

# Dipole moments and potential energies of the alkaline earth monohalides from an ionic model

T. Törring, W. E. Ernst, and S. Kindt

Citation: *The Journal of Chemical Physics* **81**, 4614 (1984); doi: 10.1063/1.447394

View online: <https://doi.org/10.1063/1.447394>

View Table of Contents: <http://aip.scitation.org/toc/jcp/81/10>

Published by the [American Institute of Physics](#)

---

## Articles you may be interested in

[Energies and electric dipole moments of the low lying electronic states of the alkaline earth monohalides from an electrostatic polarization model](#)

*The Journal of Chemical Physics* **90**, 4927 (1989); 10.1063/1.456589

[Radiative lifetimes of the alkaline earth monohalides](#)

*The Journal of Chemical Physics* **60**, 2330 (1974); 10.1063/1.1681366

[Electric-dipole moment of  \$\text{CaF} \(X^2\Sigma^+\)\$  by molecular beam, laser-rf, double-resonance study of Stark splittings](#)

*The Journal of Chemical Physics* **80**, 2283 (1984); 10.1063/1.447005

[Theoretical study of the dipole moments of selected alkaline-earth halides](#)

*The Journal of Chemical Physics* **84**, 5025 (1986); 10.1063/1.450651

[Permanent and transition dipole moments in  \$\text{CaF}\$  and  \$\text{CaCl}\$](#)

*The Journal of Chemical Physics* **115**, 7450 (2001); 10.1063/1.1405118

[Hyperfine Interaction and Chemical Bonding in  \$\text{MgF}\$ ,  \$\text{CaF}\$ ,  \$\text{SrF}\$ , and  \$\text{BaF}\$  molecules](#)

*The Journal of Chemical Physics* **54**, 322 (1971); 10.1063/1.1674610

---

PHYSICS TODAY

WHITEPAPERS

### ADVANCED LIGHT CURE ADHESIVES

Take a closer look at what these environmentally friendly adhesive systems can do

READ NOW

PRESENTED BY  
 MASTERBOND  
ADHESIVES | SEALANTS | COATINGS

# Dipole moments and potential energies of the alkaline earth monohalides from an ionic model

T. Törring, W. E. Ernst, and S. Kindt

*Institut für Molekülphysik, Freie Universität Berlin, D 1000 Berlin 33, West Germany*

(Received 9 January 1984; accepted 10 May 1984)

It is shown that the Rittner model is inadequate for the calculation of dipole moments for the alkaline earth monohalides. A modified model is proposed which takes into account explicitly the large charge shifts in the metal ions arising from the polarization. The new model is shown to give results consistent with available experimental data.

## I. INTRODUCTION

Ionic molecules are useful candidates for testing simple semiclassical bond models. The dominant part of the attractive potential in this group of molecules is simply given by the Coulomb interaction which can be calculated from known properties of the free ions. Adding an exponential repulsive term and a small term for the van der Waals attraction gives a model potential which for diatomics is of the general form

$$V(r) = A \cdot \exp\{-r/\rho\} + \Phi - \frac{C}{r^6}, \quad (1)$$

where  $r$  is the internuclear distance.

The three terms on the right-hand side can be treated in different ways leading to a large variety of model potentials which have been discussed in the literature.<sup>1,2</sup> The general form of  $A$  in the repulsive term is a polynomial in  $r$ .<sup>1</sup> However, it turns out that usually this can be approximated simply by a constant. The constant  $C$  in the van der Waals term can be expressed by properties of the two free ions by using the London approximation<sup>3,4</sup>

$$C = \frac{3}{2} \alpha^+ \cdot \alpha^- \cdot \{(I^+ I^-)/(I^+ + I^-)\}, \quad (2)$$

where  $\alpha^\pm$  and  $I^\pm$  are the dipole polarizabilities and ionization potentials of the two free ions, respectively. Thus, the only two constants in Eq. (1) which must be determined from specific molecular spectroscopic data are  $A$  and  $\rho$  in the repulsive term; all other terms can be calculated from properties of the free ions. The predictive power of this simple model is potentially very high. Not only spectroscopic constants but also the dissociation energy into free ions  $D_i$  and the electric dipole moment  $\mu$  of the molecule can be calculated. A comparison with experimental data can serve as a critical test for the validity of the model.

In a crystal where symmetry is high the electrostatic part of the potential can be approximated at least roughly by  $\Phi = -e^2/r$  leading to the Born-Mayer potential.<sup>5</sup> In a free molecule  $\Phi$  needs a more elaborate treatment since mutual polarization of the two ions has to be taken into account. This can be seen from the fact that the dipole moments of all known ionic diatomics are considerably smaller than  $\mu = e \cdot r$ . Currently, the most widely accepted treatment of this problem is due to Rittner.<sup>6</sup> In this model the ions are assumed to be polarizable spherical charge distributions and multipole terms higher than dipole terms are neglected in the calculation of the mutual polarization. As already pointed

out by Rittner this should be a good approximation only if

$$r^6 \gg 4 \cdot \alpha^+ \cdot \alpha^-. \quad (3)$$

For the alkali halides this condition is well fulfilled in a large range around  $r \approx r_e$  and the Rittner model—and some slightly modified versions of this model—have been successfully applied. A complete set of experimental data, including dipole moments, exists for these species allowing a detailed and critical comparison. A list of references may be found in Ref. 7. More recently a large amount of precise spectroscopic information has become available for some of the group II A monohalides.<sup>8-33</sup> From hyperfine structure measurements it has become evident that the chemical bond in these molecules is also highly ionic.<sup>21</sup> However, the polarizabilities of the alkaline earth ions are much larger than those of the corresponding alkali ions so that the condition for the applicability of the Rittner model given by Eq. (3) is fulfilled only poorly. In order to test the validity of the model Klyning and Martin have studied the potential energy curve of CaCl.<sup>34</sup> They found that the experimentally determined RKR potential could be fitted rather well to the Rittner potential and some slightly modified versions when in addition to  $A$  and  $\rho$  at least one other parameter was treated as an adjustable variable in the fit. However, when in a later work<sup>35</sup> these results were used for a more detailed study of the polarization effects in CaCl it turned out that the resulting ground state dipole moment comes out too small by one order of magnitude. This is in contradiction to the result of Dagdigan<sup>36</sup> who calculated  $\mu = 3$  D from the so-called truncated Rittner (T-Rittner) model proposed by Brumer and Karplus<sup>7</sup> in reasonable agreement with his experimental estimate of the dipole moment from beam deflection measurements. With the precise values for the electric dipole moments for CaCl, CaBr, and CaF determined most recently with a molecular beam resonance method<sup>37-39</sup> a more reliable comparison with experimental data is now possible. It will be shown in this paper that the T-Rittner model gives reasonable dipole moments only for a few of the alkaline earth monohalides due to a fortuitous cancellation of two neglected effects. An improved model will be discussed which takes into account the large charge shifts in the alkaline earth ions arising from the polarization. This can be achieved without the introduction of a new adjustable parameter. Predictions of this model are compared with the available experimental data.

## II. THEORY

### A. The breakdown of the Rittner model

To understand the problems arising in the application of the Rittner model to the alkaline earth monohalides it is useful to go back to Rittner's original paper.<sup>6</sup> In the mutual polarization of the two ions only induced dipole moments are considered. The electrostatic energy binding the ions together is then given by charge-charge interaction, charge-dipole interaction, dipole-dipole interaction, and quasielastic energy stored in the induced dipoles

$$\Phi = -\frac{e^2}{r} - \frac{\mu^+ e}{r^2} - \frac{\mu^- e}{r^2} - \frac{2\mu^+ \mu^-}{r^3} + \frac{(\mu^+)^2}{2\alpha^+} + \frac{(\mu^-)^2}{2\alpha^-} \quad (4)$$

The induced moments  $\mu^+$  and  $\mu^-$  reduce the primary dipole moment  $e \cdot r$  so that the net dipole moment  $\mu$  of the molecule is given by

$$\mu = e \cdot r - (\mu^+ + \mu^-) \quad (5)$$

$\mu^+$  and  $\mu^-$  are calculated by

$$\mu^+ = \alpha^+ \cdot \left\{ \frac{e}{r^2} + \frac{2\mu^-}{r^3} \right\} \quad (6)$$

and

$$\mu^- = \alpha^- \cdot \left\{ \frac{e}{r^2} + \frac{2\mu^+}{r^3} \right\} \quad (7)$$

The expressions in braces are the polarizing fields written as a multipole expansion around the center of the spherical ions. Here also quadrupole and higher order terms are neglected. Simultaneous solution of Eqs. (6) and (7) yields

$$\mu^+ = \frac{r^4 \cdot e \cdot \alpha^+ + 2r \cdot e \cdot \alpha^+ \cdot \alpha^-}{r^6 - 4\alpha^+ \cdot \alpha^-} \simeq \frac{e \cdot \alpha^+}{r^2} + \frac{2e \cdot \alpha^+ \cdot \alpha^-}{r^5}, \quad (8)$$

$$\mu^- = \frac{r^4 \cdot e \cdot \alpha^- + 2r \cdot e \cdot \alpha^+ \cdot \alpha^-}{r^6 - 4\alpha^+ \cdot \alpha^-} \simeq \frac{e \cdot \alpha^-}{r^2} + \frac{2e \cdot \alpha^+ \cdot \alpha^-}{r^5}. \quad (9)$$

It is obvious from these expressions that the model will largely overestimate the polarization effects and that convergence of the power series on the right-hand side is very poor if  $r^6 > 4\alpha^+ \cdot \alpha^-$  is not fulfilled. For the alkali halides  $r_e^6/4\alpha^+ \cdot \alpha^-$  is usually of the order of 50 and higher. Polarizabilities of the alkaline earth ions are approximately one order of magnitude larger than those of the corresponding alkali ions and bond lengths of the monohalides are shorter. For CaCl this leads to  $r_e^6/4\alpha^+ \cdot \alpha^- \simeq 2$  and induced moments of  $\mu^+ = 16.9$  D and  $\mu^- = 11.5$  D, quite unreasonable results when compared to the primary moment of  $e \cdot r_e = 11.7$  D. Obviously any truncation of the power series on the right-hand side of Eqs. (8) and (9) will reduce this overestimation of the polarization effects but is hard to justify in view of the poor convergence of the series. Brumer and Karplus<sup>7</sup> have applied quantum mechanical exchange perturbation theory to the problem and have shown that in a consistent second-

order perturbation treatment only the first term occurs in the power series of Eqs. (8) and (9). This means that the contributions of the induced moments to the polarizing fields are completely neglected in this so called "truncated" Rittner (T-Rittner) model. However, while a restriction to a second-order treatment is completely justified for the alkali halides, it is much less convincing for the alkaline earth monohalides with their high metal ion polarizabilities. In the results presented in Sec. III B, we have included values of the molecular constants  $\alpha_e, \omega_e x_e, D_i$ , and  $\mu$  calculated from the T-Rittner model for comparison.

### B. An ionic model for the alkaline earth monohalides

Two effects become important for the alkaline earth monohalides which play only a minor role for the alkali halides: (i) the contribution of higher order multipole moments in the mutual polarization and (ii) the inhomogeneity of the polarizing field. Inclusion of these effects for the alkali halides<sup>40</sup> gave no improvement. In some cases the agreement with experimental data was even worsened. This may be due to the fact that these small contributions tend to cancel and may compete with other effects which have been neglected or not properly described in the model. The situation is quite different for alkaline earth compounds. An alkaline earth ion consists of a closed shell  $\text{Me}^{++}$  kernel with a single  $s$  electron in the valence shell. Polarizability of the doubly charged kernel may be neglected, so polarization of the ion is entirely due to  $s$ - $p$ - $d$ -hybridization of the single valence electron. This means that the electron's center of charge must be shifted by  $\Delta r$  to give the induced dipole moment (see Fig. 1)

$$\mu^+ = e \cdot \Delta r. \quad (10)$$

$\Delta r$  is of the order of 1 Å and thus cannot be considered as small compared to the internuclear distance. For this reason a multipole expansion of the  $\text{Me}^{++}$ -electric field around the position of the  $\text{Me}^{++}$  kernel will converge only poorly at the Hal ion. On the other hand the electric field of the Hal-ion acting on the  $\text{Me}^+$  valence electron will be significantly smaller than the field at the position of the  $\text{Me}^{++}$  kernel. For ions with a closed shell configuration this can be neglected since all valence electrons in degenerate orbitals (usually six  $p$  electrons) contribute to the polarization and polarizabilities are smaller in most cases. Then  $\Delta r$  is small compared to

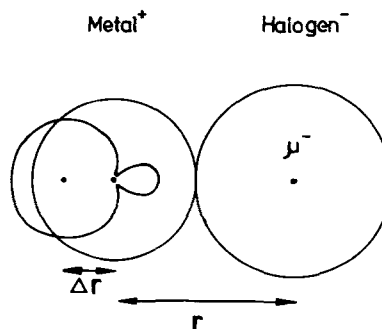


FIG. 1. Alkaline earth monohalide consisting of two closed shell ions  $\text{Me}^{++}$  and  $\text{Hal}^-$  and a strongly hybridized metal centered electron.  $r$  is the internuclear distance and  $\Delta r$  the displacement of the center of charge of the  $s$ - $p$ - $d$  hybrid from the metal nucleus.

the internuclear distance and the Rittner model is an appropriate approximation. In our new model we therefore use Rittner's treatment for the polarization of the Hal ion but write the polarizing field as a superposition of the fields arising from the  $\text{Me}^{++}$  kernel at a distance  $r$  and the valence electron at a distance  $(r + \Delta r)$ , respectively:

$$\mu^- = \alpha^- \cdot \left\{ \frac{2e}{r^2} - \frac{e}{(r + \Delta r)^2} \right\}. \quad (11)$$

Here the  $\text{Me}^{++}$  kernel is treated as a spherical charge distribution since we have neglected its polarizability. The field from the valence electron is also written as arising from a spherical charge distribution. This means that some higher order terms have been neglected even in our model, but the larger contributions due to the charge shift  $\Delta r$  are included.

In the expression for the polarization of the  $\text{Me}^+$  ion we consider the valence electron as elastically bound to the  $\text{Me}^{++}$  kernel so that the induced moment is proportional to the polarizing field. In the approximation of a spherically symmetric charge distribution for the valence electron this polarizing field has to be calculated at the center of charge, i.e., at a distance  $(r + \Delta r)$  from the negative ion

$$\mu^+ = e \cdot \Delta r = \alpha^+ \left\{ \frac{e}{(r + \Delta r)^2} + \frac{2\mu^-}{(r + \Delta r)^3} \right\}. \quad (12)$$

Equations (11) and (12) have a correct asymptotic behavior in the sense that neither  $\mu^+$  nor  $\mu^-$  can become infinite for any finite value of  $\alpha^+$  and  $\alpha^-$ . Inserting Eq. (11) into Eq. (12) we get

$$\Delta r = \frac{\alpha^+}{(r + \Delta r)^2} + \frac{4\alpha^+ \cdot \alpha^-}{r^2(r + \Delta r)^3} - \frac{2\alpha^+ \cdot \alpha^-}{(r + \Delta r)^5}. \quad (13)$$

From this expression  $\Delta r$  can be calculated numerically by a simple iteration program to any useful degree of accuracy. The electrostatic potential in our model is given by

$$\begin{aligned} \Phi = & -\frac{2e^2}{r} + \frac{e^2}{(r + \Delta r)} - \frac{2\mu^- \cdot e}{r^2} \\ & + \frac{\mu^- \cdot e}{(r + \Delta r)^2} + \frac{(\mu^+)^2}{2\alpha^+} + \frac{(\mu^-)^2}{2\alpha^-}. \end{aligned} \quad (14)$$

If in a series expansion all quadratic and higher order terms in  $\Delta r/r$  are neglected, Eq. (14) is equivalent to the Rittner potential (4). Using Eq. (11), Eq. (14) may be written more simply

$$\Phi = -\frac{2e^2}{r} + \frac{e^2}{(r + \Delta r)} + \frac{(\mu^+)^2}{2\alpha^+} - \frac{(\mu^-)^2}{2\alpha^-}. \quad (15)$$

With this expression the model potential of Eq. (1) can be calculated once the two unknown constants  $A$  and  $\rho$  have been fitted to the specific molecule under investigation. This can be done by comparing the first two derivatives of the potential (1) with experimentally determined values of  $r_e$  and  $\omega_e$ :

$$V'(r_e) = 0 \quad (16)$$

and

$$V''(r_e) = \frac{2}{r_e^2} \cdot a_0 = \frac{2}{r_e^2} \cdot \frac{\omega_e^2}{4B_e}. \quad (17)$$

From the higher derivatives the coefficients  $a_i$  of the Dunham potential<sup>41</sup>

$$V(\xi) = a_0 \cdot \xi^2 \{ 1 + a_1 \xi + a_2 \xi^2 + \dots \}$$

with

$$\xi = \frac{r - r_e}{r_e}$$

may then be derived

$$a_0 \cdot a_n = \frac{r_e^{n+2}}{(n+2)!} \cdot V^{(n+2)}(r_e), \quad (18)$$

where  $V^{(n)}(r_e)$  denotes the  $n$ th derivative of  $V(r)$  at  $r = r_e$ . Relations for the calculation of spectroscopic constants from the coefficients  $a_i$  have been given by Dunham<sup>41</sup> and Varshni *et al.*<sup>1</sup>

In the calculation of the  $V^{(n)}(r_e)$  from Eq. (1) simple analytic expressions can be obtained only for the first and the last term. Derivatives of  $\Phi$  have to be calculated numerically. To avoid errors in this calculation, especially for the higher derivatives, the accuracy in the iterative calculation of  $\Delta r$  from Eq. (13) must be sufficiently high.

### III. COMPARISON WITH EXPERIMENTAL DATA

#### A. Input data

The most important input data for the calculations are the polarizabilities of the free ions. Unfortunately no experimental data are available for the alkaline earth ions. We therefore have to use the values calculated by Hildenbrand<sup>42</sup> using the relation<sup>43,44</sup>

$$\alpha = 2n \cdot e^2 \cdot \langle R^2 \rangle / 3I, \quad (19)$$

where  $n$  is the number of valence electrons and  $\langle R^2 \rangle$  the expectation value of the squared orbital radius of a valence electron. This may give rise to comparatively large uncertainties in the results but general trends and the comparison with the Rittner model should be relatively insensitive to errors in the  $\alpha^+$  which are listed in Table I. Values for the polarizabilities of the halogen ions have been given by Pauling.<sup>45</sup> However, effective polarizabilities of the negative ion in an ionic molecule are somewhat smaller due to exchange forces. De Wijn<sup>46</sup> assumed that polarization of the two  $p_\sigma$  orbitals is completely quenched while polarization of the four  $p_\pi$  orbitals remains unaffected. This would reduce the

TABLE I. Ion polarizabilities used in this paper.

Ion	Free ion polarizabilities <sup>a,b</sup> $\alpha^+, \alpha^- (\text{\AA}^3)$	Effective polarizability <sup>c</sup> $\alpha^- (\text{\AA}^3)$
Be <sup>+</sup>	1	
Mg <sup>+</sup>	3	
Ca <sup>+</sup>	7	
Sr <sup>+</sup>	9	
Ba <sup>+</sup>	12	
F <sup>-</sup>	1.05	0.69
Cl <sup>-</sup>	3.69	2.55
Br <sup>-</sup>	4.81	3.50
I <sup>-</sup>	7.16	5.35

<sup>a</sup> Metal<sup>+</sup> polarizabilities from Ref. 42.

<sup>b</sup> Halogen<sup>-</sup> polarizabilities from Ref. 45.

<sup>c</sup> Effective polarizabilities of the halogen ions have been fitted to the alkali halide dipole moments.

polarizabilities of the halogen ions by a factor of 2/3. Brumer and Karplus<sup>7</sup> have assumed that the deviation from the free ion polarizabilities depends exponentially on the internuclear distance. Although the additional adjustable parameter introduced this way was fitted to reproduce the values of the dipole moment, errors in the prediction of the other molecular constants were reduced only slightly. We therefore preferred to use fixed effective polarizabilities listed in Table I. These values are slightly larger than those resulting from De Wijn's rule. They have been adjusted to reproduce the experimental dipole moments of the alkali halides to within  $\pm 0.15$  D except for the Li halides where the deviations go up to  $\pm 0.5$  D.

Values for the ionization potentials  $I$  and  $I^+$  and the electron affinity  $E = I^-$  listed in Table II were taken from Landolt-Börnstein.<sup>47</sup> They are necessary to calculate the constant  $C$  of the van der Waals attraction according to Eq.

TABLE II. Ionization potentials and electron affinities used in this paper.<sup>a</sup>

Atom	$I$ (eV)	$I^+$ (eV)	$E = I^-$ (eV)
Be	9.32	18.2	
Mg	7.64	15.0	
Ca	6.11	11.9	
Sr	5.69	11.0	
Ba	5.21	10.0	
F			4.1
Cl			3.78
Br			3.52
I			3.12

<sup>a</sup> All values from Ref. 47.

(2) and the dissociation energy into free ions

$$D_i = D_0^0 + 1/2\omega_e + I - E, \quad (20)$$

TABLE III. Comparison with experimental data.<sup>a</sup>

Molecule	$\Delta r/r_e$	$\mu$ (D)	$D_i$ (cm <sup>-1</sup> )	$\alpha_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )
MgF This work:	0.3767	3.64	66 400	$4.22 \times 10^{-3}$	4.29
Exp:			67 200	$4.70 \times 10^{-3}$	4.94
T-Rittner:		2.62	66 900	$4.06 \times 10^{-3}$	4.16
MgCl This work:	0.2672	4.25	53 100	$1.60 \times 10^{-3}$	2.25
Exp:			57 500	$1.58 \times 10^{-3}$	2.10
T-Rittner:		5.05	52 800	$1.64 \times 10^{-3}$	2.29
CaF This work:	0.4955	3.34	62 200	$2.40 \times 10^{-3}$	3.01
Exp:		3.07	60 700	$2.45 \times 10^{-3}$	2.91
T-Rittner:		-0.32	64 000	$2.10 \times 10^{-3}$	2.72
CaCl This work:	0.3603	4.47	49 600	$8.36 \times 10^{-4}$	1.54
Exp:		4.27	52 500	$7.99 \times 10^{-4}$	1.37
T-Rittner:		3.98	49 800	$8.28 \times 10^{-4}$	1.52
CaBr This work:	0.3268	4.80	46 500	$4.30 \times 10^{-4}$	0.99
Exp:		4.36	47 500	$4.04 \times 10^{-4}$	0.84
T-Rittner:		4.96	46 500	$4.33 \times 10^{-4}$	0.99
CaI This work:	0.2839	5.25	42 600	$2.89 \times 10^{-4}$	$7.66 \times 10^{-1}$
Exp:			45 900	$2.64 \times 10^{-4}$	$6.28 \times 10^{-1}$
T-Rittner:		6.16	42 400	$2.96 \times 10^{-4}$	$7.82 \times 10^{-1}$
SrF This work:	0.5112	3.67	59 000	$1.59 \times 10^{-3}$	2.35
Exp:			58 100	$1.55 \times 10^{-3}$	2.27
T-Rittner:		-0.84	61 100	$1.37 \times 10^{-3}$	2.07
SrCl This work:	0.3701	5.08	47 300	$4.83 \times 10^{-4}$	1.10
Exp:			49 100	$4.52 \times 10^{-4}$	0.97
T-Rittner:		4.01	47 600	$4.71 \times 10^{-4}$	1.07
BaF This work:	0.5589	3.44	57 700	$1.30 \times 10^{-3}$	2.09
Exp:			58 000	$1.16 \times 10^{-3}$	1.83
T-Rittner:		-2.70	60 500	$1.08 \times 10^{-3}$	1.77
BaCl This work:	0.4037	5.14	46 200	$3.75 \times 10^{-4}$	$9.67 \times 10^{-1}$
Exp:			48 500	$3.34 \times 10^{-4}$	$8.17 \times 10^{-1}$
T-Rittner:		3.17	46 800	$3.60 \times 10^{-4}$	$9.21 \times 10^{-1}$
BaI This work:	0.3242	6.14	40 000	$7.56 \times 10^{-5}$	$3.41 \times 10^{-1}$
Exp <sup>b</sup> :			42 000	$6.63 \times 10^{-5}$	$2.90 \times 10^{-1}$
T-Rittner:		6.07	40 000	$7.56 \times 10^{-5}$	$3.40 \times 10^{-1}$

<sup>a</sup> Experimental data and values of  $r_e$ ,  $\omega_e$  and  $D_0^0$  used in the calculations were taken from Refs. 14-16, 23-25, 48, and 49. For a better comparison with model calculations only three significant digits are given in the table.

<sup>b</sup>  $r_e$  and  $\alpha_e$  from unpublished microwave work.

where  $D_0^0$  is the experimentally determined dissociation energy into atoms relative to the lowest existing level of the molecule. All molecular constants were taken from Huber and Herzberg<sup>48</sup> or Rosen<sup>49</sup> unless more recent and more precise values were available from the microwave or laser spectroscopic work cited in the references.

## B. Results and discussion

Calculations have been carried out for all alkaline earth monohalides provided that a reliable rotational analysis was available. Calculated values of the dipole moment  $\mu$ , dissociation energy into ions  $D_i$ , and the spectroscopic constants  $\alpha_e$  and  $\omega_e x_e$  are listed in Table III. Experimental data and values calculated with the T-Rittner model are listed for comparison. The parameter  $\Delta r/r_e$  gives the charge shift in the metal ion due to the polarization in units of the internuclear distance. It is a measure for the importance of the inhomogeneity of the polarizing field.

The electric dipole moment is of particular interest since this quantity is most sensitive to changes in the model. Experimental data are presently available only for the calcium monohalides CaCl,<sup>37</sup> CaBr,<sup>38</sup> and CaF.<sup>39</sup> In Fig. 2 these data are compared with the different model calculations. The Rittner model largely overestimates polarization effects so that negative dipole moments result for all alkaline earth monohalides. The model is therefore not applicable to this group of molecules. All experimental data are reproduced very well by the new model. Agreement can even be improved by a slight adjustment of  $\alpha^+$  without worsening the results for the other constants given in Table III. Predictions from the T-Rittner model reflect the approximations made in this model. This can be seen by comparing the induced moments  $\mu^+$  and  $\mu^-$  listed in Table IV for the two models. Neglecting the charge shift and the inhomogeneity of the polarizing fields leads to an overestimation of  $\mu^+$  by the T-Rittner model. Neglecting the contribution of the induced moments of the polarizing fields has the opposite effect. This can be seen from the values of  $\mu^-$ . As a result the total induced moment ( $\mu^+ + \mu^-$ ) is highly overestimated for the fluorides since for these molecules  $\Delta r/r_e$  is large while the polarizability of  $F^-$  is small. For the heavier halides the parameter  $\Delta r/r_e$  goes down while the polarizability of the halogen ion increases rapidly. It thus may happen that both effects nearly cancel as in the case of CaCl and CaBr so that the T-Rittner model accidentally reproduces the experimental dipole moment well. However, even in this case the values of  $\mu^+$  and  $\mu^-$  differ significantly from the results

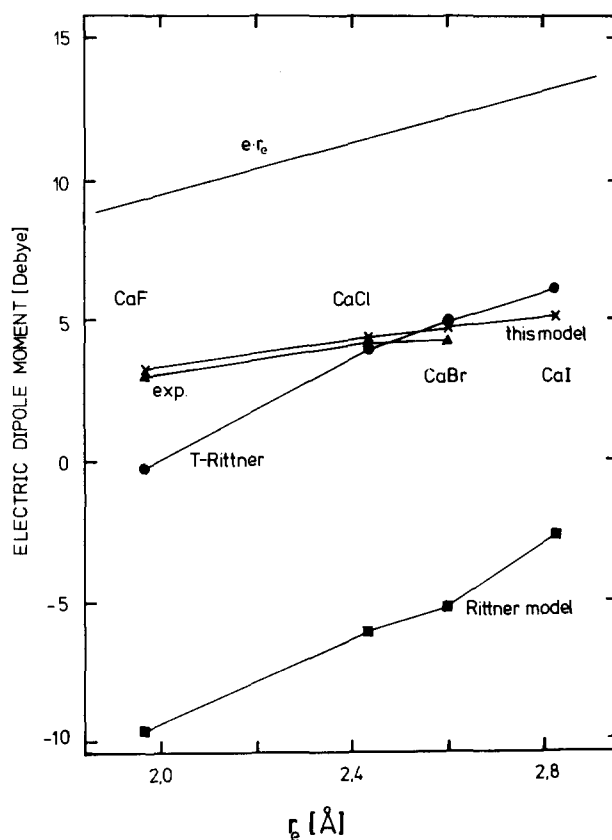


FIG. 2. Electric dipole moment of calcium monohalides from measurements ( $\blacktriangle$ ), our new model ( $\times$ ), T-Rittner model ( $\bullet$ ), and Rittner model ( $\blacksquare$ ). A plot of the primary moment  $e \cdot r_e$  is shown for comparison.

given by the new model. Despite different results for the charge distribution the two models describe the quantities  $D_i$ ,  $\alpha_e$ , and  $\omega_e x_e$  equally well for all molecules listed in Table III. Obviously the T-Rittner model is capable of reproducing the potential energy reasonably well even in the cases where the sign of the dipole moment is wrong. This may seem surprising since polarization of the ions makes an essential contribution to the attractive potential, amounting to roughly 50% of the charge-charge interaction energy. However, the total potential energy is strongly influenced by fitting the harmonic part of the potential to the experimentally determined value of  $\omega_e$ . Errors in the polarization terms are thus partly compensated. As a result the values of  $D_i$  given in Table III are changed by only about 15% when polarization effects are completely neglected. A second order treatment of the electrostatic interaction is therefore sufficient in the

TABLE IV. Induced moments  $\mu^+$  and  $\mu^-$  in the Ca monohalides.<sup>a</sup>

	T-Rittner model			This model		
	$\mu^+$	$\mu^-$	$(\mu^+ + \mu^-)$	$\mu^+$	$\mu^-$	$(\mu^+ + \mu^-)$
CaF	8.82	0.87	9.69	4.68	1.35	6.03
CaCl	5.66	2.06	7.72	4.21	3.02	7.23
CaBr	5.00	2.50	7.50	4.08	3.58	7.66
CaI	4.20	3.21	7.42	3.86	4.47	8.33

<sup>a</sup> All values in D.

ionic model of the potential energy even if the polarizabilities of the ions are high. The electric dipole moment is much more sensitive to details of the charge distribution in the molecule. For the alkaline earth monohalides the simple model presented here is expected to predict this quantity with about the same accuracy as the Rittner model does for the alkali halides.

When this work was nearly completed the first *ab initio* calculations on CaCl were published by Honjou *et al.*<sup>50</sup> Their study confirms the ionic character of the bonding and agrees well with the results of Bernath *et al.*<sup>21</sup> concerning the strong *s-p* hybridization of the Ca<sup>+</sup> ion. The *ab initio* calculations yielded a rather large equilibrium internuclear distance  $r_e$  for the  $X^2\Sigma^+$  state whereas the resulting ground state dipole moment of 4.29 D (at  $r_e$ ) agrees with our measurements strikingly well. Of course these calculations require a large computational effort and will become even more difficult when heavier alkaline earth monohalides are to be treated.

## ACKNOWLEDGMENTS

The authors want to thank Dr. W. J. Childs for communicating his result for the CaF dipole moment prior to publication. This work is part of a research program supported by the Deutsche Forschungsgemeinschaft in the Sonderforschungsbereich 161.

<sup>1</sup>Y. P. Varshni and R. C. Shukla, *J. Mol. Spectrosc.* **16**, 63 (1965).

<sup>2</sup>R. L. Redington, *J. Phys. Chem.* **74**, 181 (1970).

<sup>3</sup>H. L. Kramer and D. R. Herschbach, *J. Chem. Phys.* **53**, 2792 (1970).

<sup>4</sup>F. London, *Trans. Faraday Soc.* **33**, 8 (1937).

<sup>5</sup>M. Born and J. E. Mayer, *Z. Phys.* **75**, 1 (1932).

<sup>6</sup>E. S. Rittner, *J. Chem. Phys.* **19**, 1030 (1951).

<sup>7</sup>P. Brumer and M. Karplus, *J. Chem. Phys.* **58**, 3903 (1973).

<sup>8</sup>P. J. Dommaille, T. C. Steimle, N. B. Wong, and D. O. Harris, *J. Mol. Spectrosc.* **65**, 354 (1977).

<sup>9</sup>T. C. Steimle, P. J. Dommaille, and D. O. Harris, *J. Mol. Spectrosc.* **68**, 134 (1977).

<sup>10</sup>T. C. Steimle, P. J. Dommaille, and D. O. Harris, *J. Mol. Spectrosc.* **73**, 441 (1978).

<sup>11</sup>J. Nagakawa, P. J. Dommaille, T. C. Steimle, and D. O. Harris, *J. Mol. Spectrosc.* **70**, 374 (1978).

<sup>12</sup>P. J. Dommaille, T. C. Steimle, and D. O. Harris, *J. Mol. Spectrosc.* **66**, 503 (1977).

<sup>13</sup>P. J. Dommaille, T. C. Steimle, and D. O. Harris, *J. Mol. Spectrosc.* **68**, 146 (1977).

<sup>14</sup>M. Dulick, P. F. Bernath, and R. W. Field, *Can. J. Phys.* **58**, 703 (1980).

<sup>15</sup>P. F. Bernath, R. W. Field, B. Pinchemel, Y. Lefebvre, and J. Schamps, *J. Mol. Spectrosc.* **88**, 175 (1981).

<sup>16</sup>D. E. Reischer, P. F. Bernath, and R. W. Field, *J. Mol. Spectrosc.* **89**, 107 (1981).

<sup>17</sup>L.-E. Berg, L. Klynning, and H. Martin, *Phys. Scr.* **21**, 173 (1980).

<sup>18</sup>L.-E. Berg, L. Klynning, and H. Martin, *Phys. Scr.* **22**, 216 (1980).

<sup>19</sup>J. M. Brown, D. J. Milton, and T. C. Steimle, *Faraday Discuss. Chem. Soc.* **71**, 151 (1981).

<sup>20</sup>P. F. Bernath, P. G. Cummins, and R. W. Field, *Chem. Phys. Lett.* **70**, 618 (1980).

<sup>21</sup>P. F. Bernath, B. Pinchemel, and R. W. Field, *J. Chem. Phys.* **74**, 5508 (1981).

<sup>22</sup>Ch. Ryzlewicz and T. Törring, *Chem. Phys.* **51**, 329 (1980).

<sup>23</sup>Ch. Ryzlewicz, H.-U. Schütze-Pahlmann, J. Hoefl, and T. Törring, *Chem. Phys.* **71**, 389 (1982).

<sup>24</sup>K. Möller, H.-U. Schütze-Pahlmann, J. Hoefl, and T. Törring, *Chem. Phys.* **68**, 399 (1982).

<sup>25</sup>H.-U. Schütze-Pahlmann, Ch. Ryzlewicz, J. Hoefl, and T. Törring, *Chem. Phys. Lett.* **93**, 74 (1982).

<sup>26</sup>W. J. Childs, G. L. Goodman, and L. S. Goodman, *J. Mol. Spectrosc.* **86**, 365 (1981).

<sup>27</sup>W. J. Childs, L. S. Goodman, and I. Renhorn, *J. Mol. Spectrosc.* **87**, 522 (1981).

<sup>28</sup>W. J. Childs, D. R. Cok, and L. S. Goodman, *J. Chem. Phys.* **76**, 3993 (1982).

<sup>29</sup>W. J. Childs, D. R. Cok, G. L. Goodman, and L. S. Goodman, *J. Chem. Phys.* **75**, 501 (1981).

<sup>30</sup>W. E. Ernst and T. Törring, *Phys. Rev. A* **27**, 875 (1983).

<sup>31</sup>W. E. Ernst, *Appl. Phys. B* **30**, 105 (1983).

<sup>32</sup>W. E. Ernst and J. O. Schröder, *Chem. Phys.* **78**, 363 (1983).

<sup>33</sup>W. E. Ernst and S. Kindt, *Appl. Phys. B* **31**, 79 (1983).

<sup>34</sup>L. Klynning and H. Martin, *Phys. Scr.* **22**, 221 (1980).

<sup>35</sup>L. Klynning and H. Martin, *Phys. Scr.* **24**, 33 (1981).

<sup>36</sup>P. G. Dagdigan, *Chem. Phys. Lett.* **88**, 225 (1982).

<sup>37</sup>W. E. Ernst, S. Kindt, and T. Törring, *Phys. Rev. Lett.* **51**, 979 (1983).

<sup>38</sup>S. Kindt, W. E. Ernst, and T. Törring, *Chem. Phys. Lett.* **103**, 241 (1983).

<sup>39</sup>W. J. Childs, L. S. Goodman, K. Nielsen, and V. Pfeufer, *J. Chem. Phys.* **80**, 2283 (1984).

<sup>40</sup>W. Klemperer, W. G. Norris, A. Büchler, and A. G. Emslie, *J. Chem. Phys.* **33**, 1534 (1960).

<sup>41</sup>J. L. Dunham, *Phys. Rev.* **41**, 721 (1932).

<sup>42</sup>D. L. Hildenbrand, *J. Chem. Phys.* **48**, 3657 (1968).

<sup>43</sup>J. E. Mayer and M. G. Mayer, *Phys. Rev.* **43**, 605 (1933).

<sup>44</sup>L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill, New York, 1935).

<sup>45</sup>L. Pauling, *Proc. R. Soc. London Ser. A* **114**, 191 (1927).

<sup>46</sup>H. W. de Wijn, *J. Chem. Phys.* **44**, 810 (1966).

<sup>47</sup>*Landolt-Börnstein, Atom und Molekülphysik, 1. Teil Atome und Ionen* (Springer, Berlin, 1950).

<sup>48</sup>K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

<sup>49</sup>*International Tables of Selected Constants 17, Spectroscopic Data Relative to Diatomic Molecules*, edited by B. Rosen (Pergamon, New York, 1970).

<sup>50</sup>N. Honjou, G. F. Adams, D. R. Yarkony, *J. Chem. Phys.* **79**, 4376 (1983).