HYPERFINE STRUCTURE AND PREDISSOCIATION OF THE B $^3\Pi_{0+}$ STATE OF BROMINE

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Investigations have been carried out in bromine of the hyperfine structure of the \( B \; ^3\Pi_{0^+} \) and \( X \; ^1\Sigma^+_g \) electronic states and of the predissociation of the \( B \; ^3\Pi_{0^+} \) state by the \( ^1\Pi_{1u} \) dissociative level. The technique of laser induced fluorescence of a molecular beam was used. \(^79\)Br\(^81\)Br hyperfine spectra were recorded for various \( B \rightarrow X \) vibrational bands \((v' \leftrightarrow v'')\) with \( v' = 11 \) through 17 and \( v'' = 0, 1, \) and 2, and for various rotational transitions \((J' \leftrightarrow J'')\) with \( J' \) from 0 to 11 and \( J'' \) from 0 to 10. As well, the \(^79\)Br\(_2\) and \(^81\)Br\(_2\) hyperfine spectra of the \((13' \rightarrow 0'')\) and \((17' \rightarrow 2'')\) bands over the same range of rotational states were measured. The spectra are well described using one \( X \) state parameter: the electric quadrupole coupling constant \( eqQ_X \); and two \( B \) state parameters: the electric quadrupole coupling constant \( eqQ_B \), and the nuclear spin-rotation constant \( C_{sr} \). The results show that \( eqQ_B(\(^79\)Br) = (177.0 \pm 0.6) \text{ MHz} \) for \( v' = 11 \) and increases by approximately 0.5 MHz per vibrational quantum up to \( (180.6 \pm 1.4) \text{ MHz} \) for \( v' = 17. \) Similarly the ground state electric quadrupole coupling constant, \( eqQ_X(\(^79\)Br) = (808.1 \pm 1.4) \text{ MHz} \) for \( v'' = 0 \) and increases by about 1 MHz per vibrational quantum to \( (811.4 \pm 1.4) \text{ MHz} \) for \( v'' = 2. \) The hyperfine data also provided a check on the accuracy of some of the published rovibronic constants\(^1\) for each isotopomer. In order to reproduce the observed relative spacings of the transitions for all three isotopomers, the published term values, \( T_{00} \), have to be modified; this can be done by decreasing the published values of \( T_{00} \) for \(^81\)Br\(_2\) and \(^79\)Br\(^81\)Br by \((177 \pm 8) \text{ MHz} \) and \((326 \pm 8) \text{ MHz} \), respectively.

The phase shift technique was applied to the study of the predissociation of the \( v' = 13 \) \( B \; ^3\Pi_{0^+} \) electronic state of bromine. The lifetimes of individual hyperfine levels were

measured for the rotational states $J' = 0 - 7$ (except for $J' = 2$) for each isotopomer of bromine. Revised values are given for the radiative decay rate $\Gamma_{\text{rad}}$, the gyroscopic predissociation parameter $C_v$, and the magnetic dipole predissociation parameter $a_v$. The first observation of electric quadrupole predissociation is reported and is characterized by a new molecular parameter, $b_v$. 
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Chapter 1

Introduction

The study of the excited electronic states of the diatomic halogens has been an active area of research over the past two decades. In particular, work on molecular iodine has been extremely rewarding. Researchers have used iodine as a test molecule for developing new spectroscopic techniques, for observing predicted but previously unobserved effects, for refining spectroscopic theory, and, in the process, have discovered new, unexpected phenomena.

Molecular bromine has been somewhat less studied owing to its weaker absorption and stronger predissociation. However, bromine has several features that make it more attractive to the researcher. First, atomic bromine occurs in two isotopic forms, $^{79}\text{Br}$ and $^{81}\text{Br}$, in almost equal abundance. The molecular species, $^{79}\text{Br}_2$, $^{79}\text{Br}^{81}\text{Br}$, and $^{81}\text{Br}_2$, (called isotopomers) appear in the ratio 1:2:1, presenting an opportunity to study different molecular systems with very similar properties. Second, the nuclear spin of both the isotopes of bromine is 3/2 as compared to 5/2 for iodine. Therefore the hyperfine structure of molecular bromine is less complicated and insights into the dynamics of the excited molecules may be easier to glean. Finally, the radiative lifetime of the $^3\Pi_{0^+}$ electronic state of bromine was reported to be at least three to four times longer than that of the $^3\Pi_{0^+}$ state of iodine. With the longer lifetime, it is easier to observe interactions of the $^3\Pi_{0^+}$ state with other electronic levels. Understanding these interactions of electronic levels, especially the interactions of dissociative and bound electronic states (e.g. predissociation) has some important implications. As was observed for molecular
iodine, predissociation occurs through several different physical mechanisms, one of which arises through hyperfine interactions. This type of predissociation affects the different hyperfine levels of the molecules by different amounts. Therefore, if one understands the mechanisms that lead to predissociation then one could, perhaps, manipulate the predissociation or inverse-predissociation, so as to prepare molecules of bromine in specific states for further experimentation. In addition, for atoms in optical traps, their recombination into molecules represents one way in which the atoms can leak out. With an understanding of the recombination and predissociation processes one may be able to manipulate the conditions in the trap so as to hold the atoms for a longer period of time.

This thesis presents the results of work on the hyperfine structure of the X $^1\Sigma_g^+$ and B $^3\Pi_{0^+}$ electronic states of bromine and on the predissociation of the B state by the dissociative $^1\Pi_{1u}$ state.

The hyperfine structure of the X and B states (both are $\Omega = 0^+$ levels) is determined primarily by electric quadrupole interactions (characterized by the parameters $\text{eq}Q_X$ and $\text{eq}Q_B$, respectively) plus a small contribution from the B state nuclear spin – rotation interaction (characterized by the parameter, $C_{sr}$). For all three isotopomers, hyperfine spectra were recorded of the (13$'$–0$''$) band for the rotational transitions $P(1)$ – $P(5)$, $R(0)$ – $R(3)$ and $R(10)$. For the (17$'$ – 2$''$) band, hyperfine transitions were measured for the $P(1)$ – $P(7)$, excluding the $P(6)$, and $R(0)$ – $R(10)$, excluding the $R(9)$. In addition, for $^{79}\text{Br}^{81}\text{Br}$, the hyperfine spectra of $R(0)$ – $R(2)$ and $P(1)$ were measured for the (11$'$–0$''$), (12$'$–0$''$), (14$'$–1$''$), (15$'$–1$''$), and (16$'$–1$''$) bands. Of particular importance were the $\Delta F \neq \Delta J$ (so-called cross over) transitions which allowed one to separate the hyperfine parameters for each electronic state. The results indicated that, for both the X and B electronic states, the ratio of the molecular electric quadrupole coupling constants, $\text{eq}Q(79\text{Br}_2)/\text{eq}Q(81\text{Br}_2)$, agreed with the ratio of the nuclear quadrupole moments, $Q(79)/Q(81)$. For the B state, the parameter, $\text{eq}Q_B(79\text{Br})$, was (177.0 ± 0.6) MHz for
\( v' = 11 \), and increased by about 0.5 MHz per vibrational quantum up to \((180.6 \pm 1.4)\) MHz for \( v' = 17 \). The X state had \( \text{eq}Q_{X}(^{79}\text{Br}) = (808.1 \pm 1.4)\) MHz increasing by about 1 MHz per vibrational quantum up to \((811.5 \pm 1.9)\) MHz for \( v'' = 2 \). These results were in excellent agreement with the findings of previous workers [1, 2, 3, 4, 5, 6].

The study of the hyperfine structure of each isotopomer of bromine provided a second type of information. Because the B–X spectrum of bromine is dense, many near coincidences of transitions from different levels within an isotopomer and from levels from different isotopomers were observed. A study of the Doppler–limited B–X spectrum of \(^{79}\text{Br}_2\) had been carried out earlier by Gerstenkorn and Luc [7]. Analysis of the data provided the rovibronic (i.e. rotational, vibrational, and electronic) constants for the B and X states of \(^{79}\text{Br}_2\). Using isotopic relations, the authors of Reference [7] also calculated the corresponding parameters for \(^{81}\text{Br}_2\) and \(^{79}\text{Br}^{81}\text{Br}\). By measuring the frequency separations of the nearly coincident transitions in the current work, the accuracy of the molecular parameters was tested. The results of the hyperfine studies presented here indicated that the rovibronic parameters of Reference [7] reproduce the the observed frequency separations of transitions arising from levels of the same isotopomer to \(\pm 5\) MHz. The observed frequency separations of nearly coincident transitions arising from levels belonging to different isotopomers led to the conclusion that the term values for the different isotopomers, \(T_{00}\), reported by Gerstenkorn and Luc [7] had to be adjusted. Because the reported \(^{79}\text{Br}_2\) constants were derived directly from observed data while the constants reported for \(^{81}\text{Br}_2\) and \(^{79}\text{Br}^{81}\text{Br}\) were deduced using isotopic relations, \(T_{00}\) for \(^{79}\text{Br}_2\) was kept fixed and \(T_{00}\) for \(^{81}\text{Br}_2\) and \(^{79}\text{Br}^{81}\text{Br}\) were adjusted. The new term values are \((177 \pm 8)\) MHz and \((386 \pm 8)\) MHz lower than those reported by Gerstenkorn and Luc [7] for \(^{79}\text{Br}^{81}\text{Br}\) and \(^{81}\text{Br}_2\), respectively. With these new constants, the frequency separations between spectral features arising from different isotopomers should be accurate to \(\pm 9\) MHz (\(\pm 0.0003\) cm\(^{-1}\)).
The fluorescence from many of the rovibrational levels of the B $^3\Pi_{0^+}$ state of bromine is diminished owing to the phenomenon of predissociation. Predissociation occurs when a bound and unbound electronic state are coupled allowing some of the molecules in the bound state to fall apart into constituent atoms. The decay rate, $\Gamma$, of a level subject to predissociation is the sum of the radiative decay rate, $\Gamma_{\text{rad}}$, and the predissociation rate, $\Gamma_{\text{p}}$ (neglecting other decay channels such as collisions and stimulated emission). The strength of the predissociation rate depends upon the types of coupling and is strongest in the region where the two electronic potentials cross.

The theory of the predissociation of the B $^3\Pi_{0^+}$ state of molecular iodine by a dissociative $^1\Pi_{1u}$ state has been worked out in detail [8]. In this theory, the predissociation arises primarily from terms in the rotational Hamiltonian (gyroscopic terms), from interactions between the electrons and nuclei in the hyperfine Hamiltonian (hyperfine terms), and from the interference of these two types of coupling. The gyroscopic terms couple all of the hyperfine levels associated with a specific rovibronic state to the continuum by the same amount. By contrast, the hyperfine and interference terms lead to predissociation rates which vary from hyperfine level to hyperfine level. The hyperfine operators arise from magnetic dipole interactions, electric quadrupole interaction, magnetic octupole interactions and so on. Previous studies have determined that only the gyroscopic terms (characterized by the parameter $C_{\nu}$), and the magnetic dipole terms (characterized by the parameter $a_{\nu}$) are necessary to explain the observed predissociation rate of the B state of iodine [8, 9, 10, 11, 12].

A variety of techniques has been used to determine the predissociation of a state: (i) direct lifetime measurements of rotational levels (this yields an accurate determination of $C_{\nu}^2$) [13, 14]; (ii) direct lifetime measurements of hyperfine levels (to give $\Gamma_{\text{rad}}$, $C_{\nu}$, and $a_{\nu}$) [12]; (iii) observations of the linewidths of hyperfine transitions (giving $\Gamma_{\text{rad}}$, $C_{\nu}$, and $a_{\nu}$) [11]; (iv) measurements of relative intensities of hyperfine spectral features (producing
Chapter 1. Introduction

$C_v/\sqrt{\Gamma_{\text{rad}}}$ and $a_v/\sqrt{\Gamma_{\text{rad}}}$ [3, 4, 9]. The predissociation of the B state of bromine has been investigated by several different researchers [3, 4, 13, 14] using techniques (i) and (iv). The reported values of the parameters, $\Gamma_{\text{rad}}$, $C_v$, and $a_v$ show a great deal of variation from research group to research group, and in the case of References [3] and [4], from one rotational state to another. In particular, the radiative lifetime has been reported to lie between 1.9 and 15.7 $\mu$s [3, 13, 14, 15, 16].

In this thesis, a different experimental approach has been taken to studying the predissociation of the B state of bromine. A technique known as the phase shift method was successfully applied to the determination of the lifetimes of individual hyperfine levels. In this method, bromine molecules in a molecular beam were excited by a narrow band tunable laser. The laser's intensity was modulated at an angular frequency approaching the total decay rate of the level being studied. The resulting laser induced fluorescence signal was shifted in phase with respect to the laser's intensity modulation signal. The amount of phase shift provides a measure of the total decay rate, $\Gamma$, of the state. For example, a phase shift of $45^\circ$ is observed when $\Gamma$ equals the angular modulation frequency. This is the first time that the phase shift method has been applied to the measurement of lifetimes of individual hyperfine levels.

The decay rates of the $v' = 13$ B state hyperfine levels of $J' = 0$ through 7 (excluding $J' = 2$) were measured for each isotopomer of bromine. The previous predissociation theory including only the magnetic dipole hyperfine terms proved to be inadequate to describe the data. In this thesis the theory has been expanded to include the electric quadrupole terms. This led to the introduction of a new molecular parameter, $b_v$, corresponding to electric quadrupole predissociation. Revised values of $\Gamma_{\text{rad}}$, $C_v$, and $a_v$ are reported along with the values of $b_v$ for each isotopomer. For the first time, a determination of a quadrupole coupling constant between a bound and unbound electronic state has been made.
Chapter 1. Introduction

1.1 Thesis Organization

This thesis is organized into 7 chapters. The theoretical concepts are covered in Chapters 2 and 3 while the experimental details and results are found in Chapters 4 through 6. Chapter 7 contains a summary of the findings and some suggestions for future work.

Chapter 2 presents an overview of the basic ideas of the spectra of diatomic molecules including the Born–Oppenheimer approximation, symmetry considerations and labelling of energy states, a brief treatment of the rovibronic energy levels, and a description of hyperfine interactions and energy levels. Chapter 2 ends with a discussion of the fluorescence intensities of hyperfine transitions and their dependence upon the laser polarization as compared to absorption line intensities.

Chapter 3 introduces the topic of predissociation and presents the theory of natural predissociation of Vigué et al. [8] The theory has been expanded to include heteronuclear molecules. The chapter includes a brief discussion of which hyperfine states are the most sensitive to the various predissociation effects.

Chapter 4 discusses the molecular beam machine and laser system common to both the hyperfine structure studies and the predissociation work.

Chapter 5 contains the specific optical collection scheme and frequency calibration system used along with the results and discussion of the hyperfine structure of the B and X states of bromine. It concludes with a discussion of the accuracy of the rovibronic constants of Reference [7] and suggests that small corrections should be added to the B state term values to reconcile the calculated and observed transition frequencies.

Chapter 6 details the study of the natural predissociation of the \( \nu' = 13 \) level of the B \( ^3\Pi_0^+ \) electronic state of bromine. The various saturation and laser polarization considerations required for relative intensity measurements are pointed out as are the anomalous results that were originally observed. These were remedied by a redesign of the optical
collection system. Measurements of the lifetimes of individual hyperfine levels were performed using the phase shift method. The theory of the phase shift method is presented and the final results for the radiative decay rate, and for the gyroscopic and hyperfine predissociation parameters are given and discussed.
Chapter 2

General Theoretical Considerations

In this chapter, the main theoretical considerations for unravelling the rovibronic and hyperfine spectra of diatomic molecules will be presented. For more complete treatments of the subject the readers are referred to [17, 18], two of the excellent texts on spectroscopy.

The diatomic molecule may be conceptualized as a dumb-bell; the nuclei are separated by a distance \( R_N \) and surrounded by an electron cloud. The nuclei rotate and vibrate while interacting with the electrons. The energy levels of the molecules are determined from the time-independent Schrödinger equation,

\[
H |\psi\rangle = E |\psi\rangle
\]

(2.1)

where \( H \) is the Hamiltonian describing the system, \( |\psi\rangle \) represents the eigenfunction corresponding to eigenenergy \( E \). The Hamiltonian of the system can be written as

\[
H = T_e + T_N + V_{ee}(r_e) + V_{Ne}(r_e, R_N) + V_{NN}(R_N)
\]

(2.2)

where \( T_e \) and \( T_N \) are the kinetic energies of the electrons and nuclei respectively; \( V_{ee}(r_e) \) represents the electron–electron interactions; \( V_{Ne}(r_e, R_N) \) represents the electron–nuclear interactions; and \( V_{NN}(R_N) \) represents the internuclear interactions. (\( r_e \) and \( R_N \) represent the electron and nuclear coordinates, respectively.) In order to simplify the solution of Equation 2.1, one uses the Born-Oppenheimer approximation (BOA). The BOA relies on the fact that the electrons are much lighter than the nuclei and move much more rapidly. Therefore the orbital frequencies of the electrons are much higher than the characteristic
Figure 2.1: A schematic diagram of two bound electronic state energy potentials. The separation of the electronic states, $\Delta E_e$, is much larger than the separation of the vibrational levels, $\Delta E_v$, which is, in turn, larger than the rotational state separations, $\Delta E_r$.

The electronic motion is deduced from the Schrödinger equation keeping the nuclei fixed and treating the internuclear distance, $R_N$, as a parameter.

$$[T_e + V_{ee} + V_{Ne}][\psi_e] = U_e(R_N)[\psi_e]$$

$U_e(R_N)$ is then put back into the nuclear Schrödinger equation.

$$[T_N + V_{NN} + U_e(R_N)][\psi_N] = E[\psi_N]$$

$U_e(R_N)$ and $V_{NN}$ provide a background potential in which the nuclei vibrate and rotate.

Two typical potentials are illustrated in Figure 2.1. To solve Equation 2.5, the nuclear wavefunction is factored into vibrational, rotational, and nuclear spin functions as

$$|\psi_N\rangle = |\psi_v\rangle|\psi_r\rangle|\chi_N\rangle$$
The total energy of the molecule, excluding nuclear spin interactions and terms that
couple different electronic states, is resolved as:

\[ E = T_e + G(v) + F_v(J) \]  \hspace{1cm} (2.7)

where \( T_e \) is the electronic term energy, \( G(v) \) is the vibrational energy of the state labelled
by the quantum number \( v \), and \( F_v(J) \) is the rotational energy of the state labelled by the
quantum number \( J \). The subscript \( v \) in the rotational energy term takes into account the
coupling between the vibrational and rotational motions of the nuclei. In general \([17]\),

\[ G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + \omega_e y_e (v + \frac{1}{2})^3 + \omega_e z_e (v + \frac{1}{2})^4 + \cdots \]  \hspace{1cm} (2.8)

\[ F_v(J) = B_v J(J + 1) - D_v (J(J + 1))^2 + H_v (J(J + 1))^3 + \cdots \]  \hspace{1cm} (2.9)

with

\[ B_v = B_e - \alpha_e (v + \frac{1}{2}) + \gamma_e (v + \frac{1}{2})^2 + \cdots \]  \hspace{1cm} (2.10)

\[ D_v = D_e - \beta_e (v + \frac{1}{2}) + \delta_e (v + \frac{1}{2})^2 + \cdots \]  \hspace{1cm} (2.11)

Typically, \( T_e >> \omega_e >> B_e \). That is, the separation between different electronic states is
much greater than the separation of vibrational states which is, in turn, larger than the
separation of neighbouring rotational states. This is shown schematically in Figure 2.1.
The energy of an electronic-vibrational-rotational level is known as the rovibronic energy.

### 2.1 The Labelling of Electronic Wavefunctions

An infinite number of electronic potentials are possible depending upon the configurations
of the valence electrons. These potentials may be bound or repulsive; the latter are
called dissociative and molecules excited into these potentials break apart into constituent
atoms.

When several molecular electronic states are known, the letters X, A, B, ... and a, b, c, ... are used to label them. The state lowest in energy is traditionally called X. In itself, this labelling is insufficient to distinguish all the states and determine the allowed transitions from one electronic state to another. In order to do better, one must consider the symmetry properties of the electronic energy levels.

2.1.1 Electronic State Labels

The diatomic molecule, here visualized as a dumb-bell, has cylindrical symmetry; i.e. there is a symmetry axis along the line joining the two nuclei. As pointed out in References [17, 18], the electric fields in the molecule are symmetric about the internuclear axis. This leads to a precession of the total orbital angular momentum of the electrons, \( \mathbf{L} \), about the internuclear axis. Thus, in general, \( \mathbf{L} \), is not conserved but its projection along the internuclear axis, \( L_z \), (with eigenvalue \( M_L \)) is. The states with the same absolute value of \( M_L \) have the same energy. Using the convention of Reference [18] the label \( \Lambda = M_L \) is used to classify the different electronic states. (As is evident, states with \( \Lambda \neq 0 \) are doubly degenerate.) By analogy with atomic spectroscopy the electronic states are labelled according to:
Similarly, the total electronic spin angular momentum, $\mathbf{S}$, is the vector sum of the spins of the individual electrons. The corresponding quantum number, $S$, is integral or half-integral depending upon the whether the total number of electrons in the molecule is even or odd [17]. $\mathbf{S}$ is coupled to the internuclear axis by the magnetic field resulting from the orbital motion of the electrons. $\mathbf{S}$ precesses about the internuclear axis and its projection along the internuclear axis, $S_z$, (with eigenvalue $M_S$) is conserved. By convention $\Sigma = M_S$, which may take on $2S+1$ different values.

The quantity, $\Omega$, is defined as

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

(2.12)

In general, the different electronic states are labelled with the electron spin multiplicity, $2S+1$, indicated as a superscript to the left of the $|\Lambda|$ label and $\Omega$ is added as a subscript.

$$^{2S+1} |\Lambda|_{\Omega}$$

(2.13)

This labelling is sufficient for the most commonly encountered singlet, doublet, and triplet states. However, for quartet or higher spin multiplicity electronic states the $\Omega$ label may be insufficient to distinguish all of the different components. For example, consider a $^4\Pi$ state; here $|\Lambda| + \Sigma = 5/2, 3/2, 1/2,$ and $-1/2$ are the four distinct components.
Using Equation 2.13 to denote the states leads to the same label for the 1/2 and -1/2 components, even though they are distinct. Therefore, in such cases it is preferable to list the levels as,

\[ ^{2S+1} \Lambda_{\Lambda+\Sigma} \]  

(2.14)

2.2 Hund's Coupling Cases

In addition to the electron orbital, \( L \), and spin, \( S \), angular momenta, diatomic molecules possess the nuclear end over end rotation, \( R \), and nuclear spin, \( I \), angular momenta. Neglecting the nuclear spin for the moment, there are various different schemes for coupling \( L \), \( S \) and \( R \) together to form \( J \), the total angular momentum exclusive of nuclear spin. In general,

\[ J = R + L + S \]  

(2.15)

Usually, \( R \), \( L \), and \( S \) are not conserved. One describes the molecules in terms of the eigenvalues (represented by quantum numbers) of conserved quantities. The most appropriate angular momentum quantum numbers with which to describe the molecular system depend upon the manner in which the various momenta are coupled together. The different types of idealized couplings were first treated by Hund and are called Hund's coupling cases [17, 18]. The specific case applied to a given molecule depends upon the relative strengths of the couplings of the various angular momenta to the internuclear axis and to each other. For the purposes of this thesis only cases (a) and (c) will be briefly presented.

2.2.1 Hund's Case (a)

Hund's coupling case (a) is characterized by both \( L \) and \( S \) being strongly coupled to the internuclear axis. Thus, the operators \( L_z \) and \( S_z \) (the projections of electron orbital and
Figure 2.2: Hund's coupling case (a). The electron orbital angular momentum, $L$, and spin, $S$, are strongly coupled to the internuclear axis ($Z$ axis) making their projections, $\Lambda$ and $\Sigma$, respectively, good quantum numbers. $\Omega$ (see text) is then coupled to the rotation of the nuclei, $R$, to form $J$.

Spin angular momenta on the internuclear axis, respectively) have well-defined quantum numbers $\Lambda$ and $\Sigma$. In this description the mixing of different electronic levels is ignored; a vector $\Omega$ is defined whose magnitude is $|\Lambda + \Sigma|$ and whose direction lies along the internuclear axis. (See Figure 2.2.) $\Omega$ and $R$ are coupled together to form $J$. The energy levels are labelled by the quantum numbers $J$, $\Lambda$, $\Sigma$, and $\Omega$. The basis functions are written as

$$|\gamma \Lambda \Sigma J \Omega\rangle$$

(Here $\gamma$ is used as a label for the rest of the quantum numbers that have been omitted.) In this case the description of the electronic levels given in Equation 2.14 is the appropriate one.
Chapter 2. General Theoretical Considerations

2.2.2 Hund's Case (c)

For heavy molecules, like bromine or iodine, \( L \) and \( S \) are more strongly coupled to each other than to the internuclear axis. Thus, \( L \) and \( S \) form the resultant, \( J_a \), which precesses around the internuclear axis with a well defined projection along the internuclear axis. (See Figure 2.3.) As in case (a), the coupling between different electronic states is neglected and the projection of \( J_a \) is called \( \Omega \). \( \Omega \) is coupled to \( R \) to give \( J \). Here, \( \Lambda \) and \( \Sigma \) are no longer defined so that the energy levels are labelled by the quantum numbers \( J \) and \( \Omega \) and the basis functions are written,

\[
|\gamma J\Omega\rangle \tag{2.17}
\]

For molecules which follow case (c) coupling, (such as bromine and iodine), the electronic states are given labels such as, \( 0_g^+, 0_u^+, 1_u \), where the integer is the value of \( \Omega \).
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2.3 Electronic symmetries

For diatomic molecules, any plane passing through the two nuclei is a plane of symmetry. For $\Omega = 0$ states, a reflection of the electrons through this plane of symmetry multiplies the wavefunction by a phase factor $\lambda_v$. This operation will be called $\sigma_v$ here and it is easily demonstrated that $\lambda_v$ must be either 1 or $-1$.

$$\sigma_v |\psi\rangle = \lambda_v |\psi\rangle$$  \hspace{1cm} (2.18)

This allows the labelling $+$ or $-$ for these levels. (e.g. $^1\Sigma^+$, $^1\Sigma^-$, $^3\Pi_{0}$, etc.)

Parity, $P$, is the operation in which the spatial coordinates of all of the electrons and nuclei are reflected through the origin of the coordinate system. ($r_e \rightarrow -r_e$ and $R_N \rightarrow -R_N$). The parity of each level, $\lambda_P$, is well defined.

$$P |\psi\rangle = \lambda_P |\psi\rangle$$  \hspace{1cm} (2.19)

Here $\lambda_P = \pm 1$.

Finally, when the nuclei have the same charge (e.g. H$_2$ or HD), the molecular charge distribution has a center of symmetry half way between the two nuclei [17]. The reflection of all of the electrons through the center of symmetry is denoted here by the operator $R_{ug}$. Under this operation the electronic wavefunction again either changes sign or remains unchanged.

$$R_{ug} |\psi\rangle = \lambda_{ug} |\psi\rangle$$  \hspace{1cm} (2.20)

where $\lambda_{ug} = \pm 1$. The states with $\lambda_{ug} = -1$ are labelled $u$ and those with $\lambda_{ug} = 1$ are labelled $g$.

$$^1\Sigma^+_g, \ ^3\Pi_{0^+}, \ ^3\Pi_{1u}, \ldots$$  \hspace{1cm} (2.21)

It should be noted that for heteronuclear molecules such as $^{79}$Br$^{81}$Br, when the rotation and vibration of the nuclei are taken into account the $u$ and $g$ electronic levels
are mixed [19, 20, 21]. (For homonuclear molecules the u–g symmetry remains.) The mixing is usually weak so the u–g label will be retained here.

A final word about nomenclature: for both diatomic iodine and bromine the electronic states have been described in the literature according to the description 2.21. That is the X and B states are labelled $^1\Sigma_g^+$ and $^3\Pi_{0^+}$, respectively. Being relatively heavy molecules, the B states of iodine and of bromine are better described using a Hund's case (c) description, B $0^+$. In this thesis the prevalent Hund's case (a) description of the B state will be used but it should be understood that only the quantum number $\Omega$ is relevant. (i.e. $\Lambda$ and $\Sigma$ are not defined.)

2.4 Nuclear Spin

Each of the nuclei in a diatomic molecule may have nuclear spin, $i_x$, where $x (= 1$ or 2) labels the nucleus being referred to. A first approximation to the energy levels neglects any coupling between the nuclear spin and electronic motion. The total nuclear spin of a given state is the vector sum of the nuclear spins of the two nuclei, $I$.

$$I = i_1 + i_2$$  \hspace{1cm} (2.22)

The various nuclear spin states are represented in the coupled representation as

$$|\chi_N\rangle = |(i_1i_2)IM_I\rangle$$  \hspace{1cm} (2.23)

$$= \sum_{m_1,m_2} C(i_1,i_2,m_1,m_2;IM_I)|i_1m_1;i_2m_2\rangle$$  \hspace{1cm} (2.24)

where $C(i_1,i_2,m_1,m_2;IM_I)$ is the Clebsch-Gordan coupling coefficient [22] between the two representations. It is more convenient to use the symmetric 3-j symbols [22] which are simply related to the Clebsch-Gordan coefficients.

$$|(i_1i_2)IM_I\rangle = \sum_{m_1,m_2} (-1)^{i_2-i_1-M_I}\sqrt{2I+1} \begin{pmatrix} \begin{array}{ccc} i_1 & i_2 & I \\ m_1 & m_2 & -M_I \end{array} \end{pmatrix} |i_1m_1;i_2m_2\rangle$$
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Figure 2.4: The effect of interchanging nuclear spin and spatial coordinates. \( R(12) \) is equivalent to the operation \( \chi_{12} \) followed by \( R_{ug} \) and the parity operation, \( P \). The two nuclei are represented by the large black and a white circles, each with its own nuclear spins (arrow). The small black and white dots represent two different electrons.

\[
R(12) = \chi_{12} R_{ug} P
\]

(2.25)

When the nuclear spin interactions are neglected, the energy levels of different total nuclear spin states are degenerate.

The wavefunction of a homonuclear molecule either remains the same or changes sign when the (identical) nuclei are interchanged. That is,

\[
R(12)|\psi\rangle = \pm|\psi\rangle
\]

(2.26)

where \( R(1,2) \) denotes the operator which interchanges the nuclear spatial and spin coordinates. As illustrated in Figure 2.4, \( R(12) \) is equivalent to

\[
R(12) = P \cdot R_{ug} \cdot \chi_{12}
\]

(2.27)
In Equation 2.27 $P$ is the parity operation, $R_{ug}$ is the reflection of the electronic coordinates through the center of symmetry of the molecule, and $\chi_{12}$ is the operator which interchanges the nuclear spin coordinates. Therefore to deduce the effect of $R(12)$ on the wavefunction of a homonuclear molecule one needs to know the effect of these three operations on the wavefunction.

The results of the operations $P$ and $R_{ug}$ on a wavefunction were defined previously in Equations 2.19 and 2.20, respectively. From Reference [22]

\[
\begin{pmatrix}
i_1 & i_2 & I \\
m_1 & m_2 & -M_I
\end{pmatrix}
= (-1)^{i_1+i_2+I}
\begin{pmatrix}
i_2 & i_1 & I \\
m_2 & m_1 & -M_I
\end{pmatrix}
\]

(2.28)

It follows, then, that the effect of $\chi_{12}$ on the nuclear spin wavefunction described in Equation 2.25 is,

\[
\chi_{12}|(i_1i_2)IM_I\rangle = (-1)^{i_1+i_2+I}|(i_2i_1)IM_I\rangle
\]

(2.29)

Thus,

\[
R(12)|\psi\rangle = P \cdot R_{ug} \cdot \chi_{12}|\psi\rangle
= \lambda_P \lambda_{ug} (-1)^{i_1+i_2+I}|\psi\rangle
= \pm |\psi\rangle
\]

(2.30) (2.31) (2.32)

For nuclei, like bromine and iodine, with half integer nuclear spin, the wavefunction changes sign under $R(12)$. This allows one to rewrite Equation 2.32 as

\[
-|\psi\rangle = \lambda_P \lambda_{ug} (-1)^{i_1+i_2+I+J}|\psi\rangle
\]

(2.33)

From Equation 2.33 and the fact that $\lambda_P = (1)^J$ for the $\Omega = 0^+$ electronic states of interest here, if follows that

\[
-1 = \lambda_{ug} (-1)^{i_1+i_2+I+J}
\]

(2.34)
Equation 2.34 can be simplified knowing that \( i_1 (= i_2) \) is half integral. This gives,

\[
1 = \lambda_{ug} (-1)^{I+J}
\]  

(2.35)

Consequently, in the \( X \; ^1\Sigma_g^+ \) electronic state, for the even rotational states \( J \) only the even nuclear spin states \( I \) are populated. For the odd \( J \) states only odd \( I \) levels are populated. The inverse is true for the \( B \; ^3\Pi_0^+ \) electronic levels. This correlation between the nuclear spin and the rotational state leads to a further label for homonuclear diatomic molecules. The rotational states with the higher nuclear spin degeneracy are called ortho-levels while the rotational levels with the lower degeneracy are called para-levels. To give an example, consider \(^{79}\text{Br}_2\) in which each nucleus has nuclear spin 3/2. In the \( X \; ^1\Sigma_g^+ \) electronic state the para-levels are the even \( J \) levels coupled to the \( I = 0 \) and 2 nuclear spin states, and the ortho-levels are the odd \( J \) states which are coupled to the \( I = 1 \) and 3 nuclear spin states.

For heteronuclear molecules there are no such ortho-para considerations and each rotational level has the full complement of nuclear spin states (e.g. for \(^{79}\text{Br}^{81}\text{Br} \) \( I = 0, 1, 2, \) and 3).

### 2.5 Hyperfine Interactions

The hyperfine effects arise from the interaction of the nuclear multipole moments with the electric and magnetic fields produced by the electrons and other nuclei in the molecule. For a diatomic molecule where both nuclei have the same nuclear spin, \( i_1 = i_2 = i_z \), the two nuclear spins are coupled together to form the total nuclear spin, \( I \). In turn, the total nuclear spin is coupled to \( J \) to form the total angular momentum,

\[
F = I + J
\]  

(2.36)
The hyperfine interactions result in the splitting of the rotational states into several levels each labelled by a quantum number $F$. The separations of the hyperfine levels are usually much smaller than the separation of the rotational states.

### 2.5.1 Hyperfine Symmetries

Symmetry considerations allow one to deduce some of the properties of the hyperfine Hamiltonian, $H_{hf}$, without knowing its explicit form. To obtain the hyperfine energies, one calculates the matrix elements

$$\langle \psi | H_{hf} | \psi' \rangle$$

(2.37)

in the uncoupled $I$ and $J$ basis and then diagonalizes the resulting matrix to obtain the eigenvalues, $E_F$, and eigenstates, $|\psi_F\rangle$. The hyperfine Hamiltonian must have positive parity. That is,

$$H_{hf} = (PH_{hf}P^\dagger)$$

(2.38)

($P^\dagger$ is the hermitian conjugate of $P$.) Equation 2.38 implies that the only non-zero hyperfine interactions are those electric and magnetic terms which have positive parity; namely the electric $2k$-pole and magnetic $(2k+1)$-pole terms [18].

The hyperfine Hamiltonian for a diatomic molecule can be expressed as the sum of the interactions between nucleus 1 and the electrons, $H_{hf}(1)$, between nucleus 2 and the electrons, $H_{hf}(2)$, and between nucleus 1 and nucleus 2, $H_{hf}(1,2)$.

$$H_{hf} = H_{hf}(1) + H_{hf}(2) + H_{hf}(1,2)$$

(2.39)

The behaviour of $H_{hf}(1)$ and $H_{hf}(2)$ is different from that of $H_{hf}(1,2)$. The first two, because they act on both the electronic and nuclear coordinates, can couple different electronic states, while $H_{hf}(1,2)$, which acts only on the nuclear coordinates, is diagonal.
in the molecular electronic state. When calculating the hyperfine structure of the rovibronic levels within an electronic state, both the nuclear-electronic and nuclear-nuclear interaction must be taken into account. However, hyperfine predissociation, the coupling of a bound and a dissociative electronic state can only be accomplished through $H_{hf}(1)$ and $H_{hf}(2)$. The electron–nuclear hyperfine interactions are considerably larger than the nuclear–nuclear terms [23, 24].

For homonuclear molecules, upon interchange of the nuclear spatial and spin coordinates,

$$R(12)H_{hf}(1)R(12)^\dagger = H_{hf}(2)$$ (2.40)

Remember that the nuclear interchange operator, $R(12) = R_{ug} \cdot \chi_{12} \cdot P$. Hence,

$$H_{hf}(2) = R(12)H_{hf}(1)R(12)^\dagger$$

$$= R_{ug} \chi_{12} (P H_{hf}(1) P^\dagger) \chi_{12}^\dagger R_{ug}^\dagger$$

$$= R_{ug} \chi_{12} H_{hf}(1) \chi_{12}^\dagger R_{ug}^\dagger$$ (2.41)

From Equations 2.31 and 2.41 it follows that the matrix element of the hyperfine Hamiltonian, $H_{hf}(1)$, between the states $|\psi'I\rangle$ and $|\psi I\rangle$ obeys the condition

$$\langle \psi'I | H_{hf}(2) | \psi I \rangle = (-1)^{I'+I'} \lambda_{ug}^\prime \lambda_{ug} \langle \psi'I | H_{hf}(1) | \psi I \rangle$$ (2.42)

The labels $I$ and $I'$ are the total nuclear spin quantum numbers associated with the states $|\psi I\rangle$ and $|\psi'I\rangle$, respectively.

Similarly for the nuclear–nuclear interactions,

$$R(12)H_{hf}(1,2)R(12)^\dagger = H_{hf}(1,2)$$ (2.43)

The $H_{hf}(1,2)$ terms involve only the nuclear coordinates and therefore must be invariant with respect to $R_{ug}$, i.e.

$$R_{ug} H_{hf}(1,2) R_{ug}^\dagger = H_{hf}(1,2)$$ (2.44)
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Similarly, it follows from the definition of $R(1, 2)$, Equation 2.38, and Equation 2.44, that

$$\chi_{12} H_{hf}(1, 2) \chi_{1,2}^\dagger = H_{hf}(1, 2)$$  \hspace{1cm} (2.45)

This leads to the following condition on the matrix elements:

$$\langle \psi' I' | H_{hf}(1, 2) | \psi I \rangle = (-1)^{I+I'} \delta(\lambda_{ug}, \lambda'_{ug}) \langle \psi' I' | H_{hf}(1, 2) | \psi I \rangle$$  \hspace{1cm} (2.46)

As a consequence of Equation 2.42, electronic $u$ and $g$ states can be coupled via

$$\langle \psi' u I' | H_{hf}(1) + H_{hf}(2) | \psi g I \rangle = \left(1 + (-1)^{I+I'}\right) \langle \psi' u I' | H_{hf}(1) | \psi g I \rangle$$  \hspace{1cm} (2.47)

Thus $H_{hf}(1)$ and $H_{hf}(2)$ can couple $u$ and $g$ electronic states if $I + I'$ is odd. This means that ortho $u$ states are mixed with para $g$ states and vice-versa. On the other hand, the ortho-para character of the states is preserved when a $g$ (or $u$) state interacts with another $g$ (or $u$) state.

As mentioned in Section 2.3, for $\Omega = 0$ electronic states, $\sigma_v$, a reflection of the electrons in a plane containing the nuclei is a symmetry operation. States, $|\psi, \Omega = 0, \lambda_v\rangle$, that have $\lambda_v = \pm 1$ are labelled

$$|\psi, \Omega = 0, \lambda_v\rangle = |\psi_{\Omega = 0, \lambda_v}\rangle = |\psi_{0\pm}\rangle$$  \hspace{1cm} (2.48)

The $\sigma_v$ symmetry operator can be applied to the hyperfine Hamiltonian matrix elements between two $\Omega = 0$ states.

$$\langle \psi_{0\pm} | H_{hf} | \psi'_{0\pm} \rangle = \langle \psi_{0\pm} | (\sigma_v^\dagger \sigma_v) H_{hf} (\sigma_v^\dagger \sigma_v) | \psi'_{0\pm} \rangle = \lambda'_v \lambda_v \langle \psi_{0\pm} | (\sigma_v H_{hf} \sigma_v^\dagger) | \psi'_{0\pm} \rangle$$  \hspace{1cm} (2.49)
Equation 2.49 indicates that of the hyperfine matrix elements that couple two $\Omega = 0$ states, the only ones which can be nonzero are those which satisfy:

$$H_{hf} = \chi'_u \chi_v \left( \sigma_v H_{hf} \sigma_v^\dagger \right)$$

(2.50)

The $\sigma_v$ operation changes the sign of the magnetic dipole operators which couple two $\Omega = 0$ electronic states while the electric quadrupole operators are unchanged. Therefore, the magnetic dipole terms can only couple $0^+ \leftrightarrow 0^-$ levels and the electric quadrupole terms couple only $0^+ \leftrightarrow 0^+$ and $0^- \leftrightarrow 0^-$ electronic states [25].

### 2.6 Calculation of Hyperfine Energies

A nucleus with spin $i_1$ can take on $(2i_1 + 1)$ different orientations in an external field. Therefore to describe completely the energy level structure of the nucleus one needs only $(2i_1 + 1)$ labels or properties [18]. One label is taken up by the total charge of the nucleus, $Z$, leaving $2i_1$ labels. These are the electric and magnetic multipoles of the nucleus. Therefore the hyperfine Hamiltonian can be expressed as the sum of the multipole interactions,

$$H_{hf} = H_{MD} + H_{EQ} + H_{MO} + \cdots$$

(2.51)

where $H_{MD}$ represents the magnetic dipole interactions, $H_{EQ}$ represents the electric quadrupole interactions, $H_{MO}$ represents the magnetic octupole interactions, and so on. Although a nucleus having spin $i_1$ can have up to $2^{2i_1}$ multipoles, the resolution of most experimental data in visible spectroscopy is insufficient to observe anything but the magnetic dipole and electric quadrupole effects. Consequently these are the only two hyperfine interactions that will be discussed.
2.6.1 Hyperfine Interactions Between the Electrons and the Nuclei

The interactions between each nucleus and the electrons will be discussed first. The magnetic dipole terms are the interaction between the magnetic dipole moment of the nucleus, \( \mu_m(x) \) and the magnetic fields produced by the electrons, \( \mathbf{H} \).

\[
H_{MD}(x) = \sum_x -\mu_m(x) \cdot \mathbf{H}
\]  

(2.52)

The hyperfine magnetic dipole Hamiltonian is made up of three terms \([23, 25]\).

\[
H_{MD}(x) = H_{LI}(x) + H_{SI}(x) + H_{FI}(x)
\]  

(2.53)

(Here \( x (= 1 \text{ or } 2) \) is a label for the nucleus.) The first term, the nuclear spin–orbit term, is the interaction of the nuclear spin with the electron orbital angular momentum, \( l_e(x) \). (To simplify the discussion \( x = 1 \) is used.)

\[
H_{LI}(1) = -\sum_e 2g_i \mu_B \mu_N \left( \frac{\mu_0}{4\pi} \right) \frac{i_1 \cdot l_e(1)}{r_{1e}^3}
\]  

(2.54)

(In the equations presented here, all units are in MKS. The conventions of Reference \([23, 25]\) are adopted; namely, the Bohr magneton is negative, \( \mu_B < 0 \), the nuclear magneton is positive, \( \mu_N > 0 \), and the charge of the electron is \( e \), where \( e < 0 \). The magnetic moment of the nucleus is \( \mu_m(x) = g_i \mu_N i_1 \), where \( g_i \) is the nuclear g-factor of nucleus 1.) Here,

\[
r_{1e} = r_e - r_1
\]  

(2.55)

where \( r_e \) is the position of the electron and \( r_1 \) is the position of nucleus 1. As well,

\[
h_1 l_e(1) = r_{1e} \times p_e
\]  

(2.56)

The second term in Equation 2.53 is the nuclear spin–electron spin interaction, a tensor dipole–dipole coupling between the nuclear spin and the electron spins, \( s_e \),

\[
H_{SI}(1) = -\sum_e g_s g_i \mu_B \mu_N \left( \frac{\mu_0}{4\pi} \right) \frac{3(s_e \cdot r_{1e})(i_1 \cdot r_{1e}) - (i_1 \cdot s_e)(r_{1e} \cdot r_{1e})}{r_{1e}^5}
\]  

(2.57)
(\(g_e\) is the electron spin g-factor.) The third is the Fermi contact term,

\[
H_{FI}(1) = \sum_\varepsilon g_\varepsilon g_\varepsilon 1 \mu_B \mu_N \left( \frac{\mu_0}{4\pi} \right) \left( \frac{8\pi}{3} \right)^{1} i_1 \cdot s_{ie} \delta(r_{1e})
\]  

(2.58)

Following References [23, 25], each of the magnetic dipole interactions has the same form and can be re-expressed as

\[
H_{MD}(1) = \sum_\varepsilon \sum_q (-1)^q Q_q^1(i_1) V_{-q}^1(j_e(1))
\]  

(2.59)

[Here, \(j_e(1) = l_e(1) + s_e(1)\).] \(Q_q^1(i_1)\) and \(V_{-q}^1(j_e(1))\) are spherical tensor operators of rank 1 constructed from \(i_1\) and \(j_e(1)\), respectively.

The electric quadrupole contributions to \(H_{hf}(x)\) are from the interactions of the quadrupole moment of the each nucleus, \(Q(x)\), with the gradient of the electric field of the electrons, \(\nabla E\). For nucleus 1,

\[
H_{EQ}(1) = \sum_\varepsilon \sum_q (-1)^q Q_q^2(i_1) V_{-q}^2(j_e(1))
\]  

(2.60)

\(Q_q^2(i_1)\) and \(V_{-q}^2(j_e(1))\) are spherical tensor operators of rank 2. They arise from the multipole expansion of the Coulomb potential. It can be shown that [23, 25]

\[
Q_q^2(1) = \sum_p |e|r_p^2 C_q^2(\theta_p, \phi_p)
\]  

(2.61)

The sum over \(p\) represents the sum over the charge distribution in nucleus 1. \(r_p, \theta_p, \text{ and } \phi_p\) are the spherical coordinates of proton, \(p\), of nucleus 1. Similarly

\[
V_{-q}^2(1) = \frac{e}{4\pi \varepsilon_0 r_{1e}^3} C_q^2(\theta_{1e}, \phi_{1e})
\]  

(2.62)

Here \(\theta_{1e}\) and \(\phi_{1e}\) are the angular coordinates of the vector \(r_{1e}\). In Equations 2.61 and 2.62

\[
C_q^2(\theta, \phi) = \sqrt{\frac{4\pi}{5}} Y_q^2(\theta, \phi)
\]  

(2.63)
and the $Y_{q}^{2}(\theta, \phi)$ are spherical harmonics.

In summary, both the magnetic dipole and electric quadrupole interactions between the electrons and the nuclei can be expressed as

$$H^{k}(x) = \sum_{e} \sum_{q} (-1)^{q} \mathcal{Q}_{q}^{k}(l_{x}) \mathcal{V}_{q}^{k}(j_{e}(x))$$

(2.64)

where $k = 1$ is the magnetic dipole interaction and $k = 2$ is the electric quadrupole interaction.

The matrix elements of the electron–nuclear hyperfine interactions can be worked out in terms of the coupled basis set.

$$M_{h_{f}}^{k}(x, F', v', F, v) = \langle \gamma'(J' I') \Omega' v' F' M' | H^{k}_{h_{f}}(x) | \gamma(J I) \Omega v F M \rangle$$

(2.65)

These can be expressed as the product of a reduced matrix element of intrinsic molecular parameters, $f_{k}(x, \Omega', v', \Omega, v)$, and calculable rotational and nuclear factors. The matrix elements have been worked out previously for homonuclear iodine [23, 25] and may be applied to $^{79}\text{Br}_{2}$, $^{81}\text{Br}_{2}$, and $^{79}\text{Br}_{81}\text{Br}$ using $i_{1} - i_{2} = 3/2$.

$$M_{h_{f}}^{k}(1, F', v', F, v) = \delta_{F,F'} \delta_{M,M'} (-1)^{k+i_{1}+i_{2}+F+I'+J+J'} N_{k} f_{k}(1, \Omega', v', \Omega, v)$$

(2.66)

where

$$N_{k} = \sqrt{(2I + 1)(2I' + 1)(2J + 1)(2J' + 1)}$$

$$\times \left( \begin{array}{ccc} J' & k & J \\ -\Omega' & \Delta \Omega & \Omega \end{array} \right) \left\{ \begin{array}{ccc} i_{2} & i_{1} & I \\ k & I' & i_{1} \end{array} \right\} \left\{ \begin{array}{ccc} F & I' & J' \\ k & J & I \end{array} \right\}$$

(2.67)

The total matrix element for the electron-nuclei interactions can then be written:

$$M_{h_{f}}^{k}(F, \Omega', \Omega) = M_{h_{f}}^{k}(1, F, \Omega', \Omega) + M_{h_{f}}^{k}(2, F, \Omega', \Omega)$$

$$= \delta_{F,F'} \delta_{M,M'} (-1)^{k+i_{1}+i_{2}+F+I'+J+J'} N_{k}$$

$$\times \left( f_{k}(1, \Omega', v', \Omega, v) + \epsilon_{u_{g}}(-1)^{I'+J'} f_{k}(2, \Omega', v', \Omega, v) \right)$$

(2.68)
Here,

\[ \epsilon_{ug} = \begin{cases} 
1 & \text{if both states are } u \text{ or } g \\
-1 & \text{if one state is } u \text{ and the other is } g 
\end{cases} \]

(The quantum number \( F' \) has been dropped owing to the delta function in Equation 2.66.)

The explicit forms for \( f_1(1, \Omega', v', \Omega, v) \) and \( f_2(1, \Omega', v', \Omega, v) \) have been given by Reference [23] in terms of Hund’s case (a) coupling. Since the magnetic terms do not directly contribute to the hyperfine structure of the \( X \,^1\Sigma_g^+ \) and \( B \,^3\Pi_u^+ \) states of \( ^79\text{Br}_2 \), \(^81\text{Br}_2 \), and \(^79\text{Br}^81\text{Br} \) they are expressed in a condensed form,

\[
f_1(1, \Omega', v', \Omega, v) = (-1)^{\Omega'} B(1, S', S, \Lambda', \Lambda, \Omega', \Omega, v', v) \sqrt{i_1(i_1+1)(2i_1+1)} \quad (2.69)
\]

\( B(1, S', S, \Lambda', \Lambda, \Omega', \Omega, v', v) \) is the sum of three different reduced matrix elements corresponding to the nuclear spin-electron orbital interaction, the nuclear spin-electron spin interaction and the Fermi contact term defined in Equations 2.54 through 2.58.

For the electric quadrupole term

\[
f_2(1, \Omega', v', \Omega, v) = (-1)^{\Omega'} \frac{|e| q_{\Omega\Omega} Q(1)}{4} \left[ \frac{(2i_1+3)(2i_1+2)(2i_1+1)}{2i_1(2i_1-1)} \right]^{1/2} \quad (2.70)
\]

Here,

\[
Q(1) = \langle i_1 i_1 | \sum_p (3z_p^2 - r_p^2) | i_1 i_1 \rangle \quad (2.71)
\]

This is the electric quadrupole moment of nucleus 1. (As in Equation 2.61, the sum over \( p \) represents the summation over the protons in nucleus 1.)

\[
\frac{q_{\Omega\Omega}}{2} = \langle \Omega' \nu' || \sum_e \frac{e}{4\pi \epsilon_0 r_{1e}^3} C_{\Delta \Omega}^2(\theta_{1e}, \phi_{1e}) || \Omega \nu \rangle \quad (2.72)
\]

\( q_{\Omega\Omega} \) is the electric field gradient produced by the electrons at nucleus 1. (Remember that \( e \) is the charge of the electron so that \( e < 0 \).) The constant \( |e| q_{\Omega\Omega} Q(x) \) is referred to as \( eqQ(x) \). (Note that the \( e \) in \( eqQ(x) \) is not the electron charge but \( |e| \).)
2.6.2 Hyperfine Interactions Between the Nuclei

The two nuclei interact magnetically and electrically in a manner analogous to the electrons and the nuclei. The magnetic interactions occur in two forms. First, the nuclear magnetic moment of nucleus 1 is coupled to the magnetic field produced by nucleus 2 as the molecule rotates in analogy with the $H_{LI}$ term in the previous section. In this case, $I_e$ is replaced by $R$, the rotational angular momentum of the nuclei about the center of mass of the molecule.

$$ R = J - (L + S) $$  \hspace{1cm} (2.73)

This gives [23],

$$ H_{IK(1,2)} = 2(2g_I - 1)\mu_N^2 \frac{\mu_0}{4\pi} \frac{Z}{M_N} \left( \frac{I \cdot J}{R_{12}^3} - \frac{I \cdot (L + S)}{R_{12}^3} \right) $$  \hspace{1cm} (2.74)

where $R_{12}$ is the internuclear separation. Second, there is a nuclear dipole–dipole interaction analogous to the electron spin–nuclear spin interaction of Equation 2.75.

$$ H_{i_1i_2} = g_1g_2\mu_N^2 \frac{\mu_0}{4\pi} (i_1 \cdot i_2)(R_{12} \cdot R_{12}) - 3(i_1 \cdot R_{12})(i_2 \cdot R_{12}) $$  \hspace{1cm} (2.75)

The electric quadrupole terms are the interactions of the quadrupole moment of nucleus 1 with the gradient of the electric field produced by the charge distribution of nucleus 2 and vice versa.

$$ H_{EQ(1,2)} = \sum_q (-1)^q \left[ Q_q^2(1)V_q^2(1,2) + Q_q^2(2)V_q^2(2,1) \right] $$  \hspace{1cm} (2.76)

$Q_q^2(x)$ was defined in Equation 2.61 and

$$ V_q^2(1,2) = \frac{Z|e|}{4\pi \epsilon_0 R_{12}^3} C_q^2(\theta_{12}, \phi_{12}) $$  \hspace{1cm} (2.77)
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The matrix elements for $H_{EQ}(1,2)$,

$$M_{h_f}^2(1,2)(F,\Omega',\Omega) = \langle \gamma'(J'I')\Omega'F'M'|H_{EQ}(1,2)|\gamma(JI)\Omega FM\rangle$$  \hspace{1cm} (2.78)

are very similar to those of the corresponding electron–nuclear interaction,

$$M_{h_f}^2(1,2)(F,\Omega',\Omega) = \delta_{F,F'}\delta_{M,M'}\delta_{\Omega'}\Omega(-1)^{k+i_1+i_2+F+I+I'+\Omega}$$

$$\left[ \frac{(2i_1+3)(2i_1+2)(2i_1+1)}{2i_1(2i_1-1)} \right]^{\frac{3}{2}} \sqrt{(2I+1)(2I'+1)(2J+1)(2J'+1)}$$

$$\left( \begin{array}{ccc} J' & 2 & J \\ -\Omega & 0 & \Omega \end{array} \right) \left\{ \begin{array}{ccc} i_2 & i_1 & I \\ 2 & I' & i_1 \end{array} \right\} \left\{ \begin{array}{ccc} F & I' & J' \\ 2 & J & I \end{array} \right\}$$

$$\left( \frac{Ze}{2} \right) (Q(1) + (-1)^{I+J'}Q(2)) \langle \Omega v'| \frac{1}{4\pi\epsilon_0 R_{12}^3} |\Omega v\rangle$$  \hspace{1cm} (2.79)

(The definition of $Q(x)$ was given in Equation 2.71.) The matrix elements $M_{h_f}(F,\Omega,\Omega)$ in Equation 2.68 and $M_{h_f}^2(1,2)(F,\Omega,\Omega)$ have exactly same dependence on the quantum numbers, $J, J', I, I'$, and $F$.

The magnetic term of the most interest in this work is the first part of $H_{IR}(1,2)$, namely

$$H_{IJ}(1,2) = (4g_I - 2)\mu_N^2 \frac{\mu_0}{4\pi M_N} \frac{Z}{R_{12}^3} \left( \mathbf{I} \cdot \mathbf{J} \right)$$  \hspace{1cm} (2.80)

This has matrix elements,

$$M_{sr}(F,\Omega',\Omega) = \delta_{\Omega'\Omega}\delta_{I'I}\delta_{JJ'}\delta_{FF'}\delta_{MM'} \frac{C_{sr}^1}{2} (F(F+1) - J(J+1) - I(I+1))$$  \hspace{1cm} (2.81)

where

$$C_{sr}^1 = (4g_I - 2)\mu_N^2 \frac{\mu_0}{4\pi M_N} \frac{Z}{R_{12}^3} \langle \Omega v'| \frac{1}{R_{12}^3} |\Omega v\rangle$$  \hspace{1cm} (2.82)

Other electronic states interact with the electronic states being studied. As is pointed out by Broyer et al [23], many of these interactions, treated using second order perturbation theory, lead to energy shifts which have the same dependencies on the quantum
numbers $F, J, J', I, I'$ as do the shifts produced by the matrix elements, $M^k_{FJ}(x, F', \Omega', \Omega)$ and $M_{sr}(F, \Omega', \Omega)$. These two types of shifts are not easily separated. The net effect is that the measured hyperfine parameters are mixtures of arising from the two different effects.

In particular, the second order terms which behave the same way as $M_{sr}(F, \Omega', \Omega)$ are important. It can be shown [23] that the nuclear–spin rotation contribution of $H_{1J}(1, 2)$ in Equation 2.80 is negligible. The observed nuclear spin–rotation effects in the B $^3\Pi_{0^+}$ state of bromine are due primarily to the second order interactions between the B state and other electronic states [6, 23].

The selection rules for the various hyperfine Hamiltonians are summarized in Table 2.1. As noted previously, for the homonuclear bromine isotopomers, only the I and I±2 nuclear states interact in the $X^1\Sigma^+_g$ and in the B $^3\Pi_{0^+}$ electronic states. In addition, for $\Omega = 0$ electronic states, only the J and J±2, ±4, ±6, ... levels are coupled together.

To deduce the hyperfine energies of the $X^1\Sigma^+_g$ and B $^3\Pi_{0^+}$ states of bromine, one begins by working out the matrix representation, $M$, of each term of the Hamiltonian in terms of the basis set, $|\gamma(JI)\Omega \nu FM\rangle$. These include the rovibronic $M_{rv}$, the nuclear spin–rotation $M_{sr}$, and hyperfine electric quadrupole $M_{EQ(1)} + M_{EQ(2)} + M_{EQ(1,2)}$, 

Table 2.1: The selection rules for the magnetic dipole, ($H'(x)$, and $H'(x, 2)$) and the electric quadrupole ($H'(x)$, and $H'(x, 2)$) hyperfine Hamiltonians.
matrices. It should be noted that for $^{79}\text{Br}^{81}\text{Br}$ the nuclear spin–rotation interaction is really characterized by two constants, one for each nucleus. However, for the spectra observed in this research the nuclear spin–rotation contribution to the energy is extremely small and, therefore, this interaction will be treated in the same manner for both the homonuclear and heteronuclear molecules. Then,

$$
\mathcal{M} = \mathcal{M}_{rv} + \mathcal{M}_{sr}
$$

$$
+ \mathcal{M}_{\text{EQ}(1)} + \mathcal{M}_{\text{EQ}(2)} + \mathcal{M}_{\text{EQ}(1,2)}
$$

(2.83)

In practice, the final electric quadrupole term is much smaller than $\mathcal{M}_{\text{EQ}(1)}$ and $\mathcal{M}_{\text{EQ}(2)}$. It also has the same explicit dependence on the quantum numbers. Therefore it is absorbed into them to give,

$$
\mathcal{M} = \mathcal{M}_{rv} + \mathcal{M}_{sr}
$$

$$
+ \mathcal{M}_{\text{EQ}(1)} + \mathcal{M}_{\text{EQ}(2)}
$$

(2.84)

The matrix, $\mathcal{M}$, is diagonalized for each hyperfine level to produce the hyperfine energy, $E(F,\epsilon)$, and the corresponding eigenfunction,

$$
|F\epsilon M\rangle = \sum_{JI} \alpha_{JIE\epsilon}^{F} |\gamma(JI)\Omega v FM\rangle
$$

(2.85)

The label $\epsilon$ is adopted to remind the reader that more than one hyperfine level may have the same quantum number $F$.

2.7 Transition Intensities

In this work spectra were taken in a molecular beam apparatus using laser induced fluorescence (LIF). That is, the molecules were excited with a tunable laser and then relaxed back down to the ground state by emitting a photon. A fraction of these photons was collected and detected with a photomultiplier. It is important to appreciate that
absorption and fluorescence measurements are not the same. In the absence of external electric or magnetic fields absorption measurements are independent of the polarization of the laser field exciting the molecules. Fluorescence, on the other hand, is sensitive to the polarization of the laser. In addition, fluorescence measurements also depend on the positioning of the detector, and the amount of solid angle collected. A simple way of seeing this is to imagine the detector and emitter arranged as shown in Figure 2.5, and to treat the molecules as classical dipoles. A classical dipole oscillating in the Z direction will radiate primarily in the X-Y plane. Therefore, if a molecule, sitting at the origin, is excited by a laser beam polarized in the Z direction, one expects to observe relatively little fluorescence at the detector. Conversely, if the molecule is excited by a laser polarized in the Y direction, the dipole radiates primarily in the X-Z plane and one expects to observe a strong signal. Thus, the fluorescence signal measured should depend upon the laser polarization. Furthermore, in the limit that all of the fluorescent light is collected (i.e. one observes over 4π steradians) the signal observed must be independent of the laser polarization just as for the absorption signal.

In the quantum mechanical treatment of the problem, such polarization effects persist and are important especially when one observes transitions between low J levels. If one is interested in making measurements of relative intensities of LIF spectral features then the laser polarization, the detector geometry, and the amount of solid angle observed must be taken into account.

2.7.1 Allowed Transitions

The laser induced transitions studied here were the electric dipole allowed ones. The selection rules for an electric dipole transition are, [17]
Figure 2.5: With the coordinate system shown above, the laser beam propagates along the X axis, the molecular beam travels along the Y axis and the detector is situated along the Z axis.
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\[ 0^+ \leftrightarrow 0^+ \]
\[ 0^- \leftrightarrow 0^- \]
\[ u \leftrightarrow g \]
\[ u(g) \not\leftrightarrow u(g) \]
\[ \Delta J = 0, \pm 1 \]
\[ \Delta J \neq 0 \text{ for } \Omega = 0 \leftrightarrow \Omega = 0 \]
\[ \Delta S = 0 \]

The + and - refer to \( \sigma_v \) symmetry here. The transitions studied were between hyperfine levels of the \( X \ 1\Sigma_g^+ \) and \( B \ 3\Pi_{\sigma g}^+ \) electronic states of bromine. This adds the selection rules \( \Delta F = 0, \pm 1 \) and \( \Delta I = 0 \).

2.7.2 Fluorescence

Consider the geometry shown in Figure 2.5, in which the molecular beam is travelling along the Y direction, the laser radiation propagates along the X axis, and the detector is on the Z axis. (This coordinate system is chosen so as to simplify the calculations.) With this arrangement the laser may be polarized either in the Y or Z directions. To be detected, the molecules must emit photons which travel into the detector, namely in the Z direction. Therefore the emitted light observed must be polarized in the X–Y plane only.

Before discussing the details of the calculations, it is instructive to consider a simple system composed only of the rotational states \( J'' = 0 \) in the X state and \( J' = 1 \) in the B state with no hyperfine structure. With the laser polarized in the Z direction the only allowed excitation transition is \( |J'' = 0, M'' = 0\rangle \rightarrow |J' = 1, M' = 0\rangle \). In order to be detected, the emitted light must be polarized in the X–Y plane. This implies a \( \Delta M = \pm 1 \) transition. However, this would mean making the transition \( |J' = 1, M' = \)}
0) → |J'' = 0 M'' = ±1) which is ruled out. Therefore, no fluorescent light is observed. When the laser light is polarized along the Y direction, the excitation transitions |J'' = 0 M'' = 0) → |J' = 1 M' = ±1) occur. As before, to be detected, the emitted light must be polarized in the X-Y plane implying decay transitions ΔM = ±1. Namely, |J' = 1 M' = ±1) → |J'' = 0 M'' = 0) and fluorescent light should be detected. In this simplified example, one recovers the classical result that the LIF signal depends upon the polarization of the laser light. Of course, the existence of hyperfine structure and other rotational levels for the molecules to decay to reduces the polarization sensitivity but it is not completely eliminated.

This example offers another useful insight. Consider the coordinate system rotated as shown in Figure 2.6, with the laser beam propagating along the Z'-axis, the detector on the Y'-axis, and the molecular beam travelling along the X'-axis. The results of the physical measurements must be independent of the coordinate system used. Therefore, when the laser is polarized along the detector axis (which was the Z-axis of Figure 2.5 and is now the Y'-axis) one should observe exactly the same result as above, namely no signal. With the new coordinate system the excitation transitions are ΔM = ±1. i.e. |00) → |1±1). To be observed, the emitted light must be polarized along the X' or Z' axes, giving ΔM = 0, ±1 decay transitions. The emitted light polarized in the Z' direction (ΔM = 0 or |1 ± 1) → |0 ± 1)) is ruled out, while the emitted light polarized in the X' direction (ΔM = ±1) is not. This would seem to imply that one expects to observe some fluorescence with Y'-polarized light, in contradiction with the previous calculation. (See Figure 2.6.) In reality there is no difficulty because the observed signal is the square of the sum of the amplitudes of the transitions [|00) → |11) → |00)] and [|00) → |1-1) → |00)]. When the laser is polarized along the Y'-axis (parallel to the detector) these amplitudes cancel out and they add up when the laser is polarized along the X'-axis (perpendicular to the detector), in exact agreement with the results of the (X,Y,Z) coordinate system.
Figure 2.6: The laser–detector–emitter system using a different coordinate system. The molecular beam is travelling along the $X'$ axis. With this arrangement, the transitions $\Delta M = \pm 1$ from the ground state to upper states and back down, shown for the X state $J''=0$ and B state $J'=1$ system, are allowed for both laser polarization directions.
Chapter 2. General Theoretical Considerations

With the \((X',Y',Z')\) system, one has an excellent demonstration of the 2 slit problem in which the slits here correspond to the \(M' = \pm 1\) levels of the upper state and the phase difference between the two paths, \([|00\rangle \rightarrow |11\rangle \rightarrow |00\rangle\) and \([|00\rangle \rightarrow |1-1\rangle \rightarrow |00\rangle\), is determined by the relative orientations of the detector and laser beam polarization.

The fluorescent light signal detected is proportional to the product of the probability of absorption and the probability of detection.

\[
S_{\text{obs}} \propto P(\text{absorption})P(\text{detection})
\]

\[
\propto |\langle \psi | \mu \cdot E_{\text{laser}} | \psi' \rangle \langle \psi' | \mu \cdot \epsilon_{\text{emitted}} | \psi'' \rangle|^2
\]

where \(E_{\text{laser}}\) is the electric field of the laser, and \(\epsilon_{\text{emitted}}\) is the unit vector along the direction of polarization of the emitted photons. For bromine the states under study are the eigenfunctions

\[
|\psi\rangle = \sum_{J,I} \alpha_J^I \gamma(JI) \Omega FM
\]

It is easiest to solve the above expressions when the electric dipole moments and electric fields are expressed in spherical tensor notation [22]. For example,

\[
\mu_z = \frac{1}{\sqrt{2}} (\mu^1_1 - \mu^1_1)
\]

\[
\mu_y = \frac{i}{\sqrt{2}} (\mu^1_1 + \mu^1_1)
\]

\[
\mu_z = \mu_0^1
\]

Consider the signal, \(S_z(z)\), observed by a detector situated along the Z-axis from a molecule sitting at the origin excited by a laser polarized along the Z-axis.

\[
S_z(z) \propto |\mu_0|^2 \frac{\mu_0^2}{2} \sum_{F',M',I,M} \left\{ \sum_{all J, all I} T(F,F',J,J',I,M) \cdot T(F',F'',J',J'',I'',M) \right\} \left[ \pm \left( \begin{array}{cc} F' & 1 \\ -M & M' \end{array} \right) \right]^2
\]

\[
\left( \begin{array}{cc} F & 1 \\ -M & M \end{array} \right) \left[ \pm \left( \begin{array}{cc} F' & 1 \\ -M & M' \end{array} \right) + \left( \begin{array}{cc} F' & 1 \\ -M & M'' \end{array} \right) \right]^2
\]
where

\[
T(F, F', J, J', I, M) = \alpha_{JF}^{F'} \alpha_{J'F'}^{F} \left( -1 \right)^{F+F'+J+J'+I+M} \delta(I, I') \\
\times \sqrt{(2F+1)(2F'+1)(2J+1)(2J'+1)} \\
\times \left\{ \begin{array}{ccc}
I & J & F \\
1 & F' & J'
\end{array} \right\} \left( \begin{array}{ccc}
J & 1 & J' \\
\Omega & -\Delta \Omega & -\Omega'
\end{array} \right)^2
\]

(2.93)

Consider now the signal, \( S_z(y) \), observed with the detector along the Z-axis produced by a molecule at the origin excited by a laser polarized along the Y-axis.

\[
S_z(y) \propto \frac{|\mu_0|^2}{2} \sum_{F''} \sum_{M''} T(F, F', J, J', I, M) \cdot T(F', F'', J', J'', I'', M) \\
\times \left[ \begin{array}{ccc}
F & 1 & F' \\
-M & 1 & M
\end{array} \right] + \left[ \begin{array}{ccc}
F & 1 & F' \\
-M & -1 & M'
\end{array} \right] \\
\times \left[ \begin{array}{ccc}
F' & 1 & F'' \\
-M & 1 & M''
\end{array} \right] + \left[ \begin{array}{ccc}
F' & 1 & F'' \\
-M & -1 & M''
\end{array} \right] \right]^2
\]

(2.94)

By solving the above equations for transitions between the \( X^1\Sigma_g^+ \) and \( B^3\Pi_d^+ \) states of bromine, one observes that the polarization effects are most noticeable for hyperfine transitions of the lower rotational levels. The values of \( S_z(z) \) and \( S_z(y) \) for the R(0) and P(4) transitions are given in Table 2.2. The simulated R(0) hyperfine fluorescence spectra for both laser polarizations are shown in Figure 2.7.

The above fluorescence expressions may be compared with the absorption intensity expression, \( S_{abs} \),

\[
S_{abs} \propto |\mu_0|^2 \sum_{J, J'} T(F, F', J, J', I)|^2
\]

(2.95)

Equations 2.92 and 2.94 are the correct expressions when the fluorescent light is collected over a small amount of solid angle. When a large solid angle is observed the solutions must be integrated over the solid angle with the effect of decreasing the signal sensitivity to the laser polarization.
Figure 2.7: The simulated $^{79}\text{Br}_2$ B-X ($13'-0''$) R(0) hyperfine fluorescence spectra with the laser polarized along the Z-axis (Sz dotted line) and along the Y-axis (Sy solid line). The spectra are normalized to line a. The peaks labelled a and b are the transitions, $F'' = 2 \rightarrow F' = 1_1^1$ and $F'' = 0 \rightarrow F' = 1_1^1$, respectively. Those labelled c and d are $F'' = 2 \rightarrow F' = 1_1^1$, and $F'' = 0 \rightarrow F' = 1_1^1$, respectively. For clarity the Sz spectrum is displaced by 20 MHz and, in both spectra, the central peak heights are divided by a factor of 5.
Table 2.2: The calculated fluorescence signals with two different laser polarizations for the R(0) and P(4) hyperfine transitions of $^{79}$Br$_2$. The situation considered is that the detector is on the Z-axis, and the laser radiation propagates along the X-axis. $S_z(z)$ is the signal calculated with the laser polarized along the Z-axis and $S_z(y)$ is that with the laser polarized along the Y-axis. The calculated absorption signals are given under the $S_{abs}$ column. The most striking variations in the fluorescence signals occur for low J hyperfine transitions.
Chapter 3

Predissociation

In general, diatomic molecules have an infinite number of excited electronic levels, some of which are bound while others are unbound. Many of the electronic states of iodine arising from different electron configurations have been worked out by Mulliken [26]. A similar type of electronic structure is expected and observed for bromine. Many of the bound and unbound potentials intersect as illustrated in Figure 3.1. In such cases there is the possibility that the two states can interact in the region of intersection. This implies that when a molecule is excited from the ground electronic into a bound excited state which is coupled to a repulsive state, there is a significant probability that the molecule will pass from the bound excited electronic state into the unbound state resulting in the decomposition of the molecule into its constituent atoms. This phenomenon is known as predissociation.

There are various ways to couple the bound and unbound electronic states. These fall into two categories; field-induced predissociation which requires an external electric or magnetic field, and natural predissociation. Both types of predissociation have been previously observed [8, 9, 10, 27, 28, 29, 30, 31, 32]. In particular the study of the $B \ ^3\Pi_0^+$ state of iodine has been instrumental to the understanding of excited state dynamics of diatomic molecules.

Two types of natural predissociation were studied in this work; gyroscopic and hyperfine predissociation. Gyroscopic predissociation arises from part of the rotational Hamiltonian which couples the rotation of the molecule to the electronic orbital and spin
Figure 3.1: Crossing bound and dissociative potentials.
angular momenta. The hyperfine Hamiltonians $H_{hf}(1)$ and $H_{hf}(2)$ can couple different electronic states, as was pointed out in the previous chapter. An important property of hyperfine predissociation is that the different hyperfine levels of each rotational state will display different amounts of predissociation. By contrast, gyroscopic predissociation acts equally on all of the hyperfine levels of a given rotational state.

3.1 Theory

In this thesis, the natural predissociation of the $B \ ^3\Pi_{0^+}$ of $^{79}\text{Br}_2$, $^{81}\text{Br}_2$, and $^{79}\text{Br}^{81}\text{Br}$ has been studied. The coupling is primarily to the dissociative $^1\Pi_{1u}$ state which crosses the $B$ state between the $v' = 4$ and 5 vibrational levels [13]. The theory for gyroscopic and hyperfine predissociation has been worked out in detail by Vigué et al. [8] and applied to the $B \ ^3\Pi_{0^+}$ electronic state of iodine which also interacts with a repulsive $^1\Pi_{1u}$ level. The remainder of this chapter will present the theoretical results for gyroscopic and hyperfine predissociation following Vigué et al. as applied to $^{79}\text{Br}_2$, $^{81}\text{Br}_2$, and $^{79}\text{Br}^{81}\text{Br}$.

The predissociation rate, $\Gamma_p$, is given by Fermi's Golden Rule [8, 33, 34],

$$\Gamma_p = \frac{2\pi}{\hbar} | \langle \psi_c | V | \psi_b \rangle |^2$$

(3.1)

where $|\psi_c\rangle$ is the continuum wavefunction, $|\psi_b\rangle$ is the bound wavefunction, and $V$ is the Hamiltonian which couples them. The total decay rate for the level is the sum of the radiative decay rate, $\Gamma_{\text{rad}}$, the predissociation rate, $\Gamma_p$, the collisional decay rate, $\Gamma_{\text{coll}}$, and the stimulated emission rate, $\Gamma_{\text{sat}}$.

$$\Gamma = \Gamma_{\text{rad}} + \Gamma_p + \Gamma_{\text{coll}} + \Gamma_{\text{sat}}$$

(3.2)

In a molecular beam the collisional decay rate is extremely low and is neglected in the rest of the discussion. The stimulated emission rate, $\Gamma_{\text{sat}}$, can be made very small by reducing
the intensity of the laser beam which interacts with the molecules and is, therefore, neglected too.

As previously mentioned, there are two primary types of interaction terms which enter the Hamiltonian for natural predissociation: the gyroscopic and hyperfine Hamiltonians, \( V = H_G + H_{hf} \). The fact that more than one mechanism can lead to predissociation introduces the possibility of observing interference effects between \( H_G \) and \( H_{hf} \).

\[
\Gamma_p = \Gamma_G + \Gamma_{hf} + \Gamma_{int} \tag{3.3}
\]

where \( \Gamma_{int} \) are the interference terms. When Vigué et al. studied the predissociation of the \( B^3\Pi_g \) state of iodine in a magnetic field, it was the existence of these interference terms that allowed the first observation of hyperfine predissociation \[27, 28\].

### 3.1.1 Gyroscopic predissociation

The gyroscopic term is part of the rotational Hamiltonian which has matrix elements that are off-diagonal in the electronic state.

\[
H_G = -\frac{\hbar^2}{\mu R^2} \mathbf{J} \cdot (\mathbf{L} + \mathbf{S})
\]

\[
= -\frac{\hbar^2}{2\mu R^2} \left\{ J_+ (L_+ + S_-) + J_- (L_+ + S_+) + 2J_Z (L_Z + S_Z) \right\} \tag{3.4}
\]

Here \( \mu \) is the reduced mass of the molecule and \( R \) is the internuclear distance. The first two parts of Equation 3.4 which have the \( L_\pm \) and \( S_\pm \) operators are responsible for coupling different electronic states. Rewriting the Hamiltonian in terms of spherical tensors, and dropping the diagonal parts, one obtains:

\[
H_G = \frac{\hbar^2}{\mu R^2} \left\{ T^1_1(J) \left[ T^1_1(L) + T^1_1(S) \right] + T^1_{-1}(J) \left[ T^1_1(L) + T^1_1(S) \right] \right\} \tag{3.5}
\]

As per Chapter 2, the eigenfunctions of the bound hyperfine levels are written

\[
|F \epsilon M \rangle = \sum_{JJ} \alpha_{J \epsilon M}^F |\gamma(JJ)\Omega_v FM \rangle \tag{3.6}
\]
Chapter 3. Predissociation

The continuum wavefunctions are expressed

$$|\psi_c(E')\rangle = |\gamma'(J' I')\Omega' E' F'M'\rangle$$  \hspace{1cm} (3.7)

and normalized as

$$\langle \psi_c(E')|\psi_c(E)\rangle = \delta(E' - E)$$  \hspace{1cm} (3.8)

The predissociation rate between the bound and continuum levels is

$$\Gamma_p = \frac{2n}{\hbar} \sum_{J'I'\Omega'} | \sum_{I}\alpha_{J'\Omega'}^E \langle \gamma(JI)\Omega F M| \left[ H_G + \sum_k H^k(x) \right] |\gamma'(J'I')\Omega' E' F'M'| \rangle^2$$ \hspace{1cm} (3.9)

(The sum over $J'$, $I'$, $\Omega'$ has been inserted to take into account that the bound level may couple to more than one dissociative state.) To evaluate the predissociation rate it is useful to work out matrix elements of the form,

$$M_X(\Omega, \Omega') = \langle \gamma(JI)\Omega F M| H_X |\gamma'(J'I')\Omega' E' F'M'\rangle$$ \hspace{1cm} (3.10)

where $H_X$ is the gyroscopic Hamiltonian or a hyperfine Hamiltonian.

The matrix element of the gyroscopic Hamiltonian is [8]

$$M_G(\Omega, \Omega') = \delta_{FF'}\delta_{MM'}\delta_{II'}\delta_{JJ'}(-1)^J(2J+1) \sqrt{J(J+1)} \langle \Omega v \frac{\hbar^2}{\mu R^2} \left[ T^1_{-\Delta\Omega} + T^1_{\Delta\Omega}(S) \right] |\Omega' E'\rangle$$ \hspace{1cm} (3.11)

3.1.2 Hyperfine predissociation

As indicated in Chapter 2, the hyperfine Hamiltonian can be written as,

$$H_{hf} = H_{hf}(1) + H_{hf}(2) + H_{hf}(1, 2)$$ \hspace{1cm} (3.12)
Chapter 3. Predissociation

Only the hyperfine interactions between the electrons and the nuclei, $H_{hf}(x)$, are able to couple different electronic states. (Here $x = 1$ or 2 is a label for each nucleus.) Each of the first two hyperfine terms is made up of a sum of different rank interactions starting with the magnetic dipole, then the electric quadrupole, and so on.

$$H_{hf}(x) = \sum_k H^k(x)$$

The expression for the matrix element,

$$M_{hf}^k(1, \Omega, \Omega') = \langle \gamma(J)\Omega\nu FM | H_{hf}^k(1) | \gamma'(J' I')\Omega' E' F'M' \rangle$$

is [8]

$$M_{hf}^k(1, \Omega, \Omega') = \frac{\delta_{F',F} \delta_{M,M'}(-1)^{k+1+i_2+F+I'+I'} J' f_k(1, \Omega, \nu, \Omega', E')}{\sqrt{(2I+1)(2I'+1)(2J+1)(2J'+1)}} \left( \begin{array}{ccc} J & k & J' \\ -\Omega & -\Delta \Omega & \Omega' \end{array} \right) \left( \begin{array}{ccc} i_2 & i_1 & I \\ k & I' & i_1 \end{array} \right) \left( \begin{array}{ccc} F & I' & J' \\ k & J & I \end{array} \right)$$

(3.15)

$M_{hf}^k(2, \Omega, \Omega')$ is obtained by multiplying $M_{hf}^k(1, \Omega, \Omega')$ by the factor

$$\epsilon_{ug}(1)^{I+I'} [f_k(2, \Omega, \nu, \Omega', E')/f_k(1, \Omega, \nu, \Omega', E')]$$

(3.16)

where

$$\epsilon_{ug} = \begin{cases} 1 & \text{if both states are u or g} \\ -1 & \text{if one state is u and the other is g} \end{cases}$$

(3.17)

and $f_k(1, \Omega, \nu, \Omega', \nu')$ is defined in Equations 2.69 and 2.70. The predissociation rate given in Equation 3.9 can be rewritten,

$$\Gamma_p = \frac{2\pi}{\hbar} \sum_c |\langle \psi_b | H_G + \sum_k H^k(x) | \psi_c \rangle|^2$$

$$= \frac{2\pi}{\hbar} \sum_c \langle \psi_b | H_G + \sum_k H^k(x) | \psi_c \rangle \langle \psi_c | H_G + \sum_k H^k(y) | \psi_b \rangle$$

(3.18)
Table 3.1: The selection rules for three Hamiltonians: the gyroscopic, $H_G$, the hyperfine magnetic dipole, $H^1(x)$, and hyperfine electric quadrupole, $H^2(x)$.

The first sum is over all of the possible continuum levels that the Hamiltonians may couple to. Schematically, then, the predissociation rate can be seen to be the sum of several terms:

$$\Gamma_p = \Gamma_{GG} + \sum_{k,k'} \{\Gamma_{kk'}(1,1) + \Gamma_{kk'}(1,2) + \Gamma_{kk'}(2,1) + \Gamma_{kk'}(2,2)\}$$

$$+ \sum_k \{\Gamma_{Gk}(1) + \Gamma_{kG}(1) + \Gamma_{Gk}(2) + \Gamma_{kG}(2)\}$$  \hspace{1cm} (3.19)

The first term, $\Gamma_{GG}$, is the pure gyroscopic predissociation. The terms, $\Gamma_{kk'}(x,y)$, are the pure hyperfine predissociations of order $k$. (e.g. $\Gamma_{11}(x,y)$ is the pure hyperfine magnetic dipole predissociation.) The interference terms between hyperfine Hamiltonians of different rank, $\Gamma_{kk'}(x,y)$ ($k \neq k'$, and $x, y = 1$ or 2), and the gyroscopic–hyperfine interferences, $\Gamma_{Gk}(x)$, exist only when different Hamiltonians couple the bound state to the same continuum state. Table 3.1 summarizes the selection rules for three Hamiltonians: the gyroscopic, $H_G$, the hyperfine magnetic dipole, $H^1(x)$, and hyperfine electric quadrupole, $H^2(x)$. (The reader is reminded that although the B electronic state for each isotopomer of bromine is referred to as $B^3\Pi_{0^+}$ it should be thought of as an $\Omega = 0^+_u$ state.) One will observe interference terms between the gyroscopic and hyperfine Hamiltonians when the B state is coupled to an $\Omega = 1_u$ dissociative electronic state.

Following Vigué et al. [8], it is easiest to evaluate the predissociation rate using the
tensorial operator method. The method will be outlined here and given in more detail in Appendix A. Equivalent tensorial operators are derived for the gyroscopic and hyperfine Hamiltonians. This is accomplished by, first, introducing the projection operator, \( P_{\Omega v J I} \), which restricts the action of the Hamiltonian to the sublevels \( |\Omega v J I> \). Second, one defines two irreducible operator basis sets, \( \tilde{T}^{k}_{q} \) and \( U^{k}_{q} \). The former operates on all of the coordinates except for the nuclear spins and the latter acts only on the nuclear spins. \( \tilde{T}^{k}_{q} \) has non-vanishing matrix elements only between the states \( |J\Omega| \) and \( |J'\Omega'| \) and \( U^{k}_{q} \) has non-zero matrix elements only between the states \( |(i_1 i_2)I| \) and \( |(i_1 i_2)I'| \).

The matrix element of the scalar product, \( \sum_{q} (-1)^{q} \tilde{T}^{k}_{q} U^{k}_{q} \), is [8, 22]

\[
\langle \gamma(JI) \Omega FM | \sum_{q} (-1)^{q} \tilde{T}^{k}_{q} U^{k}_{q | \gamma'(J'I') \Omega' F'M'} \rangle =
\]

\[
\delta_{FJ} \delta_{M'I'} (-1)^{F+J'+I} \left\{ \frac{\tilde{F}}{k} \frac{J}{I} \frac{I}{J'} \right\} \langle J\Omega || \tilde{T}^{k}_{q} U^{k}_{q} || J'\Omega' \rangle \langle I || U^{k} || I' \rangle
\]

The equivalent tensorial form of the Hamiltonian, \( H_{X} \), is expanded in terms of these new irreducible operator basis sets as follows:

\[
P_{\Omega v J I} H_{X} P_{\Omega' v' J' I'} = \tilde{F}_{k}(\Omega, \Omega', v, E', J, J', I, I') \sum_{q} (-1)^{q} \tilde{T}^{k}_{q} U^{k}_{q}
\]

(3.21)

The factor, \( \tilde{F}_{k}(\Omega, \Omega', v, E', J, J', I, I') \), will be abbreviated as \( \tilde{F}_{k} \). The equivalent gyroscopic operator becomes

\[
P_{\Omega v J I} H_{G} P_{\Omega' v' J' I'} = V(\Omega, \Omega', v, E', J, J') \delta_{II'} \delta_{JJ'} \tilde{T}^{0}_{q}
\]

(3.22)

By comparing with the matrix element in Equation 3.11, one has

\[
V(\Omega, \Omega', v, E', J, J') = (-1)^{J-\Omega+1} (2J+1) \sqrt{J(J+1)} \begin{pmatrix} J & 1 & J \\ -\Omega & -\Delta \Omega & \Omega' \end{pmatrix}
\]

\[
\langle \Omega v | \frac{\hbar^{2}}{\mu R^{2}} \left[T^{1}_{-\Delta \Omega(L)} + T^{1}_{-\Delta \Omega(S)} \right] | \Omega' E' \rangle
\]

(3.23)
Similarly for the hyperfine Hamiltonian, $H^k(x)$,

\[ P_{\Omega J} H^k(x) P_{\Omega' J'} = w_k(x, \Omega, \Omega', v, E', J, J', I, I') \sum_q (-1)^q \frac{\Omega' \Gamma^k I_{q J'} J_I U_{q I}}{(2k + 1)} \]

(3.24)

with

\[ w_k(x, \Omega, \Omega', v, E', J, J', I, I') = (-1)^{k+I+I'+J'} f_k(x, \Omega, v, \Omega', E')/(2k + 1) \]

\[ \left( \begin{array}{ccc} J & k & J' \\ -\Omega & -\Delta \Omega & \Omega' \end{array} \right) \left\{ \begin{array}{c} i_x \\ i_x \\ I \end{array} \right\} \]

(3.25)

The coefficients $f_k(x, \Omega, v, \Omega', E')$ are defined as,

\[ f_k(x, \Omega, \Omega', E') = (-1)^\Omega \langle \Omega v | V_{-\Delta \Omega} | \Omega' E' \rangle \langle i_x | Q^k(i_x) | i_x \rangle \]

(3.26)

as per Equations 2.69 and 2.70. For the homonuclear molecules,

\[ f_k(1, \Omega, v, \Omega', E') = \epsilon_{uv} f_k(2, \Omega, v, \Omega', E') \]

(3.27)

and

\[ w_k(1, \Omega, \Omega', v, E', J, J', I, I') = (-1)^{I+I'} \epsilon_{uv} w_k(2, \Omega, \Omega', v, E', J, J', I, I') \]

(3.28)

The predissociation rates are generally of the form,

\[ \Gamma = \frac{2\pi}{\hbar} \sum_c \langle \psi_b | H^k | \psi_c \rangle \langle \psi_c | H^{k'} | \psi_b \rangle \]

(3.29)

If the projection operators are introduced, this becomes

\[ \Gamma = \frac{2\pi}{\hbar} \sum_{J,J',I'} \gamma(J''I'') \Omega v F M | P_{\Omega J}^{J''I''} H^k P_{\Omega' E'}^{J'} | \gamma'(J'I') \Omega' E' F' M' \]

\[ \times \gamma(J'I') \Omega' E' F' M' | P_{\Omega' J'}^{I'} H^k P_{\Omega J} | \gamma(JI) \Omega v F M \]

(3.30)
With the help of Equation 3.21 this reduces to,

$$\Gamma = \frac{2\pi}{\hbar} \sum_{J' K'} (\gamma(J' I')) \Omega v FM | F_k \left[ \sum_{q} (-1)^q \Omega_{j j} T^k_{j j} I^q J^q U^k_{-q} \right] | \gamma(J' I') \Omega' E' F' M' \rangle$$

$$\times (\gamma(J' I') \Omega' E' F' M') | F_{k'} \left[ \sum_{q'} (-1)^q' \Omega'_{j j} T'^{k'}_{j j} I'^{q'} J'^{q'} U'^{k'}_{-q'} \right] | \gamma(J I) \Omega v FM \rangle$$

$$= \frac{2\pi}{\hbar} \sum_{J' K'} F_k F_{k'} (\gamma(J' I')) \Omega v FM \left[ \sum_{q} (-1)^q \Omega_{j j} T^k_{j j} I^q J^q U^k_{-q} \right] | \gamma(J' I') \Omega' E' F' M' \rangle$$

$$\times (\gamma(J' I') \Omega' E' F' M') \left[ \sum_{q'} (-1)^q' \Omega'_{j j} T'^{k'}_{j j} I'^{q'} J'^{q'} U'^{k'}_{-q'} \right] | \gamma(J I) \Omega v FM \rangle \quad (3.31)$$

The evaluation of the matrix elements of the irreducible tensor operator basis sets is presented in Appendix A. The results indicate that the predissociation rates can be written as the product of a molecular parameter which is to be determined experimentally, and some rotational and nuclear factors to be denoted $R_{XY}(a, b)$. (The labels $X$ and $Y$ refer to the type of predissociation term; $a$ and $b$ label the nuclei.) The $R_{XY}(a, b)$ are sums of products of 3-, 6-, and 9-j symbols. (For example see Equation 3.36.) Specializing to the states, $B^3\Pi_{0^+} (\Omega = 0^+)$ and $^1\Pi_{1u} (\Omega' = 1u)$, one can define the molecular parameters, $(i_1 = i_2 = i_x)$

$$C_v = \sqrt{\frac{\pi}{\hbar}} (0_u^+ v) \Omega v FM | T^1_{-\Delta n}(L) + T^1_{-\Delta n}(S) | 1u E' \rangle \quad (3.32)$$

$$a_v(x) = \sqrt{\frac{2\pi}{\hbar}} f_1(x, 0_u^+, v, 1u, E') \left/ \left[ i_x(i_x + 1)(2i_x + 1) \right]^{\frac{1}{2}} \right. \quad (3.33)$$

and

$$b_v(x) = \sqrt{\frac{2\pi}{\hbar}} f_2(x, 0_u^+, v, 1u, E') \left[ \frac{2i_x(2i_x - 1)}{(2i_x + 1)(2i_x + 2)(2i_x + 3)} \right]^{\frac{1}{2}} \quad (3.34)$$

$C_v$ is the gyroscopic predissociation parameter, $a_v(x)$ is the hyperfine magnetic dipole $(k = 1)$ predissociation parameter for nucleus $x$, and $b_v(x)$ is the hyperfine electric
quadrupole ($k = 2$) predissociation parameter for nucleus $x$. $b_y(x)$ is a new parameter that is introduced in this thesis.

The rotational and nuclear factors are now considered. For the purely gyroscopic term,

$$R_{GG} = J(J + 1)\delta_{JJ''}\delta_{II'}$$  \hspace{1cm} (3.35)

For the interference terms between the gyroscopic and hyperfine Hamiltonian of order $k$,

$$R_{Gk}(x) = \sum_{J,I,J'',I''} \alpha_j^{F} \alpha_j^{F'} \alpha_{J''I''} X_k(i_1)$$

$$\times (-1)^{k+2I'+F+I''+I''+1} \sqrt{J''(J'' + 1)(2J'' + 1)}$$

$$\times W(J, J'', I, I'') S^k(J, J'', I, I'') \begin{pmatrix} i_x & i_x & I \\ k & I'' & i_x \end{pmatrix}$$  \hspace{1cm} (3.36)

The factor arising from the product of two hyperfine matrix elements which both couple nucleus $x$ to the continuum is

$$R_{kk'}(x, x) = \sum_{J,I,J''} \alpha_j^{F} \alpha_j^{F'} \alpha_{J''I''} (-1)^{F+\Omega+k+k'} W(J, J'', I, I'') X_k(i_x) X_{k'}(i_x)$$

$$\times \sum_K (2K + 1) Z^{kk'}_K(J, J'', I, I'') \begin{pmatrix} i_x & i_x & I \\ K & I'' & i_x \end{pmatrix} \begin{pmatrix} i_x & k & i_x \\ K & i_x & k' \end{pmatrix}$$  \hspace{1cm} (3.37)

The factor from the product of two hyperfine matrix elements which couple different nuclei ($x \neq y$) to the dissociative electronic state is

$$R_{kk'}(x, y) = \sum_{J,I,J''} \alpha_j^{F} \alpha_j^{F'} \alpha_{J''I''} (-1)^{F+\Omega+I''} W(J, J'', I, I'') X_k(i_x) X_{k'}(i_x)$$

$$\times \sum_K (-1)^K (2K + 1) Z^{kk'}_K(J, J'', I, I'') \begin{pmatrix} i_x & I & i_x \\ k & K & k' \end{pmatrix} \begin{pmatrix} i_x & I'' & i_x \end{pmatrix}$$  \hspace{1cm} (3.38)
In these equations

\[ X_1(i_x) = \left[ \frac{i_x(i_x + 1)(2i_x + 1)}{2i_x(2i_x - 1)} \right]^{\frac{3}{2}} \]  (3.39)

\[ X_2(i_x) = \left[ \frac{(2i_x + 1)(2i_x + 2)(2i_x + 3)}{2i_x(2i_x - 1)} \right]^{\frac{3}{2}} \]  (3.40)

\[ W(J, J'', I, I'') = \sqrt{(2J + 1)(2J'' + 1)(2J + 1)(2J'' + 1)} \]  (3.41)

\[ S^k(J, J'', I, I'') = \begin{pmatrix} J'' & 1 & J'' \\ -\Omega & -\Delta\Omega & \Omega' \end{pmatrix} \begin{pmatrix} J'' & k & J \\ -\Omega' & \Delta\Omega & \Omega \end{pmatrix} \begin{pmatrix} F & I'' & J'' \\ k & J & I \end{pmatrix} \]  (3.42)

\[ Z^{kk'}(J, J'', I, I'') = \begin{pmatrix} F & I'' & J'' \\ K & J & I' \end{pmatrix} \begin{pmatrix} k & k' & K \\ \Delta\Omega & -\Delta\Omega & 0 \end{pmatrix} \begin{pmatrix} J & J'' & K \\ \Omega & -\Omega & 0 \end{pmatrix} \]  (3.42)

The predissociation rate for a level with wavefunction

\[ |F_{eM} = \sum_{JJ} \alpha_{eJ}^M \gamma(JI) \Omega \nu FM) \]  (3.43)

expanded up to the electric quadrupole hyperfine terms \((k = 2)\) is

\[ \Gamma_p(F_{e\nu}) = C_{\nu}^2 R_{GG} + \left[ a_\nu^2(1) + a_\nu^2(2) \right] R_{11}(1, 1) + 2a_\nu(1)a_\nu(2)R_{11}(1, 2) \]

\[ + 2\sqrt{2}C_\nu [a_\nu(1) + a_\nu(2)] R_{G1}(1) + 2\sqrt{2}C_\nu [b_\nu(1) + b_\nu(2)] R_{G2}(1) \]

\[ + 2 [a_\nu(1)b_\nu(1) + a_\nu(2)b_\nu(2)] R_{12}(1, 1) \]

\[ + \left[ b_\nu^2(1) + b_\nu^2(2) \right] R_{22}(1, 1) + 2b_\nu(1)b_\nu(2)R_{22}(1, 2) \]  (3.44)

Equation 3.44 must be used to describe the predissociation rate of \(^{79}\text{Br}^{81}\text{Br}\). However the expression can be simplified for \(^{79}\text{Br}_2\) and \(^{81}\text{Br}_2\) by realizing that \(a_\nu(1) = a_\nu(2)\) and
b_\nu(1) = b_\nu(2) for these molecules. This gives

\[ \Gamma_p(F, \epsilon, \nu) = C^2 R_{GG} + 2a_\nu^2 [R_{11}(1, 1) + R_{11}(1, 2)] + 4\sqrt{2}a_\nu C_\nu R_{G1}(1) + 4\sqrt{2}b_\nu C_\nu R_{G2}(1) + 4a_\nu b_\nu R_{12}(1, 1) + 2b_\nu^2 [R_{22}(1, 1) + R_{22}(1, 2)] \]  

(3.45)

### 3.1.3 Special Cases

For the homonuclear molecules, \(^79\)Br\(_2\) and \(^81\)Br\(_2\), the predissociation rates of some of the B \(^3\Pi_{0^+}\) state hyperfine levels are sensitive to only one or to a specific combination of the predissociation parameters. In particular, the hyperfine levels associated with the \(J' = 0\) state and the two \(F' = J'\) hyperfine levels associated with the odd \(J'\) rotational states (para-states) are discussed below.

Previous workers [3, 4, 8, 11, 14] have expanded the predissociation rate only up to the magnetic dipole hyperfine terms. This was sufficient to fit the observed predissociation rates for the hyperfine levels of the B \(^3\Pi_{0^+}\) state of iodine and reported to be sufficient to describe the predissociation of the B \(^3\Pi_{0^+}\) of bromine as well. When this simplification is made, a new selection rule appears, \(I = I''\). (This arises because the selection rules for hyperfine Hamiltonians that couple two \(u\) electronic states provide \(|\Delta I| = 0, 2, 4,\ldots\) while the magnetic dipole selection rule is \(|\Delta I| \leq 1\).)

\[ \Gamma_p(F, \epsilon, \nu) = \sum_{J_1} |a_{JJ_1}^F|^2 \left\{ C_\nu^2 J^2 - \sqrt{2}a_\nu C_\nu I \cdot J + \frac{a_\nu^2}{3} \left[ J^2 + \frac{3(I \cdot J)^2 + \frac{3}{2}I \cdot J - I^2 J^2}{(2J - 1)(2J + 3)} \right] \right\} \]  

(3.46)

The usual definitions apply,

\[ Z^2 = Z(Z + 1) \]  

(3.47)
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\[ \mathbf{I} \cdot \mathbf{J} = \frac{1}{2} \left( \mathbf{F}^2 - \mathbf{J}^2 - \mathbf{I}^2 \right) \]  

(3.48)

Recall that for homonuclear bromine, each nucleus has spin \( i_1 = i_2 = 3/2 \). The para states (the odd-J levels in the B electronic state) are those with total nuclear spin \( I = 0 \) and \( 2 \). This produces a very simple and symmetric hyperfine pattern. The two \( F = J \) hyperfine states are shifted equally to either side of the hyperfine-free energy. (The \( F \neq J \) hyperfine states lie close to the hyperfine-free energy.) The level shifted to higher energy will be labelled \( F^+ \) and the level shifted to lower energy will be called \( F^- \). (See Figure 3.2.) To a good approximation the two \( F = J \) states can be described by the eigenfunctions,

\[ |F_-^M\rangle = \frac{1}{\sqrt{2}} \left[ |\gamma(J0)JM\rangle - |\gamma(J2)JM\rangle \right] \]  

(3.49)

\[ |F_+^M\rangle = \frac{1}{\sqrt{2}} \left[ |\gamma(J0)JM\rangle + |\gamma(J2)JM\rangle \right] \]  

(3.50)

In the limit that \( b_\nu \to 0 \) (i.e. no hyperfine electric quadrupole predissociation) the predissociation rates for these hyperfine levels will be denoted \( \Gamma_p^{MD}(F_\pm^J, \nu) \). Using Equation 3.46 and eigenfunctions 3.49 and 3.50 one has:

\[ \Gamma_p^{MD}(F_\pm^J, \nu) = C^2 \nu (J + 1) + \frac{3}{2} \sqrt{2} a_v C_\nu \]

\[ + \frac{2}{6} \left[ 6 + \frac{3(3)^2 - \frac{3}{2}(3) - 6J(J + 1)}{(2J - 1)(2J + 3)} \right] \]  

(3.51)

Both the \( F_+^J \) and \( F_-^J \) hyperfine levels have the same predissociation rate.

When the electric quadrupole predissociation is included, \( |\Delta I| = 0 \) and \( 2 \), and the expressions for the predissociation rates are not so simple as the above equation. One important deduction is that the predissociation rates for the \( F_+^J \) and \( F_-^J \) hyperfine levels are no longer equal:

\[ \Gamma_p(F_\pm^J, \nu) = \Gamma_p^{MD}(F_\pm^J, \nu) + \beta b_\nu^2 \pm \epsilon \{ \sqrt{2} C_\nu + a_v \} b_\nu \]  

(3.52)
Figure 3.2: The hyperfine structure and spectrum characteristic of para-bromine (even $J$ in the $X \, ^1\Sigma_g^+$ and odd $J$ in the $B \, ^3\Pi_{0^+}$). The $F \neq J$ levels are nearly degenerate and lie close to the hyperfine-free energy with the $F_\pm$ levels lying symmetrically to high and low energy. The strong $\Delta F = \Delta J$ transitions produce a central peak composed of several nearly coincident transitions, a low frequency $F'' = F_J^+ \rightarrow F' = F_J^-$ transition, and a high frequency $F''' = F_J^+ \rightarrow F' = F_J^-$ peak.
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<table>
<thead>
<tr>
<th>$F^J_\pm$</th>
<th>$\Gamma_p(F^J, \epsilon, \nu)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^-$</td>
<td>$2C_0^2 + 1.5\sqrt{2}a_vC_v + 1.35a_v^2 - 2.18(\sqrt{2}C_v + a_v)b_\nu + 2.6b_\nu^2$</td>
</tr>
<tr>
<td>1$^+$</td>
<td>$2C_0^2 + 1.5\sqrt{2}a_vC_v + 1.35a_v^2 + 2.21(\sqrt{2}C_v + a_v)b_\nu + 2.6b_\nu^2$</td>
</tr>
<tr>
<td>3$^-$</td>
<td>$12C_0^2 + 1.5\sqrt{2}a_vC_v + 0.818a_v^2 - 1.79(\sqrt{2}C_v + a_v)b_\nu + 2.1b_\nu^2$</td>
</tr>
<tr>
<td>3$^+$</td>
<td>$12C_0^2 + 1.5\sqrt{2}a_vC_v + 0.815a_v^2 + 1.79(\sqrt{2}C_v + a_v)b_\nu + 2.1b_\nu^2$</td>
</tr>
<tr>
<td>5$^-$</td>
<td>$30C_0^2 + 1.5\sqrt{2}a_vC_v + 0.775a_v^2 - 1.75(\sqrt{2}C_v + a_v)b_\nu + 2.0b_\nu^2$</td>
</tr>
<tr>
<td>5$^+$</td>
<td>$30C_0^2 + 1.5\sqrt{2}a_vC_v + 0.777a_v^2 + 1.75(\sqrt{2}C_v + a_v)b_\nu + 2.0b_\nu^2$</td>
</tr>
<tr>
<td>7$^-$</td>
<td>$56C_0^2 + 1.5\sqrt{2}a_vC_v + 0.762a_v^2 - 1.74(\sqrt{2}C_v + a_v)b_\nu + 2.0b_\nu^2$</td>
</tr>
<tr>
<td>7$^+$</td>
<td>$56C_0^2 + 1.5\sqrt{2}a_vC_v + 0.765a_v^2 + 1.74(\sqrt{2}C_v + a_v)b_\nu + 2.0b_\nu^2$</td>
</tr>
</tbody>
</table>

Table 3.2: The predissociation rates for several the odd--J' (para-bromine) $F^J_\pm$ hyperfine levels including up to the electric quadrupole terms. As is evident, the difference in the rates for $F^J_-$ and $F^J_+$ would vanish if $b_\nu = 0$.

where $\beta$ and $\epsilon$ are numerical factors. One has the remarkable result that the difference in the predissociation rates of the $F^J_+$ and $F^J_-$ hyperfine levels is directly proportional to the hyperfine electric quadrupole predissociation constant, $b_\nu$. The expressions for $\Gamma_p(F^J_\pm, \nu)$ for a few para hyperfine levels are given in Table 3.2. These have been calculated from the eigenfunctions which included the contributions of the $|\gamma(J, IJM)\rangle$ and $|\gamma(J \pm 2, IJM)\rangle$, $I = 0$ and 2, basis states.

The homonuclear P(1) hyperfine transitions present another important test case. The upper rotational state in these transitions is the $J' = 0$ level with corresponding hyperfine states, $F' = 1$ and 3. To a good approximation,

$$|\psi F' = 1\rangle = |\gamma(0, 1)JM')\rangle \quad (3.53)$$

$$|\psi F' = 3\rangle = |\gamma(0, 3)JM')\rangle \quad (3.54)$$
These levels suffer no gyroscopic or gyroscopic–hyperfine interference predissociation. They have predissociation rates,

\[
\Gamma_p(F' = 1, v) = \frac{2}{3} a_v^2 + 2.4 b_v^2 \\
\Gamma_p(F' = 3, v) = 4 a_v^2 + 2.4 b_v^2
\]

and total decay rates

\[
\Gamma(F', v) = \Gamma_{\text{rad}} + \Gamma_p(F', v)
\]

As is evident, the difference in decay rates between these two hyperfine levels is directly proportional to the hyperfine magnetic dipole predissociation parameter, \(a_v^2\). Notice that if the electric quadrupole predissociation is not negligible then the parameter derived from relative intensity measurements of the \(P(1)\) hyperfine spectral lines will be

\[
\frac{a_v^2}{\Gamma_{\text{rad}} + 2.4 b_v^2}
\]

and not

\[
\frac{a_v^2}{\Gamma_{\text{rad}}}
\]

as reported by other authors [3, 4].
Chapter 4

General Experimental Considerations

The experimental work for this thesis divided naturally into two parts. The first was a study of the hyperfine structure of the $X \ 1\Sigma_g^+$ and $B \ 3\Pi_0^+$ electronic states of bromine. The second part was a measurement of the natural predissociation of the $B \ 3\Pi_0^+$ state of bromine by a dissociative $^1\Pi_{1u}$ state. Each type of experiment had its own unique experimental requirements but they also had many common aspects. The measurements of the hyperfine structure of bromine were considerably simpler than the predissociation measurements in which saturation effects and optical collection efficiency were of great importance. This chapter will describe the experimental features common to both studies while the specifics of the hyperfine and the predissociation measurements will be covered in Chapters 5 and 6, respectively.

Both of the experimental studies involved direct observations of the individual hyperfine transitions between the $B$ and $X$ electronic states. These transitions occurred in the visible spectral region around 5700 Å. The technique for observing the transitions was laser induced fluorescence (LIF). This technique relies on a laser with a tunable frequency. When the laser is brought into resonance with a molecular transition, the molecules absorb light and jump into an excited state. They de-excite by falling apart, by colliding with another object, or by relaxing back down to a lower level by emitting a photon. For bromine, the probability of dropping back into the original state is very low. This means that the emitted (fluorescent) light is shifted, usually to the red, of the excitation source. This allows the detector to be conveniently "blinded" to the scattered laser light by using
an appropriate red-pass filter which blocks out the laser light but allows light of longer wavelength (red shifted) through. The transitions are, therefore, recorded against a dark background giving the LIF technique a very high sensitivity. A further enhancement to the sensitivity is obtained by modulating either the light or the molecular source at a frequency, \( f \). This guarantees that the signal of interest is also modulated at the same frequency. By using a lock-in amplifier, a device which selectively amplifies input signals at the frequency chosen by the experimenter, (the modulation frequency, \( f \), of the laser light or molecular source, here), much more of the residual background may be filtered out of the detector signal.

The requirements of the excitation light source are determined by the type of experiment planned and the system being studied. Here both studies required that measurements be performed on individual hyperfine levels of bromine. The natural width of the \( B \) state bromine levels is of the order of 0.1 MHz and the separations of the hyperfine levels vary from a few to tens of MHz. Therefore the light source could not exceed 10 MHz in width in order to resolve at least some of the hyperfine transitions. A Coherent CR699-21 dye laser system operating with Rhodamine 6G dye and pumped by the 5145 Å line from a Coherent Innova 420 argon ion laser was used. The dye laser had a line width of about 2 MHz and with this dye could operate in the range \( 560 \text{ nm} \leq \lambda \leq 600 \text{ nm} \) with a power \( \geq 200 \text{ mW} \) and a maximum at about 570 nm of 800 mW. The system is able to sweep continuously through a frequency window of between 10 and 30000 MHz in a time of 2.5 seconds to 10 minutes.

The studies conducted here are difficult to perform in a static cell for several reasons. At 20°C bromine has a vapour pressure of about 170 Torr and a Doppler width of roughly 400 MHz. At this temperature the maximum in the rotational state population occurs at \( J = 35 \). This presents two difficulties; first, the hyperfine structure of the transitions are hidden under the Doppler width and second, the most interesting states
to study are those with low J which are weakly populated. To measure the electric quadrupole constants of both the X and B states separately one must be able to observe the $\Delta F \neq \Delta J$ transitions. These decrease in intensity at least as fast as $1/J^2$ compared to the $\Delta F = \Delta J$ transitions [18]. Therefore, for high rotational states, only the differences in the hyperfine parameters of the B and X electronic states can be determined from the spectra. As for the predissociation measurements, the gyroscopic term and gyroscopic – magnetic dipole interference terms increase as $J^2$ and $J$, respectively, while the other terms remain constant or decrease slowly with $J$. To best measure the hyperfine predissociation parameters, one must study the hyperfine levels of the low lying J states. Furthermore, in a sealed gas cell the collisions between bromine molecules quench the fluorescence and affect the lifetimes of the upper states.

These difficulties are eliminated by studying bromine in a molecular beam. A molecular beam is produced by sending molecules through a small nozzle into a vacuum chamber. The molecules, especially when mixed with a noble carrier gas, collisionally cool in the nozzle concentrating the molecules into low lying rotational and vibrational states. After passing through the nozzle, the molecules may be further collimated. The molecules in such a beam are free of collisions and travel primarily in one direction with only a small residual velocity perpendicular to the molecular beam axis. Now, if a laser beam intersects the molecular beam at $90^\circ$, the Doppler broadening, which is caused by the velocity distribution of the molecules along the axis of the laser, is greatly reduced. The amount of residual Doppler width depends upon the degree of collimation of the molecular beam and the angle between the laser and molecular beam axes. In our experiments the Doppler shift was reduced from about 400 MHz down to 4 MHz or better.

The molecular beam machine, shown schematically in Figure 4.1, consisted of an injection chamber and a high vacuum section separated by a gate valve, GV. The injection chamber was evacuated with a roots blower (Edwards Mechanical Booster Pump model
EH500), RB, backed by a mechanical pump (Edwards mechanical pump model E2M40), M2, to a pressure of about 1 mTorr. (The cold trap, C1, was used to trap excess bromine.)

The high vacuum side consisted of two cylinders joined together; the first will be referred to as the main chamber where all the measurements were made and the second will be called the auxiliary chamber. The main chamber was evacuated with a 4.5 inch diameter diffusion pump (Norton diffusion pump model 0161), D1, backed by a roughing pump (Duo Seal model 1402), M3. The auxiliary chamber was evacuated with a 6 inch diameter diffusion pump (CVC model 88), D2, backed by a mechanical pump (Duo Seal model 1402), M4. (Both diffusion pumps were preceded by cold traps, C2 and C3 in Figure 4.1.)

The high vacuum side of the molecular beam machine achieved a pressure of $4 \times 10^{-6}$ Torr with no gas load. Both chambers had flanges attached to the top and the two sides perpendicular to the molecular beam axis as shown in Figure 4.1. The auxiliary chamber also had an end flange closing it off. The inner surfaces of both chambers were coated with graphite to minimize scattered laser light.

The main chamber was an aluminum cylinder 12 inches high with a diameter of roughly 18 inches. The flanges perpendicular to the molecular beam axis had various entrance and exit windows for the laser radiation. The laser beam interacted with the molecules in the region labelled A during the predissociation study and in the region labelled B during the hyperfine structure work. The photomultiplier (RCA model 31034A), housed in a cooling jacket (Products for Research model TE104RF) which brought it to a temperature of roughly $-30^\circ$ C, sat on top of the main chamber over either the A or B region. An optical stack holding a series of lenses to collect the LIF was mounted inside the vacuum chamber and the light was fed through a port on the top flange to the active area of the photomultiplier. (The exact arrangement of the lenses was different for the hyperfine and predissociation studies and will be presented in detail in Chapters 5 and 6.) The mount for the cooling jacket – photomultiplier housing was designed so that a
Figure 4.1: The molecular beam machine. (See text for explanation of symbols.)
colored glass filter could be placed in front of the photomultiplier to cut out the scattered laser light.

The gas, typically a mixture of 20% bromine in argon, was introduced through a pyrex nozzle, Nl, ranging from 20 to 40 microns in diameter. After expanding through the nozzle into the injection chamber, the gas passed through a 1 mm diameter skimmer, Sk, to help collimate it. The beam then entered the high vacuum side. A pair of adjustable stainless steel slits, Sl, mounted vertically, were placed about 10 cm downstream of the skimmer. These were followed by an adjustable iris 1 cm further downstream. By varying the slit width the amount of residual Doppler width in the fluorescence signals could be reduced.

Before evacuating the beam machine, the skimmer, iris, and optical stack were aligned optically. The end flange of the auxiliary chamber was removed and replaced by a cardboard alignment plate which had a small hole cut in its center. A HeNe laser beam was then sent through the centers of the alignment plate, the iris, and the skimmer — defining the molecular beam axis. The optical stack was then positioned so that the HeNe laser beam passed through the center of the optical collection region. The stack was then locked in place.

The nozzle was mounted so that its distance from the skimmer as well as its position in the plane perpendicular to the molecular beam propagation direction could be varied. Initial alignment was performed by placing the nozzle about 3 mm away from the skimmer and injecting a pure argon beam into the high vacuum chamber. The pressure inside the main chamber was monitored with an ion gauge and the nozzle's position in the perpendicular plane was adjusted until the pressure was maximized. The optimal distance between the nozzle and skimmer was determined by introducing a bromine beam and monitoring its LIF. The best signal to noise was usually obtained when the nozzle – skimmer distance was from 1.5 to 2.0 cm.
The gas delivery system consisted of a 500 ml stainless steel lecture bottle holding about 100 ml of liquid bromine connected by a needle valve (Whitey model SS 22RS4), N, to a piece of copper tubing feeding into the nozzle. A 0 – 760 Torr pressure gauge (Matheson model 63-5601), P, was attached to the copper tubing to allow a measurement of the gas pressure behind the nozzle. The gas system was designed so that the argon could be fed directly into the copper tubing or into the bromine cylinder. The bromine cylinder plug was designed so that the argon could be fed into the inlet and a mixture of bromine and argon was carried through the outlet. The cylinder was charged up with argon and then left for at least an hour before use to allow the two gases to mix. The system could be operated on a single charge for roughly 5 hours. The entire delivery system could be evacuated with a roughing pump, M1.

The pressure of the argon and bromine mixture behind the nozzle was measured with the pressure gauge and controlled with the needle valve. The best signal to noise depended upon the nozzle diameter, the backing pressure, and the pumping speed of the injection system. Using a 20 micron diameter nozzle the best results were achieved with a backing pressure of roughly 300 Torr. The resulting rotational temperature of the molecular beam was about 6 K.
Chapter 5

Hyperfine Structure of Bromine

The first part of this thesis involved the measurement of sub-Doppler spectra of the B $^3\Pi_0^+$ – X $^1\Sigma_g^+$ rovibronic transitions of each isotopomer of bromine. Bromine has several features that make it particularly attractive to study. Bromine occurs naturally in two isotopes, $^{79}$Br and $^{81}$Br, in almost equal abundance, providing three isotopomers of molecular bromine $^{79}$Br$_2$, $^{81}$Br$_2$, and $^{79}$Br$^{81}$Br in the ratio 1:1:2. Each isotope has the same nuclear spin, $i = 3/2$, but quite different nuclear magnetic and electric quadrupole moments [35]. As well, bromine is a heavy molecule so that the rovibronic spectra of each isotopomer are very dense. Therefore, when studying molecular bromine in natural abundance, one observes many near coincidences of transitions arising from different isotopomers. This gives the experimenter the ability to compare sub-Doppler spectra and hyperfine structure of three distinct, yet very similar molecular systems. Recently, an atlas of the rovibronic B–X transitions of $^{79}$Br$_2$ was prepared [36]. The B $^3\Pi_0^+$ and X $^1\Sigma_g^+$ rovibrational constants were deduced from these measurements and were published along with the rovibrational parameters of the other two isotopomers, $^{81}$Br$_2$, and $^{79}$Br$^{81}$Br derived from those for $^{79}$Br$_2$ [7]. The near coincidences of bromine transitions provides an opportunity to investigate the accuracy of these published constants.

There are two main techniques of observing sub-Doppler spectra. The first is to use saturation spectroscopy on the molecules in a sealed glass cell. Saturation techniques are very sensitive but, as discussed, they generally yield information about the high $J$ states. The second technique, measurement of LIF of a molecular beam, provides
information mainly about low-lying rotational states. Previous authors [1, 2, 3, 4, 5, 6] have reported measurements of the hyperfine structure of the B and X electronic states of bromine. Half of the studies [1, 5, 6] used saturation spectroscopy techniques, and the others [2, 3, 4] measured the LIF of a molecular beam of bromine. The observed spectra have been adequately described by the molecular constants, $\text{eqQ}_X$, $\text{eqQ}_B$, (the molecular electric quadrupole coupling constants of the X and B electronic states respectively) and $C_{sr}$ (the nuclear spin-rotation constant of the B state). Since both the B and X levels are $\Omega = 0^+$ states, the predominant hyperfine splitting of the rovibronic levels is due to the electric quadrupole interaction given by Equation 2.84. The hyperfine splitting patterns are very similar in the two electronic states with their magnitudes being set by $\text{eqQ}_X$ and $\text{eqQ}_B$. Transitions between levels with $\Delta F = \Delta J$ only yield information about $\Delta \text{eqQ} = (\text{eqQ}_B - \text{eqQ}_X)$. In order to deduce $\text{eqQ}_B$ and $\text{eqQ}_X$ separately one must observe some of the $\Delta F \neq \Delta J$ (so-called crossover) transitions. As mentioned in Chapter 4, the crossover transitions decrease in intensity at least as fast as $J^2$ compared to the $\Delta F = \Delta J$ peaks. Thus, the hyperfine spectra of the low rotational states are of particular importance. The trade-off is that the nuclear spin-rotation interaction is very small for low lying rotational states and increases in magnitude with J. Thus, molecular beam studies are suited to the study of the hyperfine parameters $\text{eqQ}_X$ and $\text{eqQ}_B$ while the saturation spectroscopy techniques are useful for measuring $\Delta \text{eqQ}$ and $C_{sr}$.

In this chapter the experimental details and results of the hyperfine structure study are presented and compared with the findings of previous authors.
5.1 Experimental Details

The hyperfine spectra of various B-X rovibronic transitions of bromine were recorded using the molecular beam machine and laser system described in Chapter 4. The experimental apparatus is shown schematically in Figure 5.1. The argon-ion (AL) pumped dye laser (DL) beam was steered through the molecular beam machine using mirrors M1, M2, and M3. The laser induced fluorescence (LIF) was collected with the optical system and imaged on the photomultiplier (PMT). The signals were fed into a lock-in amplifier (LIA) tuned to the frequency of the mechanical chopper which modulated the molecular beam. Part of the laser beam was sent into two reference etalons, Et1 and Et2, using beam splitters S1 and S2 and mirror M4. Et1 was pressure and temperature stabilized with a 750 MHz free spectral range (FSR) and Et2 was a passive 150 MHz FSR etalon. The etalon transmission peaks along with the LIA signal were recorded on a µVax computer.

The optical collection system, shown schematically in Figure 5.2, had a f/0.88 condenser lens (Melles Griot aspheric glass condenser number 01 LAG 007, focal length 26.5 mm, diameter 30 mm), L1, one focal length above the laser–molecule interaction region. In addition a spherical mirror (Melles Griot concave spherical reflector number 01 MCG 007, focal length 25.0 mm, diameter 30.0 mm), M1, was located one focal length below the interaction region to enhance the collection efficiency of the laser induced fluorescence (LIF). This light collected was then fed into a spatial filter consisting of two f/0.88 condenser lenses (L2 and L3) held 2f apart with a plate having a 2mm hole in it half way between them. This allowed the on axis light to travel up the optical stack and blocked much of the scattered (off-axis) light. The spatially filtered light was then focussed by a 110 mm focal length lens (Melles Griot symmetric convex glass lens number 01 LDX 183,
focal length 110.0 mm, diameter 35.0 mm), L4, onto the active area of the photomultiplier. (L4 also acted as the window from inside to outside the vacuum chamber.) The system was designed so that a red pass filter could be inserted above L4 to reduce the stray laser light detected. To further cut down the noise, the molecular beam rather than the laser beam was modulated with a mechanical chopper inside the vacuum chamber. When one modulates the laser beam, the scattered light is also modulated allowing any scattered light which reaches the photomultiplier to be detected by the lock in amplifier, LIA. However, in the absence of absorption, the molecular beam does not give off any visible light so that it presents a dark background to the detector.

Crucial to this work was the calibration system, designed and built by Adam et al. [37], which supplied the frequency scale for the observed hyperfine spectra. The system consists of two confocal Fabry-Perot etalons. The first etalon, Et1, has a free spectral range (FSR) of 750 MHz and is housed in a temperature controlled vacuum chamber. It is locked to a transmission peak of a polarization stabilized HeNe laser and was calibrated to allow absolute frequency measurements. The second is a passive etalon, Et2, with a FSR of 150 MHz. Part of the laser beam used to probe the molecules was split off and sent into these two etalons (using beam splitters S1 and S2 and mirror M4 as per Figure 5.1). As the laser was scanned over the frequency region of interest, the etalon transmission peaks were recorded along with the spectral features providing frequency markers to be used for analyzing the data. The designers have determined that this system provides absolute frequency measurements accurate to ±25 MHz and relative frequency measurements accurate to slightly better than ±1.0 MHz [37].

Unfortunately, during these studies, the stabilized HeNe laser used to lock the calibration system was under repair. The 750 MHz etalon (FSR = (750.83 ± 0.30) MHz) was no longer fixed to a HeNe transmission peak but was still pressure and temperature regulated. This, of course, ruled out absolute frequency measurements but had almost
Figure 5.1: A schematic of the apparatus used for studying the hyperfine structure of bromine. (See text for explanation of symbols.)
Figure 5.2: A schematic of the optical collection system used in the hyperfine structure studies.
no effect on relative frequency measurements. For example, an error in the free spectral range of 1 MHz yielded only an error of 1 MHz in the relative frequency separations of peaks which were 750 MHz apart. To put this in perspective, recall that the FSR of a confocal Fabry-Perot etalon is given by:

$$\text{FSR} = \frac{c}{4n d}$$  \hspace{1cm} (5.1)

where $c$ is the speed of light, $n$ is the index of refraction of the material between the mirrors, and $d$ is the mirror separation. For an etalon built with invar spacers, one may overestimate the thermal expansion coefficient, $\alpha$, as $5 \times 10^{-5}/\circ C$. For a change in temperature $\Delta T$, the change in FSR is,

$$\frac{\Delta\text{FSR}}{\text{FSR}} = -\alpha \Delta T$$  \hspace{1cm} (5.2)

To obtain a 1 MHz change in FSR would require a temperature change of 26 $\circ$C. Certainly a more realistic change in temperature for an etalon which is not in a temperature controlled container would be $\Delta T = 5 \circ C$ giving a change in FSR of only 0.19 MHz. Similar considerations for a catastrophic failure of the vacuum chamber housing the etalon ($\Delta P = 1$ atmosphere) show that the FSR would only change by 0.24 MHz. Therefore, one is confident that the measurements were reliable to at least 1.0 MHz for a 750 MHz frequency separation (0.13%).

The data were recorded on a microVAX ($\mu$VAX) minicomputer which took 2048 channels per scan. The 150 MHz markers were used to interpolate between the 750 MHz peaks allowing the frequency separations between spectral lines to be deduced.

The list of B–X rovibronic hyperfine spectra recorded is given in Table 5.1. The hyperfine spectrum of each transition studied was recorded at least 3, and usually 4 times. The results are contained in 379 data sets comprising over 3000 hyperfine spectral features.
### Table 5.1: A list of the rovibronic transitions whose hyperfine spectra were recorded in this study.

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>$(v' - v'')$</th>
<th>Rotational Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{79}\text{Br}_2$</td>
<td>$(11' - 0'')$</td>
<td>R(18)</td>
</tr>
<tr>
<td></td>
<td>$(13' - 0'')$</td>
<td>R(0) – R(3), R(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(1) – P(5), P(15) – P(17)</td>
</tr>
<tr>
<td></td>
<td>$(14' - 1'')$</td>
<td>R(11), R(12), R(14)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(7), P(17)</td>
</tr>
<tr>
<td></td>
<td>$(17' - 2'')$</td>
<td>R(0) – R(8), R(10), R(15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(1) – P(5), P(7), P(12)</td>
</tr>
<tr>
<td></td>
<td>$(19' - 2'')$</td>
<td>P(6)</td>
</tr>
<tr>
<td>$^{79}\text{Br}^{81}\text{Br}$</td>
<td>$(11' - 0'')$</td>
<td>R(0) – R(2), P(1)</td>
</tr>
<tr>
<td></td>
<td>$(12' - 0'')$</td>
<td>R(0) – R(2), P(1)</td>
</tr>
<tr>
<td></td>
<td>$(13' - 0'')$</td>
<td>R(0) – R(3), R(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(1) – P(5)</td>
</tr>
<tr>
<td></td>
<td>$(14' - 1'')$</td>
<td>R(0) – R(2), R(8), R(11)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(1), P(5), P(7)</td>
</tr>
<tr>
<td></td>
<td>$(15' - 1'')$</td>
<td>R(0) – R(2), P(1)</td>
</tr>
<tr>
<td></td>
<td>$(16' - 1'')$</td>
<td>R(0) – R(2), P(1)</td>
</tr>
<tr>
<td></td>
<td>$(17' - 2'')$</td>
<td>R(0) – R(8), R(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(1) – P(5)</td>
</tr>
<tr>
<td>$^{81}\text{Br}_2$</td>
<td>$(13' - 0'')$</td>
<td>R(0) – R(3), R(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(1) – P(5)</td>
</tr>
<tr>
<td></td>
<td>$(17' - 2'')$</td>
<td>R(0) – R(8), R(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(1) – P(5)</td>
</tr>
</tbody>
</table>
5.2 The Model

The B $^3\Pi_{0^+}$ and X $^1\Sigma_g^+$ electronic states are both $\Omega = 0$ levels. For this work, it is sufficient to include only the electric quadrupole Hamiltonian and the nuclear spin-rotation Hamiltonian to adequately describe the observed hyperfine spectra.

$$E_{sr} = \frac{C_{sr}}{2} [F(F+1) - J(J+1) - I(I+1)]$$

(5.3)

To the accuracy needed here, the nuclear spin-rotation Hamiltonian can be treated as diagonal in I, J, and F. (In addition, even though one has one constant, $C_{sr}$, for each nucleus for $^{79}\text{Br}^{81}\text{Br}$, characterizing the energy by a single, effective constant was sufficient.) The electric quadrupole terms couple different nuclear spin states, $|\Delta I| \leq 2$, and rotational states, $|\Delta J| \leq 2$. For $\Omega = 0$ levels, one has the added restriction that only the $J$ and $J \pm 2$, $\pm 4$, ..., states are mixed. All of the even $J$ levels are connected to one another as are all the odd $J$ levels. This implies that one must set up and diagonalize an $N \times N$ matrix which includes all of the rotational and nuclear spin states. In practice it is sufficient to truncate this matrix to include only the $J$ and $J \pm 2$ rotational states and the appropriate nuclear spin states (see Chapter 2) to fit the observed hyperfine spectra.

It is convenient to begin by describing the hyperfine states with a coupled basis set, $|\gamma(J,I)\Omega \nu FM\rangle$, and work out the matrix elements for the hyperfine electric quadrupole Hamiltonian. Then one adds the nuclear spin-rotation terms and, finally, the rovibronic energies for the states. Schematically, for each electronic rotational–vibrational hyperfine level, one must diagonalize a matrix, $\mathcal{M}$, which is the sum of a (diagonal) rovibronic energy matrix, $\mathcal{M}_{rv}$, a (diagonal) nuclear spin–rotation matrix, $\mathcal{M}_{sr}$, and symmetric electric quadrupole matrices, $\mathcal{M}_{EQ}^1$ and $\mathcal{M}_{EQ}^2$. (The superscripts 1 and 2 refer to the electric quadrupole contributions from nucleus 1 and 2 respectively.)

$$\mathcal{M} = \mathcal{M}_{rv} + C_{sr} \cdot \mathcal{M}_{sr} + \frac{eqQ(1)}{2} \cdot \mathcal{M}_{EQ}^1 + \frac{eqQ(2)}{2} \cdot \mathcal{M}_{EQ}^2$$

(5.4)
For the homonuclear molecules Equation 5.4 may be simplified by recognizing that 
\( \text{eqQ}(1) = \text{eqQ}(2) \) and combining the two matrices into \( \mathcal{M}_{\text{EQ}} \). Diagonalization gives the eigenenergies, \( E(F, \epsilon) \), and eigenvectors, labelled here as

\[
|F\epsilon M\rangle = \sum_{JI} \alpha_{FJI}^\epsilon |(J, I)\Omega \nu FM\rangle
\]

(5.5)

The label \( \epsilon \) is used to emphasize that several hyperfine states can have the same \( F \) quantum number but different eigenenergies and wavefunctions.

As with any energy calculation, one has an arbitrary zero point. In this work, where only relative frequencies were measured, it was convenient to subtract off the energy of the hyperfine-free rovibrational level, \( E_{v,J,\Omega}^0 \), from \( \mathcal{M} \).

\[
\mathcal{M}' = \mathcal{M} - E_{v,J,\Omega}^0 \cdot I
\]

(5.6)

\[
= \mathcal{M}'_{\nu
} + C_{sr} \cdot \mathcal{M}_{sr} + \frac{\text{eqQ}(1)}{2} \cdot \mathcal{M}_{\text{EQ}}^1 + \frac{\text{eqQ}(2)}{2} \cdot \mathcal{M}_{\text{EQ}}^2
\]

(5.7)

where \( I \) is the identity matrix. This manipulation does not change the eigenfunctions but translates the eigenenergies by an amount \( E_{v,J,\Omega}^0 \). For each electronic state, the new energies are,

\[
E(F, \epsilon) = E(F, \epsilon) - E_{v,J,\Omega}^0
\]

(5.8)

(Of course, \( E_{v',J',B}^0 - E_{v'',J'',X}^0 \) is the \( B - X \) \( (v', J') \leftrightarrow (v'', J'') \) rovibronic energy difference.)

The calculated hyperfine contribution to the transition between the \( X ^1\Sigma_g^+ |F''\epsilon''M\rangle \) level and the \( B ^3\Pi_{0^+} |F'\epsilon'M\rangle \) level is

\[
\nu(F', F'') = E(F', \epsilon') - E(F'', \epsilon'')
\]

(5.9)

The absolute transition frequencies are obtained by adding to these values the appropriate rovibronic energy differences, \( (E_{v',J',B}^0 - E_{v'',J'',X}^0) \).

The observed frequencies were not absolute frequency measurements so that one had the freedom to arbitrarily choose a zero point for the experimental frequency scale. The
difference between this arbitrary zero and the center of the hyperfine free rovibronic transition frequency, \( \delta \), was an adjustable parameter applied to the data.

\[
\nu_{\text{obs}}(F', F'') = \delta + \nu(F', F'')
\]

(5.10)

where \( \nu(F', F'') \) is the calculated transition frequency and depends upon the hyperfine parameters, \( \text{eq}Q_X, \text{eq}Q_B, C_{sr} \), and the known rovibronic constants for the X and B electronic states [7]. The nuclear spin – rotation constant, \( C_{sr} \), was measured for the vibrational levels, \( 16 \leq v' \leq 28 \), of the B state of \( ^{79}\text{Br}_2 \) in Reference [6]. This parameter increases with vibrational state, and for B state vibrational levels studied here is less than 0.100 MHz. Therefore its overall contribution to the energy of a hyperfine level for \( J' = 5 \) is less than 1.5 MHz and smaller for hyperfine levels of lower \( J' \) states, compared to electric quadrupole hyperfine contributions of tens to hundreds of MHz. Therefore, the data were fit for \( \text{eq}Q_X, \text{eq}Q_B \), and \( \delta \) holding \( C_{sr} \) fixed at the value appropriate for the vibrational state, \( v' \), of the transition under study. (The values of \( C_{sr} \) were interpolated from the \( ^{79}\text{Br}_2 \) data presented in Reference [6]. The values used for \( ^{81}\text{Br}_2 \) were scaled by the ratio of nuclear magnetic dipole moments, \( g(^{81}\text{Br})/g(^{79}\text{Br}) \). The values used for \( ^{79}\text{Br}^{81}\text{Br} \) were taken as the average of the \( ^{79}\text{Br}_2 \) and \( ^{79}\text{Br}^{81}\text{Br} \) constants.)

The heteronuclear data could, in theory, be used to deduce the parameters \( \text{eq}Q(^{79}\text{Br}) \) and \( \text{eq}Q(^{81}\text{Br}) \) for both electronic states. However, these were highly correlated so that the restriction,

\[
\frac{\text{eq}Q(^{79}\text{Br})}{\text{eq}Q(^{81}\text{Br})} = \frac{Q(^{79}\text{Br})}{Q(^{81}\text{Br})} = 1.19707(3)
\]

(5.11)

was imposed [35]. The heteronuclear data were fit for \( \text{eq}Q(^{79}\text{Br}) \) (for both electronic states) and \( \delta \). Each hyperfine spectrum was recorded 4 to 5 times and the results for each vibrational band were averaged.

To test the validity of constraint 5.11 on the heteronuclear data hyperfine spectra, the \((13'-0'')\) and \((17'-2'')\) bands were recorded for each isotopomer. The deduced
Table 5.2: The electric quadrupole parameter for the (13' - 0") and (17' - 2") bands of
79Br2 and 81Br2. The ratio of eqQ for the different homonuclear isotopomers agrees,
within experimental uncertainty, with the ratio of nuclear electric quadrupole moments
of the two isotopes.

The measured ratios of the electric quadrupole moments between the two isotopes equal
Q(79Br)/Q(81Br) to within the experimental uncertainty. This implies that the gradient
of the electric field, q, at the nuclei is the same for both 79Br in 79Br2 and 81Br in
81Br2.

5.3 Results and Discussion

For each data set, the unblended transitions were selected, weighted by their relative
heights, and then subjected to a nonlinear least squares fit for the parameters, eqQB,
eqQX, and δ. Having recorded over 3000 transitions in 379 data sets, it is not practical to
list completely the observed and calculated transition frequencies. Instead, Appendix B
shows, in tabular form, the raw data (νobs), the calculated hyperfine transition frequencies
(νcalc), and their differences (νobs - νcalc) referred to as (obs-calc), for the B-X (17' - 2")
P(1) hyperfine spectra of each isotopomer. In addition a summary of the average values
of νobs and their (νobs - νcalc) is given. These data, with a root-mean-square (rms)
Table 5.3: The B state eqQ parameters for each isotopomer.

<table>
<thead>
<tr>
<th>v'</th>
<th>$^{79}\text{Br}_{81}\text{Br}$ eqQ($^{79}\text{Br}$) (MHz)</th>
<th>$^{79}\text{Br}_{2}$ eqQ($^{79}\text{Br}$) (MHz)</th>
<th>$^{81}\text{Br}_{2}$ eqQ($^{81}\text{Br}$) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>177.0 ± 0.6</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>12</td>
<td>177.8 ± 3.2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>13</td>
<td>178.8 ± 0.5</td>
<td>178.1 ± 1.0</td>
<td>148.3 ± 1.0</td>
</tr>
<tr>
<td>14</td>
<td>179.8 ± 1.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>15</td>
<td>180.1 ± 0.4</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>16</td>
<td>179.9 ± 0.5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>17</td>
<td>180.6 ± 1.4</td>
<td>180.7 ± 1.8</td>
<td>150.0 ± 2.1</td>
</tr>
</tbody>
</table>

obs–calc of about 0.7 MHz, are typical of most of the data recorded and well within the experimental uncertainty. The exceptions are the (13' − 0") band data which had an experimental uncertainty that was larger than the rest. The B–X (13' − 0") P(2) hyperfine data are also summarized in Appendix B demonstrating the slightly worse rms (obs–calc) of 1.2 MHz.

The deduced electric quadrupole coupling constants for the different vibrational levels of the B and X state studied are given in Tables 5.3 and 5.4, respectively. These are compared with the results reported by previous authors [2, 3, 4, 5, 6] in Tables 5.5 and 5.6.

As can be seen, the values presented in this thesis are in excellent agreement with those of previous workers and, with the exception of results reported by Katzenellenbogen and Prior [5], have comparable or better error limits on the B state eqQ($^{79}\text{Br}$) parameters. The molecular electric quadrupole coupling constants increase with vibrational quantum in both electronic states. Performing a linear least squares fit on the molecular constants
Table 5.4: The X state $\Theta Q$ parameters for each isotopomer.

<table>
<thead>
<tr>
<th>$v''$</th>
<th>$^{79}\text{Br}^{81}\text{Br}$ $\Theta Q(^{79}\text{Br})$ (MHz)</th>
<th>$^{79}\text{Br}_2$ $\Theta Q(^{79}\text{Br})$ (MHz)</th>
<th>$^{81}\text{Br}_2$ $\Theta Q(^{81}\text{Br})$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>808.1 ± 1.4</td>
<td>808.3 ± 7.0</td>
<td>676.1 ± 5.6</td>
</tr>
<tr>
<td>1</td>
<td>810.8 ± 0.7</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>811.5 ± 1.9</td>
<td>810.9 ± 1.8</td>
<td>675.1 ± 3.5</td>
</tr>
</tbody>
</table>

Table 5.5: A comparison of the observed electric quadrupole coupling constants, $\Theta Q(^{79}\text{Br})$, for different vibrational levels of the $B^3\Pi_0^+$ state.

<table>
<thead>
<tr>
<th>$v'$</th>
<th>Reference</th>
<th>$\Theta Q(^{79}\text{Br})$ (MHz)</th>
<th>$v'$</th>
<th>Reference</th>
<th>$\Theta Q(^{79}\text{Br})$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>[3]</td>
<td>(176.5 ± 1.0)</td>
<td>15</td>
<td>this work</td>
<td>(180.1 ± 0.4)</td>
</tr>
<tr>
<td></td>
<td>[4]</td>
<td>(176.97 ± 0.62)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>this work</td>
<td>(177.0 ± 0.6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>this work</td>
<td>(177.9 ± 3.2)</td>
<td>16</td>
<td>[2]</td>
<td>(178.5 ± 1.2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[4]</td>
<td>(180.05 ± 0.69)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[6]</td>
<td>(180.9 ± 2.7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>this work</td>
<td>(179.9 ± 0.5)</td>
</tr>
<tr>
<td>13</td>
<td>[2]</td>
<td>(179.1 ± 1.6)</td>
<td>17</td>
<td>[6]</td>
<td>(179.7 ± 2.2)</td>
</tr>
<tr>
<td></td>
<td>[4]</td>
<td>(177.12 ± 0.98)</td>
<td></td>
<td>[5]</td>
<td>(180.20 ± 0.03)</td>
</tr>
<tr>
<td></td>
<td>this work</td>
<td>(178.8 ± 0.5)</td>
<td></td>
<td>this work</td>
<td>(180.6 ± 1.4)</td>
</tr>
<tr>
<td>14</td>
<td>[2]</td>
<td>(178.7 ± 1.6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>this work</td>
<td>(179.8 ± 1.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 5. Hyperfine Structure of Bromine

<table>
<thead>
<tr>
<th>$\nu''$</th>
<th>[2]</th>
<th>[3]</th>
<th>[4]</th>
<th>this work</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>(808.7 ± 0.9)</td>
<td>(809.32 ± 0.59)</td>
<td>(808.1 ± 1.4)</td>
</tr>
<tr>
<td>1</td>
<td>(810.0 ± 0.6)</td>
<td></td>
<td>(809.91 ± 0.82)</td>
<td>(810.8 ± 0.7)</td>
</tr>
<tr>
<td>2</td>
<td>(810.0 ± 1.1)</td>
<td></td>
<td>(810.15 ± 0.62)</td>
<td>(811.5 ± 1.4)</td>
</tr>
</tbody>
</table>

Table 5.6: A comparison of observed electric quadrupole coupling constants for different vibrational levels of the $X^1\Sigma_g^+$ state of $^{79}$Br$_2$.

determined here gives,

$$B\text{ state}: \text{eqQ}(^{79}\text{Br}) = (170.82 \pm 1.91) + (0.598 \pm 0.134)v' \text{ (MHz)} \quad (5.12)$$

$$X\text{ state}: \text{eqQ}(^{79}\text{Br}) = (808.76 \pm 1.14) + (1.70 \pm 0.99)v'' \text{ (MHz)} \quad (5.13)$$

The calculated values are shown in Tables 5.7 and 5.8. Liu et al. [6] have reported the B state electric quadrupole coupling constants for the vibrational levels, $16 \leq v' \leq 28$, using polarization spectroscopy. Because this technique investigates the high rotational states, the eqQ($^{79}$Br) values reported in Reference [6] for the B state were deduced from the measurements of $\Delta$eqQ and the values of the X state eqQ($^{79}$Br) parameters of Reference [4]. (See Table 5.9.) Fitting these data in the same manner yields:

$$B\text{ state}: \text{eqQ}(^{79}\text{Br}) = (172.06 \pm 3.52) + (0.484 \pm 0.158)v' \text{ (MHz)} \quad (5.14)$$

again, in excellent agreement with this work.

The authors of Reference [5] report uncertainties in the B state electric quadrupole coupling constants about 30 times lower than those of all other authors. Like Liu et al. [6],
### Table 5.7: The $eqQ(7^9\text{Br})$ values for the B state vibrational levels recorded as measured and calculated from Equation 5.12.

<table>
<thead>
<tr>
<th>$v'$</th>
<th>$eqQ(7^9\text{Br})_{\text{obs}}$ (MHz)</th>
<th>$eqQ(7^9\text{Br})_{\text{calc}}$ (MHz)</th>
<th>obs - calc (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>177.0 ± 0.6</td>
<td>177.40</td>
<td>-0.40</td>
</tr>
<tr>
<td>12</td>
<td>177.9 ± 3.2</td>
<td>178.00</td>
<td>-0.10</td>
</tr>
<tr>
<td>13</td>
<td>178.8 ± 0.5</td>
<td>178.60</td>
<td>0.20</td>
</tr>
<tr>
<td>14</td>
<td>179.8 ± 1.0</td>
<td>179.20</td>
<td>0.60</td>
</tr>
<tr>
<td>15</td>
<td>180.1 ± 0.4</td>
<td>179.80</td>
<td>0.30</td>
</tr>
<tr>
<td>16</td>
<td>179.9 ± 0.5</td>
<td>180.39</td>
<td>-0.49</td>
</tr>
<tr>
<td>17</td>
<td>180.6 ± 1.4</td>
<td>180.99</td>
<td>-0.39</td>
</tr>
</tbody>
</table>

### Table 5.8: The $eqQ(7^9\text{Br})$ values for the X state vibrational levels recorded as observed and calculated from Equation 5.13.

<table>
<thead>
<tr>
<th>$v'$</th>
<th>$eqQ(7^9\text{Br})_{\text{obs}}$ (MHz)</th>
<th>$eqQ(7^9\text{Br})_{\text{calc}}$ (MHz)</th>
<th>obs - calc (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>808.1 ± 1.4</td>
<td>808.76</td>
<td>-0.66</td>
</tr>
<tr>
<td>12</td>
<td>810.8 ± 0.7</td>
<td>810.47</td>
<td>0.33</td>
</tr>
<tr>
<td>13</td>
<td>811.5 ± 1.4</td>
<td>812.17</td>
<td>-0.67</td>
</tr>
</tbody>
</table>
Table 5.9: The observed B state $eqQ^{(79}\text{Br})$ values from Reference [6] and the corresponding values calculated from Equation 5.14.

<table>
<thead>
<tr>
<th>$\nu'$</th>
<th>$eqQ^{(79}\text{Br})_{\text{obs}}$ (MHz)</th>
<th>$eqQ^{(79}\text{Br})_{\text{calc}}$ (MHz)</th>
<th>$\text{obs} - \text{calc}$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>180.9 ± 2.7</td>
<td>179.80</td>
<td>1.10</td>
</tr>
<tr>
<td>17</td>
<td>179.7 ± 2.2</td>
<td>180.28</td>
<td>-0.58</td>
</tr>
<tr>
<td>18</td>
<td>180.0 ± 1.9</td>
<td>180.76</td>
<td>-0.76</td>
</tr>
<tr>
<td>19</td>
<td>180.6 ± 1.8</td>
<td>181.25</td>
<td>-0.65</td>
</tr>
<tr>
<td>20</td>
<td>181.5 ± 1.7</td>
<td>181.73</td>
<td>-0.23</td>
</tr>
<tr>
<td>21</td>
<td>183.0 ± 1.8</td>
<td>182.22</td>
<td>0.78</td>
</tr>
<tr>
<td>22</td>
<td>183.5 ± 1.8</td>
<td>182.70</td>
<td>0.80</td>
</tr>
<tr>
<td>23</td>
<td>184.6 ± 2.0</td>
<td>183.18</td>
<td>1.42</td>
</tr>
<tr>
<td>24</td>
<td>182.2 ± 2.5</td>
<td>183.67</td>
<td>-1.47</td>
</tr>
<tr>
<td>25</td>
<td>183.8 ± 1.8</td>
<td>184.15</td>
<td>-0.35</td>
</tr>
<tr>
<td>26</td>
<td>185.3 ± 1.9</td>
<td>184.63</td>
<td>0.67</td>
</tr>
<tr>
<td>27</td>
<td>185.2 ± 2.0</td>
<td>185.12</td>
<td>0.08</td>
</tr>
<tr>
<td>28</td>
<td>184.3 ± 2.3</td>
<td>185.60</td>
<td>-1.30</td>
</tr>
</tbody>
</table>
Table 5.10: The electric quadrupole parameters reported by Ref. [5] for the B state of bromine.

Table 5.10: The electric quadrupole parameters reported by Ref. [5] for the B state of bromine.

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>ν'</th>
<th>eqQ(79Br) (MHz)</th>
<th>eqQ(81Br) (MHz)</th>
<th>Csr (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>79Br2</td>
<td>17</td>
<td>180.20 ± 0.03</td>
<td>—</td>
<td>90.18 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>185.17 ± 0.07</td>
<td>—</td>
<td>98.30 ± 0.08</td>
</tr>
<tr>
<td>81Br2</td>
<td>17</td>
<td>—</td>
<td>151.39 ± 0.04</td>
<td>91.77 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>—</td>
<td>150.04 ± 0.12</td>
<td>103.07 ± 0.08</td>
</tr>
<tr>
<td>79Br81Br</td>
<td>17</td>
<td>179.06 ± 0.03</td>
<td>151.29 ± 0.07</td>
<td>91.93 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>181.02 ± 0.06</td>
<td>151.48 ± 0.06</td>
<td>101.35 ± 0.09</td>
</tr>
</tbody>
</table>

The technique employed by Katzenellenbogen and Prior [5] was polarization spectroscopy on a sealed cell of bromine. The hyperfine structure of the states J' = 30 to 100 of the ν' = 17 and 18 vibrational levels were used to deduce, for each isotopomer, the parameters eqQ, Csr, and Γ, the half–width at half maximum (HWHM) of the hyperfine peaks. (The HWHM values will be discussed in more detail in Chapter 6.) Csr and eqQ are summarized in Table 5.10. The work of Reference [5] should only be sensitive to ΔeqQ and not eqQ directly. To obtain the reported values, Katzenellenbogen et al. fixed the X state parameters eqQ(79Br) = 810.0 MHz and eqQ(81Br) = 676.7 MHz. The former was chosen from Reference [2] and the latter, it must be assumed, was deduced from the ratio Q(79Br)/Q(81Br). The uncertainty in the value of eqQ used by the authors was the order of 0.8 MHz. No account was taken of this uncertainty to the errors given in Reference [5] and quoted here in Table 5.10. The variation in the electric quadrupole coupling constant from ν' = 17 to ν' = 18 is markedly different from isotopomer to isotopomer considering the quoted accuracy. As well, the B state ratio eqQ(79Br)/eqQ(81Br) is considerably
different from the ratio assumed for the ground state. Thus, the reported uncertainties seem optimistic. (In passing, it should be noted that the rovibronic transition frequencies for the B–X (17' – 2") and (18' – 2") hyperfine spectra shown in Reference [5] are both roughly 4.8 cm\(^{-1}\) too high. These are probably calculated values and point to a trivial error in the term value for the X state \(v'' = 2\) level used in the calculation.)

In general, the observation of the hyperfine spectra corresponding to the low-lying rotational B–X transitions were particularly important for obtaining both the signs and the magnitudes of the electric quadrupole parameters. For example, the P(1) hyperfine spectrum for each isotopomer is almost entirely due to the hyperfine energy pattern of the X \(^1\Sigma^+_g\) \(J=1\) level and, therefore, a direct measure of eqQ of the ground state. For each isotopomer this pattern is quite asymmetric so that the sign of the ground state electric quadrupole coupling constant, eqQ\(_X\), may be determined along with the magnitude. The observed spectra lead to the conclusion that the sign of eqQ\(_X\) is positive as indicated in Table 5.4. From this observation, and measurements of other hyperfine splitting patterns one may further deduce that the upper state quadrupole coupling constant, eqQ\(_B\), is also positive as reported in Table 5.3. (It should be noted that, in eqQ, the symbol, e, is treated as positive.)

### 5.4 Observation of Near Coincident Transitions

The B–X spectrum of the three species of bromine is extremely dense. Even with the rotational and vibrational cooling inherent in the molecular beam there are many accidental near coincidences of rovibronic transitions. For each isotopomer, a rotational band head was observed between the R(1) and R(2) transitions. This allowed the recording of either the R(0) and R(2) or the R(1) and R(2) hyperfine structures in a single laser scan. By fitting the observed hyperfine spectra for each rovibronic transitions separately
one obtained, in addition to the molecular hyperfine constants, values for δ for each transition. For transitions recorded in the same scan these δ could be used to deduce the hyperfine free frequency separation, Δν, of the two rovibronic transitions. That is,

\[
\Delta \nu \equiv (\delta_1 - \delta_2) = [E^0(1) - \text{(scale zero)}] - [E^0(2) - \text{(scale zero)}] = E^0(1) - E^0(2)
\]

(5.15)

where \(E^0(i)\) is the (hyperfine free) rovibronic transition energy of peak \(i\) (\(i = 1, 2\)). The measurements of \(\Delta \nu\) in the R branch band head region for the different vibrational levels studied are shown in Table 5.11. The entries in the column labelled \(\Delta \nu(\text{calc})\) are the corresponding values deduced from the constants published by Gerstenkorn and Luc [7]. In their work, Gerstenkorn and Luc measured the B–X absorption of \(^79\)Br\(_2\) using Fourier transform spectroscopy, recording 80,000 rovibronic transitions in the region 11,600 cm\(^{-1}\) to 19,577 cm\(^{-1}\). The data were fit with 39 Dunham coefficients and one empirical scaling factor to take into account the centrifugal distortion effects higher in order than the detecic term. The equivalent constants for \(^81\)Br\(_2\) and \(^79\)Br\(^{81}\)Br were deduced from isotopic relations. These authors claim an uncertainty in the absolute transition frequencies of ±0.0016 cm\(^{-1}\) (±48 MHz). The agreement shown Table 5.11 indicate that the predicted spacings of the rovibronic transitions within a given isotopomer (for low rotational states) are accurate to at about ±5 MHz.

The study of the \((17' - 2'')\) band of each type of molecular bromine was particularly useful. For this band the molecular constants are such that the P(J) and R(J+3) transitions are nearly coincident allowing them to be recorded within one data set. (See Table 5.12.) The frequency difference between these rovibronic transitions, including
### Table 5.11: The observed hyperfine free separations, $\Delta \nu$, of the transitions listed compared with the theoretical values based upon the rovibronic constants of Reference [7].

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>Vibrational Band</th>
<th>Rotational Transitions</th>
<th>$\Delta \nu_{\text{obs}}$ (MHz)</th>
<th>$\Delta \nu_{\text{calc}}$ (MHz)</th>
<th>obs-calc (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{79}\text{Br}_2$</td>
<td>(13' - 0'')</td>
<td>R(1) - R(2)</td>
<td>538.0 ± 4.0</td>
<td>538.2</td>
<td>-0.1</td>
</tr>
<tr>
<td></td>
<td>(17' - 2'')</td>
<td>R(2) - R(0)</td>
<td>46.6 ± 1.4</td>
<td>48.2</td>
<td>-1.6</td>
</tr>
<tr>
<td></td>
<td>(13' - 0'')</td>
<td>R(1) - R(0)</td>
<td>1054.2 ± 1.2</td>
<td>1052.1</td>
<td>1.9</td>
</tr>
<tr>
<td>$^{81}\text{Br}_2$</td>
<td>(13' - 0'')</td>
<td>R(2) - R(0)</td>
<td>754.1 ± 1.0</td>
<td>757.1</td>
<td>-3.0</td>
</tr>
<tr>
<td></td>
<td>(17' - 2'')</td>
<td>R(1) - R(2)</td>
<td>514.5 ± 2.1</td>
<td>504.2</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>(13' - 0'')</td>
<td>R(2) - R(0)</td>
<td>6.2 ± 1.6</td>
<td>2.0</td>
<td>4.2</td>
</tr>
<tr>
<td>$^{79}\text{Br}^{81}\text{Br}$</td>
<td>(11' - 0'')</td>
<td>R(1) - R(2)</td>
<td>276.2 ± 0.8</td>
<td>278.2</td>
<td>-2.0</td>
</tr>
<tr>
<td></td>
<td>(12' - 0'')</td>
<td>R(2) - R(0)</td>
<td>947.3 ± 2.3</td>
<td>954.6</td>
<td>-7.3</td>
</tr>
<tr>
<td></td>
<td>(13' - 0'')</td>
<td>R(1) - R(2)</td>
<td>396.2 ± 1.2</td>
<td>397.8</td>
<td>-1.6</td>
</tr>
<tr>
<td></td>
<td>(14' - 1'')</td>
<td>R(2) - R(0)</td>
<td>756.7 ± 5.1</td>
<td>749.2</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>(13' - 0'')</td>
<td>R(1) - R(2)</td>
<td>516.3 ± 0.8</td>
<td>521.0</td>
<td>-4.7</td>
</tr>
<tr>
<td></td>
<td>(15' - 1'')</td>
<td>R(2) - R(0)</td>
<td>593.8 ± 4.6</td>
<td>594.4</td>
<td>-0.6</td>
</tr>
<tr>
<td></td>
<td>(14' - 1'')</td>
<td>R(1) - R(2)</td>
<td>614.7 ± 1.3</td>
<td>610.1</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>(16' - 1'')</td>
<td>R(2) - R(0)</td>
<td>377.0 ± 1.4</td>
<td>376.3</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>(15' - 1'')</td>
<td>R(1) - R(2)</td>
<td>740.4 ± 1.4</td>
<td>741.0</td>
<td>-0.6</td>
</tr>
<tr>
<td></td>
<td>(16' - 1'')</td>
<td>R(2) - R(0)</td>
<td>150.8 ± 3.0</td>
<td>151.5</td>
<td>-0.7</td>
</tr>
<tr>
<td></td>
<td>(15' - 1'')</td>
<td>R(1) - R(2)</td>
<td>873.0 ± 2.2</td>
<td>876.0</td>
<td>-3.0</td>
</tr>
<tr>
<td></td>
<td>(17' - 2'')</td>
<td>R(2) - R(0)</td>
<td>456.2 ± 1.4</td>
<td>452.4</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>(16' - 1'')</td>
<td>R(1) - R(2)</td>
<td>21.0 ± 0.4</td>
<td>22.8</td>
<td>-1.8</td>
</tr>
</tbody>
</table>
Chapter 5. Hyperfine Structure of Bromine

Table 5.12: The observed hyperfine free frequency separations, $\Delta \nu$, for some $P(J) - R(J+3)$ lines of the $(17' - 2'')$ band of $^{79}\text{Br}_2$, $^{81}\text{Br}_2$, and $^{79}\text{Br}^{81}\text{Br}$. terms up to those involving the quartic distortion constant ($D_v$) satisfies the relationship:

$$\frac{\nu(P(J)) - \nu(R(J + 3))}{(J+2)} = \alpha + \beta(J + 2)^2 \quad (5.16)$$

where

$$\alpha = [(-10B'_{17} + 6B''_2) + (120D'_{17} - 24D''_2)] \quad (5.17)$$

$$\beta = (20D'_{17} - 12D''_2) \quad (5.18)$$

Tables 5.13 and 5.14 contain the results of a least squares fit for $\alpha$ and $\beta$ for each isotopomer and compares the results with the values of Reference [7]. The observed and calculated values of $\beta$ are in good agreement. However, there is a systematic difference between the observed and calculated values of $\alpha$ of $(-0.304 \pm 0.017)$ MHz – well outside of the experimental uncertainties. The higher order centrifugal distortion terms (sextic and above) only contribute corrections of the order of tens of Hz to the calculated value of $\alpha$ so that the discrepancy appears to be significant. The determination made here of
Chapter 5. *Hyperfine Structure of Bromine*

### Table 5.13: The difference between the observed and calculated values of $\alpha$.

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>$\alpha_{\text{obs}}$ (MHz)</th>
<th>$\alpha_{\text{calc}}$ (MHz)</th>
<th>$\text{obs} - \text{calc}$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{79}\text{Br}_2$</td>
<td>47.872 ± 0.134</td>
<td>48.124</td>
<td>-0.252</td>
</tr>
<tr>
<td>$^{79}\text{Br}^{81}\text{Br}$</td>
<td>22.447 ± 0.035</td>
<td>22.758</td>
<td>-0.311</td>
</tr>
<tr>
<td>$^{81}\text{Br}_2$</td>
<td>-(2.376 ± 0.061)</td>
<td>-2.060</td>
<td>-0.316</td>
</tr>
</tbody>
</table>

### Table 5.14: The observed and calculated values of $\beta$.

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>$\beta_{\text{obs}}$ (MHz)</th>
<th>$\beta_{\text{calc}}$ (MHz)</th>
<th>$\text{obs} - \text{calc}$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{79}\text{Br}_2$</td>
<td>0.0288 ± 0.0023</td>
<td>0.0304</td>
<td>-0.0016</td>
</tr>
<tr>
<td>$^{79}\text{Br}^{81}\text{Br}$</td>
<td>0.0298 ± 0.0006</td>
<td>0.0294</td>
<td>0.0004</td>
</tr>
<tr>
<td>$^{81}\text{Br}_2$</td>
<td>0.0268 ± 0.0013</td>
<td>0.0284</td>
<td>-0.0016</td>
</tr>
</tbody>
</table>

This linear combination of molecular parameters may prove useful in the future in refining the values of the rotational and distortion constants.

Finally, the observations of frequency spacings between transitions arising from different bromine isotopomers provided an unusual opportunity to measure the relative positioning of the electronic potentials of $^{79}\text{Br}_2$, $^{79}\text{Br}^{81}\text{Br}$, and $^{81}\text{Br}_2$. A list of the observed frequency differences is given in Table 5.15 along with the predicted values. The results are divided into three groups for clarity. The first consists of 12 $^{79}\text{Br}_2 \rightarrow ^{79}\text{Br}^{81}\text{Br}$ observations. The second consists of 4 $^{79}\text{Br}^{81}\text{Br} \rightarrow ^{81}\text{Br}_2$ observations, and the third consists of a single $^{79}\text{Br}_2 \rightarrow ^{81}\text{Br}_2$ observation. Clearly the experimental frequency separations are systematically larger than the calculated values. This leads to the conclusion that the term values are slightly in error. For example, the $^{79}\text{Br}_2 \rightarrow ^{79}\text{Br}^{81}\text{Br}$
### Table 5.15: Observed hyperfine free frequency differences, $\Delta \nu$, between rovibronic transitions for different isotopomers as compared with the calculated differences based upon Reference [7].

<table>
<thead>
<tr>
<th>Transitions</th>
<th>$\Delta \nu$(obs) (MHz)</th>
<th>$\Delta \nu$(calc) (MHz)</th>
<th>obs - calc (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(11'-0'')^79$ R(18) - $(11'-0'')^79,81$ R(0)</td>
<td>$(427.9 \pm 2.8)$</td>
<td>$(251.8)$</td>
<td>$(176.1 \pm 2.8)$</td>
</tr>
<tr>
<td>$(11'-0'')^79$ R(18) - $(11'-0'')^79,81$ R(2)</td>
<td>$-(720.1 \pm 4.4)$</td>
<td>$-902.1$</td>
<td>$(182.0 \pm 4.4)$</td>
</tr>
<tr>
<td>$(13'-0'')^79$ P(15) - $(13'-0'')^79,81$ R(3)</td>
<td>$(1038.6 \pm 5.2)$</td>
<td>$(854.7)$</td>
<td>$(183.9 \pm 5.2)$</td>
</tr>
<tr>
<td>$(13'-0'')^79$ P(16) - $(13'-0'')^79,81$ P(4)</td>
<td>$(511.0 \pm 1.4)$</td>
<td>$(330.8)$</td>
<td>$(180.2 \pm 1.4)$</td>
</tr>
<tr>
<td>$(13'-0'')^79$ P(17) - $(13'-0'')^79,81$ R(10)</td>
<td>$(1219.5 \pm 1.6)$</td>
<td>$(1031.6)$</td>
<td>$(187.9 \pm 1.6)$</td>
</tr>
<tr>
<td>$(17'-2'')^79$ R(15) - $(17'-2'')^79,81$ R(4)</td>
<td>$(299.6 \pm 0.6)$</td>
<td>$(117.8)$</td>
<td>$(181.8 \pm 0.6)$</td>
</tr>
<tr>
<td>$(17'-2'')^79$ P(12) - $(17'-2'')^79,81$ R(4)</td>
<td>$(1057.8 \pm 2.3)$</td>
<td>$(875.0)$</td>
<td>$(182.8 \pm 2.3)$</td>
</tr>
<tr>
<td>$(14'-1'')^79$ P(7) - $(17'-2'')^79,81$ R(3)</td>
<td>$(1071.1 \pm 1.9)$</td>
<td>$(897.8)$</td>
<td>$(173.3 \pm 2.8)$</td>
</tr>
<tr>
<td>$(14'-1'')^79$ R(11) - $(17'-2'')^79,81$ R(5)</td>
<td>$(693.1 \pm 1.6)$</td>
<td>$(525.4)$</td>
<td>$(167.7 \pm 1.6)$</td>
</tr>
<tr>
<td>$(14'-1'')^79$ R(12) - $(17'-2'')^79,81$ R(7)</td>
<td>$(971.9 \pm 4.0)$</td>
<td>$(807.7)$</td>
<td>$(164.2 \pm 4.0)$</td>
</tr>
<tr>
<td>$(14'-1'')^79$ R(14) - $(17'-2'')^79,81$ R(10)</td>
<td>$(829.8 \pm 2.2)$</td>
<td>$(662.7)$</td>
<td>$(167.1 \pm 2.2)$</td>
</tr>
<tr>
<td>$(19'-2'')^79$ P(6) - $(13'-0'')^79,81$ P(2)</td>
<td>$(459.4 \pm 2.2)$</td>
<td>$(283.9)$</td>
<td>$(175.5 \pm 2.2)$</td>
</tr>
<tr>
<td>$(14'-1'')^79,81$ R(8) - $(17'-2'')^81$ R(1)</td>
<td>$-(106.7 \pm 3.5)$</td>
<td>$-317.4$</td>
<td>$(210.7 \pm 3.5)$</td>
</tr>
<tr>
<td>$(14'-1'')^79,81$ P(7) - $(17'-2'')^81$ P(4)</td>
<td>$(337.8 \pm 0.5)$</td>
<td>$(134.4)$</td>
<td>$(203.4 \pm 0.5)$</td>
</tr>
<tr>
<td>$(14'-1'')^79,81$ P(5) - $(17'-2'')^81$ R(3)</td>
<td>$-(458.9 \pm 3.0)$</td>
<td>$-669.0$</td>
<td>$(210.1 \pm 3.0)$</td>
</tr>
<tr>
<td>$(14'-1'')^79,81$ R(11) - $(17'-2'')^81$ R(8)</td>
<td>$(1086.1 \pm 2.2)$</td>
<td>$(874.4)$</td>
<td>$(211.7 \pm 2.2)$</td>
</tr>
<tr>
<td>$(14'-1'')^79$ P(17) - $(17'-2'')^81$ R(10)</td>
<td>$(126.1 \pm 2.1)$</td>
<td>$-260.0$</td>
<td>$(386.1 \pm 2.1)$</td>
</tr>
</tbody>
</table>
data show that the discrepancy between the observed and calculated values is about 180 MHz. (The value of $\Delta \nu$ for $(14'-1'') \rightarrow (17'-2'')$ data is an exception. The fact that the $\Delta \nu$ in this case shows a discrepancy of about 167 MHz may be evidence for some vibrationally dependent correction or may be a reflection of the uncertainty in the constants of Reference [7]. More data are required to resolve this question.) The $^{79}\text{Br}^{81}\text{Br} \rightarrow ^{81}\text{Br}_2$ data display a 210 MHz correction. That is,

\[
^{79}T_{00} - ^{79,81}T_{00} = (177 \pm 8)\text{MHz} \quad (5.19)
\]

\[
^{79,81}T_{00} - ^{81}T_{00} = (209 \pm 4)\text{MHz} \quad (5.20)
\]

Adding Equations 5.19 and 5.20 leads to the prediction,

\[
^{79}T_{00} - ^{81}T_{00} = (386 \pm 9)\text{MHz}, \quad (5.21)
\]

in remarkable agreement with the observation of $(386.1 \pm 2.1)$ MHz given in Table 5.15.

Because Gerstenkorn and Luc directly observed the $^{79}\text{Br}_2$ spectra and subsequently calculated the molecular constants for the other two isotopomers, it is reasonable to assume this shift is due to small terms that were neglected in the constants deduced for $^{81}\text{Br}_2$ and $^{79}\text{Br}^{81}\text{Br}$. To correct these, one needs only to shift the term values, $^{79,81}T_{00}$ by $-(177 \pm 9)$ MHz and $^{81}T_{00}$ by $-(386 \pm 9)$ MHz. The original ($T_{00}$) and corrected ($T'_{00}$) term values are shown in Table 5.16. The absolute values reported in the table are still only accurate to $\pm 0.0016$ cm$^{-1}$ ($\pm 48$ MHz), but the relative positions should be accurate to about $\pm 0.0003$ cm$^{-1}$ ($\pm 9$ MHz).
Table 5.16: The values of the B state term values reported by Reference [7], $T_{00}(B)$, and the values deduced from this work, $T'_{00}(B)$.

<table>
<thead>
<tr>
<th></th>
<th>$T_{00}(B)$ (cm$^{-1}$)</th>
<th>$T'_{00}(B)$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{79}\text{Br}_2$</td>
<td>15823.4297</td>
<td>15823.4297</td>
</tr>
<tr>
<td>$^{79}\text{Br}^{81}\text{Br}$</td>
<td>15823.9199</td>
<td>15823.9140</td>
</tr>
<tr>
<td>$^{81}\text{Br}_2$</td>
<td>15824.4146</td>
<td>15824.4018</td>
</tr>
</tbody>
</table>
Chapter 6

Natural Predissociation of the B state of Bromine

In the presence of predissociation the lifetime of a state decreases from its nonpredissociated lifetime. This is easy to understand as, in addition to radiation and collisions, the molecule now has another decay channel available. As a result the molecule will spend less time in the excited state. Two of the consequences of predissociation are that the level broadens and the fluorescence yield of the radiative transition is decreased owing to the molecules which fall apart without emitting a photon. These suggest different experimental techniques for studying the predissociation of excited state levels: (i) measurements of transition linewidths, (ii) direct lifetime measurements of the predissociated state, and (iii) relative intensity measurements of spectral lines. The approach taken depends upon the properties of both the molecular system under study and the type of predissociation being investigated. In this thesis the gyroscopic and hyperfine predissociation of molecular bromine was studied so that a technique that is sensitive to the properties of the individual hyperfine levels was required.

The method of making measurements of the linewidths of different hyperfine transitions has been performed on iodine [11] but the technique is very difficult to set up and use. Most of the levels of interest have sub-MHz linewidths whereas the linewidths of the lasers available for experiments are larger than 1 MHz. The authors of study [11] relied on a 2 photon resonant scattering technique in which the forward scattered light is recorded. The technique employed two frequency stabilized lasers, whose beams were made to pass colinearly through a long absorption cell. Direct lifetime measurements
have previously been performed on the rotational states of bromine [13, 14] and, in one case, on individual hyperfine levels of the B $^3\Pi_{0^+}$ state of iodine [12]. The studies used a laser beam that was pulsed on and off and the fluorescence decay of the excited molecules was recorded. The lifetime, $\tau$, is related to the radiative, predissociation, and collisional decay rates by,

$$\tau^{-1} = \Gamma_{\text{rad}} + \Gamma_P + \Gamma_{\text{coll}}$$  

(6.1)

$$\tau^{-1} = \Gamma_{\text{rad}} + C^2_v J(J+1) + \Gamma_{\text{p}^{\text{hf, int}}} + \Gamma_{\text{coll}}$$  

(6.2)

where the $C^2_v J(J+1)$ term is the pure gyroscopic predissociation rate, and $\Gamma_{\text{p}^{\text{hf, int}}}$ represents the sum of the hyperfine and interference predissociation terms. One can obtain accurate values of the gyroscopic predissociation parameter, $C^2_v$, by measuring the lifetimes of a series of rotational levels. The measurement for each rotational state must be performed at various different pressures to enable the researcher to extrapolate the results to zero pressure, thereby eliminating the collisional effects. By plotting the extrapolated inverse lifetimes as a function $J(J+1)$ one obtains $C^2_v$ from the slope. Theoretically, the intercept can provide the radiative decay rate and the predissociation parameters of the hyperfine levels underlying the rotational transitions. However, because the intercept is very small, and because one must correctly account for the different lifetimes of the hyperfine states, it is not possible to obtain very accurate values of $\Gamma_{\text{rad}}$ from the intercept of such a plot. To measure the decay rates of individual hyperfine levels using this laser pulsed technique is much more difficult. Such experiments are best performed on a molecular beam and require a laser which has a very narrow linewidth to avoid exciting several hyperfine transitions at the same time.

The simplest and most widely used technique [3, 4, 9] to measure the hyperfine predissociation relies on the fact that hyperfine predissociation couples different hyperfine states to the continuum by different amounts. This implies that the fluorescence yield
will be different for different hyperfine levels of a given rotational state. Thus, the hyperfine fluorescence spectra will display anomalies in the relative intensities of the spectral lines. The intensity of a peak may be fit to the model

$$ S(x) \propto S_0(x) \frac{\Gamma_{\text{rad}}}{\Gamma_{\text{rad}} + \Gamma_p} $$

(6.3)

where $S_0(x)$ is the intensity of the transition in the limit that $\Gamma_p = 0$. The predissociation rate, $\Gamma_p$, has been described in Chapter 3. It is very difficult to measure the absolute intensity of a given transition as this requires a very detailed knowledge of the detector efficiency, the laser beam profile, and so on. It is much easier to measure the relative intensities of two transitions labelled here as a and b.

$$ \frac{S(a)}{S(b)} = \frac{S_0(a)}{S_0(b)} \left[ \frac{\Gamma_{\text{rad}} + \Gamma_p(b)}{\Gamma_{\text{rad}} + \Gamma_p(a)} \right] $$

(6.4)

One of the problems with this technique is that it only produces the ratios of the predissociation parameters to the square root of the radiative decay rate, namely, $C_\nu/\sqrt{\Gamma_{\text{rad}}}$, $a_\nu/\sqrt{\Gamma_{\text{rad}}}$, and $b_\nu/\sqrt{\Gamma_{\text{rad}}}$. The main advantage of the relative intensity measurement technique is that it is comparatively easy to set up and use, requiring almost exactly the same experimental apparatus as was used for observing the hyperfine structure of bromine.

There are some serious drawbacks to this technique as well. First, the amount of time required to collect the data for the hyperfine structure of a single rotational transition was of the order of ten minutes. Thus, any variations in the intensities of either the laser beam or the molecular beam over this time introduce errors into the relative intensity measurements. Second, as was discussed in Chapter 2, the peak intensities of the different hyperfine transitions are sensitive to the polarization of the laser beam, to the positioning of the detector, and to the amount of solid angle observed by the optical system. Third, care had to be taken to ensure that the transitions were not saturated. A final, more
subtle point is that the experiment had to be designed so as to collect the fluorescent light with equal efficiency from the shortest to the longest-lived states being observed. If this is not done then many of the molecules excited into long-lived states will move out of the detection region without radiating while most of the molecules excited into short-lived states will decay inside the detection area. The net result is to enhance the relative strength of the states with short-lifetimes as compared to those with long lifetimes. This experimentally introduced bias will be reflected in the predissociation parameters obtained.

The radiative lifetime of the B state of bromine has been reported by two different authors [13, 14]. Clyne et al. [13] determined $\tau_{\text{rad}}$ by measuring the lifetimes of rotational states of $^{79}\text{Br}_2$, $^{81}\text{Br}_2$, and $^{79}\text{Br}^{81}\text{Br}$ for various vibrational states and extrapolating to $J = 0$. The lifetimes reported varied from 5 to 16 $\mu$s. A second study of the B $^3\Pi_0^+$ state of $^{81}\text{Br}_2$ by Peeters et al. [14] using a similar direct lifetime measurement technique found $\tau_{\text{rad}}$ to be from 2 to 5 $\mu$s. The values of $\tau_{\text{rad}}$ reported by Clyne et al. displayed a large variation with vibrational state and no attempt was made to take into account the hyperfine predissociation. In contrast, the work of Peeters et al. [14] attempted such a correction. Consequently, the latter work was accepted and it was initially assumed here that the radiative lifetime of the B state of bromine was of the order of 3 $\mu$s. Since the predissociation decreases the lifetime of a state, $\tau_{\text{rad}} = \Gamma_{\text{rad}}^{-1}$, is the longest lifetime of any state. The optical stack described in Chapter 5 could image a circle of roughly 3 mm in diameter where the laser and molecular beams intersected. Assuming that the average velocity of the molecules in the beam was 400 m/s, this meant that a molecule with a 3 $\mu$s lifetime travelled, on average, 1.2 mm from the point of excitation to the point of emitting a photon. With the existing optics, one could observe about 2.5 decay lengths or longer, sufficient for measurements with accuracy better than 10%.

With this in mind, work was started on measuring the predissociation of the B $^3\Pi_0^+$
state of $^{79}\text{Br}_2$, $^{81}\text{Br}_2$, and $^{79}\text{Br}^{81}\text{Br}$ employing the relative intensity technique. Several previous studies [3, 4, 14] had already characterized the hyperfine predissociation of bromine by the model developed by Vigué et al. [8] for iodine. This model included only up to the magnetic hyperfine predissociation terms. The results reported for bromine by References [3, 4] displayed some anomalous variation of the parameters with rotational state. This difficulty was thought to be not very serious and that the relative intensity measurements could be used to refine the previous results.

6.1 Saturation Tests

The first step in performing the predissociation measurements was to ensure that the laser was not saturating the transitions under study. The signal from a specific hyperfine transition was recorded several times as the laser intensity was varied. The signal intensity as a function of the laser intensity could be plotted. From this plot the point at which the laser began to saturate the transition could be estimated as the point where the plot deviated significantly from a straight line. In practice this was difficult because the observed LIF signals were sensitive to the variations in the position of the laser beam. Initially two consecutive polarizers were placed in the laser beam path with the second polarizer’s transmission axis held fixed (as shown in Figure 6.1) aligned with the laser’s initial axis of polarization. This was to ensure that the polarization of the laser beam interacting with the molecules remained constant to eliminate the possibility that changes in the LIF were due to variations of polarization of the laser beam. The intensity of the laser beam passing through the two polarizers is,

$$I(\beta) = I_0 \cos^4(\beta) \quad (6.5)$$

where $\beta$ is the angle between polarizer (P1) and fixed polarizer (P2) axes. With this arrangement the intensity of the laser beam interacting with the molecular beam could be
continuously varied. Unfortunately, as P1's axis was changed the direction of propagation of the laser beam also changed. The beam could be displaced by about one beam diameter over a 2 meter path length ruling out this arrangement.

A method of rotating the polarization of the laser beam without displacing the beam's position was required. The solution was to place a Pockels cell between two fixed polarizers as shown in Figure 6.2. A Pockels cell is an isotropic material which becomes birefringent when a voltage is applied across it. The result is that the axis of polarization of the light can be rotated as a function of the voltage. This provides a straightforward technique for varying the laser's intensity while maintaining the polarization of the laser light passing through the polarizer – Pockels cell arrangement. With this technique no displacement of the laser, to better than 0.1 beam diameter, was observed over a 6 meter
Figure 6.2: The polarizer–Pockels cell (PC) arrangement for varying the intensity of a laser beam while maintaining the direction of polarization of the transmitted light.
Table 6.1: The Franck–Condon factors for various B–X vibrational transitions for $^{79}$Br$_2$ as given by Reference [38] and the calculated saturation laser powers based on Equation 6.6.

<table>
<thead>
<tr>
<th>$(v' - v'')$</th>
<th>Franck–Condon Factor</th>
<th>$P_{\text{sat}}^{\text{calc}}$ ($\Delta F = \Delta J$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(13' - 0'')$</td>
<td>0.00041</td>
<td>60 mW</td>
</tr>
<tr>
<td>$(16' - 1'')$</td>
<td>0.00799</td>
<td>3 mW</td>
</tr>
<tr>
<td>$(17' - 2'')$</td>
<td>0.02405</td>
<td>1 mW</td>
</tr>
</tbody>
</table>

The intensities of the B–X P(4), $F'' = 4$ to $F' = 4$ and the $F'' = 4$ to $F' = 3_{-}$ hyperfine transitions for the $(13' - 0'')$, $(16' - 1'')$, and $(17' - 2'')$ vibrational bands of $^{79}$Br$_2$ were recorded as a function of laser power. The results are shown in Figures 6.3 to 6.5. For transitions from the same lower state to different upper states, the stronger the transition, the easier it is to saturate. Therefore, the $F'' = 4$ to $F' = 4$ peaks should show a higher saturation threshold than the $F'' = 4$ to $F' = 3_{-}$ peaks, exactly as observed.

The vibrational band to vibrational band saturation dependence is primarily determined by the Franck–Condon factors (FCF) for the transitions. The larger the FCF, the stronger the transition, and the easier it is to saturate. The FCF’s for these three bands, quoted from [38] are given in Table 6.1. Again observed transitions follow the behaviour expected with the $(13' - 0'')$ band being the hardest to saturate and the $(17' - 2'')$ the easiest. The laser power required to saturate transitions from different vibrational bands may be estimated from the data in Figures 6.3 to 6.5 and the FCF’s. i.e.

$$P_{\text{sat}}(v' - v'') = \frac{\text{FCF}(13' - 0'')}{\text{FCF}(v' - v'')} P_{\text{sat}}(13' - 0'')$$ (6.6)
Figure 6.3: The observed laser power dependence of the signal intensities of two $^{79}\text{Br}_2$ B–X (13'–0'') P(4) hyperfine transitions: (a) the $\Delta F = \Delta J F'' = 4 \rightarrow F' = 3$ transition and (b) the $\Delta F \neq \Delta J F'' = 4 \rightarrow F' = 4$ transition. Transition (b) shows a linear response, i.e. no saturation, for laser powers of up to 250 mW while the stronger transition (a) displays nonlinear behaviour at an input power of about 60 mW.
Figure 6.4: The observed signal intensities of the $^{79}\text{Br}_2$ B–X (16' – 1") P(4) (a) and (b) hyperfine transitions as a function of laser power. These both display nonlinear behaviour beginning at very low laser power, $P < 15\text{mW}$.
Figure 6.5: The observed signal intensities of the $^{79}$Br$_2$ B–X (17'–2'') P(4) (a) and (b) hyperfine transitions as a function of laser power. These transitions are more easily saturated than their (16'–1'') and (13'–0'') band counterparts.
A final note is made here that, although the laser intensity should be quoted in power per unit area, the saturation intensity has been written as a power. This is done because the area of the laser beam when it intersects the molecular beam is constant (roughly 6 mm²) and it is more convenient to measure the laser power than the intensity before it enters the molecular beam machine.

6.2 Polarization Effects

As discussed in Chapter 2, the LIF signal depends upon the polarization of the laser and the positioning of the detector. The LIF signals of the low J hyperfine levels are the most sensitive to the polarization of the laser radiation. To test this effect, a similar arrangement as was used for the saturation tests was employed (Figure 6.2). The second polarizer, P2, was removed and, by using the Pockels cell, the polarization of the laser could be rotated from vertical (z direction) to horizontal (y direction) without changing the direction of propagation of the laser beam. The ⁷⁹Br₂ B–X (13′ – 0′) R(0) transition was chosen as suitable for study because the hyperfine spectrum provides pairs of resolved peaks, labelled a, b and c, d in Figure 6.6, which start in separate lower hyperfine states and end in the same upper hyperfine state. Thus any change in relative intensities for a:b or c:d will be due solely to polarization effects and not to any differences in predissociation of the upper hyperfine states. The observed and predicted relative intensities are given in Table 6.2.

The discrepancy between the theoretical and experimentally observed ratios is due to the fact that the theoretical values were calculated assuming that the detector collected light only over a very small solid angle. These measurements of the polarization dependence of the LIF may be used to calculate the amount of solid angle observed. This, in turn, must be used to deduce the expected relative intensities of the different hyperfine
Figure 6.6: The observed $^{79}\text{Br}_2$ B–X ($13'-0''$) R(0) hyperfine spectrum with the laser polarized vertically (z-direction) and horizontally (y-direction). The relative intensities of peak a ($F'' = 2 \rightarrow F' = 1_-$) compared to peak b ($F'' = 0 \rightarrow F' = 1_-$) and peak c ($F'' = 2 \rightarrow F' = 1_+$) compared to peak d ($F'' = 0 \rightarrow F' = 1_+$) show a strong polarization dependence.
Chapter 6. Natural Predissociation of the B state of Bromine

<table>
<thead>
<tr>
<th></th>
<th>z polarization $S_z$</th>
<th>y polarization $S_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(a:b)_{\text{theory}}$</td>
<td>2.70</td>
<td>0.76</td>
</tr>
<tr>
<td>$(a:b)_{\text{obs}}$</td>
<td>1.26 ± 0.15</td>
<td>0.96 ± 0.10</td>
</tr>
</tbody>
</table>

Table 6.2: The intensity ratios of the B - X R(0) (13$'$ - 0$''$) hyperfine transitions a:b ($F'' = 2 \rightarrow F' = 1^1$) to ($F'' = 0 \rightarrow F' = 1^1$) for $^{79}\text{Br}_2$ with the laser polarized vertically (z-direction) and horizontally (y-direction).

transitions in the absence of predissociation. Without taking this correction into account, the values obtained for the predissociation parameters obtained from relative intensity measurements will be in error.

6.3 Relative Intensity Measurements

A series of measurements of the relative intensities of the hyperfine transitions of $^{79}\text{Br}_2$, $^{81}\text{Br}_2$, and $^{79}\text{Br}^{81}\text{Br}$ was made for various upper electronic state vibrational levels. The relative intensities for the levels in $v' = 11$, 12, and 13 appeared to be in agreement with the results previously published [3, 4]. However, our investigation of the $v' = 5$, $J' = 0$ hyperfine levels with $F' = 1$ and 3, showed inconsistent results from day to day and between isotopomers. To make sense of this observation one must realize that the $v' = 5$ level is strongly predissociated [13] so that the ($J' = 0$) hyperfine levels have very different lifetimes.

One can picture the apparatus as follows. The molecules in the beam travel in the positive x direction with a constant velocity, V. Let $x = -S$ be defined as the position of the molecular source. The optical system collects LIF photons emitted between the
positions \( x = -B \) and \( x = B; x = 0 \) lies at the center of this region. The laser radiation intersects the molecular beam at 90° at position \( X \). If one studies two levels, one with a (long) lifetime, \( \tau_L \), and the other with a (short) lifetime \( \tau_S \), then the observed relative intensities of the two transitions will depend upon the velocity of the molecular beam, \( V \), the length of the detection region, \( 2B \), the position of the laser beam–molecular beam interaction, \( X \), and the two lifetimes, \( \tau_L \) and \( \tau_S \). As a concrete example, let \( V = 500 \text{ m/s} \), \( 2B = 5 \text{ mm} \), \( \tau_L = 10 \mu\text{s} \), and \( \tau_S = 1 \text{ ns} \). This implies that the molecules excited into the long-lived state travel 5 mm before emitting a photon (on average) and those excited into the short-lived state travel only 0.5 \( \mu\text{m} \) before decaying (on average). The consequences of this are illustrated by the following three experiments.

(i) Suppose that the interaction point is at the center of the detection region (\( X = 0 \)). In this case one will observe virtually all of the fluorescence from the short-lived level, \( \tau_S \), and about 40% of the fluorescence from the long-lived level, \( \tau_L \). (i.e. Almost all of the short-lived molecules decay within the detection region while only about 40% of the long-lived decay in the same region.) Thus one records a spectrum with two peaks.

(ii) The laser radiation and molecular beam intersect 5 mm before the detection region (i.e. \( X = -B - 5 \text{ mm} \)). Here, almost none of the molecules excited into the short-lived level will be observed while about 24% of the molecules excited into the long-lived level are seen. One observes only one spectral line and could conclude that the absence of the transition from the short-lived level is evidence for strong predissociation of this level.

(iii) Finally, the laser beam is arranged so as to intersect the molecules 1 mm behind \( B \) (\( X = B - 1 \text{ mm} \)). With this arrangement one observes almost all of the LIF from the \( \tau_S \) level and almost no LIF from the \( \tau_L \) level. Again one records a spectrum with
Table 6.3: The intensities, $S$, of the two $^{81}$Br$_2$ B–X ($5' - 1''$) P(1) hyperfine transitions as a function of the laser beam–molecular beam interaction position, $X$. $S(F' = 3)$ arises from the transition $F'' = 4 \rightarrow F' = 3$, and $S(F' = 1)$ arises from the transition $F'' = 1 \rightarrow F' = 1$.

<table>
<thead>
<tr>
<th>X (mm)</th>
<th>$S(F' = 3)$ (arb.)</th>
<th>$S(F' = 1)$ (arb.)</th>
<th>$S(F' = 3)/S(F' = 1)$</th>
<th>$\alpha_x^2/\Gamma_{rb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.54</td>
<td>3.32 ± 0.13</td>
<td>4.42 ± 0.53</td>
<td>0.76 ± 0.09</td>
<td>(2.154 ± 0.255)</td>
</tr>
<tr>
<td>0.00</td>
<td>4.77 ± 0.32</td>
<td>4.53 ± 0.38</td>
<td>1.06 ± 0.08</td>
<td>(0.866 ± 0.065)</td>
</tr>
<tr>
<td>1.24</td>
<td>3.94 ± 0.21</td>
<td>2.56 ± 0.24</td>
<td>1.52 ± 0.11</td>
<td>(0.366 ± 0.026)</td>
</tr>
<tr>
<td>2.46</td>
<td>2.15 ± 0.13</td>
<td>1.90 ± 0.26</td>
<td>1.14 ± 0.12</td>
<td>(0.726 ± 0.076)</td>
</tr>
</tbody>
</table>

only one peak. This time one would conclude that the long-lived level is completely predissociated.

The point of this discussion is that if the optical system does not collect the LIF from the long- and short-lived states under study with equal efficiency, then the predissociation parameters deduced from the measurements of the relative intensities of spectral features will be in error.

In light of the anomalous findings for the $(v' = 5, J' = 0)$ hyperfine levels of bromine the optical system used for the relative intensity measurements was tested. A flat glass plate was placed in the path of the laser beam so that the laser beam–molecular beam interaction position, $X$, could be varied simply by rotating the plate. The intensities of the two hyperfine components were studied as a function of $X$ in the P(1) rotational transition of the $(5' - 1'')$ band. The transitions selected were $(F'' = 4 \rightarrow F' = 3)$ and $(F'' = 1 \rightarrow F' = 1)$. The former had a much shorter lifetime than the latter. The results are summarized in Table 6.3. As is evident, the signal from the longer-lived $F' = 1$ hyperfine level decreased rapidly as the laser was moved away from the source.
The signal from the shorter-lived $F' = 3$ state dropped less rapidly when the laser beam was moved away from the source and also decreased when the laser was translated closer to the molecular beam source with respect to the center of the optical detection region. These observations are easily understood in the light of experiments (i), (ii), and (iii) described above. The final column in Table 6.3 lists the parameter,

$$\frac{a_v^2}{\Gamma_{rb}} = \frac{a_v^2}{\Gamma_{rad} + 2.4b_v^2} \text{ (6.7)}$$

deduced from the different measurements. (Note that previous authors [3, 4, 14] have assumed $b_v = 0$.) These findings clearly indicated that the optical collection system was inadequate and had to be re-designed. As well, they pointed to the possibility that the radiative lifetime of the B state of bromine was much longer than the value of about $3\mu$s initially assumed.

6.4 The Lifetime Plan

The active area of the photomultiplier was a rectangle $(22 \times 7)$ mm$^2$ arranged so that the long axis coincided with the molecular beam axis. With an optical system of unity magnification one could, at most, detect light from a 22 mm length along the molecular beam. For molecules travelling at 500 m/s, this distance represents 3 decay lengths for a molecule excited into a 14.5 $\mu$s lifetime level. The new optical design relied upon the lens arrangement shown in Figure 6.7. With a lens (L1) placed 2 focal lengths (2f) in front of an object (O), an inverted, unity magnification image (I1) is formed 2f behind the lens. A second lens (L2) placed 4f behind the first forms another unity magnification, inverted image of I1 2f behind the second lens (I2). This process can be continued with more lenses to transport a unity magnification image of the original object along a distance $D = 4Nf$ (where N is a positive integer). This arrangement can be refined by adding a lens identical to L1 2f away from it, as shown in Figure 6.8. One of the advantages
Figure 6.7: Illustration of the design principle used for the final optical stack.

of using pairs of lenses separated by 2f is that the image formed is 4f away from the original object even if the object position is considerably different from 2f away from the first lens. In addition the second lens helps to collect more light and correct some of the aberrations of the first lens giving a brighter, sharper image. Three such lens pairs (Melles Griot aspheric glass condensers number 01 LAG 007, focal length 26.5 mm, diameter 30 mm) were used to collect the fluorescent light and pipe it up to the active surface of the photomultiplier. The final optical arrangement is shown in Figure 6.9. The 110 mm focal length lens was kept out of convenience as this acted as a the vacuum seal for the molecular beam apparatus. Direct measurements of the final optical arrangement found that the new stack imaged an area of \((18 \times 7) \text{ mm}^2\).

Next the input and exit laser windows were enlarged from 3 mm to roughly 1.2 cm to allow the laser beam to interact with the molecular beam at various positions, X. (As in the previous discussion, X = 0 represents the center of the optical collection region, X < 0 is closer to the source of the molecules, and X > 0 is farther downstream.) This arrangement allowed one to make relative intensity measurements as a function of the number of decay lengths observed in the optical collection region, and a determination
Figure 6.8: A pair of identical lenses separated by 2 focal lengths, 2f, produces the image of an object 4f away from the object independent of changes in the position of the object with respect to the lenses.

of the response of the optical system. The response across the detection region, shown in Figure 6.10, was measured by recording the strength of the B-X (13'-0'') R(9) F'' = 11 → F' = 12 hyperfine transition as a function of X. The optical stack's collection region was −9 mm ≤ X ≤ 9 mm. By making X < 0 the laser intersected the molecular beam closer to the molecular beam source, and one had a longer LIF collection length. Conversely, making X > 0 the optical collection length was shortened. With the new design the laser beam could be translated from X approx −8 mm to X ≈ 2.5 mm. By observing this relatively short-lived transition, \( \tau \approx 1 \mu s \), one did not have to worry about losing signal due to molecules decaying outside the viewing region over the range of X tested. The response of the optical stack was assumed to be symmetric about \( X = 0 \) and the data was fit with to a quadratic,

\[
R(X) = 0.96 - 0.000239X - 0.00207X^2
\]  

(6.8)

This large window also allowed a determination of the velocity of the molecular beam.
Figure 6.9: The new optical arrangement. Three pairs of identical lens doublets L1–L2, L3–L4, and L6–L7, were used to move the LIF onto the photomultiplier (PMT) with unity magnification. The 110 mm focal length lens, L5, was used as a window out of the vacuum chamber and slightly demagnified the image. This arrangement allowed the detection of an area of (18×7) mm².
Figure 6.10: The response of the optical collection system across the viewing area.
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By recording a hyperfine spectrum with the laser beam reflected back through the molecular beam as shown in Figure 6.11 (a), one observed two overlapping spectra shifted in frequency by amounts,

\[
\frac{\Delta \nu_a^1}{\nu} = \frac{v}{c} \sin \alpha \tag{6.9}
\]
\[
\frac{\Delta \nu_a^2}{\nu} = \frac{v}{c} \sin(\beta - \alpha) \tag{6.10}
\]
\[
\delta_a = \frac{\Delta \nu_a^1 - \Delta \nu_a^2}{\nu} = \frac{v}{c} (\sin \alpha - \sin(\beta - \alpha)) \approx \frac{v}{c} (2\alpha - \beta) \tag{6.11}
\]

Similarly one observes two overlapping spectra with the arrangement in Figure 6.11 (b) shifted by,

\[
\frac{\Delta \nu_b^1}{\nu} = \frac{v}{c} \sin(\alpha + \gamma) \tag{6.12}
\]
\[
\frac{\Delta \nu_b^2}{\nu} = \frac{v}{c} \sin(\alpha + \gamma) \tag{6.13}
\]
\[
\delta_b = \frac{\Delta \nu_b^1 - \Delta \nu_b^2}{\nu} = 2\frac{v}{c} \sin(\alpha + \gamma) \approx \frac{v}{c} (2\alpha + 2\gamma) \tag{6.14}
\]

By measuring these two frequency shifts one obtains the molecular beam velocity, \(v\), according to:

\[
v = \frac{c}{\nu} \left[ \delta_b - \delta_a \right] \tag{6.15}
\]

Using a nozzle of diameter \((21.8 \pm 3.6)\mu m\), a skimmer of 1 mm diameter and a mixture of 20% bromine in argon at a backing pressure of roughly 300 Torr, the velocity of the molecular beam was measured to be

\[v_{Ar+Br_2} = (420 \pm 60)m/s\]
For a pure bromine beam using the same nozzle and skimmer at a backing pressure of 180 Torr, the velocity was,

\[ v_{\text{Br}_2} = (350 \pm 80) \text{m/s} \]

Using the new lens configuration, very different LIF spectra were observed. Figure 6.12 shows the hyperfine spectrum of the B–X (13′ − 0″) P(1) transition of \(^{79}\text{Br}_2\) as observed with the old optical system (A) and the new system (B). As can be seen, the relative intensities of the spectral lines arising from the long-lived F′ = 1 levels were much larger with the re-designed optical system. This was clear evidence that the previous LIF optical collection arrangement was inadequate.

This re-design worked well but had three drawbacks: first, the results of the relative intensity measurements had to be corrected for the variations in collection efficiency across the optical viewing region; second, the new optical stack collected roughly 4 times less light compared to the original design; third, the new stack had more components leading to more reflection losses. The signal to noise with the new system dropped by about a factor of 8 to 10 compared to the previous arrangement. To compensate, the slits collimating the molecular beam were widened to increase the size of the molecular beam, regaining a factor of 2 in signal to noise. This led to an increase in the residual Doppler widths of the observed hyperfine lines from 3–4 MHz to about 8 MHz. In the end, the overall signal to noise was decreased by a factor of 4 to 5.

6.5 The Phase Shift Method

Direct measurements of the lifetimes of individual hyperfine levels is the best way to determine not only the predissociation parameters but also the radiative lifetime of the
Figure 6.11: The two types of measurements used to deduce the molecular beam velocity. (a) The laser beam crosses the molecular beam (moving at an angle $\alpha$ to the y-axis shown), is reflected back at an angle $\beta$, and crosses the molecular beam again, resulting in the two overlapping hyperfine spectra shown. (b) The laser beam crosses the molecular beam at an angle $\frac{\pi}{2} - \gamma$ to the y-axis and is reflected back on itself give the two overlapping spectra shown.
Figure 6.12: The observed $^{79}\text{Br}_2 (13' - 0'') P(1)$ hyperfine spectra using the initial optical collection system (A) and the redesigned system (B). The long-lived $F' = 1$ levels show a dramatic increase in intensity relative to the short-lived $F' = 3$ levels with the longer viewing length indicating that the initial collection system was inadequate. The peaks labelled with both a 1 and 3 are blended lines with the * indicating the stronger of the two forming the feature.
electronic state being studied. Unfortunately, with the available equipment it was not possible to rapidly switch the laser beam off and on to directly monitor the LIF decay. However, there was an alternative technique which could be applied here: the phase shift method [39]. In this technique the laser beam's intensity is modulated at angular frequency, $\Omega$, and the resulting LIF lags behind the excitation by phase, $\phi$, according to

$$\tan \phi = -\Omega \tau$$  \hspace{1cm} (6.16)

where $\tau$ is the lifetime of the state being studied.

To understand the technique one can conceptualize the molecular system as consisting of the levels, $n_0$ and $n_1$, the lower and upper states respectively. Molecules are excited out of $n_0$ with a modulated resonant laser beam into level $n_1$ with lifetime $\tau$. For simplicity the laser intensity, $I_{\text{laser}}$, will be described by

$$I_{\text{laser}} = I_0(1 + \sin \Omega t)$$  \hspace{1cm} (6.17)

where $\Omega$ is the angular modulation frequency. The excited molecules then decay at rate $\Gamma = \tau^{-1}$ into other levels. Assuming that the population of the lower level, $n_0$, is not appreciably altered by the laser field (i.e. weak laser intensity) one has,

$$\frac{dn_1}{dt} = n_0 I_{\text{laser}} - \Gamma n_1$$

$$= n_0 I_0(1 + \sin \Omega t) - \Gamma n_1$$  \hspace{1cm} (6.18)

Choosing the trial solution,

$$n_1(t) = M \sin \Omega t + N \cos \Omega t + O$$  \hspace{1cm} (6.19)

one obtains,

$$n_1(t) = n_0 I_0 \left[ \frac{\Gamma}{\Omega^2 + \Gamma^2} \right] \sin \Omega t - n_0 I_0 \left[ \frac{\Omega}{\Omega^2 + \Gamma^2} \right] \cos \Omega t + \frac{n_0 I_0}{\Gamma}$$  \hspace{1cm} (6.20)
This solution is of the form,

\[ n_1(t) = N_0 \sin(\Omega t + \phi) + O \]

\[ = N_0 \cos \phi \sin \Omega t + N_0 \sin \phi \cos \Omega t + O \]  \hspace{1cm} (6.21)

By inspection, the phase shift is given by

\[ \tan \phi = -\frac{\Omega}{\Gamma} \]

\[ = -\Omega \tau \]  \hspace{1cm} (6.22)

(where \( \tau = 1/\Gamma \)) in agreement with Equation 6.16.

It is important to realize the main advantage of this type of approach. This method is a ratiometric technique. That is, one needs only to measure the ratio of the coefficients of the \( \cos \Omega t \) and the \( \sin \Omega t \) terms to deduce the lifetime of a given state. This is achieved by detecting the LIF with a lock in amplifier. The in-phase (IP) component corresponds to the part of the signal oscillating in phase with the excitation (the \( \sin \Omega t \) part above), and the in-quadrature (IQ) component is the part of the signal 90° out of phase with the laser modulation (the \( \cos \Omega t \) term). This gives,

\[ \tan \phi = \frac{IQ}{IP} \]

\[ = -\Omega \tau \]  \hspace{1cm} (6.23)

Because one is not comparing the intensities of one hyperfine peak to the next, the results of this technique are no longer sensitive to temporal variations in the laser and molecular beam intensities. As well, the polarization, and detector efficiency variations over the field of view cancel out. In short, this method is insensitive to many of the systematic errors inherent in other techniques.
Figure 6.13: A schematic diagram of the laser beam and optical collection region with respect to the molecular beam.

6.6 Full Theory

The arrangement of the laser beam and optical collection region with respect to the molecular beam is described schematically in Figure 6.13. The molecular beam is shown with molecules travelling at velocity, $v$, along the x-axis. The laser beam intersects the molecular beam at $90^\circ$ and is idealized as being of length $L$, as having a constant electric field amplitude over this length, and is modulated according to

$$I_{\text{laser}} = I_0(1 + a \sin \Omega t)$$  \hspace{1cm} (6.24)

The optical system collects photons over the length $0 \leq x \leq W$. The probability, $P(x_D, t)$, that a photon is emitted at a position $x = x_D$ to $x_D + dx_D$ within the observation region,
and at a time \( t \), is given by the probability, \( P_e(x_0, t_0) \), that molecule was excited at a position \( x_0 \) at an earlier time, \( t_0 = t - (x_D - x_0)/v \), times the probability, \( P_d(x_D, x_0) \), that the molecule remains in the excited state from the position where it was excited to position \( x_D \), where it decays. The probability that the molecule was excited at time \( t_0 \) and position \( x_0 \) is proportional to the laser intensity, \( I_{\text{laser}} \);

\[
P_e(x_0, t_0) \propto I_0(1 + \sin \Omega t_0) \frac{dx_0}{v} \quad (6.25)
\]

The probability that the molecule remains in the excited state is proportional to a simple exponential decay;

\[
P_d(x_D, x_0) \propto \exp \left( -\frac{\Gamma(x_D - x_0)}{v} \right) \frac{dx_D}{v} \quad (6.26)
\]

Therefore, using this model, the amount of signal collected by the detector between \( x = x_D \) to \( x_D + dx_D \), at time, \( t \), is,

\[
dS(t,x_D) = N \left\{ \int \frac{dx_0}{v} \exp \left( -\frac{\Gamma(x_D - x_0)}{v} \right) \frac{dx_D}{v} \right\} (1 + \sin \Omega t_0) \quad (6.27)
\]

where \( N \) is a normalization factor. The total signal observed at time \( t \) is,

\[
S(t) = \int dS(t; x_D) \quad (6.28)
\]

These integrations must be performed for decays in two separate regions; region (I) is the area outside the laser beam, and region (II) is inside the laser beam. For region (I), the integral in Equation 6.27 is over \( 0 \leq x_0 \leq L \) and the integral in Equation 6.28 is over \( L \leq x_D \leq W \). The result is

\[
S_I(t) = N \left[ \begin{array}{c} \frac{(\exp(-\Gamma T) - \exp(-\Gamma U)) (\exp(-\Gamma T) - 1)}{\Gamma^2} \\
+ \frac{a \sin \Omega t}{(\Gamma^2 + \Omega^2)^2} \left\{ F(\Gamma, \Omega, T_1) - F(\Gamma, \Omega, T_2) - F(\Gamma, \Omega, T_3) + (\Gamma^2 - \Omega^2) \right\} \\
- \frac{a \cos \Omega t}{(\Gamma^2 + \Omega^2)^2} \left\{ G(\Gamma, \Omega, T_1) - G(\Gamma, \Omega, T_2) - G(\Gamma, \Omega, T_3) + 2\Omega \right\} \end{array} \right] \quad (6.29)
\]
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where

\[ T_1 = \frac{W}{v} \]  
(6.30)

\[ T_2 = \frac{L}{v} \]  
(6.31)

\[ T_3 = \frac{(W - L)}{v} \]  
(6.32)

and

\[ F(\Gamma, \Omega, T_1) = \exp(-\Gamma T_1) \left[ (\Gamma^2 - \Omega^2) \cos \Omega T_1 - 2\Gamma \Omega \sin \Omega T_1 \right] \]  
(6.33)

\[ G(\Gamma, \Omega, T_1) = \exp(-\Gamma T_1) \left[ (\Gamma^2 - \Omega^2) \sin \Omega T_1 + 2\Gamma \Omega \cos \Omega T_1 \right] \]  
(6.34)

By inspection one has

\[ \tan \phi_I = -\frac{G(\Gamma, \Omega, T_1) - G(\Gamma, \Omega, T_2) - G(\Gamma, \Omega, T_3) + 2\Gamma \Omega}{F(\Gamma, \Omega, T_1) - F(\Gamma, \Omega, T_2) - F(\Gamma, \Omega, T_3) + (\Gamma^2 - \Omega^2)} \]  
(6.35)

In the limiting case where \( W \to \infty \) and \( T_2 \to 0 \), \( \tan \phi_I \to -\Omega/\Gamma \) as expected.

For region (II) the integral in Equation 6.27 is performed over \( 0 \leq x_0 \leq x_D \) and the integral in Equation 6.28 is performed over \( 0 \leq x_D \leq L \). The solution for region (II) is,

\[ S_{II}(t) = N \left[ \frac{T_2}{\Gamma} - \frac{(1 - \exp(-\Gamma T_2))}{\Gamma^2} \right. \]

\[ + \frac{a \sin \Omega t}{(\Gamma^2 + \Omega^2)} \left\{ \Gamma T_2 + \frac{F(\Gamma, \Omega, T_2)}{(\Gamma^2 + \Omega^2)} - \frac{(\Gamma^2 - \Omega^2)}{(\Gamma^2 + \Omega^2)} \right\} \]

\[ - \frac{a \cos \Omega t}{(\Gamma^2 + \Omega^2)} \left\{ \Omega T_2 + \frac{G(\Gamma, \Omega, T_2)}{(\Gamma^2 + \Omega^2)} - \frac{2\Gamma \Omega}{(\Gamma^2 + \Omega^2)} \right\} \]

\[ \left. \right\} \]  
(6.36)

and

\[ \tan \phi_{II} = -\frac{\Omega T_2(\Gamma^2 + \Omega^2) + G(\Gamma, \Omega, T_2) - 2\Gamma \Omega}{\Gamma T_2(\Gamma^2 + \Omega^2) + F(\Gamma, \Omega, T_2) - (\Gamma^2 - \Omega^2)} \]  
(6.37)

Here, again, \( \tan \phi_{II} \to -\Omega/\Gamma \) as \( T_2 \to \infty \).

The total signal observed is the sum of \( S_I(t) \) and \( S_{II}(t) \),
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\[
S(t) = \mathcal{N} \left[ \frac{T_2}{\Gamma} - \frac{\exp(-\Gamma T_1)(1 - \exp(-\Gamma T_2))}{\Gamma^2} \right. \\
+ \frac{a \sin \Omega t}{(\Gamma^2 + \Omega^2)} \left\{ \frac{\Gamma T_2}{(\Gamma^2 + \Omega^2)} \left[ \frac{F(\Gamma, \Omega, T_1)}{(\Gamma^2 + \Omega^2)} - \frac{F(\Gamma, \Omega, T_3)}{(\Gamma^2 + \Omega^2)} \right] \\
- \frac{a \cos \Omega t}{(\Gamma^2 + \Omega^2)} \left\{ \frac{\Omega T_2}{(\Gamma^2 + \Omega^2)} \left[ \frac{G(\Gamma, \Omega, T_1)}{(\Gamma^2 + \Omega^2)} - \frac{G(\Gamma, \Omega, T_3)}{(\Gamma^2 + \Omega^2)} \right] \right\} \right]
\tag{6.38}
\]

with

\[
\tan \phi = -\frac{\Omega T_2(\Gamma^2 + \Omega^2) + G(\Gamma, \Omega, T_1) - G(\Gamma, \Omega, T_3)}{\Gamma T_2(\Gamma^2 + \Omega^2) + F(\Gamma, \Omega, T_1) - F(\Gamma, \Omega, T_3)}
\tag{6.39}
\]

Provided \(\Gamma T_1 = \Gamma W/v\) and \(\Gamma T_3 = [\Gamma(W - L)]/v\) are large compared to 1, the \(F(\Gamma, \Omega, T_1)\) and \(G(\Gamma, \Omega, T_1)\) terms in the expression for \(\tan \phi\) are negligible and one obtains the usual result.

\[
\tan \phi = -\frac{\Omega}{\Gamma}
= -\Omega \tau.
\tag{6.40}
\tag{6.41}
\]

Equation 6.41 holds provided one collects a large enough fraction of the LIF and the LIF is due to a single transition. The behaviour of the expression for \((\tan \phi)/\Omega\) (referred to here as the apparent lifetime) as a function of the viewing length, \(W\), is shown in Figure 6.14 for states with various different lifetimes. In Figure 6.14 it is assumed that the molecules in the molecular beam are travelling at 420 m/s and the laser beam–molecule interaction length, \(L\), is 2 mm. From the plot one observes that under such conditions, a viewing length of 16 mm is sufficient to measure lifetimes of up to 12 \(\mu s\) to within 8%. The behaviour of the apparent lifetime with molecular beam velocity is shown in Figure 6.15. As expected, the reliability of the measurement of longer lifetimes decreases as the velocity increases. For a level with an 8\(\mu s\) lifetime, the accuracy is degraded to \pm 5% when the velocity changes from 420 m/s to 500 m/s.

Another advantage of using the phase shift method was the insensitivity of the results to the variations in the efficiency of the detector over the field of view and to the exact
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Figure 6.14: The apparent lifetime as a function of the viewing length along the molecular beam that is imaged. Curves a – f are for states with true lifetimes of 12μs, 10μs, 8μs, 5μs, 2μs, and 1μs, respectively. The above calculation (with \( v = 420 \text{ m/s} \) and \( \Omega = 2\pi(10 \text{ kHz}) \)) indicates that a viewing window of 16 mm will lead to an 8% error in the lifetime of a 12μs state, a 5% error for a 10μs state, and a 3% error for an 8μs state.
Figure 6.15: The apparent lifetime as a function of the viewing length and molecular beam velocity for a state with an 8μs lifetime.
spatial profile of the laser beam. Both effects were investigated by numerically integrating the equations for the observed signal.

6.7 Experimental Arrangement

The new optical stack was placed in the beam machine as shown in Figure 6.16. The laser was modulated using the Pockels cell (Lasermetrics LM4-A), PC, placed between two crossed polarizers. The first polarizer, P1, had its axis aligned vertically while the second, P2, passed light with horizontal polarization. The Pockels cell sinusoidal modulation voltage was supplied by tunable frequency function generator (IEC F33 Function Generator), SG, fed into a power amplifier (Techron model 7560) followed by a 32:1 step up transformer, T. With this arrangement the modulation frequency could be varied from about 5 kHz up to over 40 kHz.

The laser beam power entering the molecular beam machine was kept below 45 mW for studying the B-X (13' - 0'') transitions of $^{79}$Br$_2$, $^{81}$Br$_2$, and $^{79}$Br$^{81}$Br to avoid saturation. The beam passed through the Pockels cell, PC, and entered the molecular beam machine approximately 6 – 7 mm upstream of the center of the optical stack. This provided an optical collection length of at least 15 mm for the LIF. The light collected passed through a Corning red pass filter (CS2-62) to reduce the scattered laser light before entering the photomultiplier. The signal from the photomultiplier was fed into a lock-in amplifier (EG&G model 5204), LIA, which measured both the in-phase (IP) and in-quadrature (IQ) responses of the input signal. The IP and IQ outputs were recorded on a two channel chart recorder (Phillips 8252A PM), CR. Tests were made on the lock-in to ensure that the zeroes, gains, and phase measurements were consistent between the IP and IQ channels. The zero values and gains of each channel of the chart recorder were checked as well.
Figure 6.16: A schematic of the apparatus used for measuring the lifetimes of individual hyperfine levels. (See text for description of symbols.)
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After selecting a modulation frequency, \( \Omega \), the lock-in amplifier's phase setting, \( \phi_{\text{LIA}} \), was chosen so that the hyperfine signals observed on the IP and IQ channels were roughly equal. The hyperfine transitions of interest were recorded between 5 and 8 times. The reference phase of the laser beam, \( \phi_{\text{ref}} \), was measured by closing off the molecular beam, removing the red-pass filter, and observing the scattered laser light. The phase shift of any given hyperfine signal could be deduced from

\[
\phi = \arctan \left( \frac{\text{IQ}}{\text{IP}} \right) + \phi_{\text{LIA}} - \phi_{\text{ref}}
\]

Each series of hyperfine transition measurements was repeated for at least two and usually three different modulation frequencies. By knowing the phase shift and the modulation frequency, the lifetimes of the individual B state hyperfine levels involved in the observed transitions were deduced from Equation 6.41. The hyperfine transitions for the \((13' - 0'')\) \(\text{P}(1)\) through \(\text{P}(9)\) excluding the \(\text{P}(3)\) of \({}^{79}\text{Br}_2\), \({}^{81}\text{Br}_2\), and \({}^{79}\text{Br}{}^{81}\text{Br}\) were recorded. A complete list of the hyperfine levels and lifetimes used in the analysis is given in Appendix C.

6.7.1 Fitting the Hyperfine Lifetimes

The inverse lifetime for a hyperfine level subject to both gyroscopic and hyperfine predissociation is given by,

\[
\Gamma = \Gamma_{\text{rad}} + \Gamma_p
\]

(assuming no saturation or collisions). The predissociation rate is given by

\[
\Gamma_p = C_v^2 R_{GG} + 2a_v^2 [R_{11}(1,1) + R_{11}(1,2)] \\
+ 4\sqrt{2}a_v C_v R_{G1}(1) + 4\sqrt{2}b_v C_v R_{G2}(1) \\
+ 4a_v b_v R_{12}(1,1) \\
+ 2b_v^2 [R_{22}(1,1) + R_{22}(1,2)]
\]
for $^{79}\text{Br}_2$ and $^{81}\text{Br}_2$ and by

$$
\Gamma_p = C_{\nu}^2 R_{GG} + \left[ a_{\nu}^2(1) + a_{\nu}^2(2) \right] R_{11}(1,1) + 2a_{\nu}(1)a_{\nu}(2)R_{11}(1,2)
$$

$$
+ 2\sqrt{2}C_{\nu} \left[ a_{\nu}(1) + a_{\nu}(2) \right] R_{G1}(1) + 2\sqrt{2}C_{\nu} \left[ b_{\nu}(1) + b_{\nu}(2) \right] R_{G2}(1)
$$

$$
+ 2 \left[ a_{\nu}(1)b_{\nu}(1) + a_{\nu}(2)b_{\nu}(2) \right] R_{12}(1,1)
$$

$$
+ \left[ b_{\nu}^2(1) + b_{\nu}^2(2) \right] R_{22}(1,1) + 2b_{\nu}(1)b_{\nu}(2)R_{22}(1,2)
$$

(6.45)

for $^{79}\text{Br}^{81}\text{Br}$. In the above expressions, the $R_{AB}(x,y)$ are numerical factors, described in Chapter 3, which depend upon the hyperfine state and the type of predissociation. (A complete list of the $R_{AB}(x,y)$ used in the analysis are given in Appendix C.) $C_{\nu}$, $a_{\nu}(x)$, and $b_{\nu}(x)$, respectively, are the gyroscopic, hyperfine magnetic dipole and hyperfine electric quadrupole predissociation parameters to be determined from the data. $x = 1, 2$ in Equations 6.44 and 6.45 label the different nuclei in the heteronuclear isotopomer.

Previous workers [3, 4, 14] have assumed that for bromine, like iodine, the electric quadrupole predissociation terms were too small to observe. The para-bromine $F = J$ hyperfine states provide a direct experimental measure of the relative importance of the electric quadrupole predissociation parameter. As was discussed in Chapter 3, the odd–$J$ (para) levels for the $B$ electronic state of $^{79}\text{Br}_2$ and $^{81}\text{Br}_2$ are coupled to the $I = 0$ and 2 nuclear spin states. The resulting hyperfine splitting is very simple and symmetric with the two $F = J$ levels displaced equally above ($F^J_-$) and below ($F^J_+$) the hyperfine free energy. The $F \neq J$ hyperfine levels lie close to the hyperfine free energy. The predissociation rates for the two $F = J$ levels, labelled $F^J_{\pm}$ are,

$$
\Gamma_p(F^J_{\pm}, \nu) = \Gamma_p^{MD}(F^J_{\pm}, \nu) + \beta b_{\nu}^2 \pm \epsilon \{ \sqrt{2}C_{\nu} + a_{\nu} \} b_{\nu}
$$

(6.46)

Here $\Gamma_p^{MD}(F^J_{\pm}, \nu)$, is the predissociation rate up to the magnetic dipole terms in the limit that $b_{\nu} = 0$. In this limit, $\Gamma_p$ is the same for both the $F^J_-$ and $F^J_+$ hyperfine levels. Any
Figure 6.17: The hyperfine spectrum for the B–X (13′–0″) P(4) transition of $^{79}\text{Br}_2$ observed with laser modulated at 25.5 kHz. The relative heights of the two hyperfine peaks labelled by $F^J_+$ and $F^J_-$ differ in the in-phase (IP) and in-quadrature (IQ) traces. The difference in lifetime is entirely due to electric quadrupole predissociation effects. The • indicate weak transitions with $\Delta F \neq \Delta J$. 

(4.48 ± 0.40)μs

(3.65 ± 0.26)μs

f (MHz)
Table 6.4: The total decay rates for various para bromine B–X (13'—0") hyperfine states having \( F = J \). The difference in the rates labelled \( \Delta(F^+ - F^-) \) (determined directly from the data, not by subtracting the average values for two decay rates) vanishes in the limit \( b \to 0 \).

<table>
<thead>
<tr>
<th>( ^{79}\text{Br}_2 )</th>
<th>( ^{81}\text{Br}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma \left( 10^5 \text{s}^{-1} \right) )</td>
<td>( \Gamma \left( 10^5 \text{s}^{-1} \right) )</td>
</tr>
<tr>
<td>( P(2) )</td>
<td>2.20 ± 0.14</td>
</tr>
<tr>
<td>( 1^+ )</td>
<td>1.58 ± 0.09</td>
</tr>
<tr>
<td>( 1^- )</td>
<td>0.60 ± 0.07</td>
</tr>
<tr>
<td>( \Delta(1^+ - 1^-) )</td>
<td>2.74 ± 0.20</td>
</tr>
<tr>
<td>( 3^+ )</td>
<td>2.23 ± 0.20</td>
</tr>
<tr>
<td>( 3^- )</td>
<td>0.50 ± 0.06</td>
</tr>
<tr>
<td>( \Delta(3^+ - 3^-) )</td>
<td>4.28 ± 0.59</td>
</tr>
<tr>
<td>( P(6) )</td>
<td>3.60 ± 0.30</td>
</tr>
<tr>
<td>( 5^+ )</td>
<td>0.57 ± 0.20</td>
</tr>
<tr>
<td>( 5^- )</td>
<td>6.10 ± 0.93</td>
</tr>
<tr>
<td>( \Delta(5^+ - 5^-) )</td>
<td>5.38 ± 0.50</td>
</tr>
<tr>
<td>( P(8) )</td>
<td>0.83 ± 0.90</td>
</tr>
<tr>
<td>( 7^+ )</td>
<td></td>
</tr>
<tr>
<td>( 7^- )</td>
<td></td>
</tr>
<tr>
<td>( \Delta(7^+ - 7^-) )</td>
<td></td>
</tr>
</tbody>
</table>

The observed difference in the lifetimes of these levels arises solely from interactions involving electric quadrupole (or perhaps higher order) predissociation. The best place to look for evidence of electric quadrupole effects is in the hyperfine structure of the low \( J \) levels because the gyroscopic predissociation rate increases as \( J(J+1) \) and, at high \( J \), could mask the electric quadrupole contributions. Figure 6.17 shows the in-phase (IP) and in-quadrature (IQ) signals recorded for the \( ^{79}\text{Br}_2 \) (13'—0") \( P(4) \) hyperfine spectrum. The fact that the ratio of the heights of the \( F^+ \) and \( F^- \) peaks is different in the IP trace from that in the IQ trace is direct evidence that the two levels have different lifetimes and, therefore, for the existence of electric quadrupole predissociation. The results of lifetime measurements of the \( F = J \) hyperfine levels of the B–X (13'—0") \( P(2) \), \( P(4) \), \( P(6) \), and \( P(8) \) for \( ^{79}\text{Br}_2 \) and \( ^{81}\text{Br}_2 \) are given in Table 6.4.

These data show clear evidence that the electric quadrupole parameters are important.
Chapter 6. Natural Predissociation of the B state of Bromine

for the B state of bromine. In particular, the difference in the decay rates, $\Delta(F^1_+ - F^1_-)$, for the levels $1 \frac{1}{2}$ and $3 \frac{3}{2}$ are well determined, having an experimental error of about 10%. It should be pointed out that the differences in decay rates reported in Table 6.4 were determined directly from the raw data and not by subtracting the average values of the decay rates from one another.

As explained in Appendix C, out of a total of nearly 200 hyperfine transitions studied for the three isotopomers (each recorded between three and five times for at least two and usually three different modulation frequencies), 73 were chosen as suitable for analysis. Those with a signal to noise ratio of less than 10 were rejected. As well, the blended lines in the spectra, for which Equation 6.16 does not hold, were not used. This process selected 20 clean measurements from a total of 50 for the $^{79}$Br$_2$ data and another 20 measurements out of 50 for the $^{81}$Br$_2$ data. The heteronuclear data, having more hyperfine levels associated with each rotational level, suffered a higher rate of rejection owing to blended transitions. Out of 100 hyperfine transitions, 33 were chosen from the $^{79}$Br$^{81}$Br data set. Appendix C contains the complete subset of hyperfine transitions used in the predissociation analysis of this thesis. It lists the observed and calculated decay rates, $\Gamma$, along with the differences (obs - calc). In addition, the observed and calculated lifetimes, $\tau = \Gamma^{-1}$, with their (obs - calc) are also tabulated.

The homonuclear molecules, $^{79}$Br$_2$ and $^{81}$Br$_2$, were fit individually to model 6.44 for the parameters, $\Gamma_{\text{rad}}$, $C_v$, $a_v$, and $b_v$. The results of the individual fits for both homonuclear isotopomers are given in Table 6.5.

The $^{79}$Br$^{81}$Br data were somewhat more difficult to fit because the parameters, $a_v(79)$ with $a_v(81)$ and $b_v(79)$ with $b_v(81)$ were highly correlated. The solution was to recast the model in terms of new parameters, $A_\pm$ and $B_\pm$, defined as,

$$A_\pm = \frac{1}{\sqrt{2}} (a_v(79) \pm a_v(81))$$

(6.47)
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Table 6.5: The results of fitting the $^{79}$Br$_2$ and $^{81}$Br$_2$ lifetime data separately for the radiative decay rate, $\Gamma_{\text{rad}}$, and the predissociation constants, $C_v$, $a_v$, and $b_v$. $N$ is the number of hyperfine lifetimes used in the fit and $\chi^2$ is a measure of the goodness of fit of the data. In theory $\chi^2$ should be less than or equal to the number of data points minus the number of parameters being fit.

\[
B_{\pm} = \frac{1}{\sqrt{2}} (b_v(79) \pm b_v(81))
\]

Equation 6.45 can then be written,

\[
\Gamma_p = C_v^2 R_{GG} + A^2_+ [R_{11}(1,1) + R_{11}(1,2)] + A^2_- [R_{11}(1,1) - R_{11}(1,2)]
+ 4C_v A_+ R_{G1}(1) + 4C_v B_+ R_{G2}(1)
+ 2[A_+ B_+ + A_- B_-] R_{12}(1,1)
+ B^2_+ [R_{22}(1,1) + R_{22}(1,2)] + B^2_- [R_{22}(1,1) - R_{22}(1,2)]
\]

There was still a large correlation between $A_+$ and $A_-$ and between $B_+$ and $B_-$ ultimately making it impossible to obtain meaningful results for all four of these parameters. The magnitudes of the parameters $A_-$ and $B_-$ were of the order of their uncertainties. Consequently the lifetimes were fit with both $A_-$ and $B_-$ held fixed at zero. The results are given in Table 6.6 along with the prediction for the parameters based upon the parameters derived from $^{79}$Br$_2$ and $^{81}$Br$_2$. As can be seen, the agreement between the measured and predicted parameters is very good although the uncertainty is relatively large for $B_+$. (Notice that the value of $\Gamma_{\text{rad}}$ deduced for each isotopomer is the same
Chapter 6. Natural Predissociation of the B state of Bromine

<table>
<thead>
<tr>
<th>N</th>
<th>$\chi^2$</th>
<th>$\Gamma_{\text{rad}}$ ($10^4 s^{-1}$)</th>
<th>$C_v$ ($s^{-1/2}$)</th>
<th>$A_+$ ($s^{-1/2}$)</th>
<th>$B_+$ ($s^{-1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{79}\text{Br}^{81}\text{Br}$</td>
<td>33</td>
<td>(8.98 ± 0.84)</td>
<td>(86.9 ± 2.4)</td>
<td>(309.6 ± 11.3)</td>
<td>(58.2 ± 11.7)</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td>(8.10 ± 1.05)</td>
<td>(88.0 ± 1.4)</td>
<td>(312.8 ± 11.2)</td>
<td>(54.7 ± 13.2)</td>
</tr>
</tbody>
</table>

Table 6.6: The results of fitting the $^{79}\text{Br}^{81}\text{Br}$ lifetime data are compared with the predictions based on the results for $^{79}\text{Br}_2$ and $^{81}\text{Br}_2$, labelled P. The constants $A_-$ and $B_-$ were held fixed at 0.

within the uncertainty. As expected, $\Gamma_{\text{rad}}$ does not vary much between isotopomers.)

A closer examination of the definition of the parameters shows that,

$$C_v^{a,b} = \frac{\hbar^2}{\mu(a, b)} \left< \Omega v \left| \frac{T_1^{\Delta\Omega}(L) + T_2^{\Delta\Omega}(S)}{R^2} \right| \Omega' E' \right>$$

(6.50)

$$a_{v}^{a,b}(x) = \frac{f_1(x, \Omega, v, \Omega', E')}{\sqrt{i_1(i_1 + 1)(2i_1 + 1)}}$$

(6.51)

$$b_{v}^{a,b}(x) = \frac{2i_1(2i_1 - 1)}{(2i_1 + 1)(2i_1 + 2)(2I - 1 + 3)} \left[ \frac{T_2^{\Delta\Omega}}{r_{3e}^2} \right]^{1/2}$$

(6.52)

where the superscript $(a, b)$ with each parameter refers to the particular isotopomer being studied. e.g. $C_{v}^{79,79}$ is the gyroscopic predissociation parameter for $^{79}\text{Br}_2$ . Each of the parameters may be re-expressed as the product of a known molecular property,

$$C_v^{a,b} \propto \mu(a, b) \text{ the reduced mass of isotopomer (a, b)}$$

(6.53)

$$a_v^{a,b} \propto g(x) \text{ the magnetic dipole moment of nucleus x}$$

(6.54)

$$b_v^{a,b} \propto Q(x) \text{ the electric quadrupole moment of nucleus x}$$

(6.55)
and a matrix element between the bound and continuum state. To a good approximation this matrix element may be written as the product of a measured parameter times a vibrational overlap integral for isotopomer (a,b), \( \sigma(a, b) \) (the square root of the Franck-Condon factor). Namely,

\[
C_v^{a,b} = \frac{C_v^a}{\mu(a, b)} \sigma(a, b) \\
a_v^{a,b}(x) = g(x) a_v^a \sigma(a, b) \\
b_v^{a,b}(x) = Q(x) b_v^b \sigma(a, b)
\]

Using definitions 6.56 – 6.58, one can fit the lifetime data from all 3 isotopomers simultaneously. The first fit was performed using \( \Gamma_{\text{rad}} \) and the following seven parameters:

\[
B_1 = \frac{C_v^0}{\mu(79, 79)} \sigma(79, 79) \\
B_2 = g(79) a_v^0 \sigma(79, 79) \\
A_2 = g(81) a_v^0 \sigma(79, 79) \\
B_3 = Q(79) b_v^0 \sigma(79, 79) \\
A_3 = Q(81) b_v^0 \sigma(79, 79) \\
B_4 = \sigma(81, 81)/\sigma(79, 79) \\
B_5 = \sigma(79, 81)/\sigma(79, 79)
\]

From these, one is able to deduce all of the necessary molecular constants for the predissociation expressions for each isotopomer. (e.g. \( b_v^{79,81}(81) = A_3 \cdot B_5 \).) CASTING THE MODEL IN THIS FORM HAS THE BUILT IN SELF-CONSISTENCY CHECKS: \( B_2/A_2 = g(79)/g(81) \) and \( B_3/A_3 = Q(79)/Q(81) \). The global fit results are given in Table 6.7. The ratios of the molecular parameters \( B_2/A_2 \), \( B_3/A_3 \), given in Table 6.8, are in excellent agreement with the known ratios [35] of the magnetic dipole and electric quadrupole moments of the \( ^{79}\text{Br} \) and \( ^{81}\text{Br} \) nuclei. Having verified the validity of modelling the parameters as per Equa-
Table 6.7: The results of the global eight parameter fit to lifetimes for $^{79}$Br$_2$, $^{81}$Br$_2$, and $^{79}$Br$^{81}$Br. The fit to 73 hyperfine lifetimes, gave a reduced $\chi^2 = 0.85$ (See Equation B.1).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{\text{rad}}$</td>
<td>$(8.46 \pm 0.36) \times 10^4 \text{s}^{-1}$</td>
</tr>
<tr>
<td>$B_1 = [C^0_\nu / \mu(79,79)] \sigma(79,79)$</td>
<td>$(86.5 \pm 0.8) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$B_2 = g(79)a^0_\nu(79)\sigma(79,79)$</td>
<td>$(203.7 \pm 5.2) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$A_2 = g(81)a^0_\nu(81)\sigma(79,79)$</td>
<td>$(226.8 \pm 3.9) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$B_3 = Q(79)b^0_\nu(79)\sigma(79,79)$</td>
<td>$(38.6 \pm 4.9) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$A_3 = Q(81)b^0_\nu(81)\sigma(79,79)$</td>
<td>$(34.8 \pm 4.7) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$B_4 = \sigma(81,81)/\sigma(79,79)$</td>
<td>$(1.045 \pm 0.010)$</td>
</tr>
<tr>
<td>$B_5 = \sigma(79,81)/\sigma(79,79)$</td>
<td>$(1.029 \pm 0.011)$</td>
</tr>
</tbody>
</table>

Table 6.8: The ratio of the parameters $B_2:A_2$ and $B_3:A_3$ as compared to the ratios of magnetic dipole moments and electric quadrupole moments for $^{79}$Br and $^{81}$Br. The nuclear moments were taken from Reference [35].
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Table 6.9: The results of the global six parameter fit to lifetimes for $^{79}$Br$_2$, $^{81}$Br$_2$, and $^{79}$Br$^{81}$Br. The fit to 73 hyperfine lifetimes gave a $\chi^2 = 56.5$, and a reduced $\chi^2 = 0.84$.

The predissociation parameters for each isotopomer of bromine may be derived from the appropriate combinations of global fit parameters for either the 8 parameter model or the 6 parameter model. These derived molecular parameters are compared with the molecular parameters deduced from the individual isotopomer fits in Table 6.10. The values deduced by the different models are in excellent agreement.

6.8 Discussion

The results of these predissociation measurements yielded some interesting surprises. First, the radiative lifetime of the B $^3\Pi_{0^+}$ state of bromine was determined to be $\tau_{\text{rad}} = \frac{1}{\Gamma_{\text{rad}}} = (11.9 \pm 0.5)\mu$s

$$\tau_{\text{rad}} = (11.9 \pm 0.5)\mu$s (6.66)
<table>
<thead>
<tr>
<th></th>
<th>Combined Fit</th>
<th>Individual Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6 parameter</td>
<td>8 parameter 4 Parameter</td>
</tr>
<tr>
<td>$^{79}$Br$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_{rad}$</td>
<td>$(8.40 \pm 0.34) \times 10^4 \text{s}^{-1}$</td>
<td>$(8.46 \pm 0.36) \times 10^4 \text{s}^{-1}$</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>$(86.5 \pm 0.8) \text{s}^{-1/2}$</td>
<td>$(86.5 \pm 0.8) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$\alpha_{13}$</td>
<td>$(208.3 \pm 3.1) \text{s}^{-1/2}$</td>
<td>$(203.7 \pm 5.2) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$\beta_{13}$</td>
<td>$(40.5 \pm 4.0) \text{s}^{-1/2}$</td>
<td>$(38.6 \pm 4.7) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$^{81}$Br$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_{rad}$</td>
<td>$(8.40 \pm 0.34) \times 10^4 \text{s}^{-1}$</td>
<td>$(8.46 \pm 0.36) \times 10^4 \text{s}^{-1}$</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>$(88.7 \pm 1.5) \text{s}^{-1/2}$</td>
<td>$(88.2 \pm 1.7) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$\alpha_{13}$</td>
<td>$(236.1 \pm 5.4) \text{s}^{-1/2}$</td>
<td>$(237.0 \pm 6.3) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$\beta_{13}$</td>
<td>$(35.6 \pm 3.8) \text{s}^{-1/2}$</td>
<td>$(36.4 \pm 5.3) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$^{79}$Br$^{81}$Br</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_{rad}$</td>
<td>$(8.40 \pm 0.34) \times 10^4 \text{s}^{-1}$</td>
<td>$(8.46 \pm 0.36) \times 10^4 \text{s}^{-1}$</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>$(88.0 \pm 1.8) \text{s}^{-1/2}$</td>
<td>$(89.0 \pm 1.8) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$\frac{1}{\sqrt{2}}A_+$</td>
<td>$(229.9 \pm 5.7) \text{s}^{-1/2}$</td>
<td>$(221.4 \pm 7.1) \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>$\frac{1}{\sqrt{2}}B_+$</td>
<td>$(38.3 \pm 4.2) \text{s}^{-1/2}$</td>
<td>$(37.8 \pm 5.4) \text{s}^{-1/2}$</td>
</tr>
</tbody>
</table>

Table 6.10: A comparison of the molecular parameters derived for the B $^3\Pi_{0+}$ $\nu' = 13$ level of $^{79}$Br$_2$, $^{81}$Br$_2$, and $^{79}$Br$^{81}$Br, with three different models: (i) by fitting the data from all three isotopomers together with 6 parameters; (ii) by fitting the data from all three isotopomers together with 8 parameters; (iii) by fitting the data from each isotopomer individually.
certainly in agreement with the rather broad range of values reported by Clyne and co-workers [13, 15, 16] (particularly for the value reported in Reference [16] for the $v' = 2$ level namely, $(12.4 \pm 0.2)\mu s$) but much longer than the values of Peeters et al. [14]. (See Table 6.1.) This finding played a crucial role in designing an experiment to observe the predissociation of bromine. The second surprise was the detection of the first example of electric quadrupole predissociation in any molecule. Previous workers have assumed that the $b_v$ parameter was negligible, omitting it from their analysis. In fact, both Koffend et al. [3] and Siise et al. [4] who investigated the predissociation using the relative intensity technique, did not bother to measure any para-bromine (odd $J'$) transitions assuming that the two strong, resolved hyperfine transitions in the para-bromine spectra would have exactly the same predissociation rates and, consequently, the same relative intensities. Part of the effect of neglecting the electric quadrupole predissociation is that these terms are absorbed into the $\Gamma_{\text{rad}}$ parameter. The variation with $J$ of the electric quadrupole terms will be reflected in variations with $J$ in $\Gamma_{\text{rad}}(\text{expt})$. It will also produce a slight variation with $J$ of $a_v/\sqrt{\Gamma_{\text{rad}}(\text{expt})}$ and $C_v/\sqrt{\Gamma_{\text{rad}}(\text{expt})}$. (A larger variation in the parameters with $J$ is expected if the experimental apparatus is inadequately designed as discussed below.) For $(J'=0 \ v'=13)$ in the $B^3\Pi_{0}^{+}$ state of $^{79}\text{Br}_2$, the electric quadrupole predissociation term, $2.4b_v^2$, is roughly 5% of $\Gamma_{\text{rad}}$.

Finally, the values for the ratios of the predissociation parameters to the radiative decay rate for bromine reported in References [3, 4] are much lower than the results observed here while the gyroscopic predissociation parameters reported in References [13, 14] are in satisfactory agreement with the values reported here. (One other study [5, 40] of the hyperfine structure of the $v' = 17$ and 18 levels of each isotopomer of bromine reported a value of $C_v^2$ that was an order of magnitude lower than that found in this work. This result will be addressed a little later.)

As discussed, the rotational state lifetime measurements only yield precise values of
the gyroscopic predissociation parameter, $C_\nu$, from the slope of a plot of the zero pressure inverse lifetime versus $J(J+1)$. The intercept is a combination of the radiative decay rate and the hyperfine and hyperfine – gyroscopic interference predissociation rates averaged over the hyperfine levels associated with the $J = 0$ state. In iodine these measurements provided direct evidence for hyperfine predissociation as the ortho and para rotational decay rates showed the same slope as a function of $J(J+1)$ but different intercepts [25]. No such behaviour has been observed for ortho and para rotational states of the B $^3\Pi_{\text{o,d}}$ electronic state of bromine owing to the much larger value of $C_\nu$ for bromine. Clyne et al. [13] carried out a systematic study of the gyroscopic predissociation parameter (which they called $k_\nu$ (= $C_\nu$ in this thesis)) for the vibrational bands $4 \leq v' \leq 24$ for each isotopomer of bromine. The intercepts were erroneously interpreted as the radiative decay rate of the B state of bromine. This, coupled with the relatively small values of the intercept, yielded measurements of the radiative lifetime of the different vibrational bands that varied by a factor of 3, from about 5 $\mu$s up to about 16 $\mu$s. Clyne and co-workers [16] also measured the radiative lifetime of the B state $v' = 2$ level which is not subject to any strong predissociation. The value reported for the $J' = 29$ rotational state was $\tau_{\text{rad}} = (12.4 \pm 0.2)\mu$s, in excellent agreement with the findings of this thesis. It must be pointed out, however, that lifetime measurements for many $v' = 2$ rotational states were reported in Reference [16] having values between 9.5 and 12.6 $\mu$s. For reasons that are not made clear in the publication, Clyne and co-workers [16] chose to use only the data from the $v' = 2, J' = 29$ level to deduce $\tau_{\text{rad}}$. Therefore, it is felt that the reported uncertainty of $\pm 0.2 \mu$s is underestimated.

A second group, Peeters et al. [14], also carried out rotational state lifetime measurements on the B state of $^{81}\text{Br}_2$ for the levels $13 \leq v' \leq 16$. This time the data were fit to two models, one which ignored the hyperfine predissociation and the other taking it into account (up to the magnetic dipole terms). The results obtained for $C_\nu$ varied by up to
10% depending upon the method of data analysis, but are in agreement with the values of Clyne and co-workers. The radiative decay rates quoted also vary from vibrational level to vibrational level and are roughly a factor of 6 larger than the radiative decay rate obtained in this study. As can be seen from Table 6.11, the agreement between the $C_2^v$ values reported is satisfactory but not excellent.

A final study by Katzenellenbogen and co-workers [5, 40] should be noted in which the hyperfine structure of the B state $v' = 17$ and 18 levels of each isotopomer of bromine was investigated using polarization spectroscopy. The hyperfine data were fit for the B state electric quadrupole parameter, $eqQ$, the nuclear spin–rotation constant, $C_{sr}$, and the linewidth of the hyperfine spectral lines observed, $\gamma$. In addition, each of the parameters was allowed to vary with $J$ as

$$O = O_0 + O_1 J(J + 1)$$

(6.67)

where $O = eqQ, C_{sr}$, or $\gamma$. Katzenellenbogen et al. assumed that,

$$\gamma = \gamma_0 + C_2^v J(J + 1)$$

(6.68)

The value of $C_2^v$ was taken as the slope of a plot of $\gamma$ versus $J(J+1)$. For the $v' = 18$ level of $^{81}$Br$_2$ their result was $(392 \pm 10)$ Hz [40]. This value was later revised to $(410.5 \pm 0.9)$ Hz [5], and values for the other isotopomers were also reported for the $v' = 17$ and 18 vibrational levels. The authors of Reference [40] attribute the discrepancy between their value and those of Reference [13] as the result an error in the experimental technique of Clyne and co-workers. However, Katzenellenbogen and co-workers failed to appreciate several key points. First, the linewidth used to fit their hyperfine spectra, $\gamma$, is the half-width at half-maximum (HWHM) in Hz and is related to the inverse lifetime in, $\Gamma$, in s$^{-1}$ by

$$\Gamma = 2\pi \gamma$$

(6.69)
### Table 6.11: The values for $C_v$ and $\Gamma_{\text{rad}}$ for this work compared with References [13,16] (Clyne and co-workers) and [14] (Peeters et al.). Peeters et al. fit the data in three ways: (a) using a purely gyroscopic predissociation model; (b) using a predissociation model that included gyroscopic and magnetic dipole predissociation; (c) fitting to a purely gyroscopic predissociation model and restricting the data to $3\tau$ observation window. The agreement among the three research groups is satisfactory but not excellent.

<table>
<thead>
<tr>
<th>$^{81}\text{Br}_2$ $v'$</th>
<th>$k_v = C_v^{10^3 \text{ s}^{-1}}$</th>
<th>$\Gamma_{\text{rad}}^{10^5 \text{ s}^{-1}}$</th>
<th>$\tau_{\text{rad}}^{\mu\text{s}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[16] 2</td>
<td>1.0</td>
<td>(0.806 ± 0.013)</td>
<td>(12.4 ± 0.2)</td>
</tr>
<tr>
<td>[13] 4</td>
<td>(4.4 ± 0.2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>(25 ± 1)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>(2.1 ± 0.2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>(7.4 ± 0.8)</td>
<td>(1.96 ± 0.58, −0.35)</td>
<td>(5.1 ± 1.5, −0.9)</td>
</tr>
<tr>
<td>14</td>
<td>(6.0 ± 0.2)</td>
<td>(1.35 ± 0.27, −0.18)</td>
<td>(7.4 ± 1.5, −1.0)</td>
</tr>
<tr>
<td>19</td>
<td>(4.8 ± 0.6)</td>
<td>(0.88 ± 0.15, −0.12)</td>
<td>(11.3 ± 2.0, −1.5)</td>
</tr>
<tr>
<td>20</td>
<td>(3.8 ± 0.2)</td>
<td>(1.64 ± 0.67, −0.38)</td>
<td>(6.1 ± 2.5, −1.4)</td>
</tr>
<tr>
<td>23</td>
<td>—</td>
<td>(0.64 ± 0.10, −0.08)</td>
<td>(15.7 ± 2.5, −1.9)</td>
</tr>
<tr>
<td>24</td>
<td>(2.8 ± 0.2)</td>
<td>(0.98 ± 0.14, −0.12)</td>
<td>(10.2 ± 1.5, −1.2)</td>
</tr>
<tr>
<td>[14] 13 (a)</td>
<td>(6.97 ± 0.10)</td>
<td>(5.24 ± 0.83)</td>
<td>(1.91 ± 0.30)</td>
</tr>
<tr>
<td>(b) (8.48 ± 0.50)</td>
<td>(5.8 ± 3.7)</td>
<td>(1.7 ± 1.1)</td>
<td></td>
</tr>
<tr>
<td>(c) (8.17 ± 0.61)</td>
<td>(6.2 ± 4.4)</td>
<td>(1.6 ± 1.1)</td>
<td></td>
</tr>
<tr>
<td>14 (a) (6.68 ± 0.42)</td>
<td>(4.5 ± 2.7)</td>
<td>(2.2 ± 1.3)</td>
<td></td>
</tr>
<tr>
<td>(b) (8.94 ± 0.79)</td>
<td>−(2.6 ± 5.9)</td>
<td>−(3.8 ± 8.7)</td>
<td></td>
</tr>
<tr>
<td>(c) (8.91 ± 0.82)</td>
<td>−(4.2 ± 6.1)</td>
<td>−(2.4 ± 3.5)</td>
<td></td>
</tr>
<tr>
<td>15 (a) (6.366 ± 0.076)</td>
<td>(2.26 ± 0.96)</td>
<td>(4.4 ± 1.9)</td>
<td></td>
</tr>
<tr>
<td>(b) (6.71 ± 0.16)</td>
<td>(5.1 ± 2.2)</td>
<td>(1.96 ± 0.85)</td>
<td></td>
</tr>
<tr>
<td>(c) (6.48 ± 0.30)</td>
<td>(4.9 ± 4.4)</td>
<td>(2.0 ± 1.8)</td>
<td></td>
</tr>
<tr>
<td>16 (a) (6.06 ± 0.11)</td>
<td>(2.4 ± 1.5)</td>
<td>(4.2 ± 2.6)</td>
<td></td>
</tr>
<tr>
<td>(b) (6.28 ± 0.20)</td>
<td>(6.7 ± 3.7)</td>
<td>(1.49 ± 0.82)</td>
<td></td>
</tr>
<tr>
<td>(c) (5.80 ± 0.45)</td>
<td>(7.4 ± 8.4)</td>
<td>(1.4 ± 1.5)</td>
<td></td>
</tr>
<tr>
<td>this work 13</td>
<td>(7.87 ± 0.27)</td>
<td>(0.840 ± 0.034)</td>
<td>(11.9 ± 0.5)</td>
</tr>
</tbody>
</table>
The authors of References [5, 40] used a gyroscopic predissociation rate of $C_\gamma^2 = 5.5$ kHz from Reference [13] and a radiative decay rate of $0.89$ MHz to calculate, for the $J' = 72$ hyperfine peaks, that

$$\gamma = \Gamma_{\text{rad}} + C_\gamma^2 J(J + 1)$$

$$= 0.89 \cdot 10^6 \text{Hz} + 5.5(72)(73)(10^3) \text{Hz}$$

$$= 29.8 \text{MHz} \quad (6.70)$$

In the light of Equation 6.69 this should be changed to

$$\gamma = (29.8 \text{MHz})/(2\pi)$$

$$= 4.74 \text{MHz} \quad (6.71)$$

much closer to the value of $\gamma = 5.9$ MHz which they reported. Second, the fact is not addressed that hyperfine predissociation affects different hyperfine levels in different ways, leading to different HWHM for the different features. Third, polarization spectroscopy is a saturation technique, but no discussion of the effect of saturation on the observed HWHM is made. Finally, the linewidth of the laser used in the study is not disclosed. Thus, several of the conclusions of References [5, 40] are suspect.

Two other studies [3, 4] have been carried out measuring the hyperfine predissociation using the relative intensity of hyperfine spectral lines technique. Both of these studies yielded predissociation parameters that displayed anomalous variations with the rotational state studied. This strong J dependence of the predissociation parameters is probably due to an experimental bias introduced by the optical systems used. As mentioned, if the observation region does not collect the LIF from long- and short-lived states with the same efficiency then the results are biased towards the short-lived states. The gyroscopic predissociation rate and the gyroscopic–magnetic dipole predissociation rate increase with the rotational state as $J^2$ and $J$, respectively, while the other predissociation
terms remain the same or decrease slowly with rotational quantum number. Consequently the lifetimes of the individual hyperfine states generally decrease with increasing J. The optical detection system can be inadequate for recording hyperfine lifetimes of low rotational states but adequate for measuring high J hyperfine levels. Thus, the deduced predissociation parameters will vary from rotational level to rotational level reflecting the changing amount of experimental bias introduced by the apparatus.

A second consequence of oversampling the short-lived levels with respect to the long-lived ones is to increase the relative intensity of the more highly predissociated (short-lived) states. When one relies on relative intensity measurements to deduce the predissociation parameters, as was done in References [3, 4], then an oversampling of the short-lived levels leads to an underestimate of the parameters, \( C_v/\sqrt{T_{rad}} \) and \( a_v/\sqrt{T_{rad}} \). The data reported by Koffend et al. [3] and Sieve et al. [4] display both of these characteristics supporting an experimental bias hypothesis. (See Table 6.12.)

The lifetime data obtained here for the \( B^3\Pi_{0^+} \) \( v' = 13 \) for \( ^{79}\text{Br}_2, ^{81}\text{Br}_2, \) and \( ^{79}\text{Br}^{81}\text{Br} \) are well described by the predissociation model given in Chapter 3. The existence of the interference terms between the gyroscopic and hyperfine terms verifies that the electronic state predominantly responsible for the predissociation must be the \( ^1\Pi_{1u} \) state. That is, in order to observe interference terms arising from the gyroscopic and hyperfine Hamiltonians, both these Hamiltonians must be able to couple the bound level to the same continuum level. The selection rules for the gyroscopic Hamiltonian, \( H_G \), (Table 3.1) allows the coupling \( u \leftrightarrow u \) or \( g \leftrightarrow g \) and \( |\Delta \Omega| = 1 \). Thus \( H_G \) can only couple the \( 0_u^+ \) state to a \( 1u \) state.
Table 6.12: The predissociation parameters reported by References [3,4] compared to the results of this work.
Chapter 6. Natural Predissociation of the B state of Bromine

<table>
<thead>
<tr>
<th>$v' = 13$</th>
<th>$\sigma(a, b)/\sigma(79, 79)$</th>
<th>FCF(a,b)/FCF(79,79)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{81}\text{Br}_2 : ^{79}\text{Br}_2$</td>
<td>(1.052 ± 0.008)</td>
<td>(1.107 ± 0.017)</td>
</tr>
<tr>
<td>$^{79}\text{Br}^{81}\text{Br} : ^{79}\text{Br}_2$</td>
<td>(1.030 ± 0.011)</td>
<td>(1.061 ± 0.023)</td>
</tr>
</tbody>
</table>

Table 6.13: The ratios of the vibrational overlap integrals and Franck–Condon factors (FCF) between the B $^3\Pi_{0^+}$ and $^1\Pi_{1u}$ electronic states for the different isotopomers of bromine.

6.9 A Closer look at the Molecular Parameters

From the definitions of the molecular parameters, one can compare the results of the studies presented in this thesis to work done by other authors on the Franck–Condon factors, on $C_2^v$, and on the electric quadrupole structure of the B state of bromine.

6.9.1 Franck–Condon Factors

The fact that data from all three isotopomers were fitted at once in this work made it possible to determine the relative sizes of the vibrational overlap integrals between the B $^3\Pi_{0^+}$ and $^1\Pi_{1u}$ electronic states for the different isotopomers. (See Table 6.13.) The results indicate that the overlap integrals, $\sigma(a, b)$, varied smoothly from isotopomer to isotopomer, increasing slightly with the mass.

Cyne et al. [13] have deduced the FCF between these two electronic states for $^{79}\text{Br}^{81}\text{Br}$ from the vibrational dependence of the gyroscopic predissociation parameter, $k_v = C_2^v$. These workers did not observe any significant variation of the gyroscopic predissociation parameters from isotopomer to isotopomer (except for the $v' = 7$ level where the predissociation is at a minimum). This result agrees well with the findings presented here. The gyroscopic predissociation parameter, $C_2^v$, depends upon the vibrational overlap integral.
Table 6.14: The ratios of the vibrational overlap integrals times reduced mass $Z(X, 79) = \frac{[\sigma(X)/\mu(X)][\mu(79, 79)/\sigma(79, 79)]}{\sigma}$ and $Z^2(X, 79)$ between the $B \, ^3\Pi_{0^+}$ and $^1\Pi_{1u}$ electronic states for the different isotopomers of bromine.

<table>
<thead>
<tr>
<th>$\nu' = 13$</th>
<th>$Z(X, 79)$</th>
<th>$Z^2(X, 79)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{81}\text{Br}_2 : ^{79}\text{Br}_2$</td>
<td>$(1.026 \pm 0.010)$</td>
<td>$(1.053 \pm 0.021)$</td>
</tr>
<tr>
<td>$^{79}\text{Br}^{81}\text{Br} : ^{79}\text{Br}_2$</td>
<td>$(1.017 \pm 0.011)$</td>
<td>$(1.034 \pm 0.023)$</td>
</tr>
</tbody>
</table>

Therefore, if the gyroscopic predissociation parameter displays a very small change from one isotopomer to the next, (i.e. with reduced mass) then one must conclude that the vibrational overlap integral from isotopomer to isotopomer must increase with the reduced mass in such a way that the ratio $\sigma(a, b)/\mu(a, b)$ remains nearly constant.

The ratio of gyroscopic predissociation parameters, $C_\nu(X)/C_\nu(Y)$, for isotopomers $X$ and $Y$ is given by the quantity,

$$C_\nu^{a,b} \propto \frac{\sigma(a, b)}{\mu(a, b)}$$

(6.72)

It follows that the ratio of the parameters, $k_\nu(X)/k_\nu(Y)$ (where $k_\nu(X) = C_\nu^2(X)$) reported in Reference [13] should follow $Z^2(X, Y)$. The values of $Z(X, 79)$ and $Z^2(X, 79)$ based upon the results presented in this thesis for the $\nu' = 13$ level of bromine are given in Table 6.14. As can be seen the variation of $C_\nu^2$ from isotopomer to isotopomer is predicted to be less than about 5%. Thus one concludes that the predissociation parameters, $k_\nu$ for each isotopomer should be the same to within the $\pm 5\%$ in excellent agreement the results of Clyne et al. [13].
Chapter 6. *Natural Predissociation of the B state of Bromine*

\[ v' = 13 \quad \sigma(81, 81)/\sigma(79, 79) \quad \text{FCF}(81, 81)/\text{FCF}(79, 79) \]

<table>
<thead>
<tr>
<th></th>
<th>( \sigma(81, 81)/\sigma(79, 79) )</th>
<th>( \text{FCF}(81, 81)/\text{FCF}(79, 79) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>((1.052 \pm 0.008))</td>
<td>((1.107 \pm 0.017))</td>
</tr>
<tr>
<td>(II)</td>
<td>((1.138 \pm 0.096))</td>
<td>((1.295 \pm 0.218))</td>
</tr>
</tbody>
</table>

Table 6.15: The ratios of the vibrational overlap integrals and FCF's for \(^{79}\text{Br}_2\) and \(^{81}\text{Br}_2\) as deduced from (I) the global fit results, and (II) the \(J' = 0\) hyperfine level decay rates.

The inverse lifetimes of the two hyperfine levels of the \(J' = 0\) state of the homonuclear molecules provide another estimate of the ratios of the FCF's. One recalls that for the homonuclear molecules (for \(J' = 0\)),

\[
\Gamma(F' = 1) = \Gamma_{\text{rad}} + \frac{2}{3}a^2_v + 2.4b^2_v \quad (6.74)
\]

\[
\Gamma(F' = 3) = \Gamma_{\text{rad}} + 4a^2_v + 2.4b^2_v \quad (6.75)
\]

The difference in the decay rates is directly proportional to the parameter \([a_{v}^{a,b}(x)]^2\). (Here the superscript \((a,b)\) refers to the isotopomer and \(x(=79\) or \(81)\) refers to the nucleus.) The magnetic dipole predissociation parameter, \(a_v(X)\), is proportional to the nuclear magnetic moment, \(g(x)\), times an overlap integral, \(\sigma(X)\).

\[ a_v(X) \propto g(x)\sigma(X) \quad (6.76) \]

The ratio \(\text{FCF}(81, 81)/\text{FCF}(79, 79)\) may be directly deduced from a knowledge of the decay rates, \(\Gamma(F' = 1)\) and \(\Gamma(F' = 3)\) for \(^{79}\text{Br}_2\) and \(^{81}\text{Br}_2\), and the ratio of the nuclear magnetic moments, \(g(81)/g(79)\). The ratio of vibrational overlap integrals and FCF's based upon the decay rates of the \(J' = 0\) hyperfine levels (see Tables C.8 and C.9) are given in Table 6.15. The estimates from the \(J' = 0\) hyperfine decay rates agree with the values obtained by fitting all of the lifetime data but have considerably larger errors.
Table 6.16: The overlap integral, $\sigma(a, b)$ and FCF between the B $3^{3}Π_{0+}$ and $1^{1}Π_{1u}$ electronic states for $v' = 13$. The values for $79\text{Br}_2$ and $81\text{Br}_2$ were determined here. The values with superscript $^a$ ($79\text{Br}^8\text{Br}$) were reported by Clyne et al. [13]

Clyne et al. [13] have tabulated the FCF between the B and $1^{1}Π_{1u}$ states for $79\text{Br}^8\text{Br}$ $1 \leq v' \leq 25$. Because of the normalization of the continuum wavefunctions,

$$\langle 1^{1}Π_{1u}E' | 1^{1}Π_{1u}E \rangle = \delta(E - E')$$

(6.77)

the FCF have units of 1/energy (and are quoted in cm by Clyne et al.). Using the FCF between the B $3^{3}Π_{0+}$ and $1^{1}Π_{1u}$ states for the $v' = 13$ vibrational level of $79\text{Br}^8\text{Br}$ reported in Reference [13], the corresponding FCF's and $\sigma(a, b)$ have been deduced from the measurements reported here for $79\text{Br}_2$ and $81\text{Br}_2$. (See Table 6.16.)

6.9.2 The Gyroscopic Predissociation Parameter

The gyroscopic predissociation predissociation parameter is defined in this thesis (see equation 3.32) as,

$$C_v^2 = \frac{\pi}{\hbar} \left\lvert \langle 0^+_u | \frac{\hbar^2}{\mu R^2} \left[ T_{1}^{-1}(L) + T_{-1}^{-1}(S) \right] | 1_u E \rangle \right\rvert^2$$ (6.78)

$$= \frac{\pi \hbar^3}{\mu^2 R^4} |\langle v|E|\rangle|^2 \left\lvert \langle 0^+_u | \left[ T_{1}^{-1}(L) + T_{-1}^{-1}(S) \right] | 1_u \rangle \right\rvert^2$$ (6.79)
Table 6.17: The electronic matrix elements between the B \( ^3\Pi_{0+} \) and \(^1\Pi_{1u}\) matrix elements involved in the gyroscopic predissociation term: a comparison between the current results and those of Ref. [13] as corrected here.

\[
\begin{array}{|c|c|}
\hline
\left| W_{e}^\text{corr}(\bar{R}) \right|^2 / 2 & 1.76 \times 10^{-2} \\
\left| \langle 0_u^+ \mid [T_{1-1}(L) + T_{-1}(S)] \mid 1_u \rangle \right|^2 & 1.79 \times 10^{-2} \\
\hline
\end{array}
\]

\( \bar{R} \) is an average value of the internuclear separation, \( R \). Here \(|\langle v | E \rangle|^2\) has units of Joules\(^{-1}\). To convert the units to \(1/(\text{cm}^{-1})\), one must divide by \((\hbar c)\),

\[
\begin{align*}
C_v^2 &= \frac{\hbar^2}{2\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| \left\langle 0_u^+ \mid [T_{1-1}(L) + T_{-1}(S)] \mid 1_u \right\rangle \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2 \\
&= \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2
\end{align*}
\]

In the notation of Clyne et al. [13],

\[
k_v = C_v^2 = \frac{\hbar^2}{4\mu^2 R^4 c} \left| \left\langle v \mid E \right\rangle \right|^2 \left| W_e(\bar{R}) \right|^2
\]

By comparing equations 6.80 and 6.81, it is clear that

\[
\frac{|W_e(\bar{R})|^2}{2} = \left| \langle 0_u^+ \mid [T_{1-1}(L) + T_{-1}(S)] \mid 1_u \rangle \right|^2
\]

Clyne et al. reported that \(|W_e(\bar{R})|^2 = 8.8 \times 10^{-3}\). However, this value is incompatible with the results that are presented in their paper. A quick check shows that the factor of 4 in Equation 6.81 was neglected, making \(|W_e^{\text{corr}}(\bar{R})|^2 / 4 = 8.8 \times 10^{-3}\), in excellent agreement with the findings of the current work as shown in Table 6.17.

6.9.3 Quadrupole terms

Both the electric quadrupole predissociation parameter and the electric quadrupole coupling constant of an electronic state have similar types of matrix elements. From Equation 3.34,
\[ v' = 13 \]

<table>
<thead>
<tr>
<th>( ^{79}\text{Br}_2 )</th>
<th>( ^{81}\text{Br}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (1729 \pm 188) )</td>
<td>( (1445 \pm 152) )</td>
</tr>
<tr>
<td>( (178.1 \pm 1.0) )</td>
<td>( (148.3 \pm 1.0) )</td>
</tr>
<tr>
<td>( (9.7 \pm 1.1) )</td>
<td>( (9.7 \pm 1.1) )</td>
</tr>
</tbody>
</table>

Table 6.18: The effective quadrupole coupling constant between the \( ^1\Pi_{1u} \) and \( ^3\Pi_{0+} \) states compared with the electric quadrupole coupling constant of the \( ^3\Pi_{0+} \) state of bromine.

\[
b_v(x) = \sqrt{\frac{2\pi}{\hbar}} f_2(x, \Omega, \Omega', v, E') \left[ \frac{2i_1(2i_1 - 1)}{(2i_1 + 3)(2i_1 + 2)(2i_1 + 1)} \right]^{\frac{1}{2}} 
\]

(6.83)

\[
b_v(x) = \sqrt{\frac{2\pi}{\hbar}} eQ_{0^+,1u} \langle v | E' \rangle 
\]

(6.84)

By dividing the overlap integral and the factor of \( \sqrt{2\pi/\hbar} \) out of \( b_v \), one obtains an effective electric quadrupole coupling constant between the \( ^3\Pi_{0+} \) and \( ^1\Pi_{1u} \) electronic states. (See Table 6.18.) This finding represents the first measurement of hyperfine electric quadrupole coupling between a bound and a continuum electronic state. In addition, this is the first time a value for \( eQ \) has been obtained between states which differ in \( \Omega \) by one.
Chapter 7

Conclusions

The hyperfine structure of the B $^3\Pi_{u}^{+}$ and $X^1\Sigma_{g}^{+}$ electronic states of molecular bromine has been investigated along with the natural predissociation of the $v' = 13$ level of the B electronic state.

The hyperfine spectra of the two electronic states were well described using three parameters. One is the X state electric quadrupole coupling constant, $eqQ_X$, second is the B state parameter the electric quadrupole coupling constant $eqQ_B$, and third is the nuclear spin–rotation constant $C_{sr}$, of the B $^3\Pi_{u}^{+}$ state. The ratio of electric quadrupole coupling constants of the different isotopomers agreed with the ratio of nuclear quadrupole moments of the different isotopes,

$$\frac{eqQ(79\text{Br})}{eqQ(81\text{Br})} = \frac{Q(79\text{Br})}{Q(81\text{Br})}$$ (7.1)

for both electronic states. The B state $eqQ(79\text{Br})$ was $(177.0 \pm 0.6)\text{MHz}$ for $v' = 11$ and increased by roughly $0.5 \text{ MHz}$ per vibrational quantum up to $(180.6 \pm 1.4)\text{MHz}$ for $v' = 17$. The ground state $eqQ(79)$ values were recorded for the vibrational levels $v'' = 0$ through $2$ beginning with $eqQ(79\text{Br}) = (808.1 \pm 1.4)\text{MHz}$ and increased by about $1.0 \text{ MHz per vibrational quantum}$.

The hyperfine study also determined the hyperfine free frequency differences between various B–X rovibronic transitions providing a test of the accuracy of the molecular constants reported by Gerstenkorn and Luc [7] for each isotopomer of bromine. In general, the data showed that the constants faithfully reproduced the observed frequency separations of rovibronic transitions within a given isotopomer (to within $5 \text{ MHz}$) for the low $J$
states studied \((J < 20)\). The study of the \((17' - 2'n)\) band had a near coincidence of the transitions \(P(J)\) and \(R(J+3)\) for each isotopomer. The observed frequency separations yielded values for the combination of constants, \((-10B'_{17} + 6B''_{17}) + (120D'_{17} - 24D''_{17})\) that were systematically \((0.304 \pm 0.017) \text{ MHz}\) lower than the values derived from Reference [7] for all three species of molecular bromine. Finally, the calculated frequency separations between transitions arising from different isotopomers were systematically offset from the observed values. The offsets may be interpreted as a correction to the \(B\) state term values of \(^{79}\text{Br}\), \(^{81}\text{Br}\) and \(^{81}\text{Br}_2\) reported [7]. The following adjustments to the term values are suggested:

\[
\begin{align*}
^{79}T'_{00}(B) &= ^{79}T_{00}(B) \\
^{79,81}T'_{00}(B) &= ^{79,81}T_{00}(B) - (177 \pm 8)\text{MHz} \\
^{81}T'_{00}(B) &= ^{81}T_{00}(B) - (385 \pm 8)\text{MHz}
\end{align*}
\]

(The primed quantities are the suggested new values.) This leads the calculated and observed transition frequency differences to agree to within about 8 MHz. (The absolute frequencies are still no more accurate than the \(\pm 48\) MHz value claimed by Gerstenkorn and Luc [7].)

The study of the predissociation of the \(v' = 13\) level of the \(B\) \(^3\Pi_{0+}\) state of bromine demonstrated that the dissociative \(^1\Pi_{1u}\) level was responsible for most, if not all of the observed predissociation. The radiative lifetime of the \(B\) state was found to be \((11.9 \pm 0.5)\mu\text{s}\), in agreement with the range of lifetimes reported by Clyne et al. [13, 15, 16]. However, it is much longer than the values reported by Peeters et al. [14] or assumed in References [3, 4]. Revised values of the gyroscopic \((C_v)\) and hyperfine magnetic dipole \((a_v)\) predissociation parameters have been determined and, for the first time, a hyperfine electric quadrupole predissociation has been measured. It has been characterized by the new molecular constant \(b_v\). From this parameter, the first determination of an electric
quadrupole coupling constant between a bound and continuum electronic state was made. Finally, this work has shown that the phase shift technique, which is relatively easy to set up and apply, is very well suited to the measurement of the lifetimes of individual hyperfine levels of excited molecular states.

7.1 Future Work

A recent study [6] of the vibrational dependence of the electric quadrupole coupling constant of the B state of bromine has been carried out for \( v' = 16 \) through 28. As was pointed out by Vigué et al. [8], the electric quadrupole coupling constant of the \( \Omega = 0 \) state can be "contaminated" by interactions with other electronic states. Therefore, it would be useful to continue this survey of the vibrational dependence of the hyperfine structure to lower vibrational levels of the B state of bromine, especially from the \( v' = 2 \) through 7 states. This is the region where the interaction between the \( ^1\Pi_{1u} \) and B states goes from being very small (\( v'=2 \)), through a maximum (\( v'=5 \)), and down to a minimum (\( v'=7 \)). It would be interesting to see the effect, if any, this dissociative state has on the hyperfine structure of the B state.

A second suggestion is to continue a systematic survey of the separations of different rovibronic transitions as deduced from hyperfine measurements. With more data any systematic variations with \( v \) and \( J \) may be detected and allow even finer corrections to the constants of Gerstenkorn and Luc [7]. The appeal of this is that bromine provides an unusual opportunity to directly measure the relative positions of molecular electronic potentials between different isotopomers.

Third, a systematic study of the predissociation of the same vibrational levels mentioned above of the B state of bromine could prove interesting. In particular, the \( v' = 5 \) level should have a much larger predissociation and may display further discrepancies in
the lifetimes of hyperfine states both within and between different isotopomers. As well, a systematic survey using the phase shift technique could determine the shape of the $^1\Pi_{1u}$ state for each isotopomer.

Finally, another candidate for observing hyperfine electric quadrupole predissociation is molecular chlorine. Like bromine, chlorine has a nuclear spin of 3/2 and, therefore, it is possible that a measurement of the lifetimes of the hyperfine levels of para-chlorine could display an effect similar to that observed in bromine.
Bibliography


Appendix A

Derivation of Predissociation Rates

This appendix contains the derivation of the critical equations used in this thesis to describe the gyroscopic, hyperfine, and interference predissociation rates. Specifically, the derivation of the rotational and nuclear factors (Equations 3.35 through 3.38) used in Equations 3.44 and 3.45 is given. The approach taken is that of Broyer and co-workers [8, 23].

The predissociation rate of a bound electronic state, $|\psi_b\rangle$, coupled to a continuum electronic state, $|\psi_c(E')\rangle$, is given by Fermi’s Golden Rule [33, 34]

$$\Gamma_p = \frac{2\pi}{\hbar}|\langle \psi_b | H + \sum_{k,x} H^k(x) | \psi_c(E') \rangle|^2 \quad (A.1)$$

where $H_G$ and $H^k(x)$ are the gyroscopic Hamiltonian and the nuclear–electron hyperfine Hamiltonians which couple the two states. (k refers to the rank of the multipole characterizing the particular hyperfine interaction and x refers to the nucleus involved in the coupling.) In Equation A.1 it is assumed that the continuum wavefunctions are normalized as,

$$\langle \psi_c(E)|\psi_c(E') \rangle = \delta(E - E') \quad (A.2)$$

To evaluate the predissociation rate the bound and continuum wavefunctions will be expressed as

$$|\psi_b\rangle = \sum_{Jl} \alpha_{Jl}^F |\gamma(JI)\Omega v FM\rangle \quad (A.3)$$
Appendix A. Derivation of Predissociation Rates

\[ \langle \psi_b \rangle = \sum_{J''I''} \alpha_{J''I''}^F \langle \gamma(J''I'')\Omega v FM \rangle \]  \hspace{1cm} (A.4)

\[ |\psi_c \rangle = |\gamma'(J'I')\Omega' E'F'M' \rangle \]  \hspace{1cm} (A.5)

Note that for the purposes of these calculations the wavefunctions with primed quantum
numbers (e.g. \( J', I', \Omega' \)) will refer to the continuum states while the wavefunctions with
unprimed or doubly primed quantum numbers will refer to the bound electronic levels.

By substituting Equations A.3 through A.5 into Equation A.1 one obtains:

\[ \Gamma_p = \frac{2\pi}{\hbar} \sum_{J''I''} \sum_{J'I'Q'} \alpha_{J''I''}^F \alpha_{J'I'}^F \langle \gamma(J''I'')\Omega v FM \rangle \left[ H_G + \sum_{k,x} H^k(x) \right] |\gamma'(J'I')\Omega' E'F'M' \rangle \times \langle \gamma'(J'I')\Omega' E'F'M | H_G + \sum_{k',y} H^{k'}(y) | \gamma(JI)\Omega v FM \rangle \]  \hspace{1cm} (A.6)

In Equation A.6, a sum over \( J', I' \), and \( \Omega' \) has been added to take into account the
possibility that, in general, the bound state can couple to several continuum states with
the same \( F \) quantum number.

Before going through the full mathematical details of the calculations, a brief overview
of the calculation will be given. (The predissociation calculations will be performed
following the method of Broyer and co-workers [8, 23].) The goal is to cast Equation A.6
into a form that is simpler to evaluate. The products of matrix elements that must be
evaluated to obtain the predissociation rate from Equation A.6 are of the form

\[ C = \sum_{J''I'} \langle \gamma(J''I'')\Omega v FM | H_A | \gamma'(J'I')\Omega' E'F'M \rangle \langle \gamma'(J'I')\Omega' E'F'M | H_B | \gamma(JI)\Omega v FM \rangle \]  \hspace{1cm} (A.7)

where \( H_A \) and \( H_B \) can each be either the gyroscopic Hamiltonian or a hyperfine Hamiltonian. To proceed, one recalls that the quantity,

\[ P_{\Omega'E'J'I'} = |\gamma'(J'I')\Omega' E'F'M \rangle \langle \gamma'(J'I')\Omega' E'F'M | \]  \hspace{1cm} (A.8)
Appendix A. Derivation of Predissociation Rates

is the projection operator onto the sublevels $|\gamma (J'J'O'E'F'M)\rangle$. Therefore Equation A.7 can be expressed as

$$C = \sum_{J'I'Q'} \langle \gamma (J''I'')\Omega vF'M| P_{\Omega E'J'I'} H_B |\gamma (JI)\Omega vF'M\rangle$$

(A.9)

A projection operator, $P_n = |n\rangle\langle n|$, has the following properties [34]:

$$P_n^2 = P_n$$

(A.10)

$$\sum_n P_n = 1$$

(A.11)

$$P_n|m\rangle = |n\rangle\langle n|m\rangle$$

(A.12)

If the states $|n\rangle$ and $|m\rangle$ in A.12 are orthonormal basis states then $\langle n|m\rangle = \delta_{n,m}$. Using these three properties in Equation A.9 one finds

$$C = \sum_{J'I'Q'} \langle \gamma (J''I'')\Omega vF'M| \left[ \sum_{\Omega_{1,1}J_1I_1} P_{\Omega_{1,1}J_1I_1} \right] (H_A P_{\Omega E'J'I'} H_B) \left[ \sum_{\Omega_{2,2}J_2I_2} P_{\Omega_{2,2}J_2I_2} \right] |\gamma (JI)\Omega vF'M\rangle$$

(A.13)

and

$$C = \sum_{J'I'Q'} \langle \gamma (J''I'')\Omega vF'M| P_{\Omega E'J'I'} (H_A P_{\Omega E'J'I'} P_{\Omega E'J'I'} H_B) P_{\Omega E'I'} |\gamma (JI)\Omega vF'M\rangle$$

(A.14)

This gives the desired result:

$$C = \sum_{J'I'Q'} \langle \gamma (J''I'')\Omega vF'M| (P_{\Omega E'J'I'} H_A P_{\Omega E'J'I'}) (P_{\Omega E'J'I'} H_B P_{\Omega E'I'}) |\gamma (JI)\Omega vF'M\rangle$$

(A.15)

Using projection operators, the expression for the predissociation rate given in Equation A.6 can be rewritten as

$$\Gamma_p = \frac{2\pi}{\hbar} \sum_{J'I'Q'} \sum_{J''I''} \alpha_{J''I''}^{J'I'I} \alpha_{J'I'}^{J'I}$$
Appendix A. Derivation of Predissociation Rates

\[
\times (\gamma (J''I'') \Omega \nu FM) \left[ (P_{\Omega_0 J'' J''} H_G P_{Q' E' J' J'}) + \sum_{k, x} \left( P_{\Omega_0 J'' J''} H^k(x) P_{Q' E' J' J'} \right) \right] \\
\times \left[ (P_{Q' E' J' J'} H_G P_{\Omega_0 J J}) + \sum_{k', y} \left( P_{Q' E' J' J'} H^{k'}(y) P_{\Omega_0 J J} \right) \right] |\gamma (J J) \Omega \nu FM| \tag{A.16}
\]

One observes that each Hamiltonian, $H_A$, which couples the bound and continuum levels has been replaced by the equivalent tensorial operator, $P_\eta H_A P_{\eta'}$. (The subscripts $\eta$ and $\eta'$ are shorthand for the appropriate quantum numbers.)

The equivalent tensorial operators for each Hamiltonian will be derived in terms of the irreducible tensor operator basis sets, $j j' T^k_q$ and $J J' U^k_q$ [8, 23]. $j j' T^k_q$ acts on all of the coordinates except for the nuclear spins, and $J J' U^k_q$ only acts on the nuclear spins. The extra sub- and superscripts used to label the basis sets are to remind the reader that $j j' T^k_q$ has non-vanishing matrix elements between the states, $|J \Omega \rangle$ and $|J' \Omega' \rangle$ while $J J' U^k_q$ has non-zero matrix elements between the states, $|(i_1 i_2) I \rangle$ and $|(i_1' i_2') I' \rangle$. ($i_1$ and $i_2$ are the nuclear spins of nucleus 1 and 2 respectively.) The properties of these operator basis sets will be explored further in the next section.

Once the equivalent operators have been derived, the composite operators,

\[
P_{GG} = \sum_{J'' J''} \left( P_{\Omega_0 J'' J''} H_G P_{Q' E' J' J'} (P_{Q' E' J' J'} H_G P_{\Omega_0 J J}) \right) \tag{A.17}
\]

\[
P_{kG}(x) = \sum_{J'' J''} \left( P_{\Omega_0 J'' J''} H^k(x) P_{Q' E' J' J'} \right) (P_{Q' E' J' J'} H_G P_{\Omega_0 J J}) \tag{A.18}
\]

\[
P_{kk'}(x, y) = \sum_{J'' J''} \left( P_{\Omega_0 J'' J''} H^k(x) P_{Q' E' J' J'} \right) \left( P_{Q' E' J' J'} H^{k'}(y) P_{\Omega_0 J J} \right) \tag{A.19}
\]

are introduced and evaluated. These allow the predissociation rate to be written

\[
\Gamma_p = \frac{2\pi}{\hbar} \sum_{J'' J''} \alpha^F_{J'' J''} \alpha^F_{J J} \langle \gamma (J'' I'') \Omega \nu FM \rangle \left[ P_{GG} + \sum_{k', y} P_{k' G}(y) \right]
\]
Appendix A. Derivation of Predissociation Rates

\[ + \sum_{k,x} P_{Gk}(x) + \sum_{k,x} \sum_{k',y} P_{kk'}(x,y) \mid \gamma(JI)\Omega vFM) \]  \hspace{1cm} (A.20)

Equation A.20 is of the form

\[ \Gamma_p = \sum_{J1J'1''} \alpha_{J''I''}^F \alpha_{J1}^F \left[ \Gamma_{GG} + \sum_{k',y} \Gamma_{k'G}(y) + \sum_{k,x} \Gamma_{Gk}(x) + \sum_{k,x} \sum_{k',y} \Gamma_{kk'}(x,y) \right] \]  \hspace{1cm} (A.21)

The matrix elements, \( \Gamma_{AB}(a,b) \), are

\[ \Gamma_{AB}(a,b) = \frac{2\pi}{\hbar} \langle \gamma(J''I'')\Omega vFM \mid P_{AB}(a,b) \mid \gamma(JI)\Omega vFM \rangle \]  \hspace{1cm} (A.22)

where A or B may be G, k, or k' and the indices a, b refer to nucleus 1 or 2; if A (and/or B) = G, then the index a (and/or b) is redundant.

(NOTE: for the rest of this appendix it will be assumed that all of the quantum numbers are integer except for \( i_1 = i_2 = i_z \).)

A.1 Hyperfine Predissociation Rates

The hyperfine Hamiltonians responsible for coupling the bound and continuum electronic states are the interactions between each nucleus and the electrons. As explained in Chapter 2, the electron–nuclear hyperfine Hamiltonians can be expressed as contractions of spherical tensors of rank k.

\[ H_{ij}^k(x) = \sum_e \sum_q (-1)^q V_q^k(j_e(x))Q_q^k(i_x) \]  \hspace{1cm} (A.23)

(k is the order of the multipole interaction, \( i_x \) is the nuclear spin of nucleus x (\( = 1 \) or 2), and \( j_e(x) = l_e(x) + s_e(x) \).) The definitions of the \( V_q^k(j_e(x)) \) and \( Q_q^k(i_x) \) have been given in Chapter 2 for the magnetic dipole (\( k = 1 \)) and electric quadrupole (\( k = 2 \)) hyperfine interactions.
The first step is to work out the equivalent operators, $P_{\Omega \omega J} H_{hf}^k(x) P_{\Omega' \omega' J'}$, in terms of the basis sets, $j_{ji'} T_q^k$ and $U_q^k$. To do this, some of the properties of the irreducible tensor basis sets must be presented. The reader is reminded that $j_{ji'} T_q^k$ operates on all of the coordinates except for nuclear spin and has non-zero matrix elements between the states $\langle J\Omega |$ and $| J'\Omega' \rangle$. $U_q^k$ only acts on the nuclear spin coordinates and has non-vanishing matrix elements between the states $\langle (i_1 i_2) I |$ and $| (i_1 i_2) I' \rangle$. (For bromine, both isotopes have the same nuclear spin, $i = 3/2$. Therefore, for the rest of this appendix $i_1 = i_2 = i_x$ will be used.) The matrix elements of the scalar product,

$$\sum_q (-1)^q j_{ji'} T_q^k U_{-q}^k$$

is given by (see Equation 7.1.6 of Reference [22])

$$\langle \gamma(JI)\Omega FM | \sum_q (-1)^q j_{ji'} T_q^k U_{-q}^k | \gamma'(J'I')\Omega' FM \rangle$$

$$= (-1)^{F+J'+I'} \left\{ \begin{array}{ccc} F & J' & I' \\ k & J & I \end{array} \right\} \times \langle J\Omega || j_{ji'} T_q^k || J'\Omega' \rangle \langle I || U_q^k || I' \rangle \quad (A.24)$$

From the normalization condition

$$Tr\left\{ j_{ji'} T_q^k (\sum_{i_1 q_1} T_{q_1}^{k_1} )^{+} \right\} = \delta_{J J_1} \delta_{\Omega \Omega_1} \delta_{J' J_1} \delta_{\Omega' \Omega_1} \delta_{k k_1} \delta_{q q_1} \quad (A.25)$$

one can show that [23]

$$\langle J\Omega || j_{ji'} T_q^k || J'\Omega' \rangle = \sqrt{2k+1} \quad (A.26)$$

and

$$\langle I || U_q^k || I' \rangle = \sqrt{2k+1} \quad (A.27)$$

The equivalent operator $P_{\Omega \omega J} H_{hf}^k(x) P_{\Omega' \omega' J'}$ is derived from the matrix element,

$$M_{hf}^k(x, F, \Omega, \Omega') = \langle \gamma(JI)\Omega FM | H_{hf}^k(x) | \gamma'(J'I')\Omega' FM \rangle \quad (A.28)$$

$$= \langle \gamma(JI)\Omega FM | P_{\Omega \omega J} H_{hf}^k(x) P_{\Omega' \omega' J'} | \gamma'(J'I')\Omega' FM \rangle \quad (A.29)$$
Replacing,

\[ P_{\Omega \nu J I} H^k_{h f}(x) P_{\Omega' \nu' J' I'} = w_k(x, \Omega, \Omega', v, v', J, J', I, I') \sum_q (-1)^q \Omega' J I \Omega \Omega' J I \]

\[ (A.30) \]

in Equation A.29 and using relations A.24, A.26 and A.27, one obtains,

\[ M^k_{h f}(x, F, \Omega, \Omega') = (-1)^{F + J' + I} (2k + 1) w_k(x, \Omega, \Omega') \begin{bmatrix} F & J' & I' \\ k & I & J \end{bmatrix} \]

\[ (A.31) \]

(Here \( w_k(x, \Omega, \Omega', v, v', J, J', I, I') \) has been abbreviated by \( w_k(x, \Omega, \Omega') \).) Equations 2.66 and 2.67 give

\[ M^k_{h f}(x, F, \Omega, \Omega') = (-1)^{k + 2 i_x \varepsilon + F + I' + J + J'} f_k(1, \Omega, v, \Omega', v') \]

\[ \sqrt{(2I + 1)(2I' + 1)(2J + 1)(2J' + 1)} \]

\[ \times \left( \begin{array}{ccc} J & k & J' \\ -\Omega & -\Delta \Omega & \Omega' \end{array} \right) \left( \begin{array}{ccc} i_x & i_x & I \\ k & I' & i_x \end{array} \right) \]

\[ \begin{bmatrix} F & J' & I' \\ k & I & J \end{bmatrix} \]

\[ (A.32) \]

(where \( \Delta \Omega = \Omega' - \Omega \).) Comparing Equation A.31 with Equation A.32 one deduces \( w_k(x, \Omega, \Omega') \).

\[ w_k(x, \Omega, \Omega', v, v', J, J', I, I') = (-1)^{k + 2 i_x \varepsilon + J + J'} f_k(x, \Omega, v, \Omega', v')/(2k + 1) \]

\[ \sqrt{(2I + 1)(2I' + 1)(2J + 1)(2J' + 1)} \]

\[ \times \left( \begin{array}{ccc} J & k & J' \\ -\Omega & -\Delta \Omega & \Omega' \end{array} \right) \left( \begin{array}{ccc} i_x & i_x & I \\ k & I' & i_x \end{array} \right) \]

\[ (A.33) \]

Now that the equivalent operator, \( P_{\Omega \nu J I} H^k_{h f}(x) P_{\Omega' \nu' J' I'} \), has been established, one would like to construct the composite operators

\[ P_{kk'}(x, y) = \sum_{J' I' \Omega'} \left( P_{\Omega \nu J I} H^k_{h f}(x) P_{\Omega' \nu' J' I'} \right) \left( P_{\Omega' \nu' J' I'} H^{k'}(y) P_{\Omega \nu J I} \right) \]

\[ (A.34) \]

Using Equation A.30 one obtains,
Appendix A. Derivation of Predissociation Rates

\[ P_{kk'}(x, y) = \sum_{J''J'}(w_k(x, \Omega, \Omega', v, E', J'', J', I'', I') \sum_q (-1)^q \frac{\Omega''}{J''J'} \Omega_k T^k_{q} I''_q U^k_{-q}) \]

\[ \times \left( w_k(y, \Omega', \Omega, E', v, J', J', I', I') \sum_{q'} (-1)^{q'} \frac{\Omega''}{J''J'} \Omega_k T^{k'}_{q'} I''_q U^{k'}_{-q'} \right) \]

\[ = \sum_{J''J'} \sum_{qq'} (-1)^{q+q'} w_k(x, \Omega, \Omega') w_{k'}(y, \Omega', \Omega) \]

\[ \times \left[ \frac{\Omega''}{J''J'} \Omega_k T^k_{q} \frac{\Omega''}{J''J'} \Omega_k T^{k'}_{q'} \right] [I''_q U^k_{-q} I''_{-q} U^{k'}_{-q}] \]

(A.35)

The product of irreducible tensor basis sets, \( \frac{\Omega''}{J''J'} \Omega_k T^k_{q} \frac{\Omega''}{J''J'} \Omega_k T^{k'}_{q'} \), can be developed on the irreducible basis set, \( \frac{\Omega}{J''J'} T^K_{Q} \), where \( K \) takes on the values \( |k - k'| \leq K \leq (k + k') \) [8, 23].

\[ \frac{\Omega}{J''J'} \Omega_k T^k_{q} \frac{\Omega}{J''J'} \Omega_k T^{k'}_{q'} = \sum_{KQ} \text{Tr} \left\{ \frac{\Omega}{J''J'} \Omega_k T^k_{q} \frac{\Omega}{J''J'} \Omega_k T^{k'}_{q'} (\frac{\Omega}{J''J'} T^K_{Q})^\dagger \right\} \frac{\Omega}{J''J'} T^K_{Q} \]

(A.36)

The trace of the product of the three irreducible tensor bases is

\[ \text{Tr} \left\{ \frac{\Omega}{J''J'} \Omega_k T^k_{q} \frac{\Omega}{J''J'} \Omega_k T^{k'}_{q'} (\frac{\Omega}{J''J'} T^K_{Q})^\dagger \right\} = \sum_{\Omega''} (J''\Omega'' | \frac{\Omega}{J''J'} \Omega_k T^k_{q} \frac{\Omega}{J''J'} \Omega_k T^{k'}_{q'} (\frac{\Omega}{J''J'} T^K_{Q})^\dagger | J''\Omega'') \]

\[ = \sum_{\Omega''} (J''\Omega'' | \frac{\Omega}{J''J'} \Omega_k T^k_{q} | J'\Omega') \]

\[ \times (J'\Omega' | \frac{\Omega}{J''J'} \Omega_k T^{k'}_{q'} | J\Omega) \]

\[ \times (J\Omega | (\frac{\Omega}{J''J'} T^K_{Q})^\dagger | J''\Omega'') \]

(A.37)

To evaluate the trace, one uses the following properties of irreducible tensorial basis sets [22]: First,

\[ (J\Omega | (\frac{\Omega}{J''J'} T^k_{q} | J'\Omega') = (-1)^{J-\Omega} \left( \begin{array}{cc} J & k \\ -\Omega & q \end{array} \right) | J\Omega | (\frac{\Omega}{J''J'} T^k_{q})^\dagger | J'\Omega'') \]

(A.38)

Second,

\[ (\frac{\Omega}{J''J'} T^K_{Q})^\dagger = (-1)^Q (\frac{\Omega}{J''J'} T^K_{-Q}) \]

(A.39)
Appendix A. Derivation of Predissociation Rates

Third,

$$\langle J\Omega' | \left( \frac{\Omega''}{J''} T^K \right)^\dagger | J'' \Omega'' \rangle = (-1)^J (-1)^Q \times \left( \begin{array}{ccc} J & K & J'' \\ -\Omega & -Q & \Omega'' \end{array} \right) \langle J\Omega'' | \frac{\Omega''}{J''} T^K | J'' \Omega'' \rangle$$

(A.40)

Substituting these into Equation A.37, one obtains,

$$Tr \left\{ \frac{\Omega}{J''} T^k \frac{\Omega''}{J''} T^k \left( \frac{\Omega}{J''} T^K \right)^\dagger \right\} = \sum_{\Omega \Omega''} (-1)^J (-1)^Q \sqrt{2k+1 \cdot 2k'+1 \cdot 2K+1} \left( \begin{array}{ccc} J'' & k & J' \\ -\Omega'' & q & \Omega' \end{array} \right) \times (-1)^J (-1)^Q \sqrt{2k'+1 \cdot 2K+1} \left( \begin{array}{ccc} J' & k' & J \\ -\Omega' & q' & \Omega \end{array} \right) \times (-1)^J (-1)^Q \sqrt{2K+1} \left( \begin{array}{ccc} J & K & J'' \\ -\Omega & -Q & \Omega'' \end{array} \right)$$

(A.41)

Using Equation 6.2.8 from Reference [22] one has,

$$\sum_{\Omega \Omega''} (-1)^J (-1)^J'' (-1)^J' (-1)^J'' (-1)^J'' \left( \begin{array}{ccc} J'' & k & J' \\ -\Omega'' & q & \Omega' \end{array} \right) \left( \begin{array}{ccc} J' & k' & J \\ -\Omega' & q' & \Omega \end{array} \right) \left( \begin{array}{ccc} J & K & J'' \\ -\Omega & -Q & \Omega'' \end{array} \right) = \left( \begin{array}{ccc} k' & k & K \\ q' & q & -Q \end{array} \right) \left\{ \begin{array}{ccc} k & k & K \\ J'' & J & J' \end{array} \right\}$$

(A.42)

This simplifies Equation A.41 giving,

$$Tr \left\{ \frac{\Omega}{J''} T^k \frac{\Omega''}{J''} T^k \left( \frac{\Omega}{J''} T^K \right)^\dagger \right\} = (-1)^Q \sqrt{(2k+1)(2k'+1)(2K+1)} \times \left( \begin{array}{ccc} k' & k & K \\ q' & q & -Q \end{array} \right) \left\{ \begin{array}{ccc} k' & k & K \\ J'' & J & J' \end{array} \right\}$$

(A.43)
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The product of irreducible tensor basis sets, \( \Omega, \Omega' T^k_q', \Omega^t T^{k'}_{q'} \), can now be expressed as,

\[
\sum_{KQ} (-1)^Q \sqrt{(2k+1)(2k'+1)(2K+1)}
\times \left( \begin{array}{ccc} k' & k & K \\ q' & q & -Q \end{array} \right) \left( \begin{array}{ccc} k' & k & K \\ J'' & J & J' \end{array} \right) \Omega, \Omega T^K \\
J'' T^Q_k
\] (A.44)

Similarly,

\[
\sum_{K'^I} (-1)^Q' \sqrt{(2k+1)(2k'+1)(2K+1)}
\times \left( \begin{array}{ccc} k' & k & K' \\ -q' & -q & Q' \end{array} \right) \left( \begin{array}{ccc} k' & k & K' \\ I'' & I & I' \end{array} \right) \Omega'^I U^{K'}_{-Q'}
\] (A.45)

Equations A.44 and A.45 can be substituted back into the expression for \( P_{kk'}(x, y) \) (Equation A.35).

\[
P_{kk'}(x, y) = \sum_{J''} \sum_{q} (-1)^{s+q'} w_k(x, \Omega, \Omega') w_{k'}(y, \Omega', \Omega)
\sum_{KQ} (-1)^Q \sqrt{(2k+1)(2k'+1)(2K+1)}
\times \left( \begin{array}{ccc} k' & k & K \\ q' & q & -Q \end{array} \right) \left( \begin{array}{ccc} k' & k & K \\ J'' & J & J' \end{array} \right) \Omega, \Omega T^K \\
J'' T^Q_k
\times \sum_{K'^I} (-1)^{-Q'} \sqrt{(2k+1)(2k'+1)(2K'+1)}
\times \left( \begin{array}{ccc} k' & k & K' \\ -q' & -q & Q' \end{array} \right) \left( \begin{array}{ccc} k' & k & K' \\ I'' & I & I' \end{array} \right) \Omega'^I U^{K'}_{-Q'}
\] (A.46)

By using the relation, \( q + q' = Q \), and Equation 3.7.8 from Edmonds [22], namely,

\[
\sum_{q} \left( \begin{array}{ccc} k' & k & K \\ q' & q & -Q \end{array} \right) \left( \begin{array}{ccc} k' & k & K' \\ q' & q & -Q' \end{array} \right) = \frac{\delta_{KK'} \delta_{QQ'}}{(2K+1)}
\] (A.47)
Equation A.46 can be reduced to:

\[ P_{kk'}(x, y) = \sum_{J J' Q Q'} \sum_{K K'} (-1)^{K+k+k'} (2k+1)(2k'+1) \times w_k(x, \Omega, \Omega') w_k'(y, \Omega', \Omega) \times \\begin{cases} k & k' & K \\ J J' & J' & J' \\ I I' & I' & I' \end{cases} \begin{cases} i_z & i_z & I'' \\ k & k' & I'' \\ I' & i_z & i_z \end{cases} \times \sum_{Q} (-1)^{Q} \frac{\Omega_{ij} \Omega_{ij}^{K}}{J'' J''} \frac{U_{ij} U_{ij}^{K}}{I'' I''} \] (A.48)

Next, the definition of \( w_k(a, \Omega_1, \Omega_2) \) from Equation A.33 is substituted into Equation A.48. This gives

\[ P_{kk'}(x, y) = \sum_{J J' Q Q'} \sum_{K K'} (-1)^{K+k+k'} (-1)^{2i_++k+I'+J''} (-1)^{2i_++k'+I'+J'} f_k(x, \Omega, \Omega') f_k'(y, \Omega, \Omega') \times \frac{(2J'+1)(2J''+1)(2J+1)(2J''+1)(2I+1)}{[(2J''+1)(2J+1)(2J''+1)(2I+1)]^{1/2}} \times \begin{cases} k & k' & K \\ I I' & I' & I' \end{cases} \begin{cases} i_z & i_z & I'' \\ k & k' & I'' \\ I' & i_z & i_z \end{cases} \times \begin{pmatrix} J'' & k & J' \\ -\Omega & -\Omega & \Omega' \end{pmatrix} \begin{pmatrix} J' & k' & J \\ -\Omega & -\Omega & \Omega \end{pmatrix} \begin{cases} k & k' & K \\ J J' & J' & J' \end{cases} \times \sum_{Q} (-1)^{Q} \frac{\Omega_{ij} \Omega_{ij}^{K}}{J'' J''} \frac{U_{ij} U_{ij}^{K}}{I'' I''} \] (A.49)

The case where \( x = y \) is treated first.

\[ P_{kk'}(x, x) = \sum_{J J' Q Q'} \sum_{K K'} (-1)^{K+k+k'} (-1)^{2i_++k+I'+J''} (-1)^{2i_++k'+I'+J'} f_k(x, \Omega, \Omega') f_k'(x, \Omega, \Omega') \times \frac{(2J'+1)(2J''+1)(2J+1)(2J''+1)(2I+1)}{[(2J''+1)(2J+1)(2J''+1)(2I+1)]^{1/2}} \times \begin{cases} k & k' & K \\ I I' & I' & I' \end{cases} \begin{cases} i_z & i_z & I'' \\ k & k' & I'' \\ I' & i_z & i_z \end{cases} \times \begin{pmatrix} J'' & k & J' \\ -\Omega & -\Omega & \Omega' \end{pmatrix} \begin{pmatrix} J' & k' & J \\ -\Omega & -\Omega & \Omega \end{pmatrix} \begin{cases} k & k' & K \\ J J' & J' & J' \end{cases} \times \sum_{Q} (-1)^{Q} \frac{\Omega_{ij} \Omega_{ij}^{K}}{J'' J''} \frac{U_{ij} U_{ij}^{K}}{I'' I''} \] (A.50)
Using formula 6.2.12 from Reference [22] one obtains

\[
\sum_{I'}(2I'+1)(-1)^{I'} \left\{ \begin{array}{ccc} k & k' & K \\ I & I'' & I' \end{array} \right\} \left\{ \begin{array}{ccc} i_x & i_x & I'' \\ k & I' & i_x \end{array} \right\} \left\{ \begin{array}{ccc} i_x & i_x & I \\ k' & I' & i_x \end{array} \right\} = \\
(-1)^{K+k+k'+I+I''} \left\{ \begin{array}{ccc} K & I & I'' \\ i_x & K & i_x \end{array} \right\} \left\{ \begin{array}{ccc} i_x & i_x & i_x \\ k & i_x & k \end{array} \right\}
\]

\[(A.51)\]

It follows, then, that

\[
P_{kk'}(x, x) = \sum_{J'Q'} \sum_{K} (-1)^{h+k'+J''+I''+J'} f_k(x, \Omega, \Omega') f_{k'}(x, \Omega, \Omega') \times \\
(2J'+1) [(2J''+1)(2J+1)(2I''+1)(2I+1)]^{\frac{3}{2}} \times \\
\left\{ \begin{array}{ccc} K & I & I'' \\ i_x & K & i_x \end{array} \right\} \left\{ \begin{array}{ccc} i_x & i_x & i_x \\ k & i_x & k \end{array} \right\} \times \\
\left( \begin{array}{ccc} J'' & k & J' \\ -\Omega & -\Delta \Omega & \Omega' \end{array} \right) \left( \begin{array}{ccc} J' & k' & J \\
-\Omega' & \Delta \Omega & \Omega \end{array} \right) \left\{ \begin{array}{ccc} k & k' & K \\
J & J'' & J' \end{array} \right\} \\
\times \sum_{Q} (-1)^{Q} \frac{\Omega_{Q} \Omega_{K}}{J_{Q} J_{K}} I_{Q} J_{K}^{K} (-A.52)
\]

A similar formula for the summation over J' can be obtained from Equation 2.19 of Reference [41]

\[
\sum_{J'}(2J'+1)(-1)^{J'} \left( \begin{array}{ccc} J'' & k & J' \\ -\Omega & -\Delta \Omega & \Omega' \end{array} \right) \left( \begin{array}{ccc} J' & k' & J \\
-\Omega' & \Delta \Omega & \Omega \end{array} \right) \left\{ \begin{array}{ccc} k & k' & K \\
J & J'' & J' \end{array} \right\} = \\
(-1)^{J+J''+\Omega'} \left( \begin{array}{ccc} k & k' & K \\
\Delta \Omega & -\Delta \Omega & 0 \end{array} \right) \left( \begin{array}{ccc} J & J'' & K \\
\Omega & -\Omega & 0 \end{array} \right)
\]

\[(A.53)\]

Equation A.52 can then be written
Appendix A. Derivation of Predissociation Rates

\[ P_{kk'}(x, x) = \sum_{\Omega'} \sum_{K} (-1)^{k+k'+J+I''+\Omega'} \]

\[ f_k(x)f_{k'}(x) [(2J'' + 1)(2J + 1)(2I'' + 1)(2I + 1)]^{\frac{1}{2}} \]

\[ \times \left\{ \begin{array}{ccc} K & I & I'' \\ i_x & K & i_x \end{array} \right\} \left\{ \begin{array}{ccc} i_x & i_x & i_x \end{array} \right\} \left\{ \begin{array}{ccc} k' & i_x & k \end{array} \right\} \]

\[ \times \left( \begin{array}{ccc} k & k' & K \\ \Delta \Omega & -\Delta \Omega & 0 \end{array} \right) \left( \begin{array}{ccc} J & J'' & K \\ \Omega & -\Omega & 0 \end{array} \right) \]

\[ \times \sum_{Q} (-1)^{Q} \sum_{J''J'} \sum_{I''I'} \sum_{K''K'} \]

Having deduced \( P_{kk'}(x, x) \) one now returns to Equation A.49 and considers the case \( x \neq y \). The evaluation of \( P_{kk'}(x, y) \) relies on the property that

\[ f_k(x) = (-1)^{\Delta J} \zeta \epsilon_{ug} f_k(y) \quad (A.55) \]

where

\[ \epsilon_{ug} = \begin{cases} 1 & \text{for } u \leftrightarrow u, \ g \leftrightarrow g \\ -1 & \text{for } u \leftrightarrow g \end{cases} \]

and

\[ \zeta = \begin{cases} g(x)/g(y) & \text{for } k = 1 \\ Q(x)/Q(y) & \text{for } k = 2 \end{cases} \]

The factor \( \zeta \) takes into account that the two nuclei may have different nuclear properties such as for \(^{79}\text{Br}^{81}\text{Br}\). For \( k = 1 \) (hyperfine magnetic dipole interaction) \( g(x)/g(y) \) is the ratio of the nuclear magnetic moments and for \( k = 2 \) (electric quadrupole interaction) \( Q(x)/Q(y) \) is the ratio of the nuclear quadrupole moments. As is evident from the definition, \( \zeta = 1 \) for all values of \( k \) for homonuclear molecules. Thus,
\[ P_{kk'}(x, y) = \sum_{j_i l' q_i} \sum_{K} (-1)^{K+k+k'} (-1)^{2i_x+k+l'+J''} (-1)^{2i_x+k'+l'+J'} \]

\[ \times \left\{ \begin{array}{ccc}
\{ k & k' & K \} & \{ i_x & i_x & I'' \} & \{ i_x & i_x & I \} \\
I & I'' & I' & k & I' & i_x \end{array} \right\} \]

\[
\times \left( \begin{array}{ccc}
J'' & k & J' \{ J' & k' & J \} & \{ k & k' & K \} \\
-\Omega & -\Delta \Omega & \Omega' & -\Omega' & \Delta \Omega & \Omega \end{array} \right) \] \[ \times \sum_{Q} (-1)^{Q} \frac{\Omega_{j'} \Omega_{l'} T_{Q}^{K}}{I'' I'' U_{-Q}^{K}} \] (A.56)

\[ P_{kk'}(x, y) = \sum_{j_i l' q_i} \sum_{K} (-1)^{K+k+k'} (-1)^{2i_x+k+l'+J''} (-1)^{2i_x+k'+l'+J'} \]

\[ (-1)^{l'+1+1} \zeta \epsilon_{ug} f_{k}(x, \Omega, \Omega') f_{k'}^{*}(x, \Omega, \Omega') [(2J'' + 1)(2J + 1)(2I'' + 1)(2I + 1)]^{1/2} \]

\[ \times (2J' + 1)(2I' + 1) \left\{ \begin{array}{ccc}
k & k' & K \{ i_x & i_x & I'' \} & \{ i_x & i_x & I \} \\
I & I'' & I' & k & I' & i_x \end{array} \right\} \]

\[
\times \left( \begin{array}{ccc}
J'' & k & J' \{ J' & k' & J \} & \{ k & k' & K \} \\
-\Omega & -\Delta \Omega & \Omega' & -\Omega' & \Delta \Omega & \Omega \end{array} \right) \] \[ \times \sum_{Q} (-1)^{Q} \frac{\Omega_{j'} \Omega_{j''} T_{Q}^{K}}{I'' I'' U_{-Q}^{K}} \]

\[ \zeta \epsilon_{ug} f_{k}(x, \Omega, \Omega') f_{k'}^{*}(x, \Omega, \Omega') [(2J'' + 1)(2J + 1)(2I'' + 1)(2I + 1)]^{1/2} \]

\[ \times (2J' + 1)(2I' + 1) \left\{ \begin{array}{ccc}
k & k' & K \{ i_x & i_x & I'' \} & \{ i_x & i_x & I \} \\
I & I'' & I' & k & I' & i_x \end{array} \right\} \]

\[
\times \left( \begin{array}{ccc}
J'' & k & J' \{ J' & k' & J \} & \{ k & k' & K \} \\
-\Omega & -\Delta \Omega & \Omega' & -\Omega' & \Delta \Omega & \Omega \end{array} \right) \] \[ \times \sum_{Q} (-1)^{Q} \frac{\Omega_{j'} \Omega_{j''} T_{Q}^{K}}{I'' I'' U_{-Q}^{K}} \] (A.57)
From Equation 6.4.3 in Ref. [22],

\[
\sum_{I''}(2I'' + 1)(-1)^{2I''}\begin{pmatrix} k & k' & K \\ I & I'' & I' \end{pmatrix}\begin{pmatrix} i_z & i_x & I'' \\ k & I' & i_x \end{pmatrix}\begin{pmatrix} i_z & i_x & I \\ k' & I' & i_x \end{pmatrix}
\]

\[
= \begin{pmatrix} i_z & I & i_x \\ k & K & k' \\ i_z & I'' & i_x \end{pmatrix}
\]

(A.58)

When this identity and Equation A.53 are used to simplify Equation A.57 one obtains:

\[
P_{kk'}(x, y) = \sum_{Q'} \sum_{K} (-1)^{k+k'+J+I''+J+\Omega} \epsilon_{ug} f_{k}(x, \Omega, \Omega') f_{k'}(x, \Omega, \Omega')
\]

\[
\times \left[ (2J' + 1)(2J + 1)(2I'' + 1)(2I + 1) \right]^{\frac{1}{2}}
\]

\[
\times \left( \begin{array}{ccc} k & k' & K \\ \Delta \Omega & -\Delta \Omega & 0 \end{array} \right) \left( \begin{array}{ccc} J & J'' & K \\ \Omega & -\Omega & 0 \end{array} \right)\begin{pmatrix} i_z & I'' & i_x \\ k & K & k' \\ i_z & I & i_x \end{pmatrix}
\]

\[
\times \sum_{Q} (-1)^{Q} \Omega_{\Omega'} T_{Q}^{K} \Omega_{\Omega'}^{I''} U_{Q}^{K}
\]

(A.59)

Note that in Equation A.59 the following relation has been used:

\[
\begin{pmatrix} i_z & I & i_x \\ k & K & k' \\ i_z & I'' & i_x \end{pmatrix} = (-1)^{K+k+k'+J+I''+J+4i_x} \begin{pmatrix} i_z & I'' & i_x \\ k & K & k' \\ i_z & I & i_x \end{pmatrix}
\]

(A.60)

The matrix elements of interest for the hyperfine predissociation, \(\Gamma_{kk'}(x, y)\), will now be calculated. For \(x = y\), it can be seen from Equations A.54 and A.24 that the matrix elements are of the form:
Appendix A. Derivation of Predissociation Rates

\[
\Gamma_{kk'}(x, x) = \frac{2\pi}{\hbar} \langle \gamma(J''I'')\Omega v FM | P_{kk'}(x, x) | \gamma(JI)\Omega v FM \rangle
\]  

(A.61)

\[
\Gamma_{kk'}(x, x) = \sum_{\Omega'} (-1)^{F+\Omega'+k+k'} [(2I + 1)(2I'' + 1)(2J + 1)(2J'' + 1)]^{\frac{1}{2}} \times \left[ \sqrt{\frac{2\pi}{\hbar}} f_k(x, \Omega, \Omega') \right] \left[ \sqrt{\frac{2\pi}{\hbar}} f_{k'}(x, \Omega, \Omega') \right] \times \sum_K (2K + 1) \left\{ F \ J'' \ I'' \right\} \left( k \ k' \ K \right) \left( J \ J'' \ K \right) \Delta \Omega \ -\Delta \Omega \ 0 \ \left( \Omega \ -\Omega \ 0 \right) \times \left\{ k \ I \ I'' \right\} \left\{ i_x \ K \ i_x \right\} \left\{ k' \ i_x \ k \right\}
\]  

(A.62)

Similarly for the \( x \neq y \), the hyperfine predissociation matrix elements are,

\[
\Gamma_{kk'}(x, y) = \sum_{\Omega'} (-1)^{F+\Omega'+I'''} [(2I + 1)(2I'' + 1)(2J + 1)(2J'' + 1)]^{\frac{1}{2}} \times \zeta \ \epsilon_{ug} \left[ \sqrt{\frac{2\pi}{\hbar}} f_k(x, \Omega, \Omega') \right] \left[ \sqrt{\frac{2\pi}{\hbar}} f_{k'}(x, \Omega, \Omega') \right] \times (2K + 1) \left\{ F \ J'' \ I'' \right\} \left( k \ k' \ K \right) \left( J \ J'' \ K \right) \Delta \Omega \ -\Delta \Omega \ 0 \ \left( \Omega \ -\Omega \ 0 \right) \times \left\{ k \ I \ I'' \right\} \left\{ i_x \ K \ i_x \right\} \left\{ k' \ i_x \ k \right\}
\]  

(A.63)

Expressions A.62 and A.63 may be simplified by defining the quantities

\[
W(J, J'', I, I'') = \sqrt{(2J + 1)(2J'' + 1)(2I + 1)(2I'' + 1)}
\]  

(A.64)

and

\[
Z_{kk'}^{kk'}(J, J'', I, I'') = \left\{ F \ J'' \ I'' \right\} \left( k \ k' \ K \right) \left( J \ J'' \ K \right) \Delta \Omega \ -\Delta \Omega \ 0 \ \left( \Omega \ -\Omega \ 0 \right)
\]  

(A.65)
Specializing to the $B \, ^3\Pi_{0^+}$ predissociated by the $^1\Pi_{1u}$ electronic state one obtains

$$
\Gamma_{kk'}(x, x) = \frac{2\pi}{\hbar} \langle (J''I'')0_u^+ FM | P_{kk'}(x, x) | (JI)0_u^+ FM \rangle \\
= (-1)^{F+\Omega'+k+k'} W(J, J'', I, I'') \\
\times \left[ \sqrt{\frac{2\pi}{\hbar}} f_k(x, 0_u^+, 1u) \right] \left[ \sqrt{\frac{2\pi}{\hbar}} f_{k'}(x, 0_u^+, 1u) \right] \\
\times \sum_K (2K + 1) Z_{K'}^{kk'}(J, J'', I, I'') \left\{ \begin{array}{ccc} i_x & i_x & I \\
K & I'' & i_x \end{array} \right\} \left\{ \begin{array}{ccc} i_x & k & i_x \\
K & i_x & k' \end{array} \right\}
$$

(A.66)

$$
\Gamma_{kk'}(x, y) = \frac{2\pi}{\hbar} \langle (J''I'')0_u^+ FM | P_{kk'}(x, y) | (J'I')0_u^+ FM \rangle \\
= (-1)^{F+\Omega'+I''} W(J, J'', I, I'') \\
\times \left[ \sqrt{\frac{2\pi}{\hbar}} f_k(x, 0_u^+, 1u) \right] \left[ \sqrt{\frac{2\pi}{\hbar}} f_{k'}(x, 0_u^+, 1u) \right] \zeta \\
\times \sum_K (-1)^K (2K + 1) Z_{K'}^{kk'}(J, J'', I, I'') \left\{ \begin{array}{ccc} i_x & I & i_x \\
k & K & k' \end{array} \right\}
$$

(A.67)

(NOTE: The wavefunctions describing the molecular states are chosen so as to make $f_k(x, \Omega, \nu, \Omega', E')$ real.)

A.2 Gyroscopic Predissociation Rates

Now the calculation will be performed for the term $P_{GG}$ in Equation A.17.

The gyroscopic Hamiltonian,

$$
H_G = -\frac{\hbar^2}{\mu R^2} \mathbf{J} \cdot (\mathbf{L} + \mathbf{S})
$$

(A.68)

can couple different electronic states through the $J_\pm (L_\pm + S_\pm)$ terms. The matrix element of these terms between the $B \Omega = 0_u^+$ electronic state and a dissociative $\Omega' = 1u$ electronic state is given by [8]
Appendix A. Derivation of Predissociation Rates

\[ \langle \gamma (J'' I'') \rangle_{\Omega'' F M | \Omega' F M} \gamma (J' I') \Omega' E', F, M = (-1)^{J'' - \Omega' + 1} \sqrt{(2J'' + 1)J'' (J'' + 1)} \]

\[ \delta_{J'', J} \delta_{I'', I'} \left( \begin{array}{ccc} J'' & 1 & J'' \\ 0 & -1 & 1 \end{array} \right) \]

\[ \langle 0^+_v \mid \frac{\hbar^2}{\mu R^2} [T^1_{-\Delta \Omega}(L) + T^1_{-\Delta \Omega}(S)] \mid 1u E' \rangle \]

(A.69)

The equivalent operator, \( P_{\Omega, J'' I''} H_G P_{\Omega', E', J'} \), can be written:

\[ P_{\Omega, J'' I''} H_G P_{\Omega', E', J'} = V(\Omega, v, \Omega', E', J'') \Omega'' \Omega' T^0 \]

(A.70)

where

\[ V(\Omega, v, \Omega', E', J'') = (-1)^{J'' - \Omega' + 1} (2J'' + 1) \sqrt{J'' (J'' + 1)} \]

\[ \delta_{J'', J} \delta_{I'', I'} \left( \begin{array}{ccc} J'' & 1 & J'' \\ -\Omega & -\Delta \Omega & \Omega' \end{array} \right) \]

\[ \langle \Omega v \mid \frac{\hbar^2}{\mu R^2} [T^1_{-\Delta \Omega}(L) + T^1_{-\Delta \Omega}(S)] \mid \Omega' E' \rangle \]

(A.71)

The gyroscopic predissociation rate is easily evaluated as

\[ \Gamma_{GG} = \frac{2\pi}{\hbar} \left| \langle \gamma (J'' I'') \rangle_{\Omega'' F M | \Omega' F M} \gamma (J' I') \Omega', E', F, M \rangle \right|^2 \]

\[ = \frac{2\pi}{\hbar} (2J'' + 1) J'' (J'' + 1) \left( \begin{array}{ccc} J'' & 1 & J'' \\ 0 & -1 & 1 \end{array} \right)^2 \]

\[ \left| \langle 0^+_v \mid \frac{\hbar^2}{\mu R^2} [T^1_{-\Delta \Omega}(L) + T^1_{-\Delta \Omega}(S)] \mid 1u E' \rangle \right|^2 \]

(A.72)

For \( \Omega = 0 \) and \( \Omega = 1 \) the 3–j symbol reduces to

\[ \left( \begin{array}{ccc} J'' & 1 & J'' \\ 0 & -1 & 1 \end{array} \right)^2 = \frac{1}{2(2J'' + 1)} \]

(A.73)

Then,

\[ \Gamma_{GG} = \left[ \frac{\sqrt{\pi}}{\hbar} \langle 0^+_v \mid \frac{\hbar^2}{\mu R^2} [T^1_{-\Delta \Omega}(L) + T^1_{-\Delta \Omega}(S)] \mid 1u E' \rangle \right]^2 J'' (J'' + 1) \]

(A.74)
A.3 Hyperfine – Gyroscopic Interference terms

The gyroscopic–hyperfine interference terms in Equation A.18 can be readily derived from Equations A.70 and A.30

\[
P_{Gk}(x) = \sum_{J',J''} \left[ P_{\nu',J''} H G P_{\nu',J''} JP \right] \left[ P_{\nu',J''} J' P H^k(x) P_{\nu,J} \right]
\]

\[
= \left[ V(\Omega, \nu, \Omega', E', J'') \Omega J'' J_0 \right] \times \left[ w_k(x, \Omega', \Omega, E', \nu, J'', J, I', I) \sum_q (-1)^q \frac{\Omega J'' J_0}{J'' J_1} T_q^{J'' J_1} I'' U_{-q}^k \right]
\]

\[
= V(\Omega, \Omega') \cdot w_k(x, \Omega', \Omega) \sum_q (-1)^q \left( \frac{\Omega J'' J_0}{J'' J_1} T_q^{J'' J_1} \right) I'' U_{-q}^k \tag{A.75}
\]

From equation A.44 one has:

\[
\frac{\Omega J'' J_0}{J'' J_1} T_q^{J'' J_1} = \frac{(-1)^{J''} \Omega J'' J_0}{(2J'' + 1)} T_q^{J'' J_1} \tag{A.76}
\]

Then

\[
P_{Gk}(x) = (-1)^{J'' + 1 + 1} \frac{1}{(2J'' + 1)} \sqrt{\frac{2\pi}{h}} \left( \frac{j}{2k + 1} \right) \times \sqrt{\frac{1}{h} \left[ 0^+_V | 0^+ v | \frac{h}{\mu R^2} \left[ T_1^L \Delta \Omega (L) + T_1^S \Delta \Omega (S) \right] | 1 u E' \right]}
\]

\[
\times \left( \begin{array}{ccc} J'' & J'' & k \\ 0 & 1 & 1 \end{array} \right) \left( \begin{array}{ccc} J'' & J & 1 \\ 1 & 0 & -1 \end{array} \right) \left( \begin{array}{c} i_x \ i_z \ I'' \end{array} \right) \times \sum_q (-1)^q \frac{\Omega J'' J_0}{J'' J_1} T_q^{J'' J_1} I'' U_{-q}^k \tag{A.77}
\]

The matrix element of this operator can then be written:

\[
\Gamma_{Gk}(x) = \frac{2\pi}{h} \sum_{\Omega E', J', \Omega'} \langle \gamma(J'' I'') \Omega v FM \rangle \left[ P_{\nu', J''} H G P_{\nu', J''} J P \right] \left[ P_{\Omega E', J' P} H^k(x) P_{\nu,J} \right] \gamma(JI) \Omega v FM \tag{A.78}
\]
\[\Gamma_{Gk}(x) = (-1)^{F+J''+I+I''+2i_s+k+\Omega+1} \sqrt{(2J'' + 1)} \times \sqrt{J''(J''+1)(2I + 1)(2I'' + 1)} \times \frac{2\pi}{\hbar} f_k(x, \Omega, \Omega') \times \sqrt{2} \left[ \sqrt{\frac{\pi}{\hbar}} \left( 0^+ v \right) \frac{\hbar^2}{\mu R^2} \left[ T^1_{\Delta\Omega} (L) + T^1_{-\Delta\Omega} (S) \right] |1u E'| \right] \times \begin{pmatrix} J & J'' & k \\ 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} J'' & J'' & J'' \\ 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} i_s & i_s & I'' \\ k & I & i_s \end{pmatrix} \begin{pmatrix} F & J & I \\ k & I'' & J'' \end{pmatrix} \] (A.79)

To simplify the above equation, one can define the quantity

\[S^k(J'', J, I'', I) = \begin{pmatrix} J'' & 1 & J'' \\ -\Omega & -\Delta\Omega & \Omega' \end{pmatrix} \begin{pmatrix} J'' & k & J \\ \Omega' & \Delta\Omega & \Omega \end{pmatrix} \begin{pmatrix} F & J & I \\ k & I'' & J'' \end{pmatrix} \] (A.80)

This gives:

\[\Gamma_{Gk}(x) = (-1)^{F+J''+I+I''+2i_s+k+\Omega+1} \sqrt{J''(J''+1)(2J''+1)} W(J, J'', I, I'') \times \left[ \frac{2\pi}{\hbar} f_k(x, \Omega, \Omega') \right] \times \sqrt{2} \left[ \sqrt{\frac{\pi}{\hbar}} \left( 0^+ v \right) \frac{\hbar^2}{\mu R^2} \left[ T^1_{\Delta\Omega} (L) + T^1_{-\Delta\Omega} (S) \right] |1u E'| \right] \times S^k(J'', J, I'', I) \begin{pmatrix} i_s & i_s & I'' \\ k & I & i_s \end{pmatrix} \] (A.81)

### A.4 Putting it all Together

Now that the building blocks \(\Gamma_{GG}, \Gamma_{kk'}(xy), \Gamma_{Gk}(x)\) have been developed, one recalls that the predissociation rate of a hyperfine level, \(|F\epsilon M\rangle\), is given by,

\[\Gamma_p = \sum_{J'I''I''} \alpha_{J''J''}^{F} \alpha_{J'k}^{F} \left[ \Gamma_{GG} + \sum_{k'y} \Gamma_{k'y}(y) + \sum_{kx} \Gamma_{kx}(x) + \sum_{kx k'y} \Gamma_{kk'}(x, y) \right] \] (A.82)
Appendix A. Derivation of Predissociation Rates

The predissociation terms, $\Gamma_{GG}$, $\Gamma_{kk'}(xy)$, and $\Gamma_{Gk}(x)$, can be written as the product of a molecular parameter to be experimentally determined and calculable rotational and nuclear factors. For predissociation between the $B^3\Pi_{0^+}$ ($\Omega = 0^+_u$) electronic state and the dissociative $^1\Pi_{1u}$ ($\Omega = 1u$) state the molecular parameters are defined here as,

$$C_\nu = \sqrt{\frac{\pi}{\hbar^2}} (0^+_u v) \frac{\hbar^2}{\mu R^2} \left[ T^1_{-\Delta\Omega}(L) + T^1_{-\Delta\Omega}(S) \right] |1u E'\rangle \quad (A.83)$$

$$a_\nu(x) = \sqrt{\frac{2\pi}{\hbar}} f_1(x, 0^+_u, v, 1u, E')/\left[i_x(i_x + 1)(2i_x + 1)\right]^{1/2} \quad (A.84)$$

$$b_\nu(x) = \sqrt{\frac{2\pi}{\hbar}} f_2(x, 0^+_u, v, 1u, E') \left[ \frac{2i_x(2i_x - 1)}{(2i_x + 1)(2i_x + 2)(2i_x + 3)} \right]^{1/2} \quad (A.85)$$

Here $C_\nu$ is the gyroscopic predissociation parameter, $a_\nu$ is the hyperfine magnetic dipole ($k = 1$) predissociation parameter, and $b_\nu$ is the hyperfine electric quadrupole ($k = 2$) predissociation parameter – a new molecular parameter introduced here. By including the sums over the coefficients, $\alpha_{j,k}$, in the rotational and nuclear factors, $R_{GG}$, $R_{Gk}(x)$, and $R_{kk'}(xy)$, one can rewrite the predissociation rate as,

$$\Gamma_p(F_{ev}) = C_\nu^2 R_{GG} + \sum_x \sqrt{2} C_\nu a_\nu(x) R_{G1}(x) + \sum_x \sqrt{2} C_\nu a_\nu(x) R_{1G}(x)$$

$$+ \sum_x \sqrt{2} C_\nu b_\nu(x) R_{G2}(x) + \sum_x \sqrt{2} C_\nu b_\nu(x) R_{2G}(x)$$

$$+ \sum_{xy} a_\nu(x) b_\nu(y) R_{12}(x, y) + \sum_{xy} b_\nu(x) a_\nu(y) R_{21}(x, y)$$

$$+ \sum_{xy} a_\nu(x) a_\nu(y) R_{11}(x, y) + \sum_{xy} b_\nu(x) b_\nu(y) R_{22}(x, y) \quad (A.86)$$

By inspection, the expressions for the rotational and nuclear factors can be deduced.

$$R_{GG} = J(J + 1) \quad (A.87)$$
Appendix A. Derivation of Predissociation Rates

\[ R_{Gk}(x) = \sum_{J^{''}J''I''} \sum_{J I} \alpha_{J''I''}^{F} \alpha_{J I}^{F} (-1)^{F+J''+I''+2i_{x}+k+\Omega+1} \times \sqrt{J''(J''+1)(2J''+1)} W(J, J'', I, I'') \times X_k(i_{x}) S^k(J'', J, I'', I) \left\{ \begin{array}{c} i_{x} \quad i_{x} \quad I'' \\ k \quad I \quad i_{z} \end{array} \right\} \] (A.88)

\[ R_{kk'}(x, x) = \sum_{J^{''}J''I''} \sum_{J I} \alpha_{J''I''}^{F} \alpha_{J I}^{F} (-1)^{F+\Omega'+k+k'} W(J, J'', I, I'') X_k(i_{x}) X_{k'}(i_{x}) \times \sum_{K} (2K+1) Z^k_{K'}(J, J'', I, I'') \left\{ \begin{array}{c} i_{x} \quad i_{x} \quad I \\ K \quad I'' \quad i_{z} \end{array} \right\} \left\{ \begin{array}{c} i_{x} \quad k \quad i_{z} \\ K \quad i_{z} \quad k' \end{array} \right\} \] (A.89)

\[ R_{kk'}(x, y) = \sum_{J^{''}J''I''} \sum_{J I} \alpha_{J''I''}^{F} \alpha_{J I}^{F} (-1)^{F+\Omega'+I''} W(J, J'', I, I'') X_k(i_{x}) X_{k'}(i_{x}) \times \sum_{K} (-1)^{K} (2K+1) Z^{kk'}_{K}(J, J'', I, I'') \left\{ \begin{array}{c} i_{x} \quad I \quad i_{x} \\ k \quad K \quad k' \end{array} \right\} \] (A.90)

Here

\[ X_1(i_{x}) = \sqrt{i_{x}(i_{x}+1)(2i_{x}+1)} \] (A.91)

\[ X_2(i_{x}) = \left[ \frac{(2i_{x}+3)(2i_{x}+2)(2i_{x}+1)}{2i_{x}(2i_{x}-1)} \right]^{\frac{1}{2}} \] (A.92)

The rotational and nuclear terms in Equations A.88, A.89, and A.90 have the following symmetry properties:

1. \( R_{Gk}(x) = R_{kG}(x) \).
2. \( R_{Gk}(x) = R_{Gk}(y) \).
3. \( R_{kk'}(x, x) = R_{kk'}(x, x) \).
4. \( R_{kk'}(x, y) = R_{kk'}(y, x) \).
These simplify Equation A.86 to:

\[ \Gamma_p(Fe\nu) = C^2 R_{GG} + 2\sqrt{2} C_{\nu} [a_{\nu}(1) + a_{\nu}(2)] R_{G1}(1) \]
\[ + 2\sqrt{2} C_{\nu} [b_{\nu}(1) + b_{\nu}(2)] R_{G2}(1) \]
\[ + \left[a_{\nu}^2(1) + a_{\nu}^2(2)\right] R_{11}(1,1) + 2a_{\nu}(1)a_{\nu}(2)R_{11}(1,2) \]
\[ + 2\left[a_{\nu}(1)b_{\nu}(1) + a_{\nu}(2)b_{\nu}(2)\right] R_{12}(1,1) \]
\[ + \left[a_{\nu}(1)b_{\nu}(2) + a_{\nu}(2)b_{\nu}(1)\right] [R_{12}(1,2) + R_{21}(1,2)] \]
\[ + \left[b_{\nu}^2(1) + b_{\nu}^2(2)\right] R_{22}(1,1) + 2b_{\nu}(1)b_{\nu}(2)R_{22}(1,2) \]  (A.93)

The coefficients \( R_{12}(1,2) \) and \( R_{21}(1,2) \) are completely negligible for the states of interest in this work. Therefore the predissociation rate for \( ^{79}\text{Br}^{81}\text{Br} \) can be written:

\[ \Gamma_p(Fe\nu) = C^2 R_{GG} + 2\sqrt{2} C_{\nu} [a_{\nu}(1) + a_{\nu}(2)] R_{G1}(1) \]
\[ + 2\sqrt{2} C_{\nu} [b_{\nu}(1) + b_{\nu}(2)] R_{G2}(1) \]
\[ + \left[a_{\nu}^2(1) + a_{\nu}^2(2)\right] R_{11}(1,1) + 2a_{\nu}(1)a_{\nu}(2)R_{11}(1,2) \]
\[ + 2\left[a_{\nu}(1)b_{\nu}(1) + a_{\nu}(2)b_{\nu}(2)\right] R_{12}(1,1) \]
\[ + \left[b_{\nu}^2(1) + b_{\nu}^2(2)\right] R_{22}(1,1) + 2b_{\nu}(1)b_{\nu}(2)R_{22}(1,2) \]  (A.94)

For the homonuclear molecules, \(^{79}\text{Br}_2 \) and \(^{81}\text{Br}_2 \), where \( a_{\nu}(1) = a_{\nu}(2) \) and \( b_{\nu}(1) = b_{\nu}(2) \), the predissociation rate is:

\[ \Gamma_p(Fe\nu) = C^2 R_{GG} + 4\sqrt{2} C_{\nu} a_{\nu} R_{G1}(1) + 4\sqrt{2} C_{\nu} b_{\nu} R_{G2}(1) \]
\[ + 2a_{\nu}^2 [R_{11}(1,1) + R_{11}(1,2)] \]
\[ + 4a_{\nu} b_{\nu} R_{12}(1,1) + 2b_{\nu}^2 [R_{22}(1,1) + R_{22}(1,2)] \]  (A.95)
Appendix B

Hyperfine Data

The study of the hyperfine structure of the $B^3\Pi_{0^+}$ and $X^1\Sigma^+$ electronic states involved recording, for each isotopomer of bromine, the hyperfine spectra of the following rovibronic transitions: (a) for the $(13'-0'')$ band, $P(1)$ through $P(5)$, $R(0)$ through $R(3)$ and $R(10)$; (b) for the $(17'-2'')$ band, $R(0)$ through $R(10)$ except $R(9)$ and $P(1)$ through $P(7)$ except $P(6)$. In addition, for $^{79}\text{Br}^{81}\text{Br}$, the hyperfine spectra were measured of $R(0)$ through $R(2)$ and $P(1)$ for the $(11'-0'')$, $(12'-0'')$, $(14'-1'')$, $(15'-1''')$, and $(16'-1''')$ vibrational bands. Each transition was measured at least three and usually four times producing 379 data sets with a total of over 3000 hyperfine transitions for the three isotopomers of bromine. As mentioned in Chapter 5, only the relative separations of the rovibronic hyperfine spectral features observed were recorded. Each data set was analyzed separately for the parameters $eqQ_B$, $eqQ_X$, and $\delta$, an arbitrary frequency scale offset. The unblended features were chosen, weighted by their relative heights, and then the observed frequencies were subjected to a nonlinear least squares fit. Each data set provided associated fit parameters and a reduced chi-squared value,

$$\chi^2 = \sum_{\text{data}} \frac{|\nu_{\text{obs}} - \nu_{\text{calc}}|^2}{(\sigma_{\text{obs}})(N - n)} \quad (B.1)$$

Here $\nu_{\text{obs}}$ is the observed frequency of a given hyperfine transition, $\nu_{\text{calc}}$ is the calculated hyperfine transition frequency, $\sigma_{\text{obs}}$ is the uncertainty of the observed frequency, $N$ is the total number of transitions included in the fit, and $n$ is the number of parameters varied. Ideally the reduced chi-squared value should be $\leq 1.0$. The final values for the electric quadrupole coupling constants, $eqQ$, for a given electronic and vibrational state were
deduced by averaging the values from the appropriate data sets weighted by the reduced chi-squared value.

Owing to the very large number of transitions recorded it is not practical to tabulate the (observed – calculated) frequency differences for all of the transitions. Instead the observed and calculated frequencies of the B–X (17' – 2") P(1) hyperfine data sets for each isotopomer are given in tables B.1 through B.6. These results are typical of the measurements with the exception of the (13' – 0") band which had slightly higher uncertainties. The (17' – 2") band results are summarized in Tables B.7 through B.9, which give the reader a feeling for the variation of the observed transition frequencies along with the (observed – calculated) residuals. Finally, Tables B.10 to B.12 summarize the (13' – 0") P(2) hyperfine results for each isotopomer to demonstrate the slightly higher uncertainty associated with this band. (The values and uncertainties quoted for the observed data in the tables labelled AVERAGES are the averages and standard deviations of the frequencies of the individual the data sets.)

In the tables in this appendix, the X and B hyperfine states are labelled both by J' and F'. For many of the rotational levels several hyperfine states with the same value of F' exist. These are distinguished with the further label a, b, c, and so on in order of ascending energy. (e.g. J' = 4, F' = 6a labels the lowest energy hyperfine level for the J' = 4 rotational state having F' = 6.)
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Table B.1: The \(^{79}\text{Br}_2\) (17' – 2") P(1) observed and calculated hyperfine transition frequencies for separated data sets (part I).
### Table B.2: The $^{79}\text{Br}_2$ (17$'$ − 2$''$) P(1) observed and calculated hyperfine transition frequencies for separated data sets (part II).

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Table B.3: The $^{79}\text{Br}_2 (17' - 2'') \text{ P}(1)$ observed and calculated hyperfine transition frequencies for separated data sets (part III).
### Table B.4: \( ^{81}\text{Br}_2 \) (17' - 2'') P(1) observed and calculated hyperfine transition frequencies for separated data sets (part I).

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Table B.5: The $^{81}$Br$_2$ (17' - 2'') P(1) observed and calculated hyperfine transition frequencies for separated data sets (part II).
### Appendix B. Hyperfine Data

**Isotopomer:** $^{79,81}\text{Br}_2$

**Band:** $(17' - 2'')$

**Line:** $P(1)$

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Table B.6: The $^{79}\text{Br}^{81}\text{Br} (17' - 2'') P(1)$ observed and calculated hyperfine transition frequencies for separated data sets.
### Appendix B. Hyperfine Data

#### Table B.7: A summary of the $^{79}$Br$_2$ (17' - 2") P(1) data results. The root mean square (rms) of the differences (obs - calc) is 0.56 MHz.

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<th>Line: P(1)</th>
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<td>$\nu_{\text{calc}}$ (MHz)</td>
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#### Table B.8: A summary of the $^{81}$Br$_2$ (17' - 2") P(1) data results. The (obs - calc) rms is 0.98 MHz.

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<td>-296.76 ± 1.94</td>
<td>-296.23</td>
</tr>
<tr>
<td>1a</td>
<td>0,2</td>
<td>-235.46 ± 0.96</td>
<td>-235.07</td>
</tr>
<tr>
<td>3b</td>
<td>3</td>
<td>-222.81 ± 1.14</td>
<td>-222.80</td>
</tr>
<tr>
<td>2a</td>
<td>1,2,3</td>
<td>-122.79 ± 1.61</td>
<td>-124.24</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>76.34 ± 0.53</td>
<td>77.06</td>
</tr>
<tr>
<td>1b</td>
<td>1</td>
<td>147.10 ± 1.07</td>
<td>148.22</td>
</tr>
<tr>
<td>1c</td>
<td>0,1,2</td>
<td>238.56 ± 0.67</td>
<td>238.61</td>
</tr>
<tr>
<td>2c</td>
<td>1,3</td>
<td>273.46 ± 0.80</td>
<td>273.23</td>
</tr>
</tbody>
</table>

Table B.9: A summary of the $^{79}$Br$^{81}$Br (17' – 2") P(1) data results. The (obs – calc) rms is 0.74 MHz.
Table B.10: A summary of the $^{79}\text{Br}_2$ (13' - 0'') P(2) data results. The (obs − calc) rms is 1.17 MHz.

<table>
<thead>
<tr>
<th>F''</th>
<th>F'</th>
<th>$\nu_{\text{obs}}$ (MHz)</th>
<th>$\nu_{\text{calc}}$ (MHz)</th>
<th>obs − calc (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1b</td>
<td>$-(271.94 \pm 1.59)$</td>
<td>$-272.46$</td>
<td>0.51</td>
</tr>
<tr>
<td>2a</td>
<td>2</td>
<td>$-(215.09 \pm 0.66)$</td>
<td>$-215.95$</td>
<td>0.86</td>
</tr>
<tr>
<td>2a</td>
<td>1a</td>
<td>$-(158.97 \pm 0.68)$</td>
<td>$-159.69$</td>
<td>0.85</td>
</tr>
<tr>
<td>0</td>
<td>1b</td>
<td>$-(65.89 \pm 1.66)$</td>
<td>$-67.64$</td>
<td>1.75</td>
</tr>
<tr>
<td>1</td>
<td>1b</td>
<td>$-(54.49 \pm 1.43)$</td>
<td>$-56.57$</td>
<td>2.08</td>
</tr>
<tr>
<td>0</td>
<td>1a</td>
<td>$(44.28 \pm 0.96)$</td>
<td>$45.00$</td>
<td>$-0.72$</td>
</tr>
<tr>
<td>1</td>
<td>1a</td>
<td>$(55.26 \pm 0.87)$</td>
<td>$56.07$</td>
<td>$-0.82$</td>
</tr>
<tr>
<td>2b</td>
<td>1b</td>
<td>$(157.76 \pm 0.58)$</td>
<td>$159.55$</td>
<td>$-1.79$</td>
</tr>
<tr>
<td>2b</td>
<td>2</td>
<td>$(215.76 \pm 1.43)$</td>
<td>$216.05$</td>
<td>$-0.29$</td>
</tr>
<tr>
<td>2b</td>
<td>1a</td>
<td>$(271.84 \pm 4.28)$</td>
<td>$272.19$</td>
<td>$-0.36$</td>
</tr>
</tbody>
</table>
### Appendix B. Hyperfine Data

#### Table B.11: A summary of the $^{81}\text{Br}_2$ (13' - 0') P(2) data results. The (obs - calc) rms is 1.20 MHz.

<table>
<thead>
<tr>
<th>Isotopomer: $^{81}\text{Br}_2$</th>
<th>Band: (13' - 0') AVERAGES</th>
<th>Line: P(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F''</td>
<td>F'</td>
<td>$\nu_{\text{obs}}$ (MHz)</td>
</tr>
<tr>
<td>2a</td>
<td>1b</td>
<td>(226.48 ± 5.98)</td>
</tr>
<tr>
<td>2a</td>
<td>2</td>
<td>(180.31 ± 1.19)</td>
</tr>
<tr>
<td>2a</td>
<td>1a</td>
<td>(133.16 ± 1.14)</td>
</tr>
<tr>
<td>0</td>
<td>1b</td>
<td>(54.16 ± 2.36)</td>
</tr>
<tr>
<td>1</td>
<td>1b</td>
<td>(45.76 ± 2.50)</td>
</tr>
<tr>
<td>0</td>
<td>1a</td>
<td>(39.62 ± 1.34)</td>
</tr>
<tr>
<td>1</td>
<td>1a</td>
<td>(46.99 ± 1.16)</td>
</tr>
<tr>
<td>2b</td>
<td>1b</td>
<td>(132.39 ± 0.79)</td>
</tr>
<tr>
<td>2b</td>
<td>2</td>
<td>(179.39 ± 0.33)</td>
</tr>
<tr>
<td>2b</td>
<td>1a</td>
<td>(224.94 ± 1.85)</td>
</tr>
</tbody>
</table>
### Appendix B. Hyperfine Data

#### Table B.12: A summary of the $^{79,81}$Br$_2$ (13' - 0'') P(2) data results. The (obs - calc) rms is 1.26 MHz.

<table>
<thead>
<tr>
<th>Isotopomer: $^{79,81}$Br$_2$</th>
<th>Band: (13' - 0'') AVERAGES</th>
<th>Line: P(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F''$</td>
<td>$F'$</td>
<td>$\nu_{\text{obs}}$ (MHz)</td>
</tr>
<tr>
<td>2a</td>
<td>1c</td>
<td>-(253.26 ± 3.06)</td>
</tr>
<tr>
<td>3c</td>
<td>4</td>
<td>-(231.11 ± 1.40)</td>
</tr>
<tr>
<td>2a</td>
<td>2b</td>
<td>-(200.86 ± 1.94)</td>
</tr>
<tr>
<td>3c</td>
<td>2a</td>
<td>-(187.71 ± 1.60)</td>
</tr>
<tr>
<td>4b</td>
<td>4</td>
<td>-(176.53 ± 1.30)</td>
</tr>
<tr>
<td>3c</td>
<td>3b</td>
<td>-(164.53 ± 1.16)</td>
</tr>
<tr>
<td>2a</td>
<td>1a</td>
<td>-(147.66 ± 1.39)</td>
</tr>
<tr>
<td>4b</td>
<td>3b</td>
<td>-(109.38 ± 1.34)</td>
</tr>
<tr>
<td>1a</td>
<td>0</td>
<td>-(91.00 ± 0.98)</td>
</tr>
<tr>
<td>1b</td>
<td>1c</td>
<td>-(52.10 ± 1.38)</td>
</tr>
<tr>
<td>2d</td>
<td>1b</td>
<td>-(32.40 ± 0.88)</td>
</tr>
<tr>
<td>2d</td>
<td>2a</td>
<td>(27.64 ± 0.56)</td>
</tr>
<tr>
<td>3a</td>
<td>2a</td>
<td>(78.82 ± 1.36)</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>(92.30 ± 1.48)</td>
</tr>
<tr>
<td>3a</td>
<td>3b</td>
<td>(100.35 ± 0.76)</td>
</tr>
<tr>
<td>2c</td>
<td>2c</td>
<td>(132.05 ± 0.98)</td>
</tr>
<tr>
<td>2c</td>
<td>1c</td>
<td>(139.70 ± 1.00)</td>
</tr>
<tr>
<td>2b</td>
<td>1c</td>
<td>(169.35 ± 1.69)</td>
</tr>
<tr>
<td>1c</td>
<td>2c</td>
<td>(198.70 ± 2.43)</td>
</tr>
<tr>
<td>2b</td>
<td>2b</td>
<td>(220.22 ± 2.62)</td>
</tr>
<tr>
<td>2b</td>
<td>3b</td>
<td>(270.82 ± 1.67)</td>
</tr>
<tr>
<td>1c</td>
<td>2a</td>
<td>(286.02 ± 0.86)</td>
</tr>
</tbody>
</table>
Appendix C

Phase Shift Data

This appendix contains all the lifetime data used in the analysis of the natural predisso-
ociation of the $B \, ^3Π_{0^+}$ state of bromine.

The phase shift method was applied to the hyperfine spectra of the $B–X \, (13'–0'')$
$P(1)$ through $P(9)$ transitions (excluding the $P(3)$) of $79\text{Br}_2$ and $81\text{Br}_2$ and to the $P(1)$
through $P(7)$ and $R(9)$ transitions of $79\text{Br} \, 81\text{Br}$ . A sample calculation of the lifetime of
the $79\text{Br}_2 \, P(2) \, F'=1_-$ hyperfine level is given below.

The calculated hyperfine spectrum of the $P(2)$ transition is given in Figure C.1. The
$F''=2_- \rightarrow F'=1_-$ transition is indicated by the letter A in the figure. The amplitude
of the laser radiation was modulated at a frequency, $f$, and the in-phase (IP) and in-
quadrature (IQ) signals from a lock-in amplifier were recorded as the wavelength of the
laser beam was varied. The phase setting on the lock-in amplifier, $ϕ_{\text{LIA}}$, was chosen
so as to make IP and IQ almost equal for most of the hyperfine peaks. The reference
phase, $ϕ_{\text{ref}}$ was determined from the scattered laser light signal. The data for the lifetime
measurements of the $B \, ^3Π_{0^+} \, v'=13, \, J'=1, \, F'=1_-$ level for $79\text{Br}_2$ are shown in
Tables C.1 to C.3. The phase shift of the observed signal is deduced from,

$$\phi = [ϕ_{\text{LIA}} + \arctan\left(\frac{\text{IQ}}{\text{IP}}\right)] - ϕ_{\text{ref}} \quad \text{(C.1)}$$

and

$$τ = -\frac{\tan ϕ}{2πf} \quad \text{or} \quad \frac{-\tan ϕ}{Ω} \quad \text{(C.2)}$$

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Figure C.1: A simulated hyperfine absorption spectrum for $^{79}$Br$_2$ B–X (13' – 0") P(2) transition. The peak labelled A has the F' = 1_ level as its upper state.
Appendix C. Phase Shift Data

For example from the second entry in Table C.1, $\phi_{\text{ref}} = 60.7^\circ$, $\phi_{\text{LIA}} = 70.00^\circ$, and the observed IQ/IP phase is $46.36^\circ$. Therefore,

$$\phi = [70.00 - 46.36] - 60.70$$

$$= -37.06^\circ$$

yielding,

$$\tau = -\frac{\tan(-37.06^\circ)}{2\pi(18.48)(10^3s^{-1})}$$

$$= 6.503 \times 10^{-6}s$$

For each hyperfine spectrum studied the measurements were repeated for at least 2 and usually 3 different modulation frequencies providing a test of the consistency of the data. The variation from modulation frequency to modulation frequency seen for the data shown in Tables C.1, C.2, and C.3 was typical. The average lifetime for this level was $(6.313 \pm 0.343)\mu s$.

Of the nearly 200 hyperfine transitions studied for the different isotopomers, 73 were chosen as suitable for analysis because they had a signal to noise ratio of 10 or better and were not blended with other transitions. (Equation 6.16 does not hold for blended lines.)

The coefficients, $R_{kk'}(x,y)$, used in Equations 6.44 and 6.45 for the calculation of the theoretical decay rates, $\Gamma$, for each isotopomer are given in Tables C.4 through C.7. For the homonuclear species the use of the tables is straightforward. For example, the expression for the decay rate of the $J' = 0$, $F' = 0$ hyperfine level may be read directly from the first line of table C.4 as,

$$\Gamma(F' = 0) = 0.0C_v^2 + 0.0003\sqrt{2}C_v a_v(79) + 0.6642a_v^2(79)$$

$$+0.0402\left[\sqrt{2}C_v + a_v(79)\right]b_v(79) + 2.4b_v^2(79) \quad \text{(C.3)}$$
Appendix C. Phase Shift Data

<table>
<thead>
<tr>
<th>f = 18.48 kHz</th>
<th>( \phi_{\text{ref}} = 60.7^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi_{\text{LIA}} ) (degrees)</td>
<td>-arctan(IQ/IP) (degrees)</td>
</tr>
<tr>
<td>60.7</td>
<td>35.47</td>
</tr>
<tr>
<td>70.0</td>
<td>46.36</td>
</tr>
<tr>
<td></td>
<td>46.56</td>
</tr>
<tr>
<td></td>
<td>45.54</td>
</tr>
<tr>
<td></td>
<td>48.13</td>
</tr>
<tr>
<td></td>
<td>45.84</td>
</tr>
<tr>
<td></td>
<td>43.92</td>
</tr>
<tr>
<td></td>
<td>45.55</td>
</tr>
<tr>
<td></td>
<td>46.13</td>
</tr>
</tbody>
</table>

Average (6.392 ± 0.276)

Table C.1: The deduced lifetimes of the \( v' = 13, J' = 1, F' = 1 \) hyperfine state using a modulation frequency of 18.48 kHz.

For \(^{79}\text{Br}^{81}\text{Br}\), the coefficients are split up into Tables C.6 and C.7. These tables for \(^{79}\text{Br}^{81}\text{Br}\) are used in exactly the same manner as the homonuclear tables except for new the labels,

\[
B^+ = b_\nu(79) + b_\nu(81) \quad \text{(C.4)}
\]

\[
AB^+ = [a_\nu(79)b_\nu(79) + a_\nu(81)b_\nu(81)] \quad \text{(C.5)}
\]

in Table C.7. The decay rate for one of the heteronuclear levels \((J', F')\) is given by the sum of all of the entries in Tables C.6 and C.7. For example, for the \( J' = 0, F' = 1 \) level one has
Appendix C. Phase Shift Data

Table C.2: The deduced lifetimes of the $v' = 13$, $J' = 1$, $F' = 1_-$ hyperfine state using a modulation frequency of 25.49 kHz.

<table>
<thead>
<tr>
<th>$\phi_{\text{LIA}}$ (degrees)</th>
<th>$-\arctan(IQ/IP)$ (degrees)</th>
<th>$-\phi$ (degrees)</th>
<th>$\tau$ (\mu s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.0</td>
<td>46.48</td>
<td>46.28</td>
<td>6.530</td>
</tr>
<tr>
<td></td>
<td>43.84</td>
<td>43.64</td>
<td>5.955</td>
</tr>
<tr>
<td></td>
<td>45.00</td>
<td>44.80</td>
<td>6.200</td>
</tr>
<tr>
<td></td>
<td>47.16</td>
<td>46.96</td>
<td>6.687</td>
</tr>
<tr>
<td></td>
<td>47.04</td>
<td>46.84</td>
<td>6.660</td>
</tr>
<tr>
<td></td>
<td>43.14</td>
<td>42.94</td>
<td>5.809</td>
</tr>
<tr>
<td></td>
<td>47.81</td>
<td>47.81</td>
<td>6.888</td>
</tr>
<tr>
<td></td>
<td>47.54</td>
<td>47.54</td>
<td>6.823</td>
</tr>
<tr>
<td></td>
<td>46.31</td>
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<td>6.537</td>
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<td>43.90</td>
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</tr>
<tr>
<td></td>
<td>47.54</td>
<td>47.54</td>
<td>6.823</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td><strong>(6.447 \pm 0.387)</strong></td>
</tr>
</tbody>
</table>

$f = 25.49$ kHz, $\phi_{\text{ref}} = 49.8^\circ$
Table C.3: The deduced lifetimes of the $v' = 13, J' = 1, F' = 1_-$ hyperfine state using a modulation frequency of 35.97 kHz.
### Table C.4: Coefficients, $R_{kk'}(x, y)$ for calculating of $\Gamma$ for $^{79}$Br$_2$.

<table>
<thead>
<tr>
<th>$J'$</th>
<th>$F'$</th>
<th>$C_v^2$</th>
<th>$\sqrt{2}C_v a_v(79)$</th>
<th>$a_v^2(79)$</th>
<th>$[\sqrt{2}C_v + a_v(79)] b_v(79)$</th>
<th>$b_v^2(79)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0.0</td>
<td>0.0003</td>
<td>0.6642</td>
<td>0.0402</td>
<td>2.4000</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0</td>
<td>0.0001</td>
<td>4.0231</td>
<td>0.0402</td>
<td>2.4000</td>
</tr>
<tr>
<td>1</td>
<td>1_</td>
<td>2.0</td>
<td>1.5018</td>
<td>1.3505</td>
<td>-2.1788</td>
<td>2.6027</td>
</tr>
<tr>
<td></td>
<td>1+</td>
<td>2.0</td>
<td>1.4983</td>
<td>1.3495</td>
<td>2.2029</td>
<td>2.5972</td>
</tr>
<tr>
<td>3</td>
<td>3_</td>
<td>12.0</td>
<td>1.4972</td>
<td>0.8164</td>
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<td>2.0721</td>
</tr>
<tr>
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<td>3+</td>
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<td>1.5029</td>
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</tr>
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<td>6</td>
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<td>-5.0000</td>
<td>3.3230</td>
<td>-0.9373</td>
<td>2.8964</td>
</tr>
<tr>
<td></td>
<td>7</td>
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<td>-12.0000</td>
<td>4.9125</td>
<td>1.2679</td>
<td>2.2094</td>
</tr>
<tr>
<td>5</td>
<td>5_</td>
<td>30.0</td>
<td>1.4971</td>
<td>0.7747</td>
<td>-1.7541</td>
<td>2.0303</td>
</tr>
<tr>
<td></td>
<td>5+</td>
<td>30.0</td>
<td>1.5030</td>
<td>0.7766</td>
<td>1.7541</td>
<td>2.0210</td>
</tr>
<tr>
<td>6</td>
<td>6a</td>
<td>42.0</td>
<td>1.5624</td>
<td>0.8012</td>
<td>1.7490</td>
<td>2.0199</td>
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<tr>
<td></td>
<td>7b</td>
<td>42.0</td>
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<td>-2.0346</td>
<td>1.7733</td>
</tr>
<tr>
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<td>8</td>
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<td>3.5035</td>
<td>-0.6874</td>
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</tr>
<tr>
<td></td>
<td>9</td>
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<td>-18.0000</td>
<td>5.0022</td>
<td>1.3914</td>
<td>2.1645</td>
</tr>
<tr>
<td>7</td>
<td>7_</td>
<td>56.0</td>
<td>1.4970</td>
<td>0.7623</td>
<td>-1.7437</td>
<td>2.0179</td>
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<tr>
<td></td>
<td>7+</td>
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<tr>
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<td>10</td>
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<td>-13.0000</td>
<td>3.6079</td>
<td>-0.5427</td>
<td>2.9629</td>
</tr>
<tr>
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<td>11</td>
<td>72.0</td>
<td>-24.0000</td>
<td>5.0543</td>
<td>1.4630</td>
<td>2.1352</td>
</tr>
</tbody>
</table>
# Appendix C. Phase Shift Data

<table>
<thead>
<tr>
<th>( J' )</th>
<th>( F' )</th>
<th>( C_\nu^2 )</th>
<th>( \sqrt{2}C_\nu a_\nu(81) )</th>
<th>( a_\nu^2(81) )</th>
<th>( [\sqrt{2}C_\nu + a_\nu(81)] b_\nu(81) )</th>
<th>( b_\nu^2(81) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0.0</td>
<td>0.0002</td>
<td>0.6646</td>
<td>0.0340</td>
<td>2.4000</td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>0.0001</td>
<td>4.0196</td>
<td>0.0340</td>
<td>2.4000</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1−</td>
<td>2.0</td>
<td>1.5018</td>
<td>1.3505</td>
<td>−2.1788</td>
<td>2.6027</td>
</tr>
<tr>
<td>1+</td>
<td>2.0</td>
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Table C.5: Coefficients \( R_{kk}(x, y) \) for calculating \( \Gamma \) for \( ^{81}\text{Br}_2 \).
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Table C.6: Coefficients $R_{kk'}(x, y)$ for calculating of $\Gamma$ for $^{79}$Br-$^{81}$Br (part I).
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Table C.7: Coefficients $R_{kk'}(x, y)$ for calculating $\Gamma$ for $^{79}$Br$^{81}$Br (part II).
\[ \Gamma(F' = 0) = 0.0C_{\nu}^2 + 0.0001\sqrt{2}C_{\nu}[a_{\nu}(79) + a_{\nu}(81)] \\
+ 1.2550 \left[a_{\nu}^2(79) + a_{\nu}^2(81)\right] - 1.8463a_{\nu}(79)a_{\nu}(81) \\
+ 0.0198\sqrt{2}C_{\nu}[b_{\nu}(79) + b_{\nu}(81)] + 0.0174[a_{\nu}(79)b_{\nu}(79) + a_{\nu}(81)b_{\nu}(81)] \\
+ 1.000 \left[b_{\nu}^2(79) + b_{\nu}^2(81)\right] + 0.4000b_{\nu}(79)b_{\nu}(81) \]  

(C.6)

These expressions were fit to the observed decay rates for the parameters described in Chapter 6.

The observed and calculated inverse lifetimes (decay rates) are given in Tables C.8 to C.10 along with the differences, (obs-calc). The calculated values were obtained from a global fit of the data to a six parameter model described in Chapter 6. The parameters were,

\[ \Gamma_{\text{rad}} \]  

(C.7)

\[ B_1 = \frac{C_{\nu}}{\mu(79, 79)}\sigma(79, 79) \]  

(C.8)

\[ B_2 = g(79)a_0^0\sigma(79, 79) \]  

(C.9)

\[ B_3 = Q(79)b_0^0\sigma(79, 79) \]  

(C.10)

\[ B_4 = \sigma(81, 81)/\sigma(79, 79) \]  

(C.11)

\[ B_5 = \sigma(79, 81)/\sigma(79, 79) \]  

(C.12)

The hyperfine states are labelled both by \( J' \) and \( F' \). For many of the rotational levels several hyperfine states with the same value of \( F' \) exist. These are distinguished with the further label \( a, b, c \), and so on in order of ascending energy. (e.g. \( J' = 4, F' = 6a \) is the lowest energy hyperfine level for the \( J' = 4 \) rotational state having \( F' = 6 \).) As can be seen, the agreement between the observed and calculated values is excellent.

For the readers convenience, the lifetimes of the states, \( \tau \), derived from \( 1/\Gamma \), are listed in Tables C.11 through C.13.
### Table C.8: The observed and calculated inverse lifetimes, $\Gamma$, for $^{79}$Br$_2$. The uncertainties in the observed decay rates are the standard deviations of the data.

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<th>$\Gamma_{\text{calc}}$ (10$^5$s$^{-1}$)</th>
<th>(obs - calc) (10$^5$s$^{-1}$)</th>
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<td>3 _</td>
<td>3.295 ± 0.065</td>
<td>3.154</td>
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<td>9</td>
<td>1 _</td>
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<td>8</td>
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<td>4.570 ± 0.142</td>
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<td>0.135</td>
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<tr>
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<td>2.460 ± 0.221</td>
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Table C.9: The observed and calculated inverse lifetimes, $\Gamma$, for $^{81}\text{Br}_2$. The uncertainties in the observed decay rates are the standard deviations of the data.
Appendix C. Phase Shift Data

\[ {^{79}\text{Br}}^{81}\text{Br} \, ^3\Pi_{0*} \, \nu' = 13 \]

<table>
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<tr>
<th>( J' )</th>
<th>( F' )</th>
<th>( \Gamma_{\text{obs}} ) (10^5 s(^{-1}))</th>
<th>( \Gamma_{\text{calc}} ) (10^5 s(^{-1}))</th>
<th>( (\text{obs} - \text{calc}) ) (10^5 s(^{-1}))</th>
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<td>1.213</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.933 ± 0.112</td>
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<td>0.084</td>
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<tr>
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<tr>
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</tr>
<tr>
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<td>2b</td>
<td>1.827 ± 0.213</td>
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<tr>
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<tr>
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<td>4b</td>
<td>2.394 ± 0.204</td>
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<tr>
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<td>4c</td>
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<td>5b</td>
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<td>2.005 ± 0.100</td>
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<tr>
<td></td>
<td>5c</td>
<td>3.189 ± 0.059</td>
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<td>0.059</td>
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<tr>
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<td>1.742 ± 0.075</td>
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<tr>
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<tr>
<td></td>
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<td>6a</td>
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</tr>
<tr>
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<td>6d</td>
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<tr>
<td></td>
<td>7c</td>
<td>4.320 ± 0.442</td>
<td>4.272</td>
<td>0.048</td>
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<tr>
<td></td>
<td>8b</td>
<td>3.571 ± 0.164</td>
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<tr>
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<td>11c</td>
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<td>-0.711</td>
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<tr>
<td></td>
<td>13</td>
<td>3.917 ± 0.305</td>
<td>3.770</td>
<td>0.147</td>
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</table>

Table C.10: The observed and calculated inverse lifetimes, \( \Gamma \), for \(^{79}\text{Br}^{81}\text{Br} \). The uncertainties in the observed decay rates are the standard deviations of the data.
$^{79}$Br$_2$ B $^3Π_u^+$ $v' = 13$

<table>
<thead>
<tr>
<th>J'</th>
<th>F'</th>
<th>$\tau_{\text{obs}}$ (μs)</th>
<th>$\tau_{\text{calc}}$ (μs)</th>
<th>(obs - calc) (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>8.313 ± 0.532</td>
<td>8.525</td>
<td>-0.213</td>
</tr>
<tr>
<td>3</td>
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<td>4.021 ± 0.239</td>
<td>3.802</td>
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<tr>
<td>1</td>
<td>1.−</td>
<td>6.313 ± 0.343</td>
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</tr>
<tr>
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<td>4.545 ± 0.289</td>
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</tr>
<tr>
<td>3</td>
<td>3.−</td>
<td>4.480 ± 0.391</td>
<td>4.421</td>
<td>0.059</td>
</tr>
<tr>
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<td>3.664 ± 0.270</td>
<td>3.647</td>
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<tr>
<td>4</td>
<td>5b</td>
<td>3.421 ± 0.109</td>
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<tr>
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</tr>
<tr>
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<td>6.447 ± 0.291</td>
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<tr>
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<tr>
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<tr>
<td>8</td>
<td>3.035 ± 0.060</td>
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<tr>
<td>9</td>
<td>5.685 ± 0.107</td>
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<td>0.044</td>
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<tr>
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<td>1.638 ± 0.250</td>
<td>1.671</td>
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<tr>
<td>9b</td>
<td>1.744 ± 0.037</td>
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<td>4.065 ± 0.365</td>
<td>3.965</td>
<td>0.100</td>
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</tr>
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</table>

Table C.11: The observed and calculated lifetimes, $\tau$, for $^{79}$Br$_2$. 

\( ^{81}\text{Br}_2 \text{ B } ^3\Pi_{0^+} \nu' = 13 \)

<table>
<thead>
<tr>
<th>J'</th>
<th>F'</th>
<th>( \tau_{\text{obs}} ) (( \mu\text{s} ))</th>
<th>( \tau_{\text{calc}} ) (( \mu\text{s} ))</th>
<th>(obs - calc) (( \mu\text{s} ))</th>
</tr>
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<tbody>
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<td>-0.018</td>
</tr>
<tr>
<td>1</td>
<td>1_-</td>
<td>5.195 ± 0.551</td>
<td>5.139</td>
<td>0.056</td>
</tr>
<tr>
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<td>1_+</td>
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</tr>
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<tr>
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</tr>
<tr>
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<tr>
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Table C.12: The observed and calculated lifetimes, \( \tau \), for \(^{81}\text{Br}_2\).
### Table C.13: The observed and calculated lifetimes, \( \tau \), for \( {}^{79}\text{Br}{}^{81}\text{Br} \).

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<th>( \tau_{\text{calc}} ) (( \mu s ))</th>
<th>(obs - calc) (( \mu s ))</th>
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</tr>
<tr>
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<td>5a</td>
<td>1.423 ± 0.342</td>
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<td>2.081 ± 0.279</td>
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</tr>
<tr>
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<td>8b</td>
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<td>10d</td>
<td>0.896 ± 0.145</td>
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<tr>
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<td>1.303 ± 0.285</td>
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<tr>
<td>13</td>
<td>2.553 ± 0.199</td>
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