ROTATIONAL SPECTRUM AND HYPERFINE STRUCTURE IN THE X $^2\Sigma^+$ STATE OF BaBr

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The rotational structure in the $^2\Sigma^+$ ground state of BaBr has been analysed for the first time Precise Dunham coefficients have been derived from microwave spectra in the 100 GHz range for the two isotopes ^{138}Ba^{79}Br and ^{138}Ba^{81}Br. Hyperfine structure has been partially resolved in one rotational transition of ^{137}Ba^{79}Br Hyperfine coupling parameters *b*, *c* and *eqQ* for ^{137}Ba, and *b* for ^{79}Br, have been determined

1. Introduction

In a series of papers [1–6] we have reported microwave rotational spectra of the Ca, Sr and Ba monohalides in their $^2\Sigma^+$ ground state, except CaF and BaBr For CaF very precise rotational and hyperfine coupling parameters have been given in the literature [7–12] The most recent rotational analysis of the optical spectrum was performed by Dulick et al. [9], while fine and hyperfine coupling parameters of very high precision have been determined by Childs et al [12] using the molecular-beam laser–rf double-resonance technique. We have measured one rotational transition of CaF and its spin–rotation and hyperfine splitting The transition frequencies were found to agree with predictions based on the data given in refs [9,12] well within the quoted errors and only a minor improvement of the rotational constants seemed possible Since the production of CaF was difficult under the low-pressure conditions necessary for high-resolution microwave spectroscopy, no such attempt has been made

For BaBr, on the other hand, no preliminary rotational constants were available from optical spectra Searching for microwave transitions is then expected to be a tedious and time-consuming enterprise. Fortunately the variation of internuclear distances among the alkaline earth monohalides turned out to show a very regular and smooth systematic behavior. It was thus possible to deduce the unknown rotational constants of BaBr with high accuracy and to predict the mw transitions to within 50 MHz. BaBr was produced in a high-temperature reaction

$$BaBr_2 + Ba \xrightarrow{T > 1200\ K} 2BaBr. \qquad (1)$$

The concentration of BaBr obtained in this way was just sufficient to encourage a search for the ^{137}Ba^{79}Br isotope (5 5% natural abundance) which shows a well resolved hyperfine structure due to a large Fermi contact interaction with the Ba nucleus Despite the very poor signal-to-noise ratio, we were able to observe the small additional splitting which is due to hyperfine interaction with the bromine nucleus and which cannot be resolved for the ^{138}BaBr isotopes with $I_1 = 0$

2. Rotational spectrum of ^{138}Ba^{79}Br and ^{138}Ba^{81}Br

BaBr produced by reaction (1) evaporated from a hot oven into a cold free space absorption cell entrained in a stream of argon buffer gas. The total pressure in the absorption cell was kept at about 0 01 Torr. The full width of the lines was about 200 kHz under these conditions, mainly due to pressure broadening. Saturation effect modulation [13] was used for sensitive detection

Rotational transitions of the two isotopes

Table 1
Frequencies of rotational transitions $N \to N+1, J \to J+1$ for $^{138}Ba^{79}Br$ and $^{138}Ba^{81}Br$

$^{138}Ba^{79}Br$					$^{138}Ba^{81}Br$				
v	N	J	observed frequency (MHz)	obs. − calc (kHz)	v	N	J	observed frequency (MHz)	obs. − calc (kHz)
0	35	35.5	89446.848	−3	0	36	36.5	90486.409	4
		34.5	89396.075	15			35.5	90436.438	0
1	35	35.5	89183.773	5	2	36	36.5	89958.619	−4
		34.5	89133.218	1			35.5	89909.114	−2
0	36	36.5	91928.311	−2	3	36	36.5	89695.188	−1
		35.5	91877.494	−25			35.5	89645.910	0
1	36	36.5	91657.930	5	5	36	36.5	89169.231	1
		35.5	91607.380	11			35.5	89120.413	2
2	36	36.5	91387.854	3	0	43	43.5	107578.647	−8
		35.5	91337.533	−2			42.5	107528.650	−3
3	36	36.5	91118.096	3	1	43	43.5	107264.675	1
		35.5	91068.010	−6			42.5	107214.897	4
4	36	36.5	90848.641	−10	2	43	43.5	106951.038	1
		35.5	90798.804	−9			42.5	106901.498	4
5	36	36.5	90579.522	−1	3	43	43.5	106637.763	−7
		35.5	90529.937	13			42.5	106488.458	1
0	43	43.5	109292.554	−9	4	43	43.5	106324.868	3
		42.5	109241.745	1			42.5	106275.776	−5
1	43	43.5	108971.030	3	5	43	43.5	106012.322	1
		42.5	108920.461	14			42.5	105963.466	0
2	43	43.5	108649.874	8					
		42.5	108599.517	−7					
3	43	43.5	108329.075	−4					
		42.5	108278.973	−4					
4	43	43.5	108008.667	−1					
		42.5	107958.799	−5					
5	43	43.5	107688.634	3					
		42.5	107639.009	3					

$^{138}Ba^{79}Br$ and $^{138}Ba^{81}Br$ have been measured in the frequency range between 89 and 108 GHz in vibrational states up to $v = 5$. The transition frequencies are listed in table 1. They have been fitted to the expression for the rotational energy of a $^2\Sigma$ molecule:

$$E = B_{\text{eff}} N(N+1) + \tfrac{1}{2}\gamma_{\text{eff}} N \quad \text{for } J = N + \tfrac{1}{2},$$

$$= B_{\text{eff}} N(N+1) - \tfrac{1}{2}\gamma_{\text{eff}} (N+1) \quad \text{for } J = N - \tfrac{1}{2},$$

with

$$B_{\text{eff}} = Y_{01} + Y_{11}(v+\tfrac{1}{2}) + Y_{21}(v+\tfrac{1}{2})^2 + [Y_{02} + Y_{12}(v+\tfrac{1}{2})]\, N(N+1) \tag{2}$$

and

$$\gamma_{\text{eff}} = \gamma_{00} + \gamma_{10}(v+\tfrac{1}{2}) + \gamma_{01} N(N+1).$$

The two isotopes have been fitted independently. The consistency of the measurements can then be checked by testing the mass relations between the Dunham coefficients Y_{jk} for the two isotopes labeled by superscripts 1 and 2:

$$Y^1_{jk}/Y^2_{jk} = (\mu^2/\mu^1)^{(j+2k)/2}, \tag{3}$$

where μ^1 and μ^2 stand for the reduced masses of the two isotopes. Eq. (3) should hold in the framework of the Born–Oppenheimer approximation. Small deviations of the order of 10^{-6} from this relation have been observed for the rotational constant Y_{01} of many diatomic molecules [14]. They may be due to adiabatic and non-adiabatic corrections to the Born–Oppenheimer approximation or – as has been shown recently [15] – even to isotopic changes in the nuclear

Table 2
Molecular constants of ^{138}Ba^{79}Br and ^{138}Ba^{81}Br. Numbers in parentheses represent 1σ errors

	^{138}Ba^{79}Br	^{138}Ba^{81}Br
Y_{01} (MHz)	1244.38440(24)	1224.84239(19)
Y_{11} (MHz)	−3.656110(91)	−3.570300(62)
Y_{21} (kHz)	2.1300(94)	2.0530(53)
Y_{02} (kHz)	−0.228402(74)	−0.221294(53)
Y_{12} (Hz)	−0.158(23)	−0.146(15)
γ_{00} (MHz) [a]	50.852(21)	49.997(15)
γ_{10} (MHz)	−0.2390(22)	−0.2293(13)
γ_{01} (Hz) [a]	14.9(43)	20.6(28)
ω_e (cm^{-1})	193.772(31)	192.241(23)
$\omega_e x_e$ (cm^{-1})	0.4133(25)	0.4061(17)
(amu) [b]	50.1940433(18)	50.9948919(26)
r_e (Å) [c]	2.8445286(99)	
a_0 (cm^{-1})	2.26141(63) × 10^5	
a_1	−3.28594(10)	
a_2	6.865(33)	
a_3	−10.70(26)	

[a] Perturbed by effects of unresolved hyperfine structure.
[b] Atomic masses from ref. [16].
[c] Conversion factor 505390.98 ± 3.5 from ref. [17].

charge distribution. No such effect can be observed for the two BaBr isotopes as can be seen from the results in table 2. All Y_{jk} fulfil eq. (1) within the experimental errors. The spin–rotation interaction constants γ_{jk} are expected to obey a similar mass relation [18]:

$$\gamma^1_{jk}/\gamma^2_{jk} = (\mu^2/\mu^1)^{(j+2k+2)/2} . \tag{4}$$

However, in contradiction to this prediction we find from the results of table 2 that $\gamma_{01}(^{138}\mathrm{Ba}^{81}\mathrm{Br}) > \gamma_{01}(^{138}\mathrm{Ba}^{79}\mathrm{Br})$. Obviously γ_{01} is strongly distorted. It has been shown in ref. [2] for the case of CaBr that this is due to effects of unresolved hyperfine structure. The value given in table 2 may therefore be considered only as a fit parameter and has no well defined physical meaning. Perturbation of γ_{01} will also cause a systematic shift in the values of γ_{00}. This shift may be two orders of magnitude larger than the statistical errors from the fit given in table 2. The Dunham coefficients Y_{jk} are related to r_e and to the coefficients a_i of the power series describing the internuclear potential [19]. These isotopically independent constants are also listed in table 2. The vibrational constants ω_e and $\omega_e x_e$ have been calculated from the a_i. They are consistent with data from band spectra given in the tables of Huber and Herzberg [20] but are one order of magnitude more accurate. From the internuclear distance r_e the electric dipole moment of BaBr can be estimated using an electrostatic bond model [21]. With the ion polarizabilities given in ref. [21] this model predicts μ_e(BaBr) = 5.57 D. As in all cases which have been experimentally tested so far this prediction is expected to be a few percent too large.

3. Hyperfine structure in the spectrum of ^{137}Ba^{79}Br

In a previous paper [3] we analysed the hyperfine structure in ^{137}BaF and ^{137}BaCl. It was challenging to extend these measurements to ^{137}BaBr since the result can give information if there is any noticeable trend in the electronic structure of the Ba halides. The extremely poor signal-to-noise ratio due to the low natural abundance of ^{137}Ba and the additional hyperfine splitting made this a difficult enterprise.

The hyperfine structure is dominated by the strong Fermi contact interaction between the unpaired electron spin and the ^{137}Ba nucleus with $I_1 = 3/2$. This results in a coupling of angular momenta intermediate between Hund's case $b_{\beta S}$ for low rotational states and $b_{\beta J}$ for very high N values. Coupling of the bromine nucleus is weak. So F_1 remains rather well defined and energy levels may be labeled by F, F_1, J and N. Only transitions with selection rules $\Delta F = \Delta F_1 = \Delta J = \Delta N = +1$ have been observed. Matrix elements for the calculation of energy levels in the case of two coupling nuclei are given in ref. [3].

The results of the measurements and the calculations are listed in table 3. The spectrum is mainly determined by the strong coupling of the Ba nucleus. The additional splitting of the F_1 components due to the Br coupling with $I_2 = 3/2$ is only partially resolved. For the transitions with the highest and lowest possible values of F_1 this splitting is negligible. These lines located at the upper and lower end of the spectrum have an experimental full linewidth of 200 kHz determined by pressure broadening and the Doppler effect. The next inner transitions with $F_1 = 36$ and $J = 35 \pm \frac{1}{2}$ show an experimental linewidth of 600 kHz due to unresolved hyperfine structure from the bromine interaction. This is in good agreement with the calculated spectrum. For the two transitions with $F_1 = 35$ it was possible to resolve the bromine hyperfine structure although the four lines are located within only 1 MHz.

Table 3
Rotational transition $N = 35 \to 36, J \to J + 1, F_1 \to F_1 + 1$ of $^{137}\mathrm{Ba}^{79}\mathrm{Br}$

J	F_1	F	Observed (MHz)	Calc. (MHz)	Obs. – calc (kHz)
34.5	33	31.5 34.5 32.5 33.5	89633.329	89633.316 89633.326 89633.328 89633.330	4
	36	37.5 36.5 35.5 34.5	89640.599	89640.372 89640.534 89640.692 89640.843	–11
	35	36.5	89648.956	89648.978	–22
		35.5	89649.268	89649.283	–15
		34.5	89649.565	89649.598	–33
		33.5	89649.892	89649.926	–34
	34	32.5 33.5 34.5 34.5	not observed	89655.297 89655.752 89656.198 89656.637	
35.5	34	35.5 34.5 33.5 32.5	not observed	89660.917 89661.352 89661.790 89662.231	
	35	33.5	89667.524	89667.583	–59
		34.5	89667.910	89667.921	–11
		35.5	89668.237	89668.247	–10
		36.5	89668.520	89668.562	–42
	36	34.5 35.5 36.5 37.5	89676.922	89676.655 89676.827 89676.995 89677.161	12
	37	36.5 35.5 37.5 38.5	89684.218	89684.181 89684.187 89684.190 89684.210	26

Intensity of these lines was extremely poor and extensive signal averaging had to be used. This lack of intensity unfortunately prevented the observation of the inner transition with $F_1 = 34$ which should be slightly better resolved.

It can be seen from the theory that the influence of the barium hyperfine structure on the transition frequencies of the outer components with $F_1 = 33$ and 37 is negligibly small. These frequencies can therefore be calculated using the constants of table 2 and the mass relations (3) and (4) Since the results agree with the observed frequencies within the experimental errors these constants can be kept fixed and only the hyperfine constants for both atoms have to be fitted to the observed splitting

This can be done in two steps First the three hyperfine parameters b, c and eqQ for the Ba nucleus are fitted to the six observed F_1 transitions taking the average frequency for the split $F_1 = 35 \to 36$ transitions. Information about the bromine coupling constants is contained in the observed splitting of these two transitions. Since the four components are equally spaced within the experimental uncertainties only the constant $b(^{79}\mathrm{Br})$ which has the strongest influence

Table 4
Hyperfine structure parameters of ^{137}BaX molecules (X = F, Cl or Br. All constants given in MHz)

	^{137}Ba^{19}F, ref [3]	^{137}Ba^{37}Cl, ref [3]	^{137}Ba^{79}Br, this work
b(Ba)	2301(9)	2314(9)	2306(13)
c(Ba)	75(6)	96(20)	99(23)
eqQ(Ba)	−117(12)	−134(42)	−93(60)
b(X)	60(6)		71(7)

on the line positions can be determined

Despite the very poor signal-to-noise ratio, the resulting hyperfine parameters reproduce the observed transition frequencies surprisingly well The parameters are listed in table 4 with the corresponding data for ^{137}Ba^{19}F and ^{137}Ba^{37}Cl given for comparison [3] The most striking result is that the Fermi contact interaction ($b + \frac{1}{3} c$) and therefore the percentage of s character of the unpaired electron is essentially the same in the three molecules, possible variations are less than 1%. Information about the s and p admixture to the wavefunction are contained in the constants c and eqQ A precise knowledge of the mixing coefficients would be very useful since they are related to the electric dipole moment of the molecule and could be compared with predictions from the bond model proposed in ref [21]. However, the large experimental errors of the data prevent a meaningful analysis

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