one is able to distinguish between in-plane and out-of-plane collision geometries.

An example for such a system is the ion-molecule reaction

$$\text{H}_2^+ + \text{H} \rightarrow \text{H}_3^+ + \text{H}$$

or which experiments have been performed by measuring the infrared chemoluminescence of the $\text{H}_3^+$ product. The reaction took place in a large vessel filled with low pressure $\text{H}_2 (\approx 5 \times 10^{-5} \text{Torr})$, where $\text{H}_2$-reagents were produced by electron impact, and subsequently reacted with the unionized $\text{H}_2$-gas. Infrared emission was measured in the 2.5-5.5 $\mu$m region with the use of a high throughput double monochromator specially built for this experiment. So far the spectroscopy of the $\text{H}_3^+$ system is not yet completely known, as this is the first time such ion spectra have been recorded. However, with the help of ab initio calculations one can reach at least qualitative conclusions, which show a non statistical behaviour of the appropriate distributions. Particularly one can conclude that the 3rd vibrational level of the asymmetric stretch mode is considerably populated, and the rotational distribution of the $\text{H}_3^+$ shows maxima for levels with $J \approx K$, indicating that the rotation is mainly about the axis perpendicular to the molecular plane. This is in agreement with trajectory studies on the same system, and would lead to the conclusion that the reaction predominantly proceeds via an in-plane collision encounter.

**Dr. M. Martin, Mr. M. Trainer and Dr. R. J. Donovan (Edinburgh) (communicated):**

We would like to mention some recent results which support the findings of Baughcum et al. concerning the low yield of HBr from the reaction of Br($^4P_3$) with $\text{H}_2$. In a wide range of studies involving $1(^3P_0)$ interacting with hydrides (e.g., $\text{CD}_3\text{CN}$, $\text{C}_6\text{H}_5\text{CH}$, $\text{CH}_2\text{CHO}$, $\text{C}_6\text{H}_5\text{CHO}$) for which exothermic chemical reaction to produce $\text{H}_2$ is thermodynamically favoured, we find that the dominant removal process is physical quenching.

The fact that the electronic excitation energy in these systems cannot be used efficiently for reaction is not in fact surprising as a non-adiabatic transition from the excited entrance channel hypersurface to the ground state exit channel surface is required before the hydrogen halide product can be formed. Thus adiabatic correlation rules provide a good guide to the branching into product channels for these, and many other systems.

We would emphasise that where adiabatic reaction on an excited hypersurface is possible, reaction proceeds efficiently. Examples of this behaviour are given by Baughcum et al. for reaction of Br($^4P_3$) and I($^3P_0$) with halogens and interhalogens. Further examples are provided by the reactions of $\text{F}(^2P_3)$ and $\text{Cl}(^3P_1)$ with hydrogen halides where the thermal population of the $^3P_1$ state, $\approx 300 \text{ K}$, is sufficient to give rise to substantial yields of the excited halogen atom product via the adiabatic channel:

$$X(^3P_1) + \text{HY} \rightarrow \text{HX} + Y(^3P_1).$$

**Dr. J. Wanner (Munich) said:** In this Discussion Clyne and McDermid reported on an improved method for the determination of bond dissociation energies of the

3. J. Muckerman, personal communication.