Determination of the Equilibrium Cr^+–F^- Distance in Cr^+:NaF and Cr^+:$KMgF_3$

G. FERNÁNDEZ RODRIGO AND L. PUEYO

Departamento de Química Física, Facultad de Química,
Universidad de Oviedo, 33007 Oviedo, Spain

M. MORENO

Departamento de Optica y Estructura de la Materia, Facultad de Ciencias,
Universidad de Santander, 39005 Santander, Spain

AND M. T. BARRIUSO

Departamento de Física Teórica, Facultad de Ciencias,
Universidad de Santander, 39005 Santander, Spain

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The variation of the isotropic superhyperfine constant of the octahedral CrF_6^{5-} cluster with the Cr^+–F^- distance has been obtained from the results of Hartree–Fock–Roothaan calculations on the $t_{2g}^3e_g^2$-$^6A_{1g}$ ground state. The effects of the quality of the 3d basis set, type of core–valence partition, core-projection operators, and cluster–lattice interaction on the $A_s(R)$ curve has been analyzed. From this calculation and the observed values of A_s, it is found that $R_e(Cr^+:NaF)=2.47 \pm 0.03$ Å and $R_e(Cr^+:KMgF_3) = 2.35 \pm 0.03$ Å. These are the first Cr^+–F^- distances reported to date. © 1987 Academic Press, Inc.

I. Introduction

Many properties of the transition-metal ions in ionic lattices are understood in terms of the electronic structure of the ML_n cluster formed by the metal ion M and its n nearest neighbors L. In many cases, the symmetry of the cluster is so high that its geometry is determined by just a M–L internuclear distance. Octahedral and tetrahedral species are examples. Knowledge of the equilibrium value of this coordinate, R_e, is a very important step in the study of the cluster. However, when the metal M is a substitutional impurity, R_e may be different from the perfect lattice value, R_0. In these cases, the determination of R_e is not easy. In fact, although the extended X-ray absorption fine-structure (EXAFS) technique may give accurate values of R_e, large concentrations of impurity (more than 1%) are usually needed (*1*). On the other hand, the nonempirical determination of R_e from the ground state nuclear potential of the ML_n cluster requires highly sophisticated and very expensive calculations, due to the intricacies of the M–L bond in the lattice.

To deal with this problem, Moreno *et al.*

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(*2–5*) have recently proposed a useful alternative based on the analysis of the isotropic superhyperfine constant A_s. Using it, these authors have determined ligand relaxations in alkali halides doped with copper and silver atoms (*2, 3*), and have shown that when a stable impurity is placed substitutionally in different lattices, R_e tends to be close to a value determined by the impurity, the ligand, and the coordination number (*4, 5*). In this way, for instance, the values or R_e (Mn^{2+}–F^-) in a sample of manganese-doped fluoroperovskites turn out to cluster around 2.11 ± 0.04 Å, although the corresponding values of R_0 range from 1.993 to 2.262 Å (*4*).

The method of Moreno *et al.* is based on the fact that A_s is a local observable having a definite variation with the metal–ligand distance R. To determine this variation, Moreno *et al.* assume that the covalency parameter λ_s, appearing in the definition of A_s, is proportional to the group overlap integral $S_s = \langle 3d_\sigma | \chi_s \rangle$, χ_s being the symmetry-adapted combination of s valence ligand orbitals. Since the R variation of S_s can be immediately obtained from Hartree–Fock atomic orbitals, the determination of the $A_s(R)$ function reduces to the estimation of the proportionality constant c in the assumed equation $\lambda_s = cS_s$. This constant can be obtained from a system with known values of A_s and R_e, or from the results of reliable molecular calculations (*4, 5*).

The latter alternative becomes particularly necessary when an impurity is generated in a doped sample by irradiation and there are not stable concentrated compounds of such impurity to supply a calibration for the constant c. This is the case of the Cr^+ ion generated by X-ray radiation of Cr^{2+}-containing crystals. This unstable ion has been detected in octahedral environments in NaF and $KMgF_3$ by means of resonance spectroscopy (*6–9*).

The purpose of this work is to obtain the value of R_e for the Cr^+–F^- bond in the octahedral systems Cr^+:NaF and Cr^+:$KMgF_3$ by means of the theoretically determined $A_s(R)$ curve and the observed values of A_s. The curves $A_s(R)$ have been computed from the molecular orbitals forming the ground state of the octahedral CrF_6^{5-} unit, *without* invoking the relation $\lambda_s = cS_s$. On the other hand, our calculations confirm that such an equation holds quite accurately for CrF_6^{5-}, at least for $1.7 \le R(Cr^+–F^-) \le 2.6$ Å. However, we do not analyze in this work the causes of this behavior of the covalency parameter λ_s. A study of such causes seems to be convenient, given the potential usefulness of the method of Moreno *et al.*, and it is in progress in our laboratories.

In this paper we present results of Hartree–Fock–Roothaan (HFR) calculations on the octahedral CrF_6^{5-} unit *in vacuo* and in the lattice potential of NaF and $KMgF_3$. In order to know the sensitivity of the theoretical $A_s(R)$ curves obtained from these results against methodological alternatives in the cluster calculation, we have considered several refinements and have analyzed their effects on $A_s(R)$. The quality of the $3d$ basis set, the size and structure of the core–valence partition adopted in the calculation, the core projection on the valence shell, and the cluster–lattice interaction have been investigated. These results are part of a detailed study of the geometry, bonding, and spectra of the Cr^+ in fluoride lattice (*10*). In a forthcoming report we discuss the nuclear potential of the classically repulsive CrF_6^{5-} unit and the stabilization effects produced on it by the $L \rightarrow M$ and $L \rightarrow$ lattice charge transfers, as well as by the electrostatic and nonelectrostatic, short-ranged cluster–lattice interactions.

From the work presented in this paper we find $R_e(Cr^+:NaF) = 2.47 \pm 0.03$ Å and $R_e(Cr^+:KMgF_3) = 2.35 \pm 0.03$ Å. As far as we know, these are the first Cr^+–F^- distances reported to date. When compared with the corresponding $R_e(Mn^{2+}:NaF) = 2.154 \pm 0.013$ Å and $R_e(Mn^{2+}:KMgF_3) =$

2.070 ± 0.020 Å (*4*), as well as with R_0(NaF) = 2.317 Å, R_0($KMgF_3$) = 1.993 Å, they reveal a Cr^+ ion more deformable than the stable Mn^{2+} ion, and with ionic radius larger than $r(Na^+)$.

II. Method

The HFR equations corresponding to the $t_{2g}^3e_g^2$-$^6A_{1g}$ ground state of the octahedral CrF_6^{5-} unit have been solved, following the methodology of Richardson *et al.* (*11*), at eight values of R, from 3.26 a.u. (1.73 Å) to 4.99 a.u. (2.64 Å). The STO basis set for the Cr^+ ion has been taken from Ref. *12*, but the 4*s* and 4*p* orbitals are those on Ref. (*13*). The fluoride basis has been taken from Ref. (*14*).

Four core–valence partitions (*11*) have been analyzed in this work: (a) the SPD partition, in which the valence set is formed of the 3*s*, 3*p*, and 3*d* metallic orbitals, and the 2*s* and 2*p* ligand orbitals; the remaining orbitals are kept frozen in the core (*11*); (b) the SPDD partition is the SPD one augmented with the extra $3d_I$ function, which is the inner STO of the regular 2-ζ $3d_M$ function of Ref. (*12*); (c) the valence shell of the DDSP partition contains the $3d_M$, $3d_I$, 4*s*, and 4*p* metallic orbitals, the 3*s* and 3*p* now being in the core; (d) the SPDDSP partition contains the largest metal valence: 3*s*, 3*p*, $3d_M$, $3d_I$, 4*s*, and 4*p*. We note that the ligand valence shell is the same in these four cases.

Calculations made by following the standard methodology of Ref. (*11*) will be called here *unprojected* calculations, and will be indicated by a capital U preceding the name of the partition. These calculations can be improved by the inclusion of core-projection operators in the Fock–Hamiltonian of the cluster. Such operators, defined in terms of the core orbitals, prevent the possible collapse of the valence shell into the core, due to insufficient two-center, core-valence orthogonality (*15*). We have introduced these projections in the manner discussed in Ref. (*15*). "Projected" calculations will be denoted by a capital P before the name of the core-valence partition.

The cluster–lattice interaction appropriate to the Cr^+:NaF and Cr^+:$KMgF_3$ systems has been investigated as in Ref. (*16*), namely, computing the lattice potential by the Ewald method at many points along the 100, 110, and 111 directions, representing these values by a one-electron octahedral function, and incorporating such function in the cluster Fock operator before the SCF iterations. The accurate 7P potential function discussed in Ref. (*17*) has been used here.

Finally, the isotropic superhyperfine constant A_s is given by (*6*)

$$A_s = \frac{1}{3}\lambda_s^2N^2A_{2s}^0/2S$$

where

$$A_{2s}^0 = (8\pi/3)\ g\ g_N\ \beta\ \beta_N|\psi_{2s}(0)|^2$$

and $S = 5/2$ for the $t_{2g}^3e_g^2$-$^6A_{1g}$ state considered in this work. λ_s and N are, respectively, the covalency parameter and normalization constant in the e_g antibonding molecular orbital:

$$|e_g^*> = N(3d_e - \lambda_s\chi_s - \lambda_\sigma\chi_\sigma)$$

When this *MO* is doubly occupied, the transferred spin density $f_s = \lambda_s^2N^2/3$. We have, then, for the $^6A_{1g}$ state:

$$A_s = f_sA_{2s}^0/2S.$$

In this work we deal with the SPD $|e_g^*>$:

$$|3e_g^*,\text{SPD}> = a_{13}3d_M + a_{23}\chi_s + a_{33}\chi_\sigma$$

which gives $f_s = a_{23}^2/3$, and with the DD forms

$$|3e_g^*,\ \text{DD}> = b_{13}3d_M + b_{23}3d_I + b_{33}\chi_s + b_{43}\chi_\sigma$$

for which $f_s = b_{33}^2/3$. The fluoride 2s AO used here gives $A_{2s}^0 = 13920 \times 10^{-4}\ \text{cm}^{-1}$.

III. Results and Discussion

In the table we present the values of A_s obtained in different calculations. In all these cases A_s decreases by a factor of about 20 when R increases from $R = 3.26$ to 4.99 a.u.

The last two columns of the table contain results obtained with the $3d$ wavefunction corresponding to the Cr^{3+} (*12*). These numbers show the importance of the $3d$ AO in the final value of A_s. The $3d(Cr^{3+})$ function is more contracted than the $3d(Cr^+)$ one, giving rise to a sensible reduction in A_s, in spite of the presence of the second $3d$ function in the SCF process. The extra $3d_I$ function cannot correct the effects induced by the comparatively more internal $3d(Cr^{3+})$.

The results in the first four columns of the table reveal the effects produced in A_s by the type of core-valence partition. The three DD bases give essentially the same function $A_s(R)$, showing some differences with the SPD partition that are larger at shorter R's. However, for $R > 4.19$ a.u. these differences are negligible. Accordingly, the predicted values of R_e, obtained with the observed A_s, differ by less than 0.03 Å within these calculations.

Looking at the results of the projected calculations we observe that the modifications of the cluster wavefunctions produced by the core projectors increase when R decreases. This is not surprising since the error corrected by these operators (the lack of two-center core-valence orthogonality) is a decreasing function of R. Again, the differences between the U and P calculations are negligible for $R > 4.19$ a.u. In these two types of calculations the effects of the empty $4s$ (a_{1g}) and $4p$ (t_{1u}) metallic AO's on A_s are negligible, indicating that this quantity is mainly determined in this case (with no open shells in the a_{1g}, t_{1u} blocks) by the details of the e_g MO's.

Finally, we observed in the table that the effects of the electrostatic cluster–lattice interaction on the structure of the $|3e_g\rangle$ MO are entirely negligible. This is true for any core-valence partition, as well as for the U and P calculations, although only the SPDDSP results are collected in the table.

We conclude that, apart from the calculation performed with the $3d$ (Cr^{3+}) function, the $A_s(R)$ curve obtained from 4.00 to 4.99 a.u. is essentially independent of the partition size, core-projection, and cluster–lattice interaction.

From the theoretical curves we obtain $R_e(Cr^+:NaF)$ and $R_e(Cr^+:KMgF_3)$ by using the experimental values of A_s (*6*): $A_s(Cr^+:NaF) = (12.5 \pm 0.5) \times 10^{-4}\ cm^{-1}$, $A_s(Cr^+:KMgF_3) = (19.3 \pm 0.5) \times 10^{-4}\ cm^{-1}$. Our results are: $R_e(Cr^+:NaF) = 2.47 \pm 0.03$ Å, $R_e(Cr^+:KMgF_3) = 2.35 \pm 0.03$ Å. The uncertainty in these predictions has been estimated from the uncertainty in the observed A_s and from the dispersion of our different theoretical curves.

These numbers indicate outward fluoride relaxation in NaF and $KMgF_3$ upon Cr^+ substitution. $\Delta R = R_e - R_0 = 0.15$ Å and 0.35 Å for Cr^+:NaF and Cr^+:$KMgF_3$, respectively. The first value suggests that the Cr^+ ion is larger than the Na^+ ion, since there is not charge compensation in Cr^+:NaF. From this result, the ionic radius $r(Cr^+)$ can be estimated to be about 1.14 Å. This number compares well with the known series (*18*): Cr^{6+} (0.44 Å), Cr^{5+} (0.49 Å), Cr^{4+} (0.55 Å), Cr^{3+} (0.615 Å), Cr^{2+} (0.80 Å). The large relaxation (0.35 Å) in $KMgF_3$ can be understood in terms of the large size of Cr^+ and the charge reduction in the substitution $Mg^{2+} \rightarrow Cr^+$.

These results cannot be compared with other deduced from a calibration of the constant c (in $\lambda_s = cS_s$) by means of a Cr^+ crystal with A_s and R_e known, since no previous value of R_e has been reported. However, a comparison can be made with the isoelectronic Mn^{2+}. The distances $R_e(Mn^{2+}:NaF) = 2.154 \pm 0.013$ Å and $R_e(Mn^{2+}:KMgF_3) = 2.070 \pm 0.020$ Å have been

TABLE I

CALCULATED A_s(10^{-4} cm^{-1}), BEST A AND ρ PARAMETERS IN THE FUNCTION $A_s = A \cdot \exp(-R/\rho)$, COEFFICIENT OF DETERMINATION r^2, AND VALUES OF R_e DEDUCED FROM THE THEORETICAL $A_s(R)$ CURVE AND THE OBSERVED A_s(Cr^+:NaF), A_s(Cr^+:$KMgF_3$)

	CrF_6^{5-} *in vacuo*				CrF_6^{5-} *in vacuo*			Cr^+:NaF	Cr^+:$KMgF_3$		CrF_6^{5-}–3*d*(Cr^{3+})	
R (Bohr)	USPD	USPDD	USPDDSP	UDDSP	PSPDD	PSPDDSP	PDDSP	USPDDSP	USPDDSP	PSPDDSP	USPDD	USPDDSP
3.26	145.85	179.96	183.37	183.49	145.12	146.60	147.85	184.25	184.81	147.72	72.382	73.466
3.425	110.60	126.55	129.46	130.29	110.58	112.15	113.94	130.61	131.17	113.61	50.900	51.438
3.59	83.381	91.071	93.244	94.393	83.654	84.989	86.649	94.223	94.824	86.417	36.043	36.212
3.99	41.184	43.105	43.925	44.811	41.889	42.515	43.457	44.379	45.065	43.618	15.554	15.457
4.19	28.619	29.931	30.404	31.045	29.431	29.824	30.478	30.718	31.394	30.796	—	—
4.39	19.718	20.752	21.026	21.466	20.545	20.790	21.232	21.261	21.895	21.651	6.4555	6.3944
4.59	13.458	14.310	14.480	14.772	14.225	14.386	14.677	14.670	15.236	15.137	—	—
4.99	6.0787	6.6290	6.7229	6.8434	6.6147	6.7095	6.8292	6.8640	7.2470	7.2310	—	—
A(cm^{-1})	5.8470	8.2277	8.5779	8.3558	4.9015	4.9665	4.9751	8.4454	7.6552	4.4306	7.6167	8.3052
ρ (Bohr)	0.54735	0.52939	0.52771	0.53054	0.56288	0.56289	0.56418	0.52955	0.53797	0.57460	0.46875	0.46387
r^2	0.9991	0.99998	0.9998	0.9998	0.9994	0.9994	0.9992	0.9998	0.9998	0.9996	0.9998	0.9999
R_e(Cr^+:NaF) (Å)	2.45	2.46	2.47	2.47	2.46	2.47	2.47	2.47	—	—	2.16	2.16
R_e(Cr^+:$KMgF_3$) (Å)	2.32	2.34	2.35	2.35	2.34	2.34	2.35	—	2.36	2.36	2.06	2.05

reported by Barriuso and Moreno (*4*). Applying the method described here to the SCF results on MnF_6^{4-} by Flórez *et al.* (*19*), we find $R_e(Mn^{2+}:NaF) = 2.177 \pm 0.006$ Å and $R_e(Mn^{2+}:KMgF_3) = 2.10 \pm 0.01$ Å. The close similarity between these two sets of numbers indicates that the method used here is essentially equivalent to that described in Ref. (*4*). The small differences should come from the slightly different value of A^0_{2s} (14978×10^{-4} cm^{-1} in Ref. (*4*)), and perhaps from considering $N_{eg} = 1$ in Ref. (*4*). Both calculations give $\Delta R_e = R_e(Mn^{2+}:NaF) - R_e(Mn^{2+}:KMgF_3) = 0.08$ Å. ΔR_e turns out to be 0.12 Å for Cr^+. This larger value suggests that the unstable Cr^+ is a more deformable species than the stable Mn^{2+}.

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