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A Theory of the Strong Hydrogen Bond. *Ab Initio* Calculations on HF_2^- and H_3O_2^+ ^{1a}

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Abstract: *Ab initio* calculations are presented on simple cationic and anionic "strong" hydrogen bonds. The potential surfaces for HF_2^- and H_3O_2^+ are well represented in this molecular orbital calculation. Charge density differences and molecular orbital energy shifts are used to compare hydrogen bonds with ordinary covalent bonds and to gain greater insight into the similarities and differences between "strong" and "weak" hydrogen bonds. Strong hydrogen bonds can be understood as a donor-acceptor complex quantitatively characterized by molecular orbital energy shifts, in the same manner as previously found for weak hydrogen bonds.

In chemistry the concepts of covalent and ionic have proved very useful in understanding ordinary chemical bonding, even though these idealized cases are relatively rare compared to the vast number of intermediate cases. Hydrogen bonds are different from ordinary chemical bonds because they involve two coordinate hydrogens and have a much smaller energy of formation than most normal bonds; the meaningful division in this case is into "strong" hydrogen bonds (30–60 kcal/mol) and "weak" hydrogen bonds (5–10 kcal/mol). Weak hydrogen bonds (*e.g.*, between two closed-shell neutral molecules, as $(\text{H}_2\text{O})_2^2$) can be understood in terms of small perturbations on the charge densities, geometries, and spectroscopic properties of the individual molecules involved in hydrogen bond formation. A large number of *ab initio* and semiempirical molecular orbital calculations have been carried out on weak hydrogen-bonded systems.² A further theoretical understanding of strong hydrogen bonds, which cannot be easily characterized in terms of the monomer fragments from which they are formed, is the subject of this paper.

(1) (a) Research supported by the Chemistry Section of the National Science Foundation, Grant No. NSF-GP-8907; (b) National Science Foundation Predoctoral Fellow, 1966–1970.

(2) References to many of the calculations are given in P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969); **52**, 5085 (1970).

The simplest strong anionic hydrogen-bonded system (and the easiest to study by rigorous methods) is the bifluoride ion, since it only involves the three centers which are considered the skeleton of a hydrogen bond. Experimental work on HF_2^- includes the neutron diffraction studies of Peterson and Levy^{3a} and Ibers,^{3b} X-ray diffraction work by Helmholz and Rogers,⁴ ir spectroscopy studies by Couture and Mathieu,⁵ and nmr spectroscopy by Waugh, *et al.*⁶ Bessis^{7a} and Erdahl⁸ have carried out nonempirical valence-bond calculations on this system, the former work containing a more extensive review of the experimental work on the bifluoride ion. Bessis calculated the ground and excited states of HF_2^- at the experimental geometry ($R(\text{F}-\text{F}) = 2.26 \text{ \AA}$) and computed electronic charge densities for the two lowest electronic states. His calculation yielded a lower total energy than Erdahl's, but this was due to Bessis' neglect of certain

(3) (a) S. W. Peterson and H. A. Levy, *ibid.*, **20**, 704 (1952); (b) J. A. Ibers, *ibid.*, **40**, 402 (1964).

(4) L. Helmholz and M. T. Rogers, *J. Amer. Chem. Soc.*, **61**, 2590 (1939).

(5) L. Couture and J. P. Mathieu, *C. R. Acad. Sci.*, **228**, 555 (1949).

(6) J. S. Waugh, F. B. Humphrey, and D. M. Yost, *J. Phys. Chem.*, **57**, 486 (1953).

(7) (a) G. Bessis, *Cah. Phys.*, **127**, 105 (1961). (b) Bessis reported a virial ratio of 2.12 because he neglected to include the nuclear repulsion in V .

(8) R. Erdahl, Ph.D. Thesis, Princeton University, 1965; copies available from University Microfilms, Ann Arbor, Mich.

Table I. Monomer Calculations (Distances and Energies in au)

HF (with p's on H)			HF (without p's on H)			HF ($r = 1.73$ au, vary p exponent)			
r	E		r	E		Exp	E	$F^-(1s)$	$F(2p)$
1.67	-100.03077		1.67	-100.01341		0.4	-100.02585	-99.40738	-99.38629
1.73	-100.03149		1.73	-100.01463		0.7	-100.03149		
1.79	-100.02984		1.79	-100.01361		1.0	-100.03209		
H ₂ O			H ₃ O ⁺ (with p's on H)			H ₃ O ⁺ (without p's on H)			
R	θ	E	R	θ	E	R	θ	E	
1.808	105	-76.00291	1.88	120	-76.31296	1.88	120	-76.29150	
1.84	105	-76.00203	1.88	115	-76.31164	1.88	115	-76.28671	
1.87	105	-76.00026	1.88	109.5	-76.30872	1.88	109.5	-76.27877	
1.808	110	-76.00432	1.83	120	-76.31617	1.83	120	-76.29493	
1.808	115	-76.00435	1.93	120	-76.30645	1.93	120	-76.28488	

three-center integrals and approximation of others [the virial ratio ($-V/2T$) in Bessis' calculation^{7b} (1.0075) was poorer than Erdahl's (1.0047)]. Erdahl carried out an extensive potential surface search for HF₂⁻ and calculated force constants in reasonable agreement with Ibers' ⁹ potential function analysis of the experimental frequencies of the bifluoride ions.

Molecular orbital studies of HF₂⁻ have been carried out by Hamamo,¹⁰ Nagahara,¹¹ and Clementi and McLean.^{12a} Clementi examined the effect that addition of further functions to a minimal Slater basis set had on the total energy; his best basis set was approximately 5 eV above the Hartree-Fock energy of HF₂⁻. A molecular orbital study by McLean and Yoshimine^{12b} found a much lower energy for HF₂⁻, only 1 eV above the Hartree-Fock limit estimated by Clementi^{12a} to be -199.616 au.

X-Ray studies on perchloric acid dehydrate,¹³ hydrogen chloride dehydrate¹⁴ and trihydrate,¹⁵ HAuCl₄·4H₂O,¹⁶ and nitranilic acid hexahydrate¹⁷ indicate that the H₃O₂⁺ ion plays a role in these crystals. The structure evidence for H₃O₂⁺ in different crystalline environments indicates that the bonding around the oxygens is usually pyramidal, with the hydrogen connecting the oxygens in a symmetric or near-symmetric well. No theoretical calculations have been reported for this system.

It is our purpose in this paper to discuss the electronic structure of these strong hydrogen bonds and to answer the following questions. (1) What would one predict for the most stable structure of these species? (2) How do the energy of formation and spectroscopic properties predicted compare with experiment, and how sensitive are these properties to basis set choice? (3) What is the detailed electron distribution in these strong hydrogen bonds?

Description of Calculation

The energy calculations were carried out with the aid of a set of automatic computer programs written at

(9) J. A. Ibers, *J. Chem. Phys.*, **41**, 25 (1964); **48**, 539 (1968).

(10) H. Hamamo, *Bull. Chem. Soc. Jap.*, **30**, 741 (1957).

(11) S. Nagahara, *Rep. Progr. Mol. Struct. Tokyo Univ.* [transaction 3], **17** (1954).

(12) (a) E. Clementi and A. D. McLean, *J. Chem. Phys.*, **36**, 745 (1962); (b) A. D. McLean and M. Yoshimine, *IBM J. Res. Develop.*, **11**, Tables of Linear Molecules (1967).

(13) I. Olovson, *J. Chem. Phys.*, **49**, 1063 (1968).

(14) J. O. Lundgren and I. Olovson, *Acta Crystallogr.*, **23**, 966 (1967).

(15) J. O. Lundgren and I. Olovson, *ibid.*, **23**, 971 (1967).

(16) J. M. Williams and S. W. Peterson, *ibid.*, *Sect. B*, **25**, 5113 (1969).

(17) J. M. Williams and S. W. Peterson, *J. Amer. Chem. Soc.*, **91**, 776 (1969).

Princeton University. Essentially double- ζ -quality atomic orbitals were used as a basis set: (10s, 5p) gaussian basis functions on oxygen and fluorine and 5s gaussians on hydrogen.¹⁸ The calculations on both H₃O₂⁺ and HF₂⁻ contracted the oxygen (fluorine) s functions into four groups, the oxygen (fluorine) p functions into two, and the hydrogen s's into two.¹⁹ Certain geometry points were examined with one-component p functions on the central hydrogen. Self-consistent-field calculations were carried out using the Roothaan procedure.²⁰

Geometries and Energies of Formation

The geometry searches for H-F and the energies of F(2p) and F⁻ are reported in Table I. It is important to note that, unlike the contracted Hartree-Fock basis, the basis set used in this calculation predicts F⁻ to be more stable than F. The first ionization potential of F⁻ is predicted to be 0.127 au (experimental electron affinity of F = 0.134 au), although the total energy of F⁻ is only 0.0211 au lower than that of F(2p). (In Hartree-Fock level calculations²¹ the ionization potential predicted is 0.181 au and the total energy of F⁻ is 0.050 au lower than that of F.) The geometry of HF is quite well represented; the bond distances predicted are 1.73 (no p's on hydrogen) and 1.715 au (p's on hydrogen) (experimental,²² 1.73 au).

Experimentally, the most stable geometry of the bifluoride ion is a linear symmetric structure with F-F distance in various crystals between 2.26 and 2.28 Å.²³ In this calculation, the F-F distance, the F-H distance, and the FHF angle have been varied, and a minimum energy has been found at an F-F distance of 2.285 Å, with the hydrogen symmetrically placed between the fluorines (Table II). The stabilization of FHF⁻ calculated relative to F⁻ and HF is 52 kcal/mol (experimental, 58 ± 5 kcal/mol²³). McLean and Yoshimine's calculation on HF₂⁻^{12b} is the best to date in terms of total energy, but because they used a

(18) The 10s functions were taken from J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966), and the 5p from S. Huzinaga, *ibid.*, **42**, 1293 (1965). The hydrogen function was scaled by $\sqrt{2}$, as W. Fink found appropriate for HF and H₂O (manuscript in preparation).

(19) The exponent of the p function for H₃O₂⁺ and H₃O⁺ was 0.7, which had the same radial maximum as a two-component p function of NH₃ [A. Rauk, L. C. Allen, and E. Clementi, *ibid.*, **52**, 4133 (1970)]. In HF₂⁻ and HF, the p exponent was varied between 0.4 and 1.0.

(20) C. J. Roothaan, *Phys. Rev.*, **23**, 69 (1951).

(21) E. Clementi, "Tables of Atomic Wavefunctions," a supplement in *IBM J. Res. Develop.*, **9**, 2 (1965).

(22) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, "Spectra of Diatomic Molecules," 2nd ed, Van Nostrand, New York, N. Y., 1950.

(23) T. C. Waddington, *Trans. Faraday Soc.*, **54**, 25 (1958).

Table II. Overall System Calculations (Distances and Energies in au)

H ₅ O ₂ ⁺ (sp ² eclipsed, no p's)			H ₅ O ₂ ⁺ (sp ² eclipsed, p's)	
R	r ^a	E	R	E
4.00	0	-152.33048	4.35	-152.35942
4.35	0	-152.35198		
4.35	0.10	-152.35169	H ₅ O ₂ ⁺ (sp ² staggered, R = 4.35)	
4.35	0.20	-152.35056	E = -152.34583 (no p's)	
4.50	0	-152.353473	E = -152.36230 (p's)	
4.50	0.075	-152.353464		
4.50	0.15	-152.353405	H ₅ O ₂ ⁺	
4.50	0.30	-152.35218	(tetrahedral, R = 4.35)	
4.70	0	-152.35069	E = -152.33170 (no p's)	
4.70	0.10	-152.35095	E = -152.34305 (p's)	
4.70	0.25	-152.35193		
4.70	0.45	-152.35111		
FHF ⁻				
R	r ^a	Δ ^b	E	
4.25	0	0	-199.50684	
4.50	0	0	-199.50446	
4.00	0	0	-199.49857	
4.25	0.05	0	-199.50676	
4.25	0.10	0	-199.50653	
4.25	0.20	0	-199.50536	
4.25	0	0.15	-199.50601	
4.25	0	0.30	-199.50355	
4.25	0	0	-199.52303 (with p's, p exp = 0.7)	
4.25	0	0	-199.52238 (with p's, p exp = 1.0)	
4.25	0	0	-199.51958 (with p's, p exp = 0.4)	
4.50	0.10	0	-199.50461	
4.50	0.20	0	-199.50485	
4.50	0.40	0	-199.50315	

^a Shift of hydrogen from center of F-F (O-O) bond. ^b Shift of hydrogen off F-F line.

different basis set at different internuclear separations, it is difficult to predict other properties from their wave functions.

The potential surface searches for H₂O and H₃O⁺ are given in Table I. The minimum energy geometry for H₂O is at $\theta = 112^\circ$ and $R(\text{OH}) = 1.82$ au (experimental²⁴ $\theta = 105^\circ$, $R = 1.81$ au); for H₃O⁺, the minimum energy is at $R = 1.81$ au, $\theta = 120^\circ$ (experimental²⁴ $\theta = 115\text{--}117^\circ$, $R = 1.02$ Å). Theoretical calculations on these systems have been carried out by Moskowitz and others.²⁴ After correcting for the zero-point vibration difference between H₂O (12.8 kcal/mol) and H₃O⁺ (17–19 kcal/mol),²⁴ the proton affinity for H₂O found in this calculation is 178 kcal/mol. (De Pas, *et al.*,²⁵ determined a proton affinity of 182 ± 7 kcal/mol.) The energy for the reaction $\text{H}_3\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_5\text{O}_2^+$ is calculated to be 36.9 kcal/mol (no correction for the zero-point energy difference between H₅O₂⁺ and (H₃O⁺, H₂O)), compared with an experimental value of 32 kcal/mol.²⁶ The minimum

(24) For more theoretical details on H₂O and H₃O⁺, see D. Neumann and J. W. Moskowitz, *J. Chem. Phys.*, **49**, 2056 (1968), and J. W. Moskowitz and M. C. Harrison, *ibid.*, **43**, 3550 (1965). Experimental studies on H₃O⁺ and H₅O₂⁺ are extensively discussed in G. Zundel, "Hydration and Intermolecular Interaction," Academic Press, New York, N. Y., 1969.

(25) M. De Pas, J. J. Leventhal, and L. Friedman, *J. Chem. Phys.*, **51**, 3748 (1969), find a water proton affinity of 182 kcal/mol and $\Delta E(\text{H}_2\text{O} + \text{H}_3\text{O}^+ \rightarrow \text{H}_5\text{O}_2^+) = 32$ kcal/mol. Another recent proton affinity is 165, reported by M. A. Haney and J. L. Franklin, *ibid.*, **50**, 2028 (1969). Moskowitz and Harrison (ref 24), whose basis set is slightly better than the one used here, find a water proton affinity of 180 kcal/mol.

(26) For H₅O₂⁺, an H_{ext}-O-H_{ext} angle of 120° and an O-H_{ext} bond length of 1.88 au were assumed. To calculate the energy of reaction, the energies at the optimized H₂O geometry and the H₃O⁺ energy at $\theta = 120^\circ$ and $r = 1.88$ au were subtracted from the H₅O₂⁺ energy. A more complete optimization would probably increase the energy of reaction calculated by 1–2 kcal, but the change in zero-point energies

energy O–O distance found was 2.38 Å (most crystal structures on H₅O₂⁺ find $R(\text{O}-\text{O}) \sim 2.45$ Å). Three different geometrical arrangements were considered for H₅O₂⁺ (Table II).²⁶ The least stable was a tetrahedral (sp³) configuration around the oxygens, with the hydrogens on opposite ends staggered. The two sp² arrangements were more stable. The eclipsed sp² arrangement (which had the possibility of O–H–O pπ delocalization) was the next in stability, and the staggered sp² arrangement was the most stable. It is of interest to note that H₅O₂⁺ is probably tetrahedral in some crystals,^{13,17} but seems staggered sp² in others. The energy difference between sp³ and sp² is great enough (12 kcal) that H₅O₂⁺ is most probably nearly sp² and is often distorted to an sp³ arrangement in its crystalline environment.

It is encouraging that the energies of the reactions $\text{HF} + \text{F}^- \rightarrow \text{HF}_2^-$ and $\text{H}_3\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_5\text{O}_2^+$ appear to be well represented in these near-Hartree-Fock-level calculations. A similar finding has been made by Snyder and Basch²⁷ using a basis set very similar to ours on a wide variety of reactions involving closed-shell reactants and products. As one referee pointed out to us, it would certainly be desirable to carry out a calculation on HF₂⁻ to the Hartree-Fock limit, since the Hartree-Fock energies of HF and F⁻ are known; until this is done, however, the empirical evidence certainly indicates that near-Hartree-Fock calculations give quite reliable ΔE 's for reactions involving closed-shell species.

MO Energy Analysis

Molecular orbital energy shifts as the characterizing feature of donor-acceptor complex formation have been discussed in a previous paper.²⁸ The strong H-bonded systems examined in this paper are different from those previously considered, however, because there is a significant geometry change in the individual fragments upon complex formation and the MO's are no longer assignable to individual fragments. Nevertheless, one still finds that all the MO's on the electron-pair donor decrease in energy and those on the electron-pair acceptor increase²⁹ (see Table III). In the bifluoride ion, the electron-pair acceptor (HF) dominates the donor (F⁻); *i.e.*, the MO shifts for HF are much larger than those for F⁻. In H₅O₂⁺, the electron-pair donor (H₂O) dominates the acceptor H₃O⁺. As has been found previously, the average absolute value of the MO energy changes in HF₂⁻ (0.2495 au) and H₅O₂⁺ (0.1900 au) reflect the greater energy of formation of the former system from its closed-shell fragments.

Charge Distribution in Strong H Bonds

The Mulliken atomic and overlap populations for the computed wave functions (near equilibrium geometry) are given in Table IV. In both HF₂⁻ and H₅O₂⁺, the hydrogen is significantly positive (more positive than in the monomer fragments). For the hydrogen in the

decreases the ΔE by 3–5 kcal. Thus, on the basis of these results, one would predict a ΔE of 35 ± 2 kcal/mol.

(27) L. Snyder and H. Basch, *J. Amer. Chem. Soc.*, **91**, 2189 (1969).

(28) P. A. Kollman and L. C. Allen, *ibid.*, **92**, 1142 (1970).

(29) In these systems, there is some arbitrariness in correlating the original MO's with those in the complex when symmetry doesn't give one the answer, but one gets a consistent picture by not allowing crossings in the correlation diagram. Note that all the donor (acceptor) changes in a given system are quite close in magnitude.

Table V. Comparison with Other Calculations and Experiment for HF_2^-

	Exptl	Bessis ^f	Erdahl ^e	Clementi ^g	McClean ^h	This work	Hartree-Fock limit ^o
F...F distance, Å	2.27 ^a	(2.25) ^d	2.33	(2.25) ⁱ	2.25	2.28	2.25
ΔE ($\text{HF} + \text{F}^- \rightarrow \text{FHF}^-$), kcal/mol	58 ± 5 ^b					52	
Force constants for symmetric stretch (10^5 dyn/cm)	4.0 ^c		4.8			5.3	
Force constant for asymmetric stretch (10^5 dyn/cm)	0.325 ^c		1.10			0.47	
Force constant for bend (10^5 dyn/cm)	0.22 ^d		0.40			0.38	
Total energy (au)	-200.5494 ^e	-199.57	-199.49	-199.39	-199.57	-199.52	-199.616

^a Reference 3b. ^b Reference 21. ^c Reference 9. ^d Calculated from the bending frequency in J. A. A. Ketelaar and W. Vedder, *J. Chem. Phys.*, 19, 654 (1951). ^e Reference 8. ^f Reference 7a. ^g Reference 12a. ^h Reference 12b. ⁱ Numbers in parentheses are assumed values.

nically explains the charge density difference which we find in our calculation on HF_2^- (Figure 1), as well as the difference plots on $(\text{HF})_2$, H_2OHF , and $(\text{H}_2\text{O})_2$.² In all these plots, there is a decrease of charge (node) around the hydrogen during H-bond formation. These pictorial models clearly represent the difference between three-center, four-electron (hydrogen) bonding and two-center, two-electron ordinary covalent bonding (e.g., H_2), where there is no nodal plane, and, relative to the isolated systems (2H), there is electron density increase throughout the bonding region.³¹

As noted charge density differences illustrate the pictorial appeal of the simple MO model. However, in most cases, the three centers and four electrons which make up the skeleton of the hydrogen bond cannot really be isolated from the rest of the molecule, and one has to find a set of quantities which takes the whole system into consideration. This is what we have attempted to do in the previous section (MO energy analysis).

Spectral Properties and the Proton Potential Well

Force constants for the H potential surface, the F-F (O-O) stretch, and the H bend (only in HF_2^-) were calculated for these two systems. The results for the bifluoride ion are given in Table V. Included in this table are comparisons with other calculations of spectral properties.

The potential for the proton in the F-F well (at $R(\text{F-F}) = 4.25$ au) which our SCF calculations yield is shallower than Erdahl's and much closer to Ibers's best-force-constant fit to the experimental frequencies. Both Erdahl⁸ and Ibers⁹ get similar values for the quartic-force-constant contribution to the asymmetric stretch (0.25×10^{22} dyn/cm³), and we have assumed this quartic contribution in calculating the harmonic force constant. One would expect quite good agreement with experiment for this normal mode in the SCF approximation, since its dissociation limits are $\text{F}^- + \text{HF}$. At a longer F-F distance ($R = 4.50$ au), the potential becomes a double well (see Figure 3), although the zero-point energy of proton movement (~ 700 cm⁻¹) is still greater than the energy barrier (~ 100 cm⁻¹). The force constant calculated for the symmetric stretch (F...F) is slightly worse than Erdahl's VB calculation, but reasonably close to the experimental value (Table V). The fact that this stretch is more poorly represented by this calculation than by Erdahl's is due to the SCF dissociation to $\frac{1}{2}(\text{H}^+ + \text{F}^- + \text{F}^-) + \frac{1}{2}(\text{H} + \text{F}^- + \text{F})$. (Erdahl's VB dissociates correctly to $\text{F}^- + \text{F} + \text{H}$).³²

(31) Helpful discussions on this point with Professor I. Kuntz and Mr. J. Liebman are acknowledged.

The bending force constant is slightly closer than Erdahl's to the experimental value but still quite poor. This lack of agreement with experiment may also be due to the incorrect dissociation of the SCF wave function.

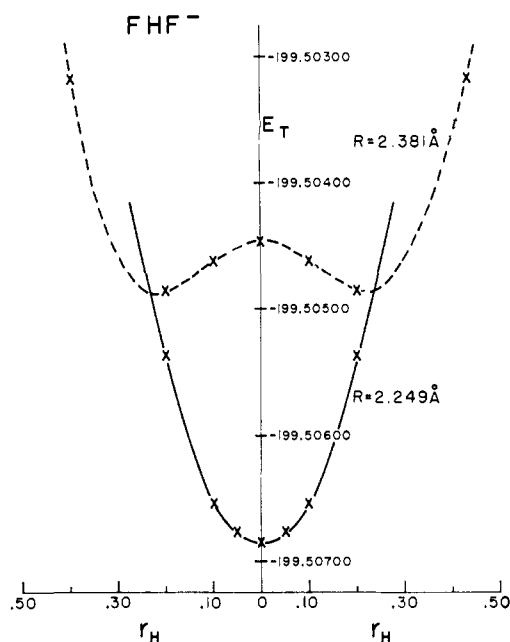


Figure 3. Proton potential for FHF^- at different F-F distances.

For H_2O_2^+ , the symmetric stretch force constant ($\text{O}\cdots\text{O}$) was 2.1×10^5 dyn/cm. The proton potential function for this cation at the minimum energy configuration ($R = 2.38$ Å) was an extremely shallow single minimum. In contrast, the bifluoride ion had a double minimum at the same heavy atom ($\text{X}\cdots\text{X}$) separation. The proton potential as a function of O-O distance is presented in Figure 4. Even at an O-O separation of 2.487 Å, the energy barrier is still only 275 cm⁻¹, less than one finds for zero-point energies. At O-O distances slightly above this, one would expect to find protons localized (zero-point energy < energy barrier); this is precisely what one

(32) Erdahl found a double minimum for the hydrogen only when an F-F distance of 5.25 au was reached. One would expect that an SCF calculation would also find a double minimum near this point. Further discussion of the question of single- vs. double-potential wells in strong H bonds is given by A. Haas and L. Feinberg, *Theor. Chim. Acta*, 10, 189 (1968). These authors find that the equilibrium geometry for H_3^+ has a double-minimum proton well. An increase in the nuclear charge of the external hydrogens causes the transition from single to double well to occur at larger R .

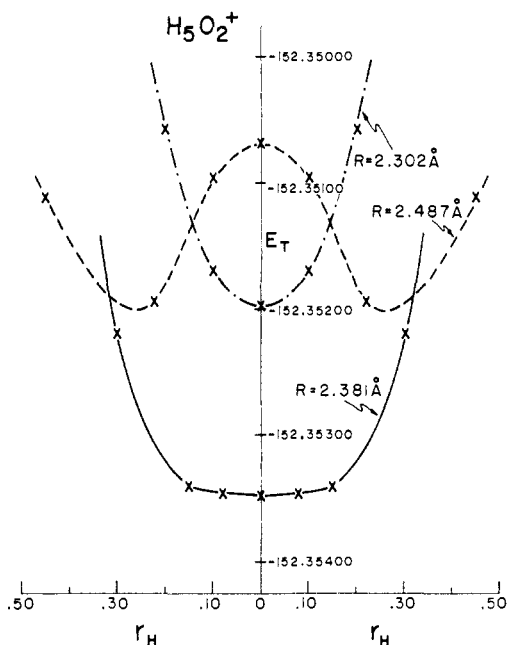


Figure 4. Proton potential for H_5O_2^+ at different O-O distances.

finds in crystal studies, where asymmetric OHO bonds are found when $R(\text{O}-\text{O}) > 2.50\text{--}2.55 \text{ \AA}$.^{16, 33}

p-Orbital Contribution

Paolini³⁴ first proposed that the p orbitals on hydrogen might play a much larger role in hydrogen bonding than they do in ordinary molecule formation. Clementi^{12a} has commented on this issue, noting that the inclusion of a 2p hydrogen function in the basis set lowers the first virtual π level in the bifluoride ion. In these strong-hydrogen-bonded systems, the p-orbital effect, if it exists, should be larger than in weak-hydrogen-bonded systems.

It is clear that the addition of any polarization functions to an imperfect wave function will lower the total energy, but the appropriate question to ask is: do p functions on hydrogen improve the representation of the hydrogen-bonded system (FHF^-) relative to the non-hydrogen-bonded system (HF)? The data in Table VI show quantitatively, in terms of the energy

Table VI. p-Orbital Contribution

	With p's on H	Without p's on H
$E(\text{H}_2\text{O} + \text{H}_3\text{O}^+ \rightarrow \text{H}_5\text{O}_2^+)$ (eclipsed sp^2)	35.3 ^a	35.1
$E(\text{HF} + \text{F}^- \rightarrow \text{FHF}^-)$	52.25	53.20
Gross population of H in $\text{HF}-\text{HF}_2^-$	0.1165	0.0671
Gross population of H in $\text{H}_3\text{O}^+-\text{H}_5\text{O}_2^+$	0.1001	0.0203

^a This value is calculated by subtracting the energy of H_2O (without p's on hydrogens), the energy of H_3O^+ (without p's on hydrogens), and one-third the difference between H_3O^+ (p's on all hydrogens) and H_3O^+ (no p's on hydrogens) from the energy of H_5O_2^+ (with p's on hydrogen).

of formation and the population analysis on the hydrogen, that the p-orbital effect on the hydrogen is not a

(33) W. Hamilton and J. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.

(34) L. Paolini, *J. Chem. Phys.*, 30, 1045 (1959).

useful concept in hydrogen bonding. In fact, the population analysis indicates that p orbitals play a much larger role in the monomers than in the hydrogen bond (this is what one would expect in terms of the nearness of H to a heavier center in the monomer, making $p\pi$ delocalization easier).³⁵

In the calculation of HF_2^- and HF, the p exponent was optimized for HF (0.8) and HF_2^- (0.9) (see Tables I and II for the energy values). A p exponent of 0.7 was assumed for H_5O_2^+ and H_3O^+ . In the range of p exponents 0.7–1.0, the calculated energy of formation is not very sensitive to p-exponent choice.³⁶

Conclusions

These studies on HF_2^- and H_5O_2^+ indicate that an LCAO-MO-SCF wave function adequately represents the geometry, energy of formation, and spectroscopic properties of strong hydrogen bonds. The agreement is not quantitative, but this is partially due to the need for further polarization functions, not to a basic defect in the molecular orbital method. The role of p-polarization functions on hydrogen in hydrogen bonds has been shown to be small, and they are not a useful concept in understanding hydrogen bonding. Charge density plots have emphasized the unique character of hydrogen bonds (a node in the "bond" charge density) which distinguishes them from ordinary covalent bonds. An analysis of the charge-density shifts around the water fragment in H_5O_2^+ emphasizes the similarities of strong and weak hydrogen bonds. The charge density shifts in strong as well as in weak hydrogen bonds are compatible with the simple four-electron, three-center view of the hydrogen bond. Both strong and weak hydrogen bonds can be unified in terms of the molecular orbital energy shifts. In particular, all the MO's on the electron-pair acceptor go up in energy and all those on the electron-pair donor go down in energy.³⁷

Table VII. Force Constant Data

	K_s , mdyn/ \AA	K_a , mdyn/ \AA	a , mdyn/ \AA^3	b , mdyn/ \AA^2
McLean and Yoshimine ^a four terms	3.31	0.22	0.74	-2.08
Noble and Kortzeborn ^b four terms	2.99	0.94	11.77	-8.78
Kollman and Allen ^c four terms	2.64	0.56	8.37	-5.52
Ibers ^d	2.04	0.65	4.90	-1.73
H_5O_2^+ , this work ^e	2.12	0.20	2.12	-2.12

^a A. D. McClean and M. Yoshimine, *J. Chem. Phys.*, 52, 5375 (1970), Table V, row 2. ^b Row 4 of the table mentioned in footnote a. ^c This work, nine points; standard deviation, 1.2 cm^{-1} ; average error, 0.6%. ^d Reference 12. ^e Eleven points (excluding $R = 4.00, r = 0.0$); standard deviation, 94 cm^{-1} ; average error 25%.

(35) It should be noted that the presence of p orbitals on hydrogen increases the σ population on the hydrogen by 0.10 e^- and the π population by 0.03 e^- in HF_2^- ; of this increase in the σ population, all goes into the $p\sigma$ orbital. In HF, the presence of p orbitals increases the σ population by 0.13 e^- and the π population by 0.06 e^- ; of the increase in the σ population, 0.08 goes into the s orbitals, 0.05 into the $p\sigma$. Thus the $p\sigma$ orbital itself contributes more in HF_2^- than in HF, but in terms of number of electrons in the σ pool, p orbitals are no more important in HF_2^- than in HF.

(36) Assuming a p exponent of 0.7 for both HF and HF_2^- , one would predict a $\Delta E(\text{HF} + \text{F}^- \rightarrow \text{HF}_2^-)$ of 52.8 kcal/mol; using a p exponent of 1.0, one gets 52.0 kcal/mol. The p exponent optimized value is 52.25 kcal/mol.

(37) NOTE ADDED IN PROOF. After this paper was submitted for publication, three other papers of relevance appeared in the literature.

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Kraemer and Dierksen [*Chem. Phys. Lett.*, **5**, 463 (1970)] carried out an SCF calculation on the sp^2 configurations of the $H_3O_2^+$ system with an extended basis set of lower total energy than ours ($E_t = -152.43$), but found essentially the same energy for the reaction $H_3O^+ + H_2O \rightarrow H_3O_2^+$ (32.2 kcal/mol) in addition to an extremely shallow proton well at the minimum 0–0 separation (2.39 Å). DePaz, Ehrenson, and Friedman [*J. Chem. Phys.*, **52**, 3362 (1970)] studied a number of hydrated ions ($H_{2n+1}O_n^+$ and $H_{2n-1}O_n^-$) by CNDO/2 molecular orbital methods. Their minimum energy structure for $H_3O_2^+$ was similar to ours, but they carried out a much more complete search. The computed reaction energies were too high, and the authors proposed a semiempirical procedure to scale the results to fit experimental data.

Noble and Kortzeborn [*ibid.*, **52**, 5375 (1970)] studied the HF_2^- ion as well as HF_2 and HeF_2 by LCAO–MO techniques. These authors, using a basis set intermediate between ours and the best basis set of McLean and Yoshimine,^{12b} found an energy of reaction of 40 kcal for $F^- + HF \rightarrow HF_2^-$ as well as estimating a lower limit of 28 kcal from McLean and Yoshimine's results. They compared their results to a more recently obtained experimental value of 37 kcal: S. A. Harrell and D. H. McDaniel, *J. Amer. Chem. Soc.*, **86**, 4497 (1964). It should be noted that our dimerization energy (52 kcal/mol) is not in as good agreement with this value. The contrast between $H_3O_2^+$ (where different basis sets give similar reaction energies) and HF_2^- (where the theoretical values differ substantially) is a further example of the fact that Hartree–Fock calculations treat positive ions much more successfully than negative ions.

Noble and Kortzeborn also fit their data to the four-term potential suggested by Ibers⁹ in his spectroscopic study of HF_2^- . In Table V we calculated K_s (the symmetric stretch force constant) by fitting the

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$D_{\infty h}$ FHF^- structures to a parabola near the minimum, and K_a (the asymmetric stretch force constant) by fitting the $R(F-F) = 4.25$ au points to a parabola after subtracting off the quartic term reported by Ibers.⁹ We have now fit our energy points to the same four-term potential used by Noble and Kortzeborn [$V = K_s Q_s^2 + K_a Q_a^2 + a Q_a^4 + b Q_a^2 Q_s$; $Q_a \equiv 1/2(rHF - rHF')$; $Q_s = (rHF + rHF')$], and the results of all the HF_2^- force field calculations are given in Table VII.

Two additional points deserve mention. First, Noble and Kortzeborn compared their calculations to Ibers' original results [*J. Chem. Phys.*, **41**, 25 (1964)], which were later corrected [*ibid.*, **48**, 539 (1968)]. Secondly, Noble and Kortzeborn used a different definition for the asymmetric stretching normal mode (by a factor of 0.5), so the Ibers' force constants⁹ have been adjusted by the following factors ($K_s = 1/2 K_1$; $K_a = 2K_3$; $a = 2K_4$; $b = 1/\sqrt{2} K_{13}$) in order to compare them with the calculated values from the molecular orbital studies. The conclusions from this are similar to those of Noble and Kortzeborn, i.e., none of the SCF calculations is in especially good agreement with Ibers' results. Also, the results do not improve with an extension of the basis set—the highest total energy calculation (ours) appears to give the best agreement with Ibers' values. This is a rather discouraging result, but is not without precedent. A single Slater basis predicts a dipole moment for H_2O of 1.82 D, and the lowest energy calculation predicts 1.99 D (experimental, 1.84 D).

We have also attempted to fit our $H_3O_2^+$ results to the same four-term potential with much less success (see Table VII). In that system, the external hydrogens must contribute significantly to the normal modes, and we have not varied any of the external O–H distances.

An LCAO MO SCF Study of “ p_π – d_π ” Bonding to Phosphorus. The H_3PO Molecule

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Abstract: SCF calculations were carried out for the hypothetical compound phosphine oxide, H_3PO . The effect was studied of adding either a d or another p orbital to a phosphorus atom depicted in terms of seven s and three p Gaussian orbitals. The added p orbital gave a considerably greater improvement in total energy than did the d because the added p contribution was particularly large in phosphorus inner shells. However, introduction of the d orbital led to a large change in the electronic population of the two highest filled molecular orbitals. Population analysis showed that a major part of this change can be attributed to p_π – d_π bonding, and that introduction of d character to the molecule leads to an overall loss of ca. 0.1 electron charge from the oxygen and a gain of ca. 0.5 electron by the phosphorus, with the difference being made up by the hydrogens. Three-dimensional plots of electron densities across the H–P–O plane are presented to illustrate the electronic structure of this phosphoryl compound.

The question of the role of outer d electrons in the bonding of second-row atoms such as silicon, phosphorus, and sulfur is still a subject of dispute.^{2,3} Although a considerable body of experimental data is readily interpreted in terms of the concept of p_π – d_π bonding involving the d orbitals of these atoms, and although semiempirical investigations of the importance of d orbitals in the binding of second-row elements have been made by Brown and Peel,⁴ using the VESCF

method, and by Santry and Pople (CNDO),⁵ the only nonempirical study of which we are aware is by Boyd and Lipscomb⁶ whose LCAO SCF results for PO and PO^- show a large contribution of phosphorus 3d orbitals to bonding. An approximate model of phosphine oxide based on the valence bond method has also been published.⁷

In order to shed further light on this matter, we have carried out the preliminary LCAO MO SCF studies⁸

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