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81. *Ab initio* SCF Calculation of the Fluoronium Ion: Geometry, Electronic Structure and Vibrational Constants

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Summary. An *ab initio* SCF calculation of 42 points of the energy hypersurface of the fluoronium ion is presented using a contracted $F(5s/3p)$, $H(2s)$ gaussian basis set. In its equilibrium structure a bond length of 1.812 a. u. and a HFH bond angle of 127.2° are predicted. The calculated vibrational frequencies for H_2F^+, HDF^+, and D_2F^+ are in good agreement with the experimental data.

1. Introduction. – The vibrational spectra of the fluoronium ions H_2F^+, HDF^+, and D_2F^+ have recently been reported by *Couzi et al.* [1]. They concluded that the molecules are bent in their equilibrium configuration and derived, by assuming HFH angles between 105° and 120°, sets of harmonic force constants. *Pople et al.* [2] employed minimal STO-3G and extended 4-31G basis sets in a systematic *ab initio* study of the geometries and energies of AH_n molecules and cations. The fluoronium ion H_2F^+, having the same electron configuration as H_2O, was predicted to have a somewhat larger bond angle than water. *Leibovici* [3] investigated the structure of H_2F^+ and the path of protonation of HF using semiempirical and *ab initio* calculations. The activation energy of protonation is thought to result from solvation effects only.

An understanding of rotational and vibrational energy transfer and of chemical reactivity can be obtained by calculating energy hypersurfaces and solving the collision dynamical problem by trajectory calculations. The description of the hypersurfaces in analytical form over an extended range, however, presents serious problems. *Schaefer et al.* [4] determined the interaction potential between two rigid HF molecules in

order to study energy transfer mechanisms. The chemical laser related family of reactions $F + H_2 \rightarrow HF + H$; $H + F_2 \rightarrow HF + F$; and $F + HF \rightarrow HF + F$ has been studied by *Schaefer et al.* [5] at four different levels of *ab initio* treatment. Finally, *Jaffe & Anderson* [6] performed a classical trajectory analysis of the reaction $F + H_2 \rightarrow$

Table 1. *Gaussian basis set* $\chi_\mu = N_\mu \cdot x^k \cdot y^l \cdot z^m \exp\{-\alpha_\mu(x^2 + y^2 + z^2)\}$[a]

μ	Center	Type[b]	Orbital exponent α_μ[c]	μ	Center	Type[b]	Orbital exponent α_μ[c]
1	F	s	23342.2	13, 19	H(1), H(2)	s	10.2465
2	F	s	3431.25	14, 20	H(1), H(2)	s	2.34648
3	F	s	757.667	15, 21	H(1), H(2)	s	0.67332
4	F	s	209.192	16, 22	H(1), H(2)	s	0.22466
5	F	s	66.7261	17, 23	H(1), H(2)	s	0.082217
6	F	s	23.3705	24, 31, 38	F	x, y, z	65.6593
7	F	s	8.62372	25, 32, 39	F	x, y, z	15.2187
8	F	s	2.70001	26, 33, 40	F	x, y, z	4.78819
9	F	s	1.08750	27, 34, 41	F	x, y, z	1.72755
10	F	s	0.396536	28, 35, 42	F	x, y, z	0.648123
11	F	s	0.172324	29, 36, 43	F	x, y, z	0.244965
12, 18	H(1), H(2)	s	68.1600	30, 37, 44	F	x, y, z	0,091537

[a] N_μ normalization constant for the basis function χ_μ.
[b] s-Type: $k = 0, l = 0, m = 0$; x-Type: $k = 1, l = 0, m = 0$; y-Type: $k = 0, l = 1, m = 0$; z-Type: $k = 0, l = 0, m = 1$.
[c] Taken from [8].

Table 2. *Contracted gaussian basis set* $\chi_\nu = \Sigma \chi_\mu C_{\mu\nu}$

χ_ν	Center	Type[a]	Gaussian[b] functions γ_μ	Contraction coefficients[c] (not normalized) $C_{\mu\nu}$
1	F	1s	1, 2, 3, 4, 5	0.0004, 0.00327, 0.01754 0.07082, 0.2129
2	F	1s	6, 7	0.42213, 0.3748
3	F	2s	8	1.0
4	F	2s	9	1.0
5	F	2s	10, 11	0.44502, 0.06182
6	H(1)	1s	12, 13, 14, 15	0,00255, 0.01938, 0.0928, 0.2943
7	H(1)	1s	16, 17	0.49221, 0.2426
8	H(2)	1s	18, 19, 20, 21	0.00255, 0.01938, 0.0928, 0.2943
9	H(2)	1s	22, 23	0.49221, 0.2426
10	F	$2p_x$	24, 25, 26, 27	0.00882, 0.05778, 0.19341, 0.35671
11	F	$2p_x$	28	1.0
12	F	$2p_x$	29, 30	0.2299, 0.03143
13	F	$2p_y$	31, 32, 33, 34	0.00882, 0.05778, 0.19342, 0.35671
14	F	$2p_y$	35	1.0
15	F	$2p_y$	36, 37	0.2299, 0.03143
16	F	$2p_z$	38, 39, 40, 41	0.00882, 0.05778, 0.19342, 0.35671
17	F	$2p_z$	42	1.0
18	F	$2p_z$	43, 44	0.2299. 0.03143

[a] Atomic orbital which corresponds most closely to the contracted gaussian function χ_ν.
[b] No. of the gaussian function listed in Table 1.
[c] See [8] [9].

HF + H. Since *ab initio* calculations of the energy surface were not available a semi-empirical hypersurface was chosen. From MONTE CARLO averages over a large number of trajectories cross sections for energy distribution among reaction products were calculated.

Table 3. *Total SCF energy E_T as a function of the geometrical parameters r_1, r_2, and α*

Calculation	r_1[a.u.]	r_2[a.u.]	α [°]	E_T[a.u.]
1	1.732	1.732	180.0	– 100.20248
2	1.732	1.732	157.5	– 100.20667
3	1.732	1.732	135.0	– 100.21384
4	1.732	1.732	112.5	– 100.21081
5	1.732	1.732	90.0	– 100.18380
6	1.732	1.732	67.5	– 100.12405
7	1.732	1.732	22.0	– 99.58674
8	1.332	1.332	135.0	– 99.99184
9	1.432	1.432	135.0	– 100.09661
10	1.532	1.532	135.0	– 100.16097
11	1.632	1.632	135.0	– 100.19719
12	1.732	1.732	135.0	– 100.21384
13	1.832	1.832	135.0	– 100.21697
14	1.932	1.932	135.0	– 100.21085
15	2.032	2.032	135.0	– 100.19853
16	2.132	2.132	135.0	– 100.18217
17	1.782	1.782	135.0	– 100.21680
18	1.782	1.832	135.0	– 100.21689
19	1.782	1.882	135.0	– 100.21586
20	1.832	1.882	135.0	– 100.21592
21	1.882	1.882	135.0	– 100.21485
22	1.782	1.782	123.25	– 100.21758
23	1.782	1.832	123.25	– 100.21772
24	1.782	1,882	123.25	– 100.21671
25	1.832	1.832	123.25	– 100.21782
26	1.832	1.882	123.25	– 100.21679
27	1.882	1.882	123.25	– 100.21573
28	1.782	1.782	112.5	– 100.21411
29	1.782	1.882	112.5	– 100.21346
30	1.832	1.832	112.5	– 100.21457
31	1.832	1.882	112.5	– 100.21363
32	1.882	1.882	112.5	– 100.21266
33	1.832	1.832	130.0	– 100.21775
34	1.757	1.807	113.0	– 100.21377
35	1.820	1.820	123.25	– 100.21799
36	1.800	1.800	129.0	– 100.21800
37	1.811	1.811	126.87	– 100.21815
38	1.737	3.000	180.0	– 100.11932
39	1.8122	1.8122	90.0	– 100.18946
40	1.8122	1.8122	120.0	– 100.21747
41	1.8122	1.8122	150.0	– 100.21269
42	1.8122	1.8122	180.0	– 100.20609

In this work we restrict ourselves to the vicinity of the equilibrium structure of the fluoronium ions and to the calculation of small oscillations. A harmonic energy hypersurface is fitted to the calculated points, thus determining the equilibrium SCF energy, the bond distance, the bond angle, and the four force constants. The calculated vibrational frequencies are compared with the measured values.

2. Calculations. – The *ab initio* calculations were carried out with a CDC version of the program IBMOL [7]. The basis set contained 44 cartesian gaussian functions of s and p type [8]. Details are given in Table 1. The gaussian functions F(11s/7p) and H(6s) were linearly combined to a contracted basis set of F(5s/3p) and H(2s) using coefficients derived from atomic calculations (Table 2). The number of linear coefficients for the SCF procedure was thus reduced from 44 to 18.

3. Results and Discussion. – *Geometry.* – An extensive search for the minimum of the SCF energy with respect to the three geometrical parameters of the fluoronium ion H_2F^+ has been performed. The assumed geometries and the calculated SCF energies are given in Table 3. First (calculations 1–7) the bond angle α was varied (Fig. 1) keeping the HF distance $r_1 = r_2 = 1.732$ a.u. (0.9168 Å) at the experimental value for the HF-molecule [10]. Although the potential energy does not vary drasti-
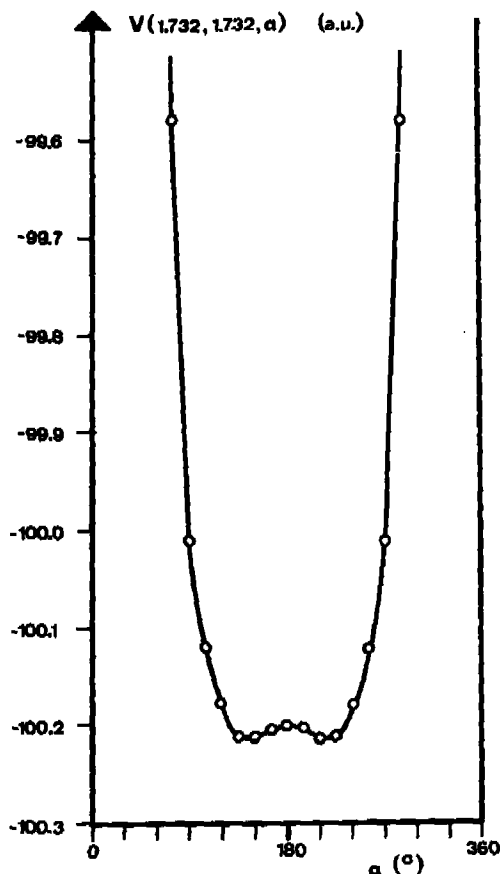

Fig. 1. *Total SCF energy of the fluoronium ion as a function of the bond angle* ($r_1 = r_2 = 1.732$ a.u.)

cally from 120°–180°, a bent geometry is clearly predicted. A second set of calculations (8–12) was performed, keeping $\alpha = 135°$ and changing $r = r_1 = r_2$ (Fig. 2). From a quadratic fit an equilibrium length of 1.832 a.u. was obtained. This value is significantly larger than the HF bond distance. The calculated geometry of the molecule was further improved by using a smaller net of the parameter surface near the expected equilibrium position.

A total of 42 points of the energy hypersurface was calculated. Near its equilibrium position the hypersurface was approximated by a potential function, containing 7 free parameters:

$$V(r_1, r_2, \alpha) = V_e(r_e, r_e, \alpha_e) + 1/2\, f_r\, \{(r_1 - r_0)^2 + (r_2 - r_e)^2\}$$
$$+ 1/2\, f_\alpha\, (\alpha - \alpha_e)^2 + f_{rr}\, (r_1 - r_e)(r_2 - r_e)$$
$$+ f_{r\alpha}\{(r_1 - r_e) + (r_2 - r_e)\}\{\alpha - \alpha_e\}$$
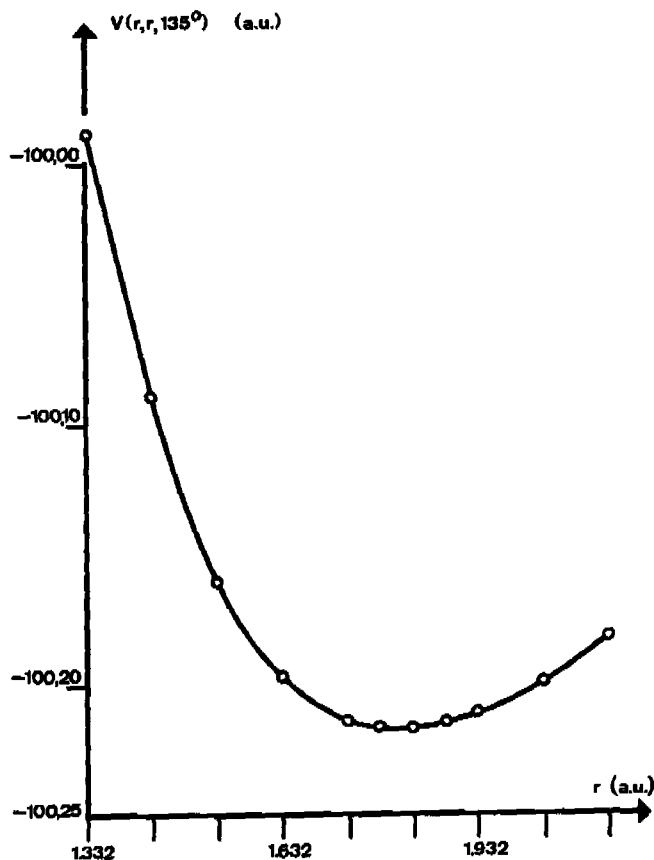

Fig. 2. *Total SCF energy of the fluoronium ion as a function of the HF bond distance* ($\alpha = 135°$)

The SCF energy at the equilibrium $V_e\,(r_e, r_e, \alpha_e)$, the equilibrium geometry parameters r_e, α_e, and the four force constants f_r, f_α, f_{rr}, and $f_{r\alpha}$ were obtained from a least square fit using various selections of the calculated points. Only the off diagonal constants f_{rr} and $f_{r\alpha}$ are sensitive to the selection of the points used (Table 4); they

Table 4. *Total SCF energy, equilibrium structure, and force constants of the fluoronium ion*

$V_e(r_e, r_e, \alpha_e)$ [a.u.]	r_e [a.u.]	α_e [°]	F_r [mdyn·Å^{-1}]	F_α [mdyn·Å^{-1}]	F_{rr} [mdyn·Å^{-1}]	$F_{r\alpha}$ [mdyn·Å^{-1}]	number of points employed
− 100.218143	1.8160	127.22	7.20	0.466	0.230	0.038	25 [a]
− 100.218175	1.8144	127.14	7.44	0.463	0.335	0.043	23 [a]
− 100.218180	1.8142	127.15	7.43	0.465	0.361	0.036	21 [a]
· 100.218184	1.8140	127.15	7.43	0.468	0.347	0.028	20 [a]
− 100.218127	1.8117	126.67	7.09	0.379	0.157	0.024	15 [a]
− 100.218142	1.8112	126.58	7.93	0.379	0.178	0.028	10 [a]
− 100.218158	1.8122	127.18	6.97	0.463	0.186	0.050	21 [b]

[a]   Points with lowest SCF energy.
[b]   Special selection of points near equilibrium position.

are not expected to be well defined by such a calculation. For the determination of vibrational frequencies to be reported below, the parameters derived from the 21 points which lie closest to the equilibrium position were employed. In its equilibrium structure the fluoronium ion has a H–F bond distance of 1.812 a.u. and a bond angle H–F–H of 127.2°. The corresponding SCF energy is − 100.21816 a.u.
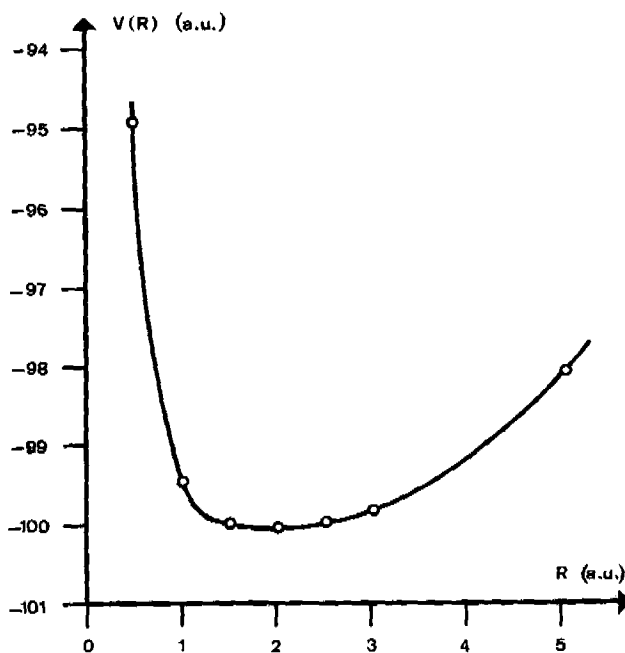

Fig. 3. *Total SCF energy of the HF molecule as a function of the bond distance*

For comparison the molecule HF was studied using the same basis set as before. The potential energy curve is given in Fig. 3. The equilibrium distance R_e, the force constant f_R, and the equilibrium SCF energy $V_e(R_e)$ were obtained by fitting the relation

$$V(R) = V_e(R_e) + 1/2\, f_R\, (R - R_e)^2$$

to 6 points near the equilibrium. The minimum was obtained at R = 1.737 a. u. with $V_e(R_e) = -100.13088$ a. u. and a bond stretching constant $f_R = 10.28$ mdyn Å^{-1}.

MO-correlation diagrams. – *Walsh* [11] has empirically constructed angular correlation diagrams for the behavior of the various MO-energy curves to rationalize the geometrical arrangements of molecules in their ground and excited states. The arguments are based upon a series of simple theoretical concepts. According to such a diagram all AH$_2$-type systems with 8 valence electrons are expected to have a bent structure.

The *Walsh*-like correlation diagram (Fig. 4) shows the variations of the *Hartree-Fock* one-electron energy (MO's) with bond angle for the H$_2$F$^+$ system with $r_e = 1.8122$ a. u., calculated in this work. Inspecting the diagram in detail we notice that the
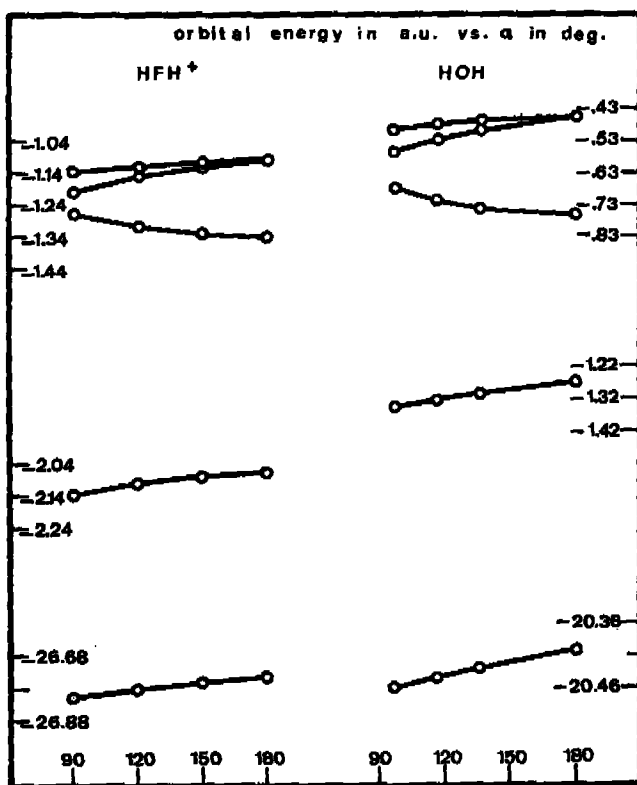

Fig. 4. *Walsh correlation diagrams for H$_2$F$^+$ and H$_2$O* (Values for H$_2$O have been taken from [12])

three highest occupied MO's are in good qualitative agreement with those estimated by *Walsh*. For the variation of the $2\sigma_g - 2a_1$ orbital *Walsh* assumed that the 2s character at the A atom in a AH$_2$ system becomes negligibly small at small bond angle, causing a destabilization of the orbital. As pointed out by *Mulliken* [18] this assumption is erroneous and our calculations show that even at 90° the 2a$_1$ MO is predominantly a 2s$_A$ orbital, causing rather a stabilizing of this MO at a smaller bond angle. Exactly the same qualitative argument may be applied to the iso-electronic H$_2$O molecule which is also shown in Fig. 4.

Proton affinity of the HF molecule. – The proton affinity may be defined as the energy difference between the protonated species and the parent molecule and it can be estimated by different experimental methods such as mass spectroscopy, the use of the thermochemical cycle, *etc.*

Table 6 contains the calculated proton affinities of the HF molecule along with the values reported previously. It is to be noticed that our value of -491.7 kJ/mol is in good agreement with data from calculations using large basis sets (*e.g.* 4-31G basis set of [2]). Values from smaller basis sets are much larger and might be in error.

It is expected that the *ab initio* SCF MO-method in the *Hartree-Fock* limit leads to a rather reliable prediction of the proton affinity. Both, the parent and the protonated molecule contain the same number of electrons and therefore electron correlation effects might play a minor role. The experimental proton affinity of HF remains yet to be determined.

Electron population analysis. – Table 5 compares the *Mulliken* electron population analysis of the HF and the H_2F^+ molecules. In H_2F^+ both, the total charge at the F and the H atoms, are decreased by about 0.2 units leaving the 'ionic' character of the H–F bond nearly unchanged.

Table 5. *Electron population in HF and H_2F^+*

Center	HF[a])	$H_2F^{+b})$
F(s)	3.96	3.9
F(p_x)	1.53	
F(p_y)	2.00	} 3.40
F(p_z)	2.00	2.00
F(total)	9.49	9.30
H(s)	0.51	0.35

[a]) The x-axis is taken along the H–F bond axis.
[b]) The z-axis is perpendicular to the molecular plane.

Estimate of electron correlation. – The lowest total energy for the HF molecule has been reported to be -100.3564 a.u., obtained from an extended *ab initio* calculation with configuration interaction [13]; the calculated electron correlation energy is approximately 0.29 a.u. The correlation energies for the 10 electron systems of Ne, HF, H_2O, and CH_4 have been estimated previously as 0.393, 0.377, 0.383, and 0.341 a.u. [14] [15]. It is safe to say that an upper limit to the correlation energy for the H_2F^+ species might be around 0.4 a.u.

Vibrational spectra. – Having obtained a description of the energy hypersurface near the equilibrium geometry, it is a straightforward matter to determine the vibrational frequencies of the species H_2F^+, HDF^+, and D_2F^+. The GF treatment for a non-linear triatomic molecule has been worked out in detail by *Wilson et al.* [16]. The corresponding frequencies are given in Table 7a, where for H_2F^+ and D_2F^+ $\tilde{\nu}_1$ refers to the symmetrical stretching, $\tilde{\nu}_2$ to the symmetrical bending, and $\tilde{\nu}_3$ to the antisymmetrical stretching mode. Diagrams of the mass weighted displacements of the atoms $\vec{q}_k = \sqrt{M_k} \cdot \Delta \vec{x}_k$, where $\Delta \vec{x}_k$ is the geometrical displacement of an atom with mass M_k, are given in Fig. 5. For HDF^+ $\tilde{\nu}_1 = 2545$ cm^{-1} describes approximately a D–F and $\tilde{\nu}_3 = 3514$ cm^{-1} a H–F stretching mode.

The measured frequencies, listed in Tables 7b and 7c, depend markedly on the nature of the surrounding counter ion. The interaction between the fluoronium ions
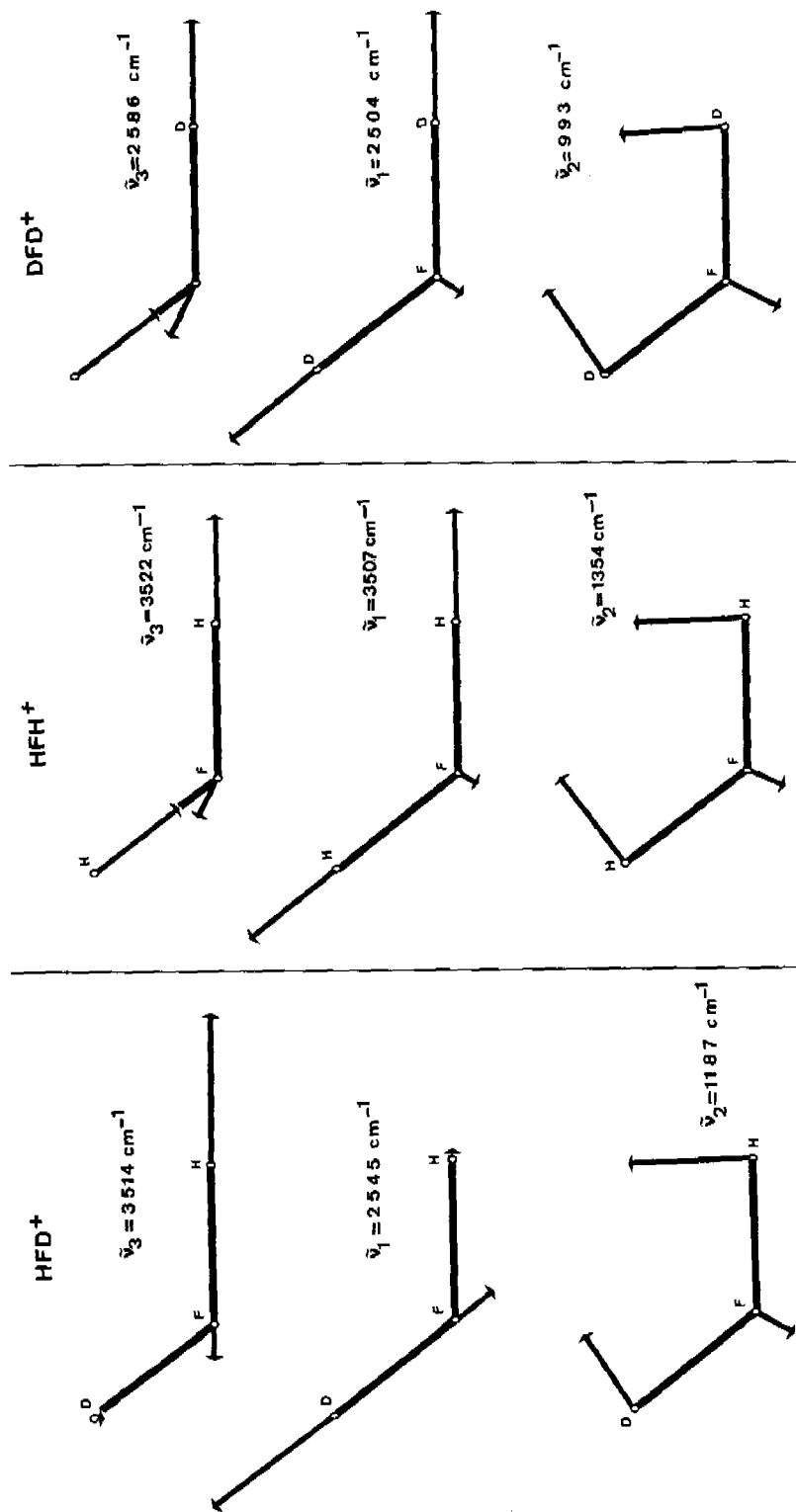
Fig. 5. *Normal coordinate displacements of H_2F^+, HDF^+, and D_2F^+ in mass weighted coordinates*

Table 6. *Total SCF energy, equilibrium structure, and force constants of H_2F^+ and HF*

$V_e(r_e, r_e, \alpha_e)$ [a.u.]	r_e [a.u.]	α_e [°]	F_r [mdyn Å⁻¹]	F_α [mdyn Å⁻¹]	F_{rr} [mdyn Å⁻¹]	$F_{r\alpha}$ [mdyn Å⁻¹]	$V_e(R_e)$ [a.u.]	R_e [a.u.]	f_R [mdyn Å⁻¹]	Proton affinity of HF $V_e(r_e, r_e, \alpha_e) - V_e(R_e)$ [kJ/mol]	
−100.218158	1.8122	127.18	6.97	0.463	0.186	0.050	−100.030889	1.738	10.28	−491.7	a)
− 98.86411	1.841	112.0					− 98.57285	1.807	11.3	−764.8	b)
−100.07787	1.831	125.5					− 99.88729	1.742	9.6	−500.4	c)
	1.960	127.15	14.91					1.900	18.34	−840	d)
−100.25838	1.781	116.0					−100.06439	1.698		−509.4	e)
							−100.0705	1.7328			f)
			5.71	1.36	−0.55	−0.79					g)
			4.97	0.96	−0.29	−0.54					h)
			±0.20	±0.14	±0.20	±0.13					i)

a) This work, results from the *ab initio* calculations. b) STO-3G basis set [2]. c) 4-31G basis set [2]. d) Semiempirical calculation (INDO) [3]. e) *Ab initio* calculation [3]. f) Near *Hartree-Fock* limit [1]. g) Force field derived from experimental data assuming a HF distance of 1.928 a.u. and a bond angle of 117° [1]. h) This work, force field derived from experimental data of [1] using the calculated equilibrium geometry. i) This work, standard deviations.

Table 7. *Vibrational frequencies of the fluoronium ions* (cm⁻¹)

a)	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$	b)	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$	c)	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$	d)	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$
H_2F^+	3507	1354	3522	H_2F^+	2970	1680	3080	H_2F^+	3112	1627	3270	H_2F^+	3017	1715	3101
HDF^+	2545	1187	3514	HDF^+	2270	1495	2980	HDF^+	–	1460	–	HDF^+	2279	1471	3038
D_2F^+	2504	993	2586	D_2F^+	2250	1240	2320	D_2F^+	2330	1200	2400	D_2F^+	2193	1235	2277

7a: Frequencies directly calculated from the *ab initio* energy hypersurface.
7b: Experimental results for $(H_2F^+)(BF_4)$, $(HDF^+)(BF_4)$, and $(D_2F^+)(BF_4)$.
7c: Experimental results for $(H_2F^+)(SbF_6)$, $(HDF^+)(SbF_6)$, and $(D_2F^+)(SbF_6)$.
7d: Best fit to the experimental data given in 7b assuming a harmonic force field. The corresponding force constants are $f_r = 4.97$, $f_\alpha = 0.96$, $f_{rr} = -0.29$, and $f_{r\alpha} = -0.54$ mdyn Å⁻¹.
We would like to thank Dr. *Meyer* for making his normal coordinate program available to us.

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and SbF_6^- is weaker than with BF_4^-. This leads to an increase in the frequency of the two stretching modes and to a lowering of the bending frequency. The calculated values from the *ab initio* hypersurface pertain to the free fluoronium ions and conform to the pattern followed by the experimental values.

A force field which leads to an optimal description of the experimental data obtained with the BF_4^- counter ion, assuming the *ab initio* equilibrium geometry, is given in Table 6 (h, i). As expected from the counter-ion effect [1], the force constant F_r is smaller, while F_α is larger than the *ab initio* values given in Table 6 (a). The magnitude and even the sign of the off-diagonal force constants F_{rr} and $F_{r\alpha}$ depend strongly on the assumed equilibrium geometry. As expected, they compare very poorly with the calculated *ab initio* values.

A comparison of the calculated and the experimental frequencies (Table 7) shows that they all lie within 20% which is typical for a SCF calculation using this kind of basis set [19] 20].

Ab initio calculations at the SCF level provide a useful tool to the quantitative understanding of structural features and of the vibrational spectra of small molecules. An extended description of the energy hypersurface and a study of the chemical reactivity by trajectory calculations will be attempted in the future.

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