State-Resolved Dynamics of Electronically Inelastic Collisions of Small Free Radicals

Colin James Randall

A thesis presented for the degree of
Doctor of Philosophy in the
Faculty of Science at the
University of Edinburgh
1998
To my family.

Thanks for everything.
Abstract

The phenomenon of collision-induced electronic energy transfer in selectively excited diatomic radicals has been investigated experimentally. Direct laser excitation of initial rovibronic states and dispersed, temporally-resolved fluorescence analysis of transitions from both parent and collisionally populated levels has allowed the collisional encounter to be quantified at a state-specific level. Theoretical modelling of these results allows the form of the potential energy surfaces which control the dynamics to be established.

In an extended series of experiments, collision-induced $C^2\Delta$-$B^2\Sigma^+$ transfer in the SiF radical has been investigated. It was observed that the product $B^2\Sigma^+$ state vibrational distributions were well correlated with the Franck-Condon overlap between vibronic wavefunctions of the two states. Dominant channels were found to involve $\Delta v=0$, which corresponds to an energy defect of $\sim 5000$ cm$^{-1}$. Rotationally resolved investigation of the $C^2\Delta, v=0 \rightarrow B^2\Sigma^+, v'=0$ channel revealed a significant fraction of this energy to be released as product state rotation. A limiting impulsive model of the energy release reproduced the main features of the observed behaviour. Polarisation resolved investigation of the transfer event revealed significant depolarisation of the product $B^2\Sigma^+$ state compared to the initial $C^2\Delta$ state. This observation was rationalised within two dynamically distinct models of rotational energy transfer. It is believed that all these observations may be explained by the valence-Rydberg nature of the electronic states involved.

In a related set of experiments, novel measurements of collision-induced transfer between the $A^2\Delta$ and $B^2\Sigma^-$ states of the CH radical have been obtained. Facile transfer in both directions between the states has been observed for collisions with CO$_2$, with potentially important ramifications for previously measured total quenching rates. Kinetic modelling of the collisional process has allowed specific electronic branching fractions to be established. Vibrationally resolved fluorescence spectra have revealed a propensity for transfer into $B^2\Sigma^-, v'=0$ from $A^2\Delta, v=1$ and 2, while direct transfer to $A^2\Delta, v'=0$ from $B^2\Sigma^+, v=0$ has been observed for the first time. Higher resolution spectra show rotational transfer propensities to be determined by the energy gap between parent and daughter levels in these electronically inelastic $A^2\Delta \rightarrow B^2\Sigma^-$ collisions.
I know not all that may be coming, but be it what it will, I'll go to it laughing.

Herman Melville.
Declaration

I declare that this thesis has been composed by myself, and that the work described in it is my own, except where due acknowledgement is made, and was carried out whilst a member of the laser group at Edinburgh University.

Signed:

Date: 4/3/99
Acknowledgements

First and foremost, thanks must be given to Ken McKendrick, my supervisor over the last four years, for his opinions, thoughts, and a seemingly endless supply of plausible explanations.

Dr Neil Jackson deserves thanks for his guidance in the early days, and for the major contributions he made to the rotationally and polarisation resolved studies of SiF. Encouraging words in the lab were received from Cameron Watson and Gillian Sweeney. Craig Murray assisted in much of the acquisition and analysis of the CH data, and now boldly forges on alone (well, sort of). The fellow laser group members, whose chat has made the last four years so enjoyable, include Mike, Craig, Andy, Scott, Alison, Angela, Michel, Neil and Pat, while Trevor got the beers in. Repeatedly. Thanks to the folks back home for the encouragement and the cash: I literally could not have done it without you. Finally, a big thank you goes to Luann for helping out over the last year, and occasionally managing to put things back into perspective.
Table of Contents

1. General Introduction ................................................................. 1
   1.1 CN Quenching .................................................................. 2
   1.2 N₂⁺ Quenching ................................................................. 4
   1.3 CO⁺ Quenching ................................................................. 5
   1.4 Conclusions ..................................................................... 6
   1.5 Scope of Current Work ..................................................... 7

2. SiF Experimental Apparatus ....................................................... 10
   2.1 Introduction ...................................................................... 10
   2.2 Gas Handling & Radical Production ................................. 12
      2.2.1 Vacuum Line ............................................................ 12
      2.2.2 Gas Flow Control .................................................... 12
      2.2.3 Microwave Discharge ............................................... 12
      2.2.4 Discharge Flow System ............................................ 13
   2.3 The Laser System .............................................................. 15
      2.3.1 The Nd:YAG Laser ................................................... 16
      2.3.2 The Dye Laser ........................................................ 17
      2.3.3 The Wavelength Extender Unit ................................. 18
   2.4 The Fluorescence Collection System ................................. 18
      2.4.1 The Two Lens System ............................................... 18
      2.4.2 The Single Lens System ............................................ 19
   2.5 Polarisation Studies .......................................................... 19
   2.6 Fluorescence Resolution and Detection ............................ 20
   2.7 Experimental Control and Signal Processing .................... 21

3. Spectroscopy of the SiF B³Σ⁺-X²Π and C²Δ-X²Π Systems .......... 24
   3.1 Introduction ..................................................................... 24
   3.2 Previous Work .................................................................. 25
   3.3 Interatomic Potentials and Spectroscopic Constants ............ 25
   3.4 Energy Level Structure ..................................................... 28
      3.4.1 The B³Σ⁺ State ....................................................... 28
      3.4.2 The X²Π State ........................................................ 29
      3.4.3 The C²Δ State ........................................................ 30
   3.5 Rovibronic Transition Selection Rules ............................... 31
      3.5.1 SiF Excitation Spectra .............................................. 36
      3.5.2 Experimental Technique ........................................... 36
      3.5.3 Results ................................................................. 36
   3.6 SiF Dispersed Fluorescence Spectra .................................. 40
9. Spectroscopy of the CH $A^2\Delta-X^2\Pi$ and $B^2\Sigma^--X^2\Pi$ Systems

9.1 Introduction ................................................................. 131
9.2 Interatomic Potentials and Spectroscopic Constants ........................................... 132
9.3 Energy Level Structure ................................................................. 135
  9.3.1 The $B^2\Sigma^-$ State ................................................................. 135
  9.3.2 The $X^2\Pi$ State ................................................................. 135
  9.3.3 The $A^2\Delta$ State ................................................................. 136
9.4 Rovibronic Transition Selection Rules ................................................................. 141
9.5 CH Excitation Spectra ................................................................. 141
  9.5.1 Experimental Technique ................................................................. 142
  9.5.2 $B^2\Sigma^--X^2\Pi (0,0)$ Excitation Spectra ................................................................. 144
  9.5.3 $A^2\Delta-X^2\Pi (1,0)$ and (2,1) Excitation Spectra ................................................................. 146
9.6 Electronic Configurations ................................................................. 150
9.7 Simulation Technique ................................................................. 150

10. Collision-Induced CH $A^2\Delta\leftrightarrow B^2\Sigma^-$ Vibrational Transfer

10.1 Introduction ................................................................. 153
10.2 Preliminary Work ................................................................. 155
10.3 A-X and B-X Waveform Analysis ................................................................. 155
  10.3.1 Kinetic Modelling of Collision-Induced $B^2\Sigma^--A^2\Delta$ Transfer ................................................................. 156
  10.3.2 Determination of $\lambda_1$ and $\lambda_2$ ................................................................. 160
10.4 Dispersed B-X and A-X Emission ................................................................. 163
  10.4.1 Determination of the Relative $A^2\Delta$ and $B^2\Sigma^-$ State Populations ................................................................. 163
  10.4.2 Determination of the Relative $A_0$ and $A_1$ Integrated Emission Intensities ................................................................. 168
10.5 Interpretation of Dispersed Fluorescence Spectra ................................................................. 175
  10.5.1 Determination of $k_{AB}$ and $k_{BA}$ Within the Three-Level System ................................................................. 175
  10.5.2 Determination of Rate Constants Within the Four-Level System ................................................................. 178
10.6 Discussion ................................................................. 181

11. Rotationally Resolved CH $A^2\Delta\rightarrow B^2\Sigma^-$ Transfer

11.1 Introduction ................................................................. 187
11.2 $N$-Specific A-X(I,0) Pumping ................................................................. 188
11.3 Collision-Induced CH $B^2\Sigma^-, v'=0$ Rotational Distributions ................................................................. 197
11.4 Conclusions ................................................................. 199

12. CH Conclusions and Discussion ................................................................. 208
  12.1 Discussion ................................................................. 208
  12.2 Future Work ................................................................. 211
Table of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Schematic of Typical Experimental Arrangement.</td>
<td>11</td>
</tr>
<tr>
<td>2-2</td>
<td>Close up of Excitation/Detection Zone.</td>
<td>14</td>
</tr>
<tr>
<td>3-1</td>
<td>Potential Energy Curves of the $X^2\Pi$, $B^2\Sigma^+$ and $C^2\Delta$ States of $^{28}\text{Si}^{19}\text{F}$.</td>
<td>27</td>
</tr>
<tr>
<td>3-2</td>
<td>Energy Level Structure and Main Branch ($\Delta N = \Delta J$) Transitions in the SiF $B^2\Sigma^+-X^2\Pi$ (0,0) System.</td>
<td>32</td>
</tr>
<tr>
<td>3-3</td>
<td>Energy Level Structure and Satellite ($\Delta N \neq \Delta J$) Transitions in the SiF $B^2\Sigma^+-X^2\Pi$ (0,0) System.</td>
<td>33</td>
</tr>
<tr>
<td>3-4</td>
<td>Energy Level Structure and Main Branch ($\Delta N = \Delta J$) Transitions in the SiF $C^2\Delta-X^2\Pi$ (0,0) System.</td>
<td>34</td>
</tr>
<tr>
<td>3-5</td>
<td>Energy Level Structure and Satellite ($\Delta N \neq \Delta J$) Transitions in the SiF $C^2\Delta-X^2\Pi$ (0,0) System.</td>
<td>35</td>
</tr>
<tr>
<td>3-6</td>
<td>SiF $C^2\Delta -X^2\Pi_{1/2}$ (0,0) LIF Excitation Spectra.</td>
<td>38</td>
</tr>
<tr>
<td>3-7</td>
<td>SiF $B^2\Sigma^+-X^2\Pi$ (3,0) LIF Excitation Spectra.</td>
<td>39</td>
</tr>
<tr>
<td>4-1</td>
<td>RKR Potential Energy Curves for the Relevant States of SiCl and SiF.</td>
<td>48</td>
</tr>
<tr>
<td>4-2</td>
<td>Parmenter-Seaver plot for total collisional removal from SiCl $B^2\Delta \nu=0$ (■) and $\nu=1$ (▲).</td>
<td>50</td>
</tr>
<tr>
<td>4-3</td>
<td>$B^2\Sigma^+$ Product State Vibrational Distributions.</td>
<td>53</td>
</tr>
<tr>
<td>4-4</td>
<td>LIF Excitation Spectrum of the $C^2\Delta -X^2\Pi_{1/2}$ (0,0) Sub-band.</td>
<td>56</td>
</tr>
<tr>
<td>4-5</td>
<td>Dispersed $C^2\Delta -X^2\Pi_{3/2}$ (0,0) Fluorescence Spectra.</td>
<td>58</td>
</tr>
<tr>
<td>4-6</td>
<td>Collision-Induced SiF B-X(0,0) Fluorescence Spectra.</td>
<td>60</td>
</tr>
<tr>
<td>4-7</td>
<td>SiF $C^2\Delta$, $\nu=0$ and $B^2\Sigma^+$, $\nu'=0$ Excited State Rotational Distributions.</td>
<td>61</td>
</tr>
<tr>
<td>4-8</td>
<td>Expanded View of $C^2\Delta -X^2\Pi_{1/2}$ (0,0) P$_1$ Branch.</td>
<td>65</td>
</tr>
<tr>
<td>4-9</td>
<td>$C^2\Delta -X^2\Pi_{3/2}$ (0,0) Dispersed Fluorescence Spectra following P$_1$ line Pumping.</td>
<td>66</td>
</tr>
<tr>
<td>4-10</td>
<td>Collision-Induced B-X (0,0) Fluorescence Spectra.</td>
<td>70</td>
</tr>
<tr>
<td>4-11</td>
<td>Best Fit SiF $C^2\Delta$ and $B^2\Sigma^+$ State Rotational Distributions .</td>
<td>71</td>
</tr>
<tr>
<td>4-12</td>
<td>Predicted $\Delta J_{\text{max}}$ Values for a given SiF $C^2\Delta$ Rotational Level, $J$, using an Impulsive Model (Equation 4-5).</td>
<td>79</td>
</tr>
<tr>
<td>5-1</td>
<td>Schematic of Excitation/Detection Geometry for Polarisation Studies.</td>
<td>83</td>
</tr>
<tr>
<td>5-2</td>
<td>SiF B-X (3,0) LIF Excitation Spectrum Showing All Band Positions.</td>
<td>90</td>
</tr>
<tr>
<td>5-3</td>
<td>$B^2\Sigma^+-X^2\Pi_{1/2}$ (3,2) Dispersed Fluorescence Spectrum.</td>
<td>91</td>
</tr>
</tbody>
</table>
Figure 5-4: C2Δ -X2Π3/2 (0,0) Dispersed Fluorescence Spectrum.

Figure 5-5: Collision-Induced B2Σ+ -X2Π3/2 (0,0) Dispersed Fluorescence Spectrum.

Figure 5-6: Geometrical Relationship between the Vectors J, ΔJ and J'.

Figure 5-7: Representation of Addition of Spherically Isotropic ΔJ to J for ΔJ/J<1.

Figure 5-8: Predictions of the ‘spherical’ (solid lines) and ‘circular’ (dashed lines) models of collisional depolarisation as function of ΔJ/J.

Figure 5-9: Representation of Addition of Circularly Isotropic ΔJ to J for ΔJ/J<1.

Figure 6-1: Schematic Reduced Dimension PESs for a SiX-Quencher Interaction.

Figure 8-1: Schematic of the experimental apparatus used in the study of CH.

Figure 9-1: Schematic Potential Energy Curves of the X2Π, A2Δ and B2Σ States of the 12C1H radical.

Figure 9-2: Energy Level Structure and Main Branch (ΔN =ΔJ) Transitions in the CH B2Σ-X2Π (0,0) System.

Figure 9-3: Energy Level Structure and Satellite (ΔN ≠ΔJ) Transitions in the CH B2Σ-X2Π (0,0) System.

Figure 9-4: Energy Level Structure and Main Branch (ΔN =ΔJ) Transitions in the CH A2Δ-X2Π (0,0) System.

Figure 9-5: Energy Level Structure and Satellite(ΔN ≠ΔJ) Transitions in the CH A2Δ-X2Π (0,0) System.

Figure 9-6: CH B2Σ-X2Π (0,0) LIF Excitation Spectra.

Figure 9-7: Overlapping CH B2Σ-X2Π (0,0) and A2Δ-X2Π (1,0) and (2,1) LIF Excitation Spectra.

Figure 9-8: CH A2Δ-X2Π (1,0) LIF Excitation Spectrum.

Figure 10-1: Vibronic Energy Level Structure of the CH X2Π, A2Δ and B2Σ States.

Figure 10-2: CH B2Σ-X2Π (0,0) and A2Δ-X2Π Δv=0 Waveforms.

Figure 10-3: Schematic of the Three-Level Kinetic Scheme.

Figure 10-4: Observed B2Σ, v=0 State Quenching Rates.

Figure 10-5: CH B-X(0,0) and A-X Δv=0 Dispersed Fluorescence Spectra Following A2Δ, v=1 Initial Excitation.

Figure 10-6: CH B-X(0,0) and A-X Δv=0 Dispersed Fluorescence Spectra Following B2Σ+, v=0 Initial Excitation.

Figure 10-7: Schematic Diagram of the Four-Level Kinetic Scheme.
Figure 10-8: CH A-X and B-X Spectra Resulting from Vibrationally and Electronically Inelastic Transfer from $A^2\Delta, v=1$ Induced by Collisions with CO$_2$. 170

Figure 10-9: CH A-X and B-X Spectra Resulting from Electronically Inelastic Transfer from $B^2\Sigma^-, v=0$ Induced by Collisions with CO$_2$. 173

Figure 10-10: Ratio of CH A0:A1 Integrated Emission Signals Induced by Collisions of A1 and B0 with CO$_2$. 174

Figure 10-11: Comparison of Predicted and Observed Integrated Signal Ratios. 184

Figure 10-12: Variation of the Components of Equation 10-3 with Pressure. 185

Figure 11-1: Expanded View of the $A^2\Delta-A^2\Pi (1,0)$ R-type Branches. 189

Figure 11-2: CH $A^2\Delta-X^2\Pi (1,1)$ Dispersed Fluorescence Spectra obtained from R(2) Pumping. 192

Figure 11-3: CH $A^2\Delta-X^2\Pi (1,1)$ Dispersed Fluorescence Spectra obtained from R(7) Pumping. 193

Figure 11-4: Best Fit CH $A^2\Delta, v=1$ Rotational Distributions obtained from R(2) Pumping. 194

Figure 11-5: Best Fit CH $A^2\Delta, v=1$ Rotational Distributions obtained from R(7) Pumping. 195

Figure 11-6: CH $B^2\Sigma^- - X^2\Pi (0,0)$ Dispersed Fluorescence Spectra. 200

Figure 11-7: CH $B^2\Sigma^- - X^2\Pi (0,0)$ Dispersed Fluorescence Spectra. 201

Figure 11-8: Best Fit CH $B^2\Sigma^-, v'=0$ Rotational Distributions from Initial $A^2\Delta, v=1$ R(2) Excitation. 202

Figure 11-9: Best Fit CH $B^2\Sigma^-, v'=0$ Rotational Distributions from Initial $A^2\Delta, v=1$ R(7) Excitation. 203

Figure 11-10: CH $A^2\Delta$ and $B^2\Sigma^-$ Rovibronic Energy Levels. 205

Figure 11-11: Initial and Product State Population Distributions Expressed as a Function of Absolute Rovibronic Term Energy. 206
Table of Tables

Table 3-1: Principle Spectroscopic Constants of the $X^2\Pi$, $B^2\Sigma^+$ and $C^2\Delta$ States of $^{28}\text{Si}^{19}\text{F}$. 26

Table 4-1: Characteristics of the SiF $C^2\Delta$ Rotational Distributions produced by $J$-Specific $P_1$ Excitation. 64

Table 4-2: Characteristics of the $B^2\Sigma^+$ $v'=0$ Rotational Distributions produced by Collisions of Rotationally State-Selected $C^2\Delta$ $v=0$ with $\text{H}_2$. 69

Table 5-1: Classical limiting high-$J$ values of $R$ obtained from Equation 5-5. 86

Table 5-2: Observed and Predicted Polarisation ratios, $R$, for $P_1 P\downarrow$ combinations of SiF Bands. 97

Table 6-1: Key Points of Comparison between the Collisional Processes SiCl $B^2\Delta$, $v$, $J\rightarrow B^2\Sigma^+$, $v'$, $J'$ and SiF $C^2\Delta$, $v$, $J\rightarrow B^2\Sigma^+$, $v'$, $J'$. 111

Table 9-1: Principal Spectroscopic Constants of the $X^2\Pi$, $A^2\Delta$ and $B^2\Sigma^-$ States of the $^{12}\text{C}^1\text{H}$ Radical. 133

Table 9-2: Band Origins and Franck-Condon Factors for the $A^2\Delta$-$X^2\Pi$ System. 143

Table 9-3: Band Origins and Franck-Condon Factors for the $B^2\Sigma^-$-$X^2\Pi$ System. 143

Table 10-1: Experimentally Observed and Calculated Relative Parent and Product State Integrated Signals for Initial Excitation of $A^2\Delta$ and $B^2\Sigma^-$ States. 177

Table 10-2: Iteratively Determined Rate Constants for the Coupling Channels between the $B_0$, $A_1$ and $A_0$ levels of CH Induced by Collisions with CO$_2$. 180

Table 11-1: Characteristics of CH $A^2\Delta$, $v=1$ Rotational Distributions Produced by Collisions of State-Selected $A^2\Delta$, $v=1$ with CO$_2$. 196

Table 11-2: Characteristics of a 300 K CH $A^2\Delta$, $v=1$ Boltzmann Rotational Distribution. 196

Table 11-3: Characteristics of CH $B^2\Sigma^-$, $v'=0$ Rotational Distributions Produced by Electronically Inelastic Collisions of State-Selected $A^2\Delta$, $v=1$ with CO$_2$. 204

Table 11-4: Characteristics of a 300 K CH $B^2\Sigma^-$, $v'=0$ Rotational Boltzmann Distribution. 204
Chapter 1

General Introduction

One of the ultimate goals of physical chemistry is to fully understand the outcome of a collision between molecules, whether it involves a chemical transformation, or the redistribution of energy among the various degrees of freedom of the collision pair. The work contained in this thesis is concerned with the study of collision-induced electronically inelastic energy transfer, where there is a change in the electronic state of a molecule arising from a bimolecular collisional encounter, with the possibility of the redistribution of electronic energy into the mechanical degrees of freedom of the collision pair.

For several decades now it has been known that the fluorescence quantum yield from electronically excited atomic and molecular species in the gas phase is dependent upon pressure, and therefore that collisions are capable of transferring population between electronic states. There exists a considerable body of work where the collisional quenching rate of the fluorescing state has been determined. A number of empirical models based on these studies have been developed in an attempt to correlate the observed quenching efficiency with various physical properties of the molecule-collider system [1,2,3,4,5,6]. However, only a small subset of these investigations have identified the product states populated by the collision event.

Recent advances in molecular beam and laser techniques have enabled the electronically inelastic event to be studied at a state-specific level. It is now possible to prepare a well-defined subset of rovibrational levels in the initial (parent) state, and determine the detailed branching over the accessible levels of a collisionally populated product electronic state. The factors which determine the branching over the various degrees of freedom of the product state are still far from completely understood. The features of the potential energy surfaces involved in the collisional interaction which govern particular dynamic outcomes, may, however, be explored from experiments which probe the collision event in a quantum-level-specific manner. The work described in this thesis
is concerned with expanding the current body of state-resolved data with the intention of furthering the understanding of the governing processes involved.

The need to understand these quenching processes is driven by their practical, as well as fundamental, importance. They will be relevant in situations where the collisional redistribution of energy affects the evolution of the system, as in combustion, plasmas, chemical laser gain media, the atmosphere and astrophysical environments. Also, since quenching affects the fluorescence quantum yield, knowledge of the rate of excited state collision processes is required to relate signal intensities resulting from optical, and particularly laser-based, probe techniques to ground state populations.

A recent review article by Dagdigian [7] has comprehensively reviewed the progress which has been made in the study of state-resolved electronically inelastic collisions of diatomic molecules, with particular emphasis on the use of laser based single- and double-resonance experimental methods in extracting state-to-state information. The remainder of this chapter is intended to provide an overview of the results which have been obtained to date on a few of the more extensively studied systems, specifically the isoelectronic series \( \text{N}_2^+ \), \( \text{CN} \) and \( \text{CO}^+ \).

### 1.1 \( \text{CN} \) Quenching

The \( \text{CN} \ A^2\Pi - X^2\Sigma^+ \) transition has been the subject of extensive studies as the possible basis of a molecular predissociation laser [8,9]. A study of the collisional removal of \( \text{CN} \ A^2\Pi (\nu'=3-9) \) with Ar by Bondenye and co-workers showed that the lifetime of the excited state decreased with vibrational energy [10], and the time dependence of the fluorescence waveform from the directly excited level was strongly double exponential. This was interpreted as arising from rapid collisional equilibration between the excited \( \text{A}^2\Delta, \nu' \) levels and the nearby vibrational levels in the \( \text{X}^2\Sigma^+ \) state. The energy mismatch between the vibrational levels of the two electronic state manifolds decreases until a minimum is reached between the \( \text{A}^2\Delta, \nu'=8 \) and \( \text{X}^2\Sigma^+, \nu=12 \) levels, resulting in the observed increases in the removal cross section as this level is approached.

Dagdigian investigated collision-induced transitions in the \( \text{CN} \ A^2\Pi - X^2\Sigma^+ \) system with Ar using an optical-optical double resonance method [11,12,13,14,15]. The rotational distributions in the \( \text{A}^2\Pi \) and \( \text{X}^2\Sigma^+ \) states were probed through laser-induced fluorescence (LIF) via the \( \text{B}^2\Sigma^+ \) state.
Chapter 1: General Introduction

Collisional transfer between the $A^2\Pi, \nu=7$ and $X^2\Sigma^+$, $\nu'=11$ vibrational levels following rotationally specific excitation of $A^2\Pi, \nu=7$ was studied [11,12]. Collision-induced transfer rates were shown to be comparable to those for pure rotational relaxation within the $A^2\Pi$ state, and largely independent of $J$, regardless of the degree of $X$ state character in the initial rotational level (heterogeneous perturbations mix the $X^2\Sigma^+$ and $A^2\Pi$ levels). The collision-induced $X^2\Sigma^+$ state rotational populations exhibited significant even-odd alternations, reflecting the near homonuclear character of the CN-Ar interaction potentials. The largest transfer cross sections were observed for transitions with small changes in rotational angular momentum.

Investigation of the collision induced $A^2\Pi, \nu=3 \rightarrow X^2\Sigma^+, \nu'=7$ channel revealed transfer to occur at a rate similar to that observed between the $A^2\Pi, \nu=7$ and $X^2\Sigma^+, \nu'=11$ levels, despite a much larger energy gap and less favourable Franck-Condon overlap. The $X^2\Sigma^+$ state rotational distribution again exhibited an even-odd alteration, as discussed above. Interestingly, this oscillation of the product state rotational distribution was not observed in the nearly isoenergetic $A^2\Pi, \nu=8 \rightarrow X^2\Sigma^+, \nu'=12$ channel [14], presumably explained by the sharp decrease in the homonuclear character of the CN-Ar interaction potential as the C-N intranuclear separation is increased.

In a closely related experiment, Dagdigian et al investigated collision induced $A^2\Pi, \nu=10 \rightarrow B^2\Sigma^+, \nu'=0$ transfer [16]. The anomalous intensity of specific rotational lines in the $B^2\Sigma^+-X^2\Sigma^+$ emission spectra observed in flames has historically been regarded as evidence for the requirement of 'gateway' levels to facilitate collision induced electronic transitions [17]. It was postulated that the preferentially formed $A^2\Pi$ state populated the $B^2\Sigma^+, \nu'=0$ level through perturbed rotational levels in the isoenergetic $A^2\Pi, \nu=10$ manifold. However, Dagdigian observed emission from $B^2\Sigma^+, \nu'=0$ after the excitation of unperturbed $A^2\Pi, \nu=10$ levels after a time delay consistent with single collision conditions, indicating efficient collisional transfer in the absence of perturbed states. The reason the perturbed B state levels appear stronger in the emission from flames is now thought to be due to the preferential chemical formation of CN in the A state, so only the B state levels with some A state character are formed initially. The rest of the B state levels are populated by collisional transfer out of the A state, or pure rotational relaxation within the B state, so the ratio of perturbed to unperturbed B state emission is...
Chapter 1: General Introduction

sensitive to pressure,

In the case of CN, experimental investigation of electronically inelastic transfer has been matched by high-level theoretical studies. Using the approach developed by Alexander and Corey [18], potential energy surfaces were calculated for the interaction of CN (X^2Σ^+ and A^2Π) with He [19]. These surfaces were consequently used to predict cross sections for rovibronic collision induced energy transfer in the CN-He system [20], and the results compared with the experimental cross sections obtained by Dagdigian for the analogous CN-Ar system [11,12,13,14]. Agreement between the predicted and observed cross sections is good for the A^2Π, ν=7 → X^2Σ^+, ν'=11 and A^2Π, ν=8 → X^2Σ^+, ν'=12 channels, but poor for A^2Π, ν=3 → X^2Σ^+, ν'=7 transfer, where the failure of the calculation was attributed to the significantly larger energy gap involved. To resolve this discrepancy, ab initio potential energy surfaces for the CN-Ar interaction were computed, and the cross sections recalculated. This resulted in a slight enhancement of the predicted values, though the agreement with experiment was still unconvincing.

Subsequently, a tandem experimental and theoretical investigation of CN A^2Π, ν=7 → X^2Σ^+, ν'=11 transfer induced by collisions with He was performed [15]. For the first time, non-Born-Oppenheimer mixing between the A^2Π_u and B^2Σ^+ states in the isolated CN molecule was included in the quantum scattering calculations. The agreement between prediction and experiment was good, although the observed even-odd alteration in the product state rotational distribution was somewhat reduced from the calculated values (an effect attributed mainly to multiple collisions in the experimental spectra).

1.2 N2^+ Quenching

The collision-induced N2^+ A^2Π_u → X^2Σ^+_g transfer channel has been studied by Katayama et al in a series of experiments, using He as the collision partner [21,22,23,24,25,26]. Perturbations between these states are strictly forbidden due to the homonuclear nature of the N2^+ molecule. The X^2Σ^+_g product state rotational distributions were determined using OODR via the B^2Σ^+_u state.

Katayama employed a pump-probe experimental approach to investigate collision induced A^2Π_u, ν=4 → X^2Σ^+_g, ν'=7,8 transfer. Rotationally specific excitation of A^2Π_u, ν=4 was accompanied by coincident double-resonance probing of the X^2Σ^+_g, ν'=7,8 rotational levels. In this way, the effect of multiple collisions could be minimised. The
results of this study showed a strong propensity for the conservation of rotational angular momentum over both the near isoenergetic $A^2\Pi_{ui}, \nu=4 \rightarrow X^2\Sigma_g^+, \nu'=8$ channel, and the exothermic $A^2\Pi_{ui}, \nu=4 \rightarrow X^2\Sigma_g^+, \nu'=7$ channel ($\Delta E=1760 \text{ cm}^{-1}$). The collision induced transitions were shown to be governed by the optical-like selection rules $a\leftrightarrow a$ and $s\leftrightarrow s$, and to proceed at rates comparable to, or faster than those observed for pure rotational relaxation.

$A^2\Pi_{ui}, \nu=3 \rightarrow X^2\Sigma_g^+, \nu'=6$ and 7 transfer was also observed to exhibit a propensity for $\Delta J=0$, despite the difference in energy gaps between the two channels (~1950 and -23 cm$^{-1}$, respectively). The transfer rate for the nearly-resonant $X^2\Pi_{ui}, \nu=3 \rightarrow X^2\Sigma_g^+, \nu'=7$ channel was observed to be only three times greater than for the $A^2\Pi_{ui}, \nu=3 \rightarrow X^2\Sigma_g^+, \nu'=6$ process.

Berning and Werner performed quantum scattering calculations for the $N_2^+ (X, A)$-He system, and obtained results which agreed in many respects with the experimental data [27]. Small nuclear rotational angular momentum changes, conservation of $s/a$ symmetry and $e/f$ spin doublet populations were all in agreement with the observed results, as were the calculated cross section trends. However, the absolute values of the cross sections predicted for the $A^2\Pi_{ui}, \nu=3 \rightarrow X^2\Sigma_g^+, \nu'=6$ channels were several orders of magnitude too small, a discrepancy which has yet to be resolved.

### 1.3 CO$^+$ Quenching

The CO$^+$ $A^2\Pi, \nu=0 \rightarrow X^2\Sigma^+$ transfer process induced by collisions with He has been probed at a rotationally resolved level by Dentamaro and Katayama using the OODR technique [28]. Unlike the studies of CN and $N_2^+$, however, transfer between unperturbed levels in the rotational manifolds of the parent and product states was not observed in CO$^+$. It has been argued that the very small Franck-Condon overlap between these two states may explain why transfer is enhanced between perturbed levels, although the role of the Franck-Condon Factor as a controlling influence on electronic energy transfer has been questioned by previous experiments [13,16,29].
Chapter 1: General Introduction

1.4 Conclusions

What is evident from the results obtained to date on electronically inelastic transfer in the isoelectronic CN-CO-N$_2^+$ series, is that there exists, as yet, no universal model which may be applied to successfully predict the collisional behaviour of even this relatively small subset of systems. Transitions occur efficiently via perturbed (gateway) levels in certain systems, but it has been shown that the existence of these levels is not a prerequisite for collisional transfer. Further, even when perturbed levels do exist, they do not always define the dominant transfer channel. The roles played by the energy gap and Franck-Condon overlap in the product state vibrational branching are also unclear at this point. While it is typical for electronically inelastic transfer to be accompanied by a moderate release of rotational energy, with a $\Delta J=0$ propensity applying in most cases, notable exceptions to this have been observed [30,31,32,33].

In relevant studies, which have not been discussed here, the collisional behaviour of various other systems has been investigated. These systems include alkali metal dimers (Na$_2$, Li$_2$, K$_2$), the diatomic hydrides of O, N, P, and an assortment of other molecules (N$_2$, NS, O$_2$, NO, I$_2$, CO). A summary of the results obtained from these studies can be found in Dagdigian's review of the field [7].

Unfortunately, due to the lack of rigorous tandem state-to-state theoretical and experimental studies (with the notable exception of work performed on the CN $A^2\Pi \rightarrow B^2\Sigma^+$ system by Alexander et al and Dagdigian et al), we are currently unable to define a general predictive model for specific transfer channel propensities and cross sections. Such a model would have to be based upon all of the variable parameters present in molecule-collider systems, such that:

$$\sigma_{i\rightarrow f} \propto f\left(J, J', v, v', \Delta E, q_{v', v}, V, \Omega\right)$$

Equation 1-1

where $V$ represents the potential energy surfaces between the quencher and the molecule in the initial and final states, and also the quencher-induced coupling between them.
1.5 Scope of Current Work

The work described in the remainder of this thesis adds to the current body of data by exploring collision-induced electronic energy transfer in the SiF $C^2\Delta \rightarrow B^2\Sigma^+$ and CH $A^2\Delta \leftrightarrow B^2\Sigma^-$ systems.

In a continuation of previous studies performed in this laboratory [31,32], collision-induced SiF $C^2\Delta \rightarrow B^2\Sigma^+$ transfer is examined at a rotationally state-specific level, revealing the electronic transition to be accompanied by a substantial release of rotational energy. More refined, polarisation resolved experiments showed the B state product molecules to be significantly depolarised compared to the parent C state. These observations are rationalised within various limiting models of the transfer event, and are believed to arise from the valence-Rydberg nature of the $C^2\Delta-B^2\Sigma^+$ electronic states.

In a novel investigation, transfer between the $A^2\Delta$ and $B^2\Sigma^-$ states of CH has been observed in collisions with CO$_2$. The product state vibrational branching has been determined for initial excitation of $A^2\Delta, v=1$ and $B^2\Sigma^-, v=0$. Rotationally state-resolved study of the $A^2\Delta, v=1 \rightarrow B^2\Sigma^-, v=0$ channel has revealed a propensity for transfer to occur between levels which lie close in energy.
Bibliography

Chapter 1: General Introduction


Chapter 2

SiF Experimental Apparatus

2.1 Introduction

In this chapter the experimental apparatus involved in studies of the SiF radical will be described in detail. The equipment employed for the investigation of CH will be discussed in Chapter 8, with reference made to this section whenever an area of overlap between the two procedures arises.

There are three general criteria which the experimental apparatus must either accomplish directly, or allow to be fulfilled through careful design:

- generation of the desired molecule
- state-specific excitation of the species to a known quantum state
- determination of the final excited states populated

Generation of SiF radicals is achieved by microwave discharge of SiF₄ in a continuous flow system. Direct laser excitation is used to achieve state-specific radical excitation, and the technique of Laser Induced Fluorescence (LIF) is employed to determine how population is partitioned amongst the various degrees of freedom in the excited electronic states involved. The apparatus used to accomplish these tasks is shown schematically in Figure 2-1.
Figure 2-1: Schematic of Typical Experimental Arrangement.

The laser beam enters the excitation zone vertically, as shown in Figure 2-2. The arrangement shown is in the two-lens fluorescence collection mode.
Chapter 2: SiF Experimental Apparatus

2.2 Gas Handling & Radical Production

2.2.1 Vacuum Line

A purpose built vacuum line was constructed to handle the precursor and bath gases. This was constructed from Pyrex glass incorporating Young’s greaseless taps, and evacuated using a cryotrapped single stage Hg diffusion pump (replaced by a small oil diffusion pump towards the latter stages of the project) backed by an Edwards M5 rotary pump. Pressures within the line were monitored using a capacitance manometer (MKS 626 Baratron, 0-1000 Torr scale), with typical base pressures of less than 0.005 Torr. Gas mixtures were admitted to the line using \( \frac{1}{4} \)" Teflon tubing via one of eight isolable sidearms, storage taking place in a 10 l glass bulb.

2.2.2 Gas Flow Control

For the majority of the gases involved in this study, admittance to the flow system was regulated by mass flow controllers (Advanced Semiconductor Materials AFC-260), with control ranges of 0-50, 0-500 and 0-2000 Standard Cubic Centimetres per Minute (sccm). These were regulated by a dedicated master control unit (Advanced Semiconductor Materials, ROE) which ensured that a constant flow was achieved regardless of the gas backing pressure. For most experiments, an accurate knowledge of the flow rate was not required, and hence it was unnecessary for the mass flow controllers to be calibrated for the different gases involved.

It was found, however, that the controllers afforded poor regulation of H\(_2\) flows, and as such were unsuitable for experiments where the effect of H\(_2\) as a quenching species was being investigated, and a reproducible total pressure was required. In these cases it was discovered that consistent control of the flow could be achieved by using a needle valve (Nupro B-4JN). So, through a combination of these two approaches to flow regulation it was possible to achieve a stable total pressure of gas in the flow tube for all combinations of gases involved.

2.2.3 Microwave Discharge

The SiF radicals required for this investigation were generated by continuous microwave discharge in a flow of SiF\(_4\) diluted in Ar. An EMS Microtron 200 Mk. 1 microwave generator was used to produce microwave radiation with a frequency of 2450 MHz at a
power of ~50 W, with typical reflected powers being ~30 %. This radiation was coupled to the plasma via an air-cooled microwave discharge cavity (EMS 214L) which enclosed the quartz discharge arm. This technique was found to effectively dissociate SiF₄ to the desired SiF radical, and other undetected species.

2.2.4 Discharge Flow System

The discharge flow system consists of three main sections: a silica quartz inlet arm (incorporating the microwave discharge cavity) allowing radical generation and admission, a quenching gas inlet downstream of this and, finally, the laser excitation/fluorescence detection zone. Pressure in the system was maintained by a high throughput cryotrapped rotary pump (Edwards E2M80, 80 m³h⁻¹).

Pressure stability in the system was found to be excellent once flows had been allowed to stabilise, with typical variations of ±0.005 Torr hour⁻¹. Pressures within the flow system were monitored using a MKS Baratron (model 627, 0-10 Torr) mounted on one arm of the six way cross which constitutes the excitation/detection region. For collisional transfer experiments, pressures were typically of the order of 1.5 Torr, while studies of total quenching rates involved pressures in the range 1 to 10 Torr.

The silica quartz arm is attached collinearly to the main flow tube using a custom made, O-ring sealed, brass coupling, and protrudes to ~5 cm upstream of the excitation/detection zone. The quenching gas enters the flow tube perpendicularly via a ground glass joint ~10 cm upstream of the excitation/detection zone. In this way adequate mixing of the two flows is ensured prior to laser excitation.

As mentioned above, the excitation/detection zone is in the form of a six way cross, as shown schematically in Figure 2-2. The excitation laser beam enters the zone vertically via sidearms fitted with quartz windows. These windows are mounted at Brewster’s angle for minimum reflection of a laser beam with its polarisation vector oriented parallel to the flow axis. Fluorescence is collected along the axis mutually perpendicular to the flow and laser propagation axes via a 5 mm thick quartz flat. The MKS Baratron is attached to the six way cross collinear with this final axis through the remaining unused sidearm.
Figure 2-2: Close up of Excitation/Detection Zone.

The laser beam is shown entering the zone vertically. Gas flow is from back to front. Fluorescence is shown collected with the two-lens arrangement.
Chapter 2: SiF Experimental Apparatus

The quartz flat through which the fluorescence is collected is susceptible to deformation under operational conditions (i.e. reduced pressure within the flow tube relative to atmosphere). As this is a known source of birefringence, it is essential to minimise this effect to ensure both polarisations of the fluorescence are transmitted through the flat without a preferential orientation. This problem was overcome by employing a 5 mm thick collection window.

A major problem associated with the discharge-flow technique employed here is radical losses arising from collisions with the walls of the flow system. Two steps were taken to minimise this effect. Firstly, the flow system was designed to be linear and have a large uniform internal diameter (25 mm). This has the effect of maximising the flow rate through the system and thereby reducing the number of radical-wall collisions. Secondly, the flow system walls were coated to reduce the chances of collisions leading to radical reformation. Previous studies in this laboratory [1,2] have shown that a combination of two approaches provides the best results in this area. Halocarbon wax and phosphoric acid had both been shown to be effective surface reaction inhibiting agents, but with differing physical properties. The walls of the excitation zone were coated with inert halocarbon wax. However, the low melting point of halocarbon wax (~60 °C) makes it unsuitable for use in the quartz discharge arm, where the local surface temperature may exceed several thousand degrees Kelvin. The surfaces here, therefore, are coated with phosphoric acid. This process requires the arm to undergo three stages of treatment:

1. cleaning the surfaces by washing with hot 5 M potassium hydroxide soln.
2. coating the surfaces with phosphoric acid then heating to ~1000 K with a blue Bunsen flame
3. overnight baking at ~700 K to produce a uniform white coating

2.3 The Laser System

The laser system employed in this study was a pulsed Neodymium Yttrium Aluminium Garnet (Nd:YAG) pumped dye laser with a Wavelength Extender Unit (WEX).
2.3.1 The Nd:YAG Laser

The Nd:YAG laser used was a model SL803 Q-switched laser as supplied by Spectron Laser Systems. This consists of separate oscillator and amplifier units, each with a flashlamp-pumped Nd³⁺-doped YAG rod.

The fundamental oscillator output wavelength of 1064.8 nm is produced by inducing lasing action between electronic energy levels of the Nd³⁺ ion embedded in the YAG matrix. Nd³⁺ has the ground electronic configuration [Kr] 4d¹⁰ 4f⁵ 5s² 5p⁶, and the main lasing action occurs between the ⁴F₃/₂ and ⁴I₁₁/₂ terms (labelled within the Russell-Saunders approximation) which arise from this arrangement [3]. In free Nd³⁺ the ⁴F₃/₂-⁴I₁₁/₂ transition is doubly forbidden, as it violates the ΔL=0,±1 and ΔJ=0,±1 selection rules for atomic electronic transitions. However, the presence of the YAG matrix splits the two levels into several non-degenerate components by crystal field interactions allowing eight different transitions to occur, the one at 1064.8 nm being dominant at room temperature.

The output characteristics of the laser pulse are greatly enhanced by Q-switching within the oscillator cavity. This operation involves lowering the quality factor, Q, of the cavity for a short interval, preventing radiation from being reflected through the gain medium. During this time the population inversion required for the lasing action is allowed to build to a much higher level than would be the case if the Q of the cavity remained permanently high [3]. Rapid increase of Q now results in a very short, intense laser pulse. Q-switching is achieved by the use of a Pockels cell in conjunction with a polariser within the oscillator cavity. A Pockels cell operates on the principle of electro-optical activity, whereby the birefringent properties exhibited by a block of potassium dihydrogen phosphate (KDP) under an applied potential are utilised. Careful timing of the switching of this voltage allows control over the power and length of the output pulses.

The fundamental YAG output at 1064.8 nm has an approximately Gaussian temporal appearance, with a full width at half maximum (FWHM) value of ~ 20 ns. The power output is ~1 J at 10 Hz repetition rate, which is intense enough to allow further harmonic wavelength generation. The laser housing allows for four possibilities of harmonic production depending on the arrangement of non-linear crystals used. The 1064 nm fundamental may be doubled in frequency by one crystal to give the second harmonic at
532 nm. The second harmonic may then be mixed with the fundamental in a second crystal to give third harmonic generation at 355 nm, or it may simply be doubled by a second crystal to give the fourth harmonic at 266 nm.

2.3.2 The Dye Laser

The dye laser system used was a type SL4000 as supplied by Spectron Laser Systems. To provide tuneable radiation in the wavelength range required, 355 nm pumping of a methanol solution of Coumarin 500 was employed, followed by frequency doubling of the dye fundamental output.

At the concentrations used in the course of these experiments, the fundamental output of the dye was tuneable over the range 485-550 nm [4]. As is common for laser dyes, the active lasing medium involved is a large organic molecule (7-ethylamino-4-trifluoromethylcoumarin), exhibiting oscillator strengths and fluorescence quantum yields close to unity. The principle of operation involves excitation of the molecules from the ground electronic state, S_0, to the first excited state, S_1 [3,5]. Collisional relaxation within the S_1 state results in a Boltzmann distribution over the associated vibrational and rotational levels, which then fluoresce to excited vibrational levels of the S_0 state according to the Franck-Condon principle. This relaxation in the S_1 state prior to emission is vital to the dye being suitable as an active medium as it shifts the fluorescence spectrum of the dye to higher wavelength than the absorption spectrum, thus avoiding self-absorption problems. Operationally, the lifetime of the dye was extended from a few hours to several weeks by the addition of DABCO (1,4-diazobicyclo[2,2,2]octane). This acts as an effective triplet quencher thereby reducing the rate of dye decomposition.

The dye laser consists of an oscillator unit followed by two amplifier stages. All dye cells are pumped in the transverse orientation with horizontally polarised 355 nm radiation. Approximately 10% of the 355 nm pump beam is split off into the oscillator dye cell, the remainder being split equally between the two amplifier cells. Two 1 litre capacity dye circulators provided constant dye circulation.

The oscillator unit consists of a dye cell, a holographic grating, a tuning mirror, an output coupler and a prism beam expander. Wavelength selection is achieved using the tuning mirror which is mounted on a sine drive and controlled by a dedicated PC (FBS 486-DX) running custom software control (Spectron Laser Systems Autotracker...
Chapter 2: SiF Experimental Apparatus

Version 8.10) via an AT101 scan controller. The alignment of the oscillator unit optical components results in a horizontally polarised output beam.

Optimum amplification of the oscillator output was achieved by ensuring overlap with the pump beams in both amplifier cells. Monitoring of the output beam power is achieved by splitting a small fraction of the total output beam, after the first amplification stage, onto a photodiode. This signal is recorded by the scanning control PC.

2.3.3 The Wavelength Extender Unit

The fundamental output of the dye laser was frequency doubled using the wavelength extender unit (Spectron Laser Systems SL4000D-FM4A). This unit also provided the opportunity for frequency mixing the dye output with the YAG fundamental, and mixing the doubled dye output with the YAG fundamental. However, these facilities were not required in this study.

The frequency doubling of the dye fundamental output takes place in a temperature regulated housing holding a single potassium dideuterium phosphate crystal. The system includes a quartz compensating block to correct beam deviations as the whole unit is angle tuned with a stepper motor for optimum frequency doubling efficiency. Power monitoring again takes place by sampling a small fraction of the doubled beam after the doubling unit, and it is this signal that a dedicated autotracker PC, running custom software (Spectron Laser Systems Auto2), uses to optimise the crystal orientation.

2.4 The Fluorescence Collection System

The purpose of the capture optics is to maximise the gathering of fluorescence photons, thereby increasing the signal to noise ratio at the photon detector. To this end, two different arrangements of lenses have been tried over the course of this project. Initially, a two lens system was employed where the fluorescence was first collimated, and then focused into the monochromator. Latterly, a single lens arrangement was used where collection and focusing were performed by a single optic.

2.4.1 The Two Lens System

In general, due to the isotropic nature of the gas mixture, and ignoring any alignment effects induced by the polarisation of the exciting laser, laser induced fluorescence will be
emitted into a solid angle of $4\pi$ i.e. into all directions of space. To collect and collimate the maximum number of these photons, a collection lens with a focal length equal to the minimum distance achievable between the excitation point and the lens position was employed. The resulting collimated beam was then focused down into the monochromator using a second lens with a $f$-number chosen to match that of the monochromator. In this way the resolution of the monochromator is maximised as the grating is completely filled, and the radiant energy reaching the detector is also as large as possible. A focusing lens of diameter 50 mm and focal length 350 mm was chosen to match the $f/7$ monochromator.

### 2.4.2 The Single Lens System

It is especially important to collect the maximum number of fluorescence photons when attempting polarisation studies as the signal to noise ratio is much lower than that encountered during straightforward wavelength dispersion scans. The reasons for this are twofold: firstly, only one polarisation of the fluorescence photons is being detected at any given time, and secondly, the exciting laser intensity is generally much less to ensure no saturation effects are present, therefore absolute signal sizes are reduced. With this in mind, the two lens assembly was replaced with a single lens system, again matching the $f$-number of the monochromator, the hope being that lower reflection losses associated with a single collection optic would increase the signal-to-noise ratio at the detector. This obviously involved a reoptimisation of the monochromator-excitation point distance, but did yield slightly improved signal sizes. There was also the added benefit of more space along the fluorescence beam path for the additional optical components required for polarisation studies.

### 2.5 Polarisation Studies

The polarisation study embarked upon here necessitated some modifications to the previous experimental arrangement. As already stated, the collection of fluorescence photons was now carried out by a single lens system. The extra space this change afforded enabled the easy inclusion of a Photoelastic Modulator (Hinds International Inc., PEM-80 Series I, FS5) and a fixed Glan-Taylor calcite polariser (Halbo Optics) into the fluorescence path. A second fixed Glan-Taylor calcite polariser was inserted directly prior to the entrance window of the excitation zone, to ensure the purity of linear
polarisation of the excitation laser.

The PEM operates on the principle of strain-induced birefringence. The strain is induced in a fused silica optical crystal by longitudinal mode vibration at the element's natural frequency of 50 MHz, driven by a piezoelectric quartz crystal transducer. The degree of birefringence exhibited by the optical element is a function of the amplitude of the oscillation induced by the vibrating quartz crystal. This allows the PEM to introduce phase differences of up to 180° between two perpendicular components of light initially in phase. The PEM was mounted in the fluorescence path with its optic axis mounted at 45° to the vertical, with the Glan-Taylor polariser positioned immediately after in the fluorescence path set to transmit horizontally polarised light only. The rotation of the incident wave polarisation is a function of where the optical element is in its compression-stretching cycle at that moment in time. The PEM driver unit itself cannot be triggered, so a phase-locked output channel is provided which is used to trigger the laser via the CAMAC-based delay generation module described below.

The fluorescence 'analyser' polariser ensures that only one polarisation of light is transmitted through the monochromator to the detector. This implies that careful selection of the laser delay settings relative to the phase of the PEM allows selective detection of the horizontal and vertical components of the laser induced fluorescence. Only transmitting one polarisation through the monochromator removes any potential problems associated with preferential transmission. The polariser was set to transmit the horizontal component as the monochromator was found to slightly favour this polarisation.

2.6 Fluorescence Resolution and Detection

Wavelength dispersion of the laser induced fluorescence was performed by a Hilger and Watts Monospek 1000 D400 grating spectrometer. This instrument has a focal length of 1 m and, as previously mentioned, an effective $f$-number of ~7. The dispersion element in the monochromator was a 1200 groove mm$^{-1}$ grating mounted in the Czerny-Turner configuration [6]. Scanning of the grating was achieved by a retro-fitted stepper motor (Hytec KS 500, 0.72° per step) attached to the grating manual adjust sine drive, and controlled by a Hytec SMC 1066 stepper motor drive system. This unit was in turn controlled through a CAMAC crate, as will be described in the next section. The spectral bandwidth of the monochromator was set by adjusting the width of the slits at
Chapter 2: SiF Experimental Apparatus

the entrance and exit windows. Previous experiments had shown the reciprocal dispersion of the instrument to be 0.82 nm/mm. Wavelength calibration was achieved by comparison of known emission line positions from a low pressure mercury discharge lamp [7].

The wavelength-resolved photons were detected by a photomultiplier tube (EMI 9789QB or 9558QB, PM28R power supply). Nominally, both tubes operate in the 300-900 nm region, but both were specifically supplied with quartz windows to extend the operational response in the UV to ~200 nm. The quantum efficiency of these tubes in the wavelength window of interest (~250-350 nm) is ~20% [8]. Both employ CsSb photocathodes and have the venetian blind arrangement of dynodes (13 dynodes for the 9789QB and 11 for the 9558QB). The 9789QB is supplied with a 10 mm effective photocathode diameter as oppose to 45 mm for the 9558QB. As is expected from such arrangements, the 9789QB exhibits a high sensitivity and low dark current count, while the 9558QB shows an enhanced temporal response. PMT output signals were amplified prior to digitising using an EMI A2 unit for x10 amplification, or a Stanford Research Systems SRS240 unit for x5 and x25.

The PMT was protected from ambient and scattered light signals at all times. This was achieved by mounting it flush to the monochromator using a light-tight flange, and subsequent draping of the whole unit with a thick black cloth. It was found that this reduced background signals to an acceptable level.

2.7 Experimental Control and Signal Processing

All experimental timing control sequences and signal processing were handled by various modules incorporated in a CAMAC (Computer Aided Monitoring And Control IEEE-583) system (DSP optima 860 crate, DSP 6001 crate controller module) coupled to a dedicated PC (Dell 433MX Optiplex) via a DSP PC004 interface card. Communication between PC and CAMAC hardware was provided by custom-written software, ‘IO’, previously developed in this laboratory [9]. IO allows central control of the experimental timing sequences and data acquisition routines.

The experimental timing sequences were generated by a LeCroy 4222 Pulse Delay Generator (PDG) controllable through the CAMAC bus via IO. This module is capable of providing 4 independent, positive-going 5V pulses, of 100 ns FWHM, up to delays of
16.7 ms, in 1 ns increments. These pulses, however, are incompatible with the trigger logic of the laser flashlamps and Q-switch circuitry. The PDG outputs were therefore used to trigger a custom built line-driver unit, which was capable of providing pulses of the required amplitude and duration whilst retaining the original relative PDG pulse delay times.

Digitisation of the amplified analogue signal from the PMT is carried out by a transient digitiser (DSP 2001A) with 100 Mhz analogue bandwidth, and minimum sample interval of 10 ns. The unit continuously digitises and stores the required number of samples until a trigger from the PDG forces it to output data to the controlling PC. A particularly useful aspect of the *JO* program was its ability to record up to 10 independent signal gates simultaneously. In this way it was possible to integrate over specific regions of waveforms, thereby revealing the temporal evolution of the process generating the fluorescence.

Scanning of the dye laser wavelength was an aspect of this experiment not controlled by *IO* or any CAMAC module. This task was accomplished by a dedicated PC running custom scanning software as previously described. One problem arising from this arrangement was the need for manual synchronisation between any wavelength scanning and the data acquisition routines in *IO*. However, absolute accuracy in starting the separate processes was unnecessary as the spectroscopic features being recorded were generally well isolated and easily recognisable through previous experiments and simulated spectra.

The inclusion of a 4 channel analogue to digital converter (Hytec ADC 520) in the CAMAC array allowed data to be recorded simultaneously with the transient digitiser output. Although unable to provide any temporally resolved information, this module was used for recording power traces of the doubled dye laser beam during polarisation experiments. This was achieved by sampling a small fraction of the excitation laser beam on its exit from the excitation zone with a Joulemeter (Molecular model J3-09DW). This produced a decaying analogue voltage signal from the Joulemeter, proportional to the exciting laser power, which was sampled by the ADC. The relative power fluctuations of the exciting laser beam over the course of a scan could therefore be recorded concurrent with the laser induced signal data.
Bibliography


Chapter 3

Spectroscopy of the SiF $B^2\Sigma^+-X^2\Pi$ and $C^2\Delta-X^2\Pi$ Systems

3.1 Introduction

The principal aim of this study is to investigate collision-induced electronic energy transfer between the $C^2\Delta$ and $B^2\Sigma^+$ states of the SiF radical. More specifically, what is desired is an insight into the factors which dictate how population transferred from the $C^2\Delta$ state is partitioned among the various degrees of freedom of the $B^2\Sigma^+$ product state. This requires a knowledge of the populations of rovibronic levels occupied immediately before and immediately after the electronic-state-changing collision. The technique of Laser-Induced Fluorescence (LIF) is employed to provide this information. The experimental approach and analysis of results is greatly simplified by a fortuitous difference between the radiative lifetimes of the two excited states involved: these are $\sim 100$ ns and $\leq 10$ ns for the $C^2\Delta$ and $B^2\Sigma^+$ states respectively. Consequently, the density of the collision partner can be arranged such that the $C^2\Delta$ state has a reasonable chance of undergoing an electronically inelastic collision during its radiative lifetime, but the product $B^2\Sigma^+$ state emits effectively instantaneously, without subsequent collisional modification of the product distribution. The B-X dispersed emission therefore contains information on the nascent product state distributions. A knowledge of the C state parent rovibrational distribution thereby allows the collisional state-to-state propensities to be deduced. As will be seen in the investigation of the CH radical in later chapters, the same result is achievable in the absence of such an advantageous lifetime ratio by gating over the earliest component of the fluorescence, but at the penalty of discarding the remainder of the signal. Regardless of the method used to acquire nascent product state spectra, a detailed knowledge of the spectral positions and transition probabilities of the C-X and B-X bands involved is essential for their quantitative analysis, and the resultant determination of excited state rovibronic populations.
Chapter 3: Spectroscopy of the SiF $B^2\Sigma^+-X^2\Pi$ and $C^2\Delta-X^2\Pi$ Systems

The spectroscopic features utilised in this work have previously been well characterised within this laboratory [1,2]. Therefore, only a brief overview of the relevant information will be presented in this section.

### 3.2 Previous Work

The SiF radical was first observed spectroscopically in 1911 [3], and since then has been the subject of both experimental and theoretical examination. The radical has been detected in stellar atmospheres [4,5] and, in a more applied context, is present during plasma etching and deposition in the manufacture of semiconductor devices[6,7,8,9,10]. The $a^4\Sigma^--A^2\Sigma^+$ system has also been used as the basis of a chemical laser [11].

### 3.3 Interatomic Potentials and Spectroscopic Constants

The potential energy curves for the two states of interest are shown in Figure 3-1. These were derived using the RKR method, employing the published molecular constants shown in Table 3-1. As can be seen from Figure 3-1, the equilibrium internuclear separation of the $C^2\Delta$ state ($r_e=1.5713$ Å) is only slightly shorter than that of the $X^2\Pi$ state ($r_e=1.6011$ Å), resulting in very weak off-diagonal Franck-Condon factors. However, the $B^2\Sigma^+$ state equilibrium bondlength is substantially shorter than the ground state ($r_e=1.5414$ Å), resulting in far more extensive vibrational progressions. The value of the $C^2\Delta$ spin-orbit splitting is ambiguous, and will be discussed in Section 3.4.3.
Table 3-1: Principle Spectroscopic Constants of the \( \text{X}^2\Pi \), \( \text{B}^2\Sigma^+ \) and \( \text{C}^2\Delta \) States of \(^{28}\text{Si}^{19}\text{F}\).

<table>
<thead>
<tr>
<th>State ( T_e^{(a)} )</th>
<th>( \text{X}^2\Pi )</th>
<th>( \text{B}^2\Sigma^+ )</th>
<th>( \text{C}^2\Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>34561.57</td>
<td>39438.07</td>
<td></td>
</tr>
<tr>
<td>( A_e^{(b)} )</td>
<td>161.689</td>
<td>-</td>
<td>0/2.46(^{(i)})</td>
</tr>
<tr>
<td>( \omega_e^{(c)} )</td>
<td>857.31</td>
<td>1011.16</td>
<td>889.70</td>
</tr>
<tr>
<td>( \omega_x e^{(d)} )</td>
<td>-4.83</td>
<td>-4.84</td>
<td>-5.62</td>
</tr>
<tr>
<td>( \omega_y e^{(e)} )</td>
<td>0.018</td>
<td>0.012</td>
<td>-0.044</td>
</tr>
<tr>
<td>( B_e^{(f)} )</td>
<td>0.58116</td>
<td>0.62675</td>
<td>0.60380</td>
</tr>
<tr>
<td>( D_e \times 10^6^{(g)} )</td>
<td>1.07</td>
<td>0.96</td>
<td>1.09</td>
</tr>
<tr>
<td>( \alpha_e^{(h)} )</td>
<td>0.00492</td>
<td>0.00464</td>
<td>0.00579</td>
</tr>
</tbody>
</table>

All values in wavenumbers (cm\(^{-1}\)); (a) electronic term value corresponding to the zero point energy gap between the ground and excited state; (b) spin-orbit interaction constant of the theoretical vibrationless energy level of the state; (c) the vibration wavenumber that a classical oscillator would possess for an infinitesimal displacement from equilibrium; (d) the first anharmonic correction constant; (e) the second anharmonic correction constant; (f) rotational constant for the hypothetical equilibrium state of the molecule at the bottom of the potential energy curve; (g) centrifugal distortion constant; (h) vibration-rotation interaction constant; (i) see Section 3.4.3 for discussion.
Chapter 3: Spectroscopy of the SiF $B^2\Sigma^+ - X^2\Pi$ and $C^2\Delta - X^2\Pi$ Systems

Figure 3-1: Potential Energy Curves of the $X^2\Pi$, $B^2\Sigma^+$ and $C^2\Delta$ States of $^{28}\text{Si}^{19}\text{F}$.

Curves calculated using the RKR method. The lower panel shows the region of interest in this study in more detail.
Chapter 3: Spectroscopy of the SiF $B^2\Sigma^+ - X^2\Pi$ and $C^2\Delta - X^2\Pi$ Systems

3.4 Energy Level Structure

To fully understand and simulate the spectroscopic transitions exploited in this study, it is necessary to consider the energy level structure in each of the spectroscopically linked states. This structure will vary in each state depending on the degree of coupling between the various forms of angular momentum present. These momenta, neglecting the nuclear hyperfine spin, are defined as:

- $L$, the total electronic orbital angular momentum
- $S$, the total electron spin angular momentum
- $R$, the total nuclear framework rotation angular momentum

The ways in which these angular momenta couple together to form the total angular momentum, $J$, will determine the energy level structure of each state.

3.4.1 The $B^2\Sigma^+$ State

The $B^2\Sigma^+$ state, for which the projection of the electronic angular momentum, $L$, onto the internuclear axis is clearly zero, exhibits pure Hund’s case (b) coupling. The quantum number $N$ is defined as the total angular momentum neglecting electron spin, which in this case is exactly equivalent to $R$. The electron spin angular momentum, $S$, is coupled to $N$ by the magnetic field arising from the rotation of the nuclear framework to form the resultant total angular momentum, $J$. Space quantisation dictates that $S$ may take $2S+1$ orientations relative to $R$, which in the case of a molecule with a spin multiplicity of 2 results in two values of $J$ being associated with each value of $N$ ($J=N+1/2$, $J=N-1/2$). For $^2\Sigma$ states the rotational energy levels are given by:

$$F_1(N) = B_J N (N+1)^{1/2} \gamma N$$

Equation 3-1

and

$$F_2(N) = B_J N (N+1)^{-1/2} \gamma(N+1)$$

Equation 3-2

where $F_1$ and $F_2$ refer to the $J=N+1/2$ and $J=N-1/2$ components, respectively. $\gamma$ is the spin-rotation constant, which determines the magnitude of the $F_1$-$F_2$ splitting for a given $N$. The energy level structure arising from this coupling scheme is illustrated in Figure 3-2.
3.4.2 The $X^2\Pi$ State

The $X^2\Pi$ state has been shown, for low values of $R$, to be well described by Hund’s coupling case (a) [12,13]. In this case the couplings within the molecule are dominated by the strong, axially symmetric electric field existing between the nuclei. This field couples the electronic angular momentum, $L$, to the internuclear axis, which in turn couples $S$ through the magnetic field induced by the rotation of the electrons around the axis. In this case, the projections of $L$ and $S$ onto the internuclear axis, $\Lambda$ and $\Sigma$ respectively, are good quantum numbers, their sum defining the value of $\Omega$, the quantum number representing the component of the total electronic angular momentum along the internuclear axis. $\Omega$ may be written as:

$$\Omega = |\Lambda + \Sigma|$$

Equation 3-3

where $\Lambda$ may be assigned any integer value between 0 and $L$, and $\Sigma$ any integer or half integer (depending on the number of unpaired electrons) value between $+S$ and $-S$. The total angular momentum, $J$, is given by the resultant of $\Omega$ and the nuclear framework rotation, $R$.

As $|\Lambda|$ has the value 1 in a $\Pi$ state, and $S$ has the value $1/2$ for a doublet state, the spin-orbit interaction gives rise to two components in the ground state, labelled $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. These two spin-orbit manifolds are split by an amount governed by the spin-orbit interaction constant, $A$. This may be seen in Figs 3-2 to 3-5, where the $^2\Pi$ state is shown split into an $F_1$ and $F_2$ manifold.

Neglecting centrifugal distortion, the rotational energy levels of a pure Hund’s case (a) molecule are given by:

$$F_v = B_v [J(J+1) - \Omega^2]$$

Equation 3-4

It may also be seen from Figure 3-2 that in the ground state, every value of $J$ in each manifold has two energy levels associated with it. The origin of this phenomenon lies in an effect known as $\Lambda$-doubling, arising for states with $\Lambda \neq 0$. A given value of $\Lambda$ can take two orientations with respect to the internuclear axis, giving rise to two components of
Chapter 3: Spectroscopy of the SiF $B^2\Sigma^+ - X^2\Pi$ and C$^2\Delta - X^2\Pi$ Systems

each value of $J$ for a given $\Omega$. These two components may usefully be thought of as the sum and difference of the two wavefunctions corresponding to the clockwise and anticlockwise classical rotation of the electrons about the internuclear axis. These symmetry-adapted wavefunctions are degenerate to a first approximation, but split when coupled with the rotation of the nuclear framework by an amount proportional to $R$.

The quantum number $N$ corresponds to the total angular momentum neglecting electron spin. This quantum number is ill-defined when an electronic state corresponds rigorously to a Hund’s case (a) classification, but as $R$ increases, and the molecule rotates faster, the electronic spin is gradually decoupled from the internuclear axis, and couples to the rotation vector $R$ through the magnetic field arising from the rotation of the nuclei. In the limit of high $R$, the molecule conforms to a Hund’s case (b) coupling scenario with $\Omega$ no longer defined, but with $\Lambda$-doubling still present. A theoretical investigation by Hill and Van Vleck [14] showed that the rotational term values for doublet states with $\Lambda \geq 1$ undergoing a Hund’s case (a)-(b) transition are given by:

$$F_1(J) = B_v \left[ (J + \frac{1}{2})^2 - \Lambda^2 + \frac{1}{2} \sqrt{4(J + \frac{1}{2}) + Y(Y - 4)\Lambda^2} \right] - D_v J^4$$

Equation 3-5

and

$$F_2(J) = B_v \left[ (J + \frac{1}{2})^2 - \Lambda^2 + \frac{1}{2} \sqrt{4(J + \frac{1}{2}) + Y(Y - 4)\Lambda^2} \right] - D_v (J + 1)^4$$

Equation 3-6

where $Y = A/B_v$.

3.4.3 The C$^2\Delta$ State

Exactly the same arguments applied to the $X^2\Pi$ state may be used when discussing the energy level structure of the C$^2\Delta$ state. However, in this case the magnitude of the spin-orbit coupling and $\Lambda$-doubling observed is much less than in the ground state, and the transition to Hund’s case (b) occurs at much lower values of $R$.

As mentioned in Table 3-1, there is some ambiguity as to the magnitude of $A$, the spin-orbit splitting constant, in the C$^2\Delta$ state, leading to uncertainty about the coupling case
Chapter 3: Spectroscopy of the SiF $B^2\Sigma^+-X^2\Pi$ and $C^2\Delta-X^2\Pi$ Systems

present [15]. This situation arises as equivalent term value expressions are obtained for all but the lowest A-doubled level from Equation 3-5 and Equation 3-6 with either $A=0$ or $A=4B$, where $B$ is the rotational constant. Spectral congestion in the region where transitions from this level occur have prevented a definitive assignment of $A$. However, our own observations of the relative intensities of low-$J$ lines in $C^2\Delta- X^2\Pi$ LIF excitation spectra are matched better to simulations with $A=4B$ (2.46 cm$^{-1}$), and it is with this value that the $C^2\Delta$ state is depicted in Figure 3-4 and Figure 3-5.

3.5 Rovibronic Transition Selection Rules

The electric dipole selection rules operating for rovibronic transitions in diatomic molecules are[13,16,17]:

- $\Delta A=0, \pm 1$
- $\Delta S=0$ (transitions with $\Delta S\neq 0$ become more strongly allowed as spin-orbit interactions increase with heavier atoms)
- $\Sigma^+ \leftrightarrow \Sigma^+, \Sigma^- \leftrightarrow \Sigma^-, \Sigma^+ \leftrightarrow \Sigma^-$ (Only electronic states of the same parity can interact)
- $\Delta J=0, \pm 1$
- $+ \leftrightarrow -, + \leftrightarrow +, - \leftrightarrow -$ (only rovibronic levels of opposite parity are connected)
- $s \leftrightarrow s, a \leftrightarrow a, s \leftrightarrow a$ (for homonuclear diatomics)
- $g \leftrightarrow u, g \leftrightarrow g, u \leftrightarrow u$ (for centrosymmetric molecules)

Using these rules in conjunction with the previously determined energy level structures allows the nature and energy of all possible transitions between the ground state and the two excited states to be rationalised. The intensity of the transitions will be governed by the population in a given level, the frequency of the transition photons, and the transition moment integral [13,16,17]. The transitions marked on Figs. 3-2–3-5 are labelled according to convention, where the main letter indicates the value of $\Delta A$, the preceding superscript the value of $\Delta N$, and the subscripts indicate the upper and lower manifolds of the transition respectively.
Figure 3-2: Energy Level Structure and Main Branch ($\Delta N = \Delta J$) Transitions in the SiF $B^2\Sigma^+-X^2\Pi$ (0,0) System.

$\Lambda$-splitting in the ground state is shown on a much enlarged scale. Term energies calculated from the Zare simulation program, as discussed in Section 3.7.
Figure 3-3: Energy Level Structure and Satellite ($\Delta N \neq \Delta J$) Transitions in the SiF $B^2\Sigma^+ - X^2\Pi$ (0,0) System.

$\Lambda$-splitting in the ground state is shown on a much enlarged scale. Term energies calculated from the Zare simulation program, as discussed in Section 3.7.
Figure 3-4: Energy Level Structure and Main Branch ($\Delta N = \Delta J$) Transitions in the SiF $\text{C}^2\Delta-\text{X}^2\Pi$ (0,0) System.

$\Lambda$-splitting in the ground state is shown on a much enlarged scale. $\Lambda$-doubling in the $\text{C}^2\Delta$ state has been omitted for clarity, although the transitions from each $\Lambda$-doublet in the ground state are shown. Term energies calculated from the Zare simulation program, as discussed in Section 3.7.
Figure 3-5: Energy Level Structure and Satellite ($\Delta N \neq \Delta J$) Transitions in the SiF $C^2\Delta-X^2\Pi$ (0,0) System.

$\Lambda$-splitting in the ground state is shown on a much enlarged scale. $\Lambda$-doubling in the $C^2\Delta$ state has been omitted for clarity, although the transitions from each $\Lambda$-doublet in the ground state are shown. Term energies calculated from the Zare simulation program, as discussed in Section 3.7.
Chapter 3: Spectroscopy of the SiF B^2Σ⁺-X^2Π and C^2Δ-X^2Π Systems

3.5.1 SiF Excitation Spectra

Previous work in this laboratory had established the assignment and wavelength regions of most of the spectral features utilised in this study [1], but some new work was required to carry out the polarisation studies.

3.5.2 Experimental Technique

The apparatus used to obtain excitation spectra has already been described in Chapter 2. Radical generation was accomplished by continuous microwave discharge in a 10% mixture of SiF₄/Ar (50 sccm) combined with a larger Ar flow (2 slm) prior to the discharge region. At the pumping speed employed, this resulted in a steady pressure of 1.4 Torr in the flow tube. The 10% SiF₄/Ar mixture was prepared in advance in a 10 dm³ Pyrex bulb using SiF₄ (Union Carbide, 99.99% or Fluorochem 99.5%) and Ar (BOC 99.99%), and typically left overnight to equilibrate before use. All gases were used without further purification.

The excitation spectra were recorded by setting the monochromator to detect fluorescence emitted on a known SiF spectroscopic feature as the dye laser wavelength was scanned across transitions connected to upper state levels known to fluoresce in the region being monitored. The monochromator slits were set such that the spectral bandwidth of the detection function encompassed all the returning fluorescence on the specified band, thus allowing meaningful comparison of relative line intensities. The PMT was protected from exposure to scattered laser light by ensuring the excitation and detection wavelengths were well separated. Operationally, this was achieved either by pumping the lower lying ground state spin-orbit manifold, and detecting the red-shifted fluorescence to the upper (i.e. in the case of C^2Δ -X^2Π scans, pumping on C^2Δ -X^2Π₁/₂ and detecting on C^2Δ -X^2Π₃/₂), or by detecting the fluorescence on another vibrational band altogether.

3.5.3 Results

For the purposes of this study it is important to ensure that a well-characterised level of a single excited electronic state is occupied prior to the electronic energy state-changing collision i.e. that no accidental promotion of population to more than one initial rovibronic level takes place. Examples of vibronic states to which specific excitation is
required are the C$^2\Delta$, $v=0$ and B$^2\Sigma^+$, $v=3$ levels. To ensure clean excitation to these levels, and to assess the number of available rotational lines via which it might be achieved, excitation scans over the C$^2\Delta$ -X$^2\Pi_{\frac{1}{2}}$ (0,0) and B$^2\Sigma^+$-X$^2\Pi$ (3,0) bands were performed. These spectra are shown in Figure 3-6 and Figure 3-7, along with simulations (generated as described in Section 3.7). As can be seen, the excellent agreement between experiment and simulation shows the spectroscopy of these two systems to be well characterised.
Figure 3-6: SiF $C^2\Delta$ -$X^2\Pi_{1/2}$ (0,0) LIF Excitation Spectra.

(a) Experimentally observed excitation spectrum. Fluorescence detected on the $C^2\Delta$ -$X^2\Pi_{3/2}$ sub-band. (b) Simulation as described in Section 3.7 assuming an excitation laser bandwidth of 0.4 cm$^{-1}$. 
Figure 3-7: SiF $B^2\Sigma^+-X^2\Pi$ (3,0) LIF Excitation Spectra.

(a) Experimentally observed spectrum showing transitions from both $X^2\Pi$ spin-orbit manifolds. Fluorescence detected on $B^2\Sigma^+-X^2\Pi$ (3,2) band. Features marked with (*) are due to minority isotopes of Si. (b) Simulation as described in Section 3.7 assuming an excitation laser bandwidth of 0.4 cm$^{-1}$.
3.6 SiF Dispersed Fluorescence Spectra

Having shown that it was possible to characterise unambiguously the required excitation spectra, the next step was to identify and simulate the associated dispersed emission spectra. A complete understanding of the spectroscopy is again necessary here, as it is through the simulation of dispersed fluorescence spectra that the partitioning of population amongst the degrees of freedom of the excited states before and after the electronic state-changing collision will be assessed. Rotationally resolved dispersed fluorescence spectra will be discussed in Chapter 4, with associated simulations and conclusions, but for now only vibrationally resolved spectra will be discussed. Previous work in this laboratory had probed the vibronic transition probabilities of the relevant bands at a quantitative level, and an overview of these results will be presented here.

3.6.1 Experimental Technique

The dispersed fluorescence spectra were obtained by fixing the excitation laser wavelength on a known spectroscopic feature and scanning the monochromator over fluorescence originating from the excited states populated either directly, or by subsequent inelastic collisions. When investigating relative transition probabilities, the laser was always tuned to the Q-head of the band in question, as this afforded the maximum signal intensity. As optical saturation is not a problem in these experiments, the dye laser power was also maximised. Because only vibrational resolution was required in these spectra, the bandwidth of the monochromator was set to 0.4 nm.

3.6.2 B²Σ⁺-X²Π Emission Spectra

Previous work in this laboratory had investigated the spectroscopy of the B²Σ⁺ (v′=0-5) - X²Π (v′=0-12) [1,2] emission bands. A brief summary of these results is presented here.

The deduction of excited state populations from the simulation of dispersed fluorescence spectra requires the relevant vibrational transition probabilities to be known. These were calculated first by solving the radial Schrödinger Equation to obtain the wavefunctions for each state using a program written by Lawley and Wheeler [18], and then computing the transition moment integral. The spectral intensities of all the B-X bands were found to be well reproduced using an invariant \( R_e(r) \) function across the region investigated \((r\sim1.40-1.75 \text{ Å})\), with calculated Franck-Condon Factors agreeing well with literature.
The electronic configurations of the $X^2\Pi$ and $B^2\Sigma^+$ states of SiF have been well characterised [12,15,20,21,22,23] and found to be directly related to the analogous states of the SiCl radical (also previously investigated in this laboratory [24,25]). The configurations are:

$$X^2\Pi \quad (1\sigma...7\sigma)^2(1\pi2\pi)^4(3\pi)^1$$

$$B^2\Sigma^+ \quad (1\sigma...7\sigma)^2(1\pi2\pi)^4(4\sigma)^1$$

The $B^2\Sigma^+-X^2\Pi$ transition therefore involves promotion of an electron between the $3\pi$ and $4\sigma$ orbitals. Both these orbitals are predicted to be centred predominantly on the Si atom [26], so it is unsurprising that the transition dipole moment function is best represented as invariant with internuclear separation. This picture is also consistent with the short lifetime (<10 ns, instrumentally limited) observed for the $B^2\Sigma^+$ state, as the $B^2\Sigma^+-X^2\Pi$ system is analogous to a strongly allowed pure atomic Si 3p-4s transition.

### 3.6.3 C$^2\Delta - X^2\Pi$ Emission Spectra

As for the B-X system, the calculated Franck-Condon Factors were in good agreement with literature values [27]. However, in this case agreement with the experimental vibrational band strengths could only be achieved by incorporating a quadratic form of $R_o(r)$ which declines sharply with $r$. Consideration of the electronic configuration of the C$^2\Delta$ state again rationalises this observation. The C state is primarily described by the valence configuration $(1\sigma...6\sigma)^2(7\sigma)^1(1\pi2\pi)^4(3\pi)^2$ [15,26,28,29]. The C-X transition therefore involves the movement of an electron between the $3\pi$ and $7\sigma$ orbitals. LCAO predicts that the $7\sigma$ orbital contains a major contribution from the fluorine 2p atomic orbital, so the C-X transition involves moving an electron between orbitals centred mainly on different nuclei. This results in the degree of overlap between the orbitals decreasing as $r$ increases, hence the transition dipole moment decreases. This difference is also reflected in the longer C$^2\Delta$ state radiative lifetime of ~100 ns.
3.7 Simulation Technique

The transition frequencies and rotational linestrengths required for all SiF simulations were calculated using a program supplied by Prof. R. N. Zare [30] using published molecular constants. The output from this program was convoluted with the occupancy of the rovibronic levels in the excited state of the band being modelled. This operation was achieved by a custom-written program which allowed the populations in both spin-orbit manifolds of a doublet state to be independently adjusted. As will be discussed later, this feature was essential for accurate simulation of collisionally modified rotational distributions. The simulation then had the correct weighting for each rotational transition, but required the impartion of a finite bandwidth. This was achieved by a further program which convoluted the delta functions associated with each line position with a Gaussian instrumental resolution function, with a half-width matching the experimentally determined value.

When modelling vibrationally resolved directly excited dispersed emission spectra, no rotational features can be discerned, so for this reason it was assumed the population in the excited rotational levels corresponded to a Boltzmann temperature distribution. As will be seen in the next chapter, when the resolution of the monochromator was sufficient to observe rotational contours, the excited state rotational populations required for an accurate simulation are often very far removed from thermal.

Successful simulation of experimental excitation spectra requires that the intensities of individual rotational transitions be well matched. These simulations were performed assuming the bandwidth of the exciting laser to be the limiting factor in the resolution of the spectrum. This value was measured to be 0.4 cm\(^{-1}\). A rotational population corresponding to a 300 K thermal distribution was found to adequately model the observed intensities in Figure 3-6 and Figure 3-7.
3.8 Conclusions

Laser-induced fluorescence excitation spectra have been recorded and analysed to allow the unambiguous assignment of transitions to identified rovibronic states of SiF, thereby enabling the production of well-defined initial state distributions for energy transfer studies. The successful modelling of excitation spectra has shown the spectroscopy of the relevant systems to be well understood. This will allow dispersed emission spectra to be simulated and hence reveal the nature of the partitioning of energy amongst the various degrees of freedom of the excited states resulting from inelastic processes.
Bibliography

Chapter 3: Spectroscopy of the SiF $B^2\Sigma^+ - X^2\Pi$ and $C^2\Delta - X^2\Pi$ Systems


Chapter 4
SiX (X=Cl, F) Vibrationally and Rotationally Resolved Results

4.1 Introduction

Previous experiments carried out in this laboratory had probed collisional transfer between the \( B^2\Delta-B^2\Sigma^+ \) states of SiCl and the corresponding \( C^2\Delta-B^2\Sigma^+ \) states of SiF \([1,2,3,4,5,6,7]\). Despite the difference in labelling, the \( ^2\Delta \) and \( ^2\Sigma^+ \) states in both molecules are electronically analogous, both having the configurations discussed in Sections 3.6.2 and 3.6.3. The fortuitous ratio of excited state radiative lifetimes that allows the facile acquisition of nascent product state population partitioning, discussed in Section 3.1, is also present in SiCl (\( B^2\Delta \sim 1 \mu s, B^2\Sigma^+ \leq 10 \text{ ns} \ [5,8,9] \)). The relevant potential energy curves are shown in Figure 4-1.

The extended series of experiments comprising the whole of this study recently formed the basis of a review article \([10]\), and the reader is directed to this and the original papers for detailed information on experimental procedure and results. It is the intention in this chapter to briefly summarise the work previously performed on the SiF/SiCl radicals (Sections 4-2 to 4-3-3), and then focus on the new results obtained during the course of the present work (from Section 4-3-4 onwards).

Collisional coupling of the \( B^2\Delta-B^2\Sigma^+ \) states in SiCl was first studied at the vibronic level by Jeffries \([8]\). Subsequent work in this laboratory extended the range of quenching molecules investigated at this level, and also provided the first information on rotational branching. Product state vibrational distributions and electronic branching fractions were found to be remarkably sensitive to the identity of the quencher.

Subsequently, the iso-electronic SiF radical was studied in this group, and found to exhibit startling different behaviour. The dominant vibronic branching channels from SiF \( C^2\Delta, v=0 \) and \( 1\rightarrow B^2\Sigma^+ \) involve \( \Delta v=0 \), and therefore startlingly large vibronic energy gaps
Chapter 4: SiX (X=Cl, F) Vibrationally and Rotationally Resolved Results

of ~5000 cm⁻¹. Contrary to SiCl, the vibrational transfer propensities are well matched by the Franck-Condon overlap between $C^2\Delta$ and $B^2\Sigma^+$ vibrational wavefunctions, and are relatively independent of quencher. Rotational effects in $C^2\Delta$-$B^2\Sigma^+$ transfer were probed by pumping at two different bandheads to produce distinct initial $C^2\Delta J$ distributions. This study revealed that a significant proportion of the vibronic energy defect was partitioned into SiF rotation. It was this (surprising) observation which prompted the author's involvement in this work, extending the previous results by carrying out a study of the rotational propensities in $C^2\Delta$-$B^2\Sigma^+$ transfer upon excitation of individual rotational levels of the $C^2\Delta$ state.
Figure 4-1: RKR Potential Energy Curves for the Relevant States of SiCl and SiF.

The lower panels show the regions of interest in greater detail. Curves constructed from established molecular constants; (a) SiCl; (b) SiF.
4.2 Summary of Previous SiF and SiCl Vibronically Resolved Results

4.2.1 Total Collisional Removal of the $^2\Delta$ State

The total removal rate constants for the $^2\Delta$ states were determined by analysing the pressure dependence of fluorescence decay curves, and fitting to the well known expression:

$$k = \frac{1}{\tau_{\text{nd}}} + k_Q P_Q$$

Equation 4-1

where, in principle, both the radiative lifetime, $\tau_{\text{nd}}$, and the quencher-specific bimolecular rate constant, $k_Q$, will depend on the initial rovibronic level.

The original study by Jeffries [8] revealed the SiCl $B'^2\Delta$ state to be remarkably efficiently quenched by the noble gases He, Ne and Ar, with rate constants representing significant fractions of the gas-kinetic values. The range of quenchers was extended [3] to include the non-polar molecules H$_2$, N$_2$, CO$_2$, CH$_4$ and CF$_4$, all of which also proved to be efficient quenchers. A reasonable correlation between the thermally averaged total removal cross section and the attractive intermolecular force as expressed by the Parmenter-Seaver model [11] was observed, and is illustrated in Figure 4-2. The quenching efficiencies of the SiCl $B'^2\Delta \upsilon=0$ and 1 levels are not notably different overall, although there is considerable variation with partner identity. No experiments on rotational-level dependent quenching have been performed.

The equivalent measurements on the SiF $C'^2\Delta$ state revealed a far more limited range of efficient quenching partners (H$_2$, N$_2$, CO$_2$ and CH$_4$), quenching by He and Ar being too low to be observed until later work with improved precision. Unlike SiCl $B'^2\Delta$, these quenching efficiencies show no obvious correlation with any molecular property. The rotational-level dependence has been investigated [5] over the range $J=2.5-21.5$, with no systematic variation observed.
Figure 4-2: Parmenter-Seaver plot for total collisional removal from SiCl $B'^2\Delta$ $v=0$ (■) and $v=1$ (▲).

The data for $v=1$ have been displaced vertically for display purposes, and the results for $H_2$ were excluded when calculating the best fit to the remaining points. $\sigma(B' - (B,D))$ is the cross section for total removal of the $B'$ state.
Chapter 4: SiX (X=Cl, F) Vibrationally and Rotationally Resolved Results

4.2.2 Electronic Branching Fractions

The electronic branching fraction, $f_B$, is defined as the fraction of the population collisionally removed from the $B'/C^2\Delta$ state which is specifically transferred to the $B^2\Sigma^+$ state. It may be determined from the ratio of integrated emission intensities $I(B)/I(B'$ or $C)$ on the relevant bands for a specified pressure of quencher, provided $k_Q$ (the collisional removal rate constant) and $\tau_{rad}$ (the radiative lifetime) for the relevant $B'/C^2\Delta$ state are known. Assuming negligible secondary quenching of the $B^2\Sigma^+$ state, the dependence is given by:

$$f_B = \frac{I(B')\tau_{rad}^{-1}}{I(B' or C)k_QP_Q}$$

Equation 4-2

The $f_B$ values for the SiCl $B'\rightarrow B$ process, as originally established by Jeffries for He, Ne and Ar [8], and later extended to other molecules [3,4], span the range ~10-100%. They vary with the identity of the collision partner in a way not obviously correlated with any molecular property, but there does appear to be a tendency, for molecular partners at least, for $f_B$ to be larger for SiCl $B'^2\Delta v=0$ than $v=1$ with the same partner.

The $f_B$ values for the SiF $C\rightarrow B$ process are generally found to be smaller than the equivalent SiCl case, spanning the range ~0-20% [5]. Again, no obvious correlation with any molecular property is observed, but a tendency for similar values of $f_B$ for SiF $C^2\Delta v=0$ and $v=1$ quenching with the same partner is apparent.

4.2.3 Vibrational Partitioning

Dispersed fluorescence spectra following vibrationally specific $B'/C^2\Delta$ excitation allow the $B^2\Sigma^+$ product state vibrational distributions to be established using measured vibrational transition probabilities and band positions[4]. Product state vibrational distributions are shown in Figure 4-3 for initial excitation of $B'/C^2\Delta v=0$ and 1.

It is immediately obvious from Figure 4-3a that the SiCl product $B^2\Sigma^+$ vibrational distribution varies considerably with the collision partner for both $B^2\Delta v=0$ and $v=1$. Neither set of distributions show any correlation with the $B^2\Delta-B^2\Sigma^+ (v, v')$ Franck-Condon overlap, included in Figure 4-3a for comparison. The results do show an overall tendency for the mean of the distributions to be shifted to lower $B^2\Sigma^+$ vibrational levels.
as the molecular complexity of the collision partner increases i.e. more energy is removed to unobserved degrees of freedom. It has also been shown that the cross sections for near degenerate $B'2\Delta, v=0\rightarrow B^2\Sigma^+, v'=2$ transfer correlate well with the attractive intermolecular forces, as indicated by the Parmenter-Seaver model [11].

Once again, the results observed for SiF show a regularity which contrasts to the SiCl case, as shown in Figure 4-3b. Here we see a clear order in the collision-induced $B^2\Sigma^+$ vibrational distributions arising from a given $C^2\Delta$ state, regardless of the identity of the collision partner. It can also be seen that the distributions arising from $C^2\Delta v=0$ and $v=1$ match rather closely the $C^2\Delta-B^2\Sigma^+ (v, v')$ Franck-Condon overlap between the two vibrational manifolds. Surprisingly, in both cases, the favoured channel for vibrational transfer between the two excited states involves $\Delta v=0$, and therefore an energy gap of $\sim 5000 \text{ cm}^{-1}$. 
Figure 4-3: B²Σ⁺ Product State Vibrational Distributions.

Collisional transfer from (a) SiCl B²Δ, and (b) SiF C²Δ. In each case (i) \(v=0\) and (ii) \(v=1\). Symbols represent different quenching gases as shown in the panel. FCF represents the Franck-Condon Factor.
4.3 SiCl and SiF Rotationally Resolved Results

4.3.1 Introduction

Investigation of the rotational transfer propensities accompanying the electronically inelastic collision event was achieved through selective laser excitation, and dispersed fluorescence measurements. The results of previous work are presented in Section 4-3-2, with those of the present study in Section 4-3-4. The magnitude of the rotational constant, B, in both SiCl and SiF prevents the resolution of fluorescence spectra down to individual rotational lines. Therefore, to derive rotational information from the emission spectra, it was necessary to substantially decrease the spectral bandwidth of the monochromator to a point where rotational contours became resolved.

To be able to draw valid conclusions on the effect that initial rotational excitation in the B'/C^2Δ state has on the rotational distribution of the product B^2Σ^+ state, it is important that the population in both states be characterised in a quantum-level-specific fashion immediately before and after the electronically inelastic collision. This criterion is easily fulfilled by the B^2Σ^+ states by virtue of their radiative rate being more rapid than any collisional processes operating at the pressures employed in this study (SiCl/SiF B^2Σ^+ ≤ 10 ns). Collision-induced B^2Σ^+-X^2Π fluorescence spectra therefore carry the signature of the nascent product state rotational distributions. The situation is more complex for the B'/C^2Δ states due to the longer lifetimes involved (SiCl B^2Δ~1 μs, C^2Δ~100 ns). During their residence in the excited state, the populations evolve from an initial delta function, associated with single level excitation, towards a thermal distribution. The extent to which this degradation occurs is determined by competition between energy transfer processes which redistribute the population among internal energy levels (i.e. rotationally and, in principle for higher vibrational levels, vibrationally inelastic collisions), and processes which remove the molecule from the excited state altogether (i.e. quenching collisions and spontaneous emission). The B'/C^2Δ -X^2Π fluorescence spectra therefore reflect the extent to which the initially excited population is collisionally modified during its time in the B'/C^2Δ state.

Two approaches were adopted to achieving initial B'/C^2Δ rotational distributions. These varied in the width of the excited rotational distribution, and correspondingly the absolute magnitude of the fluorescence signal. In previous studies, the difference in J at
which the B'\r/C-X (0,0) Q_{1+}P_{21} and P_{1} bandheads form was used to prepare distinct rotational distributions in the B'/C^2\Delta, v=0 state [4,7]. The present investigation involved the preparation of more J-specific distributions in the C^2\Delta, v=0 state, achieved by pumping individual rotational lines in the P_{1} branch [12].

4.3.2 Previous SiCl and SiF Head Pumping Results

High resolution fluorescence spectra of SiCl B'^2\Delta-X^2\Pi emission following excitation at the Q_{1+}P_{21} bandhead had revealed the rotational population within the B'^2\Delta, v=0 level to be approximately thermalised within the excited state lifetime of the molecule at the pressures employed. This obviously limits the amount of information available on the \Delta J propensities accompanying the B'\rightarrow B transfer. However, from the observation that the B^2\Sigma^+, v'=0 level produced in collisions with CF_{4} had a similar, near thermal rotational contour, it may be concluded that this particular vibronic channel at least is not accompanied by large \Delta J values.

The opportunity for producing a non-thermal initial distribution is enhanced in the SiF radical by virtue of the shorter C^2\Delta state radiative lifetime (~100 ns). In preliminary investigations, the C^2\Delta-X^2\Pi_{1/2} (0,0) Q_{1+}P_{21} and P_{1} bandheads, as indicated in Figure 4-4, were pumped to prepare distinct rotational distributions centred around different values of J. These features offer enhanced signal magnitude at the expense of pumping a range of initial J values, thereby reducing the quality of state-specific data which may be obtained. The P_{1} bandhead is predicted to form at J\approx34.5, while the Q_{1+}P_{21} branches form heads at J\approx11.5. Pumping at these two features therefore allows the excitation of distinct ranges of J. As can be seen from Figure 4-4, the P_{1} branch is completely isolated, so pumping on this transition exclusively populates the F_{1} manifold of C^2\Delta v=0. The Q_{1} branch, however, forms a head concurrent with its Q_{P21} satellite branch. Pumping here therefore populates both the F_{1} and F_{2} manifolds of the C^2\Delta state. These would be populated in the ratio ~3:1 (reflecting the relative line strengths of the main branch and satellite transitions) at low laser powers, but in practice, this ratio is reduced through optical saturation.
Figure 4-4: LIF Excitation Spectrum of the $C^2\Delta - X^2 \Pi_{1/2}$ (0,0) Sub-band.

Fluorescence detected on the $C^2\Delta - X^2 \Pi_{3/2}$ (0,0) sub-band.
4.3.2.1 SiF \( \text{C}^{2}\Delta \) Rotational Distributions

The degree of inelastic transfer within the \( \text{C}^{2}\Delta \) state was minimised by ensuring that the product of the total pressure and the effective \( \text{C}^{2}\Delta \) lifetime was sufficiently low. This leads to the standard compromise between strict “single-collision” conditions and the magnitude of the desired collisionally induced signal. The extent of rotational relaxation in the \( \text{C} \) state was independently assessed by recording high resolution dispersed C-X fluorescence spectra, as shown in Figure 4-5. By pumping \( \text{C}^{2}\Delta - \text{X}^{2}\Pi_{1/2} \) and observing \( \text{C}^{2}\Delta - \text{X}^{2}\Pi_{3/2} \), any problems associated with interference from the scattered laser light could be avoided.

It is immediately obvious from inspection of Figure 4-5 that the spectra obtained from excitation at the two separate features are very different, confirming that two distinct rotational distributions have indeed been achieved and that rotational relaxation is incomplete during the \( \text{C}^{2}\Delta \) state lifetime. In all cases conditions were \(-1.4\) Torr Ar, \(-0.5\) Torr H\(_{2}\) and trace \((-1\) mTorr\) SiF\(_{4}\). The directly returning fluorescence was collected in a 400 ns gate starting just before the exciting laser pulse. This exceeds the \( \text{C} \) state zero-pressure radiative lifetime of \(-100\) ns, and, more significantly, the measured fluorescence lifetime under these conditions \((-45\) ns).

The rotational distributions associated with the simulations in Figure 4-5 are shown in Figure 4-7. These were obtained using the procedure described in Section 3.7, adjusting the rotational distributions iteratively until an acceptable match between experiment and simulation was achieved. The \( \text{F}_{1}:\text{F}_{2} \) ratio in the \( \text{C}^{2}\Delta \) state was treated as an adjustable parameter in the fitting process, but the distribution in each manifold was constrained to be the same. Unsurprisingly, the best fits involved ratios of the \( \text{F}_{1}:\text{F}_{2} \) levels of around unity for \( \text{Q}_{1}^{+} \text{P}_{21} \) pumping, and \(-3:1\) for \( \text{P}_{1} \) pumping. It is clear from these distributions that substantial memory of the initially pumped levels is retained by the system in each case, and that rotational relaxation is far from complete.
Figure 4-5: Dispersed $C^2\Delta - X^2\Pi_{3/2}$ (0,0) Fluorescence Spectra.

Spectra produced after excitation of (a) $Q_1 + ^2P_{21}$ head and (b) $P_1$ head with ~1.4 Torr Ar, 0.5 Torr H$_2$ and trace (~1 mTorr) SiF$_4$. In both cases (i) experimental result and (ii) simulation.
Chapter 4: SiX (X=Cl, F) Vibrationally and Rotationally Resolved Results

4.3.2.2 SiF $B^2\Sigma^+$ Rotational Distributions

The collision-induced $B^2\Sigma^+ - X^2\Pi (0,0)$ dispersed fluorescence spectra produced from the $C^2\Delta, v=0$ state rotational distributions characterised in Section 4.3.2.1 are shown in Figure 4-6 with the relevant simulations. Collision-induced fluorescence was again collected over the full range of the fluorescence decay (400 ns gate), with the time dependence of the B-X emission being controlled by the effective $C^2\Delta$ state lifetime. It is clear by inspection that there is significant variation in the spectra originating from the different $C$ state distributions. The B-X spectrum corresponding to initial $P_1$ C state excitation appears significantly hotter than the analogous $Q_1+P_21$ spectrum. Included for comparison is the $Q_1+P_21$ excited spectrum obtained with $N_2$ as the quenching partner. The simulations were generated in this case assuming the $F_1:F_2$ ratio in the $B^2\Sigma^+$ state to be equal. The $B^2\Sigma^+$ rotational distributions generated are shown in Figure 4-7.

4.3.3 Preliminary Conclusions from Excitation at Bandheads

Due to the limited resolution of the dispersed spectra, the rotational distributions derived for both excited states are not unique. However, the populations do possess well defined features, such as the location of the peak of the distribution and the upper and lower limits. What is clearly obvious from Figure 4-7 is that rotational relaxation is far from complete in the $C^2\Delta$ state, and that a considerable fraction of the large vibronic energy deficit (~5000 cm$^{-1}$) involved in the $C^2\Delta, v=0 \rightarrow B^2\Sigma^+, v'=0$ transition is partitioned into product state rotation. It is probable that the agreement between experiment and simulation of the $C^2\Delta - X^2\Pi_{3/2} (0,0)$ band could be improved by allowing the rotational populations in the $C$ state $F_1$ and $F_2$ manifolds to vary independently of each other. It is anticipated that simulation of the $P_1$ spectrum would benefit most from this analysis, allowing the $F_2$ population to reflect the efficiency of spin-orbit changing/rotationally inelastic collisions.

Having established that the SiF C→B transfer process involves a substantial release of energy in the form of B state rotation, it was decided to investigate the correlation between initial and final rotational levels in the $C^2\Delta, v=0 \rightarrow B^2\Sigma^+, v'=0$ transition in a more detailed manner. This was achieved in the present study by preparing individual levels in the $C^2\Delta, v=0$ state, as described in the next section.
Figure 4-6: Collision-Induced SiF B-X(0,0) Fluorescence Spectra.

Collision partners (a) and (b) H₂; (c) N₂. Initial excitation of C²Δ, ν=0; (a) and (c) Q₁⁺P₂₁ head and (b) P₁ head. In all cases, (i) experimental result and (ii) simulation. Spectra recorded with ~1.4 Torr Ar, 0.5 Torr quencher and trace (~1 mTorr) SiF₄.
Chapter 4: SiX (X=Cl, F) Vibrationally and Rotationally Resolved Results

Figure 4-7: SiF $C^2\Delta$, $\nu=0$ and $B^2\Sigma^+$, $\nu'=0$ Excited State Rotational Distributions.

Initial excitation of $C^2\Delta$, $\nu=0$: (a) $Q_1 P_{21}$ head, (b) $P_1$ head. Initial $C^2\Delta$, $\nu=0$ rotational distribution: (o). Collisionally produced $B^2\Sigma^+$ rotational distributions with: (△) $H_2$; (□) $N_2$ collider.
4.3.4 J-Specific Pumping Results from Present Investigation

Inspection of Figure 4-4 shows that, at the dye laser resolution available, spectral congestion to the short wavelength side of the Q$_1^+$$^0$P$_{21}$ bandheads would make excitation of single rotational levels in the C state difficult. However, the P$_1$ branch to longer wavelength is isolated and sufficiently resolved, at least for low lines away from the bandhead, to allow the selection of individual rotational lines for excitation. The lines chosen are indicated in Figure 4-8. At the expense of reduced signal magnitudes, this approach produces much tighter initial rotational distributions, therefore allowing the ΔJ propensities observed in the C→B transfer process to be more rigorously quantified. The acquisition of state-specific data was carried out in this laboratory in conjunction with Dr Neil Jackson [13], with the analysis, simulations and development of any software being the responsibility of the author.

4.3.4.1 SiF C$_2^\Delta$ Rotational Distributions

As in the less sophisticated case of head-pumping, rotational relaxation within the C state following excitation to a single J level was assessed by dispersing the directly returning C-X fluorescence. The rotational lines chosen to excite specific levels in the C state are shown in Figure 4-8, and the corresponding fluorescence spectra and simulations are shown in Figure 4-9. Again, it is immediately obvious from the starkly contrasting appearance of each spectrum in Figure 4-9 that rotational equilibration is far from complete. The rotational distributions associated with each spectrum are characterised by a single dominant peak, corresponding to a substantial fraction of the overall population residing in the initially pumped level. As can be seen from Figure 4-9 though, there is evidence of some rotational relaxation, with wings on the sharp features in the spectra extending well beyond the bandwidth of the detection system. We are aided in modelling the degree of relaxation in the C state by spectroscopic details of the C-X transition. As mentioned in Section 3.4.3, each rotational level in the C$_2^\Delta$ state is spin-split into an F$_1$ and F$_2$ component, corresponding to the $^2\Delta_{3/2}$ and $^2\Delta_{5/2}$ manifolds of a Hund's case (a) state, or the J=\(N\pm1/2\) spin-rotation levels of a Hund's case (b) state. The F$_1$ and F$_2$ levels are connected to the ground state by separate spectroscopic branches, some of which appear isolated in the C-X emission spectrum even in the absence of full rotational resolution.
In the case of exciting on the $C^2\Delta - X^2\Pi_{1/2}$ P$_1$ branch, only the F$_1$ manifold is populated in the C state. Therefore, if no spin-orbit changing collisions occurred, the $C^2\Delta - X^2\Pi_{3/2}$ emission would contain only three branches: $^3R_{12}$, $^3Q_{12}$ and $^3P_{12}$. However, it was found that the spectra could only be satisfactorily reproduced by including the additional three branches (R$_2$, Q$_2$ and P$_2$) originating exclusively from collisionally populated F$_2$ levels. In the same way that the P$_1$ branch is isolated in the $C^2\Delta - X^2\Pi_{1/2}$ band, so the $^3P_{12}$ branch is isolated in the $C^2\Delta - X^2\Pi_{3/2}$ band. Therefore, the rotational distribution in the F$_1$ levels could be unambiguously assigned by selectively fitting only to the $^3P_{12}$ branch, and the F$_2$ population iteratively adjusted to fit the remainder of the spectrum.

The best fit simulations were achieved by assuming that a large fraction of the excited population, typically ~40% of the F$_1$ component (~30% of the total), remains in the initially excited level, superimposed on a relatively broad F$_1$ distribution of J's, populated through collisional relaxation. The F$_2$ population was independently found to mirror only the rotationally relaxed component of the F$_1$ distribution, but surprisingly it was found that only ~1/3 of the collisionally modified molecules were transferred to the F$_2$ manifold. This propensity for retention of the spin label has not yet been examined in greater detail. The F$_1$ distributions are shown in Figure 4-11. The quantitative characteristics of the distributions associated with each pump line are shown in Table 4-1. For ease of comparison with B state distributions, we have defined an operational maximum, $J_{\text{max}}$, which may safely be said to be populated within the experimental signal-to-noise. $J_{\text{max}}$ is defined as the highest J value for which the cumulative population is less than 95% of the total.
### Table 4-1: Characteristics of the SiF $C^2\Delta$ Rotational Distributions produced by $J$-Specific $P_1$ Excitation.

<table>
<thead>
<tr>
<th>$J^{(a)}$</th>
<th>$p_1^{(b)}$</th>
<th>$F_1:F_2^{(c)}$</th>
<th>$&lt;J&gt;_x^{(d)}$</th>
<th>$J_{max}^{(e)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>29%</td>
<td>2.4</td>
<td>7.6</td>
<td>17.5</td>
</tr>
<tr>
<td>8.5</td>
<td>27%</td>
<td>1.7</td>
<td>9.9</td>
<td>18.5</td>
</tr>
<tr>
<td>13.5</td>
<td>33%</td>
<td>2.0</td>
<td>12.8</td>
<td>19.5</td>
</tr>
<tr>
<td>16.5</td>
<td>37%</td>
<td>1.6</td>
<td>15.3$^{(f)}$</td>
<td>20.5$^{(f)}$</td>
</tr>
</tbody>
</table>

(a) Initially populated $C^2\Delta$ $F_1$ rotational level.

(b) Fraction of total excited population remaining in pumped level.

(c) Ratio of collisionally produced $F_1$ to $F_2$ populations summed over all levels other than the one initially pumped.

(d) The average rotational quantum number considering all rotational levels occupied.

(e) The 95$^{th}$ percentile of the $C^2\Delta$ $v=0$ rotational distribution.

(f) Values calculated excluding high $J$ component from returning $P_1$ bandhead, see discussion in the text.
Figure 4-8: Expanded View of $C^2\Delta -X^2\Pi_{1/2} (0,0) P_1$ Branch.

Rotational lines selected for excitation marked with (*): $J=4.5, 8.5, 13.5$ and 16.5 respectively.
Chapter 4: SiX (X=Cl, F) Vibrationally and Rotationally Resolved Results

Figure 4-9: C^2Δ -X^2Π_{3/2} (0,0) Dispersed Fluorescence Spectra following P_1 line Pumping.

The solid lines are simulations using adjustable rotational F_1/F_2 distributions as discussed in the text. Spectra recorded with ~1.4 Torr Ar, 0.5 Torr H_2 and trace (~1 mTorr) SiF_4.
When simulating the experimental C-X spectrum associated with initial excitation of $J=16.5$, it was found that a satisfactory match could only be achieved by including a secondary component of population, corresponding to $\sim 5\%$ of the total, centred on $J=58.5$. This additional population element arises from an accidental overlap of the pump laser with a high $J$ line returning from the $P_1$ bandhead. This shows the difficulties involved in cleanly exciting individual $J$ states beyond the limited range included in this work.

C-X fluorescence spectra recorded with longer integration gates, under the same conditions as above, showed a proportional progression towards rotational equilibration. However, increasing the concentration of an effective C state quencher, such as $H_2$, showed little increase in the fraction of redistributed population. This may be rationalised through the fact that the quenching cross section for these molecules is large, and total removal from the C state therefore occurs at a rate comparable to rotationally inelastic processes. The main effect of increasing the quencher pressure is, therefore, to reduce the effective lifetime of the C state, thereby reducing the average number of rotationally inelastic collisions.

The fraction of the excited population retained in the initially excited level can be seen from Table 4-1 to increase with $J$. This is a well known phenomenon, arising from the non-linear increase in rotational term energies with $J$. The $\sim J^2$ dependence of rotational energy has the effect of increasing the size of the energy gaps between adjacent states as $J$ increases, thereby reducing the probability of a given collision successfully inducing a transfer between neighbouring $J$ levels.

The results of this section show that it is possible to prepare distinct C state rotational distributions, over an admittedly limited range, which are only partially affected by rotationally inelastic collisions.

### 4.3.4.2 SiF $B^2\Sigma^+$ Rotational Distributions

The dispersed B-X $(0,0)$ fluorescence spectra obtained following the excitation of specific C-X $(0,0) P_1$ lines are shown in Figure 4-10 along with the relevant simulations. As in the C-X case, the resolution is only sufficient to reveal the contours of the rotational distribution in each case. The spectra were recorded under identical conditions to those of the directly returning C-X fluorescence in Figure 4-9. As
mentioned earlier, the much shorter B state lifetime ensures no collisional modification of the nascent B state population under these conditions.

Because of the limited wavelength resolution and signal-to-noise ratio associated with the B-X spectra, there is inevitably a degree of flexibility in the rotational distributions which will give satisfactory simulations. Operationally, it is difficult to establish conclusively the peak of a relatively broad distribution, the limit of the high $J$ tail where the signal-to-noise ratio is at its worst, and relative populations of the lowest few levels, where the congestion of lines is well below the bandwidth of the detector. In practice, a smoothly varying function of $J$ with a single maximum was iteratively adjusted, avoiding any sharp discontinuities or inflexions, until a satisfactory "by eye" agreement between experiment and simulation was achieved. It was found that this could be accomplished, within the signal-to-noise of the experiment, by assuming identical populations and equal weighting to each of the $F_1$ and $F_2$ manifolds within the $B^2 \Sigma^+$ state. The characteristics of the collision-induced B state rotational distributions are shown in Table 4-2. The $F_1/F_2$ B state distributions are shown in Figure 4-11 along with those from the corresponding C state for easy comparison.

Despite the uncertainties associated with the B state distributions, certain parameters, such as the average $J$ and the width, are well determined. It is particularly noticeable that the B state rotational distributions are very significantly broader than the C state distributions they originated from. This point is emphasised in Figure 4-10, where an example of a B-X simulation assuming the original C state rotational distribution is shown. This simulation is clearly a very poor fit to the observed B-X spectrum. It is also clear from Figure 4-11 and Table 4-2 that the initial C state angular momentum adds to the substantial product B state rotational motion induced in electronic state-changing collisions. This correlation between the B state rotational distribution and the parent C state population is revealed through the ratio of the major to minor heads in the B-X spectra ($Q_{1+}^+P_{21}$ to $P_1$ in the $B^2 \Sigma^+ - X^2 \Pi_{1/2}$ sub-band, and $P_2 + ^PQ_{12}$ to $^OP_{12}$ in the $B^2 \Sigma^+ - X^2 \Pi_{3/2}$ sub-band). Because the $Q_{1+}^+P_{21}$ and $P_2 + ^PQ_{12}$ heads form at relatively low $J$ ($\sim 6.5$) compared to the $P_1$ and $^OP_{12}$ heads ($\sim 19.5$), the shift in the major:minor head ratio as higher $J$'s are pumped in the C state reflects a shift in B state population from low to medium $J'$, consistent with the distributions in Figure 4-11.
Chapter 4: SiX (X=Cl, F) Vibrationally and Rotationally Resolved Results

Table 4-2: Characteristics of the $B^2\Sigma^+ v'=0$ Rotational Distributions produced by Collisions of Rotationally State-Selected $C^2\Delta v=0$ with $H_2$.

<table>
<thead>
<tr>
<th>$J^{(a)}$</th>
<th>$&lt;J^{(b)}$</th>
<th>$&lt;\Delta J^{(c)}$</th>
<th>$J_{\text{max}}^{(d)}$</th>
<th>$\Delta J_{\text{max}}^{(e)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>24.9</td>
<td>17.3</td>
<td>56.5</td>
<td>39</td>
</tr>
<tr>
<td>8.5</td>
<td>26.9</td>
<td>17.0</td>
<td>59.5</td>
<td>41</td>
</tr>
<tr>
<td>13.5</td>
<td>28.4</td>
<td>15.6</td>
<td>61.5</td>
<td>42</td>
</tr>
<tr>
<td>16.5</td>
<td>30.2</td>
<td>14.9$^{(0)}$</td>
<td>64.5</td>
<td>44$^{(i)}$</td>
</tr>
</tbody>
</table>

(a) Initially populated $C^2\Delta F_1$ rotational level.
(b) Average collisionally produced rotational quantum number in $B^2\Sigma^+ v'=0$.
(c) Average change in rotational quantum number between the parent $C^2\Delta v=0$ and daughter $B^2\Sigma^+ v'=0$ distributions i.e. $<\Delta J> = <J'> - <J>$.
(d) The 95th percentile of the $B^2\Sigma^+ v'=0$ rotational distribution.
(e) The difference between the 95th percentiles of the C and B state distributions i.e. $\Delta J_{\text{max}} = J_{\text{max}}^{\text{B}} - J_{\text{max}}^{\text{C}}$.
(f) As in Table 4-1, neglecting the $C^2\Delta$ high $J$ component.
Figure 4-10: Collision-Induced B-X (0,0) Fluorescence Spectra.

Spectra resulting from collisions of C$^2\Delta$ with H$_2$ quencher. Initially excited C state rotational levels as indicated. The solid lines indicate the simulations obtained using the B state distributions shown in Figure 4-11. The dashed line in $J=8.5$ is a B state simulation assuming the original C state rotational distribution remained unchanged upon transfer.
Figure 4-11: Best Fit SiF $C^2\Delta$ and $B^2\Sigma^+$ State Rotational Distributions.

(a) Initial $C^2\Delta$ populations derived from the spectra in Figure 4-9. Only the $F_1$ component is shown for clarity. (b) Product $B^2\Sigma^+$ populations derived from the spectra in Figure 4-10. $F_1$ and $F_2$ populations identical. Distributions corresponding to initially excited $C^2\Delta J$ levels indicated by the symbols: (□) 4.5; (○) 8.5; (◇) 13.5; (△) 16.5. Quenching by H$_2$ in all cases.
4.4 Discussion

The quenching behaviour of the SiF $C^2\Delta$ state has been shown in this chapter to exhibit some striking peculiarities, probably the most remarkable of which is the substantial release of rotational energy involved in the $C^2\Delta, \nu=0 \rightarrow B^2\Sigma^+, \nu'=0$ channel. Any mechanism proposed to explain the results obtained from $J$-specific experiments in the present study, however, must also be consistent with the quenching results obtained from previous studies in this laboratory [5,6]. To summarise briefly, it has been discovered that irrespective of the nature of the collision partner, there is relatively little, if any, influence of the SiF $C^2\Delta$ rotational state on the quenching efficiency, on the electronic branching fraction, and on the product vibrational distribution [5]. In contrast, however, the initial rotational angular momentum is seen here to add to the substantial fraction of the $\sim 5000$ cm$^{-1}$ vibronic energy defect released as SiF product rotation during the C$\rightarrow$B electronically inelastic transfer. The identity of the collision partner has also been shown to affect the product state rotational distributions significantly [6]. The remainder of the available energy is assumed to be partitioned largely to relative translation of the collision pair. The SiF B state vibrational distribution shows little variation with collision partner and strongly reflects the Franck-Condon overlap between initial and final vibrational wavefunctions [5].

The absence of any strong $J$ dependence on the various properties, other than the product state rotational distribution, tends to suggest there is no strongly preferred quencher-radical orientation for collisional removal from the $C^2\Delta$ state. If this were the case, a decrease in quenching efficiency would be expected as the initial $J$ is increased, corresponding to a disruption of the preferred collision geometry. The large absolute values observed for the total quenching rate constants are also consistent with a lack of steric constraints.

Clearly, the most interesting aspect of the results so far is the release of rotational energy associated with the C$\rightarrow$B transfer process, which is in contrast to the $\Delta J=0$ propensities normally reported to accompany electronically inelastic events. The extent to which this observation was particularly unexpected in the SiF-H$_2$ system may be appreciated by considering the interaction in terms of the simplest kinematic picture: collinear repulsion between the SiF radical and the H$_2$ molecule.
As may be seen from Figure 4-1, the dominant $C^2\Delta, v=0\rightarrow B^2\Sigma^+, v'=0$ channel involves a vibronic energy defect of $\sim 5000 \text{ cm}^{-1}$. The simplest scenario would involve all of this energy being partitioned to relative translation of the collision partners. Assuming the most extreme limit of an impulsive force acting between two spherical 'hard' potentials, and neglecting any contributions from the initial translational and rotational energies of the collision pair, conservation of momentum dictates that the much lighter $H_2$ molecule carry away $-47/49$ of the total recoil energy ($\sim 4800 \text{ cm}^{-1}$). Even if some mechanism existed to convert the remaining energy ($\sim 200 \text{ cm}^{-1}$) to SiF rotation, this would still be hopelessly insufficient to populate the high $J'$s observed experimentally.

A more realistic approach to the system would recognise from the outset that the SiF radical is substantially anisotropic, and that the potential would be better described by an ellipsoidal than a spherical hard shape. This allows for the possibility of a collision with non-zero impact parameter, relative to the SiF centre of mass, imparting a torque to the molecule. In some limiting perpendicular geometries, the $H_2$ molecule would effectively only feel an impulse involving the lighter F atom end of the SiF radical, thereby optimising the fraction of the energy released to SiF rotation. However, conservation of momentum decrees that only $\sim 500 \text{ cm}^{-1}$ can be partitioned to product rotation, still well short of the experimentally observed high-$J'$ population.

Thus, it is clear that simple kinematic arguments, based purely on the release of the vibronic energy defect as a repulsive force between the collision pair, are insufficient to account for the high degree of product state rotational excitation observed. We have therefore developed a more refined model for the prediction of the maximum product rotational level, $J'$. This model correctly allows for three distinct sources of product state angular momentum, $J'$:

- addition of the initial $C$ state angular momentum, $J$
- conversion of initial linear momentum of the collision pair to $J'$
- conversion of the released electronic energy, $\Delta E$, to $J'$

The last two contributions arise as a result of forces acting along a line which does not pass through the SiF centre of mass, thereby imparting a torque.

If we treat the problem as that of an inelastic collision between a 'hard-shape' and a 'hard-sphere', it is clear that if no additional electronic energy defect were present, the
maximum transfer of linear momentum to rotation will occur in the case of collisions which result in back-scattering in the centre-of-mass frame. This is equivalent to the well known problem involving rotationally inelastic collisions within a single electronic state [14,15]. Using this approach as the basis for our model, we can say there exists at every point of the hard-shape perimeter an extrapolated normal, which, in general, does not pass through the SiF centre-of-mass, and is therefore capable of delivering a torque. The perpendicular distance from this surface normal to the centre of mass defines the lever arm (an effective impact parameter, $b$), and therefore the torque imparted by an impulse at the surface. If the force is not directly along the surface normal, the remaining component of the impulse acts through the SiF centre of mass, adding to the linear momentum of the radical. Assuming that the conversion of linear to angular momentum and the electronic energy release both occur suddenly, at the instant that contact takes place between the bodies, the same value of $b$ applies to both these processes and the transfer is impulsive. The maximum value of $b$ is labelled $b_{\text{max}}$.

The maximum change in product rotational state, $\Delta J_{\text{max}}$, will occur when the initial angular momentum vector, $J$, lies along the normal to the plane containing the SiF internuclear axis and the point of contact, and the initial linear momentum vector, $P$, lies along the surface normal at the point of contact. In other words, the initial orbital, $L$, and rotational $J$, angular momentum vectors are parallel prior to the collision. After the collision, $J'$ remains parallel to $L$, but its magnitude is greatly increased. Angular momentum is conserved by the contribution from $L'$, as $p'$ is in the opposite direction to $p$ for a back-scattered collision.

The system as a whole must simultaneously obey energy conservation and conservation of angular momentum. Expressing these constraints in a mathematical form gives us:

\[
\frac{p^2}{2\mu} + \frac{\hbar^2 J^2}{2I} + \Delta E = \frac{p'^2}{2\mu} + \frac{\hbar^2 J'^2}{2I}
\]

Equation 4-3

and

\[\hbar J + \hbar b_{\text{max}} = \hbar J' - p'b_{\text{max}}\]

Equation 4-4
where $\mu$ is the reduced mass of the collision pair, and $I$ is the moment of inertia of the SiF hard shape. Elimination of $p'$ from Equation 4-4 using Equation 4-3, and of $J'$ through the relation $J' = J + \Delta J_{\text{max}}$ yields a quadratic expression for $\Delta J_{\text{max}}$, the more positive root of which is the desired solution:

$$\Delta J_{\text{max}} = \frac{b_{\text{max}}}{h(1 + \eta)} \left\{ \alpha + \left[ \alpha^2 + 2\mu AE(1 + \eta) \right]^{1/2} \right\}$$

Equation 4-5

where $\eta$ is defined by

$$\eta = \frac{\mu b_{\text{max}}^2}{I}$$

Equation 4-6

and $\alpha$ by

$$\alpha = p - \frac{h\mu b_{\text{max}} J}{I}$$

Equation 4-7

The principal unknown quantity in this model is the value of $b_{\text{max}}$, and without detailed calculation of the intermolecular potentials it is impossible to evaluate this accurately. However, in their closely related (and more developed) work on the modelling of rotational energy transfer within single electronic states, McCaffrey and co-workers [14,15] have consistently found that the equivalent $b_{\text{max}}$ parameter has a physically realistic value close to half the homonuclear bondlength. We therefore suggest that in the current case of a heteronuclear diatomic, the value of $b_{\text{max}}$ is unlikely to exceed the average distance of 0.92 Å between the F nucleus and the SiF centre-of-mass in the $C^2\Delta v=0$ level.

Figure 4-12 illustrates the predicted variation of $\Delta J_{\text{max}}$ with initial $J$ level for $b_{\text{max}}=0.92$ Å and various relative contributions to $J'$ from the sources discussed above. The mass parameters used are specific to SiF-H$_2$ collisions, except the uppermost trace (see caption), which is for SiF-N$_2$. The lowest trace illustrates the modest rotational release achievable if $\Delta E=0$ and the relative collision velocity is taken as the thermal average.
(<v_{rel}>=1820 \text{ ms}^{-1} \text{ at } 300 \text{ K}) \text{i.e. any increase in rotation arises purely from } l \text{ to } J' \text{ conversion. The } \Delta J_{\text{max}} \text{ values decrease approximately linearly with } J, \text{ reflecting the decrease in the magnitude of the impulse between the quencher and the F nucleus as } J \text{ increases, and the } \sim J^2 \text{ dependence of the rotational energy.}

The next four solid line plots illustrate the effect of introducing an impulsive energy release, AE, of 4816 cm\(^{-1}\) at the point of SiF-H\(_2\) contact. This corresponds to the energy defect in the dominant C\(^2\Delta, v'=0\rightarrow B^2\Sigma^+, v'=0\) quenching channel. Successive multiples of <v_{rel}> have been taken in each of the plots to illustrate the effect of varying the collision velocity. It can be seen that the \(\Delta J_{\text{max}}\) values achieved from an impulsive release of 4816 cm\(^{-1}\), with no contribution from \(l\) to \(J'\) conversion, are significantly larger, and decrease less rapidly with \(J\), than those with an average thermal velocity and \(\Delta E=0\). This reflects the smaller amount of collision energy available at average thermal velocity, and the \(J\) dependence of the rotational energy. As \(J\) increases, the amount of energy impulsively partitioned into rotation from the energy defect increases, even though the momentum change remains constant. This occurs because the addition of a constant impulse to a moving body results in a non-linear variation of the kinetic energy of that body, determined by the magnitude of the initial velocity. However, \(\Delta J_{\text{max}}\) still decreases with \(J\) due to the \(\sim J^2\) dependence of the rotational energy term values. As expected, increasing the initial average velocity produces proportional increases in \(\Delta J_{\text{max}}\), with the gradients changing slightly due to the increasing contribution made by \(l\) to \(J'\) conversion.

The absolute magnitude of \(\Delta J_{\text{max}}\) values predicted by the model are clearly very much larger than those implied by the simple kinematic models initially discussed above. The physical reason for this becomes clear by considering the reference frames in which the collision occurs. For collisions resulting in the maximum product state rotation, the F atom is receding from the H\(_2\) molecule in the laboratory frame (\(J\parallel l\)). After the collision, the H\(_2\) molecule recoils from the SiF radical in the centre of mass frame, but is moving relatively more slowly as viewed in the laboratory frame, therefore absorbing much less energy in translation than was crudely estimated above.

It can be seen from Table 4-2 that the \(\Delta J_{\text{max}}\) values observed experimentally in SiF-H\(_2\) collision are \(~40\) (bearing in mind the difficulties involved in defining exactly the highest populated level). Figure 4-12 shows that only very high collision velocities (\(~3<v_{rel}>\)) are capable of reproducing these values using the given \(b_{\text{max}}\). We note that collisions
Chapter 4: SiX (X=Cl, F) Vibrationally and Rotationally Resolved Results

involving relative velocities of one, two and three times \(<v_{\text{rel}}><\) would be exceeded in around 60\%, 4\% and 0.01\% of collisions, respectively, in a 300 K velocity distribution (including the weighting of the rate of collisions by the velocity). We conclude, therefore, that the experimentally observed values of \(\Delta J_{\text{max}}\) are produced in collisions where the relative velocities of the collision pair approach those present in the high velocity tail of a thermal sample. It should be remembered that collisions involving \(\Delta J_{\text{max}}\) constitute only a tiny minority of all the collisional transfer events, the average observed \(\Delta J\) being \(-16\). It would be possible to increase the percentage of thermal collisions resulting in \(\Delta J_{\text{max}}\) by increasing the value of \(b_{\text{max}}\). However, it is hard to see any independent physical justification for this.

The assumptions that have been made so far, regarding the suddenness of the interaction and using the maximum physically realistic value of \(b_{\text{max}}\), all work toward placing an upper limit on the predicted product rotational motion. We believe, therefore, that the success of this model in predicting \(\Delta J_{\text{max}}\) indicates that a strongly repulsive interaction operates between SiF and H\(_2\) at the instant of the collision-induced electronic transition, and that some of these collisions must occur through substantially bent geometries. This impulsive energy release model is also supported by the observation that the degree of SiF product state rotational excitation is greater with N\(_2\) quenching than H\(_2\). This is consistent with the impulsive kinematic scheme described above, and is illustrated in the top trace in Figure 4-12, with the thermal average SiF-N\(_2\) collision velocity of 602 m s\(^{-1}\) and the same value of \(b_{\text{max}}\). The experimentally observed \(\Delta J_{\text{max}}\) values of \(-50\) (see Figure 4-7) are comfortably explained within the model. However, some care must be taken here in applying the same assumptions to N\(_2\) as were given to H\(_2\). Because of the low moment of inertia associated with H\(_2\), and the correspondingly high rotational constant, it was valid to assume that the H\(_2\) molecule was precluded from carrying away a substantial component of angular momentum following the collision. While this assumption is clearly less valid for N\(_2\), it is nevertheless true that the homonuclear N\(_2\) molecule will appear substantially less electronically anisotropic than the SiF radical. Treating the N\(_2\) molecule as a hard-sphere is therefore not too extreme an assumption, and it seems reasonable to suppose that N\(_2\) should be less rotationally excited during a collision than the SiF radical.
Further evidence to support the sudden nature of the C→B transfer mechanism may be seen from the SiF $B^2\Sigma^+$ product state vibrational distributions. As discussed in Section 4.2.3 and shown in Figure 4-3, the B state vibrational distributions show only a weak dependence on the nature of the collision partner, and are well matched by the Franck-Condon overlap of the vibrational wavefunctions between the two electronic states. Franck-Condon control is generally indicative of sudden transfer between the two states, and not of the statistical redistribution of energy which would be expected if transfer occurred via a long-lived collision complex. This point will be discussed more fully in Chapter 6.

In conclusion, it has been shown that the propensity for large rotational energy release during SiF $C^2\Delta, v=0\rightarrow B^2\Sigma^+, v'=0$ transfer is consistent with a mechanism whereby a sudden, strongly repulsive interaction between the collision pair accounts for the large vibronic energy defect involved. To account for the $\Delta J_{\text{max}}$ values observed, it is necessary to assume the contributions made to $J'$ from $J$, from $l$, and from $\Delta E$ all add constructively, that the collision occurs with an effective impact parameter $b_{\text{max}}$, close to the intuitively anticipated maximum, and that the collision energy corresponds to the high tail of a thermal distribution. The extent to which this behaviour is consistent with the electronic characters of the states involved will be discussed in Chapter 6.
Figure 4-12: Predicted $\Delta J_{\text{max}}$ Values for a given SiF $C^2\Delta$ Rotational Level, $J$, using an Impulsive Model (Equation 4-5).

In all cases, $b_{\text{max}}=0.92$ Å. All filled symbols refer to H$_2$ quenching. Solid lines refer to $\Delta E=4816$ cm$^{-1}$, with collision velocities equal to multiples of the average thermal relative velocity, $\langle v_{\text{rel}}\rangle=1820$ ms$^{-1}$: (●) $v=0$; (■) $v=\langle v_{\text{rel}}\rangle$; (▲)$v=2\langle v_{\text{rel}}\rangle$; (▼)$v=3\langle v_{\text{rel}}\rangle$. Long dashed line and (●); $\Delta E=0$, $v=\langle v_{\text{rel}}\rangle$. Short dashed line and (□); N$_2$ quencher, $\Delta E=4816$ cm$^{-1}$, $v=\langle v_{\text{rel}}\rangle=602$ ms$^{-1}$. 
Chapter 4: SiX (X=Cl, F) Vibrationally and Rotationally Resolved Results

Bibliography


Chapter 5
Polarisation Effects in Collision-Induced SiF
\[ C^2\Delta + H_2 \rightarrow B^2\Sigma^+ + H_2 \] Transfer

5.1 Introduction

The preceding chapter discussed in detail the scalar partitioning of energy observed in collision-induced SiF \( C^2\Delta, \nu=0 \rightarrow B^2\Sigma^+, \nu'=0 \) transfer. We have argued that the conversion of a substantial fraction of the vibronic energy defect (~5000 cm\(^{-1}\)) to product state rotation is consistent with a sudden, repulsive interaction between the collision partners. The current chapter describes an attempt to assess whether the degree of retention of polarisation during the collision process is consistent with these mechanistic conclusions. A positive correlation would reflect a tendency for the plane of rotation of the molecule to be conserved during the transfer event. This experiment requires polarisation-sensitive fluorescence detection in order to determine the degree of molecular alignment present in the parent and product states.

The experiment comprised of three main stages. In the first stage, which was not strictly necessary from a theoretical point of view, linearly polarised light was used to excite SiF to the \( B^2\Sigma^+ \) state, and the directly returning B-X fluorescence was dispersed. The short lifetime of the \( B^2\Sigma^+ \) state (<10 ns) ensures no collisional modification of the alignment of the excited population. The polarisation ratios measured for a known combination of spectroscopic branches in excitation and detection were compared with well established theoretical predictions [1], allowing the correct functioning of the apparatus to be established. The second stage involved determining the polarisation ratios of directly returning \( C^2\Delta, \nu=0 \) laser induced fluorescence. As discussed in Chapter 4, inelastic transfer processes within the C state occur on a timescale competitive with total removal rates, resulting in a degree of collisional redistribution of the initially excited population. Measurement of the C-X fluorescence polarisation anisotropy allows the degree of
Polarisation Effects in Collision-Induced SiF $C^2\Delta+H_2\rightarrow B^2\Sigma^+H_2$ Transfer

collisional depolarisation of the C state to be assessed. Establishing the polarisation ratio associated with the parent C state rotational distribution enables a meaningful interpretation of the final stage, in which polarisation of the collision-induced B-X (0,0) emission was measured.

This experiment was again performed in conjunction with Dr Neil Jackson, with his contribution being weighted toward acquisition of the experimental data, and mine to initial experimental design and subsequent model development.

5.2 Theoretical Basis of Polarisation Measurements

The polarisation dependence of optical absorption and emission by isolated molecules has been thoroughly treated by Zare [1]. Assuming photon absorption occurs in the low power limit, the probability of a molecule being laser-excited from an initial state $|i\rangle$, to an excited state, $|e\rangle$, is proportional to the square of the projection of the linear polarisation vector, $\hat{E}_a$, onto the transition dipole moment vector, $\hat{\mu}_{ae}$:

$$\text{probability of absorption} \propto |\hat{E}_a \cdot \hat{\mu}_{ae}|^2$$

Equation 5-1

This results in positive alignment (alignment parameter $A^{(2)}_0 \rightarrow 2$ [2,3,4]) of $\hat{\mu}_{ae}$ about $\hat{E}_a$ in the excited state. Correspondingly, the probability of detecting a fluorescence photon emitted as the molecule makes the transition from $|e\rangle$ to some final state, $|f\rangle$, is proportional to the square of the associated transition dipole moment vector $\hat{\mu}_{ef}$ onto the detection polarisation vector, $\hat{E}_d$:

$$\text{probability of detection} \propto |\hat{E}_d \cdot \hat{\mu}_{ef}|^2$$

Equation 5-2

The two electronic band systems used for excitation and detection in this study (i.e. $C^2\Delta-X^2\Pi$ and $B^2\Sigma^+-X^2\Pi$) both involve $\Delta \Lambda = \pm 1$. The electronic transition dipole moment, $\hat{\mu}$, therefore lies perpendicular to the internuclear axis, $\mathbf{r}$, in both these cases. In the limit of high $J$, $\hat{\mu}$ lies parallel to $\mathbf{J}$ for Q type transitions, and perpendicular to $\mathbf{J}$ and $\mathbf{r}$ for P and R type.
Figure 5-1: Schematic of Excitation/Detection Geometry for Polarisation Studies.

Double headed arrows indicate polarisation vectors: \( \hat{E}_a \) is the excitation laser polarisation vector, \( I_\parallel \) and \( I_\perp \) indicate detected polarisations of fluorescence parallel and perpendicular to \( \hat{E}_a \) respectively. All fluorescence is collected perpendicular to \( \hat{k}_a \), the laser propagation vector, and to \( \hat{E}_a \).
The extent to which the linear polarisations of the absorbed and emitted photons is correlated is measured by determining the relative intensities of the two components of the fluorescence, \( I_\parallel \) and \( I_\perp \), corresponding to \( \hat{E}_d \) parallel to and perpendicular to \( \hat{E}_a \) respectively. The orientation of these vectors with respect to the experimental geometry is shown in Figure 5-1.

Having excited an aligned population, several processes occur which reduce the degree of fluorescence polarisation observed. The most rapid of these, which is present in all experiments, is due to rotation of the molecule in the excited state. In the case of a Hund’s case (a) molecule, this can be envisaged as precession of \( \Omega \) and \( \vec{R} \) (see Section 3.4.2) about \( \vec{J} \), which is constant in magnitude and direction. This so-called nutation of the internuclear axis about \( \vec{J} \) has the effect of degrading the spatial distribution of \( \vec{\mu} \) from its initial alignment. However, as the typical rotational period of a molecule is \( \sim 10^{-11} \) s, and the typical excited state lifetime is \( \sim 100 \) ns, the disruption caused by molecular rotation on the observed fluorescence polarisation quickly averages to a new, constant (if reduced) polarisation ratio. Physically, this arises because the projection of \( \vec{J} \) onto the laser polarisation axis, \( m_J \), remains constant throughout the rotational motion, thus a fraction of the degree of alignment initially present in the sample is conserved. To assess the degree of fluorescence anisotropy, we have chosen to use the polarisation index defined by \( R \) [1]:

\[
R = \frac{I_\parallel - I_\perp}{I_\parallel + 2I_\perp}
\]

Equation 5-3

\( R \) corresponds to the average degree of alignment relative to an isotropic sample (correctly allowing for the two orientations in which light may be \( I_\perp \) compared to \( I_\parallel \) in an isotropic array). \( R \) may also be directly related to the average angle between absorption and emission dipole moment vectors through [1, 5]:

\[
R = \frac{2}{5} \left\langle P_2 \left( \frac{\vec{\mu}_a \cdot \hat{\mu}_d}{\vec{\mu}_a \cdot \hat{\mu}_d} \right) \right\rangle
\]

Equation 5-4
where \( P_2(\chi) \) is the second order Legendre polynomial and the averaging is over several rotational periods. Physically, \( \left( \hat{\mu}_a \cdot \hat{\mu}_\nu \right) \) expresses the projection of one transition dipole onto the other.

Exact expressions of \( R \) for electronic transitions in linear molecules have been derived [1]. The predicted degree of polarisation anisotropy depends on \( J \), the type of electronic transition involved (parallel or perpendicular), and the combination of spectroscopic branch types used in excitation and detection. As would be expected, \( R \) converges on limiting high-\( J \) values for various permutations of \( P \), \( Q \) and \( R \) branches in pumping and detection. An insightful way of understanding these is to appeal to the Azimuthally Averaged Addition Theorem (AAAT) [4,6] for two otherwise uncorrelated distributions sharing a common axis of cylindrical symmetry. This allows \( R \) to be expressed as:

\[
R = \frac{2}{5} \left\langle P_2(\hat{\mu}_a \cdot \hat{\mu}_\nu) \right\rangle
\]

Equation 5-5

Simple geometric arguments may now be used to predict the limiting high-\( J \) values of \( R \), as shown in Table 5-1. In the limit of low \( J \), where space quantisation effects are more pronounced, the expressions for \( R \) are functions of \( J \) and require explicit evaluation.

The effect of collisions or other dynamical effects which may reorient the plane of rotation of the excited state, \( |e> \), prior to emission may be accounted for by a further application of the AAAT. Assuming now that \( J \) is no longer a constant in \( |e> \), and collisions occur which reorient \( J \), or transfer the system to some new \( J' \) state, we may write:

\[
R = \frac{2}{5} \left\langle P_2(\hat{\mu}_a \cdot \hat{\mu}_\nu) \right\rangle \left\langle P_2(\hat{\mu}_a \cdot \hat{\mu}_\nu) \right\rangle
\]

Equation 5-6
Table 5-1: Classical limiting high-$J$ values of $R$ obtained from Equation 5-5.

$\uparrow$ refers to excitation on a given branch type while $\downarrow$ refers to detection.
Chapter 5: Polarisation Effects in Collision-Induced SiF C^2\Delta+H_2\rightarrow B^2\Sigma^+ + H_2 Transfer

The quantity \((\hat{J} \cdot \hat{J}')\) is the cosine of the ‘tipping angle’, \(\alpha\) between the initial and final total angular momentum vectors, \(\hat{J}\) and \(\hat{J}'\). In many situations it is convenient to separate any dynamical effects on the observed polarisation ratio from those arising purely from the spectroscopy of the molecule. To this end, the parameter \(R_0\) is defined as the value of \(R\) obtained from Equation 5-5 in the absence of collisions. This allows Equation 5-6 to be expressed in the pleasingly simple form:

\[ \langle P_3(\hat{J} \cdot \hat{J}') \rangle = \frac{R}{R_0} \]

Equation 5-7

from which the value of \(\langle P_3(\hat{J} \cdot \hat{J}') \rangle\) may easily be determined, and hence the average value of the tipping angle, \(<\alpha>\).

5.3 Experimental Procedure

The experimental apparatus used in this study has already been described in Section 2.5, so only a brief overview of the technique shall be described here. Radical generation and fluorescence detection was accomplished as previously discussed.

To ensure that the pump beam was linearly polarised, it was passed through a fixed calcite Glan-Taylor polariser before entering the excitation zone via quartz windows set at Brewster’s angle. The polariser is set such that \(\hat{E}_a\), lies parallel to the flowtube axis. The fluorescence is collected perpendicular to \(\hat{E}_a\) and \(\hat{k}_a\) (see Figure 5-1), and passed through the PEM, which is mounted with its optic axis set at 45° to the vertical, bisecting \(\hat{E}_a\) and \(\hat{k}_a\).

The PEM has no provision for external triggering, so it was necessary to trigger the laser and detection electronics relative to a phase-locked output from the PEM driver unit. This allows careful timing of the laser pulse delay settings, relative to the phase of the PEM cycle, to determine whether the PEM acts as a transparent optic or a half-wave plate on the resulting fluorescence. Thus, it is possible to arrange for it to transmit the fluorescence completely unchanged, or with all polarisation components rotated through 90°. Experiments to determine the relative efficiency with which polarised photons are detected revealed the monochromator to transmit horizontally polarised light ~20% more
Chapter 5: Polarisation Effects in Collision-Induced SiF C$^2\Delta$+H$_2$→B$^2\Sigma^+$+H$_2$ Transfer 88

Thus, a second polariser was set with its polarisation axis parallel to $\hat{E}$ after the PEM in the fluorescence path, which, depending on the phase of the PEM, would transmit the parallel, $I_1$, or perpendicular, $I_2$, component of the fluorescence to the monochromator. This method removes any problems with relative transmission efficiencies, and with physical realignment of mechanically rotated passive polarising optics.

Finally, the ability of $\text{JO}$ [8] to simultaneously record data using several different delay settings allowed spectra of the parallel and perpendicular components of the fluorescence to be collected on an alternate shot basis, thereby ensuring any long term drifts in the experimental conditions affected both components equally.

5.4 Directly Excited B-X Emission

Theoretically, polarisation measurements could be made using any combination of spectroscopic branch types in absorption and emission. Ideally, the permutation resulting in the largest polarisation ratio would be most desirable. However, in practice the number of viable combinations is limited by the congested nature of the B$^2\Sigma^+$-X$^2\Pi$ spectroscopy combined with the finite resolution of the exciting laser and, more severely, the detecting monochromator. As a test of the ability of the apparatus to properly determine the fluorescence polarisation, it was decided to investigate the B$^2\Sigma^+$-X$^2\Pi$ (3,0) band, as this was a sufficiently strong transition lying within the wavelength region covered by the same laser dye as the C-X (0,0) band. A typical LIF excitation spectrum of the B-X (3,0) band is shown in Figure 5-2. The two distinct structures correspond to transitions originating in the well separated $^3\Pi_{1/2}$ and $^3\Pi_{3/2}$ components of the ground state. The congested nature of the spectrum to the blue of the main bandhead feature in each sub-band is obvious. Fluorescence was detected on the B-X (3,2) band, as it has the largest Franck-Condon factor of bands originating in B$^2\Sigma^+$, $\nu$=3.

As can be seen from Figure 5-2, there are a possible 12 distinct spectroscopic transitions for a $^2\Sigma^+\rightarrow^2\Pi$ band [9]. In the excitation step, pumping at a bandhead maximises the overall fluorescence signal, at the expense of defining a broad distribution of $J$'s. This, however, turns out not to be a severe limitation for the SiF B-X (and C-X) bands, as the relevant bandheads form at levels where the polarisation properties are approaching the limiting high $J$ values, and are relatively independent of $J$. Only the P$_1$ and $^3$P$_{1/2}$
bandheads of the respective $B^2\Sigma^+ - X^2\Pi_{1/2}$ and $B^2\Sigma^+ - X^2\Pi_{3/2}$ sub-bands are spectroscopically isolated from contamination by other branch types, and are therefore suitable for excitation. Of these two, the $P_1$ head is the more intense because of the larger thermal population of the lower lying $F_1$ ground state levels. The $P_1$ head forms at $J\sim 20.5$.

Figure 5-3 shows a typical $B^2\Sigma^+ - X^2\Pi_{1/2}$ (3,2) dispersed fluorescence spectrum following B-X (3,0) $P_1$ head excitation. The two components of the fluorescence polarisation are shown on the same plot for easy comparison. Due to the short $B^2\Sigma^+$ state lifetime (<10 ns) collisional depolarisation or redistribution of the initial population should be negligible. Therefore, only the three main branches between the $F_1$ components of the B and X states appear in the fluorescence spectrum ($P_1$ excitation exclusively populates $F_1$ levels in the B state). The $P^\uparrow P\downarrow$ and $P^\uparrow R\downarrow$ combinations show an enhancement of $I_\parallel$ over $I_\perp$, while the reverse is true for $P^\uparrow Q\downarrow$, consistent with simple geometrical arguments for a perpendicular transition.

The polarisation ratios, $R$, were calculated for different branch combinations by integrating the fluorescence intensity over the wavelength range spanning each branch, starting from the minimum point between partially resolved branches. This was performed on repeated measurements of the type shown in Figure 5-3, and a statistical analysis applicable for genuine counting experiments used to generate the final $R$ ratio from the integrated intensities. Previous experiments had established a working laser power whereby an acceptable compromise between absolute signal magnitude and saturation of the B-X transition was achieved. In the case of the B-X (3,0) band, this unavoidable trade-off was helped by the relatively weak Franck-Condon factor for the transition.

Spectral congestion also proved to be a problem in determining $R$ for directly excited C state populations, as will be discussed below, and it transpires that the numerical value of $R$ for the $P^\uparrow P\downarrow$ combination is the most reliable for both the B-X and C-X band systems (see Table 5-2). Agreement between theory and experiment is seen to be good, which was interpreted as confirmation of the validity of the experimental approach. A less rigorous analysis of the $P^\uparrow R\downarrow$ and $P^\uparrow Q\downarrow$ combinations gave qualitatively correct signs, but quantitatively less satisfactory values of $R$. We believe this may be due to unresolved overlap of the $Q_1$ and $R_1$ branches in the fluorescence spectrum.
Fluorescence detected on the B-X (3,2) band, so transitions to both ground state spin-orbit manifolds are observed. Features marked with (*) correspond to minority isotopes of Si.
Figure 5-3: $B^2\Sigma^+ - X^2\Pi_{1/2} \ (3,2)$ Dispersed Fluorescence Spectrum.

$I_1$ (---) and $I_1$ (---) components of fluorescence generated by pumping the B-X (3,0) $P_1$ bandhead.
Chapter 5: Polarisation Effects in Collision-Induced SiF $C^2\Delta+H_2\rightarrow B^2\Sigma^++H_2$ Transfer

5.5 Directly Excited C-X Emission

Analysis of directly returning C-X fluorescence gives an indication of the degree of alignment present in the C state, which is essential if any meaningful conclusions are subsequently to be drawn from the polarisation ratios observed in B-X collision-induced emission. The problems associated with cleanly exciting the $C^2\Delta$, $v=0$ state have already been discussed in Section 4.3.1, and for these reasons pumping again took place on the $C^2\Delta\rightarrow X^2\Pi_{1/2}$ (0,0) P$_1$ head (see Figure 3-6). This excites a broad rotational population in the F$_1$ levels of the C state, centred on $J\sim 34.5$.

As in the directly excited B-X transition, the polarisation properties of the directly returning C-X fluorescence were investigated. The fluorescence was collected on the $C^2\Delta\rightarrow X^2\Pi_{3/2}$ (0,0) sub-band, as the large spin-orbit splitting ($\sim 160$ cm$^{-1}$) in the ground state means the excitation and detection wavelengths are well separated. As discussed in Section 4.3.4.1, the conditions of interest include sufficient partial pressure of H$_2$ to induce the collisional transfer of a substantial proportion of the $C^2\Delta$ state population to the $B^2\Sigma^+$ state during the C state lifetime. As discussed at length in the previous chapter, rotationally resolved, dispersed fluorescence spectra of the C-X emission showed rotationally inelastic transfer processes within the $C^2\Delta$, $v=0$ level to be competitive with total removal rates [10]. Collisional transfer between F$_1$ and F$_2$ levels was also observed to be competitive with rotational relaxation within the F$_1$ manifold. Thus, the fluorescence observed on the $C^2\Delta\rightarrow X^2\Pi_{3/2}$ (0,0) sub-band contains contributions from all six possible branches (ignoring the $\Lambda$-doubling in the C state). The only transition to remain spectroscopically isolated is the $^0P_{1/2}$ branch to longer wavelength (c.f. $B^2\Sigma^+-X^2\Pi$ spectroscopic details, as shown in Figure 5-2). Thus, the only meaningful polarisation measurements which can be made are again for the $P_{1/2}P_{1/2}$ combination.

Optical saturation of the C-X transition is a concern here due to the relatively high Franck-Condon factor of the (0,0) band, although this is offset by the weaker C-X electronic transition probability [11]. Towards the limit of high laser power, as saturation effects become significant, the degree of alignment in the initially excited population will degrade towards an isotropic distribution. In this limit, no information about the retention of the plane of rotation during the C$\rightarrow$B transfer process may be inferred. Operationally, the laser pulse energy was varied whilst simultaneously monitoring the linearity of the total signal magnitude and any trends in the observed
polarisation ratios. Despite some curvature in the variation of the total signal, the polarisation ratios were found to be statistically invariant for pulse energies up to \sim 500 \mu J, although increasing scatter about the mean polarisation was observed for low pulse energies.

Statistical analysis of integrated $I_1$ and $I_1$ intensities of the $^3P_{12}$ band fluorescence over repeated measurements of the type shown in Figure 5-4 yields the C-X (0,0) R value. The result reported in Table 5-2 represents an average over the pulse energy range \sim 50-500 \mu J. The reported value of $R=0.060 \pm 0.010$ is significantly less than the theoretical prediction ($R=0.0918$) for the $P^\uparrow P^\downarrow$ combination calculated for the $J$ level at which the $P_1$ bandhead forms. It is believed this discrepancy is primarily due to collisional depolarisation during the C state excited lifetime, with a possible contribution from optical saturation. Nevertheless, the measured polarisation ratio for the C-X (0,0) fluorescence indicates that a significantly polarised $C^2\Delta$ state sample had been prepared, allowing the observed $B^2\Sigma^+$ state polarisation to be interpreted meaningfully.
Figure 5-4: $C^2\Delta - X^2\Pi_{3/2} (0,0)$ Dispersed Fluorescence Spectrum.

$I_1$ (○-○) and $I_1$ (●-●) components of fluorescence generated by pumping the C-X (0,0) $P_1$ bandhead. Only branches originating in the $C^2\Delta F_1$ manifold are labelled.
Chapter 5: Polarisation Effects in Collision-Induced SiF C²Δ+H₂→B²Σ⁺+H₂ Transfer

5.6 Collisionally Produced B-X Emission

The final stage of this study was to determine the extent to which the plane of rotation was conserved in the SiF B²Σ⁺ state produced from C, ν=0→B, ν'=0 transfer, induced by collisions with H₂. As both F₁ and F₂ levels of the B state are populated by the collision event, only the P-type branches to longest wavelength in each B-X sub-band remain spectroscopically isolated, and are therefore suitable for polarisation measurements (see Figure 4-10). However, as discussed in Section 4.4, the B state collision-induced rotational populations are substantially hotter than the parent C state distributions. A high-J component of the B²Σ⁺-X²Π₃/₂ sub-band underlies the B²Σ⁺-X²Π₁/₂ P₁ branch, thereby rendering it unsuitable for analysis (see Figure 5-2 for comparison). Therefore, polarisation resolved B-X fluorescence was collected on the B²Σ⁺-X²Π₃/₂ (0,0) O₁₂ branch.

Figure 5-5 shows a typical dispersed fluorescence spectrum over the head-forming features of the collision-induced B²Σ⁺-X²Π₃/₂ emission. Although the signal-to-noise ratio is poorer than any of the scans over directly returning fluorescence, there does appear to be slightly more intensity associated with the parallel component of the O₁₂ fluorescence over the perpendicular. Statistical analysis over repeated measurements of the O₁₂ I₀/I₁ ratio yields R=0.020 ± 0.016. This result is included in Table 5-2, with the R values for directly returning fluorescence. Thus, R is found to be statistically significantly reduced from the value obtained from directly returning C-X fluorescence, but still (more marginally) greater than zero.
Figure 5-5: Collision-Induced $B^2\Sigma^+-X^2\Pi_{3/2} (0,0)$ Dispersed Fluorescence Spectrum.

$I_\parallel$ (- - - -) and $I_\perp$ (- - - -) components of collision-induced fluorescence after initial excitation of the $C^2\Delta -X^2\Pi_{1/2} (0,0)$ $P_1$ bandhead in the presence of $H_2$ (1.5 Torr) and $Ar$ (1 Torr). Only the head-forming features are labelled (full description shown in Figure 5-2).
<table>
<thead>
<tr>
<th>P-type transition (excited)</th>
<th>P-type transition (observed)</th>
<th>Polarisation ratio, R (predicted)</th>
<th>Polarisation ratio, R (observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-X₁/₂ (3,0)</td>
<td>B-X₁/₂ (3,2)</td>
<td>0.0861 (b)</td>
<td>0.089 ± 0.033</td>
</tr>
<tr>
<td>C-X₁/₂ (0,0)</td>
<td>C-X₃/₂ (0,0)</td>
<td>0.0918 (c)</td>
<td>0.060 ± 0.010 (e)</td>
</tr>
<tr>
<td>C-X₁/₂ (0,0)</td>
<td>B-X₃/₂ (0,0)</td>
<td>0.020 ± 0.016 (e)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5-2: Observed and Predicted Polarisation ratios, R, for P↑P↓ combinations of SiF Bands.

(a) Predicted using the expressions in [1].
(b) Assuming \( J \sim 20.5 \) excited at B-X (3,0) \( P_1 \) bandhead.
(c) Assuming \( J \sim 34.5 \) excited at C-X (0,0) \( P_1 \) bandhead.
(d) Error limits correspond to 1σ uncertainties.
(e) Measured in the presence of \( H_2 \) (1.5 Torr) and Ar (1 Torr).
5.7 Discussion

Taking $R_0$ to be the observed degree of polarisation on the directly returning C-X fluorescence, and $R$ as that of the collisionally produced B-X emission, the ratio $R/R_0$ reflects any alignment changes caused by the electronic state-changing collision. The $B^2\Sigma^+-X^2\Pi$ and $C^2\Delta-X^2\Pi$ bands are both perpendicular transitions with the same polarisation properties, so a positive value of $R/R_0$ corresponds to some retention of the original alignment during the C→B transfer process. From the values listed in Table 5-2, the experimental value of $R/R_0$ is $0.33 \pm 0.27$. A principal conclusion of this study is therefore that with a high statistical probability (>98% confidence) $R/R_0$ differs from unity. This implies that the product state SiF $B^2\Sigma^+$ molecules are not aligned to the same extent as the $C^2\Delta$ molecules from which they are produced by collisions with H$_2$. It is also true, although statistically less certain (~80% confidence), that the non-zero value of $R/R_0$ suggests there may be some partial retention of the SiF polarisation.

At a qualitative level, the depolarisation of the product $B^2\Sigma^+$ state is intuitively consistent with our previous conclusion that a large $\Delta J$ is imparted during the C→B transfer process (as discussed in Section 4.4). Depending on the anisotropy of the imparted $\Delta J$ vector, and the relative magnitudes of $\Delta J$ and $J$, the product state alignment will be degraded from that of the parent distribution. In the extreme case of completely random addition of $\Delta J$ where $|\Delta J| \gg |J|$, the product state alignment will tend toward an isotropic distribution of $J'$. The degree of $B^2\Sigma^+$ state alignment may be investigated through models of $\Delta J$ addition assuming different dynamical approximations. The simplest of these approximations would assume an initially aligned distribution of vectors, $J$, of a fixed magnitude. The $\Delta J$ vector is then also assumed to be of fixed magnitude, but distributed isotropically in space in the usual, spherical sense that the probability density function of $\Delta J$ relative to $J$ is $w(J, \Delta J)$ with a normalised distribution function given by:

$$w(J, \Delta J) \, d\Omega = \frac{1}{4\pi} \, d\Omega = \frac{1}{4\pi} \sin \theta \, d\theta \, d\phi$$

$$= \frac{1}{2} \sin \theta \, d\theta = \frac{1}{2} \, d(J \cdot \Delta J)$$

Equation 5-8

The geometrical relationship between the vectors $J$, $\Delta J$ and $J'$ is shown in Figure 5-6.
Figure 5-6: Geometrical Relationship between the Vectors $J$, $\Delta J$, and $J'$. The polar angles $\alpha$ and $\theta$, and the azimuthal angle $\phi$ are shown.
Chapter 5: Polarisation Effects in Collision-Induced SiF $^2\Sigma^+ + \text{H}_2 \rightarrow B^2\Sigma^+ + \text{H}_2$ Transfer

The polar angle, $\theta$, and cylindrically symmetric azimuthal angle, $\phi$, have their usual significance as shown in Figure 5-6. As stated in Equation 5-7, the value of $R/R_0$ is then obtained from the expectation value of $P_2(\hat{j} \cdot \hat{j'})$ averaged over all angles and weighted by the probability of each orientation of $\Delta J$:

$$\frac{R}{R_0} = \langle P_2(\hat{j} \cdot \hat{j'}) \rangle = \int_0^{2\pi} \int_0^\pi P_2(\hat{j} \cdot \hat{j'}) w(J, \Delta J) d\Omega$$

Equation 5-9

This equation may be re-expressed using the trigonometric relationships between the angles $\theta$ and $\alpha$ to give:

$$\langle P_2(\hat{j} \cdot \hat{j'}) \rangle = \frac{1}{4} \int_0^\pi \left\{ \frac{3(J + \Delta J(\hat{j} \cdot \Delta J))^2}{J^2 + \Delta J^2 + 2\Delta J(\hat{j} \cdot \Delta J)} - 1 \right\} d(\hat{j} \cdot \Delta \hat{j})$$

Equation 5-10

This integral may be manipulated into a form which has the analytical solution [12]:

$$\langle P_2(\hat{j} \cdot \hat{j'}) \rangle = \frac{1}{8} \left\{ 5 - 3\left( \frac{\Delta J}{J} \right)^2 + \frac{3\left( \frac{\Delta J}{J} \right)^2 - 1}{2\left( \frac{\Delta J}{J} \right)} \times \ln \left( \frac{\Delta J + 1}{\Delta J - 1} \right) \right\}$$

Equation 5-11

The addition of a spherically isotropic distribution of $\Delta J$ to $\hat{j}$ is shown schematically in Figure 5-7. As would be expected on an intuitive basis, the degree of depolarisation depends only on the relative magnitudes of $\Delta J$ and $J$. Figure 5-8a shows a plot of $\langle P_2(\hat{j} \cdot \hat{j'}) \rangle$ as a function of $\Delta JJ$. The behaviour seems reasonable, with relatively little degradation of the initial degree of alignment when $\Delta J$ is substantially smaller than $J$, which becomes substantial when the magnitude of the two vectors becomes comparable. The alignment asymptotically approaches zero for large $\Delta JJ$ when the contribution to $\hat{j'}$ from the isotropic $\Delta J$ vector becomes totally dominant.
Figure 5-7: Representation of Addition of Spherically Isotropic $\Delta \mathbf{J}$ to $\mathbf{J}$ for $\Delta J/J < 1$.

Schematic representation of the isotropic addition of $\Delta \mathbf{J}$ (dashed lines) to $\mathbf{J}$ (solid dark line) to form $\mathbf{J}'$ (solid light line) for $\theta = 90^0$ (most heavily weighted polar angle in an isotropic distribution). The light dashed circles indicate the resultant sphere over which $\mathbf{J}'$ will be distributed for a constant $\Delta J$. 
To compare the experimentally observed degree of depolarisation with the isotropic $\Delta J$ model prediction, it is necessary to assess an appropriate value of the ratio $\Delta J/J$. An approximation to this value may be obtained by comparing the average magnitude of product rotation, $\langle J' \rangle$ with $J$, because this relationship is also determined by $\Delta J/J$. Therefore, we also require an expression to predict the average value of $J'$ assuming an isotropic distribution of $\Delta J$. This is given by:

$$\langle J' \rangle = \int_{0}^{1} J' w(J', \Delta J) d\Omega$$

$$= \frac{1}{2} \int_{-1}^{1} \frac{1}{\sqrt{(J^2 + \Delta J^2 + 2\Delta J (J' \cdot \Delta J))}} d(J' \cdot \Delta J)$$

Equation 5-12

where the trigonometric relationships between $J$, $\Delta J$ and $J'$ have again been used. Analytical integration (enforcing a physical condition on the sign of the roots) yields the result:

$$\langle J' \rangle \approx \frac{1}{6J^2 \Delta J} \left( (J + \Delta J)^3 - (J - \Delta J)^3 \right)$$

Equation 5-13

which simplifies to:

$$\langle J' \rangle \approx \left( 1 + \frac{1}{3} \left( \frac{\Delta J}{J} \right)^2 \right) \text{ for } \Delta J \leq J.$$  

Equation 5-14

$$\langle J' \rangle \approx \left( \frac{\Delta J}{J} \right)^2 \left( 1 + \frac{1}{3} \left( \frac{J}{\Delta J} \right) \right) \text{ for } \Delta J \geq J.$$  

Equation 5-15

Again, it can be seen that only the relative magnitudes of $\Delta J$ and $J$ are important in determining the behaviour of the function. The variation of $\langle J' \rangle / J$ with $\Delta J/J$ is shown in Figure 5-8b. Previous work (discussed in Section 4.3.2) characterised the parent $C^2\Delta, v=0$ rotational distribution produced from $P_1$ head pumping in the presence of $H_2$ (and some Ar), and that of the $B^2\Sigma^+, v'=0$ product state. The average rotational quantum
number of the parent C state rotational distribution, \( \langle J \rangle \), is measured to be 25.5, while that of the product B state, \( \langle J' \rangle \), was 35.5 [13]. The ratio of final to initial average rotational magnitudes is characterised by the ratio \( \frac{\langle J' \rangle}{\langle J \rangle} \approx 1.4 \). Ignoring the fact that the initial C state rotational distribution is in reality quite broad, the connection between \( \frac{\langle J' \rangle}{\langle J \rangle} \) and the isotropic model may be made by equating the experimentally observed \( \frac{\langle J' \rangle}{\langle J \rangle} \) ratio with the predicted \( \frac{\langle J' \rangle}{\langle J \rangle} \) ratio. Interpolation on Figure 5-8b yields a corresponding \( \Delta J/J \) ratio of 1.08. This allows an estimation of \( \bar{P}_2(\vec{J} \cdot \vec{J}') \) of 0.20 to be made from Figure 5-8a. Within the error bounds stated, this value agrees with the experimentally observed degree of depolarisation, \( R/R_0 = 0.33 \pm 0.27 \), lending support to the idea that the observed relatively large average change in rotational state is consistent with the observed significant degree of depolarisation.
Figure 5-8: Predictions of the ‘spherical’ (solid lines) and ‘circular’ (dashed lines) models of collisional depolarisation as function of $\Delta J/J$.

(a) Expectation value of the depolarisation ratio, $\langle p_2(J, J') \rangle$, averaged over all angles.  (b) Expectation value of the ratio of magnitudes of final and initial vectors, $<J'>/J$ averaged over all angles.
However, caution must be exercised when drawing conclusions from comparison between the predictions of the spherically symmetric model and experimental observations: in the model, no attempt has been made to average over the initial distribution of magnitudes $J$, or take into account the unknown distribution of magnitudes of $\Delta J$ for a given $J$. It is therefore unreasonable to infer anything significant from the remaining discrepancy between the mean experimental $R/R_0$ and the predictions of the spherically isotropic model.

Inherent in the spherically symmetric model is the assumption that the collisionally imparted $\Delta J$ vector has no preferential direction in space relative to the initial $J$ vector. However, in the limit that $\Delta J$ is imparted impulsively to $J$ in a sudden collision between the partner and a linear rotor, the direction of $\Delta J$ is dynamically constrained to be perpendicular to the rotor axis, $r$. As the point of impact is cylindrically symmetric about the rotor axis, the resulting $\Delta J$ distribution forms a circle in a plane perpendicular to $r$ and containing $J$ (see Figure 5-9) with no weighting by the polar angle, $\theta$ (see Figure 5-6). Averaging over all possible azimuthal orientations of $r$ in the plane perpendicular to $J$ results in a $\Delta J$ distribution over $4\pi$ solid angles, which is peaked along (and against) the direction of $J$. This phenomenon is analogous to the forward-backward peaking of product translational vectors in the decomposition of long lived complexes in molecular beam scattering [14].

In this dynamically distinct, 'circularly isotropic' model of the collision event, the $\Delta J$ vector is still constrained to be of fixed magnitude, but is distributed in space such that the normalised distribution function analogous to Equation 5-8 is given by:

$$w(J, \Delta J) d\Omega = \frac{1}{2\pi^2 \sin \theta} d\Omega = \frac{1}{2\pi^2} d\theta d\phi = \frac{1}{\pi} d\theta$$

$$w(J, \Delta J) = \frac{1}{\pi \sqrt{1 - (J \cdot \Delta J)^2}} d(J \cdot \Delta J)$$

Equation 5-16
Figure 5-9: Representation of Addition of Circularly Isotropic $\Delta J$ to $\mathbf{J}$ for $\Delta J/J<1$.

Schematic representation of the circularly isotropic addition of $\Delta J$ (dashed lines) to $\mathbf{J}$ (solid dark line) to form $\mathbf{J'}$ (solid light line). The $\Delta J$ distribution associated with a single value of $\phi$ is shown bounded by the dashed ellipse. The light dotted circle indicates the resultant sphere over which $\mathbf{J'}$ will be distributed for a constant $\Delta J$ once averaged over all $\phi$. 
Substitution of Equation 5-16 into Equation 5-9 yields a corresponding analogue of Equation 5-10 for a system constrained to impart ΔJ perpendicular to r. We were unable to find a general closed form integral for the resulting \( \left\langle P_2(\mathbf{j} \cdot \mathbf{j'}) \right\rangle \) expression, so the results of a numerical evaluation are shown in Figure 5-8a. Comparison of the values of \( \left\langle P_2(\mathbf{j} \cdot \mathbf{j'}) \right\rangle \) predicted by the two models shows the circularly isotropic system to exhibit slightly less depolarisation than the spherically isotropic for \( \Delta J/J < 1 \). This is intuitively consistent with the greater weighting \( \mathbf{j} \) receives along the direction of \( \mathbf{J} \) in the circular model. The curves converge at \( \Delta J/J = 1 \), where \( \left\langle P_2(\mathbf{j} \cdot \mathbf{j'}) \right\rangle = 1/4 \) (exactly). Above \( \Delta J/J = 1 \) the circular model can be seen to predict a constant degree of product state alignment, in contrast to the continued decline exhibited by the spherical model. This, initially surprising, behaviour may be rationalised by the fact that in the limit of very large \( \Delta J \), the product \( \mathbf{j'} \) vectors are evenly distributed in a plane perpendicular to \( \mathbf{r} \). It is therefore the memory of the anisotropic distribution of \( \mathbf{r} \) rather than \( \mathbf{J} \) which causes the product state to be aligned. The correct limiting value is deduced by realising that the average acute angle, \( \alpha \), between a fixed \( \mathbf{j} \) vector and \( \mathbf{j'} \) vectors distributed uniformly over a circle in a plane which contains \( \mathbf{j} \) is \( \pi/4 \), so \( \cos^2 \alpha = 1/2 \) and \( P_2(\cos \alpha) = 1/4 \). This value is produced whenever the magnitude of \( \Delta J \) exceeds \( J \), allowing \( \mathbf{j'} \) to explore all directions in the plane containing \( \mathbf{j} \).

As before, we require the value of \( \left\langle \mathbf{j'} \right\rangle \) predicted by the circular model to compare the calculated degree of depolarisation with experiment. This was achieved by substituting the distribution function defined in Equation 5-16 into Equation 5-12. Again, a closed form analytical solution to the expression could not be found, so the results of a numerical evaluation are plotted in Figure 5-8b. The dependence of \( \left\langle \mathbf{j'} \right\rangle /J \) on \( \Delta J/J \) is very similar for both models.

Interpolation on Figure 5-8b using the experimental \( \left\langle \mathbf{j'} \right\rangle /J \) ratio of 1.4 yields a \( \Delta J/J \) value of 1.15 with the circular model, which allows an estimation of \( \left\langle P_2(\mathbf{j} \cdot \mathbf{j'}) \right\rangle = 0.25 \) to be made from Figure 5-8a. As with the spherical model, within the stated uncertainties this value agrees with the experimentally observed degree of depolarisation, \( R/R_0 = 0.33 \pm 0.27 \). The experimental value of \( R/R_0 \) agrees with the predictions of both models within
the relatively broad error limits, therefore not distinguishing between them.

However, an interesting conclusion to be drawn from the modelling performed here is that a system which conforms strictly to this extreme impulsive limit of energy release must, even when carefully averaged over all contributions from $J$ and $\Delta J$, retain a degree of alignment $R/R_0 \approx 1/4$. The extent to which it will exceed $1/4$ will depend on the contribution to the average made from collisions which impart $\Delta J < J$. If such a system were probed by pumping a low $J$ level in the parent state, the degree of alignment of the product levels with $\Delta J$ much larger than $J$ would be a sensitive diagnostic of the impulsiveness of the collision process. Also, there should exist a correlation for larger $J$ between the alignment of $J'$ and its magnitude. As was argued for the SiF $\Delta J_{\text{max}}$ values discussed in Section 4.4, the highest $J'$ values require $\Delta J$ and $J$ to be parallel prior to the collision for the maximum conversion of orbital angular momentum to $J'$. The highest $J'$ levels populated should therefore exhibit some memory of the initial plane of rotation, and show correspondingly large, positive polarisation ratio, $R/R_0 \to 1$.

5.8 Conclusions

The results of this study show that an aligned sample of SiF $C^2\Delta, v=0$ molecules has been prepared using linearly polarised laser excitation, and the degree of depolarisation caused by collisions within the C state lifetime determined by measuring the fluorescence polarisation ratio on a known combination of excitation and detection bands. The degree to which the plane of rotation is conserved during transfer to the $B^2\Sigma^+$, $v'=0$ level in collisions with $H_2$ has been measured. The resulting value of $R/R_0 = 0.33 \pm 0.27$ implies significant depolarisation of the product B state compared to the parent C state. This observation is consistent with our earlier findings, that the $C \rightarrow B$ transfer process imparts a large $\Delta J$ to the initial $J$ vector. To account for the observed degree of depolarisation, two models of the vector addition of $\Delta J$ to $J$ were developed. A dynamically unconstrained, spherically isotropic distribution of $\Delta J$ relative to $J$ leads to the expected monotonic decline in product state alignment as the ratio $\Delta J/J$ increases. However, in an alternative dynamical limit in which $\Delta J$ is constrained to be perpendicular to the molecular axis, $\ell$, the degree of alignment never falls below $1/4$ of that of the initial state. This observation has general implications for processes of this type, where energy is converted to product rotation in a sudden, impulsive fashion. Unfortunately, the results of this experiment are not sufficiently resolved to distinguish between the two cases.
Chapter 5: Polarisation Effects in Collision-Induced SiF $C^2\Delta+H_2\rightarrow B^2\Sigma^+ + H_2$ Transfer

Bibliography

12 M. Abramowitz, I. Stegun (Eds), *Handbook of Mathematical Functions* (Dover, New York, 1965).
Chapter 6
Mechanistic Conclusions on SiX (X=Cl, F) $^2\Delta \rightarrow ^2\Sigma^+$ Transfer

The previous two chapters have discussed in some detail the extensive body of work accumulated on collision-induced SiCl and SiF $^2\Delta \rightarrow ^2\Sigma^+$ transfer. The main points on which to compare the behaviour of the two molecules are summarised in Table 6-1. The challenge now is to understand the dynamics behind the observed collisional behaviour in terms of the potential energy surfaces (PESs) for the interaction of the SiX (X=Cl, F) excited states with the colliding partner. Ideally, the features of these surfaces should be justifiable in terms of some independent property of the molecules, and provide satisfactory mechanistic explanations of the collisional behaviour of each system.

Dealing initially with the SiF radical, the absence of any significant variation in the total quenching rate, or the electronic branching fraction, on the initial $J$ populated in the C$^2\Delta$ state, is usually interpreted as evidence for there being no preferred radical-quencher orientation for collisional removal from the C state. Otherwise, a well established argument suggests that increased initial rotation will tend to disrupt the most efficient collisional removal geometry, thereby lowering the probability of a successful quenching collision. The large absolute values for the total removal rates are also consistent with a lack of any steric constraints in the system. The lack of any angular dependence (defined as the angle between the SiF molecular axis, $\mathbf{r}$, and the vector joining the SiF centre of mass and the collision partner, $\mathbf{q}$) allows the construction of simplified 3-dimensional PESs as a function of $r$ and $q$ alone (see Figure 6-1). The potential energy curves shown in Figure 4-1 correspond to the asymptotically separated SiF-quencher limits ($q \rightarrow \infty$) in which the isolated excited states have not been modified by the approach of the quencher molecule.
Table 6-1: Key Points of Comparison between the Collisional Processes SiCl $B'^2\Delta, v, J \rightarrow B^2\Sigma^+, v', J'$ and SiF $C^2\Delta, v, J \rightarrow B^2\Sigma^+, v', J'$.

(a) Total quenching rate constant for the B'/C state.
(b) Electronic branching fraction, $B'/C^2\Delta \rightarrow B^2\Sigma^+$.
(c) Product $B^2\Sigma^+$ vibrational distribution.
(d) Product $B^2\Sigma^+$ rotational distribution.
(e) Retention of alignment of initial and product rotational vectors during $^2\Delta \rightarrow ^2\Sigma^+$ transfer.
(f) Franck-Condon overlap between the $B'/C^2\Delta, v$ and $B^2\Sigma^+, v'$ vibronic levels.

<table>
<thead>
<tr>
<th>Measured Quantity</th>
<th>SiCl</th>
<th>SiF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_Q^{(a)}$</td>
<td>Large for all quenchers studied. (He, Ne, Ar, H₂, N₂, CO₂, CH₄, CF₄)</td>
<td>Large for some quenchers (H₂, N₂, CO₂, CH₄). Small for noble gases (He, Ar). No observable $J$ dependence. No force correlations.</td>
</tr>
<tr>
<td></td>
<td>Attractive force correlation.</td>
<td></td>
</tr>
<tr>
<td>$J_B^{(b)}$</td>
<td>Quencher sensitive. Major channel (~10-100%). $v=0 \rightarrow v=1$ (for molecular quenchers).</td>
<td>Quencher sensitive. Minor channel (~0-20%). $v=0 \rightarrow v=1$.</td>
</tr>
<tr>
<td>$v'$ distribution$^{(c)}$</td>
<td>Quencher sensitive. No obvious pattern. Variable $&lt;\Delta E&gt;$.</td>
<td>Similar for all quenchers. Well correlated with $q_{v,v}^{(f)}$. Consistently large $&lt;\Delta E&gt;$.</td>
</tr>
<tr>
<td>$J'$ distribution$^{(d)}$</td>
<td>Some evidence for moderate $\Delta J$. (not studied in detail)</td>
<td>Large $\Delta J$. Quencher dependent. Correlation of $&lt;J&gt;$ with $&lt;J'&gt;$.</td>
</tr>
<tr>
<td>$I$ - $J'$ correlation$^{(e)}$</td>
<td>(not studied)</td>
<td>Significant product state depolarisation.</td>
</tr>
</tbody>
</table>
Chapter 6: Mechanistic Conclusions on SiX (X=Cl, F) \(^2\Delta \rightarrow ^2\Sigma^+\) Transfer

The \(q\) dependence of the potential energy functions has been qualitatively inferred from the remaining experimental evidence. It can be seen from Figure 4-1 that the SiF \(C^2\Delta\) and \(B^2\Sigma^+\) potential energy curves are nested in the isolated molecule, without a classical crossing in the energy region of interest. Therefore, for transfer to take place between these two states, the crossing must presumably occur on the higher dimensional hypersurface representing the approach of the quencher molecule. The fact that collisional transfer between the two excited states occurs efficiently at thermal energies, at least for some partners, implies that this seam of intersection between the two surfaces must be relatively easily accessible on the \(C^2\Delta\) surface. The \(C^2\Delta\) state has therefore been drawn as only mildly repulsive in the region of the crossing. The partitioning of the significant vibronic energy defect involved in the dominant \(C \rightarrow B \,(0,0)\) channel (\(\sim 5000\) cm\(^{-1}\)) into product state rotation and relative translation of the collision pair is consistent with a sudden, impulsive mechanism of energy release. This is also true of the large \(\langle \Delta I \rangle\) imparted to the product state and the consequential substantial depolarisation of \(J\) relative to \(J\). For these reasons, the lower surface in Figure 6-1a which correlates asymptotically with the \(B^2\Sigma^+\) state, is shown substantially more repulsive than the upper state in the \(q\) co-ordinate. The observation that the SiF \(B^2\Sigma^+\) product state vibrational distributions are well described by the Franck-Condon overlap between the vibronic wavefunctions of the two states is also indicative of the sudden nature of the electronic transition, and rapid subsequent separation of the collision pair. This Franck-Condon control also suggests that the potentials in the Si-F co-ordinate are not substantially distorted from those in the asymptotically separated limit at the hypersurface intersection. The formation of a long-lived collision complex can be discounted as a significant SiF quenching channel leading to \(B^2\Sigma^+\) production, as this would result in a statistical distribution of energy in the product state, and a positive correlation of total removal rates with attractive forces.

The schematic form of the PES in Figure 6-1a for a SiF-quencher interaction has now been justified on purely mechanistic grounds. In summary, a representative trajectory begins on the SiF \(C^2\Delta\) state, and reaches the seam of intersection between the hypersurfaces fairly easily, even with only thermal kinetic energies. The trajectory then transfers between hypersurfaces over a quite localised range of SiF-quencher distances, \(q\), switching to the steeply repulsive surface asymptotically connected with the \(B^2\Sigma^+\)
state. The collision pair now recoil rapidly, converting the asymptotic energy gap, $\Delta E$, primarily into translational and rotational energy, preserving the Franck-Condon control of the vibrational distribution.

Turning now to SiCl, there is no particular reason to believe that the functional form of the potentials in the SiCl-quencher co-ordinate, $q$, will be fundamentally different from those assumed for the SiF-quencher interaction, apart from some minor rescaling to reflect the sizes and (more importantly) the polarisabilities of the molecules (recall, the SiF and SiCl molecules are electronically analogous). The question then arises as to the origin of the major differences in the $^2\Delta \rightarrow ^2\Sigma^+$ transfer propensities of the two species. It is proposed that the critical difference between the two systems lies in the position of the classical crossing point between the excited states in the asymptotically separated limit. In the SiF molecule, the $^2\Delta$ and $^2\Sigma^+$ are 'nested' in the energy region of interest, without an accessible classical crossing in the vicinity of the energy levels populated in these experiments. However, due to relatively subtle shifts in the equilibrium internuclear distances and relative energies of the excited states in SiCl, a classical crossing between the $^2\Delta$ and $^2\Sigma^+$ excited states occurs in the isolated molecule very close to the outer turning points of the $B^2\Delta$, $\nu=0$ and $B^2\Sigma^+$, $\nu'=2$ levels (see Figure 4-1). The two hypersurfaces which correlate asymptotically with the $B^2\Delta$ and $B^2\Sigma^+$ excited states in SiCl therefore have a complicated seam of intersection in the $q$ co-ordinate which extends all the way out to the isolated molecule. A crossing between the two surfaces can therefore be induced at a point where the interaction between the quencher and the excited states is only weakly perturbative. This allows transfer to occur without requiring the quencher to penetrate to a depth where the intermolecular repulsion is significantly different between the two hypersurfaces. The probability of transitions between the hypersurfaces will be dependent on the internuclear separation through the variation of the matrix element coupling the two states with the degree of electronic distortion induced by the quencher. It is assumed the perturbation mixes the $A'$ components of the $^2\Delta$ and $^2\Sigma^+$ surfaces in the reduced symmetry of the collision pair [1].

A schematic plot of the SiCl-quencher PESs is shown in Figure 6-1b. Defining a trajectory along the $q$ co-ordinate is not so straightforward now, with the possibility of multiple crossings and recrossings of the seam of intersection between the surfaces. It is perhaps unsurprising therefore, that SiCl departs from the sudden limit, in which the
Franck-Condon overlap has a strong influence on the preferred product channels, to a situation where the quencher-dependent details of the surfaces dictate the partitioning of energy in the product state. The correlation of total quenching rate constants with the SiCl-quencher attractive forces (consistent with a quenching mechanism dominated by processes occurring at relatively long range) is also reasonable. This is found to be especially true for the 'softest' collisions, which transfer population between the nearly isoenergetic levels $B^2\Delta, \nu=0$ and $B^2\Sigma^+, \nu'=2$ (see Figure 4-1) [2]. The same reasoning may be applied to the electronic branching fractions $f_B$, in which the largest $f_B$ values are observed for SiCl $B^2\Delta, \nu=0$ as this level requires the least perturbation to induce a transition to the $B^2\Sigma^+$ state.

Thus far, the variation of the respective $^2\Delta$ and $^2\Sigma^+$ PESs in the $q$ co-ordinate of the SiX-quencher systems has been justified in terms of being consistent with the experimental observations. However, we believe the origin of the two distinct types of $q$ dependence to be the respective electronic characters of the two states. The $^2\Delta$ states are thought to be predominantly excited valence configurations, while the $^2\Sigma^+$ states are quite unambiguously assigned as the lowest members of the $n\sigma$ Rydberg series [2]. The physical significance of this distinction lies in the volume of electron density associated with the two types of orbital. The Rydberg electron occupies a significantly larger volume than the more compact valence state. As a result, the electron-electron repulsion terms become significant at larger intermolecular distances for the approach of the quencher to a Rydberg state as compared to a valence state. Thus, when the transition between states occurs, the molecule is transferred from, what is at most, a mildly repulsive surface, $^2\Delta$, to a surface which is substantially repulsive at that value of $q$, $^2\Sigma^+$. This couples the asymptotic energy defect between states into rotation and relative translation of the collision pair. This argument is consistent with the observed blue shifting of lower members of Rydberg series relative to excited valence states in condensed phases [3]. More recent, time-resolved measurements of this phenomenon have confirmed the idea of ‘bubble’ formation as the matrix cage is repelled by a molecule excited to a Rydberg state. Direct spectroscopic measurements of related Van der Waals dimers, such as NO-Ar [4,5], have similarly shown that the position of the intermolecular potential minimum is shifted by $\sim 1$ Å to longer range when the NO molecule is excited to a Rydberg state as compared to the ground state.
It is possible to set this argument on an approximately quantitative footing by estimating the effective size of each orbital. As discussed in Chapter 3, the highest occupied \( C^2\Delta \pi^* \) orbital is primarily associated with the Si 3p valence orbital. The size of the molecular orbital may therefore be estimated from:

\[
r \approx \frac{n^2 a_o}{Z^*}
\]

Equation 6-1

where \( r \) represents the average distance of the valence electron from the nucleus, \( n \) is the principal quantum number, \( a_o \) is the Bohr radius, and \( Z^* \) is the effective nuclear charge experienced by the valence electron (the effect of screening from inner electrons may be estimated using Slater’s rules to arrive at a value of \( Z^* \)) [6]. Equation 6-1 results in an estimation of the radius of the Si 3p orbital (and hence \( C^2\Delta \pi^* \)) of 1.15 Å. The Rydberg orbital radius may be obtained from:

\[
r \approx n^{*2} a_o
\]

Equation 6-2

where \( n^* \) represents the effective quantum number, given by:

\[
n^* = n - \delta
\]

Equation 6-3

The quantum defect, \( \delta \), may be calculated from experimentally observed ionisation potentials and term energies, and is known [7] for both the atomic Si 4s Rydberg orbital and the SiF \( B^2\Sigma^+ \) state to be \( \sim 1.9 \). The calculated mean radius of the \( B^2\Sigma^+ \) state is therefore found to be 2.4 Å. This independent measure of the properties of the electronic states in the isolated molecule lends further support to the functional form of the hypersurfaces shown in Figure 6-1a, and hence to the proposed mechanism of energy transfer.

However, the form of the surfaces shown in Figure 6-1 should not be interpreted too literally. Rather they should be viewed as a first order approximation of the true representation. In particular, the spectroscopic assignment of the \( C^2\Delta \) level as a valence
state has recently been called into question [8]. The equilibrium internuclear distance, \( r_c = 1.571 \, \text{Å} \), of the \( C^2\Delta \) state lies almost exactly halfway between that of the \( X^2\Pi \) (valence) ground state and the \( B^2\Sigma^+ \) (Rydberg) state (1.601 Å and 1.542 Å respectively). The \( C^2\Delta \) \( r_c \) was not well reproduced in ab-initio calculations [7,9,10], and it was realised that to account for the energy of the state it was necessary to include Rydberg-type orbitals in the basis set [9]. It has now been suggested [8] that outstanding limitations of the basis set led to an underestimation of the \( 3d\delta \) Rydberg component of the \( C^2\Delta \) state (this Rydberg state had previously been associated with the experimentally observed higher lying \( D^2\Delta \) state).

Furthermore, a knowledge of the degree of Rydberg and valence character present in an excited state is not in itself sufficient to accurately predict the form of the surface this state will give rise to. Simply assuming that electron-electron repulsion terms will dominate the interaction ignores the substantial attractive term which may arise through the charge-charge induced dipole interaction between a quencher and the positive ion core of a Rydberg state. However, this effect has generally been presumed only to become significant at high values of \( n \), where the core becomes less shielded by the remote Rydberg electron [5,11,12].

Care must also be taken in drawing comparisons between behaviour in the condensed phase and the gas phase. It has recently been proposed that the repulsive interaction experienced by a Rydberg molecule surrounded on all sides by multiple partners may differ greatly from the response induced in the potential by the approach of a single partner. It is argued that the Rydberg orbital may spatially reorientate itself such that the electron density is maximised in the direction opposite to the approach of the quencher, thereby increasing the attractive and decreasing the repulsive terms in the potential [8]. Indeed, we note that the results presented for the SiX systems do not preclude the possibility of the Rydberg PESs being substantially more attractive to longer \( q \) than has been indicated in Figure 6-1. Assuming this scenario, the seam of intersection between the two SiF excited states would be reached at value of \( q \) where the lower Rydberg surface was less repulsive. Provided the kinetic energy of the collision pair was not efficiently coupled to SiF vibration during the journey along the \( B^2\Sigma^+ \) surface, and an impulsive rebound followed at the inner wall of the product state, then the SiF \( B^2\Sigma^+ \) product state partitioning would not be easy to distinguish from that predicted by the
In summary, collision-induced SiX $^2\Delta \rightarrow ^2\Sigma^+$ transfer has been investigated through an extended series of experiments. Reduced dimension PESs have been constructed for the SiX-quencher interaction which are consistent with the experimentally observed scalar and vector propensities. While further experimentation would undoubtedly resolve some of the questions which are still outstanding concerning the behaviour of these systems, the major obstacle to a complete understanding of the dynamics is the lack of reliable PES calculations.
Figure 6-1: Schematic Reduced Dimension PESs for a SiX-Quencher Interaction.

(a) SiF A$^2\Delta$ and B$^2\Sigma^+$ hypersurfaces and (b) SiCl B$^2\Sigma^+$ and B$^2\Delta$ hypersurfaces. The parameter $r$ represents the SiX intramolecular co-ordinate, while $q$ shows the intermolecular SiX-quencher distance. A Lennard-Jones 12-6 potential [13] is used to model the functional behaviour in the $q$ co-ordinate. The $r$ co-ordinate for both surfaces is described by a Morse Potential incorporating known molecular constants for the relevant molecules and electronic states.
Chapter 6: Mechanistic Conclusions on SiX (X=Cl, F) $^2\Delta \rightarrow ^2\Sigma^+$ Transfer

Bibliography


Chapter 7

CH Introduction

Since its identification in 1918 [1], the CH radical has formed the subject of numerous spectroscopic and kinetic investigations, playing an important role in the development of an understanding of the doublet spectra of diatomic molecules. The emission spectrum of this molecule in the visible region, consisting of the $A^2\Delta-X^2\Pi$ and $B^2\Sigma^+_e-X^2\Pi$ band systems, is responsible for the familiar violet colouration of hydrocarbon flames, and its presence has also been detected in the sun, stellar atmospheres, interstellar space and comet atmospheres. As with the other first-row diatomic hydrides, CH is of fundamental interest to theoreticians and experimentalists studying the dynamics of collisional quenching and energy transfer processes of small molecules.

The total quenching of the $A^2\Delta$ state by specific quenching partners has been studied by a number of groups [2,3,4,5,6,7,8,9]. In the high temperature work of Stuhl and Crosley (950 K and 1300 K respectively) [8,9], the quenching rates of various colliders were found to be significantly higher than their 300 K values. This temperature dependence indicates that repulsive forces are involved in the quenching of CH $A^2\Delta$, suggesting the process may be governed by the inner turning point region of the CH-collider interaction, or possibly the presence of a barrier further out in the intermolecular co-ordinate [10]. Consistent with this observation, ab-initio calculations of the potential energy surfaces involved in the CH+$H_2$ system, performed by Veigiri and Farantos [11], indicate the presence of barriers in the hypersurface entrance channels. In a study of collisional relaxation within the $A^2\Delta$ state, Whitehead observed the rates of rotational relaxation to be comparable to gas kinetic for collisions with Ar and $N_2$, with vibrational relaxation about an order of magnitude slower [12]. Dixon obtained a similar rate of rotational relaxation in his study with He as the collision partner [13].

In contrast to the large body of work on $A^2\Delta$ quenching, the only information on the total removal rates of the $B^2\Sigma^+$ state are from a study by Whitehead, where the quenching
propensities of an extensive range of collision partners was undertaken [14]. He concluded that quenching of the $B^2\Sigma^-$ state was largely by chemical reaction, with rate constants which exceed those for $A^2\Delta$ state quenching and are comparable to those for CH $X^2\Pi$ ground state removal. A study of relaxation within the $B^2\Sigma^-$ state, again by Whitehead, found the rotational relaxation rates for Ar and N₂ to approach gas kinetic, with vibrational relaxation rates of a similar order of magnitude [15].

The first direct observation of collision-induced electronic energy transfer between the $A^2\Delta$ and $B^2\Sigma^-$ states is reported in a study by Crosley on the energy transfer processes in CH $A^2\Delta$ and $B^2\Sigma^-$ in an atmospheric pressure flame [16]. Following state-specific laser excitation to the $A^2\Delta$, $v=0$ and $v=1$ levels, he observed the collisional transfer of population into $B^2\Sigma^-$, $v'=0$. Interestingly though, only fluorescence from the $A^2\Delta$, $v'=1$ level was detected after pumping $B^2\Sigma^-$, $v=0$. Rotationally resolved spectra from the collisionally populated product states revealed no memory of the parent state distributions were retained for transfer in either direction, even though rotational relaxation in the parent state had been shown to be far from complete. Due to the high density of collider species in the flame environment, Crosley was unable to determine absolute rate constants for any of the energy transfer processes taking place. However, he reports the ratios of the electronic energy transfer rate to the collisional quenching rate for the three vibronic levels as lying in the order $B^2\Sigma^-$, $v=0 > A^2\Delta$, $v=1 > A^2\Delta$, $v=0$.

In their experiments in a low pressure flame, following direct excitation of the $B^2\Sigma^-$, $v=0$ level, Copeland et al. [17] obtained time resolved B-X (0,0) and collisionally produced A-X ($v,v$) fluorescence waveforms (the A-X (1,1) and (0,0) bands were unresolved within his detection system). They estimated the size of the collision-induced A-X emission to be between 30 and 50% of the directly excited B-X signal.

Encouraged by these observations of $A^2\Delta \leftrightarrow B^2\Sigma^-$ transfer in flames, it was decided to undertake a systematic investigation of the electronically inelastic process under single-collision conditions with individual quenching partners.
Bibliography

1 T. Heurlinger, Dissertation, University of Lund, 1918.
Chapter 8

CH Experimental Apparatus

8.1 Introduction

This chapter will describe in detail the experimental apparatus used to probe collision-induced transitions between the $A^2\Delta$ and $B^2\Sigma^-$ states of the CH radical. As in the SiX radical studies, Laser Induced Fluorescence (LIF) was employed to determine the state-to-state propensities of CH $A^2\Delta$-$B^2\Sigma^-$ collisional transfer.

The CH radical is present over a wide range of research fields, from combustion to interstellar environments. In order to fully understand the role it plays in these varied systems, the state-specific collisional behaviour of the molecules must be determined. The excited states involved in this study ($A^2\Delta$ and $B^2\Sigma^-$) do not possess the fortuitous ratio of lifetimes exhibited by the SiX radicals, and the acquisition of spectra reflecting nascent product state CH distributions is, accordingly, more involved.

CH radicals were produced directly in the excitation/detection zone using UV laser photolysis of bromoform (CHBr$_3$). While this proved to be an efficient means of generation, the $A^2\Delta$ and $B^2\Sigma^-$ states were found to be major products of the photolysis process, which resulted in a wavelength overlap between fluorescence associated with the photolysis pulse, and probe-induced A-X or B-X fluorescence. This enforced a substantial time delay (~5 μs) between the photolysis and probe lasers, during which the excited states were quenched and, correspondingly, the ground state population increased. An unavoidable consequence of this delay was that the density of CH radicals in the excitation beam path, and subsequently the size of the probe-induced signal, was reduced by reaction and 'flyout' from the excitation zone. The delay between the two lasers discussed above separated the signals temporally, but the large magnitude of the photolysis signal complicated the observation of probe-induced fluorescence. The resolution of this problem is discussed in Section 8.4.
8.2 Gas Handling and the Vacuum System

Generation and investigation of the CH radical was performed in a stainless steel, 6 way cross reaction chamber (Vacuum Generators UK Ltd), represented in plan view in Figure 8-1. The chamber was evacuated using a cryobaffled diffusion pump (Edwards 100/300M) backed by two cryotrapped rotary pumps (Edwards E2M8), with typical base pressures $\sim 10^{-6}$ mbar. Pressures in the vacuum system were regulated via a combination of Pirani (Edwards PR10K) and ion (Vacuum Generators VIG 8) gauges, monitored through an ion gauge controller (Vacuum Generators IGC 17F). Chamber pressures outwith the range of the ion gauge ($10^{-3}$-$10^{-9}$ mbar) could be monitored using two MKS Baratron capacitance manometers (model 627, 0-10 Torr, and type 127, 0-1 Torr). As indicated in Figure 8-1, the photolysis and probe lasers counter propagate along the same axis into the chamber via two quartz flats mounted at Brewster’s angle. The laser entrance windows are deliberately rotated through $90^\circ$ relative to each other, reflecting the orthogonal polarisations of the photolysis and probe beams. Fluorescence was collected perpendicular to the laser propagation and pumping axes, and transmitted out of the chamber to two separate detection systems, one involving a monochromator and the other using interference filters (as shown in Figure 8-1).

Control over the flow of gases into the vacuum system, and the preparation of gas mixtures, was performed by a gas inlet network connected to the chamber. Due to its low vapour pressure (~4.6 Torr @ 20°C), the precursor molecule, CHBr$_3$, was prepared as a 17% CHBr$_3$/Ar premixture at a total pressure of 30 Torr in a stainless steel reservoir (Whitey). A combination of isolation valves enabled the flow of quenching and precursor gases into the chamber to be independently varied through separate needle valve arrangements (Whitey SS 22RS4). A Baratron (type 222, 0-100 Torr) was used to monitor the rate of loss of precursor mixture at a steady chamber pressure, allowing the flow rate (and hence the partial pressure of CHBr$_3$) to be kept constant. Quenching gases were taken straight from the cylinder (through the gas line) without further purification. Liquid CHBr$_3$ was kept in a stainless steel cold finger (Whitey) and purified by repeated freeze-pump-thaw cycles prior to premixture preparation. Quenching and precursor gases were mixed in a T-piece (Swagelock) prior to admission into the chamber as an effusive source through an inlet in the top flange. Pressures in the reaction chamber were routinely set by throttling the diffusion pump at a given
premixture flow rate to 40 mTorr, and then introducing the quencher species at a sufficient flowrate to achieve the required total pressure. In this way, the partial pressure of premixture in all experiments was consistently set to 40 mTorr, giving a CHBr₃ pressure of ~7 mTorr.

8.3 The Laser Systems

As mentioned above, this investigation utilised independent photolysis and probe laser sources. The probe laser system was a Spectron Nd:YAG pumped dye combination, very similar to the one discussed in Section 2.3. Over the course of this study three different photolysis systems have been employed, operating at two wavelengths.

8.3.1 The Probe Laser System

The excitation laser system consisted of a Q-switched Nd:YAG laser (SL803S), a dye laser unit (SL400G), and a wavelength extender unit (WEX) (SL400EX), as supplied by Spectron Laser Systems. The principle of operation of these components is very similar to that described in Section 2.3, the only operational difference being that the dye laser amplifier cells are pumped in a longitudinal configuration. Control of the fundamental frequency output of the dye laser was achieved through a dedicated scan controller unit (Spectron SL4000SC) interfaced to the central PC (Dell 486/33S) through a RS-232 serial port (this eliminates the need for manual synchronisation of the scanning and data collection cycles). Optimum phase matching conditions in the doubling/mixing units of the WEX were maintained by an autotracker unit (Spectron SL400) linked to a BBC microcomputer running custom software. The wavelengths required in this investigation were generated by 532 nm pumping of the dye laser, operating with a methanol solution of a mixture of R610 and R640 dyes, and mixing the output with the residual 1064 nm Nd:YAG fundamental. This generated vertically polarised radiation, tuneable over the range 380-395 nm, with maximum pulse energies up to ~15 mJ. Separation of the frequency-mixed output from the dye and Nd:YAG fundamental radiation was achieved using a pair of highly reflecting UV dichroic mirrors.

8.3.2 The Photolysis Laser System

As stated above, three different photolysis lasers were employed over the course of this project. Initially, a Questek Series 2000 Gas Discharge (excimer) laser was used to
effect the multiphoton dissociation of CHBr$_3$. This laser was operated at 193 nm, with nominal pulse energies of ~60 mJ over a rectangular beam profile (~30 mm by 15 mm). The resulting, unpolarised, beam was brought to a focus inside the chamber, spatially overlapping the probe beam, with a quartz lens (f=50 cm). After the Questek laser, a Lambda Physik COMPex 200 excimer laser from the Central Laser Facility Loan Pool, Rutherford Appleton Laboratory, was utilised. This system was operated in the same configuration as the Questek, with the power stability and gas lifetimes found to be much improved (the COMPex laser system incorporated a halogen generator module, allowing automatic gas refills and rendering the need for external halogen tanks redundant). The final photolysis source was the quadrupled output of the Nd:YAG laser previously described in Section 2.3.1 (SL803). 266 nm radiation was generated by frequency doubling 532 nm light from the Nd:YAG laser within the doubling unit of the WEX housing. In this way, the intensity of 266 nm light produced could be monitored, and the orientation of the doubling crystal constantly adjusted for optimum phase matching conditions (as described in Section 2.3.3). This was found to be necessary as self-absorption of a small fraction of the 266 nm light generated varied the temperature of the doubling crystal, which in turn varied the optimum phase matching angle. The resulting horizontally polarised laser beam was steered into the chamber (without focusing) using a Pellin-Broca prism as shown in Figure 8-1. Typical 266 nm pulse energies were measured to be ~40 mJ.

8.4 Fluorescence Resolution and Detection

As indicated in Figure 8-1, fluorescence generated in the excitation/detection zone was collected by two separate short focal length quartz lenses, and transmitted out of the chamber along the axis perpendicular to the laser propagation and probe beam polarisation vectors. In one direction the monochromator (Hilger and Watts Monospek 1000) was used in the same configuration as discussed in Section 2.6, with the fluorescence focusing lens matching the f-number of the resolving optics. Dispersed photons were detected using the 9789QB PMT discussed in Section 2.6.

Fluorescence transmitted in the opposite direction to the monochromator was detected using a gated PMT, as shown in Figure 8-1. The inclusion of a second PMT allowed the recording of total LIF signals which could be used to normalise the dispersed LIF spectra. This was achieved by selectively detecting the normalising signal on a vibronic
band originating from the pumped/collisionally populated excited state of interest, using a wide bandpass interference filter (FWHM 10 nm). The fluorescence emitted on a given vibronic band is proportional to the total excited state population. The intensity of this fluorescence therefore reflects the relative variation of the excited population, which is obviously a function of the number of CH radicals generated, and the efficiency with which they are pumped to the excited state of interest. In this way the effect of fluctuations in photolysis power, excitation power, laser overlap and excitation wavelength on the excited population could be quantified.

As mentioned above, a large nascent fluorescence signal from electronically excited CH is associated with the photolysis process. When viewed through an interference filter, this nascent signal appears many times larger than the probe-induced signal, causing problems in gaining sufficient amplification of the desired signal without saturating the PMT. To address this problem, a gated PMT was employed (EMI 9813QB, gating circuit GB1B), operating on the principle of fast voltage switching of the focusing dynode. Careful timing of the switching pulse reduced the gain of the PMT by ~1000 over the nascent signal, protecting the tube from saturation effects. In this way, the probe-induced signal could be easily observed without fear of damaging the PMT. This problem does not arise when highly resolved fluorescence is observed through the monochromator, where the population of individual rotational levels dictates the ratio of signal sizes. In this case, the nascent and probe signals were typically of comparable size.

8.5 Experimental Control and Signal Processing

Timing control sequences and signal processing were performed in a manner very similar to that described in Section 2.7, with a few modifications reflecting the different experimental arrangement. The CAMAC modules were again controlled through a dedicated central PC (Dell 486/33S) running the custom software 'JO' [1] via a DSP PC004 card, with each module operating in the same mode as previously described. The primary differences between the two configurations arose from the presence of two laser systems, and a second PMT.

A Lecroy 4222 Pulse delay Generator (PDG) was used to fire the flashlamps and Q-switch in each laser system, determining the absolute delay between photolysis and probe pulses. This occupied all four independent channels available from the LeCroy PDG.
The pulse required to switch the gated PMT 'on' was provided by a Farnell Pulse Delay Generator (PG102). The resulting analogue probe signal from the gated PMT was integrated over a 100 ns gate (set just after the end of the probe laser pulse) using a boxcar integrator (SRS Gated Integrator and Boxcar Averager), triggered from the remaining Farnell PDG channel. A second Farnell PDG (triggered synchronously with the first through a cascade configuration) triggered an analogue to digital converter (Hytec ADC 520), used to digitise the boxcar last sample output. If desired, the power of the probe laser could be also be recorded simultaneously with the dispersed fluorescence signal by sampling the analogue output of a pyroelectric joulemeter (Molectron J3-09DW) using one of the three remaining ADC channels.
Figure 8-1: Schematic of the experimental apparatus used in the study of CH.

The configuration shown represents the arrangement employed in the latter stages of the study, with 266 nm photolysis radiation.
Bibliography

Chapter 9
Spectroscopy of the CH $A^2\Delta$-X$^2\Pi$ and $B^2\Sigma^-$-X$^2\Pi$
Systems

9.1 Introduction
As in the study of the SiF radical, the principal aim of this investigation was to determine the factors which dictate how the collisionally produced population is partitioned amongst the various degrees of freedom of the product state. Again, a complete characterisation of the spectroscopic features used in excitation and detection is necessary to quantify the collision process at a state-specific level using LIF.

The recovery of CH fluorescence spectra which reflect nascent excited state distributions is complicated by the relative lifetimes of the two states involved (the $A^2\Delta$ and $B^2\Sigma^-$ states have radiative lifetimes of $\sim540$ ns and $\sim350$ ns [1,2,3,4] respectively). If the pressure of the quenching partner is arranged such that the parent state has a high probability of undergoing a quenching collision over its lifetime, then the chances of collisional modification of the nascent product state distribution over its lifetime are also high. The extent of this relaxation is determined by the competition between vibrationally and rotationally inelastic collisions, which redistribute the population within internal levels, and quenching processes, which remove the molecule from the excited state. This problem may be overcome by selectively gating over short intervals at early times in the fluorescence waveform, when the probability of collisional modification is low. This technique recovers the nascent character of the product state distribution, but at the expense of reduced signal-to-noise ratios in the resulting spectra.

The difficulties associated with obtaining CH spectra which reflect nascent population distributions are, however, offset by the quality of the state-specific information which they yield. The low reduced mass of the CH diatomic hydride results in widely spaced rotational term energies, allowing individual rotational lines to be resolved in excitation
Chapter 9: Spectroscopy of the CH $\text{A}^2\Delta$-$\text{X}^2\Pi$ and $\text{B}^2\Sigma^-$-$\text{X}^2\Pi$ Systems

and emission spectra (in regions where the lines are well separated from congested, head-forming features). This allows the preparation of well defined initial rotational distributions through single line excitation, and, in emission, the unambiguous assignment of population to a specified excited state rotational level.

9.2 Interatomic Potentials and Spectroscopic Constants

The potential energy curves of the electronic states of interest in this study are shown schematically in Figure 9-1. The relevant molecular constants are given in Table 9-1 [5,6]. It can be seen from Figure 9-1 that the equilibrium internuclear separations of the $\text{X}^2\Pi$ ($r_e=1.116$ Å) and $\text{A}^2\Delta$ ($r_e=1.083$ Å) states are only slightly different from each other. The similarity of these two potential energy curves results in a high degree of diagonality in the overlap between the vibrational wavefunctions associated with the $\text{A}^2\Delta$ and $\text{X}^2\Pi$ states. This phenomenon is quantified by the high Franck-Condon Factors observed for $\text{A}^2\Delta$-$\text{X}^2\Pi$ vibrational transitions which involve $\Delta \nu=0$; $q_{\nu'\nu}\approx 0.98$ for $\text{A}^2\Delta$-$\text{X}^2\Pi$ (0,0), (1,1) and (2,2) bands [5,7,8,9,10]. Accompanying this high propensity for the emission of $\text{A}^2\Delta$-$\text{X}^2\Pi$ fluorescence on diagonal bands is a corresponding overlap in the wavelengths at which $\Delta \nu=0$ transitions occur. This spectral congestion takes place at $\sim 430$ nm, and renders the A-X diagonal bands unsuitable for vibrationally or rotationally state-specific analysis.

The $\text{B}^2\Sigma^-$ state equilibrium internuclear separation, $r_e=1.200$ Å, is slightly larger than the ground state $r_e$. $\text{B}^2\Sigma^-$-$\text{X}^2\Pi$ transitions are therefore still dominated by $\Delta \nu=0$ bands, but the off-diagonal Franck-Condon factors for bands with $\Delta \nu\neq 0$ also have appreciable intensity in this case.
<table>
<thead>
<tr>
<th>State</th>
<th>X^2Π</th>
<th>A^2Δ</th>
<th>B^2Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_e^(a)</td>
<td>0</td>
<td>23151.4925</td>
<td>26060.0376</td>
</tr>
<tr>
<td>A_e^(b)</td>
<td>28.0528</td>
<td>-1.1147</td>
<td>—</td>
</tr>
<tr>
<td>ω_e^(c)</td>
<td>2860.7508</td>
<td>2914.0990</td>
<td>2246.4153</td>
</tr>
<tr>
<td>ω_xe^(d)</td>
<td>64.4387</td>
<td>81.4002</td>
<td>225.7</td>
</tr>
<tr>
<td>ω_ye^(e)</td>
<td>0.3634</td>
<td>-3.3881</td>
<td>—</td>
</tr>
<tr>
<td>B_e^(f)</td>
<td>14.4599</td>
<td>14.8997</td>
<td>13.3813</td>
</tr>
<tr>
<td>D_e×10^3^(g)</td>
<td>1.4744</td>
<td>1.5398</td>
<td>1.6313</td>
</tr>
<tr>
<td>α_e^(h)</td>
<td>0.5365</td>
<td>0.6354</td>
<td>1.4823</td>
</tr>
<tr>
<td>H_e×10^7^(i)</td>
<td>1.1922</td>
<td>—</td>
<td>8.94</td>
</tr>
<tr>
<td>γ×10^2^(j)</td>
<td>-2.6223</td>
<td>4.340</td>
<td>-2.953</td>
</tr>
<tr>
<td>p_e^(k)</td>
<td>3.408×10^{-2}</td>
<td>3.1×10^{-7}</td>
<td>—</td>
</tr>
<tr>
<td>q_e^(k)</td>
<td>3.9359×10^{-2}</td>
<td>4.6×10^{-8}</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 9-1: Principal Spectroscopic Constants of the X^2Π, A^2Δ and B^2Σ States of the ^12C^1H Radical.

All values in wavenumbers (cm^{-1}); labels (a)-(h) as defined in Table 3-1; (i) second order centrifugal distortion constant; (j) spin-rotation interaction constant; (k) Λ-doubling constants.
Figure 9-1: Schematic Potential Energy Curves of the $X^2\Pi$, $A^2\Delta$ and $B^2\Sigma^-$ States of the $^{12}$C$^1$H radical.

Diagram reproduced in schematic form from [15].
9.3 Energy Level Structure

To understand the spectroscopy of the \( \Lambda^2 \Delta - \chi^2 \Pi \) and \( \beta^2 \Sigma^- - \chi^2 \Pi \) systems, it is necessary to consider the energy level structure in both the ground and excited electronic states. The relevant angular momentum coupling schemes applicable for \( \chi^2 \Sigma, \chi^2 \Pi \) and \( \chi^2 \Delta \) states have been discussed in Section 3.4 in relation to the SiF radical, and the arguments presented there are equally applicable in the case of CH. Therefore, only the major differences in energy level structure between the CH and SiF radicals, arising from the different strengths of coupling between the various sources of angular momentum, will be discussed here.

9.3.1 The \( \beta^2 \Sigma^- \) State

The \( \beta^2 \Sigma^- \) state is accurately described by Hund’s coupling case (b), with the projection of orbital angular momentum onto the internuclear axis, \( \Lambda \), equalling zero. The negative electronic parity of the state reflects the antisymmetric nature of the electronic wavefunction to reflection through any plane containing the internuclear axis. The negative value of the spin-rotation constant in this case results in a reversal of the ordering of the \( F_1 \) and \( F_2 \) components associated with a given \( N \) as compared to the SiF \( \beta^2 \Sigma^+ \) state.

Each rovibronic level in the \( \beta^2 \Sigma^- \) state is labelled according to the convention for molecules with half-integer \( J \) values[11]:

- levels with total parity \( +(\Lambda) \) are \( e \) levels
- levels with total parity \( -(\Lambda) \) are \( f \) levels

where \( J \) is the quantum number for total angular momentum excluding nuclear spin. The principal advantage of this labelling scheme is that it does not depend on the coupling case exhibited by the molecule, only the total angular momentum and the parity of a particular level.

9.3.2 The \( \chi^2 \Pi \) State

The \( \chi^2 \Pi \) state is again well described by Hund’s coupling case (a) at low \( R \), but the transition to a case (b) description is rapid in the CH radical. This arises through a combination of two factors, both of which may be attributed to the low atomic masses of
C and H. The spin-orbit coupling of $S$ to the internuclear axis by $\Lambda$ is relatively weak, allowing the electron spin to become easily decoupled by the strong magnetic field generated perpendicular to the plane of rotation of the molecule. The low spin-orbit splitting constant in the ground state, $A_e=28.0528$ cm$^{-1}$, is consistent with this argument. The magnetic field increases quickly with $J$ in a low reduced mass diatomic due to the large rotational constant, $B_e$, effectively coupling $S$ to $R$, and conforming to a Hund’s case (b) description.

The large energy associated with rotational motion of the CH radical is also responsible for the appreciable $\Lambda$-doubling present in the ground state, as reflected by the relatively large values of $p_e$ and $q_e$. This splitting is sufficiently large that transitions originating from both $\Lambda$-doublets of a given rotational level may be resolved in laser excitation spectra, giving rise to a total of 12 and 24 branches in the $B^2\Sigma^+ - X^2\Pi$ and $A^2\Delta - X^2\Pi$ systems, respectively. The energy level structure of the $X^2\Pi$ state is shown in Figs 9-2 to 9-5, with the magnitude of the $\Lambda$-doubling shown much enlarged on the scale of the term energies. The individual levels are again labelled within the $elf$ convention.

9.3.3 The $A^2\Delta$ State

The same arguments presented for the $X^2\Pi$ state may be applied when discussing the $A^2\Delta$ state, but differences in the strengths of the various forms of coupling again result in marked contrasts between the two energy level structures. The transition of the $A^2\Delta$ state from Hund’s case (a) $\rightarrow$ (b) occurs at even lower values of $N$, as $S$ is easily decoupled from the internuclear axis to $R$. $\Lambda$-doubling is again observed to be much smaller in the $A^2\Delta$ state, and is not shown on any of the energy level diagrams. The $A^2\Delta$ state is inverted, as shown in Figs 9-4 and 9-5, with the $^2\Delta_{5/2}$ manifold lying below the $^2\Delta_{3/2}$ (within the Hund’s case (a) description).
Figure 9-2: Energy Level Structure and Main Branch ($\Delta N = \Delta J$)

Transitions in the CH $B^2\Sigma^+ - X^2\Pi$ (0,0) System.

$\Lambda$-doubling in the ground state is shown on an enlarged scale.
Figure 9-3: Energy Level Structure and Satellite ($\Delta N \neq \Delta J$) Transitions in the CH $B^2\Sigma^- - X^2\Pi$ (0,0) System.
Figure 9-4: Energy Level Structure and Main Branch (ΔN=ΔJ)

Transitions in the CH $A^2\Delta$-$X^2\Pi$ (0,0) System.

For clarity, A-doubling in the $A^2\Delta$ state has been omitted, and only transitions which terminate in rotational levels with the parity label $e$ have been shown. Another six main branches exist, corresponding to transitions with the $A^2\Delta$ rovibronic $f$ levels as the upper state.
Figure 9-5: Energy Level Structure and Satellite($\Delta N \neq \Delta J$) Transitions in the CH $A^2\Delta$-$X^2\Pi$ (0,0) System.

As in Figure 9-4, only one example of each satellite branch is shown originating from each parity doublet. In practice, another six transitions are observed, which leads to a doubling of all the branches shown here.
The transitions shown on Figs 9-2 to 9-5 are labelled according to the usual convention for $\Delta J$, $\Delta N$ and manifold levels, with the parity of the upper and lower levels also indicated by the $e/f$ subscripts. Due to the low value of the spin-orbit interaction constant in both the $X^2 \Pi$ and $A^2 \Delta$ states, $N$ is a good quantum number for all energy levels. For this reason, A-X and B-X spectroscopic transitions are defined according to the value of the ground state $N$.

### 9.4 Rovibronic Transition Selection Rules

The general selection rules discussed in Section 3.5 for electric dipole-induced transitions in diatomic molecules are still completely valid. However, the rules concerning $\Delta J=0$, $\pm 1$ and $+ \leftrightarrow -$ transitions may now be re-expressed in term of $e$ and $f$ labels as [11]:

- $\Delta J=0, e \leftrightarrow f$
- $\Delta J=\pm 1, e \leftrightarrow e$, and $f \leftrightarrow f$

This labelling scheme also allows the selection rules for perturbations between states to be simply expressed as:

- $\Delta J=0, e \leftrightarrow e, f \leftrightarrow f$

although, as discussed earlier, perturbations between $^2 \Delta$ and $^2 \Sigma^-$ states are forbidden in a first order approximation.

### 9.5 CH Excitation Spectra

The spectroscopy of the CH radical has been the subject of numerous studies in the past, and as a result most of the bands utilised in this study had already been well characterised in terms of rotational line positions and vibronic intensities. This greatly aided the interpretation of spectra, and provided an absolute test as to the accuracy of the calculated transition frequencies used in spectral simulations. However, in addition to corroborating the results of previous spectroscopic investigations, we also report here what we believe to be the first experimental observation of the $A^2 \Delta-X^2 \Pi$ (2,1) band. This was achieved by scanning the probe laser over the weak A-X (2,1) band using reasonably high pulse energies (~15 mJ), and detecting fluorescence on the strong A-X (2,2) band (see Table 9-2 for A-X (2,1) and (2,2) Franck-Condon Factors).
Chapter 9: Spectroscopy of the CH $A^2\Delta$-$X^2\Pi$ and $B^2\Sigma^-$-$X^2\Pi$ Systems

9.5.1 Experimental Technique

The apparatus used in the recording of excitation spectra has previously been described in Chapter 8. CH radical generation was achieved through photolysis of a 17% mixture of CHBr$_3$/Ar at a partial pressure of 40 mTorr in the presence of a larger pressure of quenching gas which had been added upstream from the reaction chamber. The 17% CHBr$_3$/Ar mixture was prepared in advance using CHBr$_3$ (Fisons, Sp. Gr. 2.86-2.90) and Ar (BOC 99.99%), and stored in stainless steel reservoirs (Whitey). The CHBr$_3$ was purified by repeated freeze-pump-thaw cycles prior to use. All other gases involved in this study (CH$_4$, MG 99.5% and CO$_2$, BOC 99.995%) were used without further purification.

The principle behind recording CH excitation spectra is the same as that discussed in Section 3.5.2, but in practice the spectroscopy of the CH radical necessitated some modifications to the technique. CH excitation spectra were recorded with the gated PMT, using interference filters to detect fluorescence emitted from laser-excited states on selected vibronic bands. Two different interference filters were necessary to record the required excitation spectra, centred at 430 nm (Ealing Electro-Optics, FWHM 10 nm) and 390 nm (CVI Laser Corporation, FWHM 10 nm), respectively. These filters isolated fluorescence associated primarily with $A^2\Delta$-$X^2\Pi$ ($A$-$X$) $\Delta v=0$ and $B^2\Sigma^-$-$X^2\Pi$ ($B$-$X$) (0,0) transitions respectively.

The diagonal nature of the A-X and, to a lesser extent, B-X systems required that some spectra be recorded by detecting fluorescence on the same vibronic band used for excitation. The degree of spin-orbit splitting in the ground state does not lead to two well-separated sub-bands associated with the $F_1$ and $F_2$ manifolds, therefore scattered light from the exciting laser is inevitably detected with the resulting fluorescence. The magnitude of this prompt signal was reduced by painting the interior of the reaction chamber black, and placing baffles along the sidearms connecting the laser entrance and exit windows to the main chamber. Selective gating over the fluorescence signal after the scattered probe laser spike ensured a true baseline was recorded.

Table 9-2 and Table 9-3 summarise the positions and Franck-Condon Factors of the A-X and B-X vibronic bands utilised in the course of this study. Inspection of these tables reveals not only the extent to which diagonal transitions are favoured in each electronic band, but also the degree of overlap of vibronic bands both within and between the
### Table 9-2: Band Origins and Franck-Condon Factors for the $A^2\Delta-X^2\Pi$ System.

<table>
<thead>
<tr>
<th>$v'' \setminus v'$</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0: $q_{v',v''}$</td>
<td>0.9913</td>
<td>8.523x10$^{-3}$</td>
<td>—</td>
</tr>
<tr>
<td>Origin</td>
<td>431.5 nm</td>
<td>385.9 nm</td>
<td>—</td>
</tr>
<tr>
<td>1: $q_{v',v''}$</td>
<td>8.010x10$^{-3}$</td>
<td>0.9802</td>
<td>1.036x10$^{-2}$</td>
</tr>
<tr>
<td>Origin</td>
<td>489.2 nm</td>
<td>431.4 nm</td>
<td>388.7 nm</td>
</tr>
<tr>
<td>2: $q_{v',v''}$</td>
<td>—</td>
<td>9.411x10$^{-3}$</td>
<td>0.9802</td>
</tr>
<tr>
<td>Origin</td>
<td>—</td>
<td>486.1 nm</td>
<td>432.5 nm</td>
</tr>
<tr>
<td>3: $q_{v',v''}$</td>
<td>—</td>
<td>—</td>
<td>4.738x10$^{-3}$</td>
</tr>
<tr>
<td>Origin</td>
<td>—</td>
<td>—</td>
<td>484.6 nm</td>
</tr>
</tbody>
</table>

### Table 9-3: Band Origins and Franck-Condon Factors for the $B^2\Sigma^- - X^2\Pi$ System.

<table>
<thead>
<tr>
<th>$v'' \setminus v'$</th>
<th>0</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0: $q_{v',v''}$</td>
<td>0.8768</td>
<td>—</td>
</tr>
<tr>
<td>Origin</td>
<td>388.9 nm</td>
<td>—</td>
</tr>
<tr>
<td>1: $q_{v',v''}$</td>
<td>0.1036</td>
<td>0.4913</td>
</tr>
<tr>
<td>Origin</td>
<td>435.2 nm</td>
<td>403.6 nm</td>
</tr>
<tr>
<td>2: $q_{v',v''}$</td>
<td>1.6723x10$^{-3}$</td>
<td>—</td>
</tr>
<tr>
<td>Origin</td>
<td>490.9 nm</td>
<td>—</td>
</tr>
</tbody>
</table>
A-X and B-X systems. Of particular concern is the overlap of the B-X (0,0) band with both the A-X (1,0) and (2,1) bands. For some experiments, the overlap of the B-X (0,1) and A-X diagonal bands is also a significant problem. The generation of well defined, initial rotational populations in the B^2Σ^-, ν=0 and A^2Δ, ν=1 and 2 vibrational states depends crucially upon clean excitation of distinct rotational lines i.e. no underlying transitions which excite population to another rotational level within the parent electronic state, or, even more undesirable, directly to the product state. To ensure the spectroscopy of these systems was well understood, and to determine suitable lines for initial state preparation, excitation spectra were recorded over the regions of these three bands.

9.5.2 B^2Σ^--X^2Π (0,0) Excitation Spectra

From the Tables 9-2 and 9-3, comparison of the ratio of Franck-Condon Factors for the B-X (0,0) and A-X (1,0) or (2,1) bands reveals the B-X (0,0) transition to be approximately two orders of magnitude stronger than either of the overlapping A-X bands (neglecting the contributions made by the electronic transition moment integrals). In a low laser power limit, very little population would be excited on either of the overlapping A-X bands, and only a very small fraction of the resulting A-X fluorescence would be emitted on the weak, off-diagonal transitions observed through an interference filter centred at 390 nm. Spectra which reflect only the B-X (0,0) rotational transition intensities and ground state populations were therefore recorded by exciting with low probe pulse energies and detecting on the B-X (0,0) vibronic band.

The Q- and P-type branches to the red of the B-X (0,0) band origin form a congested region of the spectrum. For this reason attention was focused on the R-branch, which is well resolved at values of N sufficiently removed from the branch-head. An example of an excitation scan over the B^2Σ^--X^2Π (0,0) R-branch is shown in Figure 9-6, along with the appropriate region of a complete B-X (0,0) band simulation. The agreement between simulated and experimental line positions is seen to be excellent. The intensities of the lines are well reproduced from a 300 K Boltzmann distribution which has been modified to include more population in the higher N levels.
Figure 9-6: CH $B^2\Sigma^- - X^2\Pi$ (0,0) LIF Excitation Spectra.

(a) Experimentally observed excitation spectrum with 40 mTorr 17% CHBr$_3$/Ar, 500 mTorr CO$_2$, and a photolysis-probe delay of 5μs. Fluorescence detected through an interference filter centred at 390 nm, with laser power ~20μJ. Only the main R branch transitions are shown for clarity. (b) Simulation as described in Section 9.7 assuming an excitation laser bandwidth of 0.4 cm$^{-1}$.
Chapter 9: Spectroscopy of the CH $A^2\Delta$-X$^2\Pi$ and $B^2\Sigma^-$-X$^2\Pi$ Systems

As the power of the exciting laser is increased, substantial populations will be promoted on the weak A-X off-diagonal transitions overlapping the B-X (0,0) band, while the corresponding B$^2\Sigma^-$, $v=0$ population does not continue to increase linearly because of saturation. Therefore, before any decision could be made as to a suitable rotational line for preparing a B$^2\Sigma^-$, $v=0$ rotational distribution, the underlying structure of the $A^2\Delta$-X$^2\Pi$ (1,0) and (2,1) bands have to be established.

9.5.3 $A^2\Delta$-X$^2\Pi$ (1,0) and (2,1) Excitation Spectra

Excitation spectra of the A-X (2,1) and (1,0) bands were routinely recorded by increasing the probe pulse energy and observing the $A^2\Delta$ state fluorescence on the strong diagonal bands. Through the window defined by an interference filter centred at 430 nm (FWHM 10 nm), inspection of Tables 9-2 and 9-3 shows that fluorescence emitted on the A-X (2,2) and (1,1) bands is approximately an order of magnitude more intense than that on the B-X (0,1). At increased laser powers it is therefore possible to record excitation spectra of the A-X (2,1) and (1,0) bands whilst discriminating against B-X (0,1) emission.

A relatively high probe power (~15 mJ) excitation spectrum recorded over the B-X (0,0) band region, detecting the resulting A-X (1,1), (2,2) and B-X(0,1) fluorescence at ~430 nm, is shown in Figure 9-7. Simulation of the B-X (0,0) R-branch in Figure 9-7b was achieved by assuming a limiting detection bandwidth of 1.2 cm$^{-1}$ to imitate the effect of saturation line broadening. The A-X lines reflect the excitation laser bandwidth of 0.4 cm$^{-1}$. It is believed that the discrepancies between experimental and simulated line intensities in the A-X (2,1) band reflect the varying degrees of saturation present in the main and satellite branches, and the slow decline of probe laser power at the red end of the dye envelope. As mentioned earlier, we believe this to be the first laboratory observation of the $A^2\Delta$-X$^2\Pi$ (2,1) band, and excellent agreement is found between the experimentally observed line positions, and line positions predicted from both the $A^2\Delta$ and X$^2\Pi$ term energies of Zachwieja [5], and Zare's spectrum simulation program [12].

To ease congestion of the labelling of branches in Figure 9-7, only one example of each A-doubled A-X transition type, and only the main A-X (1,0) branches are shown. The simulations assumed variable ground state rotational populations for each band to reproduce the observed relative intensities, and an increased laser bandwidth for the B-X
Figure 9-7: Overlapping CH $B^2\Sigma^+ - X^2\Pi$ (0,0) and $A^2\Delta - X^2\Pi$ (1,0) and (2,1) LIF Excitation Spectra.

(a) Experimentally observed excitation spectrum with 40 mTorr 17% CHBr$_3$/Ar, 500 mTorr CO$_2$, and a photolysis-probe delay of 5μs. Recorded using an interference filter, centred at 430 nm, with probe laser power ~15mJ. For clarity, not all branches are shown. (b) Simulation assuming variable excitation laser bandwidth as described in Section 9.7. Lines marked with (*) represent B-X (0,0) $^5R_{21}$ lines, not simulated with the correct intensity due to the saturation of the B-X(0,0) main branch transitions.
Chapter 9: Spectroscopy of the CH A^2\Delta-X^2\Pi and B^2\Sigma^- -X^2\Pi Systems

(0,0) band to mimic the effects of saturation broadening.

Figure 9-7 shows that although the B-X (0,0) band region is heavily congested through overlap with the A-X (1,0) and (2,1) bands, some B-X (0,0) R-branch lines remain spectroscopically uncontaminated, and are therefore suitable for state-specific preparation of the B^2\Sigma^-, \(v=0\) level. In the case of the A-X (2,1) band, although only one reasonably well isolated line exists within the B-X (0,0) R-branch, spectroscopically pure lines from this transition are be found to the blue of the B-X (0,0) R-head (see Figure 9-7), allowing the A^2\Delta, \(v=2\) level to be generated in a rotationally-specific manner.

In the case of the A-X (1,0) band, it can be seen from Figure 9-7 that no lines with any significant intensity exist around the B-X (0,0) R-branch region, and the density of lines in the A-X (1,0) Q-branch is too great to allow single-line excitation. However, the A-X (1,0) R-branch was found to lie in an uncongested and spectroscopically isolated area, providing well separated, intense rotational lines as shown in Figure 9-8. The only possible source of contamination in this region comes from the high \(N\) tail of the B-X (0,0) \(^8\)R\(_{21}\)-branch, which is well characterised by the simulation in Figure 9-8b. It is interesting to note the bimodal nature of the ground state rotational population, as suggested in Figure 9-8 by the variation of line intensities as a function of \(N\). This phenomenon is typical of diatomic hydrides, reflecting the decreasing efficiency of rotationally inelastic collisions as the energy gap between neighbouring levels increases with \(N\). The reduced delay between photolysis and probe laser employed in this spectrum, \(\Delta t=3\ \mu s\), limits the number of collisions experienced by molecules in the ground state prior to excitation. This allows the rotational population to retain some memory of the distributions initially present in the states formed during the photolysis pulse. The population distribution in the simulation was iteratively adjusted from a 300 K Boltzmann rotational distribution until a 'best fit' with the experimental spectrum was achieved.
Figure 9-8: CH $A^2\Delta$-$X^2\Pi$ (1,0) LIF Excitation Spectrum.

a) Experimentally observed excitation spectrum with 40 mTorr 17% CHBr$_3$/Ar, 500 mTorr CO$_2$, and a photolysis-probe delay of 3\(\mu\)s. Recorded using an interference filter centred at 430 nm, with laser power \(\sim\)15mJ. All relevant branch types are shown. (b) Simulation as described in Section 9.7 assuming an excitation laser bandwidth of 0.4 cm$^{-1}$. 
Chapter 9: Spectroscopy of the CH A^2\Delta-X^2\Pi and B^2\Sigma^-X^2\Pi Systems

9.6 Electronic Configurations

The predominant electronic configurations of the of the X^2\Pi, A^2\Delta and B^2\Sigma^- states of CH have been established from ab initio studies\cite{13,14,15} to be:

\[ X^2\Pi: 1\sigma^22\sigma^23\sigma^21\pi^1 \]
\[ A^2\Delta: 1\sigma^22\sigma^23\sigma^1(1\pi^2, 1\Delta) \]
\[ B^2\Sigma^-: 1\sigma^22\sigma^23\sigma^1(1\pi^2, 3\Sigma^-) \]

These valence configurations describe the states well at equilibrium internuclear separations, but a formal treatment of the X^2\Pi state at large \( r \) requires the inclusion of extra configurations containing a 4\sigma orbital, to ensure proper dissociation to the correct separated atom limit \cite{13}.

Inspection of Figure 9-1 reveals the presence of a barrier in the potential energy curve of the B^2\Sigma^- state. Historically, this was attributed to an avoided crossing of the B^2\Sigma^- state with a higher-lying ion-pair state of the same symmetry \cite{13}. However, the origin of this maximum is now thought to arise from the gradual outweighing of a repulsive contribution to the potential energy from the electron exchange integral (dominant at long range), by the bonding character acquired by the 3\sigma orbital as the internuclear distance decreases. Operationally, predissociation by tunnelling through the barrier causes a drop in the intensity of emission from the B^2\Sigma^- \( N=15 \) rotational level in \( v=0 \), and the \( N=6 \) level in \( v=1 \), with no emission at all above or at \( v=0, N=16 \) and \( v=1, N=7 \), respectively \cite{16,17}.

9.7 Simulation Technique

The simulation of CH excitation and dispersed emission spectra was performed using a process similar to that described in Section 3.7, with only slight modifications required to allow for the presence of \( \Lambda \)-doubling. The inclusion of \( \Lambda \)-doubling in the X^2\Pi and A^2\Delta states doubles the number of branches produced by CH A-X simulations compared to the SiF C^2\Delta-X^2\Pi case, effectively replacing each A^2\Delta and X^2\Pi rovibronic level with a pair of \( \Lambda \)-doublets. Operationally, it was decided to assign equal occupancies to each A^2\Delta \( \Lambda \)-doubled level associated with a given \( J \), whilst still allowing the distributions within each manifold to be independently varied. This approximation is justified as the \( \Lambda \)-
doubled branch-types are not resolved by the monochromator in emission, although they may be seen separated in excitation spectra.

The simulation program responsible for calculating transition intensities and line positions uses the Unique Perturber Approximation (UPA) Hamiltonian of Zare [12], while the molecular constants reported in Table 9-1 were obtained by analysing spectra according to the more sophisticated molecular Hamiltonian of Brown [18]. Though the difference between the matrix elements of the two Hamiltonians is not great, corrections are required to convert the tabulated constants into the necessary form. This was achieved using a set of equations derived by Brown, relating the two sets of matrix elements [19].

The ground state rotational populations in each simulation were routinely determined by iteratively adjusting a 300 K Boltzmann rotational distribution until good agreement with the experimental line intensities was achieved.
Bibliography

Chapter 10

Collision-Induced CH $A^2\Delta \leftrightarrow B^2\Sigma^-$ Vibrational Transfer

10.1 Introduction

Analysis of the time-resolved, dispersed fluorescence waveforms arising from directly laser-excited or collisionally-populated excited states of the CH radical can, in principle, distinguish the populations in three of the available degrees of freedom: rotational, vibrational and electronic motion. In this chapter, the results of a preliminary investigation into the vibrational propensities of electronically inelastic $A^2\Delta \cdot B^2\Sigma^-$ collision-induced transfer in the CH radical are presented.

The excited states of CH accessible within the wavelength envelope of the selected laser dye include the $B^2\Sigma^-, \nu=0$, $A^2\Delta, \nu=1$, and $A^2\Delta, \nu=2$ levels (as discussed in Section 9.5). However, this preliminary study concentrated on initial excitation of the $B^2\Sigma^-, \nu=0$, and $A^2\Delta, \nu=1$ levels only. As can be seen from Figure 10-1, this effectively removes the $A^2\Delta, \nu=2$ and $B^2\Sigma^-, \nu=1$ levels from any collision-induced coupling schemes, as they lie too high in energy relative to the pumped states. The collisionally-accessible levels in this investigation are therefore limited to $A^2\Delta, \nu=0$ and $\nu=1$ (referred to as A0 and A1), $B^2\Sigma^-, \nu=0$ (referred to as B0), and the $X^2\Pi$ ground state. The feasible energy transfer processes within this system include $A1 \rightarrow B0$ transfer, $B0 \rightarrow A1$ transfer, $B0 \rightarrow A0$ transfer, $A1 \rightarrow A0$ relaxation, and the quenching of any of the excited levels to unobserved (dark) states. The remainder of this chapter is concerned with the determination of the rates of these various processes.
Figure 10-1: Vibronic Energy Level Structure of the CH $X^2\Pi$, $A^2\Delta$ and $B^2\Sigma^-$ States.

The term energy of the lowest $J$ level in the rotational manifold is shown for each vibronic state. The energies are those of Zachwieja [1].
10.2 Preliminary Work

Previous observations of collision-induced CH $A^2\Delta \rightarrow B^2\Sigma^-$ transfer had all been made in flame studies [2,3], where the identity of the collision partner(s) involved in specific quenching channels is not well-defined. Therefore, the first objective of this investigation was to identify a quenching partner which induced $A^2\Delta - B^2\Sigma^-$ electronically inelastic transfer, so that the process could be studied in low pressure, controlled collision conditions, in an environment where the identity of the collision partner was known.

$B^2\Sigma^- \rightarrow A^2\Delta$ transfer was established in preliminary studies by pumping the $B^2\Sigma^-$, $\nu=0$ level, and using a system of interference filters to observe directly returning $B$-$X$ and collision-induced $A$-$X$ fluorescence. In this way, the relative effectiveness of quenching partners in collisionally transferring population to the $A^2\Delta$ state could be determined. Of the potential partners investigated, CHBr$_3$, Ar, CH$_4$ and CO$_2$ were all observed to induce $B^2\Sigma^- \rightarrow A^2\Delta$ transfer, with varying degrees of efficiency. This represents, so far as we are aware, the first study in which collisional coupling of the CH $A^2\Delta$-$B^2\Sigma^-$ excited states has been observed with well-defined, single quencher species. From these results, it was decided to concentrate on the collisional behaviour of the CH+CO$_2$ molecule-collider system for the remainder of the detailed, quantitative work (CO$_2$ exhibited a favourable transfer cross-section, coupled with a low rate of reaction with ground state CH [4]).

10.3 A-X and B-X Waveform Analysis

Initial investigations of electronically inelastic transfer between the $A^2\Delta$ and $B^2\Sigma^-$ states involved state-specific excitation of B0, followed by a novel analysis of the time-resolved emission waveforms from both the directly excited B0, and collisionally populated $A^2\Delta$ levels. Fluorescence from the parent and product states was detected on the diagonal B-$X$ (0,0) and A-$X$ $\Delta \nu=0$ bands using a combination of interference filters, centred at 390 and 430 nm respectively, to resolve the two transition types. As discussed in Section 9.5.1, this level of resolution does not discriminate between A1 and A0 fluorescence due to the overlap of the A-$X$ (1,1) and (0,0) bands. The resulting fluorescence waveforms allow the time-dependence of the excited state populations to be observed as a function of quencher pressure, revealing information on the total rates of removal from both states.
Figure 10-2 shows typical examples of B-X (0,0) and A-X Δν=0 waveforms, obtained by the method described above. In practice, the recording of A-X waveforms was made more involved through a chance overlap of the A-X Δν=0 emission with directly returning B-X (0,1) fluorescence at 435 nm (see Table 9-3), unresolved within the bandwidth of the interference filter. In an attempt to recover the component of the fluorescence corresponding exclusively to A-X emission, an appropriately scaled B-X (0,0) waveform, recorded at the same pressure, was subtracted from the total signal.

10.3.1 Kinetic Modelling of Collision-Induced B$^2\Sigma^-$→A$^2\Delta$ Transfer

In modelling the time dependence of the A$^2\Delta$ and B$^2\Sigma^-$ state populations, due to the unresolved nature of the A-X Δν=0 fluorescence it was assumed that only three levels were involved in the collisional coupling scheme. This simplified representation of the real system is illustrated in Figure 10-3. In this kinetic approximation, the rate at which the A and B state populations are removed to unobserved states is given by $k_A^Q P^Q + \tau_A^{-1}$ and $k_B^Q P^Q + \tau_B^{-1}$ respectively, where $k^Q$ are the rate constants for quenching to dark states, $P^Q$ is the quencher pressure, and $\tau^{-1}$ are the inverse radiative lifetimes. Electronically inelastic transfer between the A and B states is assumed to be a reversible process, with rates $k_{BA}^Q P^Q$ and $k_{AB}^Q P^Q$.

Within this simplified kinetic analysis, the total quenching rate, $k^{TQ}$, (the sum of all processes which remove population from a given state) is defined for the A and B states in Eqns 10-1 and 10-2 respectively.

$$k_A^{TQ} = (k_{AB} + k_A^Q) P^Q + \tau_A^{-1}$$  
Equation 10-1

$$k_B^{TQ} = (k_{BA} + k_B^Q) P^Q + \tau_B^{-1}$$  
Equation 10-2
Figure 10-2: CH $B^2\Sigma^-\cdot X^2\Pi (0,0)$ and $A^2\Delta-\cdot X^2\Pi \Delta \nu=0$ Waveforms.

(a) directly returning B-X (0,0) waveform and single exponential fit; (b) collision-induced A-X $\Delta \nu=0$ waveform and difference of two exponentials fit (Eqn 10-4 of text). Experimental signals are solid lines. The fits are shown as dashed lines. Experimental conditions were 40 mTorr 17% CHBr$_3$/Ar and 800 mTorr CO$_2$. Initial B state pumping performed on the B-X (0,0) $R_1(3)$ line.
Figure 10-3: Schematic of the Three-Level Kinetic Scheme.

All of the processes assumed to be contributing to the net loss and gain of the A and B state populations are shown.
The rates at which the A and B state populations, $N_A$ and $N_B$, change with time may be expressed by a pair of differential equations involving the various loss and repopulation processes indicated in Figure 10-3. The solution of these equations yields time dependent expressions for the excited state populations, $N_A(t)$ and $N_B(t)$. Assuming initial conditions of $N_A(0)=0$ and $N_B(0)=N_B^0$, corresponding to initial excitation of the B state, these may be written as:

$$N_B(t) = \frac{N_B^0}{\lambda_1 - \lambda_2} \left( (k_B TQ + \lambda_1) e^{\lambda_1 t} - (k_B TQ + \lambda_2) e^{\lambda_2 t} \right)$$

Equation 10-3

$$N_A(t) = \frac{N_B^0 k_{BA} P^Q}{\lambda_1 - \lambda_2} \left( e^{\lambda_1 t} - e^{\lambda_2 t} \right)$$

Equation 10-4

The time dependence of the A and B state populations is governed by the parameters $\lambda_1$ and $\lambda_2$, which are defined as:

$$\lambda_1 = \frac{1}{2} \left[ -(k_B TQ + k_A TQ) + \sqrt{\left((k_B TQ - k_A TQ)^2 + 4k_{AB} k_{BA} (P^Q)^2\right)} \right]$$

Equation 10-5

$$\lambda_2 = \frac{1}{2} \left[ -(k_B TQ + k_A TQ) - \sqrt{\left((k_B TQ - k_A TQ)^2 + 4k_{AB} k_{BA} (P^Q)^2\right)} \right]$$

Equation 10-6

Inspection of Equation 10-4 reveals that the variation of the A state population is characterised by the familiar exponential rise and fall associated with a level where there is competition between the rate of population and the rate of removal. The rate at which the population builds up is determined by the larger of the exponents in Equation 10-4 (i.e. $\lambda_1$ or $\lambda_2$), and the decay by the smaller.

At first sight, the behaviour of the B state population appears qualitatively similar to that of the A state, with the time dependent part of Equation 10-3 involving a difference of
two exponentials. However, evaluation of Eqns 10-5 and 10-6 reveals that the coefficients of both exponentials in Equation 10-3 are constrained to be positive. The B state population therefore decays in a bi-exponential manner from an initial value of \( N_B^0 \), with the contributions of the two decay constants \( \lambda_1 \) and \( \lambda_2 \) to the observed time dependence determined by the magnitudes of \( (k_B^{\text{TQ}} + \lambda_2) \) and \( (k_B^{\text{TQ}} + \lambda_1) \), respectively.

It is therefore possible, in principle, to obtain the values of \( \lambda_1 \) and \( \lambda_2 \), at a given pressure of quencher, by fitting the appropriate sum or difference of exponentials function to the B-X and A-X waveforms which arise from exciting the B state. Whilst neither exponent may be directly equated with the total quenching rates from A or B, evaluation of Eqns 10-5 and 10-6 reveal that \( \lambda_2 \) and \( \lambda_1 \) asymptotically approach \( -k_B^{\text{TQ}} \) and \( -k_A^{\text{TQ}} \), respectively, in the limit that \( \text{P}^0 \rightarrow 0 \), and that the true values of \( k_A^{\text{TQ}} \) and \( k_B^{\text{TQ}} \) are bounded by \( \lambda_1 \) and \( \lambda_2 \) at all quencher pressures. Determination of \( \lambda_1 \) and \( \lambda_2 \) at sufficiently low quencher densities should therefore provide reasonable estimates of the A and B state total removal rates. However, as a sufficiently high \( \text{P}^0 \) is required to give a measurable extent of collisional removal, it becomes increasingly difficult to accurately measure \( \lambda_1 \) and \( \lambda_2 \) as \( \text{P}^0 \rightarrow 0 \).

### 10.3.2 Determination of \( \lambda_1 \) and \( \lambda_2 \)

In practice, several factors contributed to complicate the determination of \( \lambda_1 \) and \( \lambda_2 \). In the case of the B-X waveform analysis, the difference between the two decay constants present in the bi-exponential fluorescence profile was not sufficient to allow a unique determination of either. This is, to some extent, a consequence of the accidentally similar radiative rates of the A and B states. The best that could be achieved was a single exponential fit to the data, which provided an unambiguous decay constant corresponding to some weighted average of \( \lambda_1 \) and \( \lambda_2 \). An example of a fit to a typical B-X waveform is shown in Figure 10-2a. For the A-X emission, the scatter in the values of \( \lambda_1 \) and \( \lambda_2 \) determined at different pressures from fitting a difference of exponentials function (Equation 10-4) to the recovered A-X waveforms was found to be unacceptably large. This was found to be especially true at the lower quencher pressures, where the correspondence of \( \lambda_1 \) and \( \lambda_2 \) with \( k_A^{\text{TQ}} \) and \( k_B^{\text{TQ}} \) was expected to be most valid. This method of determination was therefore abandoned.
The decay rates obtained by fitting approximate single exponential decays to the, technically, bi-exponential B-X waveforms are plotted as a function of quencher pressure in Figure 10-4. As mentioned above, these numbers will, at best, represent a weighted average of the $\lambda_1$ and $\lambda_2$ values contributing to the time dependence of the B-X decay profile, and as such will be bounded by $\lambda_1$ and $\lambda_2$ at all pressures. A best-fit line through the points predicts a zero-pressure $B^2\Sigma^-$ state radiative lifetime of $352 \pm 7$ ns, and the slope gives a quenching rate constant of $k_B^{TQ} = 1.3 \pm 0.4 \times 10^{-11}$ molecule$^{-1}$cm$^3$ s$^{-1}$. Although a linear fit to the data is only truly justified in the limit of low quencher pressure, this apparent value of the quenching rate constant will prove useful for comparison with predictions of the observed decay rate made in Section 10.6.
Figure 10-4: Observed B^2Σ, ν=0 State Quenching Rates.

Observed B0 state removal rates as approximated by single exponential fits to the bi-exponential B-X (0,0) waveforms.
10.4 Dispersed B-X and A-X Emission

Having been unable to determine the total removal rates of the \( A^2\Delta \) and \( B^2\Sigma^- \) states from a kinetic analysis of the excited state waveforms, it was decided to investigate the rates of collisional transfer in the system through the variation of the excited state populations with quencher pressure. Dispersing the fluorescence emitted from the directly excited and collisionally-populated \( A^2\Delta \) and \( B^2\Sigma^- \) states reveals information on the relative populations of the \( B_0, A_1 \) and \( A_0 \) vibronic levels. The ratios of the populations of these levels is determined by competition between the total rate of formation and the total rate of removal for each state. The rate constants for the various collision-induced transfer processes coupling the vibronic levels may therefore be evaluated by determining the integrated signal ratios from these levels at various quencher pressures.

10.4.1 Determination of the Relative \( A^2\Delta \) and \( B^2\Sigma^- \) State Populations

The ratio of the A-X and B-X fluorescence intensities is, to a first approximation, determined by the fraction of the total population which undergoes a collision-induced change in electronic character from \( A^2\Delta \rightarrow B^2\Sigma^- \) or \( B^2\Sigma^- \rightarrow A^2\Delta \), depending on which is the initially pumped state. In this experiment, the ratio of the integrated fluorescence intensities emitted on the B-X \( (0,0) \) and A-X \( \Delta v=0 \) bands was determined at two distinct pressures of quencher, for initial excitation of both \( B_0 \) and \( A_1 \) levels. Within the three-level approximation discussed in Section 10.3.1, the ratio of A and B state signals is quantified by the magnitudes of \( k_{AB}P_Q \) and \( k_{BA}P_Q \) relative to \( k_A^{TQ} \) and \( k_B^{TQ} \) respectively. Therefore, by determining the relative signals from the A and B states, limiting values of \( k_{BA} \) and \( k_{AB} \) may be assessed.

The relative signals from the A and B states were determined by integrating the dispersed fluorescence emitted on the B-X \( (0,0) \) and A-X \( \Delta v=0 \) bands at 390 and 430 nm, respectively. This was performed for initial preparation of both A and B states, at total pressures of 960 and 2860 mTorr \( \text{CO}_2 \) (including 40 mTorr 17% \( \text{CHBr}_3/\text{Ar} \)). Specifically, the \( A^2\Delta \) state was excited on the A-X \( (1,0) \) \( R_2(1) \) and \( R_2(3) \) lines (see Figure 9-8), and the \( B^2\Sigma^- \) state on the B-X \( (0,0) \) \( R_1(3) \) and \( R_1(5) \) lines (see Figure 9-6).

To allow a meaningful comparison of the integrated fluorescence intensities from the A and B states, the A-X \( \Delta v=0 \) and B-X \( (0,0) \) spectra were recorded with an identical PMT voltage. This leaves the frequency response of the fluorescence transmission and
detection components unknown, but the overall system efficiency is unlikely to vary substantially over the relatively short wavelength range involved between the diagonal B-X and A-X bands. The effects of fluctuations in the experimental conditions were minimised by determining the excited state population ratios from 'short' spectra alternately recorded over the Q-branch features of each band system. By scaling spectra previously recorded over the whole of the relevant band to these 'short' spectra, the effects of long term drifts in the experimental conditions could be largely overcome. Normalisation signals were recorded in all cases using directly returning, undispersed fluorescence from the pumped state, isolated with the appropriate interference filter and recorded with the gated PMT, as described in Section 8.4.

The results of the experiments for initial excitation of $A^2\Delta$, $v=1$ and $B^3\Sigma$, $v=0$ are shown in Figure 10-5 and Figure 10-6 respectively. In each case, the directly returning and collision-induced spectra are shown normalised to the most intense feature, allowing the effects of pressure and parent state rotational level on the transferred population to be seen. Regardless of the initial state populated, the relative size of the collision-induced signal can be seen to increase significantly with the density of quencher, suggesting that radiative loss from both states is still a dominant removal process in this pressure regime. Perhaps more interestingly, however, comparison of the two sets of experimental results for A and B state pumping clearly show that $A^2\Delta \rightarrow B^3\Sigma$ collision-induced transfer is more efficient in promoting B state fluorescence than the reverse $B^3\Sigma \rightarrow A^2\Delta$ process is in promoting A state fluorescence.

In order to quantify the results from Figure 10-5 and Figure 10-6 in terms of ratios of integrated signals, it is first necessary to correct the A-X spectra for the presence of the overlapping B-X (0,1) band (discussed in Section 10.3.2). This feature may be seen most clearly in Figure 10-6 in the A-X $\Delta v=0$ P-branch region. Operationally, a fixed multiple of the total B-X (0,0) signal was subtracted from the sum of the integrated A-X $(v,v)$ and B-X (0,1) fluorescence intensities. The relevant B-X (0,0) scaling factor is determined by the ratio of B-X (0,0)/(0,0) Einstein emission coefficients, measured by Crosley to be $0.031\pm0.005$ [5].

To correctly recover the integrated emission intensity ratios from the B-X (0,0) and A-X $\Delta v=0$ spectra, the integrated fluorescence emitted on each band should be weighted by the appropriate transition probability. Unfortunately, reliable absolute quantities for
these numbers could not be found in the literature. However, due to the diagonal nature of both the B-X and A-X band systems, this overall scaling factor should not affect the ratios obtained by a large degree, and is therefore ignored in this preliminary analysis. The resulting excited state integrated signal ratios are presented in Table 10-1.
Figure 10-5: CH B-X(0,0) and A-X \Delta v=0 Dispersed Fluorescence Spectra Following A^2\Delta, v=1 Initial Excitation.

Experimental conditions: (a)(i) and (a)(ii) 960 mTorr CO_2; (b)(i) and (b)(ii) 2860 mTorr CO_2. The A^2\Delta state was excited on the A-X (1,0) R_2(1) line for spectra (a)(i) and (b)(i), and R_2(3) for (a)(ii) and (b)(ii). Monochromator bandwidth=0.82 nm in each case. Excitation laser power \sim 15 mJ.
Figure 10-6: CH B-X(0,0) and A-X Δν=0 Dispersed Fluorescence Spectra Following B^2Σ, ν=0 Initial Excitation.

Experimental conditions: (a)(i) and (a)(ii) 960 mTorr CO₂; (b)(i) and (b)(ii) 2860 mTorr CO₂. The B^2Σ state was excited on the B-X (0,0) R₁(3) line for spectra (a)(i) and (b)(i), and R₁(5) for (a)(ii) and (b)(ii). Monochromator bandwidth=0.82 nm in each case. Excitation laser power ~ 4 mJ.
10.4.2 Determination of the Relative A0 and A1 Integrated Emission Intensities

The variation of the total $A^2\Delta$ and $B^2\Sigma^-$ state signals with pressure allows the rate constants for total $A \leftrightarrow B$ transfer to be assessed. However, at a greater level of detail there will be, in principle, some branching ratio for transfer out of $B0$ into both $A1$ and $A0$. Further complications arise because of the possibility of pure vibrational relaxation within the $A^2\Delta$ state from $A1$ to $A0$. The rate constants for these processes may be assessed by obtaining integrated emission intensities from the $A0$, $A1$ and $B0$ levels at known pressures of quencher, when either of the $A1$ or $B0$ levels is initially populated. The four-level kinetic coupling scheme appropriate to this level of resolution is shown in Figure 10-7.

As discussed in Section 9.2, the degree of overlap between the diagonal $A^2\Delta-X^2\Pi (0,0)$ and $(1,1)$ bands is too exact to allow the $A0$ and $A1$ fluorescence intensities to be resolved. For this reason, the A-X $(0,1)$ and $(1,2)$ off-diagonal bands, centred at 489.2 nm and 486.1 nm respectively, were used to obtain the integrated fluorescence ratios. The Einstein emission coefficients of these off-diagonal bands have been measured by Crosley to be two orders of magnitude smaller than the corresponding diagonal transitions [6]. However, these off-diagonal bands are sufficiently separated to allow the fluorescence from the $A1$ and $A0$ levels to be resolved, justifying the additional experimental effort involved. Serendipitously, the B-X $(0,2)$ band origin lies at 490.9 nm, allowing the relative variations in fluorescence intensity from all these collisionally-coupled excited vibronic levels to be observed in a single spectrum over a relatively short wavelength range.

The vibrational relaxation rate constant for the collision-induced $A1 \rightarrow A0$ process, $k_{A1A0}$, was determined by assessing the relative populations of the $A1$ and $A0$ levels following excitation of the $A1$ state. This experiment was performed at three distinct quencher pressures (960 mTorr, 1820 mTorr and 2800 mTorr) for initial pumping of two $A1$ rotational levels. The resulting excited state emission was integrated over a total gate length of 1.5 $\mu$s, which comfortably exceeded the observed fluorescence lifetimes. The $A1$ state was initially prepared by pumping the A-X $(1,0)$ $R2(1)$ and $R2(3)$ lines, as in Section 10.4.1. The combined off-diagonal A-X and B-X spectra
Figure 10-7: Schematic Diagram of the Four-Level Kinetic Scheme.

All processes assumed to remove population from the relevant $A^2\Delta$ and $B^2\Sigma^-$ vibronic levels are shown.
Figure 10-8: CH A-X and B-X Spectra Resulting from Vibrationally and Electronically Inelastic Transfer from $A^2\Delta$, $\nu=1$ Induced by Collisions with CO$_2$.

Total pressures (inclusive of 40 mTorr 17% CHBr$_3$/Ar): (a) 960 mTorr; (b) 1820 mTorr; (c) 2800 mTorr. Experimental spectra shown as bold solid lines, simulations of individual bands as faint solid lines, and overall simulations as dotted lines. The position of the Q-branch origin of each simulated band is indicated with an arrow. Experimental spectra recorded (and simulations generated) with resolution 1.64 nm.
resulting from A-X (1,0) R_r(1) excitation are shown in Figure 10-8 normalised to the height of the most intense feature. The band simulations in Figure 10-8 assumed reasonably broad rotational distributions in the collisionally populated vibronic levels, with the pumped state distribution remaining peaked about the initially excited level (initial and product state rotational distributions are discussed fully in the next chapter).

It is immediately obvious from the relative heights of the three main features in Figure 10-8 that the A-X (0,1) and B-X (0,2) bands 'grow in' relative to the A-X (1,2) as the total pressure is increased. This reflects the increasing contribution made to the total removal of the A1 state by collisional quenching to A0 and B0. The populations of each vibronic level are proportional to the integrated intensity of the relevant band simulation. The ratio of the A-X (1,2) to A-X (0,1) transition probabilities may be estimated from Crosley to be 1.6±0.4 [6], allowing the relative integrated emission intensities from the A1 and A0 levels to be determined. The A0 to A1 signal ratios resulting from initial excitation of both A-X (1,0) rotational lines are presented in Figure 10-10a.

The relative rate constants for the collision-induced B0→A0 and B0→A1 processes, \( k_{B0A0} \) and \( k_{B0A1} \), may be determined by assessing the ratio of collisionally transferred A0 and A1 populations following direct B0 excitation. This ratio was determined at three distinct quencher pressures (960 mTorr, 1820 mTorr and 2800 mTorr) from excitation of the B0 state on the \( R_1(3) \) line (see Figure 9-6), with the direct and collision-induced fluorescence from the A0, A1 and B0 levels integrated over a total gate length of 1.5 μs. The A-X (1,2), A-X (0,1) and B-X (0,2) spectra resulting from B-X (0,0) \( R_1(3) \) excitation are shown normalised to the height of the most intense feature in Figure 10-9. As in the case of \( A^2\Delta \) pumping, the product state bands are simulated assuming relatively broad rotational distributions, while the initial state distribution is constrained to remain peaked about the pumped rotational level.

As in Figure 10-8, the relative heights of the three main features in Figure 10-9 reveal the variation of the A-X (1,2), A-X (0,1) and B-X (0,2) bands. Unsurprisingly, the A-X (1,2) and (0,1) bands are seen to gain at the expense of the B-X (0,2) as the quencher density increases, and more molecules are collisionally removed from the B0 state. The ratio of the A-X (0,1) to (1,2) band increases with quencher density, reflecting the growing contribution made to the A1 total removal rate by A1→A0 collisional relaxation as the pressure is increased. The relative A0 and A1 signals arising from B0 state
excitation were determined as described above, and the resulting integrated emission ratios are presented Figure 10-10b. A crude 'by eye' extrapolation of the data to the $P^0 \rightarrow 0$ limit suggests that even here, the $A0:A1$ ratio is significantly different from zero, implying that some of the $A0$ population arises from direct $B0 \rightarrow A0$ transfer. This represents, so far as we are aware, the first direct observation of collision-induced $B0 \rightarrow A0$ transfer.
Figure 10-9: CH A-X and B-X Spectra Resulting from Electronically Inelastic Transfer from B^2Σ^+, ν=0 Induced by Collisions with CO₂. Total pressures (inclusive of 40 mTorr 17% CHBr₃/Ar): (a) 960 mTorr; (b) 1820 mTorr; (c) 2800 mTorr. Experimental spectra shown as bold solid lines, simulations of individual bands as faint solid lines, and overall simulations as dotted lines. The position of the Q-branch origin of each simulated band is marked with an arrow. Experimental spectra recorded (and simulations generated) with resolution 1.64 nm.
Chapter 10: Collision-Induced $\text{CH} \ A^2\Delta \leftrightarrow \text{B}^2\Sigma^-$ Vibrational Transfer

Figure 10-10: Ratio of CH A0:A1 Integrated Emission Signals Induced by Collisions of A1 and B0 with CO$_2$.

(a) Initial pumping of A1 state: ($\rightarrow \triangle$) $R_2(3)$ line; ($\rightarrow \bullet$) $R_2(1)$ line.

(b) Initial pumping of B0: ($\rightarrow \blacksquare$) $R_1(3)$ line.
10.5 Interpretation of Dispersed Fluorescence Spectra

10.5.1 Determination of $k_{AB}$ and $k_{BA}$ Within the Three-Level System

Returning to the results presented in Table 10-1, the ratios of the $A^2\Delta$ and $B^2\Sigma^-$ state integrated signals are determined by the competition between electronically inelastic transfer and total quenching in each state. An attempt to quantify the rates of these processes was made by modelling the observed population ratios within the three-level coupling scheme, discussed in Section 10.3. To this end, a Maple [7] worksheet was constructed to analytically integrate the differential equations describing the A and B state populations, assuming all of the populating and removal processes shown in Figure 10-3 to be in operation. For the three-level system, these equations take the form:

$$\frac{dN_B(t)}{dt} = -N_B(t)k_B^{eq} + N_A(t)k_{BA}P$$

Equation 10-7

$$\frac{dN_A(t)}{dt} = -N_A(t)k_A^{eq} + N_B(t)k_{AB}P$$

Equation 10-8

The integrated signal intensity from a given level $Y$ may be evaluated from:

$$Y \text{ state integrated signal} \propto \int_0^\infty \tau_f^{-1}N_y(t)dt$$

Equation 10-9

By integrating over the whole fluorescence waveforms, the effect of varying the total quenching and electronic transfer rates on the ratio of excited state populations could be observed, and a set of values consistent with the experimental observations iteratively worked towards.

Operationally, to define a limiting value for $k_{BA}$, it was assumed that every quenching collision suffered by the B state resulted in the transfer of a molecule to the A state i.e. $k_B^{eq}=0$. In the case of the A state, previous work by Stuhl on the quenching of $A^2\Delta$, $\nu=0$ had determined the quenching rate constant to be $0.04\times10^{11}\text{ molecules}^{-1}\text{cm}^3\text{s}^{-1}$ [8]. This figure is unlikely to involve removal to $B_0$, because of the large endothermic energy gap.
involved, and so corresponds to the rate of A0 quenching to dark states. There is no intuitive reason to believe that the rate constant for the removal of A1 to unobserved states will differ significantly from this value, so, within the three-level approximation, the quenching rate constant of A to dark states, $k_A^0$, was assumed to be $0.04 \times 10^{-11}$ molecule$^{-1}$cm$^3$s$^{-1}$. If the true value is no bigger than this, the value of $k_{AB}$ obtained from the analysis will represent an upper limit to the real figure. The radiative rates of the two states were taken as $\tau_A^{-1} = 1.85 \times 10^6$ s$^{-1}$ and $\tau_B^{-1} = 3.07 \times 10^6$ s$^{-1}$ [9,10,11,12].

The results of a preliminary analysis suggest that the experimental results are best reproduced by setting $k_{AB}$ to $2.5 \times 10^{-11}$ molecule$^{-1}$cm$^3$s$^{-1}$, and $k_{BA}$ to $2.2 \times 10^{-11}$ molecule$^{-1}$cm$^3$s$^{-1}$. The excited state integrated signal ratios resulting from these transfer rate constants are given in Table 10-1.

Comparison of the calculated and experimentally observed ratios of excited state populations, presented in Table 10-1 show that the iteratively determined rate constants for electronic transfer reproduce the observed behaviour of the collisionally coupled A$\leftrightarrow$B system reasonably well. However, this analysis has neglected the existence of a second A$^2\Delta$ state level (A0) which effectively acts as a sink in the kinetic scheme, removing molecules from the reversible A1$\leftrightarrow$B0 coupling. The fact that the fluorescence emitted from this A0 level is indistinguishable from that emitted from A1 in this experiment suggests the value of $k_{BA}$ will be overestimated in this model (compare with the estimate of $k_B^{TQ} = 1.3 \pm 0.4 \times 10^{-11}$ molecule$^{-1}$cm$^3$s$^{-1}$ made from the B-X (0,0) fluorescence waveform analysis).
Chapter 10: Collision-Induced CH $A^2\Delta \leftrightarrow B^2\Sigma^-$ Vibrational Transfer

Table 10-1: Experimentally Observed and Calculated Relative Parent and Product State Integrated Signals for Initial Excitation of $A^2\Delta$ and $B^2\Sigma^-$ States.

(a) Total pressure of CO$_2$ (including 40 mTorr 17% CHBr$_3$/Ar).
(b) Electronic state initially excited.
(c) Rotational line pumped to prepare the parent state.
(d) Experimentally observed ratio of product to initial state integrated emission signals.
(e) Predicted ratio of product to initial state integrated emission signals.

Results calculated assuming $k_{AB} = 2.5 \times 10^{-11}$ molecule$^{-1}$cm$^3$s$^{-1}$ and $k_{BA} = 2.2 \times 10^{-11}$ molecule$^{-1}$cm$^3$s$^{-1}$. 

<table>
<thead>
<tr>
<th>$P^{(Q\alpha)}$</th>
<th>960 mTorr</th>
<th>2880 mTorr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial State$^{(b)}$</td>
<td>$A^2\Delta$</td>
<td>$B^2\Sigma^-$</td>
</tr>
<tr>
<td>Rotational Line$^{(c)}$</td>
<td>$R_2(1)$</td>
<td>$R_2(3)$</td>
</tr>
<tr>
<td>Expt Product:Initial$^{(d)}$</td>
<td>0.35</td>
<td>0.31</td>
</tr>
<tr>
<td>Calc Product:Initial$^{(e)}$</td>
<td>0.34</td>
<td>0.16</td>
</tr>
</tbody>
</table>
10.5.2 Determination of Rate Constants Within the Four-Level System

The determination of the rate constants for the collisional processes in the four-level system (as discussed in Section 10.4.2 and illustrated in Figure 10-7) was achieved by modelling the observed vibronic integrated emission intensities as a function of quencher pressure. The differential equations describing the A0, A1 and B0 populations within the four-level coupling scheme were analytically integrated within a Maple worksheet [7] to reveal the effect of varying the collisional transfer rate constants on the relative populations. In this manner, as in Section 10.5.1, a set of rate constants which reproduced relative integrated signals consistent with the experimental observations were iteratively determined. Within the four-level kinetic coupling scheme, the excited state vibronic populations are described by:

\[
\frac{dN_{B0}(t)}{dt} = -N_{B0}(t)k_{B0} + N_{A1}(t)k_{A1B0}P^Q
\]

Equation 10-10

\[
\frac{dN_{A1}(t)}{dt} = -N_{A1}(t)k_{A1} + N_{B0}(t)k_{B0A1}P^Q
\]

Equation 10-11

\[
\frac{dN_{A0}(t)}{dt} = -N_{A0}(t)k_{A0} + N_{B0}(t)k_{B0A0}P^Q + N_{A1}(t)k_{A1A0}P^Q
\]

Equation 10-12

The integrated emission signal from a given level may be evaluated from Equation 10-9. We are greatly aided in this analysis by a knowledge of the ratio of A0:A1 signals at various quencher pressures (from the two sets of expts recorded in Figure 10-10). The ratio of the rate constants for collisional transfer of the B0 population into A0 and A1, \(k_{B0A0}\) and \(k_{B0A1}\), may be determined by extrapolating the observed A0:A1 ratios in Figure 10-10b, obtained following B0 excitation, to the zero pressure limit, where the effects of secondary A1 → A0 relaxation may be effectively ignored. A first estimate of this number was made by linear regression to the data in Figure 10-10b, yielding a y-axis intercept of \(-0.69\). The \(k_{B0A0}\) and \(k_{B0A1}\) rates were therefore initiated from this ratio in the iterative procedure.
In the case of direct $A_1$ excitation, a limiting value of the rate constant for direct $A_1\rightarrow A_0$ relaxation may be estimated by determining the pressure at which the $A_1$ and $A_0$ integrated signal ratio is unity (c.f. Figure 10-10a). Neglecting any effects of differential quenching of $A_1$ and $A_0$ to 'dark' states, at this point, the total rate of $A_1\rightarrow A_0$ transfer, including direct $A_1\rightarrow A_0$ relaxation and $A_1\rightarrow B_0\rightarrow A_0$ multiple-collision transfer, is equal to the rate of radiative emission from the $A_1$ state, $\tau_{A_1}^{-1}$. This total $A_1\rightarrow A_0$ rate constant therefore represents an upper limit to the direct $A_1\rightarrow A_0$ channel. The pressure at which the $A_1$ and $A_0$ populations become equal was estimated by extrapolating a straight line, determined from the average linear fit to both sets of data in Figure 10-10a, from the origin to unity. The pressure at which the total rate of $A_1\rightarrow A_0$ transfer was found to equal the $A_1$ radiative rate was determined to be $\sim 5$ Torr, which, assuming an $A_1$ state lifetime of $\tau_{A_1}=540$ ns, yields a limiting value of $k_{A_1A_0}$ to be $\sim 1.1 \times 10^{-11}$ molecule$^{-1}$cm$^3$s$^{-1}$.

Operationally, the effects of sequentially varying the collisional transfer rate constants on the calculated $A_0:A_1$ and $(A_0+A_1):B_0$ population ratios for initial excitation of the $A_1$ and $B_0$ states were investigated, and the results compared with the experimental data in Table 10-1 and Figure 10-10. The radiative lifetimes of the three states were treated as constants in the iteration process, and set to $\tau_{B_0}=325$ ns, $\tau_{A_1}=540$ ns and $\tau_{A_0}=536$ ns [9-12]. The quenching rate constants of $A_1$ and $A_0$ to dark states, $k_{A_1X}$ and $k_{A_0X}$, were again assumed to be $0.04 \times 10^{-11}$ molecule$^{-1}$cm$^3$s$^{-1}$, and $k_B^Q$ was again set to zero.

This analysis showed that reasonable agreement between the experimentally observed and calculated integrated signal ratios is achieved when the rate constants for the various collision-induced processes are set to the values presented in Table 10-2. Due to the large number of adjustable parameters in this analysis, these numbers do not represent a totally unique set of rate constants, but rather a specific example from a small range of acceptable permutations. The signal ratios predicted at various quencher pressures from this set of rate constants are presented in Figure 10-11 along with the experimental results for comparison.
Table 10-2: Iteratively Determined Rate Constants for the Coupling Channels between the B0, A1 and A0 levels of CH Induced by Collisions with CO2.

Values determined from the four-level kinetic scheme, as described in Section 10.5.2, with $k_{B_Q}$ set to zero within the analysis.

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Value/10^{-11} molecule^{-1} cm^{3} s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{B0A1}$</td>
<td>1.0</td>
</tr>
<tr>
<td>$k_{B0A0}$</td>
<td>0.5</td>
</tr>
<tr>
<td>$k_{A1X}$</td>
<td>0.04</td>
</tr>
<tr>
<td>$k_{A0X}$</td>
<td>0.04</td>
</tr>
<tr>
<td>$k_{A1A0}$</td>
<td>0.9</td>
</tr>
<tr>
<td>$k_{A1B0}$</td>
<td>2.5</td>
</tr>
</tbody>
</table>
10.6 Discussion

The agreement between experimentally observed integrated signal ratios and predictions made from the four-level kinetic scheme illustrated in Figure 10-11, is not perfect in every case, indicating that the iteratively determined rate constants for the collisional transfer processes are not yet fully optimised, or possibly some systematic error in the analysis of the experimental data (e.g. uncorrected detection sensitivities at different wavelengths, or imperfect simulations). Even so, the model reproduces the (admittedly limited) set of experimental ratios reasonably well, indicating that the rate constants obtained from this preliminary analysis must not be very different from the true values.

A further test of the accuracy with which the rate constants model the collisionally-coupled system is revealed by the time dependence they predict for the excited state fluorescence waveforms. The equation describing the time dependence of the B0 level population is essentially unchanged from that of the B state discussed in Section 10.3.1. The differences between the two descriptions arise in the form of the coefficients and exponents in Equation 10-3, reflecting the fact that transfer to the A0 state removes population from the reversible A1↔B0 coupling. We now have enough information to explicitly evaluate $\lambda_1$ and $\lambda_2$ within this system, allowing the time dependence of the directly excited B0 population to be established from Equation 10-3. $\lambda_1$ and $\lambda_2$ (as defined in Eqns 10-5 and 10-6 respectively) may be determined from the rate constants obtained within the four-level system by making the assignments:

\begin{align*}
  k_{Ba} &= k_{B0A1} \\
  k_{AB} &= k_{A1B0}
\end{align*}

Equation 10-13

\begin{align*}
  k_{B0} &= \tau_B^{-1} + \left(k_{BA} + k_{B0A0} + k_B^Q\right)p^Q \\
  k_{A0} &= \tau_A^{-1} + \left(k_{A1A0} + k_{A1B0} + k_A^Q\right)p^Q
\end{align*}

Equation 10-15

The resulting values of the exponents $\lambda_1$ and $\lambda_2$ are plotted as a function of pressure in Figure 10-12, as are the pre-multiplying coefficients of the $e^{\lambda_1 t}$ and $e^{\lambda_2 t}$ terms in
The contributions made to the bi-exponential time-dependence of the B-X fluorescence waveform from the two single-exponential components may be determined from the relative magnitudes of the coefficients, \(- (k_B^{TQ} + \lambda_2)\) and \((k_B^{TQ} + \lambda_1)\), in Figure 10-12. At low pressure, it can be seen that the coefficient of \(e^{\lambda_1 t}\), \(- (k_B^{TQ} + \lambda_2)\), tends to zero, and the resulting bi-exponential function is dominated by \(e^{\lambda_2 t}\) (resulting in an effectively single exponential function). However, as the pressure increases, the two coefficients become comparable in size, and the B-X waveform is described by a weighted sum of \(e^{\lambda_1 t}\) and \(e^{\lambda_2 t}\). In the limit of high pressure, \(- (k_B^{TQ} + \lambda_2)\) becomes much larger than \((k_B^{TQ} + \lambda_1)\), and the resulting waveform again becomes more single-exponential in nature, with a time-dependence dominated by the \(e^{\lambda_2 t}\) term.

The evolution of the B-X waveform with pressure, from an essentially single- to a bi-exponential function, means care must be taken when analysing the apparent fluorescence lifetime as measured from a single-exponential fit. It can be seen from Figure 10-12 that the \(e^{\lambda_2 t}\) function will always decay faster than \(e^{\lambda_1 t}\), as \(|\lambda_2|\) is greater than \(|\lambda_1|\) at all pressures. The gradual weighting of the fluorescence waveform by the longer-lived \(e^{\lambda_1 t}\) component has the effect of lowering the apparent total removal rate, as determined from a single exponential fit, below the true value of \(k_B^{TQ}\), which is approached by \(\lambda_2\) at low pressure. This point is illustrated in Figure 10-12, where the quenching rates determined from single exponential fits to simulated B-X waveforms, correctly weighted for the contributions of \(e^{\lambda_1 t}\) and \(e^{\lambda_2 t}\), are shown. The deviation from the true total quenching rate, \(k_B^{TQ}\), can be seen to increase with pressure, as the contribution from \(e^{\lambda_1 t}\) becomes more significant, resulting in a degree of curvature in the 'observed' quenching rate data points. The physical reason for this behaviour is the increase in the proportion of molecules collisionally transferred to the longer-lived \(A^2\Delta\) state (\(\tau_A=540\) ns), which are transferred back to the \(B^2\Sigma^+\) state (\(\tau_B\approx350\) ns). The net result of this effect is to underestimate the value of the quenching rate constant, \(k_B^{TQ}\), by an amount dependent on the pressure range over which the measurements are made.

As discussed in Section 10.3.2, single exponential fits to directly excited B-X (0,0) waveforms, recorded over a series of pressures yielded, an apparent quenching rate constant of \(1.3\pm0.4\times10^{-11}\) molecule\(^{-1}\)cm\(^3\)s\(^{-1}\). The large uncertainty associated with this
Chapter 10: Collision-Induced CH $A^2\Delta \leftrightarrow B^2\Sigma^-$ Vibrational Transfer

number obviously limits the certainty with which conclusions may be made from comparisons between it and predicted values. However, it is interesting to note that the independently iteratively determined four-level scheme value of $k_B = 1.5 \times 10^{-11}$ molecule$^{-1}$ cm$^3$s$^{-1}$ lies above this figure, while the rate constant obtained by fitting a straight line through the predicted 'observed' total quenching rates in Figure 10-12 gives a value of $k_B = 1.28 \pm 0.03 \times 10^{-11}$ molecule$^{-1}$ cm$^3$s$^{-1}$. This agreement, albeit within relatively large error bounds, illustrates another aspect of the collisional behaviour of the system that is reasonably well reproduced by the iteratively determined rate constants.

In conclusion, the results presented in this Chapter represent, so far as we are aware, the first systematic investigation into the vibrational-level propensities of electronically inelastic CH $A^2\Delta \leftrightarrow B^2\Sigma^-$ transfer. Direct B0$\rightarrow$A0 transfer has been observed for the first time, and shown to be of comparable efficiency to the B0$\rightarrow$A1 channel for collisions with CO$_2$. Removal from the A1 state is seen to occur through electronically inelastic A1$\rightarrow$B0 transfer, and via direct A1$\rightarrow$A0 relaxation. Preliminary modelling of the excited state integrated fluorescence signals has produced a set of vibrationally specific rate constants for all of these collision-induced transfer processes which reproduce the observed experimental population ratios and B-X time-dependent waveforms reasonably well.
Figure 10-11: Comparison of Predicted and Observed Integrated Signal Ratios.

(a) Total product:parent state ratios: (b) A0:A1 following A1 pumping: (c) A0:A1 following B0 pumping. Experimental ratios produced from initial excitation of $\cdots$ A-X (1,0) $R_2(3)$; $\cdots$ A-X (1,0) $R_2(1)$; $\cdots$ B-X (0,0) $R_1(3)$; $\cdots$ B-X (0,0) $R_1(5)$. Predicted ratios from the four-level kinetic scheme in each case indicated by $\cdots$. 

(a) 
(b) 
(c)
Figure 10-12: Variation of the Components of Equation 10-3 with Pressure.

The predicted 'observed' total quenching rate as determined from single-exponential fits to the simulated bi-exponential B-X (0,0) waveforms is shown as (—O—). Simulated waveforms calculated using the rate constants obtained for CH $A^2\Delta$ and $B^2\Sigma^-$ state quenching given in Table 10-2.
Chapter 10: Collision-Induced CH $A^2\Delta \leftrightarrow B^2\Sigma^+$ Vibrational Transfer

Bibliography

7 Maple V Release 4.00a, Waterloo Maple Inc.
Chapter 11
Rotationally Resolved

$\text{CH A}^2\Delta \rightarrow \text{B}^2\Sigma^-$ Transfer

11.1 Introduction

This chapter will describe in detail the results obtained in a rotationally-resolved study of $\text{CH A}^2\Delta \rightarrow \text{B}^2\Sigma^-$ transfer. Preliminary investigation of the rotational propensities accompanying $\text{CH A}^2\Delta, \nu=1 \rightarrow \text{B}^2\Sigma^-, \nu'=0$ electronically inelastic transfer, induced by collisions with CO$_2$, was achieved through selective laser excitation, and time resolved, dispersed fluorescence measurements. The low moment of inertia of CH allows individual rotational lines to be resolved in dispersed fluorescence spectra, providing high quality state-specific information on the collision-induced transfer event.

Evaluation of the effect of parent state rotational excitation on the product state rotational distribution requires that the populations of both states, immediately before and after the electronically inelastic collision, be characterised in a quantum-level-specific fashion. While quantum level occupancies may be obtained with relative ease from dispersed fluorescence spectra, the fluorescence lifetimes of both states complicates the determination of distributions arising from single CH-quencher collisions. At the pressure required to ensure an acceptable signal-to-noise ratio in the transfer spectra, radiative emission is still the dominant removal process from both the A$^2\Delta$ and B$^2\Sigma^-$ states. As the rate of emission of fluorescence from the excited states is of the same order of magnitude as the rate of collisions at that pressure, collisional modification of both the nascent parent and product state distributions occurs over the excited state lifetimes. This problem was overcome by integrating the time-resolved A-X and B-X fluorescence waveforms over a series of time gates, allowing the temporal evolution of the rotational populations in both states to be followed.
Chapter 11: Rotationally Resolved CH $A^2\Delta \rightarrow B^2\Sigma^+$ Transfer

11.2 N-Specific A-X(1,0) Pumping

As discussed in Section 9.5.3, the A-X (1,0) R-type transitions provide a convenient route to $A^2\Delta$, $v=1$ rotationally-specific excitation. At ~500 mTorr of CO$_2$, excitation spectra of the A-X (1,0) R-branch region have revealed that a significant fraction of the ground state rotational population remains unthermalised when the photolysis-probe laser delay is set to 3 $\mu$s, as shown in Figure 11-1. This allows the preparation of distinct parent state distributions by exciting at two rotational features which terminate in well separated $A^2\Delta$ rovibronic levels (indicated in Figure 11-1). Close inspection of the A-X (1,0) branch structure reveals that both of the rotational lines selected for parent state preparation are actually blends of more than one branch type, unresolved within the bandwidth of the exciting laser. Pumping on the more intense of the marked features simultaneously excites the $R_{11\sigma}(2)$, $R_{11\Pi}(2)$, $R_{Q21\sigma}(2)$ and $R_{Q21\Pi}(2)$ transitions, while the weaker marked line is a combination of the $R_{11\Pi}(7)$, $R_{22\Pi}(7)$ and $R_{Q21\Pi}(7)$ lines. Operationally, this results in excitation to both spin-rotation ($J$) states associated with a specific $N$ level (for, $N=8$, $J=8.5$ and 7.5, and for, $N=3$, $J=3.5$ and 2.5), as may be verified from Figure 9-4 and Figure 9-5. These two features shall, for convenience, be referred to as the R(2) and R(7) lines from this point onwards.

The resulting $A^2\Delta$-$X^2\Pi$ and $B^2\Sigma^-$-$X^2\Pi$ waveforms were selectively integrated over a series of five time gates, all set to start immediately after the exciting laser pulse. The gate lengths increased progressively from 100 ns to 1300 ns in 300 ns increments, the final gate significantly exceeding the observed fluorescence lifetimes of both excited states. A-X and B-X dispersed fluorescence spectra were recorded on the diagonal bands of both systems. Rotational resolution was achieved with the monochromator resolution set to 11.1 and 14.2 cm$^{-1}$ for the A-X and B-X emission respectively. In all cases the total pressure was 550 mTorr, with a partial pressure of 40 mTorr 17% CHBr$_3$/Ar. Concurrent normalisation signals were recorded on the directly returning A-X (1,1) fluorescence, integrating over a 100 ns gate, again set directly after the exciting laser pulse. Average dissociation and excitation laser pulse energies were ~40 mJ and 15 mJ respectively.
Figure 11-1: Expanded View of the $^2\Delta$-$^2\Pi$ (1,0) R-type Branches.

Rotational features used for $^2\Delta$, $\nu=1$ state-specific excitation marked with (*): $N''=2$ and 7 respectively. Spectrum recorded with 510 mTorr CO$_2$ and 40 mTorr 17% CHBr$_3$/Ar, with fluorescence detected on the A-X (1,1) band. Photolysis-probe delay=3 μs.
The $A^2\Delta-X^2\Pi \Delta v=0$ dispersed fluorescence spectra resulting from $A-X$ (1,0) R(2) and R(7) excitation are shown in Figure 11-2 and Figure 11-3 respectively, along with the corresponding simulations. The evolution of each spectrum over the first four integration gates only is presented. The 1300 ns gate spectra are ignored as they contain very little information different from that recorded over the 1000 ns gate, reflecting the small fraction of initially excited molecules still present in the $A^2\Delta$ state during this final time increment. All spectra are shown normalised to the height of the most intense feature (this is always the Q-branch in this experiment). The rotational distributions associated with the four time gates in each experiment are shown in Figs 11-4 and 11-5 normalised to the same total population, allowing the temporal evolution of the populations to be observed. The characteristics of the two sets of rotational distributions are presented in Table 11-1. A simulation of a rotationally equilibrated $A-X$ (1,1) spectrum is presented with both sets of experimental spectra for comparison purposes, with the relevant features of the $A^2\Delta$, $v=1$ 300 K Boltzmann distribution given in Table 11-2.

It is assumed that the contribution of $A-X$ (0,0) fluorescence, arising from $A^2\Delta v=1\rightarrow0$ relaxation, is negligible when fitting the experimental spectra. Fluorescence emitted from the two vibrational levels on the diagonal bands lies too close in wavelength (at least for low values of $N'$) to be resolved by the monochromator when the slit widths are set to provide an acceptable signal-to-noise ratio. However, given the low $A1\rightarrow A0$ rate constant, $k_{A1A0}=0.9\times10^{-11}$ molecule$^{-1}$cm$^3$s$^{-1}$, determined in Section 10.5.2, it seems unlikely that emission from $v=0$ will account for more than a few percent of the total A state signal (especially in the shorter time gate spectra) at the low quencher pressure employed in this experiment.

The population distributions arising from R(7) excitation are obviously far from rotationally equilibrated within the $A^2\Delta$ state fluorescence lifetime, with spectra (a)-(d) in Figure 11-3 being dominated by single P, Q and R peaks. Correspondingly, the R(7) rotational populations, shown in Figure 11-5, reveal that a substantial percentage of the total excited population remains in the initially pumped $N=8$ level. It can be seen from Table 11-1 that, as expected, this collisionally unmodified fraction of the population decreases (along with the average $N$) as the fluorescence waveform is integrated over longer times. This relaxation reflects the comparable rates of rotationally inelastic
Chapter 11: Rotationally Resolved CH $A^2\Delta \rightarrow B^2\Sigma^-$ Transfer

transfer within the $A^2\Delta, v=1$ state, and quenching processes. The near-unity ratios of $F_1:F_2$ populations deduced from the simulations (see Table 11-1) must be treated with caution due to the inability of the experiment to completely resolve transitions from the $F_1$ and $F_2$ manifolds. However, the equal weighting given to the two populations may be rationalised by the direct pumping of both states with the main branch transitions underlying the $R(7)$ feature.

R(2) line excitation produces the fluorescence spectra (a)-(d) shown in Figure 11-2, with the corresponding rotational distributions given in Figure 11-4. Comparison of the characteristics of the rotational distributions associated with the experimental and the 300 K simulations (Table 11-1 and Table 11-2) show that even over the longest integration gate, rotational equilibration of the $A^2\Delta, v=1$ state is far from complete. Transitions from the two $A^2\Delta$ spin-rotation manifolds are better resolved at low $N$, allowing a more confident assessment of the relative $F_1:F_2$ occupancies following R(2) excitation. It can be seen from Table 11-1 that the ratio of $F_1:F_2$ populations decreases as the integration gate length is increased. The lowering of the ratio is caused by the collisional transfer of population from $F_1$ to $F_2$, and reflects the difference in the initial populations of the two manifolds caused by the discrepancy between the linestrengths of the main $R_{11}(2)$ and satellite $RQ_{21}(2)$ transitions at low $N$.

The results presented in this Section show that selective laser excitation of A-X (1,0) R-type transitions allows the preparation of distinct $A^2\Delta, v=1$ rotational distributions, which are only partially modified by rotationally inelastic collisions over the A state fluorescence lifetime.
Figure 11-2: CH $A^2\Delta$-$X^2\Pi$ (1,1) Dispersed Fluorescence Spectra obtained from R(2) Pumping.

The solid lines are experimental spectra, while the dashed are simulations assuming negligible relaxation to $A^2\Delta$, $v=0$. Spectra (a)-(d) were recorded with 550 mTorr CO$_2$ (including 40 mTorr 17% CHBr$_3$/Ar), and correspond to gate lengths of; (a) 100 ns; (b) 400 ns; (c) 700 ns; (d) 1000 ns. Spectrum (e) shows a 300 K thermal A-X (1,1) simulation, included for comparison.
Figure 11-3: CH $A^2\Delta$-$X^2\Pi$ (1,1) Dispersed Fluorescence Spectra obtained from R(7) Pumping.

The solid lines are experimental spectra, while the dashed are simulations assuming negligible relaxation to $A^2\Delta$, $v=0$. Spectra (a)-(d) were recorded with 550 mTorr CO$_2$ (including 40 mTorr 17% CHBr$_3$/Ar), and correspond to gate lengths of: (a) 100 ns; (b) 400 ns; (c) 700 ns; (d) 1000 ns. Spectrum (e) shows a 300 K thermal A-X (1,1) simulation, included for comparison.
Initial $A^2\Delta, v=1$ rotational distributions derived from spectra (a)-(d) in Figure 11-2 after R(2) excitation. The distributions shown correspond to spectra recorded with gate lengths of; (a) 100 ns; (b) 400 ns; (c) 700 ns; (d) 1000 ns. $F_1$ and $F_2$ distributions indicated by (---) and (--O--) respectively.
Figure 11-5: Best Fit CH $A^2\Delta$, $v=1$ Rotational Distributions obtained from R(7) Pumping.

Initial $A^2\Delta$, $v=1$ rotational distributions derived from spectra (a)-(d) in Figure 11-3 after R(7) excitation. The distributions shown correspond to spectra recorded with gate lengths of: (a) 100 ns; (b) 400 ns; (c) 700 ns; (d) 1000 ns. $F_1$ and $F_2$ distributions indicated by (— — ) and (—-O—- ) respectively.
Table 11-1: Characteristics of CH $A^2\Delta$, $v=1$ Rotational Distributions Produced by Collisions of State-Selected $A^2\Delta$, $v=1$ with CO$_2$.

<table>
<thead>
<tr>
<th>$A^2\Delta$, $N^{(e)}$</th>
<th>3</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>gate / ns$^{(b)}$</td>
<td>$p_i^{(c)}$</td>
<td>$F_1/F_2^{(d)}$</td>
</tr>
<tr>
<td>100</td>
<td>52</td>
<td>2.81</td>
</tr>
<tr>
<td>400</td>
<td>41</td>
<td>1.97</td>
</tr>
<tr>
<td>700</td>
<td>36</td>
<td>1.88</td>
</tr>
<tr>
<td>1000</td>
<td>36</td>
<td>1.82</td>
</tr>
</tbody>
</table>

Table 11-2: Characteristics of a 300 K CH $A^2\Delta$, $v=1$ Boltzmann Rotational Distribution.

<table>
<thead>
<tr>
<th>$A^2\Delta$, $v=1$</th>
<th>$p_{(3)}^{(f)}$</th>
<th>$p_{(8)}^{(g)}$</th>
<th>$F_1/F_2^{(d)}$</th>
<th>$&lt;N&gt;^{(e)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>21.96</td>
<td>3.39</td>
<td>1.29</td>
<td>5.2</td>
</tr>
</tbody>
</table>

(a) Initially populated $A^2\Delta$, $v=1$ $N$ level.
(b) Length of integration gate.
(c) Percentage of total excited population remaining in pumped level.
(d) Ratio of $A^2\Delta$, $v=1$ spin-rotation populations.
(e) Average $A^2\Delta$, $v=1$ $N$ quantum number.
(f) Percentage of total rotational population in $N=3$ in a 300 K Boltzmann Distribution.
(g) Percentage of total rotational population in $N=8$ in a 300 K Boltzmann Distribution.
Chapter 11: Rotationally Resolved CH $A^2\Delta \rightarrow B^2\Sigma^-$ Transfer

11.3 Collision-Induced CH $B^2\Sigma^-, \nu'=0$ Rotational Distributions

The collision-induced $B^2\Sigma^-, X^2\Pi (0,0)$ dispersed fluorescence spectra obtained following $A^2\Delta, \nu=1$ R(2) and R(7) excitation are shown in Figure 11-6 and Figure 11-7 respectively, along with the relevant simulations. The spectra were recorded by integrating the B-X waveform over the same time windows used in the A-X experiment, allowing the direct comparison of collision-induced $B^2\Sigma^-, \nu'=0$ rotational populations with the corresponding $A^2\Delta, \nu=1$ parent distribution. All spectra are again normalised to the height of the most intense feature. The rotational distributions associated with the four integration gates of the R(2) and R(7) experiments are shown normalised to the same total population in Figs 11-8 and 11-9 respectively, revealing the relative variation of the B state populations with time. The characteristics of the two sets of rotational distributions are given in Table 11-3. A simulation of a rotationally equilibrated B-X (0,0) spectrum is presented with both sets of experimental spectra for comparison purposes, with the relevant features of the $B^2\Sigma^-, \nu'=0$ 300 K Boltzmann distribution given in Table 11-4.

The two sets of collision-induced $B^2\Sigma^-, X^2\Pi (0,0)$ dispersed fluorescence spectra, and the corresponding rotational populations, clearly show the considerable influence of parent state rotational excitation on the product state distributions. $B^2\Sigma^-$ state rotational distributions produced from $A^2\Delta$ R(7) pumping exhibit a higher degree of rotational excitation than is observed in the corresponding R(2) pumped experiment (see Table 11-3). This difference is illustrated in the spectra through the R-head to Q-branch origin ratio. Because the $R_{11}$ and $R_{22}$ branches form a bandhead at $N=7$, and the $Q_{11}$ and $Q_{22}$ branches are most heavily congested at the band origin, the ratio of the two features gives an indication of the relative populations present at low and high $N$. The reversal of the ratio of the two features between Figure 11-6 and Figure 11-7, as the $A^2\Delta$ parent state distributions are varied, reflects a shift in B state population from low to high $N$, as seen in Figure 11-8 and Figure 11-9. Thus, there is an obvious correlation between the parent state population, and the observed product state rotational distribution. Within both sets of experimental spectra, the ratio of R-head to Q-branch origin can be seen to decrease as the gate length is increased, reflecting a shift in the mean of the rotational distributions to lower $N$ (see Table 11-3). This relaxation of the nascent product state distribution reflects not only rotationally inelastic transfer within the $B^2\Sigma^-$ state, but also
the parallel degradation of the parent \( A^2\Delta \) state population (see Table 11-1). However, the characteristics of the rotational distributions derived from both experiments, shown in Table 11-3, show that rotational equilibration (as defined by a 300 K Boltzmann distribution and characterised in Table 11-4) is far from complete within the product state fluorescence lifetime.

The \( F_1:F_2 \) ratios quoted in Table 11-3 must again be treated with caution due to our inability to resolve transitions from the B state spin-rotation manifolds. However, it is interesting to note that the product state ratios are weighted in the same direction as the parent state distributions.

Perhaps the most interesting feature of the \( A^2\Delta, \nu=1\rightarrow B^2\Sigma^-, \nu'=0 \) collision-induced process is the apparent propensity for the maximum probability of transfer being between *isoenergetic* levels of the two rovibronic manifolds. This channel is most apparent in the 100 ns gate B-X spectra, which carry the most state-specific information about the transfer mechanism. In the R(2) pumped experiment, spectrum (a) in Figure 11-6 shows a peaking of the main branch R(3), Q(4) and P(5) lines relative to the surrounding branch structure. This corresponds to a nascent B state product distribution with a maximum at \( N=4 \), as shown in graph (a), Figure 11-8. Exciting at the \( A^2\Delta \) R(7) line produces a nascent B-X spectrum with a clear enhancement of the main branch Q(9) and P(10) lines, as shown in Figure 11-7(a). The R(8) line is unresolved within the intense R-head structure. The dominance of the \( N=9 \) population relative to the rest of the rotational distribution is seen in graph (a) of Figure 11-9.

An explanation for the observed weighting given to the \( N'=4 \) and \( N'=9 \) populations in the product state may be seen from Figure 11-10, which shows the absolute energies of the rovibronic manifolds in the A and B states. Transfer from the initially excited \( A^2\Delta \) states to energetically nearby \( B^2\Sigma^- \) rovibronic levels can be seen to result in the observed maxima in the product state rotational distributions. In the case of \( A^2\Delta \) R(2) excitation, it can be seen from Figure 11-10 that the pumped \( N=3 \) level lies closer in energy to \( N=5 \) than \( N=4 \) in the B state. However, the \( N=5 \) level lies slightly higher in energy than \( N=3 \), resulting in the exothermic channel to \( N=4 \) becoming the dominant transfer route. In the R(7) pumping experiment, only the B state \( N=9 \) level lies close in energy to the A state \( N=8 \), so it is unsurprising that transfer to this level is favoured over all others.
The populations of the product state rotational levels adjacent to the distribution maxima in both experiments suggest that the size of the energy gap between the initial and final rotational state is crucial in determining the transfer efficiency. This point is illustrated in Figure 11-11, where the (normalised) population distributions, determined from the A-X and B-X spectra recorded over the 100 ns integration gate, are plotted as a function of absolute rovibronic term energy. The major transfer channel from the initially pumped $A^2\Delta$, $v=1$ rovibrational level is clearly seen in both cases to populate the nearest lower-lying $B^2\Sigma^-$, $v=0$ level. However, the fact that the product state distributions are significantly broader than those in the initial state implies that there is not a one-to-one mapping between nearest lying A and B state levels. We do not have sufficiently 'clean' state-resolved data to determine the propensities for transfer to surrounding levels, but it appears likely that some form of energy gap scaling law is dictating the collision-induced transfer probabilities.

Due to the limited number of $A^2\Delta$ rovibronic levels initially prepared in this experiment, we are unable to determine with confidence any possible influence the rotational quantum number of the initial and final states may have on the transfer propensities.

11.4 Conclusions

The rotational propensities of $A^2\Delta$, $v=1 \rightarrow B^2\Sigma^-$, $v'=0$ transfer in the CH radical, induced by collisions with CO$_2$, have been investigated for the first time. The preparation of distinct $A^2\Delta$, $v=1$ rotational distributions has been achieved through selective laser excitation. Dispersed, time-resolved fluorescence analysis has allowed the degree of relaxation within the parent state to be assessed, and revealed conservation of internal rovibronic energy of the CH molecule to be of prime importance in transfer to the product state.
Figure 11-6: CH $B^3\Sigma^+ - X^3\Pi$ (0,0) Dispersed Fluorescence Spectra.

The solid lines are collision-induced B-X spectra generated from $A^2\Delta$, $v=1$ $N=3$ parent distributions. The dashed lines are the corresponding simulations. Spectra (a)-(d) were recorded with 550 mTorr CO$_2$ (including 40 mTorr 17% CHBr$_3$/Ar) over gate lengths of: (a) 100 ns; (b) 400 ns; (c) 700 ns; (d) 1000 ns. Spectrum (e) shows a 300 K thermal B-X (0,0) simulation, included for comparison.
Figure 11-7: CH $B^2\Sigma - X^2\Pi$ (0,0) Dispersed Fluorescence Spectra.

The solid lines are collision-induced B-X spectra generated from $A^2\Delta$, $v=1$ $N=8$ parent distributions. The dashed lines are the corresponding simulations. Spectra (a)-(d) were recorded with 550 mTorr CO$_2$ (including 40 mTorr 17% CHBr$_3$/Ar) over gate lengths of; (a) 100 ns; (b) 400 ns; (c) 700 ns; (d) 1000 ns. Spectrum (e) shows a 300 K thermal B-X (0,0) simulation, included for comparison.
Figure 11-8: Best Fit CH $B^2\Sigma^-$, $v=0$ Rotational Distributions from Initial $A^2\Delta$, $v=1$ R(2) Excitation.

$B^2\Sigma^-$, $v'=0$ rotational distributions from spectra (a)-(d) in Figure 11-6, derived from collisions of $A^2\Delta$, $v=1$ $N=3$ with CO$_2$. The distributions shown correspond to spectra recorded with gate lengths of; (a) 100 ns; (b) 400 ns; (c) 700 ns; (d) 1000 ns. $F_1$ and $F_2$ distributions indicated by (---) and (---O---) respectively.
Figure 11-9: Best Fit CH $B^2\Sigma^-$, $v'=0$ Rotational Distributions from Initial $A^2\Delta$, $v=1$ R(7) Excitation.

$B^2\Sigma^-$, $v'=0$ rotational distributions from spectra (a)-(d) in Figure 11-7, derived from collisions of $A^2\Delta$, $v=1$ $N=8$ with CO$_2$. The distributions shown correspond to spectra recorded with gate lengths of: (a) 100 ns; (b) 400 ns; (c) 700 ns; (d) 1000 ns. $F_1$ and $F_2$ distributions indicated by (-----) and (--o--) respectively.
Table 11-3: Characteristics of CH B²Σ⁺, ν'=0 Rotational Distributions Produced by Electronically Inelastic Collisions of State-Selected A²Δ, ν=1 with CO₂.

<table>
<thead>
<tr>
<th>A²Δ, N(8)</th>
<th>3</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>gate / ns(b)</td>
<td>P₁(5)</td>
<td>F₁/F₂(6)</td>
</tr>
<tr>
<td>100</td>
<td>21</td>
<td>1.33</td>
</tr>
<tr>
<td>400</td>
<td>18</td>
<td>1.28</td>
</tr>
<tr>
<td>700</td>
<td>19</td>
<td>1.28</td>
</tr>
<tr>
<td>1000</td>
<td>18</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Table 11-4: Characteristics of a 300 K CH B²Σ⁺, ν'=0 Rotational Boltzmann Distribution.

<table>
<thead>
<tr>
<th>B²Σ⁺, ν=0</th>
<th>P₀(0)</th>
<th>P₀(6)</th>
<th>F₁/F₂(6)</th>
<th>&lt;N'&gt;(8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>15.98</td>
<td>1.90</td>
<td>1.44</td>
<td>3.91</td>
</tr>
</tbody>
</table>

a) Initially populated A²Δ, ν=1 N level.
(b) Length of integration gate.
(c) Percentage of total transferred population in dominant product state rotational level (N'=4 and N'=9).
(d) Ratio of B²Σ⁺, ν'=0 spin-rotation populations.
(e) Average B²Σ⁺, ν'=0 N' quantum number.
(f) Percentage of total rotational population in N'=4 in a 300 K Boltzmann Distribution.
(g) Percentage of total rotational population in N'=9 in a 300 K Boltzmann Distribution.
The various splittings present in the two electronic states have been omitted for clarity, with the levels labelled according to $N$. The term energies are those of Zachwieja [1].
Figure 11-11: Initial and Product State Population Distributions Expressed as a Function of Absolute Rovibronic Term Energy.

Initial excitation of $A^2\Delta, \nu=1$ (a) R(7) and (b) R(2). $A^2\Delta, \nu=1$ $F_1$ and $F_2$ populations shown as (—■—) and (—●—), respectively. $B^2\Sigma^-, \nu=0$ $F_1$ and $F_2$ populations shown as (—□—) and (—O—), respectively.
Bibliography

Chapter 12

CH Conclusions and Discussion

12.1 Discussion

The previous three Chapters have presented the results obtained during an investigation of collision-induced CH A^{2}Delta+CO_{2} \leftrightarrow B^{2}Sigma^{+}+CO_{2} transfer. Preliminary analysis of the vibrationally resolved data for the collisional processes linking the A0, Al and B0 levels suggests that B^{2}Sigma^{+} \rightarrow A^{2}Delta transfer is the dominant collisional removal process for the B state. B0 \rightarrow A0 transfer has been shown to be of comparable efficiency to the B0 \rightarrow Al channel, and removal from the Al state has been observed via electronically inelastic transfer to B0, and also via direct relaxation to A0. Rotationally resolved studies of the A^{2}Delta, v=1 \rightarrow B^{2}Sigma^{+}, v'=0 channel have shown a definite propensity for transfer between rotational levels that lie close in energy.

Considering the vibrationally-specific rate constants obtained for transfer between the two excited states, it appears at first sight rather surprising that collisional A1 \rightarrow B0 transfer should be more efficient than the reverse B0 \rightarrow Al process. A 300 K Boltzmann distribution calculated over the rotational manifolds of both A1 and B0 levels suggests the equilibrium A1:B0 population ratio to be \sim 1:0.77. This reflects the extra twofold degeneracy of the A^{2}Delta state outweighing the fact that the A1 level lies 284 cm^{-1} higher in energy than the B0. The principle of microscopic reversibility therefore predicts that B0 \rightarrow A1 transfer should be favoured by a factor of \sim 1/0.77 over A1 \rightarrow B0. However, we believe this argument to be inapplicable in this situation as rotational equilibration is incomplete in the parent and product states following single-level excitation, as discussed in Chapter 11 for the initial excitation of Al. The equilibrium populations discussed above arise as a result of the net transfer from all levels populated in a thermal distribution. Because the initial distributions we prepare are significantly removed from rotational equilibrium, the constraints of microscopic reversibility on the relative A1 \rightarrow B0 and B0 \rightarrow A1 transfer rates are removed. This argument may be illustrated by considering
the case of initial \( B_0 \) excitation to low \( N \). It can be seen from Figure 11-10 that \( B_0 \rightarrow A_1 \) transfer is endothermic from every \( B_0 \) rotational level below \( N=5 \). Initial excitation of these low \( N \) levels therefore weights the \( B_0 \) population, regardless of the favourable \( A \) state degeneracy. In a related argument, the possibility of sub-level selectivity in the observed \( A_1 \leftrightarrow B_0 \) transfer rates is introduced by the incomplete equilibration of the pumped state, again rendering the microscopic reversibility argument invalid.

Within this argument there is also the possibility that shortcomings in the experimental procedure have influenced the observed ratio of \( A_1 \leftrightarrow B_0 \) transfer rates. The response of the detection system has not, as yet, been calibrated at the relevant \( B-X \) (0,0) and \( A-X \) \( \Delta \nu=0 \) emission wavelengths. This could, in principle, result in the higher frequency fluorescence from the \( B_0 \) state receiving a greater weighting in analysis than the \( A^2\Delta \), \( \Delta \nu=0 \) emission. However, it is felt that this is unlikely to be a significant source of error due to the relatively small difference in wavelength between the two bands. In terms of the analysis itself, as stated in Section 10.5.2, the values of \( k_{B_0}^Q \) and \( k_{A_1}^Q \) have not been directly determined. While setting \( k_{B_0}^Q=0 \) appears to be a reasonable assumption, as illustrated by the agreement between the observed and predicted \( B-X \) (0,0) waveforms discussed in Section 10.6, \( k_{A_1}^Q \) awaits investigation via directly excited \( A-X \) (1,1) waveform analysis.

The value of the \( B^2\Sigma^-, \nu=0 \) collisional removal rate constant obtained from this study for \( CO_2 \) quenching, \( k_B^{Q,Y}=1.5\times10^{-11} \) molecule\(^{-1}\)cm\(^3\)s\(^{-1}\), is approximately double that quoted by Whitehead, \( k_B^{Q,Y}=0.77\times10^{-11} \) molecule\(^{-1}\)cm\(^3\)s\(^{-1}\) [1]. We believe Whitehead's number to be an underestimate of the true value, resulting from a failure to appreciate the effects of facile \( A \leftrightarrow B \) transfer on the observed \( B-X \) waveform, as discussed in Section 10.6. The discrepancy between the true total quenching rate, and that determined from a single exponential fit to the \( B-X \) waveform, would be greater in his experiment than in ours for two reasons. Firstly, his measurements were made in a higher pressure regime, \( \sim 3 \) Torr, resulting in a larger proportion of the \( B_0 \) population collisionally transferred to the longer-lived \( A^2\Delta \) state being collisionally returned. Secondly, and more importantly, his analysis was performed on the \textit{nascent} \( B-X \) waveforms generated by the photolysis of \( CHBr_3 \). As discussed in Section 8.1, the photolysis process generates \( CH \) in both \( A^2\Delta \) and \( B^2\Sigma^- \) excited states. The nascent \( B-X \) signal therefore contains a large component of long-lived fluorescence arising from \( A \rightarrow B \) transfer out of an \textit{initially} highly populated
Chapter 12: CH Conclusions and Discussion

A$^2\Delta$ state, far more so than would occur from specific excitation of the B0 level only. This effect may warrant the re-examination of A$^2\Delta$ and B$^2\Sigma^-$ state quenching rate constants derived from similar experimental approaches where the collision partner induces transfer between the two states.

The results obtained in this thesis allow several conclusions to be drawn about the mechanism operating during collisional transfer. The formation of a long lived collision-complex resulting in A$^2\Delta \leftrightarrow$B$^2\Sigma^-$ transfer may be discounted from both the rotationally resolved A$^2\Delta$, $v=1 \rightarrow$B$^2\Sigma^-$, $v'=0$, and vibrationally resolved B$^2\Sigma^-$, $v=0 \rightarrow$A$^2\Delta$, $v'=0$ and 1 results. The observed propensity for transfer between isoenergetic rotational levels in A1$\rightarrow$B0 transfer, and the preferential population of the A1 level over the A0 in B0$\rightarrow$A$^2\Delta$ transfer, both show that the internal energy of the CH molecule is not being statistically redistributed during the collision process. The transfer mechanism seems inefficient at converting electronic energy into the mechanical degrees of freedom of the collision pair, as evidenced by the tendency for transfer to occur through channels involving $\Delta E=0$. The $\Delta J$ propensities observed in A1$\rightarrow$B0 transfer are the same as those involved in rotationally inelastic transfer within a single electronic state, implying that the CO$_2$-A$^2\Delta$ surface must be very similar to the CO$_2$-B$^2\Sigma^-$ surface (i.e. the molecule hardly realises that a change of electronic state has taken place). All of this would tend to suggest that neither electronic state is significantly modified by the presence of the CO$_2$ molecule.

The Franck-Condon overlap between the B0 and A0 states has been calculated to be $\sim 5$ times greater than that between the B0 and A1 states. The fact that the B0$\rightarrow$A1 transfer is approximately twice as efficient as B0$\rightarrow$A0 (as discussed in Section 10.6) implies that the 'sudden' transfer approximation is not applicable in this case. The empirical model suggested by Katayama et al to correlate the transfer cross sections with the energy gap and Franck-Condon overlap [2] may be expressed as:

$$\sigma_{\text{obs}} = \sigma_{\text{el}} q_{\text{FC}} \exp\left(-\frac{|\Delta E|}{kT}\right)$$

Equation 12-1

where $\sigma_{\text{obs}}$ is the experimentally observed cross section, $\sigma_{\text{el}}$ is the hypothetical intrinsic electronic quenching cross section, $q_{\text{FC}}$ is the Franck-Condon Factor and $\Delta E$ the energy gap between initial and product states. This model overestimates the population of the
A1 state relative to the A0 by three orders of magnitude, and so is clearly not applicable in this case.

Collision-induced CH $A^2\Delta \leftrightarrow B^2\Sigma^-$ transfer is allowed within the reduced symmetry environment created by the approach of the quencher molecule, as described by Alexander and Corey [3]. What is perhaps surprising is that collisional transfer between the A and B states occurs more efficiently than quenching to the ground state. Recalling the electronic configurations of the states discussed in Section 9.6 ($A^2\Delta$: $1\sigma^22\sigma^23\sigma^1(1\pi^2, 1\Delta)$, $B^2\Sigma^-$: $1\sigma^22\sigma^23\sigma^1(1\pi^2, 3\Sigma)$ and $X^2\Pi$: $1\sigma^22\sigma^23\sigma^11\pi$), A-X and B-X transfer both involve the movement of just one electron between the 3σ and 1π orbitals. However, transfer between the A and B states involves the movement of one electron accompanied by a spin flip, or alternatively, two sequential 3σ→1π transitions. *Ab initio* work is clearly required to identify an operator capable of causing this.

### 12.2 Future Work

There are several avenues of experimentation through which the understanding of CH $A^2\Delta+CO_2 \leftrightarrow CH B^2\Sigma^++CO_2$ collision-induced electronic energy transfer may be furthered. The analysis of vibrationally resolved A-X (0,1) and (1,2) waveforms produced from direct A0 and A1 excitation will provide kinetic information on the total rates of removal from both states, allowing the rate constants used in the modelling process to be further refined. As mentioned above, high resolution spectra of the collisionally induced A-X (1,1) and (0,0) bands will determine whether reversible transfer from high $N$ levels of the A0 state plays a significant role in the coupling scheme, and possibly give an indication of the role of the rotational quantum number in dictating transfer efficiencies. A revealing experiment would be the rotationally resolved investigation of the $B^2\Sigma^-$, $\nu=0 \rightarrow A^2\Delta$, $\nu'=1$ channel. As the low $N$ B0 levels lie below the A1 rovibronic manifold, a systematic study of the transfer propensities as $N$ is increased will provide important information on the role of the energy gap in $B^2\Sigma^- \rightarrow A^2\Delta$ transfer. Perhaps even more interesting is the question of the rotational propensities in B0→A0 transfer. If rotational energy is conserved, some mechanism must exist to remove the energy defect between the initial and final states. An investigation of the vibrational propensities of various quenchers would determine the importance of internal degrees of freedom in the collision partner in removing energy from the collision system.
Another area of potential research lies in the collisional quenching of the $A^2\Delta, v=2$ ($A2$) level. Initial studies, not reported in the bulk of this thesis, observed emission from the B0 and B1 levels following state-specific A2 excitation. No attempt to quantify the relative magnitudes of the B0 and B1 populations has been made so far, but the integrated intensity of the B-X (0,0) band appears many times larger than the (1,1). Whether this reflects the relative transition probabilities of the two bands, a propensity for vibrational transfer over a large energy gap, or predissociation of the collisionally produced B1 population is as yet undetermined. Interestingly, vibrational relaxation from the A2 level is observed to be highly efficient, indicating the possibility of a cascade-type mechanism.

In an early study, quenching of the $B^2\Sigma^-$ state by Ar was investigated. Though the quenching rate was low, $B \rightarrow A$ transfer was observed at high total pressures (>10 Torr) and waveform analysis of the A-X ($\nu,\nu$) emission allowed $\lambda_1$ and $\lambda_2$ to be estimated. This experiment was initially abandoned because of the high pressure required to observe transfer, complicating the retrieval of spectra produced under single-collision conditions. However, in view of the tractability of the CH+Ar collision system, it may be that this experiment should be resurrected, in the hope that any state-specific results might stimulate renewed fundamental theoretical studies. Hopefully, potential energy surfaces for the CH+Ar system may be generated, allowing the $A^2\Delta \leftrightarrow B^2\Sigma^-$ process to be simulated by the appropriate scattering calculations.
Bibliography

Appendix A

Conferences Attended

Gas Kinetics Discussion Group, University of Northumbria, Newcastle-upon-Tyne, January 1995.


6th Annual Informal Northern Universities Meeting on Chemical Physics, University of Northumbria, July 1996.


Dynamics of Molecular Collisions Conference, Gull Lake, Minnesota, July 1997.
Appendix B

Courses Attended

Inelastic and Reactive Scattering Theory
Lasers1
Lasers2
Molecular Quantum Mechanics
Infrared Spectroscopy: Theory and Practice
MaxEnt
Chemometrics

Introduction to Unix
Enhancing your Unix Skills
C Programming