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H-F⁻ Potential Interaction and Local Mode Frequencies for an Interstitial Hydrogen Atom in Alkaline Earth Fluorides*

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The potential interaction between a hydrogen atom and a fluorine ion in an alkaline earth fluoride has been calculated and used to predict the local mode frequencies for $AF_2:H^0$, where A = Ca, Sr, or Ba. Born parameters for the repulsive H-F⁻ interaction are obtained by a semiempirical method and also from self-consistent-field calculations using the Hartree-Fock-Roothaan method. The effect of the crystal field, which prevents electron detachment and leads to a repulsive interaction between the H and F⁻ ions in the crystal, is simulated by restricting the basis sets. The repulsive potential is used to calculate the local mode vibration frequency for an interstitial hydrogen atom in the alkaline earth fluorides. The semiempirical and SCF potential curves are in reasonable agreement, and the calculated local mode frequency for $CaF_2:H^0$ agrees with the observed value.

I. INTRODUCTION

The adiabatic potential curves for the HF⁻ molecule ion in a crystal field are of interest for investigations of interstitial hydrogen atoms in alkaline earth fluorides.[1-5] The ground-state potential curve for a molecule ion in a crystal is quite different from the adiabatic curves for a free molecule ion, so that the former cannot be deduced from the latter. When a fluorine ion and a hydrogen atom are brought together outside of a crystalline environment, the hydrogen orbital expands and the energy of the system decreases uniformly until the electron detaches at a point where the HF and HF⁻ potential curves intersect.[6,7] The crystal field suppresses the orbital expansion and electron detachment, and changes the purely attractive interaction into an interaction which has a small long-range attractive component and a large short-range repulsive component. One can take this into account either by introducing a crystal field which increases the separation between the HF⁻ and HF + e^- levels, thereby reducing the level interaction and decreasing the separation at the point of intersection to a very small value, or by introducing directly constraints which prevent the hydrogen orbital from expanding. The two means are equivalent; constraining the orbitals will, in effect, increase the level separation, while introducing a crystal field in order to separate the levels will suppress the orbital expansion. The use of constraints has been adopted herein because it is much easier to implement for Hartree-Fock calculations using the Roothaan expansion method.

Since the procedure used is *ad hoc*, justification for its validity depends entirely on the agreement of calculated observables with experimental measurements and with semiempirical estimates obtained by independent means. We are able to make three such comparisons: One is the comparison of the polarizability of H obtained from the SCF potential curve with the known value. This comparison is of particular importance for determining whether the expansion of the hydrogen orbital has been suppressed in such a manner that one is dealing with an entity which has the properties expected of an interstitial hydrogen atom. The second is a comparison of the calculated repulsive force with an estimate obtained from considerations based on an additivity rule for repulsive forces between closed-shell atoms and ions. A third is a comparison of the calculated and observed local mode frequencies for $CaF_2:H^0$. Any one of these comparisons, taken alone, would not be sufficient to justify the *ad hoc* procedure used for obtaining the interaction between H and F⁻. But taken together, they provide a basis for arguing that we are able to obtain a reasonable and useful approximation to the interaction between an interstitial hydrogen atom and a fluorine ion in alkaline earth fluorides. The investigation was undertaken, and the results are presented, in a heuristic spirit rather than as a definitive answer to the problem of the forces acting on interstitial hydrogen atoms in fluorides.

The semiempirical estimate of the H-F$^-$ interaction is presented in Sec. II below. The results for the SCF calculations on HF$^-$ are presented in Sec. III, where they are compared with the results obtained in Sec. II. In Sec. IV the repulsive part of the HF$^-$ potential is used to calculate the local mode vibrational frequency of an interstitial H atom in alkaline earth fluorides. The frequency of the harmonic vibrations of the H atom in a static cage of fluorine ion neighbors is increased relative to the initial calculation both by approximately including the effect of the motion of the neighbors and by including quartic anharmonic terms in the expansion of the potential. The former correction is calculated in the simplest possible model, in which the fluoride neighbors vibrate as uncorrelated Einstein oscillators with the resulting changes in the local mode expressed as renormalized static force constants. Including both corrections leads to a predicted local mode frequency in agreement with experiment.

II. SEMIEMPIRICAL ESTIMATE OF H-F$^-$ INTERACTION

The potential curve for the ground state of HF lies 3.448 eV above the lowest HF$^-$ potential curve in the separated-atom limit.[8] As the internuclear distance decreases, the HF curve drops rapidly.[9] The HF$^-$ curve decreases uniformly, with a small positive slope which increases near the point of intersection of the HF and HF$^-$ curves at $R \approx 2$ bohr.[6,7] Below the intersection the HF$^-$ molecule ion does not exist because it is unstable with respect to the loss of an electron. Since the HF$^-$ potential curve decreases uniformly, the free HF$^-$ ion cannot exist even as a metastable species.

The electrostatic potential for an F$^-$ ion in the CaF_2 lattice is 8 eV lower than for a free F$^-$ ion.[10] The separation between the HF and HF$^-$ curves is, therefore, increased by 8 eV, and the crossover will not occur until the internuclear separation becomes very small. The first excited state for HF$^-$ is a state which corresponds to H$^-$ + F. The H$^-$ + F state will lie 2.694 eV higher than the H + F$^-$ state for free atoms and ions in the separated-atom limit.[11] The electrostatic field in CaF_2 will increase this by 3.853 eV.[12]

We infer from these considerations that, in the crystal, the H + F$^-$ level will not have an appreciable interaction with any other electronic level. This suggests that the interaction will consist of a relatively long-range attractive interaction due to dispersion and induced multipole forces and a short-range repulsive interaction which is analogous to the repulsive interaction between closed-shell atoms and ions. The essential part of the analogy is that both systems have a ground level which is well separated from adjacent excited levels. Although it is true that the ground level for HF$^-$ is doubly degenerate, while the ground level for closed-shell atoms and ions is nondegenerate, the degeneracy for HF$^-$ is a Kramers spin degeneracy which is not lifted by the interaction, so that it is not unreasonable to assume that it behaves as if there were no degeneracy insofar as the potential interaction is concerned. Proceeding from this intuitive picture, we may obtain an estimate of the H-F$^-$ interaction as follows.

The asymptotic form of the attractive interaction will be

$$-\tfrac{1}{2}e^2\alpha_H/R^4 - C/R^6 - \tfrac{3}{4}e^2\beta_H/R^6\ldots \quad ,$$

where the first term is the monopole-induced dipole interaction, the second term is the dipole-dipole dispersion term, and the third term is the monopole-induced quadrupole interaction. R is the internuclear distance, and e the magnitude of the electronic charge. The polarizability of the hydrogen atom is $\alpha_H = 4.49$ bohr^3.[13] The dispersion constant may be estimated to be $C \approx 0.4$ hartree-bohr^6 using the London formula.[14] The second term is, therefore, small compared to the first over the range of distances in which we are interested. No estimates of the quadrupole polarizability β_H are available, but it seems reasonable to assume that the last term is also small compared to the first, so that only the leading term of the attractive interaction between H and F$^-$ need be taken into account.

In order to obtain a rough estimate of the repulsive interaction, we make use of an empirical additivity rule for the Born-Mayer parameters which has been verified for repulsive interactions between alkali ions and halide ions.[15] According to this rule, the repulsive potential between an arbitrary pair of ions labeled by i and j has the form $U_{ij}(R) = (\rho_i + \rho_j) f \exp[(R_i + R_j - R)/(\rho_i + \rho_j)]$, where f is an arbitrary constant which may be used to scale the soft-sphere radii, R_i are the individual soft-sphere radii, and ρ_i are the individual hardness parameters. Using a constant of $f = 0.014$ hartree/bohr (which scales the radii to make the sums $R_i + R_j$ correspond to crystal lattice parameters in the alkali halides), the radius and hardness parameters for F$^-$ are found to be $R_{F^-} = 2.59$ bohr and $\rho_{F^-} = 0.338$ bohr, respectively.[15] Empirical values for the radius and hardness of a hydrogen atom are not available; however, if one assumes that there is a direct correlation between these parameters and the charge distribution in the free ion and uses the empirically determined relation between these quantities for the alkali halides in order to relate the charge distribution with the radius and hardness of hydrogen, rough estimates of the latter parameters may be obtained. These estimates are $R_H = 1.5$ bohr and $\rho_H = 0.33$ bohr.[16] From these estimates we obtain $V(R)=4.3\,e^{-R/0.67}$ for the repulsive interaction between an F^- ion and a hydrogen atom in atomic units.

The prescriptions described above lead to the following estimate for the dominant contribution to the interaction between a fluorine ion and an interstitial hydrogen atom polarized by a *single* fluorine ion in an alkaline earth fluoride:

$$U(R)=-2.25/R^4+4.3\,e^{-R/0.67}\;. \tag{1}$$

R is measured in bohrs (1 bohr = 0.529 17 Å), and U is given in hartrees (1 hartree = 27.211 eV). The first term will, of course, be missing for an interstitial hydrogen atom in a real crystal because the net field due to all neighbors vanishes at the center of symmetry, so that the hydrogen atom has no dipole moment.

III. SCF CALCULATION OF H-F⁻ INTERACTION

The computer program used for the SCF calculations, the analysis on which it is based, and the notation have been fully described elsewhere.[17,18]

The molecular basis set consisted of eleven σ basis functions (nine for F^-, two for H) and five π basis functions (four for F^-, one for H). The exponents for the F^- basis functions were taken from the atomic calculations of Bagus and Gilbert.[19] The exponents for the H basis functions were optimized as follows.

A common exponent $\zeta_H(R)$ was used for all three H basis functions. This exponent was optimized at $R=4.01$, 4.46, and 4.91 bohr. A least-squares fit,

$$\zeta_H'(R)=\exp(-0.4918/R+0.08423), \tag{2}$$

reproduced these values to an accuracy of $\Delta\zeta(4.01)=0.000$, $\Delta\zeta(4.46)=0.001$, and $\Delta\zeta(4.91)=0.000$, where $\Delta\zeta(R)=\zeta_H(R)-\zeta_H'(R)$. This formula was used to obtain ζ_H at $R=3.11$, 3.56, 4.28, and 5.36 bohr. The basis function data are summarized in Tables I and II.

The single-configuration energies [relative to $E(\infty)=E_H+E_{F^-}$], the virial ratio, and the first- and second-multipole moments of the total charge are tabulated in columns 2–7 of Table III. The parameters A, B, and ρ in the function

$$U(R)=-A/R^4+Be^{-R/\rho} \tag{3}$$

were determined by a least-squares fit to the calculated energy values. The parameters obtained by fitting this curve to all seven points and also to the last six points are given in Table IV. The six-point fit is probably closest to what one would obtain from a rigorous Hartree-Fock calculation because the expansion error increases rapidly with decreasing distance and is probably not negligible for $R=3.11$ bohr. The rms error for the six-point fit is less than the roundoff error; it is only slightly greater than the roundoff error in the case of the seven-point fit. The numbers in parentheses are the percentage differences between the calculated values and the semiempirical estimates given by Eq. (1).

TABLE I. Fluorine basis functions.

λ	p	nl	$\zeta(R)$[a]
σ	1	1s	14.096
	2	1s	7.921
	3	3s	9.939
	4	2s	3.230
	5	2s	1.834
	6	2p	7.798
	7	2p	3.789
	8	2p	1.946
	9	2p	0.968
π	1	2p	7.798
	2	2p	3.789
	3	2p	1.946
	4	2p	0.968

[a] Basis functions centered on the fluorine nucleus are identical for all R.

An important point for our purpose is to establish that the energies and wave functions given by the SCF calculation correspond to a hydrogen atom and fluorine ion in a crystalline environment, i.e., that the H in the HF⁻ system is a hydrogen atom and not a proton with a loosely bound electron. One bit of evidence is the fact that the repulsive force is in reasonable agreement with the semiempirical estimate obtained earlier. As we shall show later, if one uses a larger basis set the repulsive contribution to the potential disappears completely. However, if we want to use the repulsive force obtained from the SCF calculations, rather than the semiempirical estimate, in order to interpret observations of local mode frequencies, we need some independent evidence to show that the hydrogen atom has the properties which one would expect of an interstitial hydrogen atom in an

TABLE II. Hydrogen basis functions.

λ	P	nl	$\zeta(3.11)$	$\zeta(3.56)$	$\zeta(4.01)$	$\zeta(4.28)$	$\zeta(4.46)$	$\zeta(4.91)$	$\zeta(5.36)$
σ	10	1s	0.927	0.947	0.962	0.970	0.975	0.984	0.992
	11	2p	0.927	0.947	0.962	0.970	0.975	0.984	0.992
π	5	2p	0.927	0.947	0.962	0.970	0.975	0.984	0.992

TABLE III. Ground-state potential curve and multipole moments for HF^-.

R bohr	$U(R)=E(R)-E(\infty)$[a] hartree	$-V_{el}/T_{el}$[b]	Z_F[c] bohr	$\langle X^2\rangle$[d] bohr^2	$\langle Z_F^2\rangle_{tot}$[e] bohr^2	$3\langle Z_F^2\rangle-\langle R_F^2\rangle$[f] bohr^2
3.11	0.002 49	1.999 4340	−0.6589	6.3721	9.5195	25.6390
3.56	−0.001 05	1.999 8189	−0.4676	6.3646	8.9875	30.5930
4.01	−0.002 14	1.999 9874	−0.3356	6.3576	8.5827	36.6103
4.28	−0.002 29	2.000 0263	−0.2784	6.3511	8.3834	40.7014
4.46	−0.002 28	2.000 0338	−0.2472	6.3456	8.2641	43.6201
4.91	−0.002 06	2.000 0451	−0.1893	6.3370	8.0295	51.6013
5.36	−0.001 73	2.000 0217	−0.1500	6.3264	7.8394	60.4853
∞	0	2.000 0044	0	6.3190	6.3190	∞

[a] $E(\infty) = -99.95938$ hartree.

[b] T_{el} and V_{el} are the kinetic energy of the electron and the potential energy of the electron and fixed nuclei, respectively. The total energy is $E(R) = T_{el} + V_{el}$.

[c] First moment of total charge (− electronic + nuclear) relative to fluorine nucleus.

[d] Second moment, $\langle X^2\rangle = \langle Y^2\rangle$, of electronic or total charge relative to molecular axis.

[e] Second moment of total charge relative to fluorine nucleus.

[f] Quadrupole moment of electronic charge relative to fluorine nucleus. Subtract $2R^2$ to obtain quadrupole moment for total charge relative to fluorine nucleus. Quadrupole moment for total charge vanishes for $R\rightarrow\infty$.

alkaline earth fluoride.

To this end, we observe that the polarizability is very sensitive to small changes in the wave function. In general, the polarizability is more sensitive than the repulsive force to small perturbations in the wave function. Hence, the agreement between the parameter A obtained by fitting the potential curve and the semiempirical estimate $A = \frac{1}{2}\alpha_H$ provides a sensitive independent test that the SCF wave function does describe an HF^- system in which the electron is tightly bound to the proton (see column 1 of Table IV). We note that the value of A obtained from the potential curve is smaller than $\frac{1}{2}\alpha_H$, whereas an interaction with the FH + e^- level, which would cause a dilation of the hydrogen orbital, would tend to increase the magnitude of A. This difference is, presumably, a consequence of overlap screening, distortion dipoles, and limitations of the model.

The first moment of the charge distribution relative to the fluoride nucleus $Z_F(R)$ is tabulated in column 4 of Table III. This displacement can be regarded as the sum of the dipole moment induced in the hydrogen atom by the fluoride ion and a distortion-dipole moment produced by overlap and other short-range effects. The electric field at the hydrogen nucleus is, in first approximation $E = -1/R^2$, so that the induced dipole moment is $P = -\alpha_H/R^2$. The true effective field acting on the hydrogen atom will be $-1/R^2 + \delta E$, where δE is a contribution from overlap screening, but there is no reliable way to estimate δE, so we must include the field-induced dipole moment $\alpha_H\delta E$ as part of the distortion-dipole contribution. We assume that the distortion-dipole contribution varies exponentially and have determined the parameters in the expression $-\alpha'/R^2 - C\,e^{-R/\gamma}$ by a least-squares fit to $Z_F(R)$. The value of α' obtained in this manner is 20–30% below the experimental value of α_H (see Table IV).

In principle, the distortion-dipole moment $Z_D = -C\,e^{-R/\gamma}$ may be used to calculate the integrated infrared absorption for the local mode in $CaF_2:H^0$ which is (in cm^{-2})

$$\bar{K} = (\pi e_a^2 n/\eta\, mc^2)\,[\tfrac{1}{3}(\eta^2+2)]^2\,, \tag{4}$$

where η is the refractive index at the local mode frequency ≈ 1, n is the number of defects per cm^3, and c is the speed of light. The apparent charge on the hydrogen atom[20] e_a, is in our case

$$e_a = \frac{8}{3}\left(\frac{2Z_D}{R} - \frac{\partial Z_D}{\partial R}\right)\Bigg|_{R_0}\,, \tag{5}$$

which, for the six-point fit, is 0.1210 electrons. The observed absorption strength at 100 °C is 73 cm^{-2} corresponding to $e_a = 0.071$ electrons. This

TABLE IV. Calculated Born-Mayer parameters and spectroscopic constants.

	6-point fit	7-point fit
A	1.931 (−14%)	1.806 (−20%)
B	3.291 (−23%)	4.013 (− 7%)
ρ	0.624 (− 7%)	0.596 (−11%)
rms fitting error for $U(R)$	$\pm 0.4\times10^{-5}$	$\pm 3\times10^{-5}$
R_e	4.35 bohr	4.32 bohr
$U(R_e)$	−0.063 eV	−0.063 eV
$\alpha' \approx \alpha_H$	3.571 (−20%)	3.139 (−30%)
C	9.740	6.701
γ	0.8994	1.0383
rms fitting error for $Z_F(R)$	±0.0005	±0.002
e_a	−0.1210	−0.1254

TABLE V. Orbital energies (a.u.).

R	$\epsilon_{1\sigma}$ $\sigma 1s(\mathrm{F}^-)$	$\epsilon_{2\sigma}$ $\sigma 2s(\mathrm{F}^-)$	$\epsilon_{3\sigma}$ $\sigma 2p(\mathrm{F}^-)$	$\epsilon_{4\sigma}$ $\sigma 1s(\mathrm{H})$	$\epsilon_{1\pi}$ $\pi 2p(\mathrm{F}^-)$	$\epsilon_{4\sigma}-1/R$
3.11	−25.8646	−1.1159	−0.2451	−0.1333	−0.2187	−0.4548
3.56	−25.8523	−1.1002	−0.2204	−0.1930	−0.2049	−0.4739
4.01	−25.8442	−1.0907	−0.2052	−0.2374	−0.1962	−0.4868
4.28	−25.8408	−1.0869	−0.1991	−0.2580	−0.1926	−0.4916
4.46	−25.8391	−1.0849	−0.1959	−0.2698	−0.1908	−0.4940
4.91	−25.8360	−1.0814	−0.1905	−0.2941	−0.1875	−0.4978
5.36	−25.8340	−1.0792	−0.1871	−0.3129	−0.1855	−0.4995
∞	−25.8295	−1.0744	−0.1808	−0.5000	−0.1808	−0.5000

discrepancy is markedly larger than that in other observables, but it is not disturbingly large in view of the crude procedure used to extract the distortion-dipole contribution. A more sophisticated procedure for determining the distortion-dipole contribution and the effect of overlap screening will be needed before the calculated absorption can be taken seriously.

The second moments of the charge distribution have been tabulated in columns 5–7 of Table III. At the present time we do not know of any experimental data or semiempirical estimates with which they may be compared.

The orbital energies are listed in Table V. When an appropriate correction is made to the $\sigma 1s(\mathrm{H})$ level to take into account the electrostatic interaction with the F⁻ ion (last column), the orbital energies are all rather close to the values for the dissociated system and approach these limiting values smoothly as the internuclear distance

TABLE VI. Basis function coefficients $C_{i\lambda p}(R)$.

iλ	Center	p	R=3.11	3.56	4.01	4.28	4.46	4.91	5.36	∞
1σ	F	1	-0.08744	-0.08745	-0.08745	-0.08745	-0.08745	-0.08745	-0.08745	-0.08758
	F	2	-0.95251	-0.95251	-0.95251	-0.95251	-0.95251	-0.95251	-0.95251	-0.95234
	F	3	0.04299	0.04298	0.04298	0.04298	0.04298	0.04297	0.04298	0.04291
	F	4	-0.00285	-0.00283	-0.00281	-0.00281	-0.00280	-0.00280	-0.00279	-0.00277
	F	5	0.00004	0.00001	-0.00001	-0.00002	-0.00003	-0.00004	-0.00004	-0.00006
	F	6	-0.00012	-0.00007	-0.00004	-0.00003	-0.00003	-0.00002	-0.00001	0
	F	7	-0.00004	-0.00002	0.00000	0.00000	0.00000	0.00000	0.00000	0
	F	8	0.00003	0.00000	-0.00001	-0.00001	-0.00001	-0.00001	-0.00001	0
	F	9	0.00003	0.00003	0.00003	0.00003	0.00003	0.00002	0.00002	0
	H	10	-0.00008	-0.00006	-0.00004	-0.00003	-0.00003	-0.00002	-0.00001	0
	H	11	-0.00004	-0.00004	-0.00003	-0.00003	-0.00003	-0.00002	-0.00002	0
2σ	F	1	-0.00453	-0.00465	0.00471	0.00473	0.00474	0.00475	0.00476	0.00477
	F	2	0.27246	0.27285	-0.27302	-0.27307	-0.27309	-0.27313	-0.27315	-0.27319
	F	3	0.02597	0.02532	-0.02502	-0.02492	-0.02488	-0.02481	-0.02478	-0.02475
	F	4	-0.64175	-0.63989	0.63894	0.63864	0.63850	0.63832	0.63825	0.63817
	F	5	-0.45613	-0.46192	0.46450	0.46526	0.46559	0.46604	0.46625	0.46647
	F	6	-0.00052	-0.00032	0.00020	0.00016	0.00014	0.00010	0.00007	0
	F	7	-0.00083	-0.00036	0.00018	0.00011	0.00008	0.00001	-0.00002	0
	F	8	-0.01134	-0.00657	0.00404	0.00309	0.00261	0.00176	0.00123	0
	F	9	0.00403	0.00195	-0.00099	-0.00071	-0.00060	-0.00043	-0.00034	0
	H	10	-0.02124	-0.01174	0.00659	0.00475	0.00386	0.00239	0.00155	0
	H	11	-0.00519	-0.00322	0.00206	0.00164	0.00143	0.00110	0.00091	0
3σ	F	1	-0.00077	-0.00039	-0.00019	-0.00011	-0.00008	-0.00003	-0.00001	0
	F	2	0.01112	0.00615	0.00338	0.00236	0.00187	0.00106	0.00062	0
	F	3	-0.00300	-0.00136	-0.00050	-0.00023	-0.00011	0.00004	0.00008	0
	F	4	-0.01211	-0.00791	-0.00539	-0.00432	-0.00373	-0.00258	-0.00179	0
	F	5	-0.06298	-0.03078	-0.01424	-0.00875	-0.00625	-0.00262	-0.00102	0
	F	6	0.02329	0.02321	0.02305	0.02294	0.02288	0.02273	0.02264	0.02251
	F	7	0.31158	0.32044	0.32653	0.32906	0.33039	0.33268	0.33401	0.33564
	F	8	0.52976	0.52759	0.52458	0.52276	0.52165	0.51945	0.51802	0.51644
	F	9	0.19014	0.22000	0.23978	0.24784	0.25198	0.25900	0.26290	0.26694
	H	10	0.17723	0.11840	0.07712	0.05945	0.05001	0.03294	0.02199	0
	H	11	0.03849	0.02798	0.01948	0.01540	0.01309	0.00867	0.00568	0
4σ	F	1	0.00061	0.00061	0.00052	0.00045	0.00041	0.00030	0.00022	0
	F	2	-0.02918	-0.02090	-0.01460	-0.01167	-0.01002	-0.00683	-0.00461	0
	F	3	-0.00149	0.00006	0.00061	0.00069	0.00068	0.00061	0.00048	0
	F	4	0.07377	0.04695	0.02974	0.02271	0.01902	0.01216	0.00783	0
	F	5	0.08976	0.07153	0.05285	0.04298	0.03714	0.02571	0.01743	0
	F	6	0.00861	0.00653	0.00475	0.00389	0.00341	0.00241	0.00170	0
	F	7	0.11692	0.09133	0.06994	0.05928	0.05298	0.04015	0.03026	0
	F	8	0.19066	0.14280	0.10378	0.08537	0.07499	0.05382	0.03880	0
	F	9	0.11720	0.09782	0.07894	0.06820	0.06141	0.04758	0.03615	0
	H	10	-1.02417	-1.01969	-1.01381	-1.01052	-1.00856	-1.00501	-1.00265	-1.00000
	H	11	0.18402	0.13770	0.10832	0.09554	0.08840	0.07407	0.06317	0
1π	F	1	0.02323	0.02290	0.02272	0.02265	0.02262	0.02257	0.02254	0.02251
	F	2	0.33330	0.33429	0.33486	0.33509	0.33520	0.33540	0.33551	0.33564
	F	3	0.53038	0.52381	0.52020	0.51893	0.51833	0.51743	0.51699	0.51644
	F	4	0.24782	0.25697	0.26194	0.26366	0.26447	0.26567	0.26624	0.26694
	H	5	0.01044	0.00717	0.00491	0.00389	0.00332	0.00224	0.00152	0

TABLE VII. Added functions for augumented HF⁻ basis set.

λ	Center	P	nl	$\zeta(3.11)$	$\zeta(3.56)$	$\zeta(4.01)$
σ	F	12	$3s$	0.427	0.425	0.412
	H	13	$2s$	0.679	0.728	0.771
	H	14	$2p$	0.679	0.728	0.771
π	H	6	$2p$	0.679	0.728	0.771

increases.

The basis-function expansion coefficients are listed in Table VI. We note again that they approach the asymptotic values smoothly. The coefficients which do not vanish as $R\rightarrow\infty$ change very little in going from the molecule to the separated atoms. The largest change is in the coefficients which vanish in the limit. This suggests that the most important contributions are from overlap and electrostatic polarization. It would be desirable to extract these contributions directly from the *ab initio* calculations by an analysis based on appropriately chosen localized orbitals, but this would require major modifications of the program and is beyond the scope of the present investigation.

It is of interest to examine the wave function and energies one obtains with an extended basis set which does not inhibit the dilation of the hydrogen orbital with decreasing internuclear distance. Calculations at $R = 3.11$, 3.56, and 4.01 bohr were, therefore, carried out using four additional basis functions: $3s\sigma$(F), $2s\sigma$(H), $2p\sigma$(H), and $2p\pi$(H). The exponent for the $3s\sigma$(F) basis function and the common exponents for the three basis functions centered on the proton were optimized independently. The results are summarized in Tables VII, VIII, and IX.

We note that the use of this extended set completely eliminates the repulsive component and leads to a potential curve which decreases monotonically with decreasing internuclear separation. The added contribution to the outer orbitals corresponds to a rather diffuse charge shared by both atoms. It is a relatively small contribution and is not reflected in an increase in the hydrogen orbital energy until one reaches $R = 3.11$, the closest separation at which calculations were done.

TABLE VIII. Orbital and total energies for HF⁻ with augmented basis.[a]

R	3.11	3.56	4.01
$\epsilon_{3\sigma}$[b] $\sigma 2p(\mathrm{F}^-)$	−0.2544 (−93)	−0.2225 (−19)	−0.2056 (−4)
$\epsilon_{4\sigma}$[b] $\sigma 1s(\mathrm{H})$	−0.1295 (+38)	−0.1937 (−7)	−0.2391 (−17)
$\epsilon_{1\pi}$[b] $\pi 2p(\mathrm{F}^-)$	−0.2310 (−123)	−0.2080 (−31)	−0.1969 (−7)
$-V_{el}/T_{el}$	···	2.000 1097	2.000 0974
$U(R)$	−0.003 06	−0.002 92	−0.002 91

[a] All quantities in a.u.

[b] The numbers in parentheses are the change in the final digits relative to the values in Table V.

TABLE IX. Outer-shell basis-function coefficients for augmented HF⁻ basis set.

$i\lambda$	Center	p	$R = 3.11$	3.56	4.01
3σ	F	7	0.311 45	0.323 16	0.329 37
	F	8	0.516 55	0.516 25	0.515 91
	F	9	0.203 33	0.239 65	0.255 66
	H	10	0.230 84	0.145 70	0.093 63
	H	11	0.071 70	0.045 69	0.029 66
	F	12	0.016 78	0.007 41	0.002 80
	H	13	−0.094 23	−0.062 94	−0.041 34
	H	14	−0.054 30	−0.029 95	−0.016 93
4σ	*F*	7	0.118 40	0.090 73	0.067 98
	F	8	0.168 46	0.129 73	0.097 06
	F	9	0.152 09	0.111 34	0.080 08
	H	10	−0.935 61	−0.986 65	−1.001 54
	H	11	0.066 18	0.059 14	0.040 76
	F	12	−0.034 42	−0.021 19	−0.014 88
	H	13	−0.124 20	−0.042 77	−0.010 96
	H	14	0.138 14	0.092 01	0.078 67
1π	*F*	1	0.023 21	0.022 87	0.022 70
	F	2	0.335 32	0.335 04	0.335 12
	F	3	0.531 71	0.523 67	0.520 00
	F	4	0.246 28	0.257 48	0.262 34
	H	5	0.030 25	0.018 61	0.010 46
	H	6	−0.026 07	−0.014 20	−0.006 56

These results are in reasonable agreement with the results of Weiss and Krauss for a free HF⁻ molecule ion.[6] The values given in Tables VII and VIII should not, however, be regarded as an accurate representation of the potential curve for a free HF⁻ molecule ion. Further optimization using independent variations of the hydrogen basis functions, reoptimization of all the remaining basis functions, and possibly further augmentation of the basis set, would be required in order to obtain an accurate potential curve. We did not attempt to carry out these calculations because they would be rather expensive in machine time and were not needed for determining the force between a hydrogen atom and a fluorine ion in a crystalline environment.

IV. CALCULATION OF LOCAL MODE FREQUENCY IN $\mathrm{CaF_2 : H^0}$

The measured local mode frequency is 640 $\mathrm{cm^{-1}}$ at 100 °K[3] and 630 $\mathrm{cm^{-1}}$ at room temperature.[21] We make a rough theoretical calculation of the local mode frequency in two steps. We first calculate the exact harmonic local mode frequency of the hydrogen interstitial in a cage of eight fluorides taken to be Einstein oscillators. We then calculate an anharmonic correction to the local mode frequency in the static-cage approximation. In both parts we assume that the lattice is not distorted by the interstitial. The charge-induced dipole interaction must be considered in the full cage of neighbors and vanishes for the equilibrium configuration; it makes no contribution to the harmonic force constants and contributes to anharmonic force constants in the static-cage model only in sixth or higher orders.

The equations of motion are

$$(M\omega^2 - \mathbf{A})\,\vec{u} = \mathbf{C}(\vec{v} - \vec{u}) \;, \tag{6a}$$

$$m\omega^2 \mathbf{I}\vec{v} = \mathbf{C}(\vec{u} - \vec{v}) \;, \tag{6b}$$

where $\vec{u}$ and $\vec{v}$ are displacements of the fluoride neighbors of mass M and of the hydrogen interstitial of mass m. $\mathbf{A}$ is the force constant matrix of the host lattice, and $\mathbf{C}$ is a coupling matrix determined from the repulsive part V of the HF^- potential.

$$C_{0l\alpha\beta} = -\left[\delta_{\alpha\beta} V'/R_0 + (R^l_\alpha R^l_\beta / R_l^2)\,(V'' - V'/R_0)\right] , \tag{7}$$

where R^l_α is the αth component of the vector from the interstitial site to the lth fluoride ion, and derivatives are with respect to the HF^- separation evaluated at equilbrium. In the harmonic static-cage model the fluoride displacements are zero, and the local mode frequency is given by $\omega^2_{sc} = C_{00\alpha\alpha}/m$, where

$$C_{00\alpha\beta} = -\sum_{l=1}^{8} C_{0l\alpha\beta} = \delta_{\alpha\beta}\tfrac{8}{3}(V'' + 2V'/R_0) \;. \tag{8}$$

Using the six-point fit values of B and ρ from Table IV, we find that $\omega_{sc} = 578\ \mathrm{cm}^{-1}$.

A correction to this static-cage frequency due to the motion of the fluoride ions may be estimated by assuming the fluoride force-constant matrices $\mathbf{A}$ to be diagonal with elements equal to $M\omega^2_F$. Then substituting Eq. (6a) into (6b), we find that

$$\left[m\omega^2 \mathbf{I} - \mathbf{C}_{00} + g\sum\nolimits_l \mathbf{C}_{0l}(\mathbf{I} - g\mathbf{C})^{-1}\,\mathbf{C}_{l0}\right]\vec{v} = 0 \;, \tag{9}$$

where $g^{-1} \equiv M(\omega^2 - \omega^2_F)$. Because the tensor $\vec{R}\vec{R}/R^2$ is idempotent we may easily expand the denominator in (9) and sum to all orders. In terms of quantities

$$T \equiv V'/R_0 \quad \text{and} \quad b \equiv (V''/T) - 1, \tag{10}$$

we find the correction to the static-cage force constant $C_{00\alpha\beta}$ to be

$$\Delta C_{00\alpha\beta} = \delta_{\alpha\beta}\, 8gT^2 \left[3 + b + \frac{b(1+b)}{1-(1+b)gT}\right] \Big/ 3(1 - gT) \;. \tag{11}$$

If we take ω^2_F equal to the longitudinal optic frequency of CaF_2, the correction above is equal to $0.121\,C_{00}$. If we assume $u \ll v$ in Eq. (6a), the correction is

$$\Delta C_{00\alpha\beta} = \delta_{\alpha\beta}\, 8gT^2\left[1 + \tfrac{1}{3}b(2+b)\right] = 0.110\,C_{00} \;, \tag{12}$$

very close to the result from the exact treatment. The exactly corrected harmonic frequency then is $\omega_h = 612\ \mathrm{cm}^{-1}$.

However, the hydrogen atom has a large rms zero-point displacement, greater than a tenth of the nearest-neighbor spacing, and anharmonic corrections to the local mode frequency are expected to be significant. To estimate the anharmonic shift we assume that the hydrogen atom vibrates in a static cage with the Hamiltonian

$$\mathcal{H} = \tfrac{1}{2} m v^2 + \tfrac{1}{2}\vec{v}\cdot(\mathbf{C}_{00} + \Delta\mathbf{C}_{00})\cdot\vec{v} + \mathcal{H}' \;. \tag{13}$$

The cubic anharmonic terms vanish by symmetry, and we include only the quartic terms in $\mathcal{H}'$[22]:

$$\begin{aligned} \mathcal{H}' = {} & \tfrac{1}{9}\sum\nolimits_\alpha \left(\tfrac{1}{3}V^{\mathrm{IV}} + 4V'''/R_0 - 4V''/R_0^2 + 4V'/R_0^3\right) \\ & \times v_\alpha v_\alpha v_\alpha v_\alpha \\ & + \tfrac{1}{3}\sum_{\alpha\neq\beta}\left(\tfrac{1}{3}V^{\mathrm{IV}} + 2V''/R_0^2 - 2V'/R_0^3\right) v_\alpha v_\alpha v_\beta v_\beta \;. \end{aligned} \tag{14}$$

We write the unperturbed harmonic states as $|n_x n_y n_z\rangle$, where the n's are oscillator quantum numbers for the Cartesian directions.[23] Since the perturbation does not couple the three degenerate excited states $|100\rangle$, $|010\rangle$, and $|001\rangle$, we may use nondegenerate perturbation theory to first order to calculate the shifts Δ_0 and Δ_1 of the ground-state and excited-state energies. The infrared absorption energy then will be shifted from $\hbar\omega_h$ by

$$\Delta = \Delta_1 - \Delta_0 \equiv \langle 100|\mathcal{H}'|100\rangle - \langle 000|\mathcal{H}'|000\rangle . \tag{15}$$

Using the well-known expectation values of v^2_α and v^4_α in harmonic-oscillator states, we find that the energies of both ground and excited states are increased as in Fig. 1:

$$\Delta_0 = \tfrac{1}{4}(\hbar/m\omega_h)^2\left[V^{\mathrm{IV}} + (4/R_0)\,V'''\right] , \tag{16}$$

$$\Delta_1 = \tfrac{7}{12}(\hbar/m\omega_h)^2\left[V^{\mathrm{IV}} + (4/R_0)\,V'''\right] . \tag{17}$$

With the six-point-fit parameter we find that the quartic anharmonicity shifts the calculated local mode frequency to $\omega_e = 633\ \mathrm{cm}^{-1}$, in agreement with the experimental frequency. Considering the lattice dynamical approximations made (nearest-neighbor interactions, zero lattice distortion, two-body forces, as well as the possible expansion and correlation errors in the single-configuration calculation), we feel that the agreement is probably somewhat fortuitous.

Within the approximations made our calculation should equally well predict the local mode frequencies of neutral hydrogen interstitials in SrF_2 and BaF_2. The results are given in Table X. The corrections due to fluoride neighbor vibration and anharmonicity are seen from the fourth and fifth columns to be of the same order and are separately $\leq 10\%$ of ω_{sc}. The relative smallness of both

TABLE X. For three alkaline earth fluorides R_0 is the distance from a hydrogen interstitial to a fluoride site (Ref. 18). All angular frequencies are in units of cm^{-1} and are, from left to right, the static-cage harmonic local mode frequency, the harmonic frequency renormalized by oscillations of the fluoride neighbors, the static-cage frequency corrected for anharmonicity, the longitudinal optic frequency of the host lattice (Ref. 19), and the renormalized harmonic frequency corrected for anharmonicity.

	R_0(bohr)	ω_{sc}	ω_h	ω_a^0	ω_{LO}	ω_e
CaF_2	4.46	578	612	602	463	633 (−5)
SrF_2	4.80	446	476	471	374	498 (−7)
BaF_2	5.06	366	401	391	326	422 (−12)

corrections leads us to have some confidence in the perturbation model used. The numbers in parenthesis indicate the change in ω_e in cm^{-1} obtained by reversing the order of the perturbation calculations – calculating first a static-cage local mode frequency shifted by anharmonicity (given as ω_a^0 in Table X) and then allowing the cage to vibrate. As expected, this crude test indicates that the effect of the inconsistencies in our simple model becomes more severe as the local mode frequency approaches the unperturbed band.

Our results suggest that the neutral hydrogen local mode might be seen in the infrared in the other two alkaline earth fluorides as well. We would expect that the local mode frequencies of a deuterium defect would be approximately $1/\sqrt{2}$ of the frequencies given in Table X and that observation of this local mode would be hampered in all three cases by the region of strong reflectance just below ω_{LO}.

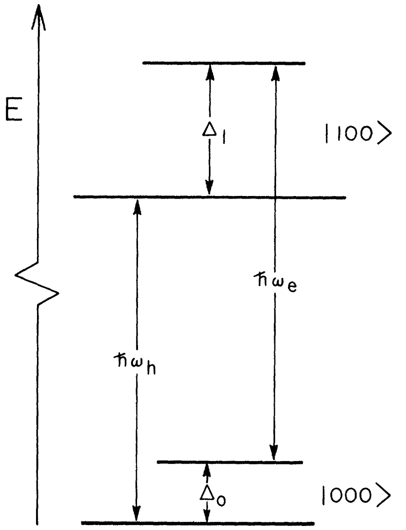

FIG. 1. Schematic diagram of the energies of the ground-state and first-excited state in the harmonic approximation and as shifted by quartic anharmonicity.

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Electron Paramagnetic Resonance Optical and Absorption Studies of the $V_1(\mathrm{Li}^+)$ Center in KCl:Li$^+$ †

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An interstitial chlorine atom created by x or γ irradiation at low temperatures can be stabilized by a Li$^+$ ion in KCl and form a $V_1(\mathrm{Li}^+)$ center, which is a bent (~ 8°) $\mathrm{Cl_2}^-$ molecule ion occupying a single negative-ion vacancy next to a substitutional Li$^+$. The two chlorine nuclei are inequivalent, and the internuclear axis is tipped 26° away from ⟨001⟩ in a {110} plane. The angular variation of the electron paramagnetic resonance (EPR) linewidth indicates a further weak hyperfine (hf) interaction with two other chlorine nuclei. One deduces that the nuclear configuration of the $V_1(\mathrm{Li}^+)$ center has the shape of a nonplanar Y, this in contrast to the H and $V_1(\mathrm{Na}^+)$ centers in KCl, whose nuclear configurations are either linear or almost linear. The symmetry of the $V_1(\mathrm{Li}^+)$ center is consistent with the well-known ⟨111⟩ off-center position of the Li$^+$ ion. The optical absorption bands of $V_1(\mathrm{Li}^+)$ are situated at 293, 354, and 618 nm and they are σ polarized. Optical anisotropy can be produced in these bands with ⟨110⟩-polarized light, and a disorientation temperature $T_D = 23.5$ °K is found.

I. INTRODUCTION

X or γ irradiation of alkali halide crystals at low temperatures results in the formation of three fundamental paramagnetic centers which have been studied very profitably with electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) techniques: (a) the well-known F center[1] which is an electron trapped by a negative-ion vacancy, (b) the self-trapped hole or V_K center[2,3] which is a positive hole stabilized and shared by two adjoining substitutional halogen ions as a ⟨110⟩-oriented X_2^- halogen molecule ion, and (c) the H center[4,5] which is an interstitial halogen atom stabilized as a ⟨110⟩-oriented[6] X_2^- halogen molecule ion occupying one negative-ion vacancy. These fundamental paramagnetic centers can interact with impurities and form a variety of other centers which are interesting in themselves and whose study often sheds light on some properties of the fundamental centers.

An important class of impurities are the foreign alkali ions. F centers for which one of the surrounding alkali ions is replaced by a foreign alkali ion have been studied extensively and are called F_A centers.[7] V_K centers stabilized to a higher temperature by a foreign alkali ion have been observed and are called V_{KA} centers.[8,9] In a recent paper[10] it was established that a center in KCl, known for a long time as the V_1 center, is an H