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Microwave spectroscopic study of the BBr molecule[1]

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Abstract

The reactive species BBr was produced by the glow discharge of the BBr_3 vapor in a free space cell. Rotational spectra of the four isotopic species were observed between 117 and 480 GHz. For lower rotational transitions the hyperfine structure owing to the bromine nucleus has been observed, and from its analysis the nuclear quadrupole interaction constant has been determined. The breakdown of the Born–Oppenheimer approximation for the rotational constant was recognized and the relevant parameters were determined. © 1997 Elsevier Science B.V.

Keywords: Microwave spectroscopy; Microwave spectrum; Millimeter wave spectrum; BBr radical; Born–Oppenheimer breakdown

1. Introduction

The labile diatomic molecules between halogen and boron atoms were investigated extensively by electronic spectroscopy [1]. Among them, boron monofluoride and boron monochloride were also studied with various spectroscopic methods including microwave spectroscopy [2–4] and high-resolution infrared spectroscopy [5–8]. However, gaseous boron monobromide was not studied by any spectroscopic techniques other than electronic spectroscopy. A triplet–singlet emission $a^3\Pi–X^1\Sigma^+$ from the discharge through BBr_3 diluted in helium was rotationally analyzed by Lebreton and co-workers [9,10] to obtain the rotational constant for ^{11}BBr. Destoky et al. [11,12] studied the $a^3\Pi–X^1\Sigma^+$ and $A^1\Pi–X^1\Sigma^+$ transitions under high resolution and derived precise vibrational and rotational constants for the most abundant $^{11}B^{79}Br$ isotopic species. However, Hassanzadeh and Andrews [13] applied infrared absorption spectroscopy to explore the reaction of laser-ablated boron atom with halogen molecules X_2. They characterized the boron halide species BX_n with $n = 1–3$ trapped in solid argon matrix. The band that was red-shifted from the gas-phase fundamental deduced from the emission study was assigned to the reactive species BX. A theoretical calculation based on AM1 predicts the dipole moment of the BBr molecule to be 2.56 D, which is larger than that of the BCl molecule (1.74 D) estimated by the same method [14].

Recently we detected the transient silicon monobromide cation produced in a glow discharge through gaseous silicon tetrabromide [15]. This stimulated us to further explore a bromine-containing molecule. In

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the present study, we have observed the microwave spectrum of various isotopic species of the boron monobromide molecule produced in the glow discharge through boron tribromide. From the analysis of the transition frequencies, we have determined the rotational and the centrifugal distortion constants through the Dunham expansion. The data yield the equilibrium bond distances with the small but distinct difference for the various isotopic species, which means that the Born–Oppenheimer approximation is not valid for this molecule.

2. Experimental

The spectrometer used has already been described elsewhere [16]. It is of a source modulation type and controlled by a small dedicated computer. The microwave source is a millimeter-wave klystron followed by a multiplier (tripler or quadrupler). The quadrupler produced spurious quintuple output which could be used to observe the spectrum in the high frequency region. The frequency of the source microwave was determined by detecting a beat signal between the millimeter wave and the phase stabilized centimeter wave. A pyrex cell was cooled with liquid nitrogen which flowed through a pipe soldered on a copper jacket. The cell temperature was monitored with thermometers composed of semiconductor diodes. A photoconductive InSb detector cooled to the liquid He temperature was used to detect the microwave absorption. The output of the detector was amplified and detected by a phase-sensitive detector and further processed by a computer.

By referring to the method of production for the boron monochloride [4] we adopted the discharge through the vapor of boron tribromide, a liquid of transparent pale yellow color with a boiling point of 91°C. The initial search for the BBr spectrum was made under the experimental conditions similar to those for the optimum production of boron monochloride. The rotational transition frequencies were calculated for the 260 GHz region, where our spectrometer had high sensitivity. For this first prediction, the rotational constant and the centrifugal distortion constant were taken for the isotopic species $^{11}B^{79}Br$ reported by Destoky et al. [12]. The rotational transition for J = 9–8 was calculated to fall around 263–245 MHz. We searched for lines ascribable to unstable molecules on an oscilloscope and detected several lines which could definitely be recognized on the oscilloscope. A line, which was observed about 65 MHz higher than the predicted frequency, disappeared quickly after the discharge was stopped. This line did not show any paramagnetic behavior, that is, the line did not vanish on application of the magnetic field. This suggested that the carrier molecule was short-lived and diamagnetic. It disappeared when oxygen was added to the system. We provisionally assigned this species to boron monobromide. Definite assignment would be possible by observing the same rotational transition of the bromine isotopic species $^{11}B^{81}Br$. The frequency was estimated from the reduced mass dependence of the rotational constants. We observed a line with almost equal intensity near the predicted frequency, to confirm the molecular species to be BBr.

The experimental conditions were then optimized by observing the rotational transition line just detected. The sample pressure was maintained at 30–40 mtorr. Higher discharge currents led to the higher intensities of the spectrum, but produced simultaneously larger noises. Thus the current was selected between 100 and 400 mA. The cell temperature was set between 0 and −30°C. Addition of helium gas to the boron tribromide did not produce any stronger signals but made the discharge more unstable at the above cell temperature.

The above frequency for the most abundant isotopic species yielded the preliminary value of the rotational constant, from which those of other isotopic species could be estimated using the following equations between the Dunham constants

$$\frac{Y^*_{lm}}{Y_{lm}} = \left(\frac{\mu}{\mu^*}\right)^{\frac{1+2m}{2}}$$

where Y_{lm} and μ are the Dunham coefficient and the reduced mass of the molecule, respectively, with an asterisk for the isotopic species. The rotational spectra of four isotopic species of BBr were thus observed. The number of rotational transitions observed is 6 for the species in the ground vibrational state. For the transitions with smaller J values, i.e. J = 7–6 and 4–3, we were able to observe hyperfine splittings owing to the nuclear quadrupole interaction of the bromine nucleus. Figure 1 shows the spectrum of the $J = 7$–6 transition for the $^{11}B^{79}Br$ species in the vibrational ground state. The spectrum shows two lines, each of which is a composite of two hyperfine components owing to the bromine nucleus with $I = 3/2$. The corresponding hyperfine splitting owing to the boron nucleus, $I(^{11}B) = 3/2$ and $I(^{10}B) = 3$, was too small to be detected in the observed transitions. In the highest frequency region the spectrum of the vibrationally excited species up to $v = 4$ could be observed. The measured frequencies for the ^{11}B and ^{10}B species are given in Tables 1 and 2, respectively, together with the rotational and vibrational assignments.

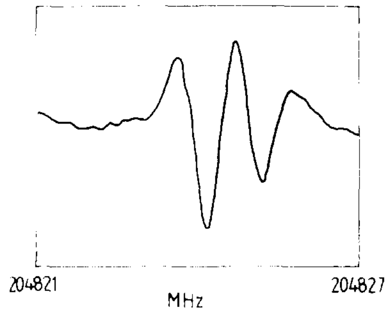

Fig. 1. The $J = 7$–6 transition of $^{11}B^{79}Br$ in the vibrational ground state near 204 825 MHz. The splitting is due to the nuclear quadrupole interaction. The lower frequency line is a composite line of $F = 17/2$–$15/2$ and $15/2$–$13/2$ and the higher one a composite of $F = 13/2$–$11/2$ and $11/2$–$9/2$.

Table 1
Observed frequencies for $^{11}B^{79}Br$ and $^{11}B^{81}Br$

v	J'	F'	←	J''	F''	Frequency (MHz)	$^{11}B^{79}Br$ O.–C. [MHz]	Weight	Frequency (MHz)	$^{11}B^{81}Br$ O.–C. [MHz]	Weight
0	4	4.5	←	3	3.5	117057.574	−0.002	0.5	116704.737	0.013	0.5
0	4	5.5	←	3	4.5	117057.574	−0.002	0.5	116704.737	0.013	0.5
0	4	2.5	←	3	1.5	117061.464	0.024	0.5	116707.952	0.000	0.5
0	4	3.5	←	3	2.5	117061.464	0.024	0.5	116707.952	0.000	0.5
0	7	7.5	←	6	6.5	204824.417	0.052	0.5	204206.850	0.034	0.5
0	7	8.5	←	6	7.5	204824.417	0.052	0.5	204206.850	0.034	0.5
0	7	5.5	←	6	4.5	204825.466	0.010	0.5	204207.731	0.004	0.5
0	7	6.5	←	6	5.5	204825.466	0.010	0.5	204207.731	0.004	0.5
0	9		←	8					262517.675	0.009	1.0
0	9	9.5	←	8	8.5	263311.320	0.064	0.5			
0	9	10.5	←	8	9.5	263311.320	0.064	0.5			
0	9	7.5	←	8	6.5	263311.873	−0.025	0.5			
0	9	8.5	←	8	7.5	263311.873	−0.025	0.5			
0	10		←	9		292545.503	−0.026	1.0	291663.622	0.032	1.0
0	13		←	12		380201.433	−0.036	1.0	379055.565	0.036	1.0
0	16		←	15		467773.025	0.035	1.0	466363.782	0.081	0.1
1	7	7.5	←	6	6.5	203061.898	0.016	0.5	202452.277	−0.016	0.5
1	7	8.5	←	6	7.5	203061.898	0.016	0.5	202452.277	−0.016	0.5
1	7	5.5	←	6	4.5	203063.009	0.036	0.5	202453.192	−0.012	0.5
1	7	6.5	←	6	5.5	203063.009	0.036	0.5	202453.192	−0.012	0.5
1	9		←	8		261045.574	−0.046	1.0	260261.935	−0.047	1.0
1	10		←	9		290027.933	−0.002	1.0	289157.299	−0.067	0.1
1	13		←	12		376929.016	0.012	1.0	375797.905	−0.008	1.0
2	9		←	8		258800.786	−0.034	1.0	258027.268	−0.021	1.0
2	13		←	12		373687.101	−0.015	1.0	372570.581	−0.037	1.0
3	9		←	8		256576.862	−0.014	1.0	255813.316	−0.011	1.0
3	13		←	12		370475.332	−0.021	1.0	369373.245	−0.023	1.0
4	9		←	8		254373.406	−0.118	0.1	253619.846	0.011	1.0
4	13		←	12		367293.342	0.006	1.0	366205.474	−0.013	1.0

Table 2
Observed frequencies for $^{10}B^{79}Br$ and $^{10}B^{81}Br$

v	J'	F'	←	J''	F''	Frequency (MHz)	$^{10}B^{79}Br$ O.–C. (MHz)	Weight	Frequency (MHz)	$^{10}B^{81}Br$ O.–C. (MHz)	Weight
0	4	4.5	←	3	3.5	127254.479	–0.007	0.5	126901.758	0.015	0.5
0	4	5.5	←	3	4.5	127254.479	–0.007	0.5	126901.758	0.015	0.5
0	4	2.5	←	3	1.5	127258.341	–0.009	0.5	126905.081	0.109	0.05
0	4	3.5	←	3	2.5	127258.341	–0.009	0.5	126905.081	0.109	0.05
0	7	7.5	←	6	6.5	222663.902	0.003	0.5	222046.578	0.022	0.5
0	7	8.5	←	6	7.5	222663.902	0.003	0.5	222046.578	0.022	0.5
0	7	5.5	←	6	4.5	222664.970	–0.020	0.5	222047.436	–0.031	0.5
0	7	6.5	←	6	5.5	222664.970	–0.020	0.5	222047.436	–0.031	0.5
0	8		←	7		254456.423	–0.052	1.0	253750.849	–0.103	0.1
0	9		←	8		286241.681	–0.096	0.1	285448.164	–0.024	1.0
0	12		←	11		381548.280	–0.008	1.0	380490.754	–0.017	1.0
0	15		←	14		476762.842	–0.056	1.0	475441.878	–0.019	1.0
1	7	7.5	←	6	6.5	220666.372	–0.024	0.5	220057.377	0.028	0.5
1	7	8.5	←	6	7.5	220666.372	–0.024	0.5	220057.377	0.028	0.5
1	7	5.5	←	6	4.5	220667.522	0.035	0.5	220058.252	–0.008	0.5
1	7	6.5	←	6	5.5	220667.522	0.035	0.5	220058.252	–0.008	0.5
1	12		←	11		378124.734	0.031	1.0	377081.422	0.019	1.0
2	7	7.5	←	6	6.5	218688.292	–0.005	0.5	218087.466	0.026	0.5
2	7	8.5	←	6	7.5	218688.292	–0.005	0.5	218087.466	0.026	0.5
2	7	5.5	←	6	4.5	218689.384	–0.004	0.5	218088.383	0.032	0.5
2	7	6.5	←	6	5.5	218689.384	–0.004	0.5	220088.383	0.032	0.5
2	12		←	11		374734.426	0.044	1.0	373705.145	0.030	1.0
3	12		←	11		371377.028	0.134	0.1	370361.609	0.130	0.1

3. Results and discussion

To analyze the observed spectrum of isotopomers separately we used the Dunham expression for the vibrational–rotational energy levels. Molecular constants were determined with a least-squares fit to the transition frequencies. The equilibrium rotational constants obtained in this analysis enabled us to calculate the bond length of the molecule. The bond lengths for the four isotopomers were found to be different from one another over the standard deviations. This suggested that the Born–Oppenheimer approximation, according to which all the isotopic species should have the same equilibrium bond length, was not applicable to this molecule.

Thus the observed frequencies for the four isotopic species were globally fitted according to the method of Watson [17]. The program used for the global fit was the same as that employed by Saleck et al. [18]. This analysis used the isotopically invariant Dunham-type expansions for various molecular constants, including the hyperfine interaction constants. In the fit the ratio of the quadrupole moments $Q(^{79}Br)/Q(^{81}Br) = 1.197052$ [19] was used instead of their absolute values. The value of the quadrupole moment $Q(^{81}Br)$ was then determined in the fit. Non-resolved hyperfine components were calculated as the intensity-weighted averages. The isotopically invariant parameters derived in the present analysis are listed in Table 3.

Also in Table 3, the equilibrium bond lengths for the isotopomers are shown. The error attached to the bond lengths mainly results from the uncertainties of the fundamental constants [21]. The difference between the isotopic bond lengths, however, is not influenced by the precision of the fundamental constants. The Born–Oppenheimer breakdown constants for boron and bromine, Δ_{01}^{B} and Δ_{01}^{Br}, are $-1.7260(61)$ and $-2.28(17)$, respectively. The uncertainty for the second constant is larger than that for the first one. This is reasonable, since the effect of the isotopic substitution of bromine will be smaller than that

Table 3
Isotopically invariant parameters for the BBr molecule

Parameter[a]	Value[b]	Unit
U_{01}^{c}	141992.006 (12)	MHz u
U_{01}^{B}	12.214 (43)	MHz u
U_{01}^{Br}	2.25 (16)	MHz u
U_{02}	−2.81008 (26)	MHz u^2
U_{11}	−3816.587 (70)	MHz $u^{3/2}$
U_{21}	55.778 (97)	MHz u^2
U_{31}	−0.705 (42)	MHz $u^{5/2}$
U_{12}	0.0279 (26)	MHz $u^{5/2}$
U_{13}	0.000264 (75)	MHz $u^{7/2}$
$eQq(^{81}Br)$	111.30 (65)	MHz
derived:		
$eQq(^{79}\mathrm{Br})$	133.23 (78)	MHz
$r_e(^{11}\mathrm{B}^{79}\mathrm{Br})$	1.88658632 (79)	Å
$r_e(^{11}\mathrm{B}^{81}\mathrm{Br})$	1.88658595 (79)	Å
$r_e(^{10}\mathrm{B}^{79}\mathrm{Br})$	1.88659439 (79)	Å
$r_e(^{10}\mathrm{B}^{81}\mathrm{Br})$	1.88659402 (79)	Å
Δ_{01}^{B}	−1.7260 (61)	
Δ_{01}^{Br}	−2.28 (17)	

[a] $U_{01} = U_{01}^{c} + U_{01}^{B}\left(1 - \frac{M_B^0}{M_B}\right) + U_{01}^{Br}\left(1 - \frac{M_{Br}^0}{M_{Br}}\right)$[20]. The atomic masses M_B^0 and M_{Br}^0 in the reference isotopomer, here $^{11}\mathrm{B}^{79}\mathrm{Br}$, were taken from Ref. [21].

[b] Values in brackets: 1σ.

owing to the boron substitution. The B–Br bond length (1.886 Å) in the BBr radical is slightly shorter than the length 1.893(5) Å in the BBr_3 molecule [22].

The nuclear electric quadrupole interaction constants eQq in BBr have been determined for the first time in the present study. The quadrupole hyperfine interaction constant reflects the electron distribution and thus is a good measure of the ionic character of a chemical bond in the molecule. The ionicity i_c of the B–Br bond is calculated from the observed eQq value using the following equation [23]:

$$eQq = -\left(\frac{1-i_c}{1+\varepsilon i_c}\right) eQq_{n10},$$

where ε is equal to 0.15 for halogen atoms other than fluorine. The atomic values of eQq_{n10} are 109.74, −769.76 and 2292.71 MHz for ^{35}Cl, ^{79}Br and ^{127}I, respectively [23]. The ionicity of the BBr bond is found to be 81% and the species can be regarded as a rather polar molecule with the electron displaced from the boron atom toward the bromine atom. The ionicity of boron monohalides is compared with that of aluminum compounds in Table 4. It can be seen that the latter molecules have generally larger ionicity. The BBr molecule has marginally smaller ionicity than aluminum monobromide and also than boron monochloride. The latter fact corresponds to the larger electronegativity of the chlorine atom in comparison with the bromine atom and thus to the higher attraction of the electron by the chlorine atom. The aluminum atom is regarded as more metallic than the boron atom, so that it has a higher tendency to transfer the electron cloud toward an electronegative halogen atom.

Table 4
Ionic character (%) i_c for boron and aluminum monohalides

	i_c	Ref.		i_c	Ref.
BCl	83	[4]	AlCl	91	[24]
BBr	81	present	AlBr	88	[25]
BI	– –	—	AlI	85	[26]

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