The Diode Laser Spectrum of Bromine Monofluoride (BrF) in the Ground Electronic State

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The infrared absorption spectra of the two isotopic forms of bromine monofluoride in natural abundance (^{79}BrF: 50.54%, ^{81}BrF: 49.46%) in their ground electronic state ($^1\Sigma$) have been measured, using a diode laser spectrometer. These data were fitted along with the published infrared and microwave spectra to produce an improved set of Dunham Y-parameters and a set of mass-independent parameters. Also, the coefficients of the Dunham potential function of bromine monofluoride were determined by a direct fit to the experimental data.

Key words: Infrared spectroscopy; Laser spectroscopy; Diatomic molecule; BrF; Dunham parameters.

Introduction

During an attempt to measure the ν_2-band of CF_2 in the gas phase (CF_2 was generated by an electrical or microwave discharge in CF_2Br_2 in a White cell) a number of intensive single lines of an unstable substance were observed. These could not come from CF_2, since in the case of CF_2, an asymmetric top, groups of lines were to be expected. These lines were later identified as transitions of bromine monofluoride.

In addition to a number of different measurements of the electronic spectra of bromine monofluoride, there are two previous investigations of the high resolution infrared spectrum by Nakagawa et al. with the diode laser [1] and by Bürger et al. [2] at medium resolution using an FTIR spectrometer with a resolution of 0.04 cm^{-1}. The microwave and milliwave spectra of BrF were observed by Nair et al. [3] and by Willis et al. [4, 5]. Some 31 lines of the two isotopic species of BrF were observed in the present work, only five of these having been observed previously by Nakagawa et al. [1]. It was decided to refit all available high resolution data for BrF to determine an optimum set of molecular parameters.

Experimental

Measurements were carried out using a White cell with a 16 m path length. The BrF sample was produced from CF_2Br_2 both by an electric discharge directly within the absorption cell and by a microwave discharge outside the White cell. A slow stream of CF_2Br_2 was passed through the discharge zone at a total pressure of about 1 mbar.

The diode laser spectrometer used was based on the laser head assembly of Spectra Physics with diodes from the same company. Measurements were carried out to a nominal accuracy of 0.001 cm^{-1}, using a calibrated confocal élaton with a FSR of 0.009784 cm^{-1} in conjunction with accurately measured absorption lines. A single diode which operated in the relevant spectral region gave fairly good coverage (with gaps) of the region from 634 cm^{-1} to 683 cm^{-1}. Absolute wavenumber calibration was carried out using accurately known absorption lines of CO_2 [6].

The signals detected by an HgCdTe infrared detector were processed by source modulation of the diode laser at 8 kHz followed by phase sensitive detection.

Spectra and Analysis

The measured rotational transitions [3, 5], a total of 34 lines ranging in N from 0 to 12 and vibrational state up to $v = 3$ for the two isotopomers, were augmented with the infrared data from Nakagawa et al. [1], and from this work (Table 1) and the whole data set was treated in three ways:

1. To these the usual Dunham [7] expression for the energy levels of a diatomic molecule

$$F = \sum_{ij} Y_{ij}(v + 1/2)^i (N(N+1))^j ,$$

was fitted. The fitted Dunham parameters and the values obtained for ^{79}BrF and ^{81}BrF are shown in Table 2. The values for these parameters available at

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Table 1. Observed infrared transitions (in cm^{-1}) of BrF.

^{79}Br	$v=1 \leftarrow 0$			$v=2 \leftarrow 1$	
P(35)	634.4447 (−07)	R(4)	665.7696 (00)	P(26)	634.7259 (02)
P(31)	637.9412 (09)	R(13)	671.6766 (−02)	R(10)	662.0984 (02)
P(23)	644.6927 (02)	R(19)	675.3749 (08)	R(16)	665.8589 (07)
P(19)	647.9483 (−03)	R(26)	679.4405 (−01)		
P (6)	657.9701 (−05)	R(32)	682.7120 (00)		
P (5)	658.7052 (−04)				
^{81}BrF	$v=1 \leftarrow 0$			$v=2 \leftarrow 1$	
P(33)	634.7635 (−04)	R (1)	662.1275 (−14)	R (6)	657.9278 (−05)
P(29)	638.2019 (04)	R (6)	665.5265 (−05)	R (7)	658.5866 (−02)
P(25)	641.5597 (−06)	R(22)	675.5125 (01)	R(12)	661.7984 (−12)
P(21)	644.8397 (−01)	R(29)	679.4475 (01)	R(13)	662.4254 (−07)
P(17)	648.0392 (−02)	R(36)	683.1122 (−12)	R(18)	665.4782 (−03)
P (3)	658.6010 (04)			R(19)	666.0735 (07)

Numbers in parentheses represent obs.−calc. in units of the last digit.

Table 2. Dunham coefficients determined for BrF (in cm^{-1}).

	^{79}BrF			^{81}BrF		
	Present study	Ref. [4], [5]	Ref. [1]	Present study	Ref. [4], [5]	Ref. [1]
Y_{10}	669.90082 (35)	(669.61 (27)) *	669.9002 (5)	668.29478 (33)	(668.00 (27) *	668.2937 (6)
Y_{20}	−3.79896 (12)	(−3.86 (8)) *	−3.7988 (2)	−3.78082 (11)	(−3.84 (8)) *	−3.7804 (2)
$Y_{01} \times 10$	3.5582767 (15)	3.5582784 (12)	3.55832 (8)	3.5412348 (16)	3.5412323 (12)	3.54121 (10)
$Y_{11} \times 10^3$	−2.59692 (33)	−2.59723 (26)	−2.5920 (13)	−2.57929 (36)	−2.57858 (26)	−2.5740 (14)
$Y_{21} \times 10^6$	−6.94 (20)	−6.72 (15)	−8.8 (5)	−6.26 (23)	−6.66 (15)	−8.8 (5)
$Y_{31} \times 10^7$	−1.76 (33)	−2.07 (26)	–	−2.74 (40)	−2.03 (27)	–
$Y_{02} \times 10^7$	−4.0206 (29)	−4.0191 (33)	−3.95 (6)	−3.9824 (43)	−3.9808 (33)	−3.90 (10)
$Y_{12} \times 10^9$	−1.51 (16)	−2.20 (37)	−2.0 (6)	−1.58 (22)	−2.20 (37)	−1.8 (11)
σ	0.00067	–	–	0.00085	–	–
IR-Lines	44	–	32	53	–	39
MW-Lines	18	15	–	16	13	–

Numbers in parentheses represent one standard deviation in units of the last digit.
* Calculated from approximate relationship.

Table 3. Mass independent parameters of BrF $\left(\text{in } cm^{-1} \times \mu^{\frac{i+2j}{2}}\right)$.

U_{10}	2621.3785 (10)
U_{20}	−58.1706 (13)
U_{01}	5.4485145 (18)
$U_{11} \times 10$	−1.55625 (15)
$U_{21} \times 10^3$	−1.575 (37)
$U_{31} \times 10^4$	−1.94 (24)
$U_{02} \times 10^5$	−9.4309 (60)
$U_{12} \times 10^6$	−1.48 (12)
σ	0.00076
IR-Lines	97
MW-Lines	34

Numbers in parentheses represent obs.−calc. in units of the last digit.

the beginning of this work are included in Table 2 for comparison.

2. The data of the two isotopic species of BrF were used simultaneously in order to fit a set of mass-independent parameters (U_{ij}) and mass scaling coefficients (Δ_{ij}) using the equation given by Watson [8]

$$E = \sum_{ij} \mu^{-(i/2+j)} U_{ij} \{1 + (m_e/m_A)\,\Delta_{ij}^{A} + (m_e/m_B)\,\Delta_{ij}^{B}\} \cdot (v+1/2)^i (N(N+1))^j ,$$

where μ is the reduced mass, m_e is the mass of the electron, m_A and m_B are the masses, and Δ_{ij}^{A} and Δ_{ij}^{B} the mass scaling factors for atom A and B, respectively.

Other than in the case of diatromic molecules such as SiS [9], SnS [10] and metal monohydrides (cf. e.g. [11, 12]), it was found to be unnecessary to include mass scaling coefficients in the energy formula above. In order to reproduce the experimental data adequately it was sufficient to consider only the simple mass dependence for a diatomic molecule

$$Y_{ij}^{*} = \left(\frac{\mu}{\mu^{*}}\right)^{(i/2+j)} Y_{ij} ,$$

Table 4. Coefficients of the Dunham potential function for ^{79}BrF, ^{81}BrF and IF *.

	^{79}BrF	^{81}BrF	IF *
ω_e [cm^{-1}]	669.92554 (96)	668.31840 (94)	610.2771 (17)
B_e [cm^{-1}]	0.35582815 (9)	0.35412375 (10)	0.279711420 (20)
a_1	−3.28779 (11)	−3.28814 (12)	−3.435165 (41)
a_2	6.39887 (61)	6.40217 (60)	7.2688 (17)
a_3	−10.862 (10)	−10.841 (12)	−13.031 (12)
σ	0.0010	0.0014	0.0003
IR-Lines	44	53	17
MW-Lines	18	16	10

Numbers in parentheses represent obs.−calc. in units of the last digit.
* Data from [15].

where μ and μ^* are the reduced masses, and Y_{ij} and Y_{ij}^* the Dunham parameters of the two isotopic species concerned. Thus the equation of Watson above could be reduced to the form

$$E = \sum_{ij} \mu^{-(i/2+j)} U_{ij} (v+1/2)^i (N(N+1))^j .$$

The results of the fitting of this equations to the experimental data are shown in Table 3.

3. Since it is well-known (e.g. [7, 9, 10, 13, 14]) that redundancies are introduced by adopting procedure 1 above, the experimental data of ^{79}BrF and ^{81}BrF respectively were used to fit directly to the Dunham potential function [7]

$$U(\xi) = a_0 \xi^2 \left(1 + \sum_{i=1}^{\infty} a_i \xi^i\right) + B_e N(N+1)(1 - 2\xi + 3\xi^2 - 4\xi^3 + \ldots),$$

where $\xi = (R - R_e)/R_e$ and $a_0 = \omega_e^2/4B_e$. In this case the fitted variables are ω_e, B_e, a_1, a_2, a_3, etc., and the values obtained are shown in Table 4, in which the values for IF [15] are also listed for comparison.

Discussion

The main advantage of the Dunham expression for the term values of the rotating and vibrating diatomic molecule is ease of computation. However, as Dunham himself recognised [7], this expression results in the introduction of redundance (i.e. more parameters are used than really necessary).

The procedure adopted here was to use the minimum number of Y-parameters which were required to reproduce the experimental data-set given (Table 1, [1, 3, 5]). In this case, the eight Y's listed with a standard deviation in Table 2 were found to be necessary. The results are compared in Table 2 with those previously obtained, and as can be seen from this table an improvement over all previous data has been achieved.

The fit of the experimental data (Table 1, [1, 3, 5]) to the Dunham potential function is carried out over the relationships between the Y-parameters and the coefficients of the function given by Dunham [7].

The superiority of this procedure is demonstrated by the fact that the residuals of a fit which included only five variables (ω_e, B_e, a_1, a_2, a_3) were identical to those produced with the eight Y's.

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