Table II. Positional Parameters (×10^4)

atom	*x*	*y*	*z*
Pd(1)	879 (0.5)	2003 (1)	2348 (1)
Pd(2)	1789 (0.5)	305 (1)	3759 (1)
Cl1	−258 (1)	2941 (4)	1779 (2)
Cl2	1738 (2)	−285 (4)	5171 (2)
N1	269 (4)	−414 (10)	2867 (6)
C10	713 (5)	346 (13)	2935 (7)
C11	−248 (6)	−1260 (12)	2857 (8)
C12	−576 (6)	−732 (12)	3342 (7)
C13	−1089 (6)	−1607 (14)	3329 (9)
C14	−1253 (7)	−2903 (16)	2844 (10)
C15	−905 (7)	−3409 (15)	2372 (10)
C16	−372 (6)	−2571 (13)	2386 (9)
C17	−387 (6)	699 (12)	3819 (8)
C18	17 (8)	−3025 (16)	1879 (11)
N2	2018 (5)	838 (10)	2101 (7)
C20	1758 (5)	967 (12)	2576 (8)
C21	2059 (5)	816 (12)	1269 (8)
C22	2652 (6)	1423 (15)	1332 (9)
C23	2686 (8)	1302 (16)	471 (10)
C24	2134 (8)	702 (19)	−382 (10)
C25	1569 (6)	118 (16)	−391 (8)
C26	1510 (6)	191 (13)	423 (8)
C27	3219 (6)	2117 (17)	2254 (10)
C28	863 (6)	−355 (16)	404 (9)
N3	2898 (4)	−18 (10)	4527 (6)
C31	3331 (6)	1096 (14)	4723 (10)
C32	4047 (7)	922 (16)	5266 (10)
C33	4340 (6)	−436 (16)	5593 (9)
C34	3883 (6)	−1561 (14)	5371 (9)
C35	3162 (6)	−1304 (12)	4838 (8)
N4	1191 (5)	3803 (10)	1858 (7)
C41	882 (7)	4148 (15)	904 (9)
C42	1118 (8)	5361 (17)	613 (10)
C43	1665 (8)	6171 (15)	1332 (11)
C44	1963 (7)	5820 (15)	2305 (11)
C45	1721 (7)	4628 (15)	2540 (10)

locate the hydrogen atoms. The positional parameters are given in Table II. Anomalous dispersion effects and atomic scattering factors were taken from the usual tabulation.[13]

Registry No. **1**, 97775-33-2; **2**, 102977-16-2.

Supplementary Material Available: Listings of nonbonded distances (SM Table I), least-squares planes and interplanar angles (SM Table II), and anisotropic thermal parameters (SM Table III) (3 pages). Ordering information is given on any current masthead page.

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Can F_2H^+ Exist in the Topological Form FHF^+?

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Although the anion[1] F_2H^- and the neutral radical[2] F_2H have been studied extensively, the cation analogue, F_2H^+, has only oblique literature references.[3] The potential energy surface of the cation is of interest in its own right. Futher, the development of the charge reversal experiment[4] and multiphoton laser techniques makes this cation accessible in the topology FHF^+ from the linear FHF^- anion. In this work we have completed ab initio calculations on both topologies FFH^+ and FHF^+ in order to ascertain whether or not the latter could have an independent existence, even if metastable. We also have calculated the proton affinity of F_2 and transition-state energies and harmonic vibrational frequencies for F_2H^+.

Table I. Energies and Structures of FHF^+

struct	method	*r*(FF), Å	*r*(FH), Å	angle, deg	energy, hartrees
$D_{\infty h}$[a]	HF	2.108	1.054		−198.690 15
	MP2	2.144	1.072		−199.177 49
	MP3	2.160	1.080		−199.146 21
C_{2v}	HF	1.394	1.183	72.2[b]	−198.800 33
	MP2	1.487	1.200	76.6	−199.296 87
	MP3	1.477	1.186	77.0	−199.248 39
C_s	HF	1.375	0.953	109.0[c]	−198.875 90
	MP2	1.427	0.984	102.6	−199.338 92
	MP3	1.416	0.972	104.4	−199.300 79
$C_{\infty v}$	HF	1.413	0.972		−198.825 59
	MP2	1.403	1.006		−199.268 66
	MP3	1.404	0.995		−199.232 94

[a] A $C_{\infty v}$ structure of this topology with FH bond lengths of 1.200 and 1.054 Å gave a HF energy of −198.685 24 hartrees and optimized to $D_{\infty h}$. [b] Measure of angle F–H–F. [c] Measure of angle F–F–H.

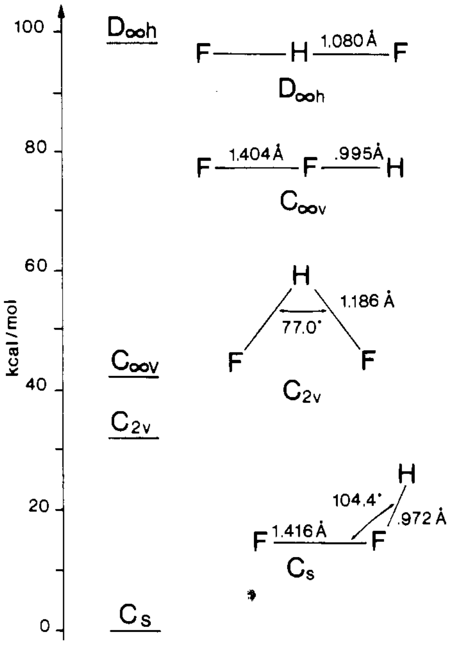

Figure 1. MP3 structures and relative energies of F_2H^+.

The GAUSSIAN 82 program package was employed for this study.[5] All calculations were executed by using the 6-311G(d,p) (also denoted 6-311G**) basis set.[6] To determine unambiguously

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Table II. Frequencies of C_s FFH$^+$

	freq, cm^{-1}			freq, cm^{-1}	
	uncor	cor		uncor	cor
HF	987.5	878.4[a]	MP2[c]	908.4	872.1[b]
	1264.7	1125.6		1165.4	1118.8
	3622.5	3224.0		3274.5	3143.5

[a] Obtained by multiplying uncorrected frequencies by 0.89.[9] [b] Obtained by multiplying uncorrected frequencies by 0.96.[9] [c] MP2 uncorrected frequencies are as follows (cm^{-1}). $D_{\infty h}$: 2187.6*i*, 2187.6*i*, 602.7, 3784.8; ZPE = 2193.8. C_{2v}: 1696.2*i*, 873.4, 2198.9; ZPE = 1536.2. $C_{\infty v}$: 1494.8*i*, 1494.8*i*, 966.1, 2193.6; ZPE = 1939.9.

the structure of F_2H^+, the molecule's structure was optimized at all possible topologies. These optimizations were carried out at the Hartree–Fock (HF) and second- and third-order Moeller–Plesset[7] (MP) levels. At each optimized geometry the harmonic vibrational frequencies were calculated. An imaginary frequency indicates that a given structure is at a saddle point, whereas real frequencies show the structure to be at a minimum (perhaps local) on the potential energy surface. Frequencies were calculated analytically at the HF level and numerically at the MP2 level.[8]

In Table I we present the structures and energies for each of the geometries that were considered; the MP3 results also are summarized in Figure 1. Two imaginary frequencies were calculated for each of the two linear structures and one for the C_{2v} structure (Table II). That is, the only minimum is that provided by the C_s structure corresponding to protonated F_2. This finding is in contrast to that of a previous study,[3b] which stated that the C_{2v} structure was a minimum. The calculated harmonic vibrational frequencies are presented in Table II along with corrected frequencies, which compensate for anharmonicity and for the overestimation of frequencies known to occur in such calculations.[9] For completeness we list as a footnote the MP2 uncorrected frequencies and zero-point energies for the three saddle-point structures. All imaginary frequencies (cm^{-1}) were in the range 1500*i*–2200*i*; it is unlikely that calculations at a higher level of theory would reveal minima at any of these geometries or alter the relative energies in any significant way.

Our study has implications for the results of a charge reversal experiment on FHF$^-$. Given the vertical nature of the experiment,[4a] one initially would expect to form the cation FHF$^+$. However, no barrier was found that would trap the FHF$^+$ topology in a metastable state. Hence, in the time scale of the experiment it will rearrange to its most stable topology, F_2H^+. (Although we did not examine the complete potential energy surface, the use of the gradient algorithms for geometry optimization shows that the energy from each of the saddle-point structures goes "downhill" to the stable C_s structure.)

The F_2H^+ cation is, of course, nothing other than protonated F_2. In the course of this study the proton affinity of F_2 also was calculated. The total energy (hartrees) of F_2 is −198.732 23 at the HF level and −199.193 33 at the MP2 level. These values coupled with the total energies of F_2H^+ given in Table I and the zero-point energy corrections in hartrees at each level (0.010 62 and 0.010 09) yield a calculated proton affinity of 83.5 kcal/mol at the HF level and 85.0 kcal/mol at the MP2 level. These numbers are slightly less than those reported by Del Bene et al.,[3c] as a result of the additional function we have in our basis set compared to theirs. The calculated diatomic F_2 bond length is 1.331 and 1.411 Å at the HF and MP2 levels, respectively. Hence, our calculations indicate that protonation will result in a slight increase in the FF bond length. The experimental proton affinity of F_2 has not been reported. We hope that this study will provide the impetus for an experimental investigation into the proton affinity of F_2 and the spectroscopic properties of the cation.

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