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Hyperfine Predissociation in Br₂

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Hyperfine structure of several rovibronic transitions in the *B-X* system of ⁷⁹Br₂ has been analyzed and the quadrupolar and nuclear spin rotation hyperfine coupling constants have been obtained. A strong hyperfine predissociation effect has been observed for the first time in Br₂ and the related hyperfine and rotational parameters were determined in the *B*(0_v⁺) *v*' = 11 level.

INTRODUCTION

Since the discovery of a predissociation due to hyperfine coupling in the iodine *B* state¹⁻² a number of studies related to this phenomenon were undertaken. A comprehensive review with a general theory has recently been published by Vigué, Broyer and Lehmann.³ However, hyperfine predissociation had, up to now, been observed only in iodine. A simple way for detecting this predissociation is through observation of intensity anomalies between the different hyperfine components of a rotational line. The research of a hyperfine predissociation in other molecules, such as Br₂, therefore implies observation of their hyperfine structure spectra.

By comparison with the extensively studied case of iodine⁴ hyperfine interactions in molecular bromine have received relatively little attention.

Hyperfine structure of some rovibrational transitions in the $B-X$ system has, however, been observed as early as 1972 by intracavity saturated absorption in a He-Ne laser.⁵ Very recently, a similar experiment was performed on a collimated molecular beam excited with a frequency stabilized dye laser.⁶ On the other hand, as in iodine, a very important rotational predissociation experienced by rovibronic levels in the B state, due to a dissociative $^1\Pi_u$ state crossing, was directly evidenced.⁷ Hanle effect,⁸ lifetime measurements⁹⁻¹⁰ and Zeeman quantum beats,¹¹ have also been performed. However, despite these precise lifetime measurements and their careful theoretical interpretation¹²⁻¹³ no hyperfine predissociation was detected in Br_2 .

In view of the precise results obtained in our study of the hyperfine interactions in iodine,¹⁴ it was thought desirable to obtain the same degree of understanding on the bromine molecule. The present paper describes the results of our first effort in this direction, the principal result of which is the unequivocal observation of a hyperfine predissociation in Br_2 .

EXPERIMENTAL

Our collimated supersonic beam machine¹⁵ was converted from iodine to bromine without any major changes. The "oven" was operated at 0°C , which ensured an adequate bromine flow. Natural bromine was used, with the resultant isotopic composition $^{79}\text{Br}_2$, $^{81}\text{Br}_2$; $^{79}\text{Br}^{81}\text{Br}$ in the ratios 0.25, 0.25, 0.5. A frequency stabilized ring laser (CR 699) operated with Rhodamine 6 G was used as the excitation source. The 30 GHz frequency scans were calibrated either with the fringes of a confocal Fabry-Perot interferometer (f.s.r. 81 MHz) or with a lambdameter. Calibration errors due to thermal drifts, a problem commonly encountered in such experiments, were minimized by using a relatively fast scan (20 MHz/s) together with digital acquisition of the data with a minicomputer. The fluorescence signal of the excitation spectrum was observed through a filter. It was, as expected, much weaker than in the case of iodine, but with our photon counting device an adequate signal to noise ratio could nevertheless be obtained (Figure 1). Typical linewidths of the observed spectra were 5 MHz, mainly due to residual Doppler effect. We verified that linewidths and relative intensities were independent of laser power in our experimental conditions (20 mW/mm² at maximum).

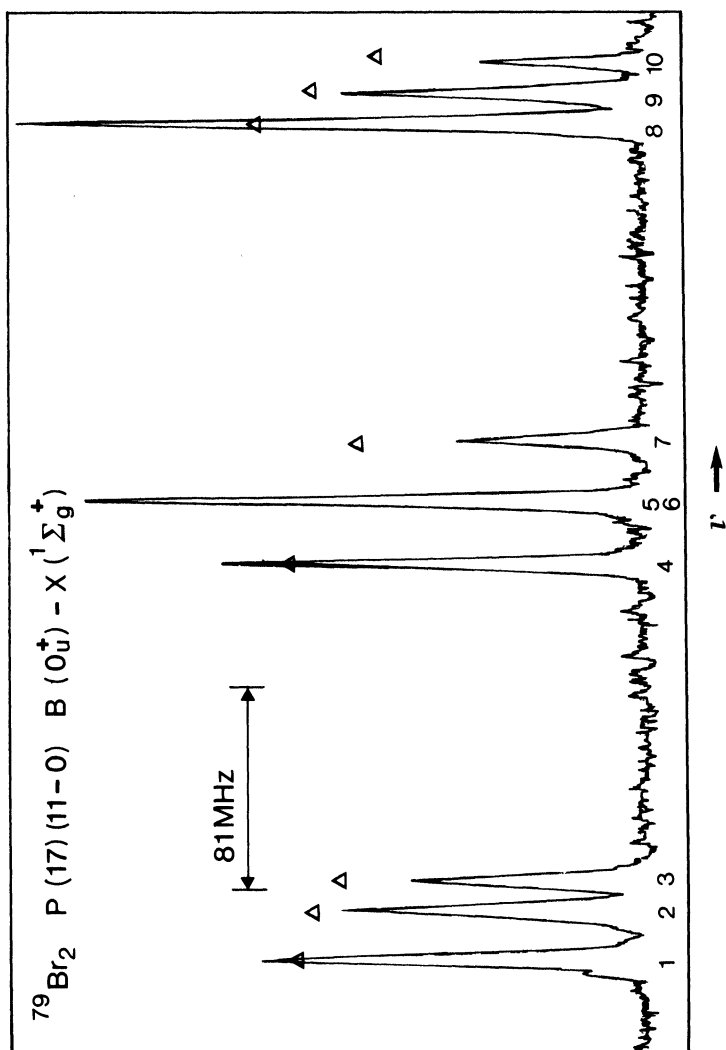


FIGURE 1 Typical record of a rotational line P(17) (11-0) of the $B(2I_{0g}^+) - X(1\Sigma_g^+)$ transition ($^{79}\text{Br}_2$). The intensities of the lines without hyperfine predissociation are noted by a triangle. They were calculated using the constants of Table I. The lines 5 [$(F-J)'' = -1$, $(F-J)' = -1$] and 6 [$(F-J)'' = 1$, $(F-J)' = 1$] are superimposed and were not used in the calculation of the hyperfine predissociation parameters. The identification of the other lines is given in Table III.

RESULTS

a) Hyperfine structure

The identification of any rovibronic line in the spectrum was made easy, from the lambdameter readings, by use of the accurate constants given by Barrow et al.¹⁶ for $^{79}\text{Br}_2$ completed by standard isotopic relations in the case of $^{79}\text{Br}^{81}\text{Br}$ and $^{81}\text{Br}_2$. In fact, as our main aim was the search for hyperfine predissociation, we concentrated our experimental effort on one isotope ($^{79}\text{Br}_2$) and one vibrational band (11-0) where the gyroscopic predissociation was expected to be relatively high.^{12,13} For this homonuclear species and a not-too-low value of J , the lines exhibit the already observed⁵ pattern of 10 or 6 $\Delta F = \Delta J$ main hyperfine component according to whether J' is odd or even (Figure 1).

The hyperfine Hamiltonian is quite similar to the one we used for iodine. The only differences are the lower value of the nuclear spin ($I = 3/2$ for both isotopes) and the existence of the heteronuclear $^{79}\text{Br}^{81}\text{Br}$ molecule for which the restrictions on the parity of the total nuclear spin number I do not hold (as was also the case for the $^{127}\text{I}^{129}\text{I}$ molecule¹⁷). A least squares fit procedure enables us to obtain the quadrupolar (eQq' , eQq'') and nuclear spin rotation (C') hyperfine coupling constants. When J was sufficiently low (≤ 9) $\Delta F \neq \Delta J$ lines were observed; the constants for the ground and excited electronic states were then not very correlated and could be determined separately. As the determinations were for low J values it was necessary to introduce the second order quadrupolar interaction ($\Delta J = \pm 2$ matrix elements). The results are gathered in Table I. They are in reasonable agreement with those of Tiemann et al.⁶ and with theoretical estimates: $eQq' = 798 \pm 15 \text{ MHz}$ ¹⁸ or $eQq'' = 770$ and $eQq' = 192$ (calculated as in Ref. 19) using $(eQq)_{410} = -769.8$.²⁰

The values obtained allow a precise calculation of the intensity of each hyperfine component. The results are in total disagreement with the observed intensities as can be seen in Figure 1. These discrepancies are explained by the hyperfine predissociation.

b) Hyperfine predissociation

The theory of hyperfine predissociation has been clearly worked out by Vigué and coworkers.³ They have shown that the lifetime τ_F of one hyperfine level is given by:

TABLE I

Hyperfine structure measurements in ⁷⁹⁻⁷⁹Br₂ : 11-0 band of the B³Π_{0_f}-X ¹Σ_g⁺ transition

	R(3)	R(4)	P(5)	R(9)	P(17)
eQq''	808.7 (9)	808.5 (20)	808.3 (10)	808.5	808.5
eQq'	176.7 (10)	175.4 (33)	175.3 (9)	176.5 (10)	177.9 (11)
ΔeQq	631.96	633.13	633.02		
C'	0.043 (17)	0.06 ^a	0.078 (20)	0.062 (10)	0.061 (8)
σ	0.43	1.2	0.54	0.56	0.55
number of lines	18	8	18	13	10

All results are in MHz.

Numbers in parentheses are two standard deviations of the last digit.

σ is the RMS deviation between observed and calculated lines.

^a Parameter held fixed in the fit (average of the three first fits).

C' held fixed to zero in the fit.

$$\frac{1}{\tau_F} = \Gamma_F = \Gamma_{\text{rad}} + C_v^2 J(J+1) + \Gamma_{\text{pred}}(\nu, J, \varepsilon, F) \quad (1)$$

where

$$\Gamma_{\text{pred}}(\nu, J, \varepsilon, F) = \sum_I |\alpha(I, \varepsilon, J, F)|^2$$

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

and

$$\mathbf{I} \cdot \mathbf{J} = \frac{1}{2} [F(F+1) - J(J+1) - I(I+1)]$$

Γ_{rad} is the pure radiative decay rate, C_v is the usual rotational (or gyroscopic) predissociation constant and a_v the hyperfine predissociation constant.

The $\alpha(I, \varepsilon, J, F)$ can be obtained by diagonalization of the hyperfine hamiltonian. Equation (1) is a simplified version of a more general relation.³ It appeared that this simplified version is in agreement with all the available

experimental results. In that case the intensity I_F of a hyperfine component in a rotational line is given by:

$$I_F = N I_F (\text{theor.}) \frac{\Gamma_{\text{rad}}}{\Gamma_{\text{rad}} + C_v^2 J(J+1) + \Gamma_{\text{pred}}(\nu, J, \epsilon, F)} \quad (2)$$

where I_F (theor.) is the intensity of this component calculated without taking account of the hyperfine predissociation and N is a normalization factor.

From a nonlinear least square fit it is possible to adjust formula (2) to the experimental intensities. From the form of expression (2) it is easy to see that the parameter Γ_{rad} is totally correlated to the a_ν and C_ν parameters and the fit can give only the value of $a_\nu/\sqrt{\Gamma_{\text{rad}}}$ and $C_\nu/\sqrt{\Gamma_{\text{rad}}}$. The normalization constant N can be considered as a free parameter or fixed at every step of the fit in such a way that the sum of the experimental and calculated intensities are the same. The two methods yield no significant difference. The results of these fits with N as a free parameter are given in Table II. The use of two parameters $a_\nu/\sqrt{\Gamma_{\text{rad}}}$ and $C_\nu/\sqrt{\Gamma_{\text{rad}}}$ allows the fit of all measured hyperfine intensities within the experimental error. It thus appears in the case of bromine that the simplified expression (2) is an excellent approximation to characterize the hyperfine predissociation, at least as it concerns intensity measurements. The ratio $Y^2 = a_\nu^2 / C_\nu^2 = 9.3$ is about two orders of magnitude lower than for I_2^3 because of the higher value of C_ν^2 for Br_2 .

In order to get a feeling about the influence of hyperfine predissociation on lifetimes, we calculated from Eq. (1) and Table II the lifetimes of eight hyperfine sublevels of the $\nu' = 11, J' = 16$ rotational level, corresponding to the hyperfine components as labeled on Figure 1. The radiative decay

TABLE II
Hyperfine predissociation parameters in the (11-0) band of Br_2 ($\text{B}^3\Pi_{0g^-} - \text{X}^1\Sigma_g^+$ transition)

	R(3)	R(5)	R(9)	P(17)	Average
C_ν	0.121 ± 0.030	0.096 ± 0.008	0.141 ± 0.074	0.072 ± 0.026	0.096 ± 0.007
$\sqrt{\Gamma_{\text{rad}}}$					
a_ν	0.294 ± 0.039	0.363 ± 0.049	0.412 ± 0.060	0.274 ± 0.017	0.292 ± 0.014
$\sqrt{\Gamma_{\text{rad}}}$					

TABLE III
Calculated lifetimes τ_F in P17(11-0) line

Line (a)	(F - J) ^{''}	(F - J) [']	10 ⁻⁵ × $\Gamma_{\text{Hyp.}}$ (s ⁻¹)	10 ⁻⁵ × $\Gamma_{\text{int.}}$ (s ⁻¹)	10 ⁻⁵ × Γ_F (s ⁻¹)	τ_F (μs)
1	1	1	1.18	-3.03	19.12	0.523
2	0	0	1.42	1.30	23.69	0.422
3	-1	-1	1.08	4.63	26.69	0.375
4	2	2	1.94	-7.14	16.02	0.624
7	-2	-2	2.17	8.79	31.93	0.313
8	3	3	2.63	-11.40	12.21	0.819
9	0	0	0.39	0.36	21.72	0.460
10	-3	-3	2.75	12.11	35.84	0.279

Calculations made with the constants:

$$C_v = 74.2 \text{ s}^{-1/2} \quad a_v = 226 \text{ s}^{-1/2} \quad \text{and} \quad \Gamma_{\text{rad}} = 6 \times 10^5 \text{ s}^{-1}$$

$$c_v^2 J(J+1) = 1.50 \times 10^6 \text{ s}^{-1} \quad (\text{pure gyroscopic term in 1})$$

$\Gamma_{\text{Hyp.}}$ is the pure hyperfine term in 1 (a_v^2 term)

$\Gamma_{\text{int.}}$ is the interference term in 1 ($a_v C_v$ term)

(a) The number corresponds to the hyperfine line noted in Figure 1.

rate Γ_{rad} was taken equal to $6 \times 10^5 \text{ s}^{-1}$ (the reason for this choice is explained below). The values obtained are gathered in Table III. Large relative variations of individual lifetimes τ_F are found (up to a factor 3) which are mainly due to the $a_v C_v$ interference term (note that, in contrast to the case of iodine, $a_v C_v$ is positive here).

Despite these variations, it is possible to see that the global decay of the population of one rotational level can still be considered as exponential during a few lifetimes. Using the expression

$$e^{-\Gamma_{\text{eff}} t} = \frac{\sum_F I_F e^{-\Gamma_F t}}{\sum_F I_F} \quad (3)$$

we can try to interpret the decay rates which were obtained for different rovibronic levels by various authors without consideration of hyperfine predissociation and which should then correspond to Γ_{eff} . For the $\nu' = 11$, $J' = 16$ level, Clyne et al. (Ref. 9a, Figure 7a) found $\Gamma_{\text{eff}} \sim 2 \times 10^6 \text{ s}^{-1}$. The same decay rate is obtained from Equation (3) if we take $\Gamma_{\text{rad}} = 6 \times 10^5 \text{ s}^{-1}$ as mentioned above. This value is somewhat higher than the experimental result given in Table 3 of Ref. 9a ($3.3 < \tau_R < 8.1 \mu\text{s}$

→ $1.2 \times 10^5 < \Gamma_{\text{rad}} < 3.0 \times 10^5 \text{ s}^{-1}$), but this difference must not be regarded as a discrepancy since hyperfine predissociation was not considered in Ref. 9a and also because of the uncertainty affecting our values of $C_v/\sqrt{\Gamma_{\text{rad}}}$ and $a_v/\sqrt{\Gamma_{\text{rad}}}$.

The global measurements, disregarding hyperfine predissociation, do not seem to give a large systematic error on the determination of C_v^2 . We find $C_v^2 = 5.5 \times 10^3 \text{ s}^{-1}$ (with $\Gamma_{\text{rad}} = 6 \times 10^5 \text{ s}^{-1}$) instead of $C_v^2 = 7.0 \times 10^3 \text{ s}^{-1}$ in Ref. 9b. Unfortunately, the nondirect determination of Γ_{rad} by our intensity measurements does not allow a precise determination of the systematic error affecting this last quantity. It is only through direct hyperfine lifetime measurements, as in Ref. 21 that Γ_{rad} could be directly determined. Future work is planned in this direction.

CONCLUSION

Precise hyperfine intensity measurements in $^{79}\text{Br}_2$ clearly show a hyperfine predissociation affecting the $B(0_u^+)$ state and yielding predissociation rates comparable with radiative decays. This is the second example after I_2 of this special type of predissociation.

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