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Energies and electric dipole moments of the low lying electronic states of the alkaline earth monohalides from an electrostatic polarization model

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A simple electrostatic polarization model is applied to the low lying electronic states $A\,^2\Pi$, $B\,^2\Sigma^+$, and $A'\,^2\Delta$ of the alkaline earth monohalides which correlate to the electronic d state of the free metal ion. The number of fit parameters can be greatly reduced using relations which are derived from the well known angular part of the free ion wave function. The model predicts energies and electric dipole moments for all Ca, Sr, and Ba monohalides in good agreement with experimental data. The model can also be applied to the C state confirming the highly ionic character of this state.

I. INTRODUCTION

Ionic models can provide a simple and powerful tool for the understanding of ionic compounds in terms of the properties of their constituent atomic ions. Although originally developed for ionic crystals, ionic models have later been extended and modified to describe small molecules and molecular aggregates, including diatomics, triatomics, dimers, clusters and molecular ions. (See Ref. 1 and references therein.) Among the diatomics, the group of alkaline earth monohalides is of particular interest. Bonding in these species is highly ionic with the unpaired electron centered at the metal, giving rise to a $^2\Sigma^+$ ground state. Excitation of this ns electron to the low lying $(n-1)d$ state forms the molecular states $A\,^2\Pi$, $B\,^2\Sigma^+$ and $A'\,^2\Delta$. During recent years a large amount of precise and detailed spectroscopic information has become available for the X, A, and B states of most of the molecules in this group. They are listed in Refs. 2 to 79 in the order of their date of publication. In the early works dissociation energies,[3,5] optical emission spectra,[2,4] and matrix ESR studies[6] have been reported. In the more recent investigations, microwaves, lasers and double resonance techniques have been employed for gas phase high resolution spectroscopy. Ground state rotational constants have been determined by microwave absorption[21,25,43–45,66,68,69] and by MODR.[10,12,16] Hyperfine structure in the ground state has been resolved by double resonance techniques, both in a cell and in a molecular beam.[24,28–32,41,42,48,49,52,54,56,57,61,72,73] Measurements of electric dipole moments have been performed with a molecular beam double resonance method for the ground states[47,50,53,58,59,64,65,70,72,74] of many molecules in the group. Dipole moments for the A and B states have been reported only for CaCl,[71] but have recently been measured for the A and C states of CaF[92] and the A and B states of SrF.[93] The remaining references refer to high resolution optical spectroscopy of excited states, mostly $A\,^2\Pi$, $B\,^2\Sigma^+$ and $C\,^2\Pi$. Information about the $A'\,^2\Delta$ state is scarce. Only for BaF[79] and BaCl[55] has this state been undoubtedly assigned and was found to be rather low in energy.

Ab initio calculations have been reported for some selected ground state dipole moments[80] and for the X,A, and B states of CaCl.[81] Extension of these calculations for the heavier molecules in this group seems to be presently out of scope. It is therefore very tempting to try to understand the general trend of the experimental data by an ionic model and perhaps to make some useful predictions. There are two possible types of ionic models which can be used. In the "crystal field" or "ligand field" approach the electrostatic interaction energy of the metal ion M^+ with the point charge and induced dipole of the ligand and the resulting change of the ionic wave function is calculated by quantum mechanics. The only molecular parameter which has to be taken from experimental data is the internuclear distance. Calculations of this type have been done successfully by Rice, Martin, and Field[82] for the Ca monohalides. Their calculations did not only include X, A, and B states but also the $C\,^2\Pi$ state which arises from excitation of the unpaired electron to the p state.

Unfortunately the knowledge of precise free ion wave functions is indispensable for ligand field calculations and Rice *et al.*[82] have shown that not only ns, np and $(n-1)d$ wave functions have to be known but that higher "Rydberg states" play an important role. For this reason no attempt has been made yet to extend ligand field calculations to the Sr and Ba monohalides.

In the second kind of ionic models the electrostatic interaction is calculated by classical physics using free ion polarizabilities. The most commonly known model of this type is the Rittner model[83] which has been very successfully applied to the ground state of the alkali halide molecules. It was shown in a previous paper that the Rittner model breaks down for the alkaline earth monohalides because of the very high polarizability of the alkaline earth ions.[84] An improved model was proposed which gives the ground state data in good agreement with experimental results. In the present paper this simple model is extended to describe the A,B and A' states for the Ca, Sr, and Ba monohalides.

II. THEORY

A. The model

The general form of a semiclassical potential for ionic compounds is

$$V(R) = A\exp(-R/\rho) - e^2/R - \Phi_{\mathrm{pol}} - C/R^6. \quad (1)$$

This is essentially the Born–Mayer potential[85] with an additional term Φ_{pol} included to describe the mutual polariza-

tion of the two ions. The various modifications of this model differ mainly in the form of this polarization term and in the treatment of the internuclear distance R in the repulsion term as an effective separation parameter to model the effects of charge overlap.

When the model is applied to the electronically excited states of the alkaline earth monohalides, slight modifications have to be made. Since the unpolarized, unpaired electron is now not in a spherically symmetric s state but in a d (or p) state, the electrostatic interaction of the quadrupole moment of this charge distribution with the point charge of the ligand has to be taken into account. Interactions of this quadrupole moment with the induced dipole moment in the ligand may be neglected. The excitation energy of the free ion E^{FI} must also be added. The potential energy then takes the form:

$$V(R) = E^{FI} + A \exp(-R/\rho) - e^2/R + \frac{e^2 Q}{2R^3}$$
$$- \Phi_{pol} - C/r^6,\qquad (2)$$

where Q of the unpaired electron is given by

$$Q = \int \Psi^* r^2 (3 \cos^2 \Theta - 1) \Psi \, dV.\qquad (3)$$

As in the ligand field calculations it is assumed here that the energies of the excited molecule states depend only on E^{FI} and on the changes in the electrostatic interaction energy compared to the ground state. Possible small changes in A, ρ, C and the internuclear distance R are neglected.

The excitation energy of the molecule is then:

$$T_i = E_i^{FI} + \frac{e^2 Q_i}{2R^3} - (\phi_{pol}^i - \Phi_{pol}^{ground}).\qquad (4)$$

In the calculation of the polarization terms one has to take into account the large charge shift which results from the strong hybridization of the unpaired electron in the field of the ligand. This is done by the model proposed in Ref. 84. The induced moment is described in this model not as usual by a point dipole but by a point charge $+e$ at the position of the metal and a point charge $-e$ shifted away from the ligand by ΔR along the internuclear axis. The resulting induced dipole moment μ^+ is related to the metal polarizability α^+ and the polarizing field of the ligand at the position of the displaced negative charge:

$$\mu^+ = e \Delta R = \alpha^+ \left(\frac{e}{(R + \Delta R)^2} + \frac{2\mu^-}{(R + \Delta R)^3} \right).\qquad (5)$$

Polarization of the ligand is described in the usual way with the polarizing field resulting from a point charge $+2e$ at a distance R plus a charge $-e$ at a distance $(R + \Delta R)$:

$$\mu^- = \alpha^- \left(\frac{2e}{R^2} - \frac{e}{(R + \Delta R)^2} \right).\qquad (6)$$

Simultaneous solution of Eqs. (5) and (6) leads to an expression for ΔR which can be calculated by a simple iteration program.

The contribution of the mutual polarization to the electrostatic energy is given by

$$\Phi_{pol} = -\frac{e^2}{R} + \frac{e^2}{(R + \Delta R)} - \frac{2\mu^- e}{R^2}$$
$$+ \frac{\mu^- e}{(R + \Delta R)^2} + \frac{(\mu^+)^2}{2\alpha^+} + \frac{(\mu^-)^2}{2\alpha^-}.\qquad (7)$$

The last two terms represent the quasielastic energy stored in the induced dipoles. It should be noted that this model for the metal polarization implicitly includes higher order than dipole polarizabilities.

Electric dipole moments are an additional and very sensitive test for the validity of the model. A few experimental values of dipole moments in electronically excited states have become available during the recent years and can be compared with the prediction from the model which gives

$$\mu = eR - (\mu^+ + \mu^-).\qquad (8)$$

B. Relations between the input parameters

The quadrupole moments Q and the ion polarizabilities α^+ which are implicitly determined in the ligand field calculations from the free ion wave functions are treated here as adjustable parameters. This has the advantage that no wave functions have to be known and that model errors are partially absorbed. On the other hand, however, the predictive power of the model is severely reduced. It is therefore essential to keep the number of independent fit parameters as small as possible. For the $A\,^2\Pi$, $B\,^2\Sigma^+$, and $A'\,^2\Delta$ states of the molecules we are in a very favorable situation, since all these three molecular states are correlated to the same atomic d state. Keeping in mind that the angular part of the free ion wave functions is given by the spherical harmonics and only the radial part is unknown one can derive relations between the fit parameters which must be fulfilled if these parameters have a distinct physical meaning.

The polarizability of an electron in a $(nd\sigma)$ state along the internuclear axis is given to second order by

$$\alpha = 2 \sum_{n'} \left(\frac{|\langle nd\sigma | z | n'p\sigma \rangle|^2}{E_{n'p} - E_{nd}} + \frac{|\langle nd\sigma | z | n'f\sigma \rangle|^2}{E_{n'f} - E_{nd}} \right),\qquad (9)$$

where the sum is over all states outside the closed shells. Note that in the corresponding expression for a $(nd\pi)$ state the energy difference in the denominator remains unchanged. The most important contribution comes from the terms with $n' = n + 1$. The second term in Eq. (9) may be neglected since the matrix elements are smaller and the energy differences much larger than in the first term. The ratio of the polarizabilities for the $(nd\sigma)$ and $(nd\pi)$ states then depends only on the angular part of the wave functions and can be calculated as:

$$\alpha^+(nd\sigma):\alpha^+(nd\pi) = \alpha^+(B\,^2\Sigma):\alpha^+(A\,^2\pi) = 4/3.\qquad (10)$$

The polarizability in the $(nd\delta)$ state is very small since only mixing with $(nf\delta)$ states is possible. A rough estimate of Eq. (9) shows that $\alpha^+ (A'\,^2\Delta)$ should not be greater than about 5% of $\alpha^+ (A\,^2\Pi)$. It may therefore be completely neglected or—in a somewhat better approximation—kept at a fixed value of about

$$\alpha^+(A'\,^2\Delta) = 0.5\ \text{Å}^3 \qquad\qquad (11)$$

for all three metal ions.

Using these relations, only one polarizability has to be treated as a free parameter to describe all monohalides of one metal in the three electronic states $A\,^2\Pi$, $B\,^2\Sigma^+$, and $A'\,^2\Delta$.

The ratio of the quadrupole moments of an electron in $(nd\sigma)$, $(nd\pi)$, and $(nd\delta)$ states is also independent of the radial part of the wave functions

$$Q(nd\sigma):Q(nd\pi):Q(nd\delta) = 2:1:-2. \qquad (12).$$

However, the expression $(1/2)(Q\,e^2/R^3)$ for the interaction energy with the ligand only holds if the point charge representing the ligand is completely outside the charge distribution of the electron. Otherwise, this energy is reduced. In the ligand field calculations this effect is explicitly taken into account.[82] Without the knowledge of the wave function Q has to be considered as an effective parameter which depends on the internuclear distance R. Fortunately, the d functions are relatively compact so that overlap with the point charge of the ligand may be neglected except for the fluorides, for which the internuclear distance is about 0.5 Å smaller than for the chlorides. This can be seen from the Ca$^+$ wavefunctions plotted in[82] and the Sr$^+$ wavefunctions in Ref. 6. So for modeling Q only one parameter has to be fitted for each metal plus an additional factor which reduces this value for the fluorides. The fact that internuclear distances vary only slightly with the metal ion suggests that the values of Q and its reduction factor for the fluorides should be nearly the same for all three ions.

The situation is much less favorable for the $C\,^2\Pi$ state which correlates with the np state. Since this state is mixed strongly with the lower lying $(n-1)d$ state, it is backpolarized and exchange forces which are not considered in the model may become important. Moreover, the np wave function is much more extended than the $(n-1)d$ function so that overlap with the ligand is severe.[6,82] The quadrupole moment in the model is therefore an effective parameter for all monohalides and has to be fitted separately for each molecule. Then no degree of freedom is left in the fit so that the validity of the model cannot be tested. For comparison with the ligand field calculations we have nevertheless tentatively included the C state in the calculations using a fixed value of Q for all monohalides except the fluorides and the same factor as in the d state for the reduction of Q for the fluorides.

TABLE I. Fixed input parameters.

Ion	Ion polarizabilities[a,b] α^+,α^- [Å^3]	Excitation energies (cm^{-1})[c] $E_{n-1,d}$	$E_{n,p}$
Ca$^+$	7	13 687	25 340
Sr$^+$	9	14 724	24 250
Ba$^+$	12	5 354	21 389
F$^-$	0.69		
Cl$^-$	2.55		
Br$^-$	3.50		
I$^-$	5.35		

[a] Metal polarizabilities from Ref. 5.
[b] Halogen polarizabilities are effective values from Ref. 84.
[c] From Ref. 91.

III. RESULTS AND DISCUSSION

There are two groups of input parameters for the calculations. Polarizabilities for the ground states and excitation energies of the ions are listed Table I. The metal polarizabilities have been calculated by Hildenbrand.[5] The polarizabilities of the halogen ions differ from the free ion values of Pauling.[86] They take into account partial quenching of the polarizability of the negative ion in a molecule[87] and have been adjusted to fit the dipole moments of the alkali halides.[84] So none of the constants in this first group has been adapted to any molecular property of alkaline earth monohalides.

The few remaining free parameters were adjusted to give best agreement between calculated and experimental values of excitation energies and excited state dipole moments. They are listed in Table II. The results of the calculations are given in Table III. Experimental data and the best ligand field results for the Ca monohalides[82] have been included for comparison. Figure 1 gives an impression of the relative importance of the different energy terms in the model [cf. Eq. (4)] for CaCl.

Looking first at the $A\,^2\Pi$ and $B\,^2\Sigma^+$ state energies one can see that the model works surprisingly well, giving significantly better results for the Ca monohalides than the ligand field calculations. Agreement with experimental data is even slightly better for the Sr and Ba halides. These numerical results depend rather critically on the choice of the input parameters listed in Table II. Changing one of the relevant parameters by only 10% results in energy shifts for the Ca monohalides between 350 and 1100 cm^{-1} with an average of about 600 cm^{-1}. This demonstrates that ligand field results will depend very critically on the quality of the available wave functions. It also shows that the relations (10) and (12) used in our model to reduce the number of independent input parameters are all well fulfilled. An independent choice of the polarizabilities $\alpha^+(A\,^2\pi)$ and $\alpha^+(B\,^2\Sigma^+)$ or of the quadrupole moments in the fit does not lead to any significant improvement. Of particular interest is the energy of the $A'\,^2\Delta$ states. Only for BaF[79] and BaCl[55] this state has been undoubtedly assigned by optical spectra and found to be lower in energy than the A and B states. Similar metastable $^2\Delta$ states have been identified in the laser induced spectra of BaH and BaD[88] which also have a highly ionic bond. The model calculations are in very nice agreement with the BaF and BaCl data. A total neglect of the $A'\,^2\Delta$ state polarizability gives energies 1500 and 1000 cm^{-1} higher for BaF and BaCl, respectively, worsening the first and improving the second.

TABLE II. Adjusted input parameters for the calculation of excited state data given in Table III.

	Ca$^+$	Sr$^+$	Ba$^+$
$\alpha^+(A\,^2\Pi)$ [Å^3]	9	14	7.5
$Q(A\,^2\Pi)^a$[Å^2]	0.9	0.9	1.0
$\alpha^+(C\,^2\Pi)$ [Å^3]	−0.35	0.00	+0.9
$Q(C\,^2\Pi)^a$ [Å^2]	−2.6	−2.6	−3.6

[a] Reduction factor for fluorides: 2/3.

TABLE III. Model calculations for the alkaline earth monohalides and comparison with experimental data and ligand field results.

		$X^2\Sigma^+$	$A^2\Pi$	$B^2\Sigma^+$	$A'^2\Delta$	$C^2\Pi$
CaF:$R = 1.952$ Å						
	model		16 340	18 620	17 690	29 850
T|cm^{-1}|	expt.[a]		16 530	18 850	···	30 270
	lig. field[b]		17 980	21 460	24 950	32 640
	model	3.34	2.57	1.59	7.73	9.21
μ|D|	expt.	3.07[c]	2.45[d]	···	···	9.24[d]
	lig. field[b]	3.00	4.09	5.71	7.57	8.23
CaCl:$R = 2.437$ Å						
	model		15 630	17 210	16 040	27 000
T|cm^{-1}|	expt.[a]		16 130	16 850	(14 800)[c]	26 540
	lig. field[b]		17 480	19 320	22 960	29 630
	this work	4.47	3.65	2.62	8.96	10.19
μ|D|	expt.	4.27[f]	3.54[g]	4.03[g]	···	···
	lig. field[b]	3.86	4.80	6.22	8.40	9.62
CaBr:$R = 2.594$ Å						
	model		15 120	16 210	16 300	27 400
T|cm^{-1}|	expt.[a]		15 950	16 380	···	25 430
	lig. field[b]		17 260	18 720	22 310	28 800
	model	4.81	3.97	2.91	9.30	10.47
μ|D|	expt.	4.36[h]	···	···	···	···
	lig. field[b]	4.19	5.08	6.45	8.71	10.09
CaI:$R = 2.829$ Å						
	model		14 590	15 140	16 420	27 680
T|cm^{-1}|	expt.[a]		15 620	15 715	(15 540)[c]	23 530
	lig. field[b]		16 870	17 880	21 380	27 760
	model	5.26	4.40	3.30	9.76	10.85
μ|D|	expt.	4.60[i]	···	···	···	···
	lig. field[b]	4.62	5.41	6.75	9.55	10.56
SrF:$R = 2.075$ Å						
T|cm^{-1}|	model		15 300	16 950	19 830	27 780
	expt.[a]		15 210	17 270	···	27 420
μ|D|	model	3.66	2.15	1.03	8.53	9.19
	expt.	3.47	2.06[i]	0.91[i]	···	···

TABLE III (continued).

		$X^2\Sigma^+$	$A^2\Pi$	$B^2\Sigma^+$	$A'^2\Delta$	$C^2\Pi$
SrCl:$R = 2.576$ Å						
T|cm^{-1}|	model		15 040	16 180	17 750	25 650
	expt.[a]		14 970	15 720	···	25 320
μ|D|	model	5.08	3.50	2.32	9.95	10.52
SrBr:$R = 2.735$ Å						
T|cm^{-1}|	model		14 700	15 430	17 850	26 030
	expt.[a]		14 850	15 350	···	24 500
μ|D|	model	5.47	3.87	2.67	10.34	10.88
SrI:$R = 2.974$ Å						
T|cm^{-1}|	model		14 360	14 660	17 830	26 320
	expt.[a]		14 590	14 815	···	22 940
μ|D	model	6.00	4.35	3.12	10.86	11.37
BaF:$R = 2.163$ Å						
T|cm^{-1}|	model		12 330	14 250	11 100	19 970
	expt.[a]		11 970	14 060	10 940[m]	20 100
μ|D|	model	3.47	4.95	4.08	9.07	8.67
	expt.	3.17[n]	···	···	···	···
BaCl:$R = 2.683$ Å						
T|cm^{-1}|	model		10 850	12 365	8 770	19 390
	expt.[a]		10 680	11 880	9 740[o]	19 260
μ|D|	model	5.14	6.66	5.77	10.68	10.32
BaBr:$R = 2.845$ Å						
T|cm^{-1}|	model		10 190	11 330	8 830	20 305
	expt.[a]		10 290	11 325	···	18 920
μ|D|	model	5.57	7.12	6.21	11.10	10.75
BaI:$R = 3.085$ Å						
T|cm^{-1}|	model		9 420	10 160	8 780	21 220
	expt.[a]		9 590	10 420	···	18 190
μ|D|	model	6.14	7.71	6.79	11.66	11.33
	expt.	5.97[p]	···	···	···	···

[a] From Ref. 89 when no other reference is given.
[b] From Ref. 82.
[c] From Ref. 58.
[d] To be published (Ref. 92).
[e] From Ref. 35.
[f] From Ref. 59.
[g] From Ref. 71.
[h] From Ref. 53.
[i] From Ref. 65.
[k] From Ref. 64.
[l] From Ref. 93.
[m] From Ref. 79.
[n] From Ref. 72.
[o] From Ref. 55.
[p] From Ref. 74.

For BaBr and BaI the $A'\,^2\Delta$ state should also be lower than the A and B states while it is expected to be higher for all Sr monohalides. Predictions for the Ca monohalides are difficult, since here the results depend even more critically on the assumed polarizability in this state. $\alpha^+(A'\,^2\Delta) = 0$ gives an upper limit of 20 000 cm^{-1} for CaF and 17 500 cm^{-1} for the other halides, still 4000 to 5000 cm^{-1} lower than the ligand field predictions. However, a polarizability of about 0.5 Å^3 as assumed in Table III seems more likely, putting the $^2\Delta$ state very near to the A and B states. No direct experimental evidence is available, but Klynning and Martin[35] have given arguments based on an analysis of perturbations between Σ, Π and Δ states that the energy of the $^2\Delta$ state may be around 14 800 and 15 540 cm^{-1} for CaCl and CaI, respectively. This would be in reasonable agreement with the model predictions.

Electric dipole moments provide a very critical test for ionic models. Unfortunately, only very few dipole moments

in excited states of the alkaline earth monohalides have been measured so far. A few of them have not yet been published.[92,93] They are enclosed in Table III. For the $A\,^2\Pi$ state data are available for CaF,[92] CaCl,[71] and SrF.[93] They are well reproduced by the model. According to Eq. (10), the polarizability in the $B\,^2\Sigma$ state is expected to be greater by a factor 4/3, giving rise to a smaller total dipole moment. While this is very nicely fulfilled for SrF it is in contradiction to the experimental result for CaCl.[71] The reason for this discrepancy is not fully understood at the moment. It may be an indication that an appreciable amount of 4s character is admixed to the $B\,^2\Sigma$ wave function by higher order polarization effects and that this is less important for the Sr and Ba compounds. More experimental data of dipole moments in $A\,^2\Pi$ and $B\,^2\Sigma$ states of the alkaline earth monohalides are highly desirable for a further critical test of the model. Dipole moments for the $A'\,^2\Delta$ states are easy to predict since metal polarizabilities are very small in this state. Here the
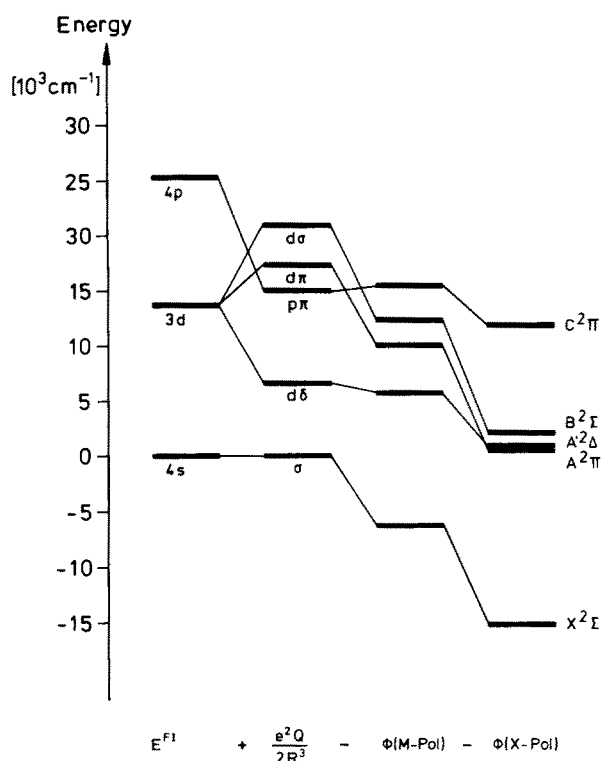
FIG. 1. The effects of the various energy terms in the model calculation for CaCl shown relative to the energies of the free Ca$^+$ ion states.

results from the ligand field and our model calculations are in complete agreement.

Results for the C states are much less conclusive although it is possible to reproduce all energies reasonably well. As for the d electron, the quadrupole moment of the p electron seems to be nearly the same for all ions. Although the agreement with experimental energies is on the average better than from ligand field calculations, the model fails to give the correct falling trend in the energies from fluorides to iodides.

For the Ca monohalides it can be tested whether this is due to the oversimplified treatment of the effective quadrupole moment by calculating these moments with the Ca$^+$ wave functions given by Weiss.[90] To take into account the extension of the electron charge distribution the operator r^2 in Eq. (3) has to be replaced by R^5/r^3 for $r > R$. Results for Q_{eff} ($3d\pi$) and Q_{eff} ($4p\pi$) are listed in Table IV. They show that assuming a constant Q_{eff} ($3d\pi$) for CaCl, CaBr, and CaI in the model is a good approximation. The calculated value of CaF is smaller by a factor of about 3/4, still in rea-

TABLE IV. Calculated effective quadrupole moments[a] of Ca$^+$ $3d\pi$ and $4p\pi$ electrons using Weiss wavefunctions 90.

	Q_{eff} ($3d\pi$)	Q_{eff} ($4p\pi$)
CaF	0.39	− 0.78
CaCl	0.49	− 1.37
CaBr	0.51	− 1.55
CaI	0.53	− 1.79

[a] All values in Å^2.

TABLE V. Energies of $C\,^2\Pi$ states of the Ca monohalides[a] using calculated Q_{eff} values of Table IV scaled up by a factor 2.2.

	Calculated	Experiment
CaF	29 990	30 200
CaCl	25 340	26 500
CaBr	24 710	25 400
CaI	24 250	23 500

[a] In cm^{-1}.

sonable agreement with the factor of 2/3 assumed in the model. However, the absolute value of Q_{eff} comes out too small. Results from the fit are larger by a factor of about 1.75. A much more pronounced dependence on the internuclear distance is found for Q_{eff} ($4p\pi$). This shows that the assumptions made in the fit for the C states are a rather poor approximation. Again all calculated values are too small. Excellent agreement between calculated and experimental energies can be obtained by scaling up the calculated Q_{eff} with a factor of 2.2. Results are listed in Table V.

Although it cannot be excluded that this excellent agreement is merely accidental we take it as a strong indication that bonding in the C state remains predominantly ionic and that the Weiss functions give expectation values $\langle \Psi | r^2 | \Psi \rangle$ which are too small.

ACKNOWLEDGMENT

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