

## THE GROUND-STATE DIPOLE MOMENT OF BaI FROM HIGH-PRECISION STARK SPECTROSCOPY

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The electric dipole moment of the  $X^2\Sigma^+$  state of BaI was measured using the molecular-beam laser-microwave double-resonance technique. From the analysis of the splitting and shift of rotational transitions in an electric field, the dipole moment of the vibrational ground state was determined as  $\mu = 5.969(6)$  D (absolute error of the measurement in parentheses). The dipole moment predicted from an ionic bonding model is 6.14 D.

### 1. Introduction

Two years ago, the application of the molecular-beam laser-microwave double-resonance technique allowed the first precise Stark effect measurements on the alkaline earth monohalides CaCl [1,2] and CaBr [3]. By this method permanent electric dipole moments were determined which stimulated the development of an ionic bonding model for this class of ionic radicals [4]. On the basis of this new electrostatic model, dipole moments were predicted for most other IIa/VIIa diatomics. Subsequent measurements on CaF by Childs et al. [5] as well as on CaI [6] and SrF [7] agreed with the predictions.

The ground states of the alkaline earth monohalides (MX) can be well described by two closed-shell ions  $M^{2+}$  and  $X^-$  with one extra electron which is mainly metal-centered. This electron is strongly s-p-d hybridized in the field of  $X^-$  which corresponds to an induced dipole moment that reduces the primary moment of the  $M^+X^-$  pair. As shown in ref. [4], the correct calculation of the induced moments is the key to a reliable prediction of dipole moments. So far all measurements have been performed on calcium and strontium monohalides [1-3,5-7] where the single electron is mainly s-p hybridized and the good agreement with the calculations shows that this effect can be accounted for by using our electrostatic model. On

the other hand, from hfs studies of  $^{137}\text{BaF}$ ,  $^{137}\text{BaCl}$  [8], and  $^{137}\text{BaBr}$  [9], it is known that the wavefunction of the single  $\text{Ba}^+$ -electron contains a significant amount of d-character for all BaX. The bonding model in ref. [4] predicts dipole moments for BaX as well. Thus measurements on a barium monohalide should show whether the model again yields the correct induced dipole moments.

Barium moniodide has been the subject of several recent spectroscopic investigations. Johnson et al. [10] performed the first rotational analysis of the  $C^2\Pi-X^2\Sigma^+$  (0,0) band around 550 nm. At the same time Törring and Doehl [11] determined very precise ground-state constants from millimetre-wave spectroscopy. Hyperfine structure (hfs) was resolved in the optical spectra (ref. [10]) and could be analyzed after the hfs constants of the  $X^2\Sigma^+$  state had been derived from independent molecular-beam laser-microwave double-resonance experiments [12]. In this work the same double-resonance technique was applied to measure the splitting and shift of hyperfine components of a rotational transition in an external electric field. From these Stark effect measurements, the electric dipole moment was determined for the BaI ground state.

## 2. Experimental

Details of the apparatus have been published [2,13] and some improvements in accuracy have been introduced [7]. An effusive BaI beam was generated from a high-temperature reaction of BaI<sub>2</sub> and Ba at about 1000°C. The beam intensity was estimated as about  $2 \times 10^{15} \text{ sr}^{-1} \text{ s}^{-1}$  BaI. Light from a single-frequency dye laser of 100 mW was used to deplete a particular ground-state level by pumping a transition in the  $C^2\Pi_{2/3}-X^2\Sigma^+$  (0,0) system of BaI around 539 nm. The population of this level was monitored further downstream in the molecular beam by observing the fluorescence induced by a 0.5 mW probe laser beam which was split off the pump beam. Between the pump and the probe zones, microwave (mw) radiation was introduced via a horn antenna. Microwave absorption inducing a transition connected to the depleted level was detected by an increase of the probe laser-induced fluorescence. Stark plates were mounted in the mw interaction region with the electric field vector parallel to the mw polarization. The Stark spectroscopy was performed around 11.2 GHz by measuring the shift of  $\Delta M_F = 0$  transitions originating from the  $N = 7 \leftarrow 6, J = 6.5 \leftarrow 5.5, F = 4 \leftarrow 3$  rotational transition (fig. 1). With a mw intensity of  $5 \mu\text{W}/\text{cm}^2$  and good shielding from the Earth's magnetic field, lines were recorded with 10 kHz fwhm. The laser frequency was fixed to the  $F'' = 4$  component of the  $Q_2(6.5)$  line in the  $C^2\Pi_{2/3}-X^2\Sigma^+$  (0,0) band at  $18569.14 \text{ cm}^{-1}$ . The optical hfs is resolved in this particular sequence (cf. ref. [12]). Because of the large density of states in BaI the sensitivity problems were worse than for any other alkaline earth monohalide. The BaI beam intensity mentioned above corresponds to about  $10^6$  radicals in the  $0.1 \text{ cm}^3$  interaction volume of the probe beam with the molecular beam. Because of the high temperature of 1300 K and the small rotational and vibrational constants [11] only about 5 BaI molecules are in the hyperfine state under investigation. About 15 min of signal averaging were necessary to record a mw line with  $S/N \approx 2$ .

## 3. Results and discussion

Stark shifts were measured for the mw transition  $N = 7 \leftarrow 6, J = 6.5 \leftarrow 5.5, F = 4 \leftarrow 3, |M_F| = 1, 2, 3$  and

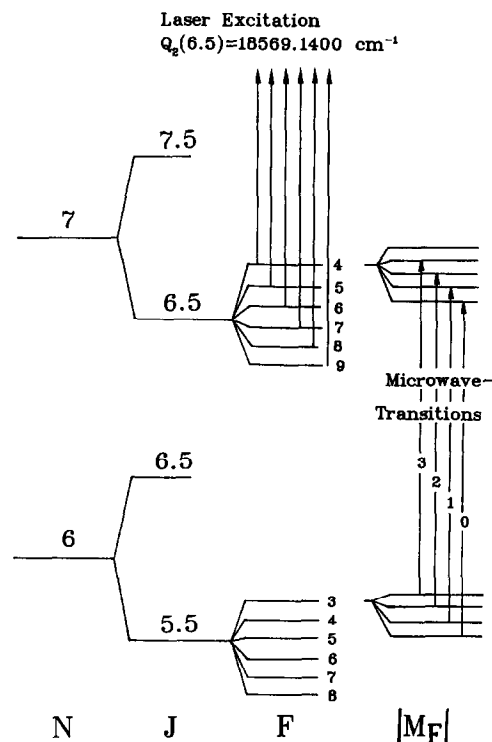


Fig. 1. Energy level diagram showing the transitions used for laser-mw double-resonance spectroscopy in the Stark field.

$\Delta M_F = 0$  in the electric field range  $0 < E < 700 \text{ V}/\text{cm}$ . The electric field strength was determined with an accuracy of 0.1%. Observed transition frequencies are listed in table 1 for different values of  $E$ . Energies of the hfs levels in an electric field are calculated by diagonalizing the effective Hamiltonian [2]

$$\hat{H} = \hat{H}_{\text{rot}} + \hat{H}_{\text{sr}} + \hat{H}_{\text{hfs}} + \hat{H}_{\text{Stark}},$$

with

$$\hat{H}_{\text{rot}} = B\hat{N}^2, \quad \hat{H}_{\text{sr}} = \gamma_{\text{sr}}\hat{N} \cdot \hat{S},$$

$$\hat{H}_{\text{hfs}} = b\hat{I} \cdot \hat{S} + c\hat{I}_z \hat{S}_z + eqQ[3\hat{I}_z^2 - I(I+1)]/[4I(I-1)],$$

$$\hat{H}_{\text{Stark}} = -|E| |\mu| \cos \theta.$$

The rotational constants and spin-rotation and hfs interaction parameters were taken from ref. [11] and ref. [12], respectively. By fitting the calculated Stark shifts to the experimentally observed shifts, the elec-

Table 1  
Transition frequencies of the mw transition  $N = 7 \leftarrow 6, J = 6.5 \leftarrow 5.5, F = 4 \leftarrow 3, \Delta M_F = 0$  at various electric field strengths  $E$ . Calculated values were derived for  $\mu = 5.9685$  D

$E$ (V/cm)	$ M_F $	Obs. $\nu_{\text{mw}}$ (MHz)	Calc. $\nu_{\text{mw}}$ (MHz)	Obs. - calc. (kHz)
0		11199.429	11199.426	3
150	1	11199.382	11199.380	2
150	2	11199.635	11199.631	4
150	3	11200.049	11200.050	-2
200	3	11200.524	11200.530	-6
200	3	11200.528	11200.530	-2
250	3	11201.145	11201.145	0
300	3	11201.891	11201.893	-2
400	3	11203.783	11203.780	3
450	3	11204.912	11204.913	-1
500	3	11206.170	11206.166	4
700	3	11212.248	11212.249	-1

tric dipole moment was determined as  $\mu = 5.9685(6)$  D with the statistical standard deviation from the fit given in parentheses. Values for observed minus calculated are shown in table 1. An absolute error of  $\pm 0.006$  D is due to uncertainty in the calibration of the Stark field.

The electrostatic bonding model of Törring et al. [4] has explained the measured electric dipole moments of the alkaline earth monohalides. This model starts with a similar approach as Rittner's model for the alkali halides [14] by subtracting dipole moments  $\mu^+$  and  $\mu^-$  induced in the positive and negative ions from the primary moment  $\mu_0 = er_e$ ,  $r_e$  being the equilibrium internuclear distance of the ionic molecule:

$$\mu = \mu_0 - (\mu^+ + \mu^-).$$

The induced moments  $\mu^+$  and  $\mu^-$  are calculated from the electric field produced by the partner ion at the ion under consideration and the appropriate polarizabilities  $\alpha^+$  and  $\alpha^-$ . The polarizabilities of the alkaline earth metal ions are particularly large due to the unpaired electron outside the closed-shell  $M^{2+}$  core. In the field of  $X^-$  this single s-electron is s-p-d hybridized and the center of charge lies outside the center of mass of  $M^+$  at a distance  $\Delta r$ , forming an induced moment  $\mu^+ = e\Delta r$  oppositely directed to the primary moment. We have shown [4] that the charge shift  $\Delta r$  has to be taken into account in the calculation of  $\mu^+$ .

For BaI a dipole moment of 6.14 D was predicted

[4]. As in the cases of CaF [5], CaCl [2], CaBr [3], CaI [6], and SrF [7] the predicted value is in good agreement with the measurement. The charge distribution in BaI is again well described by our simple bonding picture of two polarizable ions. All measurements yielded dipole moments slightly smaller than the calculated ones. On the other hand, the polarizabilities of the ions are not well known and fairly large uncertainties are possible, especially for  $M^+$ . With more experimentally determined dipole moments available, an attempt should be made to derive a new consistent set of  $M^+$  polarizabilities to reproduce the measured values even better.

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