THE THEORY OF THE HYDROGEN BOND[1a]

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Contents

I. Introduction

The hydrogen bond is an intermediate range intermolecular interaction between an electron-deficient hydrogen and a region of high electron density. Its fundamental role in the structure of DNA[2a] and the secondary and tertiary structure of proteins[2b] is well known. Several books[3-6] have been devoted solely to hydrogen bonding. Within the last 10 years numerous review articles[7-13] have discussed both the theoretical and experiment aspects of hydrogen bonding.

This work will focus on the theoretical aspects of hydrogen bonding, and we attempt to give a complete review of theoretical developments in recent years. The vast increase in theoretical studies on hydrogen bonding since Bratoz' review[11] of the theory has been due to (1) the advent of very high speed computers, which have allowed nonempirical SCF studies to be carried out on ever larger systems, and (2) the development of all-valence-electron semiempirical MO theories, which have made calculations on systems of 50 atoms and 100 valence electrons feasible. During the past few years there also have been many experimental studies on hydrogen-bonded systems, and these will be referred to where appropriate; more extensive review articles on experimental spectroscopic studies of hydrogen bonding are already in the literature.[7,9,10,13]

After brief sections in which we define hydrogen bonding and describe the theoretical methods employed, the remainder of this paper will focus on two issues. First, how well do theoretical studies on specific hydrogen-bonded systems succeed in predicting such experimentally measurable quantities as energy of complex formation, complex geometry, inter- and intramolecular force constants and potential functions, chemical shifts, and electronic transitions? Second, what has been learned recently about the detailed mechanism of hydrogen bonding and the charge redistribution accompanying hydrogen-bond formation?

A. WHAT IS A HYDROGEN BOND?

According to simple valence bond theory, a hydrogen atom should be capable of forming only one chemical bond. In many cases, however, hydrogen is formally two-valent—we

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(2) (a) See, for example, R. E. Marsh in "Structural Chemistry and Molecular Biology," W. H. Freeman, San Francisco, Calif., 1968; (b) "The Proteins," Vol. I and II, H. Neurath, Ed., Academic Press, New York, N. Y., 1964.

(3) "Hydrogen Bonding," D. Hadzi and W. H. Thompson, Ed., Pergamon Press, Oxford, 1959.

(4) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960.

(5) "Vodorondnaya Svyaz," N. D. Sokolov and V. M. Tschulanovskii, Ed., Nauka, Moscow, 1964.

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

(7) A. S. N. Murthy and C. N. R. Rao, *Appl. Spectrosc. Rev.* **2**, 1 (1968).

(8) A. S. N. Murthy and C. N. R. Rao, *J. Mol. Struct.*, **6**, 253 (1970).

(9) H. Ratajczak and W. J. Orville-Thomas, *ibid.*, **1**, 449 (1968).

(10) J. C. Davis and K. K. Deb, *Advan. Magn. Resonance*, **4**, 201 (1970).

(11) S. Bratoz, *Advan. Quantum Chem.*, **3**, 209 (1967).

(12) N. D. Sokolov, *Ann. Chim. (Paris)*, 10, 487 (1965).

(13) S. H. Lin, "Physical Chemistry—An Advanced Treatise," H. Eyring, D. Henderson, and W. Jost, Ed., Academic Press, New York, N. Y., 1970, p 439.

call this additional bond a "hydrogen bond." There are two main classes: (1) hydrogen bonds which connect atoms of electronegativity higher than hydrogen, such as that which occurs in the water dimer $H_2O\cdots H—OH$; and (2) hydrogen bonds which connect atoms of lower electronegativity, such as B—H—B bonds in the boranes. This latter type of bonding is a subject in itself,[14] and it will not be further considered here. The atoms in the periodic table with electronegativity greater than that of hydrogen are C, N, O, F, P, S, Cl, Se, Br, and I; and hydrogen bonds involving all of these elements are known. "π" hydrogen bonds involve an interaction between a partially positive hydrogen and the electrons in a double and triple bond, and these also have been the subject of some investigations.

Atoms with electronegativity greater than hydrogen have the capability of forming $A—H\cdots B$ hydrogen bonds if B has an unshared pair of electrons, but in some cases (*e.g.*, two methyl fluorides forming a $C—H\cdots F$ bond) the interaction is so weak that most chemists would consider that there is no "hydrogen bond" formed. One way to avoid this ambiguity is to add an energy criteria; *e.g.*, to be a "hydrogen bond," the energy of complex formation must be greater than dipolar or London dispersion force energies. Other criteria are structural and spectroscopic. In molecular crystals, experimental evidence for hydrogen bonding is the approach of a hydrogen in one molecule to an electronegative atom (X) in the other molecule significantly closer than the sum of the van der Waals radii of X and H.[6] An obvious example is ice I, where the nonbonded $H\cdots X$ distance of 1.75 Å is much closer than the sum of van der Waals radii (2.6 Å).

Infrared and Raman spectroscopic evidence for hydrogen bonding is the shift of the A–H stretch in a molecule toward lower frequencies, usually accompanied by broadening and enhanced ir absorption of the transition. Other intramolecular vibrations are also affected by hydrogen bonding, and in recent years the far-infrared has been examined for intermolecular hydrogen-bonding modes. Pimentel's book[4] contains an extensive discussion of infrared spectroscopic applications to H bonding, and Murthy and Rao[7] and Ratajczak and Orville-Thomas[9] review the literature on infrared studies of H bonding between 1959 and 1967.

Nuclear magnetic resonance studies of hydrogen bonding have been reviewed by Murthy and Rao[7] as well as Davis and Deb.[10] The downfield shift of the X–H proton upon hydrogen bonding is the most often studied, although recent nmr work on the ^{17}O resonance of water[15] and the N^{15} resonance of ammonia[16] indicates that studies of nonproton resonances might provide additional understanding of hydrogen bonding. Electronic transitions are affected by hydrogen bonding; in carbonyls there is a blue shift in the $n-\pi^*$ transition and, usually, a red shift in the $\pi-\pi^*$ transition. Recent electronic spectral studies of H bonding are found in Murthy and Rao's review. There are many other physical and chemical manifestations of hydrogen bonding, and these are most thoroughly discussed in Pimentel and McClellan's book.[4]

B. THEORETICAL METHODS

Although most of the theoretical approaches to the study of hydrogen bonds have been reviewed by Lin[13] as well as Pimentel[4] and Bratoz,[11] it is worthwhile to give a brief description of the principal developments.

The first attempts to understand the hydrogen bond used an electrostatic model. Pauling[17] argued that hydrogen can participate in only one covalent bond, and that a second "hydrogen bond" must be due to an ionic interaction between the partially positive hydrogen and lone pair of the neighboring molecule. Simple electrostatic calculations of the hydrogen-bond energies were carried out by a number of workers (see ref 4 and 11), among them Lennard-Jones and Pople.[18] Using a four-electron point charge model and placing the charges to fit the experimental dipole moment of water, these workers found an H-bond energy of 6 kcal/mol.

Arguments against an exclusively electrostatic model of the hydrogen bond have been given by many authors, but the strongest arguments against the electrostatic model are as follows.[19] (1) There is certainly charge redistribution upon H-bond formation, as evidenced by the infrared spectral intensity changes upon bond formation. (2) At the H-bonded distance between the two fragments, there must be considerable closed-shell (exclusion principle) repulsion between the two fragments. Inclusion of this repulsion energy nullifies the good agreement between the H-bond experimental energy and that calculated by the simple electrostatic models. This is not to say that electrostatic calculations cannot be useful in discussing certain aspects of H bonding; for example, Bader[20] was able to rationalize X–H force constant shifts in H-bonded systems with an electrostatic model.

To attempt to estimate all the contributions to the H-bond energy, Coulson and Danielson[21] and Tsubomura[22] developed an empirical valence bond approach to determine the various contributions. A similar model, emphasizing the charge-transfer aspects of H bonding, was developed by Puranik and Kumar[23] and Bratoz[11] (the role of charge transfer in H bonds is more explicitly discussed in a later section). The conclusion of the valence bond theories was that at long $A\cdots B$ distances the H-bond energy is mainly electrostatic, but at shorter distances repulsion and delocalization (intra- and intermolecular) come into play. These qualitative, valence-bond-based theories, put forth at a time when more precise, nonempirical calculations could not be carried out, constituted a very important step forward toward rationalization of many of the phenomena associated with H bonding. They did not, however, lend themselves easily to more quantitative calculations or to an understanding of why certain H bonds are stronger than others.

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[14] See, for example, W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

[15] J. Reuben, *J. Amer. Chem. Soc.*, **91**, 5725 (1969).

[16] W. Litchman, M. Alei, and A. Florin, *ibid.*, **91**, 6574 (1969).

[17] L. Pauling, *Proc. Nat. Acad. Sci.*, **14**, 359 (1928).

[18] J. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc., Ser. A*, **205**, 155 (1951); J. A. Pople, *ibid.*, **205**, 163 (1951).

[19] It should be noted that, in disagreement with the view expressed by Pimentel[4] and Bratoz,[11] the lack of correlation of H-bond energy with dipole moment of the proton acceptor is not a conclusive argument against electrostatic theories of the H bond. At the distances where H bonding occurs, the dipole moment approximation is a poor one and higher multipoles must be considered. 1,4-Dioxane forms strong hydrogen bonds because each oxygen is a good source of electron density (despite an average dipole moment of 0.4 D). The fact that amines are better proton acceptors than nitriles can be rationalized by arguing that the electrons in the amine (sp^3) lone pair extend further toward the proton donor than those in the nitrile (sp).

[20] R. F. W. Bader, *Can. J. Chem.*, **42**, 1822 (1964).

[21] C. A. Coulson and U. Danielson, *Ark. Fys.*, **8**, 205, 239 (1955).

[22] H. Tsubomura, *Bull. Chem. Jap.*, **27**, 445 (1954).

[23] P. G. Puranik and V. Kumar, *Proc. Indian Acad. Sci.*, **58**, 29, 327 (1963).

A number of the earlier studies on H bonds used an MO approach. Pimentel's model[23a] was helpful in introducing many chemists to the potential use of molecular orbital theory for the description of hydrogen bonding. However, his model does not distinguish between the very different H-bonding in FHF^- and $(H_2O)_2$. Hofacker[24] developed a localized orbital method which expressed the MO's of the complex in terms of the MO's of the fragments plus small perturbation terms. Paolini[25] used a three-center, four-electron MO wave function to represent the H bond and postulated that p orbitals on the hydrogen might play a key role in determining the H-bond properties; later studies showed this p-orbital effect to be small.[26] A more detailed discussion of the Coulson and Danielson,[21] Bader,[20] and Hofacker[24] papers is given by Lin.[13]

In recent years, nonempirical calculations using the valence bond and the molecular orbital methods have been carried out on FHF^-, the simplest and most strongly bound H-bonded system. In the valence bond calculations, the nonrelativistic Schrödinger equation is solved using a nonorthogonal atomic basis in a multideterminant wave function. Both Bessis and Bratoz[27] and Erdahl[28] carried out such a calculation on the bifluoride ion and found physically reasonable results. However, this method is very difficult to apply to larger systems in which the number of determinants for a minimal calculation becomes enormous and the resultant wave function difficult to interpret. For example, one of the main questions involves the systematic comparison of the combined and separated species: how many valence bond structures should be employed for the separated fragments ($F^- + HF$) to yield the proper relative accuracy for a particular set of valence bond structures representing the hydrogen-bonded complex (FHF^-)? In addition, Kollman and Allen find[26] that Erdahl's valence bond results are less successful in predicting R(F–F), the force constants, and $\Delta E(FHF^- \rightarrow FH + F^-)$ than molecular orbital wave functions. The valence bond method yields a more satisfactory dissociation energy for the bifluoride ion separating to $F^- + F + H$ (since the molecular orbital wave function dissociates to $2F^- + H^+$), but this is not a particularly strong advantage because in H-bonded studies one is mostly interested in predicting the closed-shell dissociation of the complex ($FHF^- \rightarrow FH + F^-$).

In net, it appears that as a starting point in understanding hydrogen bonds, molecular orbital theory is the most satisfactory approach. Ideally, one needs a multiconfiguration wave function for quantitative accuracy (configuration interaction, molecular orbital minus ionic states,[29] or multiconfiguration SCF[30]), but such calculations have not yet been attempted, and at present one is justified in hoping that most useful information is obtainable at the Hartree–Fock level. One reason for believing this comes from the correct infinite separation behavior of the molecular orbital wave function for most systems of interest, but this fact alone does not eliminate the dispersion energy problem.[31-33] The second, and most important, reason is that a large amount of existing computational experience has shown conformational energy changes and hydrogen-bond formation energies to be quite well represented within the Hartree–Fock framework.

Before proceeding further, it is useful to give a brief account of how a molecular orbital wave function is constructed. To carry out an *ab initio* molecular orbital calculation, one begins with the exact nonrelativistic Hamiltonian (assuming clamped nuclei in the well-known Born–Oppenheimer approximation) and attempts to solve the time-independent Schrödinger equation for the electronic ground state, assuming a single determinantal form of the wave function. The orthogonal molecular orbitals which make up the determinant are usually constructed as linear combinations of nonorthogonal atomic orbitals, and these coefficients are self-consistently optimized (Roothaan scheme, see ref 34, 35). Results show that neglect of relativistic effects (for low-Z atoms) and nuclear electronic coupling does not significantly affect the predictive ability of the theory. There are, however, two main problems associated with *ab initio* molecular orbital calculations. First, there is the instantaneous electron–electron correlation problem noted above. Second, with the Roothaan scheme there is obviously a wide latitude in the choice of atomic-like orbitals to be employed as a basis set. One can use atomic orbitals of near-Hartree–Fock quality or a much cruder representation. Unfortunately, the ability of the wave function to predict molecular properties does not improve monotonically with improvement in the atomic basis used. An excellent example of this is the dipole moment of H_2O; a single Slater orbital basis ($E = -75.500$ au)[36] predicts a dipole moment of 1.82 D; a near-Hartree–Fock atomic basis ($E = -76.002$ au)[37] predicts 2.57 D; and the best extended basis ($E = -76.059$ au)[38] predicts 1.99 D. The experimental dipole moment is 1.85 D, and one must carry out a configuration interaction calculation to lower the best extended basis result toward the experimental value.[39] For the tabulation of earlier molecular orbital calculations, see a compendium by Krauss;[40] an article by Allen[41] reviews more recent work.

In recent years there has been much progress toward the development of satisfactory semiempirical molecular orbital methods. These methods may be divided into two classes. (1) In one-electron theory, commonly known as extended Hückel theory,[42] the diagonal elements of the Hamiltonian are evaluated empirically, and the off-diagonal elements are an average of the diagonal elements weighted by the overlap

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[23a] G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

[24] L. Hofacker, *Z. Naturforsch. A*, **13**, 1044 (1958).

[25] L. Paolini, *J. Chem. Phys.*, 30, 1045 (1959).

[26] P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 6101 (1970).

[27] G. Bessis and S. Bratoz, *J. Chim. Phys.*, **57**, 769 (1960); G. Bessis, *Cah. Phys.*, 127, 105 (1961).

[28] R. M. Erdahl, Ph.D. Thesis, Princeton University, 1965.

[29] R. A. Kapral, Ph.D. Thesis, Princeton University, 1967.

[30] A. C. Wahl and G. Das, *Advan. Quantum. Chem.*, **5**, 261 (1970).

[31] At the distances of hydrogen bonds (~3 Å), the R^{-6} term of the dispersion energy is not a good approximation, and one must consider higher terms in the general dispersion energy expansion.[32] Another unanswered question is whether the correlation energy contribution to the intermolecular energy corresponds exactly to the dispersion energy. Margenau and Kestner[33] show that dispersion effects are not contained in the single determinant energy.

[32] J. O. Hirschfelder and W. J. Meath, *Advan. Chem. Phys.*, **12**, 1 (1967).

[33] H. Margenau and N. R. Kestner, "The Theory of Intermolecular Forces," Pergamon Press, Oxford, 1969.

[34] C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[35] F. Pilar, "Elementary Quantum Chemistry," McGraw-Hill, New York, N. Y., 1968, p 341 ff.

[36] J. Del Bene and J. Pople, *J. Chem. Phys.*, **52**, 4858 (1970); *Chem. Phys. Lett.*, **4**, 426 (1969).

[37] J. F. Harrison, *J. Chem. Phys.*, **47**, 2990 (1967).

[38] D. Neumann and J. W. Moskowitz, *ibid.*, **49**, 2056 (1968).

[39] S. Aung, R. M. Pitzer, and S. I. Chang, *ibid.*, **49**, 2071 (1968).

[40] M. Krauss, *Nat. Bur. Stand. (U. S.)*, *Tech. Note*, No. 438 (1967).

[41] L. C. Allen, *Annu. Rev. Phys. Chem.*, 20, 315 (1969).

[42] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

between the different AO's. Molecular orbitals and their associated one-electron energies are found by diagonalizing the Hamiltonian matrix, and the electrons are placed in these orbitals. The total energy E_t is taken to be the sum of the one-electron energies of the occupied orbitals. (2) Two-electron theory, in which electron–electron repulsion is considered, has been developed by Klopman[43] and Pople, *et al.*,[44] as well as several others. These two-electron theories have many forms (*e.g.*, CNDO,[44] MINDO,[45] and INDO[46]), and they differ in relatively subtle ways. The two main common features are (a) neglect of differential overlap (NDO) ($\varphi_i \cdot \varphi_j = 0$ for $i \neq j$) and (b) neglect of all three- and four-center electron repulsion integrals. (The schemes differ in their choice of certain parameters and in the detailed places where neglect of differential overlap is introduced: CNDO $\equiv$ *complete neglect* of differential overlap; NDDO $\equiv$ neglect of *diatomic* differential overlap.) The most commonly used is CNDO/2,[47] and this method approximates the one-center terms by the Mulliken electronegativity, sets the two-center attraction terms equal to the core charge of the nucleus times the electron repulsion integral between the valence s orbitals on the two centers, and evaluates the nonzero two-electron repulsion integrals using the valence shell s orbitals. As noted by Pople, the use of s orbitals only to represent all forms of the retained two-electron integrals ensures the rotational invariance of the calculation.

II. Theoretical Predictions of Observable Properties

A. GEOMETRY AND ENERGY OF FORMATION

The majority of the spectroscopic studies on hydrogen bonding have determined the enthalpy and entropy changes which accompany hydrogen-bond formation. Many of the experimental studies have been carried out in inert solvents, where the energy of complex formation is different from the gas-phase value, but not enough quantitative data exist to allow for a precise estimate of the difference between a gas-phase and solution dimerization energy.[48,49] Theoretical molecular orbital calculations should give one an estimate of the gas-phase dimerization energy and complex geometry, and a case study of theoretical calculations on different systems is presented below.

1. Ammonia–Hydrogen Chloride

The first *ab initio* molecular orbital calculation on a neutral hydrogen-bonded dimer was carried out by Clementi.[50] Clementi examined the potential surface for the NH_3–HCl dimer, assuming an H–Cl approach along the lone-pair direction of ammonia (along the C_3 axis), varying both the N–Cl and the H–Cl distance independently. By using reasonable estimates for the intermolecular vibration frequencies, thermodynamic parameters for complex formation were derived and the existence of gas-phase NH_4Cl predicted. Recently a gas-phase complex has been experimentally detected by Goldfinger,[51] but no detailed structure has been measured. No activation energy was found for the reaction $NH_3 + HCl \rightarrow NH_4Cl$. Of interest is the fact that in the gas-phase species the four hydrogens are not equivalent distances from the nitrogen, with the hydrogen forming the H bond 1.22 Å from the nitrogen and the other hydrogens 1.01 Å from N. Thus, unlike crystalline NH_4Cl, where NH_4^+ has tetrahedral symmetry and the ions are separated and stabilized by the Madelung energy term, Clementi's calculations on gas-phase NH_4Cl indicate that the molecule can be thought of as somewhere between H_3N and HCl, with the H–Cl distance significantly elongated (from 1.32 Å in isolated HCl to 1.62 Å in the complex), and hydrogen bonding between NH_4^+ and Cl^-, in which the N–H bond pointing toward the chloride is significantly longer than the other three N–H bonds.

2. The Water Dimer

To this date no less than six *ab initio* calculations on the water dimer have been reported in the literature. The first calculation by Morokuma and Pederson,[52] using a limited Gaussian basis set (5 s Gaussians and 3p on oxygen, and 3 s functions on hydrogen) found the linear (single hydrogen-bonded) configuration to be most stable, followed in stabilization by the bifurcated and cyclic structures (Figure 1). The dimerization energy was, however, considerably overestimated (12.6 kcal/mol). Second virial coefficient data imply a dimerization energy of 5.0 kcal/mol.[53] The next reported work by Kollman and Allen, using a contracted near-Hartree-Fock atomic basis set, confirmed the earlier result that a linear dimer was more stable than the bifurcated and cyclic structures (despite the two hydrogen bonds in these structures) and found a dimerization energy of 5.3 kcal/mol.[54]

Earlier ir spectroscopy work on water dimers in inert matrices was interpreted in favor of a cyclic dimer,[55] but the most recent investigation clearly favors a linear dimer.[56] Solution studies (in CCl_4) have been interpreted in terms of cyclic dimers,[57] but this interpretation has been questioned.[58] Subsequent calculations on the linear configuration by Morokuma and Winick[59] with a single Slater basis set and a complete geometry search by Del Bene and Pople[36] using a similar basis found reasonable dimerization energies for the linear structure of 6.56 and 6.1 kcal/mol. Calculations with very accurate basis sets (including d polarization functions on oxygen and p functions on hydrogen) by Hankins, *et al.*,[60] and Diercksen[61] find dimerization energies of 4.7–4.8 kcal/mol.

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[43] G. Klopman, *J. Amer. Chem. Soc.*, **86**, 4550 (1964).

[44] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129, S136 (1965).

[45] M. J. S. Dewar and G. Klopman, *J. Amer. Chem. Soc.*, **89**, 3089 (1967).

[46] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2027 (1967).

[47] J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

[48] See R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley, New York, N. Y., 1969, p 92.

[49] S. D. Christian, personal communication.

[50] (a) E. Clementi, *J. Chem. Phys.*, **46**, 3851 (1967); (b) *ibid.*, **47**, 2323 (1967); (c) E. Clementi and J. N. Gayles, *ibid.*, **47**, 3837 (1967).

[51] P. Goldfinger and G. Verhaegen, *ibid.*, **50**, 1467 (1969).

[52] K. Morokuma and L. Pederson, *ibid.*, **48**, 3275 (1968).

[53] J. A. Rowlinson, *Trans. Faraday Soc.*, **47**, 120 (1951).

[54] P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969).

[55] M. Van Thiel, E. D. Becker, and G. Pimentel, *ibid.*, **27**, 486 (1957).

[56] A. Tusi and E. Nixon, *ibid.*, **52**, 1521 (1970).

[57] L. B. Magnusson, *J. Phys. Chem.*, **74**, 4221 (1970).

[58] P. A. Kollman and A. D. Buckingham, *Mol. Phys.*, **21**, 567 (1971).

[59] K. Morokuma and J. Winick, *J. Chem. Phys.*, **52**, 1301 (1970).

[60] D. Hankins, J. Moskowitz, and F. Stillinger, *Chem. Phys. Lett.*, **4**, 581 (1970); D. Hankins, Ph.D. Thesis, New York University, 1970; D. Hankins, J. Moskowitz, and F. Stillinger, *J. Chem. Phys.*, **53**, 4544 (1970).

[61] G. Diercksen, *Chem. Phys. Lett.*, **4**, 373 (1970).

Besides the energies of formation, some geometrical parameters are of interest. The angle θ in the linear dimer was predicted to be near 0° by Morokuma and Pederson, 25° by Kollman and Allen, 40° by Diercksen and Hankins, *et al.*, and 57° by Morokuma and Winick and Del Bene and Pople. The fact that this angle is nonzero seems to support the localized orbital picture of an O–H bond approaching a lone pair of electrons (rather than between the two lone pairs in the $\theta = 0$ direction). However, it should be noted that the difference in energy between the $\theta = 0$ and minimum energy configurations is quite small, and if the dipole moment of the hydrogen donor (*e.g.*, HCN) were larger, the $\theta = 0$ configuration could be favored. The smaller basis set calculations of Pederson and Morokuma, Morokuma and Winick, and Del Bene and Pople all predict O–O distances near the ice I distance of 2.76 Å, whereas the larger basis calculations find R(O–O) = 3.0 Å. Bollander *et al.*,[62] predict R = 2.9 Å using semiempirical statistical mechanical arguments. Tursi and Nixon's[56] infrared experiments on the water dimer in inert gas matrices seem to indicate a longer O–O distance than in ice I (less red shift of the O–H stretch), but at this point no really definitive experimental value of the correct O–O distance in the dimer is available. A summary of the water dimer results is presented in Table I.

Table I

Water Dimer Calculations

	Basis set	*Dimerization energy*	*R(O–O), Å*	*θ, deg*
1.	(5,3,3) Gaussian[52]	12.6	2.68	0
2.	Hartree-Fock AO contracted Gaussian[54]	5.3	3.00	25
3.	Hartree-Fock AO "split out" Gaussian[54]	7.9	2.85	25
4.	Single Slater basis[59]	6.55	2.76	57
5.	Gaussian fit to Slater[36]	6.1	2.73	57
6.	Extended basis with polarization function[60,61]	4.7	3.00	40
7.	CNDO (exptl monomer geometry)[65,66]	5.9	2.53	0
8.	CNDO (CNDO optimized geometries)[66]	8.4	2.53	0

In addition to the *ab initio* results, numerous semiempirical calculations on the water dimer have appeared in the literature. An iterative extended Hückel calculation by Rein and Harris finds no dimerization energy for linear $(H_2O)_2$;[63] Murthy and Rao, using ordinary extended Hückel theory, have found a double minimum potential for the linear dimer (with $H_3O + OH^-$ more stable than the nonionic configuration). They do not report the monomer energies.[64]

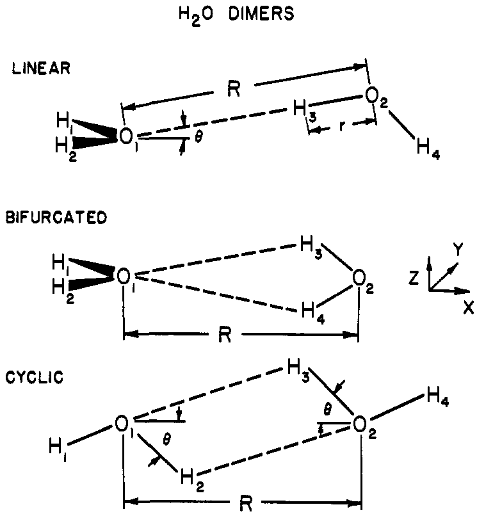

Figure 1. Linear: H_1 and H_2 are in the xy plane; H_4 and H_3 are in the xz plane. Bifurcated: H_1 and H_2 are in the xy plane; H_3 and H_4 are in the xz plane. Cyclic: All the atoms are in the xz plane.

A number of papers appearing in the literature have used CNDO/2 to calculate the water dimerization energy. Murthy and Rao[64] find a ΔE of 6.3 kcal/mol for the linear dimer, using monomer distances fixed at the experimental value [R(O–H) = 0.96 Å and θ(HOH) = 107°]. Hoyland and Kier[65] and Kollman and Allen[66] examined the three basic configurations of the water dimer, finding the linear structure to be the most stable. Kollman and Allen also found that the predicted hydrogen-bond energy was very sensitive to O–H bond length. Optimizing the O–H bond length for both monomer and dimer yielded a value of 8.4 kcal/mol [in contrast to the 5.9 kcal/mol found when R(O–H) was fixed at 0.957 Å]. In the CNDO/2 calculations (where searches were done) an angle of $\theta = 0$ was found for the linear dimer, and $R(O\cdots O)$ was considerably underestimated (calculated to be 2.53 Å). An NDDO calculation[67] predicts both the cyclic and linear water dimers to have a ΔE of 76 kcal/mol.

3. Water Polymers

Theoretical studies on water polymers have fallen into two groups: first, those calculations which attempt to give insight into the structure of ordinary water polymers; and, second, those which attempt to explain the phenomenon of "anomalous water."

The *ab initio* results of Hankins, *et al.*,[60] and Del Bene and Pople[36] give interesting new insight into the "nonadditivity" of hydrogen bonds. These authors examined the energy of three linear trimers, represented schematically by (1) O—HOH—O, (2) O—H···O···H—O, and (3) O—H···O—H···O. The stabilization energy/H bond of the first two, where the central water is functioning as a double hydrogen donor or a double hydrogen acceptor, is actually less than the stabilization in the dimer, whereas the structure (3) has a greater per-H-bond stability than that of the dimer.

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(62) R. W. Bollander, J. L. Cassner, and J. T. Zung, *J. Chem. Phys.*, 50, 4402 (1969).

(63) R. Rein and F. Harris, *J. Mol. Struct.*, 2, 103 (1968).

(64) A. S. N. Murthy and C. N. R. Rao, *Chem. Phys. Lett.*, 2, 123 (1968).

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Earlier, electrostatic calculations by Weissman, *et al.*,[67] and CNDO/2 calculations by Hoyland and Kier[65] had led to the same conclusions on the relative stability of the three trimer structures. However, Hankins, *et al.*, point out that a simple electrostatic model (assigning point multipoles and polarizabilities to each water molecule) cannot explain the large differences in the nonadditivity $V(1,2,3)$ of the three trimer interactions. The total energy of a particular orientation of the trimer can be expressed as $E(1,2,3) = 3E(1) + V(1,2) + V(1,3) + V(2,3) + V(1,2,3)$, where $E(1)$ is the isolated water energy and $V(1,2)$ the hydrogen-bond energy of molecules 1 and 2 in the absence of molecule 3. The nonadditivity energies $V(1,2,3)$ for tetrahedral coordination at $R(\text{O–O}) = 2.76$ Å are -1.36 kcal/mol for the sequential trimer (3), 0.87 kcal/mol for the double hydrogen donor (1), and 0.35 kcal/mol for the double hydrogen acceptor (2). Even though $E(1,2,3)$ for the trimer still has its minimum at 3.0 Å, Hankins, *et al.*, point out that, in tetrahedral clusters, the fact that the ratio of sequential:double donor:double acceptor trimers is 4:1:1 and that the large nonadditivity $V(1,2,3)$ of the sequential trimer is greater at shorter O–O distances rationalizes the observed ice and water O–O separation of 2.76 Å. Although the evidence is indirect (it could be argued that the inclusion of dispersion energies, left out in the SCF calculation, would cause the O–O distance to be reduced), their explanation is reasonable. Ideally, one would like to examine a tetrahedrally coordinated pentamer with their basis set but this would involve 150 contracted functions, a hefty task, for any available computer.

Del Bene and Pople[36] also examined higher polymers of water and concluded that cyclic systems should be found in the structure of liquid water. These authors as well as Hoyland and Kier[65] and Kollman and Allen[66] (the latter two using the CNDO/2 semiempirical method) carried out calculations on the tetrahedrally coordinated pentamer and found that the stability/H bond was very similar to the dimer stabilization. CNDO/2 results on a variety of cyclic structures of water polymers were very similar to Del Bene and Pople's STO-4G results (Table II) in terms of the stabilization energy found and O–O distance at the minimum energy; clearly the stabilization is exaggerated in these calculations. The CNDO/2 studies indicate that infinite OH···OH···OH sequentially H-bonded polymers should have an H-bond energy similar to the cyclic polymers.[68]

Table II

Comparison of *Ab Initio* STO-4G Calculations with CNDO/2 Results on Water Polymers

	STO-4G[a]		*CNDO/2*[b]	
	ΔE/H bond	*R(O-O)*	*ΔE/H bond*	*R(O-O)*
$(H_2O)_2$	6.1	2.76	8.4	2.53
$(H_2O)_4$	9.4	2.47	9.5	2.45
$(H_2O)_6$	12	2.44	10.8	2.45
$(H_2O)_6$ symmetric hydrogens	10–11	~2.3	10.4	2.32

[a] References 36 and 82. [b] Reference 68.

In view of these results, what can one say about the structure of liquid and solid water? Even though one should not accept the absolute value of the stabilization predicted for cyclic hexamers, the qualitative feature of additional stability for a cyclic structure should still be valid. In liquid water, the O–H stretches of the hydrogens in the cyclic structures would be shifted further downfield than those outside the cycle or those involved in O···HOH···O, cyclic, and bifurcated H bonds (the latter two dimer structures have slightly lower stability than the linear dimer but appear to be stable enough to contribute to water structure; Kollman and Allen[54] find stabilization energies of 5.3, 4.4, and 4.0 kcal/mol for linear, bifurcated, and cyclic structures). Concerning the theories of liquid water,[69] the most recent ir[70] and Raman[71] evidence seems to support a two-state model (on the time scale of vibrational spectroscopy), but it is still not really clear to what these two states correspond. They have been interpreted as representing "H-bonded" and "non-H-bonded" species with an energy difference of 2–3 kcal/mol. Unfortunately, the crudeness of CNDO/2 force constants precludes any quantitative force constant predictions for various types of clusters by that method. Extensive potential surfaces for dimers and trimers such as those carried out by Del Bene and Pople should, however, provide better potentials for Monte Carlo calculations on liquid water.[72]

The question of "anomalous water" has been, of course, the source of much controversy and excitement during the last 2 years, and the investigation of this phenomenon has produced an important new chapter in the history of chemistry. Because the problem is ultimately concerned with the potential existence of a new type of hydrogen bond, and because the experimental studies have been plagued by impurities and small amounts of material, theory has had a key role to play. It is not unexpected that a number of those theoreticians active in the theory of ordinary hydrogen bonds participated in the polywater problem, but the manner of their participation has been unusual—it is only rarely that both theoreticians and experimentalists have simultaneously been involved during that phase of research when the existence as well as the properties of a new material have been in question.

Approximately 25 theoretical papers have been published on this subject. Both semiempirical and *ab initio* methods are represented; ref 73 gives a detailed analysis and comparison of this work. One model was developed which for a time was able to compatibly interrelate all of the existing 20–25 different pieces of experimental data. Subsequent molecular weight measurements by Derjaguin, *et al.*,[74] and further high-accuracy *ab initio* calculations, however, invalidated this model. The fact that a model encompassing such a vast array of diverse experiments could be constructed from a simple structural hypothesis and that this model was then disproved is strong circumstantial evidence that a new type of hydrogen bond does not exist for water even in a low-lying metastable state.

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Experimentally, the question of polywater's existence has not been finally resolved, although many of the early investigators who felt that a new material was a good probability do not now feel this way. The general interest in polywater lent a perhaps excessive credibility to some very tentative experimental work.[75] In particular the "sweat" hypothesis has been conclusively disproved by several careful studies.[76] The problem of the amount and kind of impurities remains unanswered and the subject of wide disagreement among those who have disbelieved as well as believed in a new water allotrope.

In summary, one can say that among those who actively participated in elucidating this phenomenon, the scientific method has worked well. Faced with a genuine potential for the most important new chemistry in several decades, along with very difficult experimental and theoretical problems, a negative conclusion has been reasonably well established in a remarkably short time. In addition, theory and experiment have shared a close and fruitful partnership.

4. Hydrogen Fluoride Dimer and Polymers

Unlike water, hydrogen fluoride has a well-characterized gas-phase polymer, the cyclic hexamer. Janzen and Bartell have found,[77] using electron diffraction, that the cyclic hexamer is a puckered ring [θ(FFF) = 104° and R(F–F) = 2.53 Å]. Franck and Meyer[78] and Smith[79] have carried out extensive ir studies on HF vapor and explain their results by proposing an equilibrium between monomer, dimer, tetramer, and hexamer species. Franck and Meyer concluded that an H-bond energy of 7 kcal/mol (no nonlinear effect) is compatible with the results of their experiments.

Theoretical calculations on the HF dimer have been carried out by Kollman and Allen[80] (*ab initio*), Diercksen and Kraemers[81] (*ab initio*), Hoyland and Kier,[65] and Kollman and Allen[66] (CNDO/2). All the calculations find a near linear HF dimer to be the most stable [θ(HFH) = 140–160°], but an extremely shallow potential for bending the external hydrogen in H—F···H—F. The contracted Hartree–Fock atomic basis[80] finds a dimerization energy of 4.6 kcal/mol, and an extensive basis (including p and d polarization functions) also predicts 4.6 kcal/mol.[81] The CNDO/2 studies (using experimental monomer geometries) find a dimerization energy of 6.6–6.9 kcal/mol, but complete optimization of monomer and dimer geometries yields an energy dimerization of 9 kcal/mol. As in the case of the water dimer, the CNDO/2 studies greatly underestimate R(F–F) in the dimer (R = 2.45 Å) although no experimental value is available. The *ab initio* studies find F–F distances of 2.88[80] and and 2.85[81] Å.

Ab initio calculations[72] using near-Hartree–Fock atomic bases predict an energy of formation for HF cyclic tetramers and hexamers from the monomers to be 20 and 33 kcal/mol, respectively, with R(F–F) for the hexamer predicted to be 2.74 Å. A more complete optimization of the F–H distance in the hexamer would increase the stabilization and decrease the F–F distance. In contrast to what Janzen and Bartell's experiments seem to indicate, a planar sp^2 structure is predicted to be more stable than a chair sp^3 structure by 4.8 kcal/hexamer.

CNDO/2 calculations have been carried out on HF polymers by Hoyland and Kier[65] and Kollman and Allen.[66] The former authors, using the experimental geometry for HF (0.91 Å), computed the energy for the linear trimer, tetramer, and hexamer and cyclic planar hexamer, with the most stable structure being the cyclic hexamer (with an energy of formation of 56 kcal/mol of hexamers predicted). Kollman and Allen carried out a geometry search for the most stable linear and cyclic structure and found the most stable linear structure to be the pentamer and the most stable cyclic structure to be the planar hexamer. A complete geometry search on the cyclic HF hexamer[68] predicts a symmetrically bonded structure [R(F–F) = 2.25 Å] to be the absolute minimum energy, with an energy of formation of 100 kcal/mol relative to six HF.

5. Methanol Dimers and Polymers

Earlier matrix isolation work on the methanol dimer concluded that the minimum energy configuration was a cyclic structure,[82] but more recent calculations by Murthy, *et al.*,[83] and Hoyland and Kier,[65] as well as experimental work by Bellamy and Pace,[84] support the view that the methanol dimer is linear instead of cyclic. Experiments by Weltner and Pitzer on gas-phase methanol[85] and recent studies of methanol in various inert solvents[86] support a monomer–tetramer equilibrium (with some presence of dimer and trimer not ruled out). Murthy, *et al.*, studied methanol cyclic dimers and the linear dimer and trimer by CNDO/2 and EHT molecular orbital methods. The extended Hückel theory calculations predicted a 1.3-kcal/mol stabilization for the linear dimer and 0 for the cyclic; the corresponding values for CNDO/2 were 6.46 and 1.70 kcal/mol. The linear trimer had a greater energy of stabilization than two dimers. Hoyland and Kier examined the cyclic tetramer of methanol by CNDO/2 and found its energy of formation to be 23.9 kcal/mol, surprisingly less than four times the dimerization energy of methanol. It is possible, however, that the authors' use of the experimental monomer geometry (rather than the CNDO/2 optimized) as well as incomplete geometry optimization in the tetramer caused this lower stabilization energy. Allen and Kollman found cyclic hexamers of methanol stable by 10 kcal/H bond with respect to six monomers.[68]

The theoretical results on methanol give strong support to a linear rather than a cyclic methanol dimer. There has been some controversy in the literature on this point, and the ir work by Bellamy and Pace is the most elegant experimental proof for a linear dimer and trimer.

It is of interest at this point to review theoretical evidence for methanol, water, and hydrogen fluoride polymers. The

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experimental results that methanol forms a cyclic tetramer and HF a cyclic hexamer support the theoretical result that cyclic structures are unusually stable. In view of these facts, it is surprising that water polymers, whose energies of formation are predicted to be greater than those of HF[72,87] and comparable to those of methanol polymers,[83] should not be observable in the gas phase. This is probably due to the extensive H bonding of water liquid causing lower vapor pressures of water than HF and methanol. According to Eisenberg and Kauzmann[69] there is "no *direct* evidence for H bonds between water molecules in the vapor phase."

6. *Strong Hydrogen Bonds*

We will define strong hydrogen bonds as those in which there are significant structural changes in both members of the H-bonded complex. For example, $(HF)_2$ is a weak H bond because in its minimum energy structure, both HF monomers have a very similar structure to isolated monomeric HF. HF_2^- is a "strong" hydrogen bond because the minimum energy structure is very different from that of $HF + F^-$.

The simplest strong hydrogen-bonded system is the bifluoride ion, HF_2^-. This system has been examined theoretically by valence bond theory (Bessis and Bratoz[27] and Erdahl[28]), by *ab initio* molecular orbital calculations (Clementi,[88] McLean and Yoshimine,[89] Noble and Kortzeborn,[90] and Kollman and Allen[26]) and by CNDO/2 molecular orbital studies (Allen and Kollman[68]). The molecular orbital calculations all predict the experimental geometry within 2%; the predicted energy for the reaction $HF(g) + F^-(g) \rightarrow HF_2^-(g)$ varies from 28 kcal/mol (lowest energy SCF by McLean and Yoshimine) to 100 kcal/mol (CNDO/2). The experimental estimates for this reaction vary from 37 to 58 kcal/mol.[91] The valence bond calculations are in poorer agreement with the experimental value of the minimum energy geometry but give reasonable energies of reaction.

Ab initio calculations on $H_5O_2^+$ [26,92] and CNDO/2 calculations on various hydrated anions $O_nH_{2n-1}^-$ and $O_nH_{n+1}^+$ give good agreement with experimentally available geometries.[93,94] The energy of formation of $H_5O_2^+$ from H_2O and H_3O^+ (36 kcal/mol) is well reproduced by *ab initio* calculations, but the CNDO/2 studies significantly exaggerate the energies of formation of the various hydronium ion species. The CNDO/2 results indicate that, in both the positive and negative hydrated ions, chain structures are favored over cyclic ones.

Hoyland and Kier's CNDO/2 calculations[65] on the interaction of NH_4^+ and $MeNH_3^+$ with water yield hydrogen-bond energies in good agreement with experiment, but once again part of this agreement may be due to the use of experimental rather than CNDO/2 optimized geometries at each stage of the reaction.

7. *Carboxylic Acid Dimers and Polymers*

Carboxylic acids are one of the few sources of unequivocal hydrogen-bond gas-phase structural data. Both microwave[95] and electron diffraction[96] studies on various carboxylic acids in the gas phase confirm the cyclic structure of the dimer. In $(RCOOH)_2$, the substituent R does not affect the enthalpy of dimerization greatly (the enthalpy of dimerization is 14 kcal/mol for the formic acid dimer and 15.8 kcal/mol for the mixed formic–trifluoroacetic acid dimer). CNDO/2 studies by Schuster and Funck,[97] Murthy, *et al.*,[83] and Hoyland and Kier[65] correctly predict the cyclic dimer to be more stable than the linear; the first two papers note that the stabilization per H bond is similar in one of the linear dimers to the cyclic; this fact rationalizes the infinite linear chain crystal structure of formic acid. Schuster and Funck also determined the H-bond energy using CNDO optimized geometries for both monomer and dimer and found that the energy per H bond was 17 kcal/mol (in contrast to the experimental value of 8 kcal/mol). No one has attempted to rationalize the experimental structural difference between formic and acetic acids[98] (formic is cyclic in the gas and infinite H-bonded linear in the solid; acetic is cyclic in both phases), but it is likely that the effects are too subtle to be treated by semiempirical MO theory. Recently, Clementi has carried out an *ab initio* study of the formic acid dimer and has found a dimerization energy in very good agreement with experiment.[99]

8. *Formamide and Other Amide Hydrogen Bonds*

A number of laboratories have examined hydrogen bonding between amides in hopes of elucidating peptide structure. A small basis set *ab initio* calculation by Dreyfus, *et al.*,[100] on the cyclic formamide dimer finds dimerization energies of 14 and 19 kcal/mol with two different basis sets. Only the X-ray geometry determined dimer was considered, so it is likely that a geometry optimization would further overestimate the dimerization energy. Dreyfus and Pullman[101] also examined linear dimers of formamide, finding an H-bond energy of 8 kcal/mol. Three groups have made semiempirical MO investigation of amides. (1) CNDO/2 studies have been carried out by Pullman and Berthod[102] on the cyclic dimer of formamide. (2) Momany, *et al.*,[103] have carried out very extensive CNDO/2 calculations on dimers of formamide and *N*-methylacetamide. Their dimerization energies for linear and cyclic dimers of formamide were reasonable, but they found a huge (40 kcal/mol) stabilization when two parallel plate formamides were brought together. (3) Murthy, *et al.*,[104]

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also compared CNDO/2 and EHT predictions for internal rotation, protonation, and hydrogen bonding of amides and found that CNDO/2 gave reasonable dimerization energies whereas EHT did not. They found no difference in the dimerization energy of linear formamide and *N*-methylacetamide.

9. Formaldehyde Hydrogen Bonding

Molecular orbital studies of hydrogen bonding to the formaldehyde molecule have been examined by Morokuma (*ab initio*)[105] and Schuster.[106] Morokuma studied the H_2CO–H_2O and H_2CO–$2H_2O$ complexes using a single Slater basis set and found that in the dimer the minimum energy C—O···H angle is near 120° and the energy of dimerization is 3.5 kcal/mol. He also examined the possibilities of π hydrogen bonding and found a very small interaction energy (0.05 kcal/mol) when the water hydrogen approached the π electrons in the center of the C–O bond, 0.5 kcal/mol when the hydrogen approached the π electrons on the oxygen. The energy of C—H···O hydrogen bond in formaldehyde–water was found to be 0.61 kcal/mol. The C—H···O bond in the formaldehyde dimer would be even weaker since water is a better proton acceptor than formaldehyde. Schuster examined the complexes formaldehyde–water and formaldehyde–HF by CNDO/2 and INDO molecular orbital methods and found far greater stabilization energies than Morokuma. He also found π hydrogen bonds of comparable strength[107] to the σ (a very different conclusion from Morokuma), probably owing to a failure of CNDO/2 in this case.

10. Other Systems

There have been a number of other systems studied by molecular orbital techniques, and the energy and geometry of formation found in these studies are given in Table III.[108–124] An interesting electrostatic calculation on the dimer of HCN and the solid HCN was carried out by Rae,[125] who used a monopole–dipole representation of the exact charge distribution of the HCN monomer, bond polarizabilities, and dispersion energies and an empirical repulsion formula to compute the lattice parameters of solid HCN, finding good agreement with experiment. His potential overestimated the dimerization energy of HCN by 50%. The hydrogen bond in the HCN dimer is long (3.2 Å), and an electrostatic model should work better in estimating its energy than most other, shorter bonds, where considerable charge transfer terms may play a role.

11. Conclusions

It appears that one can have reasonable confidence in the energy and geometry of dimerization found by accurate *ab initio* calculations. There is still a significant variation of dimerization energy with basis set size, but the following general statements can be made: very accurate (d polarization functions and an extended and flexible s and p basis on the nonhydrogenic atoms and p polarization with an extensive s basis on hydrogen) *ab initio* calculations have computed dimerization energies in very good agreement with experiment; accurate (use of a double-ζ atomic basis set) calculations also give good agreement with experiment when contracted, but less agreement when more coefficients are allowed to vary; single Slater basis sets (or Gaussian fits to Slaters) give reasonable agreement with experiment for dimers, but badly exaggerate the H-bond energy in polymers; small Gaussian bases give much too large H-bond energies when allowed many SCF determined coefficients; more contracted bases give more reasonable results. The prescription is: use the most extensive basis possible if computer time is available; if not, use a highly contracted basis which well represents the monomer geometry, multipole moment, and polarizability. In any case, the uncertainties in many experimental gas-phase dimerization energies as well as the need to estimate the zero-point energy and correlation energy corrections make an exact agreement between experiment and molecular orbital dimerization energy not a reasonable goal. Further progress toward estimating correlation effects, which should be small, might be made by carrying out calculations on FHF^- and $(HF)_2$ to greater accuracy. Zero-point energy corrections[50c] in NH_3HCl lower the dimerization energy by 5 kcal/mol. However, this dimer is unusually strongly bound; the difference in zero-point energy between $(H_2O)_2$ and $2H_2O$ can be estimated from Del Bene and Pople[36] as well as Morokuma and Winick's[59] force constants for the water dimer to be 1.5 kcal/mol, which is 25% of the dimerization energy (this is most probably an upper bound to the change in zero-point energy in the water dimer). The more weakly bound dimers would have a smaller zero-point energy correction. It has been noted that energy differences for reactions involving closed-shell species should be much less affected by correlation energy effects than dissociation to atoms. However, a correlation energy difference of 1–2 kcal/mol [compared to that found in calculating the HF dissociation energy to H and F atoms (70 kcal/mol)] would be significant in view of the smallness of hydrogen-bond energies. In some cases, since the zero-point energy and correlation corrections would be of opposite sign, they might exactly cancel and the molecular orbital energy difference predict the experimental dissociation energy.

Both Kollman and Allen[80] and Diercksen and Kraemers[81] predict a greater dimerization energy for water than for HF, in contrast to what is currently experimentally accepted. Since the uncertainties in the experimental results are large, the true situation is not known at present. Evidence from ir spec-

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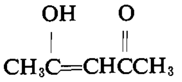
Table III[124]

System	*Method*	*Results*	*Ref*
 $CH_3\overset{\overset{\textstyle OH}{\vert}}{C}{=}CH\overset{\overset{\textstyle O}{\Vert}}{C}CH_3$	CNDO/2	The proton well is a double minimum. Replacing H with Li yields a minimum energy structure with C_{2v} symmetry in agreement with experiment. Also Be complexes found a geometry in agreement with experiment.	108
$(HCOOH)_2$ and $(CF_3COOH)_2$	CNDO/2 (modified)	Parameterization such that delocalization effects and energy are far too large	109
LiH_2^-	Small basis *ab initio*	Metastable LiH_2^- with a potential barrier of 0.15 au to decomposition to Li^- and H_2	110
Li_2H^+	Small basis *ab initio*	Stable by 59 kcal over Li^+ and LiH	111
$F^-(H_2O)_n$	Small basis *ab initio*	$n = 1, 2, 4$; average ΔE/bond $= 2$ eV; $R(O\text{–}F) = 2.33$ Å	112
Li_2H^-	Small basis *ab initio*	Stable by 7 kcal over LiH and Li^-	113
HF_2^- and $H_2F_3^-$	CNDO/2 and INDO	Nuclear spin coupling constants predicted for HF_2^- and $H_2F_3^-$	114
$H_2CO\cdots HOH$	CNDO/2	Energy and geometry of complex formation. Linear H bond (approaching an sp^2 lone pair) found to have a dimerization energy of 5–7 kcal/mol	106
Hydrated electron dimer	EHT	A model calculation for the hydrated and ammoniated electron in $(H_2O)_2$ and $(NH_3)_2$	115
$Li(NH_3)$ and $Li(NH_3)_2$	Hartree–Fock AO and extended basis	Mechanism for ammoniated electron. $Li(NH_3)_2$ unstable with respect to $LiNH_3 + NH_3$ even though $LiNH_3$ is stabilized over Li and NH_3 by 18 kcal/mol	116
$(CH_3)_2CO\cdots HOH$	CNDO/2 and EHT	Evaluate nmr shifts expected in this complex	117
$(HCOOH)_2$ and intramolecular H bonding in *o*-cresol	EHT	Too small stabilization (3.8 kcal) in formic acid dimer; charge redistribution in intramolecular H-bonding complex	118
$(NH_3)_2$, (NH_3H_2O), (NH_3HF)	Hartree–Fock AO	Reasonable ΔE of formation of various dimers. Attempt to generalize about nature of H bond in first-row dimers	119
LiFHF and $(LiF)_2$	Hartree–Fock AO	Comparison of lithium bonding with hydrogen bonding	120
Glycine–H_2O interaction	CNDO/2	Rationalization for zwitteronic structure of glycine in H_2O	121
Pyridinium–pyridine interaction	EHT	Proton potential function as a function of heavy atom distances	122
Pyridine–pyrrole	EHT	Proton potential function as a function of heavy atom distances	123

troscopy indicates that the HF dimer has a much smaller ΔE/H-bond energy than the hexamer[126] which would support the theoretical result noted above.

Of the semiempirical methods used to study hydrogen bonding, CNDO/2 is far superior to EHT and NDDO. Murthy, *et al.*, have examined various molecules by EHT and find no (or very little) stabilization in dimer formation. NDDO has the opposite weakness; it greatly exaggerates the energy of hydrogen-bond formation and predicts the cyclic dimer of water to be equal in stability to the linear. Comparison of CNDO/2 with *ab initio* calculations on dimers reveals that the CNDO/2 finds reasonable energies of dimerization in most cases, but these energies are often very dependent on the monomer geometry chosen (in contrast to the *ab initio* results). This is due to the fact that the difference in bond length between calculated and experimental in *ab initio* is small (2%), whereas CNDO/2 overestimates the bond lengths by 10%. In HF polymers CNDO/2 exaggerates the H-bond energy considerably. The energy of dimer formation calculated by CNDO/2 is greatly exaggerated when one examines π–π interactions. Momany, *et al.*,'s results[103] on the formamide dimer, Hoyland and Kier's result that a cyclic dimer of HCN is predicted to have a stabilization energy of 50 kcal/mol, and Kollman's results[127] on H_2CO-HF and H_2CO-H_2O, where the most stable hydrogen-bonded configuration finds the hydrogen from HF approaching the positive carbon in formaldehyde, show this defect. These results are in line with NDO studies on carbonium ions, where the relative stabilities of protonated acetylene and the vinyl cation and protonated ethylene and the ethyl cation are opposite to *ab initio* results.[128]

No *ab initio* calculations have been carried out on hydrogen-bonded systems where CNDO/2 fails. However, in agreement with the carbonium ion results, the fact that CNDO/2 neglects three- and four-center repulsions causes those geometrical configurations which allow more atoms to get closer together to be favored. It appears that any NDO scheme may have this defect, so it is not clear that one could reparameterize to remove this defect. Since we know that CNDO/2 overestimates the stability of multiply connected systems, we can have more confidence in CNDO/2 results which predict a linear dimer to be more stable than a cyclic (*e.g.*, water and methanol dimers).

Is there a lone-pair directionality in hydrogen bonding? This question is the subject of a review by Donahue,[129] so it deserves some comment. A number of the molecular orbital studies have attempted to give some insight into the problem. The results on the water dimer indicate that the favored configuration of a point dipole model (bifurcated structure) is not the lowest in energy. Would a lone-pair dipole model predict the geometry of the water dimer? It would predict a

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[126] P. V. Huong and M. Couzi, *J. Chim. Phys.*, **66**, 1309 (1969).

[127] P. Kollman, unpublished results.

[128] R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969).

[129] J. Donahue in ref 2a, p 443.

linear structures with θ near 54° to be most stable, which is close to the results of the most accurate dimer calculation. However, in a localized orbital picture of the water monomer, one finds a lone-pair–lone-pair angle of 140°, so that one might expect θ to be much larger. The difference in energy between the $\theta = 40°$ and $\theta = 0°$ linear structure (the latter representing an approach between the lone pairs) found by Hankins, *et al.*, is only 0.3 kcal/mol, a very small amount. These authors also note that when they move the external hydrogen of the proton donor molecule into the same plane as the hydrogens of the H acceptor water molecule (which should not affect any "lone-pair" directionality), the difference in energy between the $\theta = 40°$ and the $\theta = 0°$ (approach between the lone pairs) is less than 0.1 kcal/mol. Kollman and Allen made a similar observation in $(HF)_2$, where a "lone-pair" configuration [θ(HFH) = 120°] is higher in energy than a θ(FHF) = 180° configuration by only 0.6 kcal/mol (the minimum energy angle is 160°). When nitrogen is an sp^3 lone-pair donor, all simple models correctly favor that a hydrogen donor should approach along the lone-pair axis. No *ab initio* studies have examined the size of the force constant for moving off this line, but Schuster's CNDO/2 results[107] clearly show that this force constant should be much higher than the corresponding one for O and F sp^3 electron donors.

What about carbonyl donors? Both Morokuma and Dreyfus and Pullman have studied dimers with a carbonyl group as the base, and both find that the difference in energy between the favored lone-pair direction ($\theta = 60°$) and the approach between the lone pairs is 1.5 kcal/mol, significantly greater than that found in the sp^3 donors. Morokuma's INDO results and Schuster's CNDO/2 studies find a far smaller (0.6 kcal/mol) difference between lone-pair and dipole favored directions. Neither of these figures is very large when one considers the packing of large molecular crystals, so the wide variety of angles observed by Donahue on different carbonyl donors is not surprising.

The directionality of sp-hybridized electron donors (*e.g.*, nitriles) has not been studied theoretically, but it is likely that the force constant for bending off the N···H—X line would be higher than the corresponding angle in sp^3- and sp^2-hybridized systems.

In summary, theoretical studies imply that H bonds tend to favor those directions predicted by simple hybridization arguments. However, in the case of sp^3 O and electron donors, the potential curve for bending off the "ideal" hybrid line is quite small (~0.1–0.5 kcal/50° bend); in sp^2 donors the energy differences are about 1.5 kcal/mol between the lone-pair and dipole favored direction. Recently, Kollman has attempted to rationalize these trends in terms of the symmetry of the molecular orbitals of the donor and acceptor.[130]

B. SPECTROSCOPIC PROPERTIES

1. Vibrational Properties of Hydrogen-Bonded Systems

a. Vibrational Transitions

The method most commonly used to identify the presence of hydrogen bonding is infrared spectroscopy. A number of theoretical studies have attempted to examine the X–H stretching force constant change upon hydrogen-bond formation. Kollman and Allen have computed the infrared properties expected for $(H_2O)_2$, $(HF)_2$, and H_2O–HF[80] and have found a small increase in the X–H bond length as well as a very small decrease in the X–H force constant. (Morokuma and Winick found similar results for the water dimer.[59]) The decrease in the X–H bond force constant for water and HF dimers is much less than those found in liquid H_2O and HF, but this may be due to the closer X···X distance and different environment of the H bonds in the liquid (it is speculated that most of the large shifts observed in the liquid are due to favorable triplet configurations). The relatively small shifts found theoretically are, however, compatible with the matrix dimer work of Tursi and Nixon.[56] Dreyfus and Pullman found similar force constant changes in the linear formamide dimer.[101]

The O···O stretching force constant for the water dimer has been shown to be compatible with that found experimentally in ice;[59] very similar X···Y force constants are found in H_2O–HF and the HF dimer.[80] The hydrogen-bond bending force constant has been of interest to a number of workers. Kollman and Allen[80] have noted that the force constant for the bend in $(HF)_2$ is compatible with Pople's H-bond bending force constant[18] used to fit the experimental radial distribution function in water. They find that in the hydrogen fluoride dimer one can bend the H bond up to 20° with little energy loss; Dreyfus and Pullman find a similar flexibility in the formamide dimer.[101] Del Bene and Pople,[36] however, have examined all the intermolecular force constants in the water dimer and find the potential curves much steeper for movement of the proton donor molecule than the acceptor. In particular, their force constant for H-bond bending in the water dimer is considerably greater than Kollman and Allen's for the HF dimer. (This may be just a result of the greater H···H intermolecular repulsions in the water dimer when the H bond is bent.)

b. Infrared Intensities

Of special interest is the intensity increase observed in the X–H stretching region in hydrogen-bonded systems. Kollman and Allen[54] find relative intensity increases of 8 and 20 [$|\partial\mu/\partial r|^2_{\text{dimer}}/|\partial\mu/\partial r|^2_{\text{monomer}}$] for the linear water dimer at R(O–O) = 2.75 and 3.00 Å. Van Thiel's matrix isolation experiments[55] indicated an intensity ratio of 12, but the more recent studies of Tursi and Nixon[56] find a much smaller ratio. Kollman and Allen[80] find a much smaller intensity ratio in systems where H–F is the proton donor; Dreyfus and Pullman[101] find an intensity ratio of 11 in the formamide dimer. Quantitative comparison of these molecular orbital studies with experiment is difficult because one does not really know what the normal modes of the dimer structure are, but it appears that order-of-magnitude intensity enhancements do not require large amounts of charge transferred in hydrogen bonding; this is contrary to previous conclusions.[4,11]

Van Thiel, *et al.*,[55] observed a decrease in ir intensity of the bending mode of the water dimer in a rare gas matrix. Using Kollman and Allen's wave function,[54] one computes an intensity ratio [$|\partial\mu/\partial\theta|^2_{\text{dimer}}/|\partial\mu/\partial\theta|^2_{\text{monomer}}$] of 0.1, which is in qualitative agreement with experiment but unreasonably small (an estimate based on Van Thiel's spectra indicates that the ratio is of the order of 0.7).

c. Anharmonicity Effects in H-Bonded Systems

The change in anharmonicity in certain normal modes upon

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(130) P. A. Kollman, *J. Amer. Chem. Soc.*, **94**, 1837 (1972).

hydrogen bonding has been a subject of experimental and theoretical interest. A set of papers by Sandorfy[131] has shown that in weak hydrogen bonds there is a decrease in anharmonicity upon H-bond formation; in strong and moderate hydrogen bonds, the anharmonicity greatly increases. Fifer and Schiffer[132] have shown that in crystalline water hydrates such as $CuCl_2 \cdot 2H_2O$, the anharmonicity increases owing to stronger hydrogen bonding ($O—H \cdots Cl^-$ is stronger than $O—H \cdots O$). The qualitative conclusions of molecular orbital theory are consistent with the above results. The O–H stretch in the weak dimer $(H_2O)_2$[54,59] is still very similar to that in the water monomer, and one needs a large quartic force constant to fit the proton potential function in the strongly H-bonded HF_2^-.[26,90] In view of the well-known defects in molecular orbital calculations (overestimation of bond force constants in diatomics) and the very small perturbations observed in the water dimer spectrum, a detailed quantitative study of anharmonicity in H-bonded systems by molecular orbital calculations does not seem feasible or worthwhile.

d. Breadth of H-Bonded Ir Bands

The extreme breadth of the X–H stretching region when an $X—H \cdots Y$ hydrogen bond is formed has been explained by (a) Fermi resonance, (b) existence of different H-bonded molecular species, (c) sum and difference bands with the $X \cdots Y$ stretch (which has a frequency of 100–200 cm^{-1}), (d) anharmonicity changes upon H-bond formation, and (e) predissociation. A recent experimental study by Hall and Wood[133] gives good evidence that in phenol–pyridine systems the structure of the X–H stretch is due to overtone and combination bands of the proton donor, some of which are enhanced by Fermi resonance with the O–H stretch in these systems. Walrafen's recent Raman studies[71] on liquid water give an example where explanation b (different H-bonded species) may play a role in causing a broad O–H band. Whether one considers liquid water as two states or many, it is likely that there are hydrogen bonds of varying strength (and thus varying O–H frequencies) in water. Van Thiel, *et al.*,[55,82] pointed out that the narrow O–H stretching band of the water and methanol dimer in rare gas matrices is due to the absence of intermolecular coupling in these isolated dimers; Salthouse and Waddington have shown that the broadness of the asymmetric stretch in the bifluoride ion is due to intermolecular coupling between different FHF^- in the crystal.[134] Bertie and Millen[135] observed the X–H bands in HCl–ether complexes and explained the broad H–Cl stretching region in terms of coupling between the H–Cl and $O \cdots Cl$ vibrations (the latter having a force constant of 0.12×10^5 dyn/cm). All of the above explanations appear quite reasonable in the specific cases they have been applied to, so it is likely that in general no one of the above effects will completely explain the structure of the X–H stretch in different systems. It seems that the narrowness of the O–H stretching bands in simple H-bonded dimers at low temperature in rare gas matrices shows that the broadness of the O–H stretching bands is not intrinsic to the H bond but is caused by excitation of other modes (vibrational and rotational) of the overall complex.

e. Model Calculations

A number of model calculations have been carried out on hydrogen-bonded systems in an attempt to explain the intensity changes, spectral shifts, breadth, and temperature dependence of the infrared spectrum. Marechal and Witowski[136,137] and Singh and Wood[138] examine an interaction between the X–H stretch and the $X \cdots Y$ stretch of a hydrogen-bonded system, with the vibrational states of the complex designated by a quantum number for each mode. The former two authors studied the carboxylic acid system (two H bonds) and Singh and Wood solved the vibrational Hamiltonian (symmetric and asymmetric stretch) in a single H-bonded $A—H \cdots B$ structure. Marechal and Witowski are able to get a good fit to the experimental spectrum for the carboxylic acid dimer (and the deuterated dimer).[137] This success with the carboxylic acid spectrum, as well as the known experimental fact that in liquid water much of the breadth of the stretching mode is due to coupling between the stretches on different water molecules[139] (HO in D_2O has a far narrower O–H stretching band), is strong support that vibrational coupling plays a major role in causing a broad O–H stretching band. Recently, Robertson[140] has examined the role of predissociation as a potential cause of the broadness of the X–H stretching band. He concluded that for the types of A—H and $A \cdots B$ potentials likely in H-bonded systems, a predissociation mechanism (transition from an $A—H \cdots B$ vibrationally excited to an A-H molecule in its vibrational ground state and a B molecule infinitely separated from it) is unlikely to be an important source of line broadening. Robertson agreed with Marechal and Witowski's view that coupling between the A—H and $A \cdots B$ modes was the main source of the broadening of the A—H band in systems (such as the ones that Millen considered[135]) where Fermi resonance is not important. His attempt to quantitatively explain the HCl band in HCl–ether complexes was hampered by (1) the fact that the dependence of the H–Cl potential as a function of $O \cdots Cl$ distance is now known, and (2) the difficulty in considering the effect of low frequency intermolecular bending motions and rotational modes of the complex on the overall spectrum.

f. Semiempirical Calculations on Vibrational Properties

Examinations of X–H force constants, intensity enhancements, and $X \cdots Y$ force constants predicted in H-bonded systems by CNDO/2 show that the force constants found are similar to the results of *ab initio* calculations,[66] but that the intensity enhancements predicted by semiempirical results are too large (Table IV).

g. Strong H Bonds and the Proton Potential Function

In theoretical studies of typical "weak" H-bonded dimers

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(131) C. Berthomieu and C. Sandorfy, *J. Mol. Spectrosc.*, **15**, 15 (1965); G. Durocher and C. Sandorfy, *ibid.*, **15**, 22 (1965); A. Foldes and C. Sandorfy, *ibid.*, 20, 262 (1966).

(132) R. A. Fifer and J. Schiffer, *J. Chem. Phys.*, **52**, 2664 (1970).

(133) A. Hall and J. L. Wood, *Spectrochim. Acta, Part A*, 23, 1257 (1967).

(134) J. A. Salthouse and T. C. Waddington, *J. Chem. Phys.*, 48, 5274 (1968).

(135) J. E. Bertie and D. J. Millen, *J. Chem. Soc.*, 497 (1965).

(136) A. Witowski, *J. Chem. Phys.*, 47, 3645 (1967).

(137) Y. Marechal and A. Witowski, *ibid.*, 48, 3697 (1968).

(138) J. Singh and A. Wood, *ibid.*, 48, 4567 (1968).

(139) M. Haurie and A. Novak, *J. Chim. Phys.*, 62, 137, 146 (1965).

(140) G. Robertson, Ph.D. Thesis, Oxford University, 1970.

Table IV

Infrared Data by *Ab Initio* and CNDO/2 Calculations

	X–H stretch		X···X force constant
	$K_{\text{dimer}}/K_{\text{monomer}}$	$\left\|\partial\mu/\partial r\right\|^2_{\text{dimer}}/\left\|\partial\mu/\partial r\right\|^2_{\text{monomer}}$	(10^5 dyn/cm)
$(H_2O)_2$, *ab inito*[a]	0.96	8.2	0.18
$(H_2O)_2$, CNDO/2[b]	1.02	16	
$(HF)_2$, *ab initio*[a]	1.00	1.9	0.26
$(HF)_2$, CNDO/2[b]	1.10	180	

[a] Reference 54 and 88. [b] Reference 66.

such as $(HF)_2$ and NH_3HF, no double minimum potential well is found for the proton at the minimum energy X···Y distance, although at larger X···Y separations a second, higher energy minimum appears. These results are found in both semiempirical and *ab initio* molecular orbital calculations.[99,119,134,135,141,142] One of the main defects with extended Hückel theory is that it predicts a double minimum potential well at the minimum energy O···O distance for the water dimer and finds a lower energy for the $H_3O^+OH^-$ well than the H_2OHOH structure.[143] Bell and Barrow[144] gave experimental evidence for the existence of a double minimum potential in weak H-bonded complexes involving ethanol as proton donor. Their proposal was based on a solvent-dependent second absorption in the O–H overtone region of ethanol. However, there are other explanations for this second peak, for example, that it is due to $2\gamma_b + \gamma_s$, which interacts more strongly with $2\gamma_s$, the stronger the hydrogen bond. Based on the theoretical dimer results, one is tempted to conclude that in weak H-bonded dimers in the *gas phase*, there is only one proton minimum at the minimum energy X···Y separation. However, more extensive configuration interaction results on, for example, $(HF)_2$ are needed to substantiate this conclusion.

The potential surface for the bifluoride has been theoretically examined by McLean, Erdahl, Noble, and Kortzeborn and Kollman and Allen. Ibers'[145] best fit to the experimental ir and Raman data used a potential of the form $V = {}^1/_2 k_s Q_s{}^2 + {}^1/_2 k_a Q_a{}^2 + aQ_a{}^4 + bQ_a{}^2Q_s$, where Q_a is the "normal coordinate" for the asymmetric stretch and Q_s the "normal coordinate" for the symmetric stretch. The force constants derived from the theoretical studies[146] are not particularly encouraging; the lowest energy SCF calculation (McLean and Yoshimine[89]) gives qualitatively reasonable force constants, but the next lowest energy work (Noble and Kortzeborn[90]) found much poorer agreement; Kollman and Allen[26] actually fit the force constants best. Erdahl's valence bond results[28] were in poorer agreement with experiment than Kollman and Allen's SCF calculation.

Kollman and Allen[26] and Kraemers and Diercksen[92] have examined the proton potential well in $H_5O_2^+$. Unlike HF_2^- which has a relatively steep single proton well at the minimum energy F–F distance of 2.26 Å, $H_5O_2^+$ has an extremely shallow proton well at the minimum energy O–O distance of 2.38 Å (the energy varies only 0.04 kcal/mol when the proton is moved from the center of the O–O bond to a position 0.15 Å from the center of the bond). In addition, Kollman and Allen found that the potential could not be fit with the four-parameter function which gave qualitative agreement with experiment for HF_2^-.[26] The double well for proton motion found when the O–O distance was 2.48 Å had an energy barrier of only 300 cm^{-1}, so that the proton well was still in effectively a single well at this geometry. One would expect, however, that at distances greater than 2.5 Å the proton would become localized in one of the wells, and one would have an asymmetric hydrogen bond. This is what is observed experimentally; at distances greater than 2.5 Å the H bonds are usually asymmetric.[6] A manifestation of this is the very large isotope effect in crystals of $HCrO_2$, which has a symmetric proton well with O–O distance 2.48 Å. In $DCrO_2$, on the other hand, the deuterium is in an asymmetric proton well, with the O–O distance 2.54 Å. Rundle has given a qualitative rationalization of this.[147] This unusual isotope effect manifests itself in other systems as well.[148] The calculations of Kollman and Allen,[25] Kraemers and Diercksen,[92] and de Paz, *et al.*,[93] provide a qualitative rationalization of the unusual proton mobilities in H_2O. The CNDO/2 studies of de Paz, *et al.*, show an interesting difference between positive hydrated ions ($H_{2n+1}O_n^+$) and negative hydrated ions ($H_{2n-1}O_n^-$). In the positive series all the protons in the cluster are nearly equally positive, with the plus charge distributed evenly among the fragments. In the negative series the central protons are quite positive, whereas the external hydrogens have a slight negative charge. Thus, de Paz, *et al.*, view these species as OH^- groups held together by protons.

Schuster[108] has studied the enol form of acetylacetone by CNDO/2 and has found good structural agreement with experimental X-ray, nmr, and ir data. The H-bonded proton in acetylacetone is in a double well, although the energy barrier is less than 200 cm^{-1}. In the excited triplet state Rauh[149] finds an even shallower proton potential well.

Model calculations on proton transfer reactions have been carried out by Pshenichov and Sokolov[150] and Fischer, *et al.*[151] The former authors considered proton transfer reactions

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(141) At long enough X···Y separations, every X—H···Y system will have a double minimum proton potential function. But in view of the calculations carried out by Kollman and Allen[127] and de la Vega,[142] it appears that at the minimum X···Y separation in the *gas phase*, only one proton well exists. The best experimental evidence for a double minimum well in singly H-bonded systems is Baba, *et al.*'s,[143] study of trinitrophenol–triethylamine H bonds. It may be, however, that solvent effects play a crucial role in stabilizing the ionic structure and that a gas-phase study (or accurate theoretical calculation) would find only a single well plus an inflection point. (Baba, *et al.*,'s extrapolation to dielectric constant unity implies a finite, but shallow, second minimum for the ionic form.) Definitive gas-phase work or a more precise understanding of solvent effects is required to make any meaningful comparisons of theoretical and experimental proton potential functions in neutral X—H···Y systems. CNDO/2 studies on a number of neutral dimers have found single minimum proton potential functions at the minimum energy X···Y distance with the exception of the pyridine–methanol dimer.[8] There is no experimental evidence on whether this double well is real or spurious.

(142) Y. Fang and J. R. de la Vega, *Chem. Phys. Lett.*, **6**, 117 (1970).

(143) H. Baba, A. Matsuyama, and H. Kokubun, *Spectrochim. Acta, Part A*, **25**, 1709 (1969).

(144) C. Bell and G. Barrow, *J. Chem. Phys.*, **31**, 300 (1959).

(145) J. A. Ibers, *ibid.*, **41**, 25 (1964); **48**, 539 (1968).

(146) The force constants based on the McLean and Yoshimine[89] energies were determined by Noble and Kortzeborn.[90]

(147) R. E. Rundle, *J. Phys. Chem. Solids*, **25**, 487 (1964).

(148) S. J. Chan, L. Lin, D. Clutter, and P. Dea, *Proc. Nat. Acad. Sci. U. S.*, **65**, 1129 (1970).

(149) D. Rauh, personal communication.

(150) E. A. Pshenichov and N. D. Sokolov, *Int. J. Quantum. Chem.*, **1**, 855 (1967).

(151) S. F. Fischer, G. L. Hofacker, and M. A. Ratner, *J. Chem. Phys.*, **52**, 1934 (1970).

of the form $AH + B \rightarrow A^- + BH^+$, $A^- + BH \rightarrow AH + B^-$, and $AH^+ + B \rightarrow A + BH^+$. They noted that the first reaction was unlikely except in polar media (see above) and derived kinetic rate constants for proton transfer in the case of ionic reactants. Fischer, *et al.*, used a quasi-particle model to predict absorption spectra for ionic defects (*e.g.*, H_3O^+ in H_2O) in hydrogen-bonded solids. Singh and Wood's calculations[138] may be of great use in rationalizing much of the vibrational and isotope effects in H bonds because they present a solution to the $A—H \cdots B$ two vibrational mode Schrödinger equation for various potential parameters. The strange nature of the potential in $H_5O_2^+$,[26] however, may make this case difficult to rationalize with a single $A—H \cdots B$ fragment, and one needs a quasi-particle or nuclear dispersion force model[152] to proceed further.

h. Other H-Bond Potential Functions

Models for the proton potential function to apply to spectroscopic results have been discussed in a previous section; here we are concerned with attempts to represent the energetics of the H bond in terms of analytical functions of the intermolecular separation. Lippincott and Schroeder[153] have proposed a function which represents the H-bond potential energy as a function of $R(X \cdots Y)$ and $R(X—H)$. Others have modified this function to include H-bond bending[154] and isotope effects[155] among other things.

Even though these functions give qualitative agreement with many of the experimental properties of H bonds, they are empirical functions and not useful for understanding the underlying principles of hydrogen bonding. The need for an adequate analytical potential function for hydrogen bonding in applications is great; examples of areas where such a function is useful are the stereochemistry of biopolymers[156] and the interpretation of second dielectric virial coefficients.[157]

2. *Nmr Spectroscopy on Hydrogen-Bonded Systems*

Nmr is a very common tool for the study of hydrogen bonding, but very few theoretical studies on chemical shifts of H-bonded systems have been published. This is because, even for smaller molecules, the paramagnetic contribution to the chemical shift is large and usually requires some knowledge of excited states. It is interesting to note that in liquid HF,[158] H_2O,[15] and NH_3[16] both the proton and ^{19}F (^{17}O, ^{15}N) resonances are shifted downfield upon hydrogen bonding. Thus simple shielding–deshielding ideas do not work even qualitatively to explain both proton and ^{19}F resonances. Recent solutions of the perturbed Hartree–Fock equations to determine proton chemical shifts in NH_3 and H_2O among others give relatively poor agreement with experiment.[159] The agreement is worse if there is more than one "heavy" center in the molecule[160]. de Jeu,[117] using a more semiempirical approach to the problem, has examined the hydrogen bonding and protonation of acetone in sulfuric acid–water solutions by iterative extended Hückel theory and CNDO/2. He used the spin coupling theory of Pople and Santry[161] and estimated the paramagnetic contribution to the chemical shift with the formula of Karplus and Das.[162] Although some qualitative trends were reproduced, agreement between theory and experiment was far from satisfactory. It appears that SCF calculations will be of little predictive value in predicting the chemical shift and coupling constant changes which accompany H-bond formation, but it would certainly be of interest to see whether an *ab initio* calculation can do a significantly better job than the semiempirical methods. There are a large number of contributions to the chemical shift change which accompanies intermolecular interaction, and it is unlikely that unique hydrogen-bonding contribution can be separated from the other terms,[163] since each of them is of necessity somewhat parameterized.

All the MO studies on H-bonded systems (see section III.C) indicate that the proton loses charge on H-bonding, so it is clear that a decrease in the diamagnetic shielding is an important contribution to the downfield shift observed in hydrogen bonding studied with proton nmr. The magnitude of this charge loss ($\sim{}^1/_{20}$ electron) would predict a shift of $\sim$1 ppm, so it is likely that electric field effects are important.[163]

The change in field gradients at protons involved in H-bond formation can be determined by nmr. Weissman,[164] using an approximate MO wave function, has noted that much lower field gradient at the deuteron in ice than in gas-phase water is due more to a lengthening of the O–D bond in ice than the H-bonding effect of the nearby water. By using the wave functions reported in ref 50, we have computed the field gradient at the deuteron in the water monomer [R(O–H) = 0.96 Å], the water dimer [R(O–O) = 2.75, with H bonding toward the lone pair and r(O–H) = 0.96 Å], and the water dimer [same dimer orientation with r(O–H) = 1.01 Å]. The calculated values are compared with Weissman's and experimental deuteron quadrupole coupling observed in solid-state nmr in Table V. Our calculations support Weissman's inter-

Table V

Deuteron Coupling Constants in Water and Ice

	Water monomer r(O–H) = 0.96 Å		*Water dimer r(O–H) = 0.96 Å*		*Water dimer r(O–H) = 1.01 Å*	
	q^a	n^b	q	n	q	n
Kollman[d]	0.587	0.10	0.537	0.10	0.364	0.11
Weissman[e]	0.592	0.08	0.528	(0.08)	0.361	(0.08)
Experiment[e]	0.479	<0.12			0.330[c]	0.1

[a] Value of q_{zz} (largest component) in principal axis system; the z axis turns out to be nearly along the O–D bond. [b] Asymmetry parameter $q_{\alpha\alpha} - q_{\beta\beta}/q_{\gamma\gamma}$, where $|q_{\gamma\gamma}| \geq |q_{\beta\beta}| \geq |q_{\alpha\alpha}|$. [c] Value found in ice I. [d] Reference 54. [e] Reference 164.

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(156) D. Poland and H. A. Scheraga, *Biochemistry*, 6, 3791 (1967).

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(161) J. A. Pople and D. P. Santry, *Mol. Phys.*, 8, 1 (1964); 9, 311 (1965).

(162) M. Karplus and G. Das, *J. Chem. Phys.*, 34, 1683 (1961).

(163) See, for example, W. T. Raynes, A. D. Buckingham, and H. J. Bernstein, *ibid.*, 36, 3481 (1962).

(164) N. Weissman, *ibid.*, 44, 422 (1966).

pretation. An examination (by Kern and Karplus[165]) of the deuteron quadrupole coupling constant expected for DF_2^- found a value of $q \sim 0.15$ au [$eQq/h \sim 100$ cps] for the best basis set reported by Clementi and McLean for FHF^-.[166] A calculation of the field gradient at the deuteron using the wave function of Kollman and Allen[26] yields values of $q = 0.165$ au (no p polarization functions) and $q = 0.102$ au (with p polarization functions). To the authors' knowledge, no experimental value is available.

In Davis and Deb's review,[10] both the methods and results on recent nmr studies of H bonding are discussed. The experimental solution studies are most useful when combined with ir results on the same system. However, as Davis and Deb note, the fact that in nmr studies one sees only an average signal considering different possible interactions and proton exchange processes leaves a wide "gap" between a theoretical dimer study and a solution nmr signal. Clearly more gas-phase experimental studies are desirable, but in many systems (*e.g.*, steam), the concentration of the dimer at reasonable temperatures and pressures is so low that it will be difficult to detect, and, as noted above, it will be difficult to separate out the component of the chemical shift due to hydrogen bonding.

3. Electronic Spectral Properties of Hydrogen-Bonded Systems

Hydrogen bonding usually causes significant perturbations on the electronic transitions of the system, and the most commonly studied effects are the blue shift of the $n-\pi^*$ transition (the hydrogen bond is stronger in the ground than in the excited state) and the shift (either blue or red) in the $\pi-\pi^*$ transition of the system. Most of the reported theoretical studies on the $\pi-\pi^*$ transition of such systems have used π electron theory, modifying the core parameters to take into account the presence of the hydrogen bond. Bratoz[11] concluded that the charge-transfer model (where the change in core parameter takes into account the electron repulsion changes brought about by charge transfer) is more successful in explaining $\pi-\pi^*$ electronic transition shifts than the simple electrostatic model, but both models are too highly parameterized to give much physical insight into the problem. It is quite clear that an *ab initio* SCF-MO (including configuration interaction) on a small model system such as $H_2CO\cdots HF$ might answer such questions as (1) what is the detailed electronic redistribution in the excited $\pi-\pi^*$ and $n-\pi^*$ states and how do substituent effects change the relative energies and charge distributions of these states, (2) how can one rationalize observed electronic shifts in terms of this detailed charge redistribution, and (3) could the large intensity change in the electronic band be explained in terms of transition dipole changes upon H-bond formation? Some of these problems are now being studied by Morokuma.[167] de Jeu[168] has carried out some CNDO/2 studies on $H_2CO\cdots HOH$ and finds that the H bond is only slightly weaker in the $n-\pi^*$ triplet state of formaldehyde than in the ground state. He also finds a blue shift for the $n-\pi^*$ transition upon H-bond formation of 0.06 eV. The reader is referred to the Bratoz review for a more detailed discussion of H bonds in excited states.

4. Conclusions

Molecular orbital studies on infrared, nmr, and electronic spectral properties of H-bonded systems can at best be of a semiquantitative nature since the properties predicted by these methods for monomers are usually only accurate to 10–20%. The calculations of spectral properties can be of most use in the case of weak dimers where the experimental studies are difficult. It is important, however, that molecular orbital studies give the right qualitative behavior for force constants in H-bonded systems and also predict some constants (such as H-bond bending) difficult to determine experimentally.

Model potential functions[136–138] are of use in understanding some H-bond vibrational properties, but continue to be hampered by lack of precise *a priori* knowledge of the potential functions involved.

III. Mechanism of Hydrogen Bonding

A. DECOMPOSITION OF THE HYDROGEN-BOND ENERGY

It is well established that charge cloud repulsion and electrostatic and charge redistribution (polarization + charge transfer) are all major contributors to the hydrogen-bond energy. Thus one would hope that precise knowledge of each of the terms in different H-bonded systems would give one a greater understanding of the hydrogen bond.

Coulson and Danielson[21] and Tsubomura[22] attempted to compute the different contributions to the H-bond energy (as well as dispersion) as follows. The four electrons involved in the hydrogen bond were allowed to be distributed over three basis orbitals, x, h, y, one centered on X, H, and Y in an $X—H\cdots Y$ bond (the effect of changes in hybridization of the basis orbital on X and Y was considered). The total wave function constructed was

$$\Phi = C_1X_1 + C_2X_2 + C_3X_3$$

where

$$X_1 = N(|x_\alpha h_\beta y_\alpha y_\beta| - |x_\alpha h_\beta y_\alpha y_\beta|)$$

$$X_2 = |x_\alpha x_\beta y_\alpha y_\beta|$$

$$X_3 = N(|x_\alpha x_\beta y_\alpha y_\beta| - |x_\alpha x_\beta y_\beta y_\alpha|)$$

where the vertical rules indicate a determinantal form for the wave function and the subscripts represent the electron spin. The chemical structures represented by X_1, X_2, and X_3 are $X—H\cdots Y$, $X^-H^+\cdots Y$, and $X^-H—Y^+$, respectively. A stabilization due to a change in the coefficients C_1 and C_2 upon H-bond formation (relative to their values in the free molecule) represents the polarization energy of the hydrogen bond, and a nonzero value of C_3 is an indication of a charge-transfer contribution. The 3 × 3 Hamiltonian matrix is constructed with appropriate estimates of the covalent bond energy, short-range repulsion, ionization potential of Y and electron affinity of X and the polarization energy. The off-diagonal elements were estimated in such a way that the 2 × 2 secular equation (considering only structures 1 and 2 in the absence of the proton acceptor molecule) gives the exact O-H bond energy. The basic conclusions of the valence

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(165) C. Kern and M. Karplus, *J. Chem. Phys.*, 42, 1062 (1965).

(166) E. Clementi and A. D. McLean, *ibid.*, 36, 745 (1962).

(167) K. Morokuma, personal communication, Oct 1970.

(168) W. de Jeu, *Chem. Phys. Lett.*, 7, 153 (1970).

bond theory are: (1) the contribution to the H-bond energy of electrostatic, repulsion, and dispersion and charge transfer are of the same order of magnitude, and all absolute values are close to the total hydrogen-bond energy; (2) the contribution of C_3 to the overall wave function is a very strong function of R(X–Y) and R(X–H); and (3) for long bonds, the H bond is essentially electrostatic.

Recently, Duijneveldt, *et al.*,[169] in a series of papers has attempted to calculate directly some of the contributions to the hydrogen-bond energy using the intermediate overlap perturbation formalism developed by Murrell, *et al.*[170] Variations in the ionic character of the A–H bond and the hybridization of the B lone pair allow Duijneveldt to compare the properties of different hydrogen-bonded systems. Although the H-bond energies he computes are not in especially good agreement with more accurate calculations, he is able to rationalize the trends in first-row dimer H bonds (NH_3, H_2O, HF). The main weakness of this approach is that it uses a three-center, four-electron model, which is a great oversimplification of the problem.

One would also like to decompose the energies calculated by the *ab initio* molecular orbital approaches into the different contributions, and such decompositions have been carried out by Kollman and Allen,[171] Dreyfus and Pullman,[101] and Morokuma.[105] Kollman and Allen have divided the H-bond energy into two contributions: (a) the electrostatic and exchange repulsion energy, which is the energy of the complex with the monomer charge distributions the same as those at infinite separation, and (b) the polarization plus charge-transfer energy, which is the energy difference between the SCF converged solution for the complex and the energy found in (a). They also empirically estimated the dispersion energy. Dreyfus and Pullman further divided term a into electrostatic and exchange contributions by considering the difference in energy between (1) a completely antisymmetrized wave function at the dimer internuclear distance (electrostatic + exchange) and (2) the wave function which is antisymmetrized among the individual monomers but not between the monomers (only electrostatic energy). Morokuma's energy decomposition is the most complete in that he further subdivided the charge redistribution energy into charge transfer and polarization by finding the SCF converged solutions of wave functions 1 and 2. Kollman and Allen show, on the basis of their decomposition, that the nonlinear configuration of $(HF)_2$ is due to the charge redistribution term. Dreyfus and Pullman's calculation indicates that the electrostatic energy is significant (~2 kcal/mol) at $R(N\cdots O) = 5$ Å, but exchange terms only are nonnegligible at distances shorter than 3.75 Å. Morokuma notes that the key difference between σ and π H bonds is the larger electrostatic contribution to the former. The results of the energy decomposition studies are summarized in Table VI. While the above decompositions give interesting insight into certain H-bond properties, the various energy components are clearly more sensitive to basis set (and $X\cdots Y$ distance) than the H-bond energy. Thus a decomposition study with a much more flexible basis set is in order (*e.g.*, that of ref 60).

B. IS A HYDROGEN BOND A CHARGE-TRANSFER INTERACTION?

The role of charge transfer in hydrogen bonding is a much discussed question. As noted previously, the charge-transfer model attempts to rationalize all the "nonclassical electrostatics" aspects of hydrogen bonding in terms of an electron transfer from the proton acceptor molecule to the proton donor molecule. This model is appealing in a sense because it makes hydrogen bonding a subcategory of a more general class of compounds (all donor–acceptor complexes). However, the correlation between ionization potential of the base and K or ΔH of H-bond formation is quite limited.[173] The dipole enhancement upon H-bond formation can only be partially explained by charge transfer, and, in the infrared X–H stretch intensity enhancement, charge transfer is clearly not the only mechanism. Table VII records the intensity enhancements predicted for $(H_2O)_2$, $(HF)_2$, H_2OHF, and HFHOH assuming that the charge transferred is from one heavy atom to the other. The net enhancement found is listed in the next column. It is clear that charge transfer can explain some, but not the majority, of the observed enhancement. Dreyfus and Pullman conclude that of the 11.5 intensity enhancement in formamide, 3.5 is due to the charge-transfer effect. The most important experimental argument against using a charge-transfer model for hydrogen bonding is that there is very little evidence for charge-transfer bands in hydrogen bonding.[2]

One could not argue that "charge transfer" plays no role in hydrogen bonding, only that the qualitative phenomena associated with H bonding can be explained without invoking a large charge-transfer contribution. Hanna's work on electron donor–acceptor systems such as benzene–I_2 pursues a similar line of thought. Although the systems Hanna[174] chooses probably have a larger charge-transfer contribution than most H bonds, he shows that classical electrostatic effects are not negligible in those systems more traditionally called charge-transfer complexes. Mulliken,[175] however, argues that although electrostatic effects are important, the charge-transfer contribution is the organizing principle for most electron donor–acceptor complexes. It is our feeling that those systems which have an *experimentally* well-defined CT spectra can be treated with a charge-transfer model (with appropriate allowance for other effects); those that do not have a charge-transfer spectrum should not be examined with a charge-transfer model.

A more fundamental reason against using a two-determinant charge-transfer model to understand hydrogen bonding is that as the hydrogen bond gets stronger, the amount of "charge transferred" does not increase. [This is in contrast to charge-transfer interactions $\psi_t = a\varphi(A\text{-}B) + b\varphi(A^+B^-)$, where the stronger the complex, the larger b is.] An excellent example of this is Clementi's study[50] of the NH_3HCl reaction. At first, as one brings NH_3 closer to HCl (keeping the intramolecular distances fixed), charge is transferred from the NH_3 to the HCl. Eventually, however, the H–Cl bond length-

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[169] F. B. van Duijneveldt and J. N. Murrell, *J. Chem. Phys.*, **46**, 1759 (1967); F. B. van Duijneveldt, *ibid.*, **49**, 1424 (1968); J. G. C. M. van Duijneveldt-van de Rijdt and F. B. van Duijneveldt, *Chem. Phys. Lett.*, **2**, 565 (1968); *Theor. Chim. Acta*, **19**, 83 (1970); *J. Amer. Chem. Soc.*, **93**, 5644 (1971).

[170] J. N. Murrell and G. Shaw, *J. Chem. Phys.*, **46**, 1768 (1967); J. N. Murrell, *Chem. Brit.*, **5**, 107 (1969).

[171] P. A. Kollman and L. C. Allen, *Theor. Chim. Acta*, **18**, 399 (1970).

[172] C. A. Coulson, *Research (London)*, **10**, 149 (1957).

[173] See, for example, M. D. Johnston, F. P. Gasparro, and I. D. Kuntz, *J. Amer. Chem. Soc.*, **91**, 5715 (1969), for some exceptions.

[174] M. W. Hanna, *ibid.*, **90**, 285 (1968); M. W. Hanna and D. E. Williams, *ibid.*, **90**, 5358 (1968).

[175] R. S. Mulliken and W. B. Person, *ibid.*, **91**, 3409 (1969).

Table VI

Decomposition of H-Bond Energies (kcal/mol)[a]

System	*(1)* *Electrostatic*	*(2)* *Exchange*	*(1)* + *(2)*	*(3)* *Charge Transfer*	*(4)* *Polarization*[b]	*(3)* + *(4)*	*Dispersion*[c]
$(H_2O)_2$[d] $R = 2.8$ Å $\theta = 50°$			4.50			3.05	1.54
$(H_2O)_2$[e] $R = 2.76$ Å $\theta = 57°$	8	−9.86	−1.86	8.16	0.25	8.41	
$(HF)_2$[h] $R = 2.8$ Å $\theta = 60°$			5.25			1.49	1.53
H_2CO-H_2O[e] (minimum energy geometry)	4.64	−6.71	−2.07	5.34	0.18	5.52	
Formamide linear[f] dimer (minimum energy geometry)	10	−7	3.0			5.0	
$(H_2O)_2$[g]	6	−8.4	−2.4			8	3
H_2O as proton[h] donor [R(H···X) = 1.85 Å]	13	−11.8	1.2	2.22	0.70	2.92	1.66

[a] Stabilization is a positive quantity; destabilization is negative. [b] Polarization refers to charge redistribution within the fragments (as opposed to charge transfer). [c] Dispersion energy — long-range van der Waals attraction. [d] Reference 171. [e] Reference 105. [f] Reference 101. [g] Reference 172. [h] Reference 171.

Table VII

Comparison of Ir Intensity Enhancements Found and Those Expected on the Basis of Charge Transfer

System	$\lvert\partial\mu/\partial r\rvert^2_{\mathrm{dimer}}/\lvert\partial\mu/\partial r\rvert^2_{\mathrm{monomer}}$	$[\partial\mu/\partial r + CT]^2_{\mathrm{monomer}}/\lvert\partial\mu/\partial r\rvert^2_{\mathrm{monomer}}$
$(H_2O)_2$, R(O···O) = 2.75 Å[a]	20	4.1
$(H_2O)_2$, R(O···O) = 3.00 Å[a]	8.2	2.0
$(HF)_2$, R(F···F) = 2.88 Å[b]	1.9	1.5
H_2OHF, R(O···F) = 2.65 Å[b]	5.0	2.1
HFHOH, R(O···F) = 3.10 Å[b]	4.5	1.2
Formamide dimer, R = 2.85 Å[c]	11.5	3.5

[a] Reference 54. [b] Reference 80. [c] Reference 101.

ens, and at the minimum energy position, the H is roughly halfway between the electron donor (NH_3) and the electron acceptor (Cl). If one divides up this hydrogen's electrons and gives roughly half to Cl and half to NH_3, one sees that the electron-acceptor fragment (Cl) has actually less charge than it began with. This separation of charge is, of course, somewhat artificial, but the fundamental difference between H bonds and charge-transfer complexes can be stated as follows. In charge-transfer complexes, the amount of charge transferred increases monotonically with increase in strength of the complex; in H bonds, this is not the case.

Clementi has examined the H_3NHCl system in detail.[50] He finds that the H_3 group acts as a donor of π electrons; the nitrogen acts both as acceptor of π electrons from the ammonia hydrogens and donates σ electrons to the chlorine *via* the chlorine hydrogen. The chlorine is mainly a σ acceptor. This description of the H_3NHCl complex is much more satisfactory than a simple two-determinant analysis.

C. CHARGE REDISTRIBUTION AND MOLECULAR ORBITAL ENERGY SHIFTS

Virtually all of the workers who studied energies and geometries of H-bonded systems performed population analyses on both the complexes and the isolated monomers. Certain interesting generalizations emerge from these results.

(1) The hydrogen in the H bond loses electrons upon hydrogen bonding.

(2) The electronegative atoms gain electrons; more electrons are gained by the electronegative atom on the proton donor molecule.

(3) The largest loss of electrons occurs at the hydrogens (or carbon) immediately attached to the proton acceptor molecule.

(4) All hydrogens attached to the electronegative atom of the proton donor molecule (away from the hydrogen bond, *e.g.*, H—X—H···Y) gain electrons upon H-bond formation.

(5) The charge changes on the atoms immediately attached to the three-center hydrogen bond are of the same magnitude as those in the bond.

(6) In the reaction between, *e.g.*, $H_3N\cdots HCl$[50] or $H_3N\cdots HF$,[119] varying both the X–Y and X–H distance, the electronic effect is a transfer of charge from the hydrogens on the nitrogen to the chlorine, with the hydrogen on the chlorine losing charge and the nitrogen staying nearly neutral (at first, gaining a small amount of charge).

(7) In linear polymers (water trimer[65] and HF linear hexamer[60]) the charge shifts indicate that there is little excess charge on the middle molecules, with the charge transfer from one end molecule to the molecule on the other end. For example, in linear $(HF)_6$, the total charges in

$$\mathrm{F{-}H\cdots F{-}H\cdots F{-}H\cdots F{-}H\cdots F{-}H\cdots F{-}H}$$

Table VIII[a]

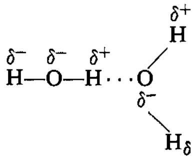
Charge Redistribution in Hydrogen-Bonded Systems

	Common protein donor				*Common protein acceptor*			
	System	ΔE	*Charge shift*	*Charge transfer*	*System*	ΔE	*Charge shift*	*Charge transfer*
NH_3	$HFHNH_2$	1.3	0.0165	0.0005	H_3NHF	11.7	0.0448	0.0313
	H_2OHNH_2	2.3	0.0280	0.0017	H_3NHOH	5.8	0.0422	0.0100
	H_3NHNH_2	2.7	0.0331	0.0036	H_3NHNH_2	2.7	0.0331	0.0036
H_2O	$HFHOH$	3.0	0.0231	0.0016	H_2OHF	9.4	0.0433	0.0218
	H_2OHOH	5.3	0.0391	0.0064	H_2OHOH	5.3	0.0391	0.0064
	H_3NHOH	5.8	0.0422	0.0100	H_2OHNH_2	2.3	0.0280	0.0017
HF	HFHF	4.6	0.0270	0.0040	HFHF	4.6	0.0133	0.0040
	H_2OHF	9.4	0.0443	0.0176	HFHOH	3.0	0.0083	0.0016
	H_3NHF	11.7	0.0448	0.0313	$HFNH_2$	1.3	0.0042	0.0005

[a] Reference 119.

are 10.039, 10.005, 10.001, 9.999, 9.996, and 9.962. In the H_2O linear duodecamer [all R(O–O) = 2.53 Å], the charges are 10.054, 10.002, 9.998, 9.999, 10.006, 10.001, 10.000, 10.001, 10.000, 9.998, 9.994, and 9.947.[176]

Kollman and Allen (KA)[80] and Dreyfus and Pullman (DP)[101] have also examined complete charge-density difference maps for the dimers $(H_2O)_2$, $(HF)_2$, H_2OHF, and formamide. The density differences near the atoms are in good agreement with the Mulliken atomic populations, but the overlap regions are much more interpretable in charge density maps. The most significant result of these is that in the H···Y region of H bonding there is a charge decrease upon complex formation. DP have shown that this effect is partially, but not all, due to exchange repulsion. Coulomb repulsion must also play a role. This effect clearly demonstrates the difference between hydrogen bonding and ordinary covalent bonds; in the latter (*e.g.*, H_2) the region in the "bond" gains electrons when the two centers come together. A very important generalization is number four. The fact that, upon dimer formation, the charge shifts are as follows



rationalizes why an (O···HOH···O) triplet is less stable than the (OH···OH···O);[36] in the (O···HOH···O) configuration the third water is donating a pair of electrons to a hydrogen which already has *more electrons* than in the water monomer. (See Table VIII for some results on *charge shift* and *charge transfer* in H-bonded systems.)

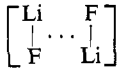
D. WHAT MAKES A HYDROGEN BOND UNIQUE?

Both Coulson[172] and Murrell[170] conclude that what makes an H bond different from other short-range intermolecular interactions is the smallness of the exchange repulsion.

Kollman, *et al.*,[120] have attempted to throw some light on this question by carrying out *ab initio* calculations on LiF···LiF, LiF···HF, HF···LiF, and HF···HF. The infrared properties in lithium-bonded systems were similar to those in the H-bonded systems, but the *charge redistribution* accompanying lithium-bond formation was different from that in hydrogen bonds. For example, the lithium gains charge (in the Mulliken population analysis) on lithium-bond formation. This gain in charge occurs because lithium has much more accessible empty π orbitals than hydrogen.

Although Kollman, *et al.*,[120] did not decompose the total energy into components, it is clear from the monomer charge distributions (LiF has a large dipole moment), the charge redistributions observed in Li-bond formation (greater than the corresponding H bonds), and the presence of a filled inner shell on lithium that the electrostatic, exchange repulsion and delocalization are all larger in magnitude than in the H-bond case. Thus, it is not really satisfying to say that the hydrogen bond is unique because of its small exchange repulsion, since a large exchange repulsion could be compensated by even larger electrostatic and charge redistribution energies (as in the Li bond).

A less general comparison of lithium bonding and hydrogen bonding is as follows. The minium energy structure of $(LiF)_2$ is cyclic



whereas that of $(HF)_2$ is linear HF···HF. This is because the bond in LiF is ionic enough that the greater electrostatic attraction and smaller charge cloud repulsion in a configuration such as $(\pm\mp)$ make up for the less charge redistribution energy (delocalization) (compared to $+\ -\ \cdots\ +\ -$). In $(HF)_2$, one does not gain enough electrostatic energy in the cyclic structure to make up for the greater delocalization energy of the linear dimer. Thus, one could say that the main difference between hydrogen and lithium bonding is the greater relative importance of charge redistribution energy in hydrogen bonding.

Molecular orbital energy shifts demonstrate a difference between H bonds and covalent bonds. In the former, the proton donor levels increase in energy and the proton acceptor levels decrease; in the covalent bonds, both sets of orbitals usually increase upon bond formation. Kollman, *et al.*,[120] have noted the correlation between size of MO energy shifts and hydrogen-bond energy (Table IX).

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[176] P. Kollman, unpublished results.

Table IX[120]

Molecular Orbital Energy Shifts upon H-Bond Formation

System	ΔE, *kcal/mol*	*Av* ΔE *donor*	*Av* ΔE *acceptor*	$\lvert\Delta E\rvert$
NH_3HF	11.7	−0.045	+0.076	0.0605
NH_3HOH	5.9	−0.023	+0.043	0.033
NH_3HNH_2	2.7	−0.012	+0.031	0.0215
H_2OHF	9.4	−0.043	+0.057	0.050
H_2OHOH	5.3	−0.026	+0.040	0.033
H_2OHNH_2	2.3	−0.010	+0.024	0.017
HFHF	4.6	−0.040	+0.036	0.038
HFHOH	3.0	−0.024	+0.024	0.024
$HFHNH_2$	1.3	−0.012	+0.017	0.0145
LiFHF	24.8	−0.066	+0.145	0.1015
HFLiF	13.5	−0.0105	+0.040	0.0694

E. EXPERIMENTAL AND THEORETICAL CORRELATIONS IN H BONDS

Dominating most of the spectroscopic H-bond literature are the efforts to critically examine correlations between the experimentally determined properties: ΔH, ΔG, $\Delta\nu_{OH}$, ν(O–O stretch), R(O–O) (in crystals), base strengths, Hammett σ constants among others. The most widely discussed correlation is that of Badger and Bauer,[177] who proposed a linear relation between ΔH and $\Delta\nu$. There has been much discussion in the literature about whether there is a general $\Delta\nu$–ΔH relationship, and Drago has given a semiempirical argument rationalizing one,[178] but it appears at present to be unlikely (see Arnett *et al.*,[179] for references). The best least-squares linear relation for hydrogen bonds with phenol as proton donor is ΔH (kcal/mol) = $0.0103\Delta\nu_{OH}$ (cm^{-1}) + 3.08.[7] There is a relatively large average difference of 0.84 kcal/mol between the data and the calculated ΔH; also, this relationship breaks down for hydrogen bonds weaker than 3 kcal/mol. A change in proton donor would certainly cause larger deviations from the above relationship. It is also worth noting that in the H-bonded complexes of phenol with cyclohexyl-X (X = F, Cl, Br, and I), the $\Delta\nu_{OH}$ decrease[180] down the periodic table, while $\lvert\Delta H\rvert$ increases.

Another important correlation has been the relation between $\Delta\nu$(OH) and $R(X\cdots Y)$ for hydrogen bonds in solids. Pimentel and Sederholm[181] and more recently Bellamy, *et al.*,[182] among others have examined this relationship. For all but the weakest hydrogen bonds, the relationship $\Delta\nu = K(R - r)$ is valid, where $\Delta\nu$ is the observed shift, r is the $X\cdots Y$ distance, and K and R are constants which are different for different (X, Y) combinations.

Many of the other experimental correlations are discussed extensively in Pimentel's[4] book. Most of these correlations and linear relationships are valid within the limits that the systems considered are closely related.

Kollman and Allen[119] have examined the first-row hydrogen bonds (H—$H\cdots Y$) where X = H_2N, OH, and F, and Y = NH_3, OH_2, and FH. They conclude that the distance $X\cdots Y$ is primarily a function of the degree of positive charge on the hydrogen in the H bond; *i.e.*, $R(N$—$H\cdots Y)$ is approximately 3.4 Å no matter what Y is (see Table X). However, once the minimum energy $X\cdots Y$ distance is reached, the Y lone-pair charge distribution is the determining factor in the charge shifts and the H-bond energy. This analysis of the importance of the positive character of the hydrogen and the "extent" of the lone pair on the proton acceptor are, interestingly enough, similar to the two main parameters in Duijneveldt's papers (K, ionicity of X–H bond, and X_s, degree of hybridization). However, one should not fall into the trap of drawing general conclusions from this limited sample; *ab initio* studies of sp^2, sp, and π proton acceptors as well as C–H, Cl–H, and HS–H proton donors are still very much needed to determine completely general aspects of H bonding.

One can make this limitation of Kollman and Allen's and Duijneveldt's studies more explicit by noting that $H_3N\cdots HCl$ has a stronger hydrogen bond than $H_3N\cdots HF$. This is due to the fact that HCl has a weaker covalent bond and a greater polarizability than HF. Because or the lower covalent bond dissociation energy, the ammonia lone pair can more easily lengthen the H–Cl bond (and give it more ionic character), as well as interacting more strongly with HCl through a dipole–polarizability mechanism.

Also, amines typically form stronger H bonds than phosphines,[7] despite the lower ionization potential and greater "p" character and "extent" of the latter lone pair. Thus, when one compares the first- and second-row electron pair donors, there are three factors one must consider in an attempt to understand the relative strengths of different H bonds: (1) the amount of excess negative charge on the electron pair donor atom, (2) the density of charge on the electron pair donor atom (the phosphorus lone pair is more diffuse than nitrogen's), and (3) the ability of the lone-pair donor to draw charge away from the atoms bonded to it (as the nitrogen pulled charge from the ammonia hydrogens in $H_3N\cdots HCl$). From the above, it is clear that the correlations developed for "first-row" H bonds must be modified to understand other H-bonded systems.

It must be emphasized that the ability of proton donors and acceptors to form hydrogen bonds (X—$H\cdots Y$) is more closely related to their respective acidity or basicity than to the electronegativities of X and Y. There has been some confusion in the past[183] on this point, so it deserves emphasis.

F. FUTURE WORK NEEDED

The ability to carry out *ab initio* calculations on larger systems and the development of all-valence-electron, semiempirical theories has enabled one to learn a significant amount about the energy and geometry of complex formation. The CNDO/2 method appears to be the most appropriate semiempirical method for study of hydrogen bonding but has some significant defects [*e.g.*, $(HCN)_2$]. Vibrational spectroscopic results derived from potential curves are in qualitative agreement with experiments; CNDO/2 particularly overemphasizes the ir intensity enhancements expected in hydrogen bonding. There are not many precise molecular orbital studies

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Table X[119]

Heavy-Atom Distances in Hydrogen-Bonded Systems

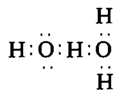
	Common proton donor			Common proton acceptor		
	System	R (Å)	ΔE (kcal)	System	R (Å)	ΔE (kcal)
NH_3	$HFHNH_2$	3.45	1.3	H_3NHF	2.75	11.7
	H_2OHNH_2	3.41	2.3	H_3NHOH	3.12	5.8
	H_3NHNH_2	3.49	2.7	H_3NHNH_2	3.49	2.7
H_2O	HFHOH	3.08	3.0	H_2OHF	2.72	9.4
	H_2OHOH	3.00	5.3	H_2OHOH	3.00	5.3
	H_3NHOH	3.12	5.8	H_2OHNH_2	3.41	2.3
HF	HFHF	2.88	4.6	HFHF	2.88	4.6
	H_2OHF	2.72	9.4	HFHOH	3.08	3.0
	H_3NHF	2.75	11.7	$HFHNH_2$	3.45	1.3

on nmr or electronic spectral properties of H bonding; it certainly would be of interest to see how charge distribution and potential curves of H-bonded systems change in the electronically excited state. Theoretical calculations have given detailed information about the charge shifts in hydrogen bonding and allow some general conclusions about the nature of H bonding, as well as allowing us to understand better the mechanism of proton transfer in aqueous solutions, and some progress has been made recently in understanding the mechanism of hydrogen bonding with both LCAO-MO and intermolecular perturbation theory approaches, but much remains to be done. In particular, the ionic character of the X-H bond and lone-pair character which are good organizing principles for first-row hydrogen bonding do not explain the relative bond strengths of NH_3HF and NH_3HCl dimers.

There are many areas for further theoretical work in hydrogen bonding. A quantitative understanding of the detailed fine structure of the X-H stretching region of certain compounds is an important issue; Marechal's formalism for $(HCOOH)_2$ could be applied to other systems to see how general the two normal mode "coupling" model is. Further decomposition of the delocalization energy might help to give more quantitative information about the amount of charge transfer and charge delocalization in hydrogen-bonded systems. Van Duijneveldt's model should be extended to allow study of substituent effects on the three-atom fragment, as well as parameterizing the method in light of *ab initio* molecular orbital calculations. Further *ab initio* studies on π H bonds, carbonyl hydrogen bonds, and non-first-row hydrogen bonds are of interest, as well as configuration interaction calculations on the smallest H bonds $(HF)_2$ and FHF^-. Finally, the unusual isotopic effect in $HCrO_2$ crystal is not at present clearly understood; that problem is certainly worthy of a theoretician's efforts.

Another area of interest, which has not been discussed in this paper, is the development of a model which treats both H bonding and boron hydride bonding. On the same footing, Pimentel's three-center molecular orbital model predicts a bonding, nonbonding, and antibonding MO for H-bonded systems. In electron-rich H bonds, the first two MO's are filled; in boron hydrides, only the bonding orbital is filled. However, there are two recent pieces of evidence, one theoretical (an *ab initio* calculation on FHF neutral[90]) and one experimental (a study of the bonding in $B_2H_7^-$ [184] which indicate that this model is faulty.

There clearly are many issues yet unresolved in hydrogen bonding, but the past 5 years have seen significant theoretical progress toward an overall understanding. Lest one become too enthralled with "progress" though, it is worth quoting from the Latimer and Rodebush[185] paper published in 1920 which proposed the hydrogen bond: "Let us compare again the compounds ammonia, water and hydrogen chloride. Ammonia adds a hydrogen readily but has little tendency to give one up. Hydrogen chloride, on the other hand, has just the opposite tendencies. Water occupies an intermediate position.... Then, in terms of Lewis theory, a free pair of electrons on one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water to bind the two molecules together. Structurally, this may be represented as



$$\mathrm{H{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}{:}H{:}\underset{H}{\overset{H}{O}}{:}}$$

The liquid may be made up of large aggregates of molecules, continually breaking up and reforming under the influence of thermal agitation...the hydrogen nucleus held between two octets constitutes a weak "bond"...gradations (should) exist all the way from ammonium chloride, where the hydrogen is definitely transferred from the chlorine to NH_3 to the case of association of water, where the hydrogen is still held quite firmly to the original water molecule." These comments made 50 years ago show a remarkable insight into the structure of water as well as appreciation for the key factors in H bonding (ability of the two molecules to accept and give up a proton).

NOTE ADDED IN PROOF. Because of the time elapsed between the submission of this article and publication, there have been quite a number of interesting papers published recently, a few of which will be mentioned here.

Pimentel and McClellan (*Annu. Rev. Phys. Chem.*, **22,** 347 (1971)) have published a general review of hydrogen bonding, emphasizing spectroscopic studies and biological applications. The similarity of the X···X force constant in HCl_2^-, HBr_2^-, HCl_2, and HBr_2 seems to indicate that the electron has been removed from a nonbonding orbital, in agreement with the predictions of Pimentel's MO theory,[4] but in disagreement with SCF studies on HF_2^- and HF_2.[90] It may be, however, that the electronegativity of the halogen is a crucial factor in how "nonbonding" this orbital is and that the "electrostatic" con-

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tribution to the H-bond energy is only very important in HF_2^- and HF_2. Clearly more work is needed to resolve this point.

Other general reviews which have been published are those of Hadzi (*Chimia*, **26,** 7 (1972)) on ir studies of strong H-bonds and a very interesting historical account of H-bond studies by Huggins (*Angew. Chem., Int. Ed. Engl.*, **10,** 147 (1971)).

Ion hydration has been a subject of considerable theoretical interest, with studies by Newton and Ehrenson (*J. Amer. Chem. Soc.*, **93,** 4971 (1971)), Schuster (*Theor. Chim. Acta*, **24,** 191 (1972)), and Dierchsen (*ibid.*, **23,** 387 (1972)) among recent publications. Newton and Ehrenson found, in contrast to earlier CNDO conclusions,[93] that H_3O^+ retains its properties even in $H_9O_4^+$, which contains an H_3O^+ unit functioning as a proton acceptor to three water molecules.

H-Bonding involving HCN (Johansson and Kollman, *Theor. Chim. Acta*, in press), intramolecular H-bonding (Johansson and Kollman, unpublished results), and second-row H-bonding (Sabin, *J. Amer. Chem. Soc.*, **93,** 3613 (1971)) have been the subject of recent *ab initio* work.

One piece of recent experimental structural work is quite relevant to the theoretical studies examined above. Klemperer's work on the HF dimer (*J. Chem. Phys.*, **56,** 2442 (1972)) supported theoretical predictions[80,81] on the structure (linear, R(F–F) $\sim$ 2.8 Å) of the dimer. This work lends calculations to successfully make H-bond structure predictions and also reinforces the fact that H-bonded dimers appear to have considerably greater X···X distances (R(F–F) = 2.5 Å in crystalline HF) than higher polymers.[130]

Marechal (*Chem. Phys. Lett.*, **13,** 237 (1972)) has continued his analysis of ir in H-bonded systems using the coupled mode model he developed previously.