Observation of Quadrupolar Hyperfine Predissociation

J. L. Booth, I. Ozier, and F. W. Dalby

Department of Physics, University of British Columbia, Vancouver, British Columbia, Canada V6R 1Z1

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Predissociation of the $(v'=13)$ $B^3\Pi_{0_u^+}$ electronic state of $^{79}Br_2$, $^{82}Br_2$, and $^{79}Br^{81}Br$ was studied by measuring the lifetimes of individual hyperfine levels. The first observation of hyperfine electric quadrupole predissociation is reported. Revised values have been obtained for the radiative decay rate, and for the parameters associated with gyroscopic and magnetic dipole predissociation. Determinations have been made of the electric quadrupole predissociation constants.

Electronic predissociation of a diatomic molecule is its decomposition into the two constituent atoms as the result of coupling between a bound state and an unbound state of the same energy. This process provides a powerful tool for studying molecular dynamics. Perhaps the most thoroughly studied case is the $B^3\Pi_{0_u^+}$ excited electron state of diatomic halogens [1–6]. In the absence of external fields, this level has been shown to interact with a repulsive $^1\Pi_{1_u}$ state by two mechanisms: gyroscopic and hyperfine magnetic dipole predissociation. The former results from the terms in the rotational Hamiltonian which couple the electron orbital angular momentum **L** and spin **S** to the total angular momentum **J** (exclusive of nuclear spin). The latter results from the dipole-dipole interaction between the electronic and the nuclear magnetic moments. Several experimental techniques have been developed initially for application to iodine [1,2]. However, only one study [2], involving pulsing a laser and observing the fluorescence decay in time, has been based on direct lifetime measurements of individual hyperfine levels.

In the current work, the phase shift technique [7] has been applied for the first time to the determination of lifetimes of individual molecular hyperfine levels. This relatively simple method has been used to study the $B^2\Pi_{0_u^+}$ state of $^{79}Br_2$, $^{81}Br_2$, and $^{79}Br^{81}Br$ [8]. Earlier work has been hampered by bromine's relatively long radiative lifetime and strong predissociation. The phase shift method combines good sensitivity with high accuracy, and is free of many of the systematic difficulties which can arise in some of the other techniques. As a result we have been able to obtain revised values of the radiative decay rate Γ_{rad} and of the parameters for gyroscopic and magnetic dipole hyperfine predissociation. A second type of hyperfine predissociation has been measured that had been predicted [3] but not previously observed. This arises from the electric quadrupole coupling between the $^3\Pi_{0_u^+}$ and the $^1\Pi_{1_u}$ states [8,9].

The main components of the experimental apparatus were a molecular beam machine and a laser system involving a ring dye laser (Coherent CR699-21). The molecular and laser beams intersected at 90°. The molecular beam, a mixture of 20% bromine in argon (by pressure), eliminated collisional effects and concentrated the molecules into low-lying rotational states ($T_{rot} \approx 6$ K) where hyperfine predissociation effects are most apparent. The velocity of the molecular beam was measured to be 420 ± 60 m/s. The critical innovation of our apparatus is an optical system that images an area of 18 mm length along the molecular beam by 7 mm width onto a cooled photomultiplier. Such a long collection length allowed us to measure lifetimes of up to 12 μs with confidence.

The laser radiation was modulated by a Pockels cell at frequencies between 18 and 40 kHz. The in-phase and in-quadrature components of the laser induced fluorescence (LIF) were recorded simultaneously with a EG&G 5204 lock-in amplifier. The phase shift Φ of the modulated LIF relative to the excitation radiation was deduced from the ratio of the in-phase to in-quadrature signals. The reference phase was determined from the scattered light. The lifetime τ of the excited state being studied was obtained from

$$\tan\Phi = -\omega\tau , \qquad (1)$$

where ω is the angular frequency of the Pockels cell modulation. The laser intensity was kept low enough to avoid saturation.

For the vibrational band $(v'=13) \leftarrow (v''=0)$ in the B-X system, the rotational transitions $P(1)$ to $P(9)$, excluding the $P(3)$, were recorded for $^{79}Br_2$, $^{81}Br_2$, and $^{79}Br^{81}Br$. The full width at half maximum for isolated hyperfine components was roughly 8 MHz.

In a preliminary study, a detailed investigation of the hyperfine splittings of the B-X system was carried out. The Hamiltonian matrix for each state was set up in the coupled basis $|JIFM\rangle$ where **I** is the total nuclear spin and $F=J+I$ the total angular momentum. Each bromine isotope has a nuclear spin of $\frac{3}{2}$ so that $I=0, 1, 2,$ or 3. The Hamiltonian for each electronic state was diagonalized to obtain the eigenvalues and the coefficients $a^F_{JI\epsilon}$ which relate the eigenvectors to the basis vectors $|JIFM\rangle$. The hyperfine levels of a given rotational state with the same F are distinguished by the label ϵ. For the homonuclear species in the B state, symmetry considerations require that only $I=0$ and 2 exist for the odd J, and only

$I=1$ and 3 exist for the even J in the B state. (The inverse is true for the X state.) The odd-J B state levels (and even-J X state levels) are called parabromine states, while the even-J B state levels (and odd-J X state levels) are referred to as ortho states.

The total decay rate for an individual hyperfine level when electric quadrupole coupling is included is given by [3]

$$\Gamma = \Gamma_{rad} + \Gamma_{GG} + \Gamma_{GM} + \Gamma_{MM} + \Gamma_{QQ} + \Gamma_{MQ} + \Gamma_{GQ}. \quad (2)$$

The last six terms are predissociation rates arising, in turn, from gyroscopic (GG), gyroscopic–magnetic-dipole interference (GM), magnetic dipole (MM), electric quadrupole (QQ), magnetic-dipole–electric-quadrupole interference (MQ), and gyroscopic–electric-quadrupole interference (GQ) effects. The gyroscopic, magnetic dipole, and electric quadrupole matrix elements between the $^3\Pi_{0_u^+}$ and the $^1\Pi_{1_u}$ states are characterized by the parameters C_v, a_v, and b_v, respectively. For a given isotopomer, the vibrational factors in these parameters can, to good approximation, be taken as proportional to a common vibrational overlap integral (the square root of the Franck-Condon factor) [3]. To simplify the notation, the overlap integral for each isotopomer will be labeled as $\sigma(x,y)$ where x and y are either 79 or 81. For example, $\sigma(79,79)$ will mean $\sigma(^{79}Br_2)$.

In previous experimental studies, the electric quadrupole contributions in Eq. (2) were neglected. This reduces Γ to [3,8]

$$\Gamma_0(v,F,\epsilon) = \Gamma_{rad} + \sum_{JI} |a_{JI\epsilon}^F|^2 \Gamma_1(v,J,I,F), \quad (3)$$

$$\Gamma_1(v,J,I,F) = C_v^2 J(J+1) - \sqrt{2}a_v C_v (\mathbf{I} \cdot \mathbf{J})$$

$$+ \frac{a_v^2}{3} \left[\mathbf{I}^2 + \frac{3(\mathbf{I} \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I} \cdot \mathbf{J}) - \mathbf{I}^2 \mathbf{J}^2}{(2J-1)(2J+3)} \right]. \quad (4)$$

When the quadrupolar contributions are included,

$$\Gamma(v,F,\epsilon) = \Gamma_0(v,F,\epsilon)$$

$$+ \sum_{J,I,J',I'} a_{JI\epsilon}^{F*} a_{J'I'\epsilon}^F \Gamma_2(v,J,J',I,I',F). \quad (5)$$

The double sums on (J',J) and on (I',I) are required because Γ_{MQ} and Γ_{QQ} are not diagonal in I and J. The general form of Γ_2 will be given in detail elsewhere [8]. The new molecular parameter which characterizes the electric quadrupole predissociation (EQP) is

$$b_v = \sqrt{2\pi/\hbar} f_2(v,\Omega,\Omega')/\sqrt{20}. \quad (6)$$

The function $f_2(v,\Omega,\Omega')$ also arises in the analysis of hyperfine splittings and its explicit expression can be found in Table II of Ref. [10]. Ω represents the sum of the components of $\mathbf{L}$ and $\mathbf{S}$ along the internuclear axis. Here $\Omega = 0$ and $\Omega' = 1$.
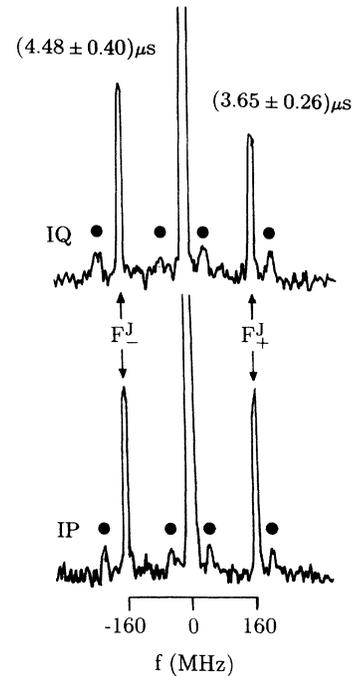
The symmetry restrictions on I and J in both the B and

FIG. 1. The hyperfine spectrum for the B-X (13'-0") $P(4)$ transition of $^{79}Br_2$ observed with the laser modulated at 25.5 kHz. The relative heights of the two hyperfine peaks labeled by F_-^J and F_+^J differ in the in-phase (IP) and in-quadrature (IQ) traces. This shows that the two upper levels have unequal lifetimes. The difference in lifetime is entirely due to effects arising from electric quadrupole hyperfine predissociation. The ● indicate weak transitions with $\Delta F \neq \Delta J$.

X electronic states of $^{79}Br_2$ and $^{81}Br_2$ produce very different hyperfine energy splitting patterns for ortho and para states [8]. The para level (B state odd J and X state even J) patterns are particularly simple with the $F \neq J$ levels forming a closely spaced multiplet, and the two levels with $F = J$ split off to either side. The high and low energy members of this pair are labeled here as F_-^J and F_+^J, respectively. If $b_v = 0$ (i.e., no EQP), these two levels have the same decay rate: $\Gamma(v,F_+^J) = \Gamma(v,F_-^J) \equiv \bar{\Gamma}_0(v, J)$. However, if $b_v \neq 0$, the decay rates are no longer equal and

$$\Gamma(v,F_\pm^J) = \bar{\Gamma}_0(v,J) + b_v^2 \beta \pm b_v \{\sqrt{2}C_v + a_v\} \eta, \quad (7)$$

where β and η are numerical factors. The electric quadrupole terms are roughly independent of J while Γ_{GG} and Γ_{GM} grow as J^2 and J, respectively. Hence, the EQP effects are most evident at low J.

Direct evidence for EQP is contained in the B-X hyperfine spectra of parabromine; see Fig. 1. For both the P and R branches, these spectra are characterized by three peaks arising from the $\Delta F = \Delta J$ transitions. (The $\Delta F \neq \Delta J$ transitions are weaker and are neglected in this discussion.) It is convenient to label the spectral features by their upper state here. The central peak ($F \neq J$) is an unresolved multiplet while the high and low frequency

TABLE I. The total decay rates for various B-X (13'-0") hyperfine states having $F = J$. The difference in the rates labeled $\Delta(F_+ - F_-)$ (determined directly from the data, not by subtracting the average values for two decay rates) is completely due to effects involving electric quadrupole predissociation.

	$^{79}Br_2$ Γ (10^5 s^{-1})	$^{81}Br_2$ Γ (10^5 s^{-1})
$P(2)$ 1$_+$	2.20 ± 0.14	2.54 ± 0.29
1$_-$	1.58 ± 0.09	1.92 ± 0.20
$\Delta(1_+ - 1_-)$	0.60 ± 0.07	0.54 ± 0.12
$P(4)$ 3$_+$	2.74 ± 0.20	3.07 ± 0.14
3$_-$	2.23 ± 0.20	2.56 ± 0.12
$\Delta(3_+ - 3_-)$	0.50 ± 0.06	0.51 ± 0.08
$P(6)$ 5$_+$	4.28 ± 0.59	4.42 ± 0.36
5$_-$	3.60 ± 0.30	3.83 ± 0.32
$\Delta(5_+ - 5_-)$	0.57 ± 0.20	0.90 ± 0.30
$P(8)$ 7$_+$	6.10 ± 0.93	6.06 ± 0.57
7$_-$	5.38 ± 0.50	5.78 ± 0.58
$\Delta(7_+ - 7_-)$	0.83 ± 0.90	0.27 ± 0.27

TABLE II. The gyroscopic (C_r), magnetic dipole (a_r), and electric quadrupole (b_r) predissociation parameters and radiative decay rate (Γ_{rad}) deduced from our lifetime measurements for the $B\,^3\Pi_{0_u^+}$ ($v' = 13$) excited state of bromine. Only the relative signs of the predissociation parameters have been determined.

	$^{79}Br_2$	$^{81}Br_2$
C_r (s$^{-1/2}$)	$+(86.5 \pm 0.8)$	$+(88.2 \pm 1.7)$
a_r (s$^{-1/2}$)	$+(208.3 \pm 3.1)$	$+(236.1 \pm 5.4)$
b_r (s$^{-1/2}$)	$+(40.5 \pm 4.0)$	$+(35.6 \pm 3.8)$
Γ_{rad} (s^{-1})	$(8.40 \pm 0.34) \times 10^4$	

lines arise solely from the F_+^J and F_-^J states, respectively. In the absence of EQP, the ratios of the intensities of the F_+^J to the F_-^J peaks should be equal for the in-phase and in-quadrature channels indicating that the corresponding upper levels have the same decay rate. Any difference in the ratios from the in-phase to the in-quadrature signals is directly proportional to b_r, as per Eq. (7).

The experimentally determined values of $\Gamma(13, F_\pm^J)$ and their differences $\Delta(F_+^J - F_-^J)$ for $^{79}Br_2$ and $^{81}Br_2$ are given in Table I. $\Gamma(13, F_+^J)$ is systematically larger than the $\Gamma(13, F_-^J)$. It should be emphasized that the model of predissociation including only the gryroscopic and magnetic dipole terms cannot account for the observed difference in lifetimes.

Over 200 hyperfine transitions were measured. Of these, 73 were chosen as suitable for analysis because they were clearly resolved and had a signal-to-noise ratio of 10 or greater. The measurements for each transition were repeated 8 to 10 times for each of at least two and usually three modulation frequencies. The data for the three isotopomers were fitted globally subject to three constraints. (i) C_r for each isotopomer was made to be inversely proportional to the molecule's reduced mass. (ii) $a_r(79)/a_r(81)$ was set proportional to the ratio of the nuclear g factors of ^{79}Br to ^{81}Br, namely, $g(79)/g(81)$. (iii) $b_r(79)/b_r(81)$ was set proportional to the ratio of the nuclear quadrupole moments of ^{79}Br to ^{81}Br, namely, $Q(79)/Q(81)$. The six parameters varied were Γ_{rad}, $C_r(79)$, $a_r(79)$, $b_r(79)$, $\zeta1 = \sigma(81,81)/\sigma(79,79)$, and $\zeta2 = \sigma(79,81)/\sigma(79,79)$. The parameters for a given isotopomer are readily deduced from these six, e.g., $a_r(81) = a_r(79)\zeta1[g(81)/g(79)]$. The results for $^{79}Br_2$ and $^{81}Br_2$ [8] are given in Table II [11]. The existence of the interference terms Γ_{GM} and Γ_{GQ} indicates that all

of the observed predissociations involve the same unbound electronic state.

Two tests of the model were carried out. First, the data for each isotopomer were fitted separately. Second a global fit was made but with two additional parameters, $a_r(81)/\zeta1$ and $b_r(81)/\zeta1$, and with constraints (ii) and (iii) relaxed. The results of these two tests were in excellent agreement with the original six parameter model.

If the EQP contributions are neglected, biased values are obtained for Γ_{rad}, C_r, and a_r. For example, our results show that for the $v' = 13$ level of the B state of $^{79}Br_2$, an error of 5% arises in Γ_{rad} if b_r is set to zero. For systems with longer lifetimes or in regions closer to the crossing of two potential curves where the predissociation rates and the radiative decay rate are comparable, the errors will be much larger. In some cases, such as when ($\Omega = 0$) and ($\Omega = 2$) electronic states overlap, the dominant predissociation contributions are the electric quadrupole terms.

Previous work on the predissociation of bromine was performed using two techniques: (A) observation of the fluorescence decay of rotational transitions but without resolving the hyperfine structure [4,6], and (B) measurement of the relative intensities of the resolved hyperfine components within a J multiplet [5]. Both are sensitive to the polarization of the laser, to the amount of solid angle collected, to variations in the detector efficiency over the field of view, and to fluctuations in the laser beam intensity and number of molecules present. The phase shift technique, being ratiometric, is considerably less sensitive to these effects. In addition, this method is relatively simple and allows for direct lifetime measurements of the individual hyperfine levels.

The fluorescence decay technique (A) involves averaging over the hyperfine states. The gyroscopic predissociation is the same for all of the hyperfine levels, but a correction must be made for residual effects due to hyperfine predissociation and the interference between hyperfine and gyroscopic predissociation. This method can be expected to yield precise values of C_r. For $^{81}Br_2$ with $v' = 13$, it was found [6] that $C_r = 83.49 \pm 0.60$ s$^{-1/2}$, which is in satisfactory agreement with our result as given in Table II. However, this fluorescence decay

technique can produce only an approximate value of Γ_{rad}, since it is obtained from the small intercept determined by extrapolating the lifetime measurements to zero pressure and to $J=0$. Furthermore, this intercept must be corrected for the residual hyperfine predissociation, a fact that is often overlooked. The values obtained [6] for Γ_{rad} are too high by a factor of about 6.

The relative intensity technique (B) is simple to apply but can only produce ratios of parameters. The results for $C_v/\sqrt{\Gamma_{rad}}$ and $a_v/\sqrt{\Gamma_{rad}}$ obtained by this method [5] are roughly 1.5 to 2 times lower than the values reported in Table II and display a large variation with rotational state.

In techniques (A) and (B) and the phase shift method, care must be taken when detecting fluorescence of relatively long-lived states. In the B state of bromine, the radiative lifetime $\tau_{rad}=11.8\pm0.5$ μs. Thus the apparatus must be designed to record lifetimes τ varying from about 1 to over 10 μs. If this is not done, molecules excited into long-lived (slightly predissociated) hyperfine levels will move out of the detection region before fluorescing, while those in short-lived (highly predissociated) levels will be detected with high efficiency. This leads to an oversampling of the short-lived states and hence to erroneous values for Γ_{rad} and the predissociation parameters. One sign of such a systematic bias in the results is that the predissociation parameters display a strong variation with J. This variation is a consequence of Γ_{GG} increasing as J^2 thereby reducing all of the hyperfine lifetimes of higher rotational levels. The amount of undersampling or oversampling is absorbed into Γ_{rad} and the predissociation parameters, causing them to change markedly from one J to the next. This mechanism is felt to be responsible for the variations reported in Ref. [5].

The existence of electric quadrupole predissociation has several important consequences. Near the dissociation limits of electronic potentials many different states converge. The interactions of these electronic levels are important for the recombination of atoms into molecules. With a good understanding of the various predissociation mechanisms (the inverse of recombination), novel approaches either to enhance or suppress them will open up new possibilities for holding atoms in traps and preparing molecules with specific physical properties.

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[8] Both homonuclear and heteronuclear species have been studied, but the wording and equations in the present work apply to the homonuclear form. Similar results are applicable to $^{79}Br^{81}Br$. The full theory will be presented elsewhere.

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