

## MICROWAVE ROTATIONAL SPECTRA OF ALKALINE EARTH MONOHALIDES: CaI AND BaI

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Rotational spectra in the  $^2\Sigma^+$  ground state of CaI and BaI have been measured in the 100 GHz range. Precise Dunham coefficients  $Y_{ik}$  and potential constants  $a_i$  can be derived from these spectra. Effects of unresolved hyperfine structure have to be considered in the interpretation of the observed  $\gamma$ -splitting

### 1. Introduction

In a series of papers we have reported millimeter wave spectra of the molecules BaF, BaCl, CaCl, CaBr, SrF and SrCl [1–4]. This systematic study of rotational spectra of the alkaline-earth monohalides is here continued with the investigation of CaI and BaI.

The optical A–X and B–X transitions in this group of molecules, especially for the heavy iodides, are very dense so that even with the use of sub-Doppler laser techniques, the spectra are often only partially resolved. The knowledge of precise ground-state data from other measurements is therefore highly desirable. This information can be obtained by a combination of different experimental techniques. The Dunham coefficients may be determined by microwave spectroscopy in the millimeter range. Although the doubling of the rotational transitions by spin–rotation interaction can also readily be observed by this technique, it has been shown that effects of unresolved hyperfine structure may give rise to systematic errors in the determination of the constant  $\gamma$  from microwave spectra [2,3]. Fully resolved spectra have been obtained either by microwave–optical polarization spectroscopy (MOPS) [5–8] or by molecular-beam, laser–rf (or laser–microwave) double resonance [9–15]. The latter technique gives by far the highest precision and resolution but it requires a rather detailed knowledge of the Doppler-free optical spectrum. Recently this technique has been applied to study elec-

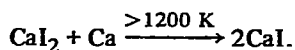
tric dipole moments of CaCl [16,17], CaBr [18], CaF [19] and SrF [20]. These results are in good agreement with predictions from a simple electrostatic bond model [21].

The first rotational analysis of the CaI optical spectrum was performed by Reisner et al. [22] in 1981. Rotational constants for several vibrational states were given from an analysis of the A–X and B–X systems. The optical data were completed by Bernath et al. [23] who derived hyperfine constants from sub-Doppler spectra. Highly precise ground-state data of hyperfine constants and the spin–rotation interaction were recently published by Childs et al. [14]. This set of precise ground-state data is now completed by the Dunham coefficients given in this paper.

Much less complete information is presently available for BaI. Only a preliminary rotational constant derived from the analysis of the optical C–X system was published by Johnson et al. [24] in 1981 although sub-Doppler techniques and population labeling had been used to unravel this highly congested spectrum. The present search for the microwave spectrum was based on this result. No reliable hyperfine structure data are presently available, the congestion of the optical spectrum preventing an unequivocal analysis. We expect that these data will be provided in the near future by a molecular-beam, laser–microwave double-resonance experiment which is in progress in our laboratory.

## 2. Calcium iodide

CaI was produced by the reaction



The substance evaporated from the oven through a small slit into a cold free space absorption cell entrained in a stream of argon buffer gas. The total oven pressure was about a few Torr under these conditions while the pressure in the absorption region was kept at about 0.01 Torr to prevent excessive pressure broadening. As in the previous experiments [1-4], saturation modulation [25] was used. The high sensitivity obtained by this technique allowed measurements of rotational transitions in vibrational states up to  $v = 4$ . The observed linewidth was about 350 kHz,

somewhat larger than expected from pressure broadening under the experimental conditions. A slight asymmetry of the lineshape indicated the presence of unresolved hyperfine structure. The observed transition frequencies are listed in table 1. Lines have been fitted neglecting all possible effects from hyperfine structure. The energy levels are then given by:

$$\begin{aligned} E &= B_{\text{eff}}N(N+1) + \frac{1}{2}\gamma_{\text{eff}}N, & \text{for } J = N + \frac{1}{2}; \\ &= B_{\text{eff}}N(N+1) - \frac{1}{2}\gamma_{\text{eff}}(N+1), & \text{for } J = N - \frac{1}{2}; \end{aligned} \quad (1)$$

with

$$\begin{aligned} B_{\text{eff}} &= Y_{01} + Y_{11}(v + \frac{1}{2}) + Y_{12}(v + \frac{1}{2})^2 \\ &+ [Y_{02} + Y_{12}(v + \frac{1}{2})]N(N+1) \end{aligned}$$

Table 1  
Frequencies of rotational transitions  $N \rightarrow N+1$ ;  $J \rightarrow J+1$  for CaI

$J$	$v$	$N$	$\nu_{\text{obs}}$ (MHz)	$\nu_{\text{calc}}$ (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (MHz)
21.5	0	21.0	91328.084	91328.092	-0.008
20.5	0	21.0	91159.605	91159.606	-0.001
21.5	1	21.0	90980.739	90980.745	-0.006
20.5	1	21.0	90813.461	90813.452	0.009
21.5	2	21.0	90634.115	90634.105	0.010
20.5	2	21.0	90468.016	90468.004	0.012
21.5	3	21.0	90288.156	90288.172	-0.016
20.5	3	21.0	90123.271	90123.262	0.009
21.5	4	21.0	89942.953	89942.945	0.008
20.5	4	21.0	89779.200	89779.227	-0.027
24.5	0	24.0	103760.544	103760.542	0.002
23.5	0	24.0	103592.054	103592.056	-0.002
24.5	1	24.0	103365.910	103365.911	-0.001
23.5	1	24.0	103198.613	103198.618	-0.005
24.5	2	24.0	102972.078	102972.083	-0.005
23.5	2	24.0	102805.976	102805.982	-0.006
24.5	3	24.0	102579.065	102579.058	0.007
23.5	3	24.0	102414.139	102414.148	-0.009
24.5	4	24.0	102186.858	102186.836	0.022
23.5	4	24.0	102023.144	102023.118	0.026
25.5	0	25.0	107903.875	107903.872	0.003
24.5	0	25.0	107735.391	107735.387	0.004
25.5	1	25.0	107493.492	107493.480	0.012
24.5	1	25.0	107326.178	107326.187	-0.009
25.5	2	25.0	107083.923	107083.923	0.000
24.5	2	25.0	106917.817	106917.821	-0.004
25.5	3	25.0	106675.196	106675.201	-0.005
24.5	3	25.0	106510.297	106510.291	0.006
25.5	4	25.0	106267.289	106267.313	-0.024
24.5	4	25.0	106103.592	106103.596	-0.004

and

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

It turned out that  $Y_{12}$  and  $\gamma_{01}$  gave no significant contribution so that they were dropped in the final fit.

The Dunham coefficients  $Y_{ik}$  are related to the coefficients  $a_i$  of the power series describing the molecular potential [26]. The coefficients  $a_0$  to  $a_3$  can thus be derived from the experimentally determined  $Y_{ik}$  and from these  $a_i$  the additional Dunham parameters  $Y_{10} \approx \omega_e$  and  $Y_{20} \approx -\omega_e x_e$  can be calculated. The results are summarized in table 2. A comparison with

the results of Reisner et al. [22] shows the high quality of these optical measurements. Most results agree within  $\pm 1\sigma$  with the microwave data. The largest deviation is for  $\omega_e$  where it is still within  $3\sigma$ . The discrepancy between our result for  $\gamma_{00}$  and the correct value given by Childs et al. [14] again demonstrates the systematic error introduced by neglecting effects of unresolved hyperfine structure. Since precise hyperfine constants are given in ref. [14] these systematic shifts of the microwave transitions can be calculated. In table 3 calculated frequencies are given for the rotational transition  $N = 25 \rightarrow 26, J \rightarrow J + 1, F \rightarrow F + 1$ .

Table 2  
Molecular constants of CaI

	This work a)	Ref. [22] b)	Ref. [14]
$Y_{01}$ (MHz)	2078.34940(40)	2078.33(25)	
$Y_{11}$ (MHz)	-7.89675(15)	-7.914(105)	
$Y_{21}$ (kHz)	8.029(29)		
$Y_{02}$ (kHz)	-0.70164(31)	-0.702	
$\gamma_{00}$ (MHz)	[169.081(10)]	168.4(3)	169.7257(1)
$\gamma_{10}$ (MHz)	-1.1919(33)	-0.93(33)	-1.1884(1)
$\gamma_{01}$ (MHz)			$-1.7463(3) \times 10^{-4}$
$a_0$ ( $\text{cm}^{-1}$ )	$2\ 05353(90) \times 10^5$		
$a_1$	-3.179772(72)		
$a_2$	6.59533(36)		
$a_3$	-10.6245(63)		
$\omega_e$ ( $\text{cm}^{-1}$ )	238.633(52)	238.7496(33)	
$\omega_e x_e$ ( $\text{cm}^{-1}$ )	0 6284(1)	0 62789(64)	
$r_e$ (Å)	2.828619(10)	2.8286(2)	

a)  $\mu_{\text{red}} = 30.39204645(60)$  amu [27] and a conversion factor  $505390.98 \pm 3.5$  amu Å<sup>2</sup> MHz [28] have been used.

b) Data have been partly converted from  $\text{cm}^{-1}$  to MHz.

Table 3  
Theoretical hyperfine splitting in the rotational transition  $N = 25 \rightarrow 26; J \rightarrow J + 1; F \rightarrow F + 1$  of CaI

$F$	$J$	$\nu_{\text{calc}}$ a)	$\nu_{\text{av}}$	$\nu_{\text{exp}}$
22	24.5	107735.305	107735.390	107735.391
27	24.5	107735.321		
23	24.5	107735.348		
24	24.5	107735.423		
26	24.5	107735.465		
25	24.5	107735.480		
25	25.5	107903.794	107903.881	107903.875
26	25.5	107903.829		
24	25.5	107003.829		
27	25.5	107903.900		
23	25.5	107903.967		
28	25.5	107903.969		

a)  $\gamma_{\text{eff}}$  and hyperfine constants from ref. [14],  $Y_{ik}$  from this paper have been used for the calculation.

$\gamma_{\text{eff}}$  and hyperfine constants taken from ref. [14] were used in these calculations together with the  $Y_{ik}$  given in this paper. The average frequency of the sextet resulting from the iodine nuclear spin of 5/2 for both  $\gamma$  components is in excellent coincidence with our experimental results.

### 3. Barium iodide

The same apparatus was used to study the rotational spectrum of BaI. This chemically unstable diatomic species was produced by reacting BaI<sub>2</sub> with Ba at temperatures >1300 K. The linewidth was only about 200 kHz and no asymmetry of the lineshape was observed. Measured transition frequencies are listed in table 4. As in the case of CaI, an excellent fit is obtained using formula (1) for the energy levels neglecting hyperfine structure. The resulting molecular constants are given in table 5. Although there is no indication for hyperfine effects from the line-width and -shape, systematic shifts of  $\gamma_{00}$  and  $\gamma_{01}$  must still be considered. For  $\gamma_{00}$  the shift can be roughly estimated by using hfs con-

Table 5  
Molecular constants of BaI

	This work <sup>a)</sup>	Previous work
$Y_{01}$ (MHz)	803.61978(24)	802.8 <sup>d)</sup>
$Y_{11}$ (MHz)	-1.98871(14)	
$Y_{21}$ (kHz)	1.0212(56)	
$Y_{02}$ (Hz)	-99.789(30)	
$Y_{12}$ (Hz)	-0.061(17)	
$\gamma_{00}$ (MHz)	[75.906(26)] <sup>b)</sup>	
	76.05(15) <sup>c)</sup>	
$\gamma_{10}$ (MHz)	-0.3439(22)	
$\gamma_{01}$ (Hz)	[-8(3)] <sup>b)</sup>	
$a_0$ (cm <sup>-1</sup> )	2.15873(65) × 10 <sup>5</sup>	
$a_1$	-3.34091(24)	
$a_2$	7.124(82)	
$a_3$	-11.37(66)	
$\omega_e$ (cm <sup>-1</sup> )	152.140(23)	152.3 <sup>e)</sup>
$\omega_e x_e$ (cm <sup>-1</sup> )	0.2746(33)	0.270 <sup>e)</sup>
$r_e$ (Å)	3.084798(11)	

a)  $\mu_{\text{red}} = 66.0881253(14)$  from ref. [27].

b) Systematic shifts due to effects of unresolved hyperfine structure.

c) Corrected value using estimated values for hyperfine constants.

d) From ref. [24], converted from cm<sup>-1</sup> to MHz.

e) From ref. [29].

Table 4  
Frequencies of rotational transitions  $N \rightarrow N + 1$ ;  $J \rightarrow J + 1$  for BaI

$\nu$	$N$	$J$	$\nu_{\text{obs}}$ (MHz)	$\nu_{\text{calc}}$ (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (MHz)
0	55	55.5	89861.780	89861.785	-0.005
0	55	54.5	89786.127	89786.127	0.000
1	55	55.5	89639.063	89639.063	0.000
1	55	54.5	89563.758	89563.740	0.010
2	55	55.5	89416.575	89416.569	0.006
2	55	54.5	89341.588	89341.599	-0.011
0	64	64.5	104269.504	104269.502	0.002
0	64	63.5	104193.863	104193.870	-0.007
1	64	64.5	104010.996	104010.995	0.001
1	64	63.5	103935.714	103935.707	0.007
2	64	64.5	103752.750	103752.754	-0.004
2	64	63.5	103677.816	103677.809	0.007
3	64	64.5	103994.768	103494.778	-0.010
3	64	63.5	103420.187	103420.178	0.009
4	64	64.5	103237.065	103237.068	-0.003
4	64	63.5	103162.798	103162.811	-0.013
5	64	64.5	102979.631	102979.623	0.008
5	64	63.5	102905.712	102905.710	0.002
0	65	65.5	105869.619	105869.613	0.006
0	65	64.5	105793.977	105793.984	-0.007
1	65	65.5	105607.132	105607.130	0.002
1	65	64.5	105531.842	105531.844	-0.002
2	65	65.5	105344.913	105344.916	-0.003
2	65	64.5	105269.979	105269.974	0.005

stants extrapolated for BaI from systematic trends in the group of II/VII compounds. This results in  $\gamma_{00} = 76.05(15)$  MHz. The given error is believed to include uncertainties from the extrapolation of hfs constants. It should be noted that the value of  $\gamma_{10}$  is not influenced by hyperfine structure effects while the systematic shift of  $\gamma_{01}$  may be quite large. The value of this constant given in brackets in table 5 may therefore be considered only as a fit parameter.

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