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# Theoretical study of the dipole moments of selected alkaline-earth halides

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*Ab initio* calculations at the self-consistent-field (SCF), singles plus doubles configuration-interaction (SDCI), and coupled pair functional (CPF) level are reported for the dipole moments,  $\mu_e$ , and dipole derivatives,  $(\partial\mu/\partial r)_{r_e}$ , of the  $X^2\Sigma^+$  ground states of BeF, BeCl, MgF, MgCl, CaF, CaCl, and SrF. For comparison, analogous calculations are performed for the  $X^1\Sigma^+$  state of KCl. The CPF results are found to be in remarkably better agreement with experiment than are the SCF and SDCI results. Apparently higher excitations are required to properly describe the radial extent along the bond axis of the remaining valence electron on the alkaline-earth metal.

## I. INTRODUCTION

The charge distribution and spectroscopic parameters ( $r_e, \omega_e, D_e$ ) for the highly ionic alkali halides are well represented by the Rittner model,<sup>1</sup> which treats the ions as spherical charge distributions and ignores terms higher than dipole in the mutual polarization. However, the polarizability of the alkaline-earth ions is much larger than the corresponding alkali atoms, and the Rittner model has failed to account for the electric dipole moment functions (EDMF), which are a sensitive measure of the charge distribution. The recent availability of accurate experimental dipole moments for the calcium halides<sup>2-6</sup> and for SrF<sup>7</sup> has motivated the development of more sophisticated models to describe the electronic structure of these molecules. Rice, Martin, and Field (RMF)<sup>8</sup> have developed a ligand field model, which approximates the halide as a polarizable negative charge perturbing the one-electron valence structure of the alkaline-earth positive ion. Application of this model to the calcium monohalides gave reasonably accurate electronic energies, transition moments, and permanent dipole moments. Töring, Ernst, and Kindt (TEK)<sup>9</sup> have proposed an ionic model that modifies the Rittner model to account for the large charge shifts in the metal ions arising from the polarization. This model gives dipole moments for the alkaline-earth halides that are in reasonable agreement with experiment, in contrast to the Rittner model.

The only previous *ab initio* dipole moments reported for the alkaline-earth halides are the results of Honjou *et al.*<sup>10</sup> for CaCl. Although their dipole moment obtained at the computed equilibrium internuclear distance,  $r_e$ , agreed well with experiment, their  $r_e$  was considerably too large owing to neglect of core-valence correlation. This introduces a large uncertainty in the determination, because the EDMF is a steep function of  $r$ . Their theoretical study indicated that the  $X$ ,  $A$ , and  $B$  states of CaCl were best described as a  $\text{Ca}^{+2}\text{Cl}^{-1}$  core with one electron in a nonbonding calcium

centered orbital polarized away from the  $\text{Cl}^{-1}$  ion.

In this work we report  $\mu_e$  and  $(\partial\mu/\partial r)_{r_e}$  for BeF, BeCl, MgF, MgCl, CaF, CaCl, and SrF. Near Hartree-Fock (HF) quality Slater basis sets are employed augmented with sufficiently diffuse functions to describe the dipole moments. Electron correlation is included using the core-valence (CV), singles plus doubles configuration-interaction (SDCI), and the coupled pair functional (CPF)<sup>11</sup> approaches. The valence electrons on both the metal and halide ions are correlated, since this is a necessary requirement for the determination of accurate potentials.<sup>12</sup> The CPF approach is found to give substantially better dipole moments than single-reference SDCI. Hence, higher than double excitations improve the radial and angular correlation, resulting in a significantly better orbital description of the unpaired electron that is polarized away from the metal by the halide ions.

In Sec. II we briefly discuss the Slater basis sets employed as well as the CV, SDCI, and CPF methods of including electron correlation. In Sec. III we compare our theoretical dipole moments with experiment. Sec. IV contains our conclusions.

## II. METHODS

Extended Slater basis sets have been used for all of the metal halides considered in the present study. Beginning with the accurate sets of Clementi and Roetti,<sup>13</sup> the basis sets were first modified slightly to reduce linear dependency and then augmented with diffuse and polarization functions. The K [10s8p4d 2f] Slater basis is given in Table I(a) of Ref. 12. The Mg [8s6p4d 2f], Ca [10s8p4d 2f], and Sr [12s10p7d 3f] Slater basis sets are given in Table I(b) of Ref. 12. The Be [6s5p3d 1f] basis is that given in Table I(b) of Ref. 12 minus the tight 2p(6.0), 3d(4.0), 3d(8.0), and 4f(2.8) functions that were required for correlating the Be 1s electrons. The F [6s5p4d 2f] and Cl [9s7p3d 2f] basis sets are given in Table

I(c) of Ref. 12. These basis sets are sufficiently flexible to describe both  $F/F^-$  and  $Cl/Cl^-$ . To assess how complete the one-particle basis sets are at the SCF level, we ran a numerical Hartree-Fock (NHF) calculation on BeCl at 3.4 bohr using an implementation of McCullough's code<sup>14</sup> on the Cray-XMP. This gave a total energy of  $-474.1972$  a.u., about 0.02 eV below the basis set calculation. The dipole moment for BeCl at 3.4 bohr at the NHF level is 1.035 D, about 0.007 D less than the basis set result. Hence, the SCF results in this paper should be near the basis set limit.

To help assess how complete our basis sets are for determining the alkaline-earth halide dipole moments, we considered CaCl with an augmented basis. Adding the following Slater functions— $4s(2.015)$ ,  $4p(1.526)$ ,  $3d(1.06)$ ,  $4d(0.75)$ , and  $4f(1.0)$ —decreased the dipole moment for CaCl by about 0.02 D at the CPF level. The dipole moments reported here are probably converged to about 0.05 D with respect to the one-particle basis sets at the SDCI and CPF levels of correlation treatment. Although rather accurate dissociation energies can be computed for these ionic systems at the SCF level (with near HF quality basis sets), the dipole moments provide a more sensitive measure of the charge distribution. Thus, the electric dipole moment functions (EDMFs) are rather sensitive to the inclusion of electron correlation. We have included electron correlation using both the single reference singles plus doubles configuration-interaction (SDCI) and coupled pair functional (CPF) approach.<sup>11</sup> Note that the  $X^2\Sigma^+$  states of all these systems are well described by one reference configuration (leading coefficient in SDCI wave function is  $\approx 0.95$ ). The CPF approach is a size-consistent formulation of SDCI obtained through the use of partial normalization denominators. The CPF approach accounts in a realistic way for higher excitations, and thus is far less sensitive to the orbital bias created by the SCF. Since the CPF procedure is based on an energy functional, the density matrix is well defined so that the dipole moment can be evaluated as an expectation value.

The eight valence electrons on the halide ions and the electrons in both the  $n$  and  $(n-1)$  shell of the metal are included in our correlation treatments. Hence, for the alkaline earths Mg–Sr, 17 electrons are correlated, while for BeF and BeCl, 9 electrons were correlated. The Be  $1s$  orbital was constrained to be doubly occupied, because it is localized on

Be, and correlating it is not expected to significantly change the dipole moment. If the  $(n-1)$  shell of the metal is not correlated, the resulting  $r_e$  are significantly too large, which introduces a considerable uncertainty into the permanent dipole moment owing to the strong dependence on  $r$ . For the heavier alkaline-earth halides such as CaCl and SrF, the SDCI and CPF procedures with 17 electrons correlated still result in bond lengths that are slightly larger than experiment. This may arise because the pair-pair terms (double excitations with one electron promoted from each center) are significantly larger, and their full differential bond shortening effect may be masked by the larger, but constant atomic correlation. For CaCl where our bond length error is largest (0.04–0.05 bohr), we have also considered a core-valence (CV) wave function, which excludes the class of double excitations where both electrons are excited from the  $(n-1)$  shell of the metal. This results in a considerable bond contraction and better agreement with experiment (see Table I). However, the resulting dipole moment is close to the SDCI results and not in very good agreement with experiment (see later discussion).

In the SDCI and CPF calculations we invoked the interacting space approximation,<sup>15</sup> i.e., only those double excitations that have nonzero matrix elements with the SCF reference configuration are included. This has a small effect on the total energy, and essentially no effect on the spectroscopic parameters and dipole moments. All core-valence calculations and constrained space orbital variation analyses were carried out on the Cray XMP using the SWEDEN codes.<sup>16</sup> The SDCI and CPF calculations were carried out on the Cyber-205 using the Karlsruhe adaptation<sup>17</sup> of the COLUMBUS codes.<sup>18–21</sup> The Slater integrals were evaluated with the diatomics integral program DERIC.<sup>22</sup>

### III. RESULTS AND DISCUSSION

The first prerequisite for accurate permanent dipole moments is the determination of accurate theoretical potentials. Otherwise, a considerable ambiguity arises depending on whether the RKR or theoretical potentials are employed in the vibrational analysis of the theoretical EDMF. This is of particular concern for the alkaline-earth halides, because the EDMFs are nearly linear and steep ( $\sim 2$ – $3$  D/bohr) functions of bond distance near  $r_e$  (see Table II). Hence, strong

TABLE I. Theoretical spectroscopic parameters ( $r_e, \omega_e$ ) for the  $X^2\Sigma^+$  states of the alkaline-earth fluorides and chlorides.<sup>a</sup>

| Molecule          | $r_e$ (bohr) |       |       |                   | $\omega_e$ (cm <sup>-1</sup> ) |      |      |                   |
|-------------------|--------------|-------|-------|-------------------|--------------------------------|------|------|-------------------|
|                   | SCF          | SDCI  | CPF   | Expt <sup>b</sup> | SCF                            | SDCI | CPF  | Expt <sup>b</sup> |
| BeF               | 2.555        | 2.577 | 2.583 | 2.5719            | 1280                           | 1250 | 1239 | 1247.36           |
| BeCl              | 3.422        | 3.413 | 3.417 | 3.3960            | 846                            | 840  | 834  | 846.7             |
| MgF               | 3.286        | 3.297 | 3.311 | 3.3070            | 738                            | 729  | 719  | 711.69            |
| MgCl              | 4.179        | 4.153 | 4.163 | 4.1557            | 468                            | 468  | 463  | 462.12            |
| CaF               | 3.740        | 3.713 | 3.716 | 3.7171            | 591                            | 587  | 583  | 581.1             |
| CaCl <sup>c</sup> | 4.719        | 4.658 | 4.650 | 4.6090            | 358                            | 361  | 355  | 367.53            |
| SrF               | 3.974        | 3.941 | 3.944 | 3.9219            | 487                            | 507  | 505  | 502.4             |

<sup>a</sup> Spectroscopic parameters are based on a parabolic fit (in  $1/r$ ) to the lowest energy points on a 0.1 bohr grid.

<sup>b</sup> Huber and Herzberg, Ref. 23.

<sup>c</sup> The core-valence results are  $r_e = 4.599$  and  $\omega_e = 369$  cm<sup>-1</sup>.

TABLE II. Dipole moment derivatives for the ground states of BeF, BeCl, MgF, MgCl, CaF, CaCl, and SrF.

| Molecule | Dipole moment derivatives (D/bohr) <sup>a</sup> |      |      |
|----------|---|------|------|
|          | SCF   | SDCI | CPF  |
| BeF      | 2.46  | 2.33 | 2.18 |
| BeCl     | 2.67  | 2.54 | 2.42 |
| MgF      | 2.71  | 2.63 | 2.39 |
| MgCl     | 2.92  | 2.87 | 2.67 |
| CaF      | 3.15  | 3.16 | 2.91 |
| CaCl     | 3.06  | 3.06 | 2.75 |
| SrF      | 3.24  | 3.25 | 3.02 |
| KCl      | 2.71  | 2.71 | 2.67 |

<sup>a</sup> Derivatives computed at experimental  $r_e$ . The EDMFs are nearly linear near  $r_e$ . The coefficient for the second derivative is positive, but very small.

infrared spectra are expected with most of the intensity going into the fundamentals.

The spectroscopic parameters  $r_e$  and  $\omega_e$  for the  $X^2\Sigma^+$  states of BeF, BeCl, MgF, MgCl, CaF, CaCl, and SrF are compared with experiment<sup>23</sup> in Table I. The theoretical values are determined from a parabolic fit in  $1/r$  to the theoretical energies on a 0.1 bohr grid. The use of the fitting variable  $1/r$  is found to give substantially more reliable values for  $\omega_e$  than using  $r$  directly.<sup>24,25</sup> However, the average error in the SDCI and CPF  $\omega_e$  values of 6–7  $\text{cm}^{-1}$  may be approaching the inherent limitations of the fitting procedure.

The SDCI and CPF  $r_e$  values are within about 0.01 Å of experiment, except for CaCl where the theoretical values are about 0.02 Å too long. The  $r_e$  values for BeF and BeCl in Table I are reduced slightly (0.01–0.02 Å) when the 1s electrons on Be are correlated (see Ref. 12), resulting in improved agreement with experiment. The bond length errors at the SCF level are larger for the heavier systems such as CaCl and SrF. The SDCI and CPF treatments reduce the bond length for these systems when the electrons in the  $(n-1)$  shell of the metal are correlated. For CaCl, how-

ever, significant errors remain in  $r_e$ , which reflect more the limitations of the correlation treatment than the one-particle basis sets. In particular, the double excitations where one electron is promoted from the  $(n-1)$  shell of the metal and one from the halide (the so-called pair-pair terms), have an important bond contraction effect, since their contribution vanishes in the asymptotic limit. These double excitations account for a relatively small amount of energy and their importance may be underestimated in the presence of the large atomic correlation present in the  $(n-1)$  shell of the metal. This observation has prompted the determination of core-valence (CV) wave functions, which exclude the class of double excitations where both electrons are promoted from the  $(n-1)$  shell of the metal. For CaCl, the CV wave function gives  $r_e = 4.599$  bohr about 0.01 bohr shorter than experiment. Hence, the CV approach can lead to a slight overestimation of the pair-pair terms without the exclusion effect of the double excitations from the metal.<sup>26</sup> Even so, the CV  $r_e$  is in best agreement with experiment and it is of interest to determine whether the CV wave function describes the charge distribution in the molecule with sufficient accuracy to give the correct permanent dipole moment.

The theoretical permanent dipole moments (D) for the  $X^2\Sigma^+$  states of selected alkaline-earth fluorides and chlorides at the SCF, SDCI, and CPF levels, evaluated at the experimental  $r_e$ , are compared with experiment and with the ionic model of TEK<sup>9</sup> in Table III. Note that vibrationally averaging the EDMF leads to a small increase of 0.01–0.02 D for  $v=0$  compared to  $\mu_e$ . The effect of electron correlation on the electric dipole moments varies from BeF and BeCl where it reduces the moment, to the heavier systems containing Ca and Sr where correlation increases the moment. This is a consequence of the increasing importance of the covalent contribution to the bonding for the lighter metals. Note also that the magnitudes of the dipole moments for BeF and BeCl are much smaller than for the heavier alkaline earths. In contrast, the dipole moments for the ionic KCl molecule included in Table III for comparison are much

TABLE III. Dipole moments (D) for the  $X^2\Sigma^+$  states of selected alkaline-earth fluorides and chlorides.

| Molecule          | Theoretical <sup>a</sup> |        |        | TEK <sup>b</sup> | Expt  |
|-------------------|--------------------------|--------|--------|------------------|---|
|                   | SCF                      | SDCI   | CPF    |                  |   |
| BeF               | 1.271                    | 1.131  | 1.086  | ...              | ...   |
| BeCl              | 1.031                    | 0.880  | 0.796  | ...              | ...   |
| MgF               | 3.098                    | 3.048  | 3.077  | 3.64             | ...   |
| MgCl              | 3.417                    | 3.381  | 3.382  | 4.25             | ...   |
| CaF               | 2.659                    | 2.590  | 3.060  | 3.34             | 3.07(7) <sup>d</sup>                            |
| CaCl <sup>c</sup> | 3.647                    | 3.629  | 4.192  | 4.47             | 4.265 ± 0.02 <sup>e</sup> , 3.6(6) <sup>f</sup> |
| SrF               | 2.579                    | 2.523  | 3.199  | 3.67             | 3.4676(1) <sup>g</sup>                          |
| KCl               | 10.569                   | 10.475 | 10.279 | ...              | 10.2384 <sup>h</sup>                            |

<sup>a</sup> Evaluated at experimental  $r_e$ .

<sup>b</sup> Predictions based on the ionic model of Törring, Ernst, and Kindt, Ref. 9.

<sup>c</sup> The value using core-valence wave functions is 3.580 D.

<sup>d</sup> Value for the  $v=0$ ,  $N=2, 3$  states based on molecular beam, laser-rf, double-resonance study of Stark splittings by Childs *et al.*, Ref. 2.

<sup>e</sup> High-precision Stark-effect measurement in the  $v=0$  level by Ernst *et al.* (Refs. 3 and 4) using the molecular-beam microwave-optical double-resonance technique. The error bars of ± 0.02 D arise from uncertainties in calibrating the Stark field.

<sup>f</sup> Estimate of Dagdigan (Ref. 27) from measuring the deflection of a molecular beam by an electric quadrupole.

<sup>g</sup> High-precision Stark-effect measurements in the  $v=0$  and  $v=1$  levels by Ernst *et al.* (Ref. 7) using the molecular beam microwave-optical double-resonance technique.

<sup>h</sup> Hebert *et al.*, Ref. 33.

larger in magnitude, but show the same correlation effects as BeCl. The significantly smaller  $\mu$  for the alkaline-earth halides as compared to the alkali halides results from the polarization of the remaining valence electron on the metal away from the halide ion. Hence, an accurate determination of  $\mu$  depends on an accurate description of this polarization.

Our theoretical dipole moment for CaF is in excellent agreement with the experimental value of Childs *et al.*<sup>2</sup> derived from a molecular-beam laser-rf, double resonance study of the Stark splittings. For an exact comparison, the theoretical EDMF should be vibrationally averaged, which leads to a small increase of 0.01–0.02 D for  $v = 0$  compared to the value for  $\mu_e$ . The  $\mu_e$  based on the ionic model of TEK is about 10% larger. Note that the model predictions of TEK tend to be high in general, and based on our theoretical results have larger errors for the lighter metals. The largest difference occurs for MgCl, which probably has some covalent character not accounted for in their model. Hence, the TEK model would probably not work well for BeF and particularly BeCl.

The SCF and SDCI dipole moments for CaCl are in good agreement with the older estimate of Dagdigian,<sup>27</sup> but are considerably smaller than the recent accurate value of Ernst *et al.*<sup>3–4</sup> based on a high-precision Stark-effect measurement. However, the dipole moment increases substantially at the CPF level giving a dipole moment in good agreement with the recent accurate experimental value. When the CPF EDMF is vibrationally averaged using the RKR potential,<sup>28</sup>  $\mu(v = 0)$  is 4.21 D about 0.05 D smaller than experiment, whereas if the theoretical potential is used,  $\mu(v = 0) = 4.31$  D about 0.05 D larger than experiment. Hence, the CPF results support the recent experimental determination, but the theoretical results are limited in accuracy by the error of 0.02 Å in  $r_e$ . This problem prompted the construction of core-valence (CV) wave functions for CaCl, since this level of correlation treatment produces the best value for  $r_e$ .

The metal valence electron polarizes away from the negative ion to reduce the repulsion. The magnitude of the dipole moment is sensitive to the degree to which this polarization is along the bond axis. The CPF results indicate that higher excitations are required to fully account for the promotion to higher angular momentum. While the CV wave function prevents the pair-pair terms from being overwhelmed by the metal atomic correlation, it does not allow the metal valence electron to mix in sufficient higher angular momentum functions. Thus, while the CV wave function results in a decrease in  $r_e$  and increase in  $D_e$  as compared with the SDCI wave function, the description of the metal valence orbital and dipole moment is not significantly changed.

The substantial increase in the dipole moment of CaCl at the CPF level can be accounted for primarily in terms of changes in the radial extent of the remaining metal valence electron. The contribution of the metal valence electron to the dipole moment is (in a.u.): SCF (–1.93), SDCI (–1.87), and CPF (–1.50). The SDCI and CPF values are derived from the 11 $\sigma$  natural orbital, and the molecule is oriented with the metal at the origin and the Cl dis-

placed in the positive direction. Hence, at the CPF level the valence electron is not pushed as far away from the metal along the bond axis. This difference is primarily due to the larger amount of higher angular momentum character in the wave functions at the CPF level, which allows better angular correlation of the open-shell electron. These statements are illustrated by the molecular orbital plots for CaF in Figs. 1 and 2. In Fig. 1 we plot the 9 $\sigma$  orbital from the  $X^2\Sigma^+$  CPF wave function for the CaF molecule at 3.7 bohr. This plot demonstrates the predominantly metal-centered character of the valence electron as well as the large degree of polarization away from the fluoride ion. In Fig. 2, we plot the difference in the CPF and SDCI densities for the 9 $\sigma$  orbital. This plot demonstrates the increased degree of higher angular momentum character in the CPF wave function, resulting in increased density perpendicular as opposed to along the bond axis.

The most accurate experimental dipole moment determination for the alkaline-earth halides is for SrF.<sup>7</sup> A very accurate value of  $\mu_e = 3.4676(10)$  was obtained from high-precision Stark effect measurements in the  $v = 0$  and 1 vibrational levels. The theoretical dipole moments for SrF show an even larger difference than CaCl between the SDCI and CPF levels. However, the CPF value is still about 0.25 D less than experiment after accounting for vibrational effects. Hence, the CPF procedure may not be accounting fully for the effect of higher excitations in these heavier systems, but does give remarkably better dipole moments than SDCI.

The EDMFs for all of the systems considered in this study are nearly linear with  $r$  for values near  $r_e$ . The first derivative,  $(\partial\mu/\partial r)_{r_e}$  at the SCF, SDCI, and CPF levels for these systems are given in Table II. The  $(\partial\mu/\partial r)_{r_e}$  at the CPF level are about 10% less than those at the SCF level. The derivatives show some correlation with  $r_e$ , increasing by about 50% from BeF to SrF. The magnitude of the deriva-

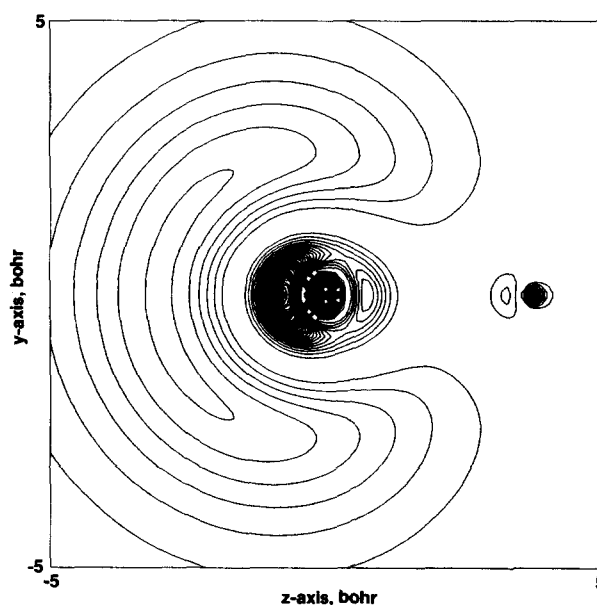


FIG. 1. Contour plot of 9 $\sigma$  natural orbital of CaF from the coupled pair functional (CPF) wave function.

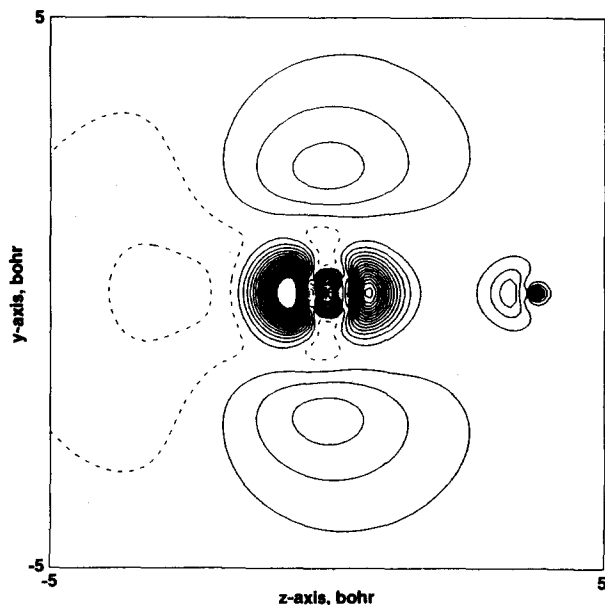


FIG. 2. Contour plot of the density difference between the  $9\sigma$  natural orbitals from the SDCI and CPF wave functions. The solid lines represent increased electron density at the CPF level, and the dashed lines represent decreased electron density.

tives are all large and comparable to that in KCl. Hence all systems including even the more covalent BeCl system are predicted to have strong infrared spectra dominated by the fundamental transitions.

The study of the dipole moments touches on the larger issues of the degree of ionic character in these molecules and whether an unambiguous measure of ionicity exists. Consider the following possible criteria for the degree of ionic character in a molecular system: (1) the dipole moment approaches  $e r_e$  in magnitude (in practice this limit is never reached—see Pauling<sup>29</sup>); (2) the dipole moment varies linearly with  $r$ —this criterion is satisfied to a high degree for all of the systems considered in this study; (3) the ratio  $r_x/r_e$  is greater than about 2.5 where  $r_x$  is the hypothetical internuclear distance where the ionic potential curve crosses the neutral asymptote.<sup>30</sup> This relation is satisfied only for KCl and for BeCl this ratio is only 1.41. (4) Mulliken population analyses which show total charge on the atoms. Although

this approach can suffer from population artifacts, especially when diffuse functions are present in the basis, it often gives some insight into the charge distribution. This criteria suggests for example that BeCl is far more covalent than the other systems considered (see Table IV). (5) Hyperfine parameters which give direct information about the charge density near the halogen nucleus. This approach suggests that all of the calcium halides are highly ionic. These five criteria give ambiguous results for the alkaline-earth halides. In this work we have applied a relatively new approach, the constrained space orbital variation (CSOV) analysis,<sup>31</sup> to gain insight into the degree of ionic bonding. In the following we demonstrate that the CSOV method leads to a clear distinction between the degree of ionicity of BeF, MgF, and BeCl, whereas the above criteria do not.

In the CSOV analysis, the orbital space, both occupied and virtual, are identified as belonging to one of the components. The need to partition the virtual orbitals necessitates a smaller basis set than the extensive STO basis sets used to determine the wave functions, and we use a Gaussian basis set of DZ quality plus diffuse functions on F and Cl, and DZ plus polarization on Be and Mg. These smaller GTO basis sets should be sufficiently complete to yield a qualitative understanding of the bonding.

The zero of energy is the metal positive ion and halide ion at infinite separation. The first step is to superimpose the two ions and evaluate the energy after orthogonalizing the orbitals of the two fragments. Since no relaxation of the fragment orbitals is allowed, we refer to this step as the frozen orbital (FO) energy. For the dipole moment at the FO step we neglect their overlap and assume the two ions are point charges. Because the diffuse valence orbital of the metal overlaps the halide ion, the major part of the orthogonalization step is to polarize the metal valence orbitals away from the negative ion. This polarization of the valence orbital is amplified when the metal is allowed to relax in the basis of the metal orbitals (occupied and virtual). For BeF, the energy associated with this polarization is quite large, and the large reduction in the dipole moment shows the movement of the metal valence charge away from the  $F^-$  ion. When the  $F^-$  ion is allowed to relax in the basis of F orbitals, the change in both energy and  $\mu$  is small. If polarization functions were added to fluorine, the changes associated with this

TABLE IV. Population differences between the SCF and CPF levels.<sup>a</sup>

| Molecule          | Metal   |         |         | Halide  |         |         | Charge <sup>c</sup> |
|-------------------|---------|---------|---------|---------|---------|---------|---------------------|
|                   | s       | p       | d       | s       | p       | d       |                     |
| BeF               | + 0.029 | + 0.045 | + 0.008 | − 0.016 | − 0.101 | + 0.032 | 0.47                |
| MgF               | + 0.039 | − 0.007 | + 0.023 | − 0.014 | − 0.079 | + 0.033 | 0.78                |
| CaF               | + 0.027 | − 0.131 | + 0.168 | − 0.013 | − 0.100 | + 0.036 | 0.76                |
| SrF               | + 0.023 | − 0.134 | + 0.166 | − 0.013 | − 0.101 | + 0.036 | 0.80                |
| BeCl              | + 0.046 | + 0.033 | + 0.003 | − 0.024 | − 0.180 | + 0.108 | 0.10                |
| MgCl              | + 0.062 | − 0.014 | + 0.022 | − 0.023 | − 0.176 | + 0.112 | 0.55                |
| CaCl <sup>b</sup> | + 0.040 | − 0.127 | + 0.154 | − 0.023 | − 0.181 | + 0.114 | 0.62                |
| KCl               | + 0.004 | − 0.092 | + 0.116 | − 0.014 | − 0.150 | + 0.115 | 0.79                |

<sup>a</sup> Positive sign indicates an increase in populations at the CPF level.

<sup>b</sup> The augmented Ca basis was used.

<sup>c</sup> Total charge at CPF level.

step might be slightly larger. If the F is allowed to donate to the metal virtual orbitals, the difference between BeF and MgF becomes clear. For BeF this step is about four times larger than that for MgF (2.40 vs 0.64 eV). Associated with this larger donation is naturally a larger reduction in the dipole moment. It is this F to metal donation that separates the Be compounds from the other alkaline-earth systems, leading to both the increased covalent bonding and decreased dipole moments. Finally, the last CSOV step is compared with an unconstrained SCF to demonstrate that the CSOV procedure has accounted for all the important bonding effects. Note that a larger degree of ionicity for MgF is supported by the Mulliken population analysis which shows a total charge of  $\text{Mg}^{+0.78}\text{F}^{-0.78}$  compared to  $\text{Be}^{+0.47}\text{F}^{-0.47}$  (see Table IV).

As a further test of the CSOV method, we have included BeCl in Table V. The Mulliken population analysis gives a total charge of only  $\text{Be}^{+0.10}\text{Cl}^{-0.10}$ . This smaller charge appears in the CSOV analysis as a larger Cl→Be back donation (2.8 vs 2.4 eV). Considerable charge transfer occurs in both the  $\sigma$  (2.07 eV) and  $\pi$  spaces (0.71 eV). The larger Cl→Be donation results in a considerably larger reduction of 1.27 D in  $\mu$  for BeCl, as compared to 0.70 D reduction from F→Be donation in BeF. The large charge transfer results in a considerable degree of covalent character. Hence, it may be appropriate to consider BeCl as a polar covalent molecule.

To gain some insight into the effect of electron correlation on the charge distribution, we have tabulated in Table IV the Mulliken population differences between the SCF and CPF wave functions for the different molecular systems for geometries near  $r_e$ . The SDCI populations lie between SCF and CPF. In all cases correlation results in charge movement from the halide to the metal. This effect is largest for BeF and BeCl and smallest for KCl. For BeF and BeCl

TABLE V. Constrained space orbital variation (CSOV) analyses for BeF, MgF, and BeCl.

| CSOV step          | $E_{\text{int}}^a$ | $\Delta E_{\text{int}}$ | $\mu$             | $\Delta\mu$ |
|--------------------|--------------------|-------------------------|-------------------|-------------|
| BeF (2.5 bohr)     |                    |                         |                   |             |
| Frozen orbital     | 5.99               | ...                     | 2.58 <sup>b</sup> | ...         |
| Relax Be           | 8.57               | 2.58                    | 1.35              | 1.15        |
| Relax F            | 9.04               | 0.47                    | 1.31              | 0.04        |
| F→Be               | 11.44              | 2.40                    | 0.61              | 0.70        |
| SCF                | 11.63              | 0.19                    | 0.53              | 0.08        |
| MgF (3.3 bohr)     |                    |                         |                   |             |
| Frozen orbital     | 6.32               | ...                     | 3.30 <sup>b</sup> | ...         |
| Relax Mg           | 7.78               | 1.46                    | 1.93              | 1.37        |
| Relax F            | 7.98               | 0.26                    | 1.78              | 0.15        |
| F→Mg               | 8.68               | 0.64                    | 1.48              | 0.30        |
| SCF                | 8.71               | 0.03                    | 1.39              | 0.09        |
| BeCl (3.4 bohr)    |                    |                         |                   |             |
| Frozen orbital     | 3.82               | ...                     | 3.40 <sup>b</sup> | ...         |
| Relax Be           | 5.69               | 1.86                    | 2.31              | 1.09        |
| Relax Cl           | 6.07               | 0.38                    | 2.06              | 0.25        |
| Cl→Be <sup>c</sup> | 8.88               | 2.78                    | 0.79              | 1.27        |
| SCF                | 9.04               | 0.16                    | 0.58              | 0.21        |

<sup>a</sup> Interaction energy (eV) with respect to ions infinitely separated.

<sup>b</sup> Dipole moment (D) assuming point charges.

<sup>c</sup> The  $\sigma$  and  $\pi$  components for the energy are 2.07 and 0.71 eV, respectively, and for  $\mu$  are 0.80 and 0.47 a.u., respectively.

this transfer of charge occurs primarily in the  $s$  and  $p$  spaces, while for the heavier systems such as CaF, CaCl, and SrF the increase is in the  $d$  space and there is considerable net  $p \rightarrow d$  promotion on the metal. The population differences for CaF and SrF are strikingly similar as are many of their other properties such as  $D_e$ .<sup>12,32</sup> Also, the population differences for the heavier alkaline-earth halides are similar to those of the truly ionic KCl molecule. The population differences at the halide also involve considerable  $p \rightarrow d$  promotion, especially for chlorine. The total charges at the CPF level tabulated in the last column are a measure of the degree of ionicity. Note that the total charges at the SCF level are uniformly slightly larger since the effect of electron correlation is to move charge to the metal. Using the total charge on KCl of 0.79 as a guide, the calculations suggest that MgF, CaF, and SrF should be very ionic while BeCl should contain considerable covalent character. The systems BeF, MgCl, and CaCl should be intermediate, but predominantly ionic.

#### IV. CONCLUSIONS

Theoretical spectroscopic parameters ( $r_e, \omega_e$ ) and dipole moments,  $\mu_e$  and  $(\partial\mu/\partial r)_{r_e}$ , are reported for the  $X^2\Sigma^+$  ground states of BeF, BeCl, MgF, MgCl, CaF, CaCl, and SrF. The theoretical  $\mu_e$  values at the CPF level are in far better agreement with the available experimental values than are the SCF or SDCI results. Hence, higher excitations, which increase the higher angular momentum components of the wave function, are found to be important in determining the proper polarization of the predominantly metal open-shell valence electron.

The theoretical study supports the conclusions drawn from the experimental hyperfine parameters that the calcium monohalides are predominantly ionic. However, BeF and particularly BeCl show signs of covalent character. The constrained space orbital variation, CSOV, procedure, which has been used to decompose the bonding into electrostatic, relaxation and charge transfer contributions, is shown to be a useful tool in assessing the degree of covalent character in a molecular system. For example, the CSOV analysis clearly shows a larger degree of covalent character in BeF than in MgF.

Finally, this work combined with our theoretical studies of the dipole moments of the alkali hydrides<sup>33</sup> and transition metal hydrides<sup>34</sup> indicate that the size consistent CPF procedure overcomes many of the limitations of the single reference SDCI procedure, providing a realistic description of the charge density in these molecules.

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