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Determination of the ground-state dipole moment of CaCl from molecular-beam laser-microwave double-resonance measurements

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The first precise ground-state dipole moment of CaCl was measured by using the molecular-beam laser-microwave double-resonance method. From the study of two vibrational states the vibrational dependence $\mu=\mu_0+\mu_1(v+\frac{1}{2})$ was determined. The result is $\mu_0=4.257(3)$ D and $\mu_1=0.016(3)$ D (with statistical standard deviation in the last digit given in parentheses). The determination of the dipole moment from measured Stark shifts of individual hyperfine levels required diagonalization of the complete energy matrix. Problems in the application of the Rittner ionic model to the alkaline-earth monohalides are discussed.

I. INTRODUCTION

When questions arise about the bonding character of a molecular species, all properties that depend on the charge-density distribution are of high interest. Information on the total charge-density distribution is provided by the electric multipole moments, especially the dipole moment. In addition, measurements of the hyperfine structure (hfs) can serve as a local probe for intramolecular fields and field gradients. Therefore, both molecular properties can be used to test bonding models which may be of a semiempirical type or be based on *ab initio* calculations. In fact, because of the different type of information both hfs constants and dipole moment should be measured to give a more complete picture of the electronic structure of a molecule.

Among diatomic species the alkaline-earth monohalides have attracted much interest. These radicals were expected to represent the molecular analog of alkali atoms since they have a single unpaired electron outside closed-shell metal (M^{2+}) and halogen ions (X^-). The spectroscopy of the species proved to be rather difficult until laser spectroscopic investigations succeeded in the analysis of the dense optical spectra[1–3] and precise rotational constants of the $^2\Sigma$ ground state were determined from millimeter-wave spectroscopy[4,5] for several alkaline-earth monohalides. First, hfs measurements were performed using Doppler-free laser spectroscopy[6] but only molecular-beam laser-rf and laser-microwave (mw) double-resonance experiments[7,8] and microwave-optical polarization spectroscopy[9] yielded a complete resolution of the hfs from the weakly coupled halogen nucleus. Highly precise hfs constants are known now for SrF (Ref. 10) and several calcium[11,12] and barium halides,[13] and Bernath *et al.* suggested a completely ionic bonding.[14] Precise dipole moments which could complete this picture had not been measured, although this property had been the matter of several estimates. Calculations by Klynning and Martin using the Rittner ionic model[15,16] resulted in $\mu=0.36$ D for the CaCl ground state,[17] a value which is by far too small when compared with that of $\mu=3.6(6)$ D estimated by Dagdigian[18] from molecular-beam deflection measurements. Very recently we were able to report the first precise dipole moment for the vibrational ground state of CaCl (Ref. 19) and now we extended the measurements to the first excited vibrational state. Dipole moments were determined from the frequency shifts of individual hfs components of rotational transitions in a homogeneous electric field. As electric fields can be more easily applied to a beam than in a reaction cell a molecular-beam laser-mw double-resonance experiment was chosen. Besides the advantage of keeping the Stark plates clean this type of beam spectroscopy offers the smallest linewidths. Low-field Stark shifts in the order of the fine and hfs splitting of an energy level exhibit a rather complicated field dependence and require an exact theoretical treatment which is also described in this paper. The theoretical results are in perfect agreement with the observed complicated shifts. The determined dipole moment can serve as a critical test for the applicability of the Rittner ionic model to the alkaline-earth monohalides.

II. STARK EFFECT IN A $^2\Sigma$ STATE WITH hfs

As an experimental result we get transition frequencies for transitions between hyperfine levels of two adjacent rotational states which belong to the same vibrational state. These levels are split and shifted in an electric field by the Stark interaction.

The alkaline-earth monohalides have a $^2\Sigma$ ground state and angular momenta are coupled according to Hund's case b.[20] The energy of hfs levels of a rotational state in a Stark field is given as solution of the Schrödinger equation using the effective Hamiltonian

$$\hat{H}_{\text{tot}}=\hat{H}_{\text{rot}}+\hat{H}_{\text{sr}}+\hat{H}_{\text{hfs}}+\hat{H}_{\text{Stark}}\ , \quad (1)$$

with

$$\hat{H}_{\text{rot}}=B\hat{N}^2 \quad (2)$$

and

$$\hat{H}_{\text{sr}}=\gamma_{\text{sr}}\hat{N}\cdot\hat{S} \quad (3)$$

describing the rotational energy and the effective electron spin rotation interaction, respectively. The hfs Hamiltonian

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

is that of Frosch and Foley[21] with terms added to include nuclear spin rotation and electric quadrupole interaction for one coupling nucleus.[22,23] The Stark effect is given by

$$\hat{H}_{\text{Stark}} = |E|\ |\mu|\,\widehat{\cos}\theta \qquad (5)$$

with θ being the angle between the electric field E and the dipole moment μ. Matrix elements are calculated in the representation $|(NS)JIFM_F\rangle$ corresponding to a Hund's case $b_{\beta J}$.[20] Table I shows the selection rules for the matrix elements of the different terms of the Hamiltonian. Without an external field there are no significant matrix elements nondiagonal in N and F. The small $\Delta N = \pm 2$ contributions from the dipolar spin-spin and electric quadrupole interaction can be neglected for the alkaline-earth monohalides. The energy matrix thus factorizes into 2×2 matrices and simple analytical expressions can be given for the energy levels.[23] The Stark effect requires a more elaborate treatment using either degenerate perturbation theory or numerical matrix diagonalization.

Matrix elements of the terms in (2), (3), and (4) are listed in Ref. 13 in terms of (nj) symbols. The matrix element for the direction cosine in (5) has been given by Dixon and Woods[24] who used the method of reversed angular momentum.[25] A recalculation using the technique applied in Ref. 13 confirmed their results:

$$\langle (NS)JIFM_F|\cos\theta|(N'S)J'IF'M_F\rangle = (-1)^t[N,N',J,J',F,F']^{1/2}\begin{pmatrix} N' & 1 & N \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} F' & 1 & F \\ M_F & 0 & -M_F \end{pmatrix}\begin{Bmatrix} J' & J & 1 \\ N & N' & S \end{Bmatrix}\begin{Bmatrix} F' & F & 1 \\ J & J' & I \end{Bmatrix}$$

with

$$t = S + J + J' + I + F + F' + 1 - M_F$$

and

$$[N,N',\ldots,F'] = (2N+1)(2N'+1)\cdots(2F'+1)\,.$$

The effective Hamiltonian in (1) contains molecular parameters which are functions of the internuclear distance. As described in Ref. 13 in more detail we adopt the notation of Childs *et al.*[11] for the vibrational and rotational dependence by writing the molecular parameters as Dunham-type series. For the transitions used in our experiments the energy matrix has the size 63×63.

The solution of the Schrödinger equation by matrix diagonalization was chosen in order to avoid limitations from a second-order perturbation theory treatment. Moreover, degenerate perturbation theory, as it was applied by Bergeman and Zare for computing second-order Stark shifts,[26] requires a similar amount of effort. As input parameters our diagonalization program received Dunham coefficients for the rotation as well as the spin-rotation and hfs terms which were taken from Ref. 13 and 11, respectively. Thus the only adjustable parameter was the electric dipole moment μ. All measured Stark field line positions were then simultaneously fitted in a nonlinear least-squares fit.

III. EXPERIMENTAL DETAILS

The molecular-beam apparatus has been described in detail in Ref. 8. An effusive CaCl beam was generated from a high-temperature reaction of $CaCl_2$ and Ca. As shown in Fig. 1 the molecular beam traversed a strong single-frequency pump beam at A which depleted a particular vibration-rotation level of the ground state. A weak probe beam split off the same laser interacts with the molecules at B in order to detect a repopulation of the depleted state. Pump and probe beam of 250 mW and 10 mW, respectively, came from a Coherent 699-21 dye ring laser operated around 593 nm to pump lines in the $B\,^2\Sigma$-$X\,^2\Sigma$ system of CaCl.

Between A and B mw radiation around 18 GHz was introduced by a horn radiator to induce transitions between different hyperfine levels of the $N=1$ and 2 rotational states. A mw intensity of about 5×10^{-6} W/cm^2 was sufficient to stimulate the allowed electric dipole transitions. The mw was amplitude modulated at 160 Hz and phase sensitive detection was used to observe the fluorescence in-

TABLE I. Conserved quantum numbers and selection rules for matrix elements in the basis $|(NS)JIFM_F\rangle$.

Matrix element	Conserved quantum numbers	Selection rule
rotation	N,J,F,M_F	
electron-spin rotation	N,J,F,M_F	
Fermi contact	N,F,M_F	$\Delta J = 0,\pm 1$
dipolar spin-spin	F,M_F	$\Delta N = 0,\pm 2$, $\Delta J = 0,\pm 1$
nuclear spin rotation	N,F,M_F	$\Delta J = 0,\pm 1$
electric quadrupole	F,M_F	$\Delta N = 0,\pm 2$, $\Delta J = 0,\pm 2$
Stark effect	M_F	$\Delta N = \pm 1$, $\Delta J = 0,\pm 1$ $\Delta F = 0,\pm 1$

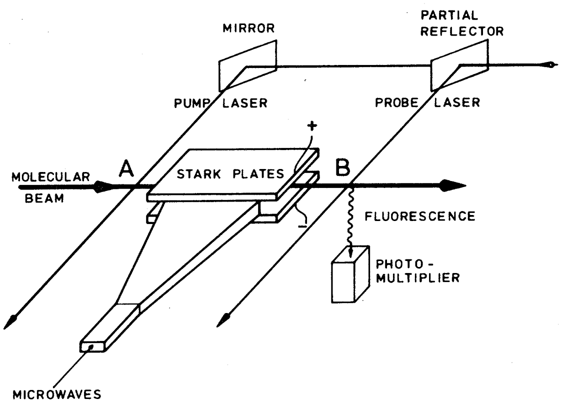

FIG. 1. Experimental scheme.

crease at B when the depleted level was refilled by an induced mw transition. In the mw interaction region an additional Stark field was applied with the field direction parallel to the mw polarization (Fig. 1). The Stark plates of 6 cm length had a separation of 2.5 cm with the voltage varied between 0 and 1200 V in 50-V steps. The electric field strength could be determined with an accuracy of 0.5%.

With the mw polarization parallel to the electric field the selection rule for induced transitions is $\Delta M_F=0$. Stark shifts were measured for the hyperfine components $J=\frac{5}{2}\leftarrow\frac{3}{2}$, $F=1\leftarrow0$ as well as $J=\frac{3}{2}\leftarrow\frac{3}{2}$, $F=1\leftarrow0$ and $F=0\leftarrow0$ of the $N=2\leftarrow1$ transitions in the $v=0$ and 1 vibrational states. The laser frequency was fixed to the appropriate $P_1(2)$ and $P_2(2)$ lines. Figure 2 shows the relevant level diagram for $v=0$. As all lines started from a level with $F=0$ they were only shifted but not split when the electric field was applied. With the interaction region carefully shielded against external magnetic fields the observed linewidth was 15–30 kHz at zero electric field and increased towards high electric fields due to field inhomogeneities at the ends of the Stark plates. At 400 V/cm, i.e., 1000-V Stark voltage, the linewidth reached about 100 kHz.

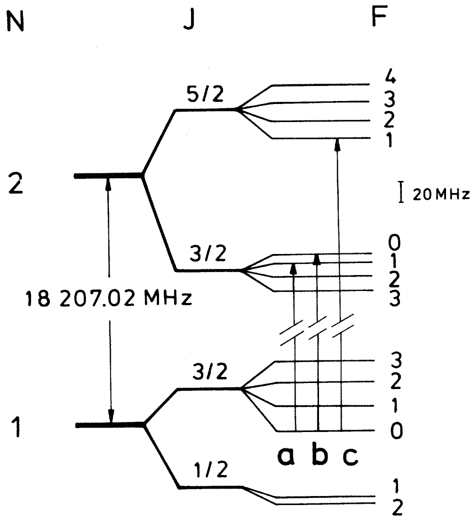

FIG. 2. Energy-level diagram of the $N=2\leftarrow1$ transition in the $X\,^2\Sigma(v=0)$ state of $Ca^{35}Cl$ showing the microwave transitions a, b, and c used for Stark effect measurements.

IV. RESULTS

Figure 3 shows the measured Stark shifts for three hfs components of the $N=2\leftarrow1$ transition in the vibrational ground state. The size of the data points represents the experimental error. Solid lines show the calculated line shifts using (1) with rotational constants from Ref. 13, spin rotation and hfs constants from Ref. 11, and a dipole moment $\mu=4.265(3)$ D. The statistical standard deviation is given in parentheses and due to the uncertainty in the calibration of the Stark field an absolute error of ±0.02 D has to be added. In the same way we got $\mu=4.281(1)\pm0.02$ D for the first excited vibrational state $v=1$. The absolute error mentioned above does not affect the relative difference of the values for $v=0$ and 1, but can only cause a shift of both together. Therefore, the first two coefficients in the usual expansion

$$\mu=\sum_i \mu_i(v+\tfrac{1}{2})^i$$

can be given as (measured in D)

$$\mu_0=4.257(3)\pm0.02$$

and

$$\mu_1=0.016(3)\,.$$

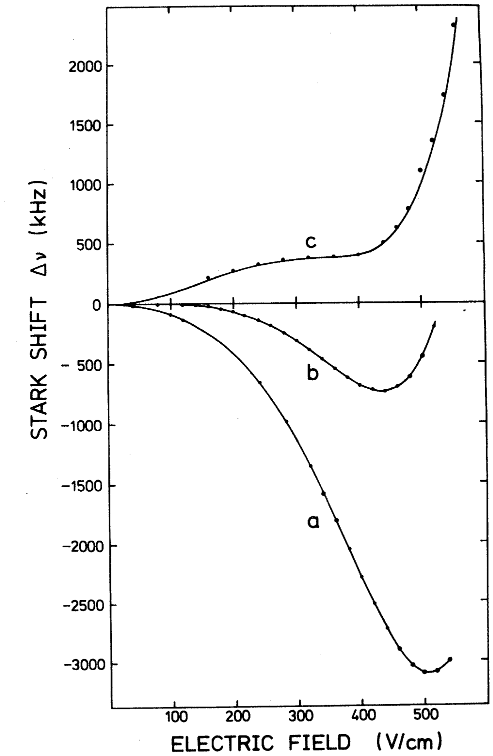

FIG. 3. Stark shift $\Delta\nu$ vs electric field for the microwave transitions a, b, and c. Measurement errors are contained in the size of the data points. The solid lines represent the calculated line shifts for $\mu=4.265$ D.

Energy eigenvalues for the $M_F=0$ components of the investigated hyperfine levels are plotted in Fig. 4 against the square of the electric field for $0 \leq E \leq 700$ V/cm. Except for the $N=2$, $J=\frac{5}{2}$, $F=1$ component the Stark effect is not quadratic in this range. The level diagram of Figs. 2 and 4 derives from the assumption of a Hund's case $b_{\beta J}$ coupling scheme in which the molecular rotation N and the electron spin S form an intermediate angular momentum J coupling with the nuclear spin I to the total angular momentum F. For low-N numbers, however, the coupling scheme is intermediate between $b_{\beta J}$ and $b_{\beta S}$. In a Hund's case $b_{\beta S}$ basis I and S are coupled to an intermediate angular momentum F_1 and the total angular momentum F is formed by a coupling of F_1 and N. In the considered Stark field range the energy shifts are in the order of the hyperfine splitting (cf. Fig. 4) and with increasing electric field, F and N stop to be good quantum numbers. In the vector model, N, S and I, or N and F_1 (in the $b_{\beta J}$ or $b_{\beta S}$ case, respectively) decouple and N starts to precess around the z axis given by the direction of the electric field. Owing to this precession of the magnetic moment of the molecular rotation, coupling of the different angular momenta with N changes more and more to a coupling with N_z. In the electric field range of Fig. 4 the described intermediate coupling scheme therefore experiences a changing basis which leads to the observed unusual shifts. Atomic spectroscopists find similarly complicated level shifts when they study magnetic field effects in the transition region between anomalous Zeeman effect and Paschen back effect.

Figure 5 shows the situation for all $M_F=0$ sublevels of $N=1$ and 2 in a Stark field range in which level shifts become much larger than spin doubling and hyperfine splitting. Then the rotational and Stark Hamiltonians are dominant in (1). The quantum numbers marking the different curves are valid only for fields below 1 kV/cm and are used in this figure only for comparing the plots with Figs. 2 and 4. In the range with $8 < E < 14$ kV/cm, all components deviating downwards exhibit a quadratic behavior whereas those starting with a positive derivative partly change the direction of shift. This is in agreement with the fact that at very high fields far outside this range all components deviate downwards because all experience the repelling interaction from more levels above than below. As the selection rule for the Stark effect is $\Delta F=0,\pm 1$ (cf. Table I) the $|1,\frac{3}{2},3\rangle$ and $|1,\frac{3}{2},2\rangle$ levels are pushed downwards first by the descending $|2,\frac{3}{2},2\rangle$ and $|2,\frac{3}{2},3\rangle$ levels. The absolute energy difference between two repelling undisturbed states determines the denominator of the interaction energy and therefore it takes higher fields until the descending levels with $N=3$ force the $|2,\frac{5}{2},4\rangle$ and $|2,\frac{5}{2},3\rangle$ levels to turn downwards.

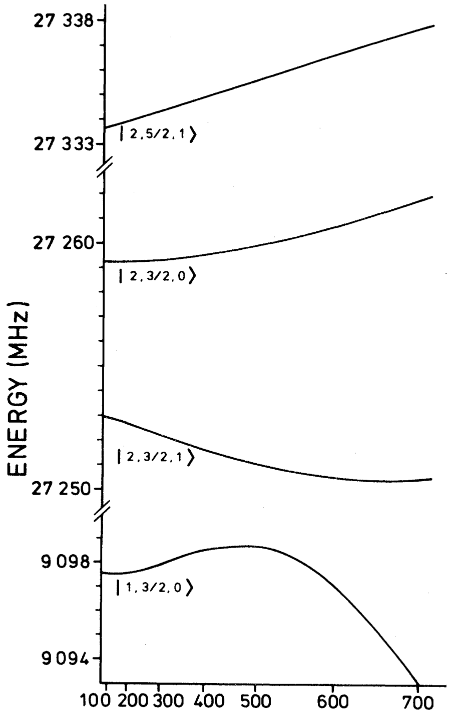

FIG. 4. Calculated Stark shifts of hyperfine levels $|N,J,F\rangle(v=0)$ for $M_F=0$.

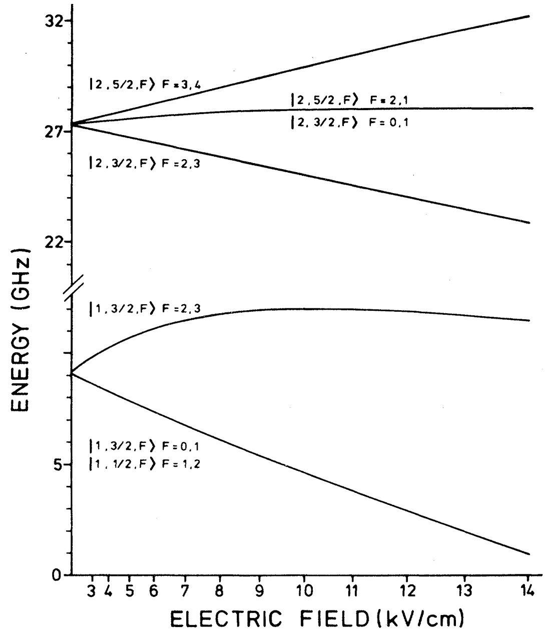

FIG. 5. Calculated Stark shifts of hyperfine levels $|N,J,F\rangle(v=0)$ for $M_F=0$ in the electric field range with $E_{\text{Stark}} \gg E_{\text{sr}}, E_{\text{hfs}}$.

The computed field dependence in the high-field range does not only agree with the qualitative considerations above but also with the much simpler Stark field behavior of ${}^1\Sigma$ states. Several authors studied ${}^2\Sigma$ molecules in electric fields where the Stark effect was large compared to the spin doubling and hyperfine interaction,[18,27] and compared the measured Stark shifts with the second-order perturbation theory result for a ${}^1\Sigma$ state:[20]

$$W=\frac{\mu^2E^2}{hB}\,\frac{N(N+1)-3M_N^2}{2N(N+1)(2N-1)(2N+3)}\ . \tag{6}$$

Taking the measured dipole moment μ and the rotational constant B of CaCl, the formula can be used to calculate shifts for $N=1$ ($M_N=0$ and 1) and $N=2$ ($M_N=0$, 1, and 2). The results are in accordance with the plots for $M_F=0$ in Fig. 5: (6) yields straight lines in this picture and that for $N=2$, $M_N=0$ is identical with the two components of $N=2$ deviating upwards. $N=2, M_N=1$ fits the slope of the four middle components and $N=2, M_N=2$ yields the same straight line as the two components pointing downwards. The same agreement is found for $N=1$ with $M_N=0$ having a positive and $M_N=1$ a negative slope. For a comparison of quantum numbers the coupling scheme described before has to be considered in which M_F is formed by coupling the projections of N, S, and I on the z axis, i.e., M_N, M_S, and M_I. Thus components with $M_N=0$, 1, and 2 can be coupled with the appropriate M_S and M_I to form $M_F=0$ yielding exactly the result of Fig. 5. Application of (6), however, cannot show deviations from quadratic behavior, since the Stark interaction with levels of adjacent N is only considered in second-order basing on the assumption of $E_{\text{Stark}} \ll E_{\text{rot}}$. According to Fig. 5 this has to be carefully checked if the simple formula (6) is used. Dagdigian applied his beam deflection measurements to the $N=2$, $M_N=0$ state of CaCl (Ref. 18) which shows a good behavior in this sense; as already pointed out, the corresponding upper component of $N=2$ in Fig. 5 has a quadratic electric field dependence.

V. DISCUSSION

Molecular-beam laser-microwave double-resonance experiments allowed the first precise Stark effect measurements of an alkaline-earth monohalide radical. So far there has been only an electric deflection study of CaCl by Dagdigian[18] yielding an estimate of 3.6±0.6 D for the ground-state dipole moment. This value is in fair agreement with our measurement.

Hyperfine studies by Childs *et al.*[11] and Bernath *et al.*[14] show the highly ionic character of these radicals. As there is reason to assume a completely ionic bonding for all calcium halides[14] the application of the Rittner ionic model[15] to this class of molecules should be possible. Klynning and Martin[17] fitted such a model to their experimental spectroscopic results of the $X\,^2\Sigma$, $A\,^2\Pi$, and $B\,^2\Sigma$ states and evaluated dipole moments, transition moments, and electronic structures of these states. Whereas some of these quantities agreed well with other experimental data their electric dipole moment now proved to be completely wrong. They predicted a dipole moment $\mu \simeq 0.36$ D for the CaCl ground state. Obviously this model of a polarizable ion pair cannot be transferred from the alkali halides to the alkaline-earth monohalides without modification.

The group-I—group-VII molecules consist of a positive closed-shell alkali ion and a negative closed-shell halogen ion. For the II-VII radicals the main difference is given by the fact that the positive alkaline-earth ion has a single electron outside a closed-shell core. In the Rittner model[15] the induced dipole moments μ_1 and μ_2 of the two ions are subtracted from the primary moment $\mu_0 = er_e$ (r_e is the equilibrium separation of the ion centers) to form the electric dipole moment of the molecule $\mu = er_e - (\mu_1 + \mu_2)$. The polarizing fields are calculated from the first two terms of a multipole expansion around the position of the two nuclei. This is a reasonable approximation if many electrons contribute to the polarizability of the ion and if the polarizability is small. In contrast to the alkali ions the singly charged positive alkaline-earth ions have a rather large polarizability[28] and it is mainly the single electron outside the closed-shell core which causes it. In addition, the internuclear distances are smaller and therefore the electric fields are larger. Thus this one electron will be displaced significantly and the center of charge will differ from the position of the nucleus. Convergence of a multipole expansion is very poor under these conditions, so that consideration of monopole and dipole terms only leads to neglect of large contributions. The dipole moment is usually approximated by the first three terms of a power series yielding[15]

$$\mu = e\left[r_e - \frac{\alpha_+ + \alpha_-}{r_e^2} - \frac{4\alpha_+\alpha_-}{r_e^5} - \cdots\right] \tag{7}$$

with α_+ and α_- being the polarizabilities of the alkaline-earth ion and the halogen ion, respectively, usually taken from Ref. 29. For CaCl all three terms in (7) are of the same order of magnitude, which shows that consideration of higher terms would yield quite a different result. Klynning and Martin[17] used (7) with only a small term of $1/r^8$ dependence added and obtained a value near zero. Dagdigian[18] points out that his experimental estimate agrees well with the truncated Rittner model of Brumer and Karplus[16] in which the dipole moment is represented by the first two terms in (7). The result of these first two terms is $\mu \simeq 3$ D. Under the conditions above we think that the agreement is more of incidental nature.

From the arguments above we conclude that significant modifications to the model are necessary which include the effects of the largely displaced electron at the alkaline-earth ion. We also want to extend the measurements to other alkaline-earth monohalides such as to base a new model on systematic experimental studies.

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