The present analysis also suggests that larger spectral red shifts could in principle be obtained through substitution of more highly conjugated substituents at the β-carbons, which would interact more strongly with orbital 1. However, such substituents might be ineffective due to loss of conjugation from steric effects. Alternatively, an anionic substituent whose π- or π^*-orbital is orbitally degenerate with orbital 1 of MgP could in principle induce large spectral changes through a strong conjugative interaction with this orbital.

Protonated Schiff Base. The spectrum of protonated NiPSB (NiPSBH$^+$) is shown in Figure 2, and it is clear that it differs significantly from that of NiPSB. As mentioned previously, protonation induces an $\sim$1200-cm^{-1} red shift of the visible band; in addition the Soret region is considerably different from that of NiPSB.

The calculated spectrum of protonated MgPSBH$^+$(30) is also shown in Figure 2, and the computed electronic states are tabulated in Table I. It is clear from these data that the change in the Soret spectral region is not due simply to an increased splitting of the degenerate metalloporphyrin Soret band but to a complete change in the composition of the constituent electronic states. The proton-induced red shift of the visible band is estimated to be $\sim$1000 cm^{-1}. To ensure that the shift was not an artifact of the computational method, a larger (ca. 2000 configurations) CI calculation designed to obtain more highly converged wave functions specifically for S_0, S_1, and S_2 was carried out on MgPSB(30) and MgPSBH$^+$(30). The energies and state compositions obtained differ insignificantly from those reported in Table I.

The effects of protonation may be understood by considering the orbital interaction diagram shown in Figure 5. In this figure the orbital energies of unsubstituted MgP and the vinyl and Schiff base substituents were obtained from SCF calculations on each isolated molecule with an additional proton placed so that its effect is equivalent to the proton in MgPSBH$^+$(30). This accounts approximately for the effect of the proton nuclear charge alone on the noninteracting molecular orbitals. For MgPSBH$^+$(30), Figure 5 shows that the vinyl orbitals interact with MgP orbitals in much the same manner as in the nonprotonated case. The Schiff base π-orbital is now much lower in energy due to the close proximity of the proton and does not perturb any of the higher lying MgP π-orbitals; it appears as an isolated "C═N" π-orbital among the orbitals of MgPSBH$^+$(30). This explains why the ^{1}H NMR and resonance Raman spectra of NiPSBH$^+$ reported by Ward et al.[11] showed that protonation effects were localized at the Schiff base and did not perturb the porphyrin macrocycle.

The principal perturbation by a substituent orbital is clearly that produced by the energetically favorable interaction of the Schiff base π^*-orbital with the 1* orbital of MgP, producing a set of three low-lying nondegenerate π^*-orbitals in MgPSBH$^+$(30), as opposed to a degenerate pair of π^*-orbitals in MgPSB(30) and MgP. Thus, we have the unusual situation in which protonation of the ground state of MgPSB(30) results chiefly in changes in the nature and location of the low-lying excited states. The red shift of the visible band may be seen as being a consequence of the differential stabilization of S_1 relative to S_0 in MgPSBH$^+$(30) due to the lower orbital energy of the 1* orbital, which causes the energetically favorable $1 \rightarrow 1^*$ excitation to become the dominant configuration in the CI composition of S_1 (see Table I). Additionally, the $S_1 \leftarrow S_0$ oscillator strength is seen to be larger than in MgPSB(30).

Among the higher lying electronic states given in Table I, it is evident that because of the new virtual orbital space, there are a number of states of moderately high oscillator strength that do not correlate with the higher lying states of MgPSB but that produce a calculated spectrum in the Soret region which is qualitatively consistent with that of NiPSBH$^+$, as shown in Figure 2.

Finally, it is also interesting to point out that the spectral effects of Schiff base protonation may be "switched off" if the Schiff base is not in conjugation with the macrocycle. This may be seen in Figure 5 for MgPSBH$^+$(90), where these is no interaction between the Schiff base π^*-orbital and the MgP 1*- and 2*-orbitals. Thus, in MgPSBH$^+$(90) orbitals 1* and 2* are the same as in MgPSB(90), orbital 3* is an isolated "C═N" π^*-orbital, and there is no significant change in the spectrum of MgPSB(90) upon protonation.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. The authors thank Professor G. T. Babcock for providing a copy of his paper on protonated Schiff base porphyrins prior to publication.

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Vibrational Frequency Shifts in Hydrogen-Bonded Systems: The Hydrogen Fluoride Dimer and Trimer

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Abstract: Ab initio molecular electronic structure theory has been used to predict the structures and harmonic vibrational frequencies of $(HF)_2$ and $(HF)_3$. Standard Huzinaga–Dunning double-ζ (DZ) and double-ζ plus polarization (DZ+P) basis sets have been used in conjunction with self-consistent-field (SCF) and configuration-interaction (CI) methods. As many as 29 161 configurations were included variationally, with analytic CI gradient methods used to precisely locate stationary point geometries. The DZ SCF, DZ+P SCF, and DZ+P CI methods all give qualitative agreement with recent high-resolution spectroscopic measurements of the H–F dimer vibrational frequency shifts. Trimer equilibrium and transition-state structures and vibrational frequencies have similarly been predicted at the DZ SCF and DZ+P SCF levels of theory.

One of the most important new developments in molecular spectroscopy is the potential for the determination of the high-resolution vibrational spectra of hydrogen-bonded systems. An excellent example of these advances is given by Pine and Lafferty's recent study[1] of rotational structure and vibrational predissociation in the HF stretching bands of the HF dimer. Pine and Lafferty's high-resolution infrared study appears to establish the "free" hydrogen H–F stretch ν_1 at 3929 cm^{-1} and the "bonded" hydrogen H–F fundamental ν_2 at 3868 cm^{-1}. Compared to the HF monomer fundamental[2] at 3961 cm^{-1}, these new experiments indicate dimer

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Table I. Theoretical Predictions of the Properties of the HF Monomer[a]

	DZ SCF	DZ CI	DZ+P SCF	DZ+P CI	exptl[b]
E, hartrees	−100.01698	−100.13789	−100.04419	−100.21382	
r_e, Å	0.931	0.960 (0.957)	0.912	0.933 (0.930)	0.917
ω_e, cm^{-1}	4103	3732 (3783)	4440	4150 (4200)	4138

[a] In parentheses are given CI results for the HF···HF system, with R = F···F = 1000 bohrs. The latter should be compared with dimer predictions, as explained in the text. [b] K. P. Huber and G. Herzberg, "Constants of Diatomic Molecules", Van Nostrand-Reinhold, New York, 1979.

red shifts of ~32 cm^{-1} for the free hydrogen stretch and ~93 cm^{-1} for the bonded hydrogen. Furthermore, recent laboratory studies[3-5] on the trimer $(HF)_3$ hold out the promise that equally reliable frequency shifts may be available for this larger system shortly.

In principle, theory should be able to provide reliable predictions of infrared vibrational shifts in hydrogen-bonded species such as $(HF)_2$ and $(HF)_3$. In practice, there are some rather serious obstacles to be overcome. First the potential energy hypersurfaces in question must be reliably described. And second, the theoretical treatment of the nuclear motion must be carried out at a sufficiently high level to guarantee success.[6] It goes without saying that the energy hypersurfaces for weakly bound systems such as $(HF)_2$ and $(HF)_3$ are expected to be significantly anharmonic. Unfortunately, the only routine treatment of the nuclear motion problem for systems of more than three atoms[7] is the harmonic approximation. Hence is seen the dilemma with respect to predicting the vibrational frequencies of small hydrogen-bonded polymers.

One cannot state with confidence, even with the exact energy hypersurface, that an harmonic treatment of the vibrational problem will yield meaningful predictions of polymer frequency shifts. Nevertheless, this approach needs to be attempted, if only as a first step toward a satisfactory theoretical treatment of the problem. To our knowledge, the first such ab initio study was that of Curtiss and Pople[8] on the HCN–HF complex. In the present research we have continued in the Curtiss–Pople framework to examine the harmonic vibrational frequencies of the HF dimer and trimer. Several distinct levels of electronic structure theory have been used in this regard to characterize the $(HF)_2$ and $(HF)_3$ potential energy surfaces.

The reader will appreciate that this is not the first ab initio study of the $(HF)_2$ or $(HF)_3$ systems. Particularly noteworthy among previous theoretical studies are those of Kollman and Allen,[9] Diercksen and Kraemer,[10] del Bene and Pople,[11] Yarkony et al.,[12] Lischka,[13,14] and Jorgensen[15,16] for the dimer and of del Bene and Pople,[11] Swepston, Colby, Sellers, and Schäfer,[17] and Clark, Emsley, Jones, and Overill[18] for the trimer. However, to our knowledge the only previous ab initio prediction of the dimer vibrational frequencies is that of Curtiss and Pople[19] (CP). CP described the $(HF)_2$ energy hypersurface by the 4-31G basis (slightly smaller than the double-ζ basis set used here) self-consistent-field (SCF) method and determined the vibrational frequencies within the harmonic approximation.

The present research is perhaps best viewed as an extension of CP's hydrogen fluoride dimer study.[19] Here larger basis sets have been used, and for the dimer the effects of electron correlation have been explicitly considered via configuration interaction (CI).[20] Also presented here are the first structural optimizations for the trimer including polarization functions[20] (d functions on F, p functions on H) and the first $(HF)_3$ vibrational frequency predictions.

Theoretical Approach

The most widely used ab initio potential energy surface for the HF–HF system is that of Yarkony, O'Neil, Schaefer, Baskin, and Bender (YOSBB).[12] The YOSBB surface has been fit to several analytic forms[21-23] and used for both scattering[24,25] and statistical mechanical[22,26] purposes. For this reason, the double-ζ plus polarization (DZ+P) basis set chosen here was precisely that used by Yarkony and co-workers.[12] Thus a secondary result of the present study was to provide additional information concerning the YOSBB DZ+P SCF potential surface for HF–HF.

The YOSBB basis set is given in Table I of their paper and is of the Huzinaga–Dunning contracted Gaussian type.[27,28] The technical description of this DZ+P basis set is F(9s 5p 1d/4s 2p 1d), H(4s 1p/2s 1p). Polarization function orbital exponents were $\alpha_d(F) = 0.7$ and $\alpha_p(H) = 0.7$. The smaller double-ζ (DZ) basis is obtained by simply deleting the polarization functions from the DZ+P set. Thus in the DZ basis set we have 12, 24, and 36 contracted Gaussian functions for HF, $(HF)_2$, and $(HF)_3$, respectively. The DZ+P basis set similarly includes 21, 42, and 63 contracted functions for monomer, dimer, and trimer, respectively.

Electron correlation was explicitly considered for the HF dimer here via the method of configuration interaction (CI).[29] Specifically, all single and double excitations (CISD) with respect to the Hartree–Fock reference configuration were included. The two lowest occupied SCF molecular orbitals (essentially fluorine 1s-like) were held doubly occupied in all configurations, and the two highest-lying virtual orbitals (core counterparts for DZ or

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Table II. Theoretical Predictions of the Properties of the HF Dimer[a]

	DZ SCF	DZ CI	DZ+P SCF	DZ+P CI	exptl
E, hartrees	−200.04439	−200.27848 (−200.26793)	−200.09587	−200.42363 (−200.41452)	
binding energy					
D_e, kcal	6.54	6.62	4.70	5.72	
D_0, kcal	4.78	3.72	3.02	3.86	D_0 = 5.1 ± 1.0[b]
vibrational freq, $\mathrm{cm^{-1}}$					
a′	4070	3773	4397	4153	3929[c]
a′	4021	3743	4349	4095	3868[c]
a′	519	523	529	607	
a″	475	459	442	486	
a′	189	196	193	218	
a′	165	166	143	156	

[a] Note that the theoretical vibrational frequencies are harmonic, while the observed fundamentals are anharmonic. Energies in parentheses are for the system HF···HF with *R* = F···F = 1000 bohrs. [b] G. Briegleb and W. Strohmeier, *Z. Electrochem.*, **57**, 668 (1953); E. V. Franck and F. Meyer, *ibid.*, **63**, 571 (1959); M. W. Chase, J. L. Curnutt, J. R. Downey, R. A. McDonald, A. N. Syverud, and E. A. Valenzuala, *J. Phys. Chem. Ref. Data*, **11**, 695 (1982). [c] Reference 1.

DZ+P basis sets) were deleted from the CI. The equilibrium geometry of $(\mathrm{HF})_2$ belongs to point group C_s. However, the determination of harmonic force constants via analytic gradient techniques[30,31] requires the consideration of C_1 geometries, i.e., geometries with no elements of symmetry other than the identity. For C_s and C_1 geometries, the DZ+P CI wave functions include 15 453 and 29 161 configurations, respectively. The latter is the largest CI gradient calculation reported to date in the literature.

Nearly all computations were carried out on the Harris Series 800 minicomputer. For the C_1 symmetry, DZ+P basis $(\mathrm{HF})_2$ case just described, complete SCF gradient times were typically 43 min. The additional time required to obtain the 29 161-configuration variational wave function is ~105 min, and thereafter ~66 min is needed for the analytic evaluation of the 12 Cartesian forces (or energy first derivatives) which comprise the CI gradient.

The HF Monomer

The emphasis in this research is on dimer and trimer property *shifts* relative to the monomer. However, a good idea of the absolute reliability of the present predictions may be found in the monomer results in Table I. Of the four sets of theoretical predictions, the DZ CI results agree worst with experiment for both the bond distance and harmonic vibrational frequency ω_e. For the bond distance r_e, best agreement with experiment is found at the DZ+P level of theory, with Δr_e(exptl − theory) = 0.005 Å. However, both DZ SCF ($\Delta r_e = -0.014$ Å) and DZ+P CI ($\Delta r_e = -0.016$ Å) give reasonable agreement with the known bond distance.

The highest level of theory used here, DZ+P CI, gives the best agreement with experiment for the harmonic vibrational frequency ω_e. In fact the difference is only 12 $\mathrm{cm^{-1}}$, or 0.3%, significantly less than typical DZ+P CI errors for stable closed-shell polyatomic molecules.[32] More generally, neither the DZ SCF nor DZ CI predictions of ω_e fit into the patterns established by earlier studies at these levels of theory.[32] DZ SCF frequencies lie typically 3.0% above the experimental results, while for HF the predicted ω_e is 0.8% *less* than experiment. Similarly DZ CI frequencies for the series of molecules HCN, H_2CO, H_2O, and CH_4 differed by an average of only 2.0% from experiment, while for HF the DZ CI ω_e value is 9.8% less than experiment. Thus we conclude that the DZ CI method may not be well suited to the prediction of vibrational frequencies for systems containing HF.

Size Consistency and Vibrational Frequency Shifts

One rather naturally defines the CI vibrational frequency shifts for the HF dimer as the differences between the dimer CI frequencies and the monomer CI frequency. Unfortunately, this procedure gives physically meaningless results, and the origin of the problem may perhaps best be discussed in this section, which is in effect a digression.

It is well-known that for most types of CI wave functions, the CI energy of the hypothetical dimer A_2 at large separations A–A is *not* twice the CI energy of the monomer A. That is, most CI methods are not size consistent,[33,34] an obvious exception being full CI. A meaningful dimer dissociation energy is thus obtained only by comparing the CI energy of equilibrium A_2 with the analogous CI energy for the supermolecule A–A, in which the A–A separation is very large.

A corollary of the above analysis is that if we wish to compare dimer and monomer CISD properties, the monomer must be treated not in isolation but as part of a dimer with a very large A–A separation. A specific example may be of help here. The DZ+P CI bond distance of the HF monomer examined in isolation is 0.9329 Å. However, if we consider the arrangement HF···HF, with the F···H distance fixed at 1000 bohrs, variation of the two H–F distances yields r_e = 0.9299 Å. And it is the latter bond distance which must be compared with the CI dimer prediction to obtain a legitimate prediction of the bond distance shift in going from monomer to dimer.

Similarly the DZ+P CI harmonic frequency for the HF monomer treated in isolation is 4150 $\mathrm{cm^{-1}}$, while the analogous prediction for the

$$\mathrm{HF}\overset{R}{\cdots}\mathrm{HF}$$

system, with *R* = 1000 bohrs, is 4200 $\mathrm{cm^{-1}}$. Comparison with the experimental frequency shifts confirms the theoretical understanding that the latter monomer frequency is the appropriate one for comparison with the dimer predictions. With this observation in mind, we have included in Table I CI results for two HF monomers separated by 1000-bohrs radii.

The HF Dimer

The microwave electric resonance study of an HF molecular beam by Dyke, Howard, and Klemperer provides considerable information concerning the geometrical structure of the dimer. However, the geometrical parameters reported in their work do not precisely correspond to any of those reported in our Figure 1. Dyke, Howard, and Klemperer,[35] assuming both HF distances in the dimer to be 0.917 Å, reported r_0(F–F) = 2.79 ± 0.05 Å. At the four levels of theory considered here, this F–F internuclear separation r_e is predicted to be 2.73 Å (DZ SCF), 2.76 Å (DZ CI), 2.80 Å (DZ+P SCF), and 2.72 Å (DZ+P CI). All four

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Table III. Predicted Vibrational Frequency Shifts (in cm^{-1}) for $(HF)_2$ and $(HF)_3$ Relative to the HF Monomer[a]

	4-31G SCF[b]	DZ SCF	DZ CI	DZ+P SCF	DZ+P CI	exptl[c]
dimer	−36	−33 (0.0019)	−10 (0.0012)	−43 (0.0029)	−47 (0.0037)	−32
	−79	−82 (0.0046)	−40 (0.0036)	−91 (0.0041)	−105 (0.0052)	−93
trimer		−170 (0.0112)		−197 (0.0115)		
		−170 (0.0112)		−197 (0.0115)		
		−229 (0.0112)		−279 (0.0115)		

[a] Note that all theoretical predictions were made within the harmonic approximation, while the experiments refer to the (anharmonic) fundamentals. [b] Curtiss and Pople, ref 19. [c] Pine and Lafferty, ref 1.

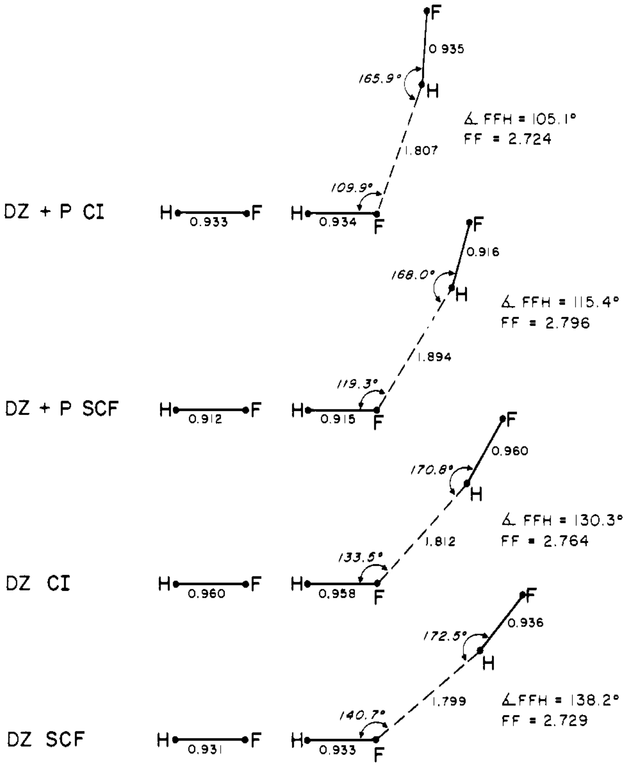

Figure 1. Equilibrium geometrical structures for the hydrogen fluoride monomer and dimer. All bond distances are in angstroms.

predictions are seen to be in good agreement with the experimental range. In addition, Klemperer's assumption of constant HF distances is seen to hold to within 0.005 Å.

Similarly Dyke, Howard, and Klemperer[35] have extracted the value θ(FFH) = 110–120° from their microwave data. Here there is a much broader spectrum of predictions from the four levels of theory. Specifically, we find θ_e(FFH) = 138° (DZ SCF), 130° (DZ CI), 115° (DZ+P SCF), and 105° (DZ+P CI). The shifting value of this angle with the level of theory is clearly illustrated in Figure 1. In summary, the agreement between the DZ+P SCF level of theory [r_e(F–F) = 2.796 Å, θ_e(FFH) = 115.4°] and experiment (2.79 ± 0.05 Å, 115 ± 5°) is sufficiently remarkable to suggest fortuitousness. This view would seem to be confirmed by the fact that the higher level DZ+P CI predictions lie just outside the experimental error basis.

Predicted vibrational frequencies for the equilibrium structure of $(HF)_2$ are given at the four levels of theory in Table II. There are no experimental values for the four "new modes", i.e., those without conterpart for the HF monomer. However, these four frequencies are surprisingly (in light of the softness of this part of the potential energy hypersurface) consistently predicted by the four distinct levels of theory. For example, the lowest frequency mode, corresponding to the HF···H bending, is predicted to be 165 cm^{-1} (DZ SCF), 166 cm^{-1} (DZ CI), 143 cm^{-1} (DZ+P SCF), and 156 cm^{-1} (DZ+P CI). It must again be emphasized, however, that these are strictly harmonic predictions. Since they characterize a portion of the energy hypersurface that is expected to be very anharmonic, these predicted harmonic frequencies may be quite different from the (yet to be) observed fundamentals.

Predicted dimer vibrational frequency shifts are compared with the experiments of Pine and Lafferty in Table III. It is seen that the 4-31G SCF results of Curtiss and Pople and the present DZ SCF, DZ+P SCF, and DZ+P CI results are all in good qualitative agreement with experiment. As could perhaps have been expected,[36,37] the DZ CI predictions are in poor agreement with the experimental vibrational frequency shifts.

Among the four successful theoretical methods, the closest agreement with experiment is found at the DZ SCF level, where the sum of the two frequency shift errors is only 12 cm^{-1}, out of a total of 125 cm^{-1}. The DZ+P SCF method yields a combined error of 13 cm^{-1}, 4-31G 18 cm^{-1}, and DZ+P CI 27 cm^{-1}. It is noteworthy that the highest of these four levels of theory yields the poorest agreement with experiment. Here it is necessary to reiterate that the theoretical predictions are exclusively made within the harmonic approximation, while the experimental shifts refer to the observed (anharmonic) fundamentals. To obtain closer agreement with experiment it will be necessary not only to include higher order correlation effects[38–40] but also to carry out a far more sophisticated treatment of the nuclear motion problem.

Also given in Table III are the monomer–dimer shifts in equilibrium bond distances. In general we find a strong correlation between dimer H–F separation increase and H–F vibrational frequency decrease. For a given system A–B, of course, one expects the stretching force constant to decrease with increasing bond distance. The largest such increase is the 0.005-Å increase in the longer H–F distance predicted at the DZ+P CI level of theory, and the accompanying decrease in the H–F stretching frequency is 105 cm^{-1}.

The HF Trimer

The success of four independent theoretical methods in qualitatively predicting the HF dimer vibrational frequency shifts gives us hope that the analogous predictions for the trimer may be meaningful. These predictions are summarized in Tables III and IV. Table III shows the shifts to be significantly greater than those for the dimer. Specifically, at the DZ SCF level, two of the HF vibrations (the two components of the e′ mode) are shifted down by 170 cm^{-1}, and the third (a′ mode) by 229 cm^{-1}. Similarly, at the DZ+P SCF level the predicted shifts are 197 cm^{-1} (e′) and 279 cm^{-1} (a′). High-resolution spectroscopic confirmation of these trimer predictions would provide considerable incentive for the analogous theoretical study of a number of related polymeric systems.

The shifts in H–F trimer equilibrium bond distances (relative to the monomer) in the trimer are in every case more than 0.01 Å, consistent with the lower H–F fundamentals predicted. As with the dimer, the DZ+P SCF method gives longer H–F distance shifts than does the less complete DZ SCF method.

The large bond distance shifts in the trimer are reflected in the large red shifts predicted for the HF stretches. The bending modes of the trimer are predicted to be blue shifted from the dimer, which is in accord with experimental trends.[41] This trend is expected

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Table IV. Theoretical Predictions of the Properties of the Cyclic Hydrogen Fluoride Trimer

		equilibrium (C_{3h})			transition state (D_{3h})	
		DZ SCF	DZ+P SCF		DZ SCF	DZ+P SCF
E, hartrees		-300.08039	-300.15634		-300.03088	-300.10937
energy D_e rel to $(HF)_2$ + HF, kcal		11.94	10.22			
D_0, kcal		8.76	7.02			
energy rel to $(HF)_3$ equil, kcal		0.0	0.0		31.07	29.47
vibrational freq, cm^{-1}	e′	3933	4243	a_1'	2143	2198
	a′	3874	4161	e′	1601	1699
	a′	895	897	e′	1576	1624
	a″	705	664	a_2''	1419	1426
	e′	476	535	e″	1049	1119
	e″	447	449	a_1'	739	783
	a′	220	201	e′	558	602
	e′	179	176	a_2'	2079i	2091i

Table V. Parallelogram and Rhombus Stationary Point Geometries of $(HF)_2$

		parallelogram			rhombus	
		DZ SCF	DZ+P SCF		DZ SCF	DZ+P SCF
E, hartrees		-200.04178	-200.09461		-199.95305	-200.01190
energy rel to dimer equil struct, kcal		1.64	0.79		57.32	52.69
vibrational freq, cm^{-1}	b_u	4062	4394	a_g	2563	2780
	a_g	4054	4376	b_{2u}	1666	1751
	a_g	591	565	b_{1u}	1373	1418
	a_u	446	414	b_{3u}	1257	1398
	a_g	167	152	a_g	800	850
	b_u	206i	189i	b_{1g}	2622i	2661i

to hold for larger polymers. Preliminary results on trimer chains continue this trend.

Table IV shows that the trimer dissociation energyt D_e relative to $(HF)_2$ + HF is 11.9 kcal at the DZ SCF level and 10.2 kcal at the DZ+P SCF level of theory. The analogous dimer predictions are 6.5 and 4.7 kcal, respectively. These results are certainly consistent with the qualitative view that *two* new hydrogen bonds are formed in the process

$$(HF)_2 + HF \rightarrow (HF)_3 \qquad (1)$$

This view, of course, is also confirmed by the predicted cyclic trimer structures seen in Figure 2.

Transition States

In addition to the equilibrium geometries discussed above, several other stationary points of $(HF)_2$ and $(HF)_3$ were also examined theoretically. The results for the dimer are summarized in Figure 3 and Table V. The parallelogram structure is a transition state for the interconversion[19,35] of the two equivalent forms of $(HF)_2$. For the HF-DF system, of course, the two isomers become distinguishable, with one carrying a D···F hydrogen bond and the other an H···F hydrogen bond. Table V shows that the barrier for this isomerization is low, 1.6 kcal at the DZ SCF level and 0.8 kcal at the DZ+P SCF level.

A much higher energy transition state is the $(HF)_2$ rhombus seen in Figure 3 and characterized in Table V. The rhombus is a transition state for the four-center exchange reaction, which might be isotopically labeled

$$DF + HF^* \rightarrow HF + DF^* \qquad (2)$$

The predicted barrier heights for this exchange reaction are 57.3 kcal (DZ SCF) and 52.7 kcal (DZ+P SCF), both low compared to the value of ~90 kcal now established[42,43] for the classic H_2 + D_2 exchange.

As shown in Figure 2 and Table IV, the equilibrium geometry of the HF trimer is of C_{3h} symmetry. There is in addition a D_{3h} stationary point structure, seen in Figure 2, with six equal H-F bond distances. This structure is a transition state for *six-center* exchange and has associated with it a remarkable low barrier

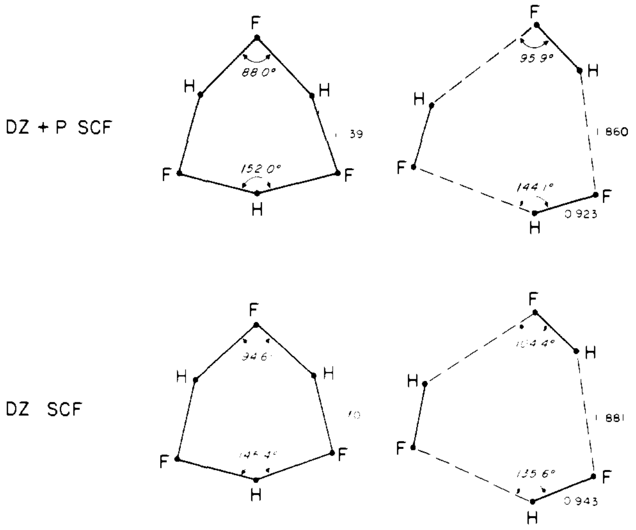

Figure 2. Stationary point geometries for the hydrogen fluoride trimer. The D_{3h} structures on the left describe the transition state for the six-atom exchange. The C_{3h} structures on the right refer to the trimer equilibrium geometry. All bond distances are in angstroms.

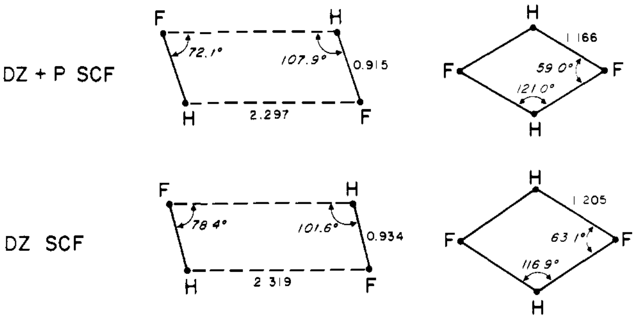

Figure 3. Transition-state geometrical structures for $(HF)_2$. On the left is the (low energy) transition state for the interconversion of the two equivalent forms of the $(HF)_2$ equilibrium geometry. On the right is the (higher energy) transition for four-center exchange. All bond distances are in angstroms.

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height. With hypothetical isotopic labeling, one could characterize this six-center exchange reaction as

$$HF + DF^* + TF^{**} \rightarrow DF + TF^* + HF^{**} \tag{3}$$

where the three product molecules are distinct from the three reactants. The predicted classical barrier height for reaction 3 is 31.1 kcal at the DZ SCF level and 29.5 kcal at the DZ+P SCF level of theory. These barriers are much lower than the 69 kcal predicted for the analogous six-center exchange reaction for three hydrogen molecules.[44]

Concluding Remarks

At four distinct levels of theory, the vibrational frequency shifts in $(HF)_2$ and $(HF)_3$ relative to the monomer have been predicted. For three of the four levels of theory, good agreement with the recent dimer experimental results of Pine and Lafferty[1] is found. It is hoped that subsequent experiments will confirm the trimer predictions presented here. The theoretical methods used to study the trimer may be readily applied to larger polymeric systems, such as $(HF)_4$ and $(HF)_5$. This and related studies on species such as the HCl dimer[45] show the widening applicability of quantum mechanics to hydrogen bonding.

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Registry No. Hydrogen fluoride, 7664-39-3.

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Hydrogen Out-of-Plane Bending in Cyclopentadienyllithium

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Abstract: An ab initio SCF MO study is presented of the out-of-plane bending of hydrogens in cyclopentadienyllithium. The effects of basis sets of varying size and possible superposition errors were evaluated. The hydrogens are found to bend away from the lithium cation to a significant degree. Comparable bending is given by an ionic model consisting of a cyclopentadienyl anion and a point positive charge at the lithium location. We attribute the hydrogen bending to a simple Coulombic effect: such bending puts more negative charge on the face of the ring toward the lithium cation. No covalency is implicated in this effect. A reasonable balance between the carbon and lithium bases is obtained by placing a diffuse sp shell on carbon.

There have been many observations of hydrogen bending in cyclopentadienyl (Cp) metal complexes (where the hydrogens bend out of the plane of the Cp ring maintaining the C_{5v} symmetry). Electron diffraction (gas phase) studies have found that the hydrogens bend out of the Cp plane toward the metal 4.6 ± 0.9° in Cp_2Fe,[1] 5° in Cp_2Ni,[2] 6.5° in Cp_2Mn,[3] and 2.9° in Cp_2Cr. X-ray studies show that the hydrogens bend out of the Cp plane away from the metal in CpIn by 4.5 ± 2°[5] and that the methyl groups of $Me_5C_5Sn^+$ bend 4° away from the metal.[6] Ab initio calculations on $CpSi^+$,[7] CpC^+,[7] and CpBeH[8] show the hydrogens bend in toward the complexed atom by 1.4°, 8.6°, and 0.8°, respectively. Other calculations on CpLi[9] (DZ basis set) found that the hydrogens bend away from the lithium by 3.6°. Two major explanations for this bending have been forwarded. Schleyer has supported a "covalency" argument where the p-orbitals of the metal parallel to the Cp ring can interact favorably with the carbon p-orbitals of the Cp ring perpendicular to the Cp plane.[8-11] Bending of the hydrogens causes the carbon p-orbitals to point in the opposite direction. The direction of the bending therefore depends on the relative size of the metal p-orbitals: metals with more diffuse p-orbitals cause the hydrogens to bend away from the metal (see Figure 1).

Alternatively, in systems best described as ion pairs, purely Coulombic forces could lead to bending in the opposite direction.[8,9] A positively charged metal center will electrostatically favor greater electron density on the face of the Cp ring adjacent to the metal. This is effectively achieved by bending the hydrogens away from the metal, essentially rehybridizing the carbons such that the carbon p-lobe on the side of the metal is increased.

The following study shows that only the latter explanation is consistent with the bending away from the metal in CpLi. Potential calculational problems which can lead to hydrogen bending are also discussed.

Method

Calculations were carried out by using the following programs: a modified version of HONDO[12] and GAMESS on the Lawrence Berkeley

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