

tions. This is to be expected, since the total energies of the two wave functions they examined are greatly above the Hartree-Fock limit (by a value of approximately 20 times the barrier height), and energy decompositions for this quality of wave function are generally very erratic. Clementi and von Niessen<sup>13</sup> have decomposed the ethane total energy as a function of rotational angle into one-, two-, three-, and four-center contributions. The three-center term undergoes the greatest change of magnitude, but the sign of its change is opposite to the barrier itself, and no physical or chemical concept emerges. A further decomposition assuming that basis functions mounted on a given center possess an energy solely associated with that center leads to a set of 26 energy *vs.* angle curves that do not reveal any chemically useful pattern. A comprehensive review of methods for analyzing barrier mechanisms has been recently made by Lehn.<sup>14</sup>

## V. Summary and Conclusions

In order to understand the origin of rotational barriers, it is necessary to analyze a considerable number and variety of molecules showing different barrier characteristics. Ethyl fluoride and ethane constitute an important pair of molecules in such a list because their barriers are surprisingly similar.

To investigate these two molecules, *ab initio* LCAO-MO-SCF wave functions with total energies reasonably close to the molecular Hartree-Fock solution were computed with an atomic orbital basis set of double- $\zeta$  quality. The computed barriers were found to be nearly equal, in agreement with experiment. This result substantiates and extends our previous conclusion that the barrier mechanism is contained within the framework of the Hartree-Fock approximation.

Energy components,  $V_{\text{att}}$  and  $V_{\text{rep}}$ , were employed to aid in understanding various aspects of the barrier mechanism. The barriers in ethane and ethyl fluoride

(13) E. Clementi and W. von Niessen, *J. Chem. Phys.*, **54**, 521 (1971).

(14) J.-M. Lehn in "Conformational Analysis," Academic Press, New York, N. Y., 1971, p 129.

are both repulsive dominant and therefore arise predominantly from the action of the Pauli principle.<sup>7,9a,15</sup> That the two barriers are quite similar can be interpreted as arising from the tail of the methyl group passing through the high potential field of the fluorine atom and adding roughly equal energy increments to both  $V_{\text{att}}$  and  $V_{\text{rep}}$  over their values for ethane. The small change in dipole moment during rotation in ethyl fluoride can also be accounted for with this type of analysis. Since this barrier is repulsive dominant, the slightly smaller moment in the eclipsed configuration arises from a reduced bond dipole in this conformation produced by the repulsion of the fluorine atom.

The possibility of using one-electron energies to characterize and predict barriers is evaluated. It is found to yield reasonably satisfactory barrier predictions for ethyl fluoride and ethane but not for several other molecules.

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(15) The first published suggestion that the Pauli principle plays the dominant role in the ethane barrier appears to have been made by J. van Dranen, *J. Chem. Phys.*, **20**, 1982 (1952). van Dranen based his hypothesis on a semiempirical estimate of the interaction between He and H<sub>2</sub>. E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959), discussed this question, and his article focused attention on the lack of adequate explanations for barrier mechanisms at that time. More recently, a significant quantitative attempt to show the central importance of the Pauli principle has been made by comparing a Hartree product of locally orthogonal bond orbitals with the corresponding antisymmetrized product: O. J. Sovers, C. W. Kern, R. M. Pitzer, and M. Karplus, *J. Chem. Phys.*, **49**, 2592 (1968). Although completely *ab initio*, the bond orbital method introduces a mixing parameter between a C-H hybrid orbital and a hydrogen 1s which constricts the wave function and considerably raises its energy over a molecular orbital wave function employing the same basis set and interaction integrals. The complexity of the interpretation in this work is illustrative of the very general difficulty inherent in any attempt to meaningfully decompose a molecular wave function which will clearly bring out the workings of the Pauli principle. Another way of approaching this problem is to make a quantitative potential energy curve analogy to the well-understood He-He case (see ref 7).

## Molecular Orbital Theory of the Electronic Structure of Organic Compounds. X. A Systematic Study of Geometries and Energies of AH<sub>n</sub> Molecules and Cations

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**Abstract:** An *ab initio* molecular orbital study of the geometries and energies of neutral systems AH<sub>n</sub> and their singly charged cations AH<sub>n</sub><sup>+</sup> (A = C, N, O, or F) is presented. Two previously reported basis sets are employed: the minimal, STO-3G, basis and the extended, 4-31G, basis in which valence shells are split into inner and outer parts. Comparisons are made between experimental and theoretically predicted properties.

Self-consistent molecular orbital theory with a well-defined set of basis functions centered at nuclear positions provides a complete theoretical model for molecular structure. Deficiencies of such models due

to partial neglect of electron correlation are widely appreciated, but it nevertheless appears that quite simple molecular orbital treatments give successful accounts of molecular geometries,<sup>1</sup> rotational po-

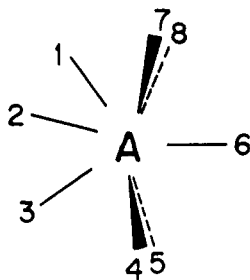


Figure 1. Hydrogen numbering for  $AH_n$  molecule with a reflection plane. Atom pairs (45) and (78) are related by reflection.

tentials,<sup>2</sup> and energy changes associated with certain types of reaction.<sup>3,4</sup> To explore the potential of such theories in depth, it is desirable to make an extended and systematic study of structural and chemical properties predicted by certain simple bases. In this paper we report theoretical equilibrium geometries and energies for the ground state and certain low-lying excited states of neutral molecules  $AH_n$  (A being C, N, O, or F) and their singly charged cations  $AH_n^+$ . Two basis sets developed in our laboratory (STO-3G and 4-31G) are used.<sup>5,6</sup> Some of the results for the hydrocarbons have been reported previously.<sup>7</sup> They are included here together with further extensions for the purpose of a full comparative survey.

## Method

The two basis sets used have been described previously and will not be discussed in detail. The simpler (STO-3G)<sup>5</sup> is a minimal basis of Slater-type atomic orbitals which are least squares fitted by three Gaussian functions. Standard molecular exponents are used. The second set (4-31G)<sup>6</sup> is an extended basis set in which inner shells are represented by a sum of four Gaussians and the valence shells are represented by inner three-Gaussian and outer one-Gaussian parts.

Given the basis set and a specified molecular geometry, the molecular orbital coefficients are found from the Roothaan equations<sup>8</sup> for closed-shell singlet states. In some cases, the lowest energies are found with complex molecular orbitals. For states of higher multiplicity, the corresponding unrestricted open-shell equations (different orbitals for different spins) are used.<sup>9</sup> This procedure leads to a calculated total energy for each molecular configuration.

The procedure adopted for the determination of equilibrium geometry is to impose certain symmetry constraints and then to vary all remaining geometrical parameters until the total energy is minimized. The final structure may, of course, have higher symmetry than that originally imposed. Details of the geometrical search procedure and the computational

(1) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).

(2) L. C. Allen, *Annu. Rev. Phys. Chem.*, **20**, 315 (1969).

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

(4) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *ibid.*, **92**, 4796 (1970).

(5) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(6) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).

(7) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

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

(9) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).

accuracy of derived structural parameters have been discussed elsewhere.<sup>1</sup>

The computations have been carried out in three stages. In the first place, the STO-3G geometry was determined with its corresponding energy. This is described as level A. Secondly, a single calculation was performed with the extended 4-31G basis using the STO-3G geometry (level B). Finally, the geometry was revised to find the structure predicted by the 4-31G basis (level C). The level B results are included here so that they may be compared in later papers with level B calculations on larger molecules where level C is impractical.

A wide range of possible molecular symmetries has been investigated for these molecules. In order to present the results in a systematic manner, we have used a common notation for hydrogen atoms. A partial list of possible symmetries for molecules with one heavy atom is given in Table I. All have at least one re-

Table I. Symmetries of Molecules  $AH_n$

Formula	Point group	Description	H atoms <sup>a</sup>	
AH	$C_{\infty v}$		1	
AH <sub>2</sub>	$C_s$		12	
	$C_{2v}$		(12)	
	$C_{\infty v}$		12	
	$D_{\infty h}$		(12)	
	$C_s$	Planar	123	
AH <sub>3</sub>	$C_s$	Nonplanar	1 (45)	
	$C_{2v}$	Planar	1 (23) <sup>b</sup>	
	$C_{3v}$	Triangular pyramid	(145)	
	$D_{3h}$	Planar	(145)	
	$C_{\infty v}$	Linear	123	
	AH <sub>4</sub>	$C_s$	Twisted	12 (45)
		$C_{2v}$	Y shape	12 (45) <sup>c</sup>
$C_{3v}$		Twisted	(12) (45)	
$C_{2v}$		Rectangular pyramid	(4578)	
$D_{2h}$		Planar rectangle	(1236)	
$D_{2d}$		Twisted	(1245)	
$C_{3v}$			1 (345) <sup>d</sup>	
$C_{4v}$		Square pyramid	(4578)	
$D_{4h}$		Square planar	(4578)	
$T_d$		Tetrahedral	(1245)	
AH <sub>5</sub>	$C_s$	I	123 (45)	
	$C_s$	II	1 (45) (78)	
	$C_{2v}$	Rectangular pyramid	1 (4578)	
	$C_{3v}$		12 (345) <sup>e</sup>	
	$C_{4v}$	Square pyramid	1 (4578)	
	$D_{3h}$	Trigonal bipyramid	(145) (26)	

<sup>a</sup> Hydrogen atoms used in Figure 1. Numbers in parentheses indicate equivalent positions. <sup>b</sup> H<sub>1</sub> on C<sub>2</sub> axis. <sup>c</sup> H<sub>1</sub>, H<sub>2</sub> on C<sub>2</sub> axis. <sup>d</sup> H<sub>1</sub> on C<sub>3</sub> axis. <sup>e</sup> H<sub>1</sub>, H<sub>2</sub> on C<sub>3</sub> axis.

flexion plane. Hydrogen atoms are numbered in the manner shown in Figure 1. Atoms 1, 2, 3, and 6 lie in the plane and the pairs 4, 5 and 7, 8 are related by reflection. For each possible symmetry the hydrogen atoms used are listed in the fourth column of the table. Hydrogens which are equivalent by symmetry are enclosed in parentheses. Thus (45) and (78) are always equivalent. For higher symmetries than the  $C_s$  point group implied by the diagram, there are further equivalences between hydrogens. Thus the symbol (23) implies that 2 and 3 are related by symmetry so that there must be a further reflection plane bisecting the angle H<sub>2</sub>AH<sub>3</sub>. Also, the symbol (145) implies the existence of a threefold rotation axis relating atoms 1, 4, and 5.

## Results

In order to present the theoretical geometries in a uniform manner, we adopt the following format.

Molecule [basis] (experimental reference if available<sup>10-17</sup>) imposed point group symmetry → point group symmetry found for lowest energy: electronic state symmetry with initial point group → electronic state symmetry with final point group: geometrical parameter = theoretical value (experimental value if available), . . . .

If the imposed and final symmetries are identical, only one is quoted. The symmetries and descriptions used refer to Table I. Geometrical parameters are quoted in ångströms for bond lengths and degrees for bond angles. The symbols  $H_{45}$  and  $H_{78}$  are used for the midpoints of lines joining pairs of equivalent hydrogens (45) and (78). All angles are measured in a counter-clockwise sense.

The detailed geometries follow. The corresponding total energies are listed in Table II.

## Discussion

We consider each system in turn. Some discussion of the hydrocarbon geometries has already been given in ref 7. Certain additional features are dealt with here.

**CH<sup>+</sup>, CH.** The CH radical and its cation are examples of diatomic hydrides AH in which the ordering of molecular orbital energies is generally assumed to be

$$1\sigma < 2\sigma < 3\sigma < 1\pi < 4\sigma$$

In most of the AH species considered in this paper, the first three  $\sigma$  orbitals are filled and the remaining electrons are in the nonbonding  $1\pi$  orbitals located on the heavy atom. All the calculations carried out are consistent with these assumptions. Thus CH<sup>+</sup> has no  $\pi$  electrons and gives a theoretical ground state of  $^1\Sigma^+$  symmetry. The CH radical has one  $\pi$  electron and a  $^2\Pi$  ground state. These results are consistent with experimental findings and other theoretical work.<sup>18</sup>

It may be noted that the STO-3G basis gives a bond lengthening of 0.04 Å on ionization of CH from 1.143 to 1.185 Å. Similar lengthenings are predicted for CH bonds in many larger hydrocarbon cations. Experimentally the bond lengthening is less (~0.01 Å) and the 4-31G basis gives a slight contraction. The STO-3G lengthening is apparently due to the poor choice of standard  $\zeta$  exponents for the positive ion. Complete optimization of both valence  $\zeta$  values and the bond length for CH<sup>+</sup> gives  $\zeta_C = 1.72$ ,  $\zeta_H = 1.41$ , and  $R_{CH} = 1.140$  Å. The optimized  $\zeta_H$  is much larger for the ion, leading to a shorter bond length close to the STO-3G value for neutral CH, where standard exponents are more nearly correct.

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(11) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1967.

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(13) L. S. Bartell, K. Kuchitsu, and R. J. DeNui, *ibid.*, **35**, 1211 (1961).

(14)  $R_e$  calculated by R. S. Berry in "Nitrenes," W. Lwowski, Ed., Wiley, New York, N. Y., 1970, p 13, from the  $B_e$  value of R. N. Dixon, *Can. J. Phys.*, **37**, 1171 (1959).

(15) K. Kuchitsu, J. P. Guillory, and L. S. Bartell, *J. Chem. Phys.*, **49**, 2488 (1968).

(16) The NH bond length is an average of those determined for NH<sub>4</sub>Cl and NH<sub>4</sub>F by J. A. Ibers and D. P. Stevenson, *ibid.*, **28**, 929 (1958).

(17) K. Kuchitsu and L. S. Bartell, *ibid.*, **36**, 2460 (1962).

(18) P. E. Cade and W. M. Huo, *J. Chem. Phys.*, **47**, 614 (1967).

**CH<sub>2</sub><sup>+</sup>, CH<sub>2</sub>.** Methylene and its cation are examples of symmetrical AH<sub>2</sub> systems which may exist in a linear ( $D_{\infty h}$ ) or bent ( $C_{2v}$ ) form. Such molecules are usually discussed in terms of the Walsh diagram<sup>19</sup> connecting the molecular orbital energy levels in the two symmetries. For the linear geometry, the ordering of energy levels is taken to be

$$1\sigma_g < 2\sigma_g < 2\sigma_u < 1\pi_u < 3\sigma_g$$

This ordering is confirmed for all molecules considered here. On bending to the  $C_{2v}$  form, the degenerate  $1\pi_u$  level splits into  $a_1$  and  $b_1$  levels, the former being lower in energy because it acquires s character in the bent form. Thus for  $C_{2v}$ , the ordering of levels is

$$1a_1 < 2a_1 < 1b_2 < 3a_1 < 1b_1 < 4a_1$$

According to the Walsh scheme, the equilibrium bond angle is determined mainly by the number of electrons in the  $1\pi_u \rightarrow 3a_1$  orbital.

The linear form of the CH<sub>2</sub><sup>+</sup> ion has a degenerate ground state with one  $\pi$  electron,  $(1\sigma_g)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)$ ,  $^2\Pi_u$ . On bending, this would lead to either a  $^2A_1$  or a  $^2B_1$  state, depending on which component molecular orbital is occupied. The theory predicts the  $^2A_1$  state to be lower, with a bond angle of about 140°. The upper state has its energy minimum in the linear form. This is consistent with the Walsh scheme.

The neutral CH<sub>2</sub> system has two  $\pi$  electrons in its lowest electron configuration in the linear form,  $(1\sigma_g)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2$ . This leads to  $^3\Sigma_g^-$ ,  $^1\Delta$ , and  $^1\Sigma_g^+$  states. The  $^3\Sigma_g^-$  state arises from assigning the two electrons with parallel spin to different  $\pi$ -type orbitals of the  $1\pi_u$  pair. On bending,  $^3\Sigma_g^-$  becomes  $^3B_1$ , with  $3a_1$  and  $1b_1$  both singly occupied. The two components of the  $^1\Delta$  state for linear CH<sub>2</sub> corresponds to configurations in which the two electrons are assigned with antiparallel spins to complex molecular orbitals  $(2p_x) + i(2p_y)$  or to  $(2p_x) - i(2p_y)$  ( $z$  axis along HCH). These are states with resultant orbital angular momentum in the  $z$  direction. One component of  $^1\Delta$  can alternatively be represented in terms of interaction between the configurations  $(2p_x)^2$  and  $(2p_y)^2$ . Since configuration interaction cannot be easily included in a general manner, we have used the complex alternative, and the energy and geometry quoted correspond to the best complex molecular orbitals. On bending, symmetry requires that the  $^1\Delta$  state splits into two distinct states of symmetries  $^1A_1$  and  $^1B_1$ .  $^1A_1$  will be lower in energy in the Walsh scheme and will ultimately correspond to the configuration  $\cdots(3a_1)^2$ . However, for slight bending, there will still be strong configuration interaction with  $\cdots(1b_1)^2$ . Also it is clear that, under these circumstances, the best single-determinant molecular orbitals in the sense of giving lowest total energies will still be complex (and unsymmetrical) even though the full  $D_{\infty h}$  symmetry is lost. The results quoted are for the configuration of real molecular orbitals  $\cdots(3a_1)^2, ^1A_1$ . For the strongly bent equilibrium angle, it is found that the use of complex molecular orbitals leads to no significant further lowering of the energy. However, for somewhat larger angles of about 120°, the best orbitals do have substantial imaginary components.

(19) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

Table II. Calculated Total Energies (hartrees)<sup>a</sup>

Molecule	Point group symmetry	State	Energy		
			A	B	C
H		<sup>2</sup> S	-0.49491 <sup>b</sup>	-0.49928 <sup>c</sup>	-0.49928 <sup>c</sup>
H <sub>2</sub> <sup>+</sup>	D <sub>∞h</sub>	<sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	-0.58270	-0.58402	-0.58408
H <sub>2</sub>	D <sub>∞h</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	-1.11751	-1.12658	-1.12683
C <sup>+</sup>		<sup>2</sup> P	-36.87134 <sup>d</sup>	-37.24348 <sup>e</sup>	-37.24348 <sup>e</sup>
C		<sup>1</sup> D	-37.16119 <sup>b,f</sup>	-37.57729 <sup>c,f</sup>	-37.57729 <sup>c,f</sup>
		<sup>3</sup> P	-37.22866 <sup>b</sup>	-37.63692 <sup>c</sup>	-37.63692 <sup>c</sup>
CH <sup>+</sup>	C <sub>∞v</sub>	<sup>1</sup> Σ <sup>+</sup>	-37.45638	-37.83680	-37.83988
CH	C <sub>∞v</sub>	<sup>2</sup> Π	-37.77026	-38.20768	-38.20801
CH <sub>2</sub> <sup>+</sup>	D <sub>∞h</sub>	<sup>2</sup> Π	-38.11074	-38.50535	-38.50849
	C <sub>2v</sub>	<sup>2</sup> A <sub>1</sub>	-38.11894	-38.50872	-38.51257
CH <sub>2</sub>	D <sub>∞h</sub>	<sup>1</sup> Δ	-38.32377 <sup>f</sup>	-38.78969 <sup>f</sup>	-38.78975 <sup>f</sup>
	C <sub>2v</sub>	<sup>1</sup> A <sub>1</sub>	-38.37230	-38.80932	-38.81035
	D <sub>∞h</sub>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	-38.41255	-38.85820	-38.85831
	C <sub>2v</sub>	<sup>3</sup> B <sub>1</sub>	-38.43623	-38.36881	-38.86963
CH <sub>3</sub> <sup>+</sup>	D <sub>3h</sub>	<sup>1</sup> A <sub>1</sub> '	-38.77948	-39.17129	-39.17512
CH <sub>3</sub>	D <sub>3h</sub>	<sup>2</sup> A <sub>2</sub> ''	-39.07671	-39.50484	-39.50497
	C <sub>3v</sub>	<sup>2</sup> A <sub>1</sub>	-39.07701	-39.50392	-39.50497
CH <sub>4</sub> <sup>+</sup>	C <sub>2v</sub>	<sup>2</sup> A <sub>1</sub>	-39.29197	-39.68864	-39.69063
	C <sub>2v</sub>	<sup>2</sup> B	-39.29262	-39.69038	-39.69291
	D <sub>2d</sub>	<sup>2</sup> B <sub>2</sub>	-39.29386	-39.69356	-39.69523
CH <sub>4</sub>	D <sub>4h</sub>	<sup>1</sup> A <sub>1g</sub>	-39.34441	-39.87147	-39.87158
	C <sub>2v</sub> (Y shape)	<sup>3</sup> B <sub>1</sub>	-39.55376	-39.99561	-39.99672
	T <sub>d</sub>	<sup>1</sup> A <sub>1</sub>	-39.72686	-40.13976	-40.13977
CH <sub>5</sub> <sup>+</sup>	D <sub>3h</sub>	<sup>1</sup> A'	-39.90885	-40.31508	-40.31571
	C <sub>4v</sub>	<sup>1</sup> A <sub>1</sub>	-39.91589	-40.31893	-40.31998
	C <sub>s</sub> (I)	<sup>1</sup> A'	-39.91887	-40.32207	-40.32715
	C <sub>s</sub> (II)	<sup>1</sup> A'	-39.91887	-40.32214	-40.32713
CH <sub>5</sub>	D <sub>3h</sub>	<sup>2</sup> A <sub>1</sub> '	-40.08006	-40.55057	-40.55198
	C <sub>3v</sub>	<sup>2</sup> A <sub>1</sub>	-40.19456	-40.63090	-40.63215
N <sup>+</sup>		<sup>3</sup> P	-53.27728 <sup>d</sup>	-53.81899 <sup>e</sup>	-53.81899 <sup>e</sup>
N		<sup>4</sup> S	-53.72010 <sup>b</sup>	-54.32792 <sup>c</sup>	-54.32792 <sup>c</sup>
NH <sup>+</sup>	C <sub>∞v</sub>	<sup>2</sup> Π	-53.83593	-54.40602	-54.41055
	C <sub>∞v</sub>	<sup>4</sup> Σ <sup>-</sup>	-53.88021	-54.45321	-54.45593
NH	C <sub>∞v</sub>	<sup>1</sup> Δ	-54.17703 <sup>f</sup>	-54.80956 <sup>f</sup>	-54.81126 <sup>f</sup>
	C <sub>∞v</sub>	<sup>3</sup> Σ <sup>-</sup>	-54.26378	-54.88340	-54.88495
NH <sub>2</sub> <sup>+</sup>	C <sub>2v</sub>	<sup>1</sup> A <sub>1</sub>	-54.45749	-55.03863	-55.04604
	D <sub>∞h</sub>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	-54.54813	-55.13467	-55.13922
	C <sub>2v</sub>	<sup>3</sup> B <sub>1</sub>	-54.55042	-55.13421	-55.13968
NH <sub>2</sub>	D <sub>∞h</sub>	<sup>2</sup> Π	-54.74327	-55.42804	-55.42875
	C <sub>2v</sub>	<sup>2</sup> A <sub>1</sub>	-54.76094	-55.42881	-55.43244
	C <sub>2v</sub>	<sup>2</sup> B <sub>1</sub>	-54.83930	-55.47092	-55.47473
NH <sub>3</sub> <sup>+</sup>	D <sub>3h</sub>	<sup>2</sup> A <sub>2</sub> ''	-55.20701	-55.79672	-55.80167
NH <sub>3</sub>	C <sub>∞v</sub>	<sup>3</sup> Σ <sup>-</sup>	-55.38157	-56.01065	-56.01248
	D <sub>3h</sub>	<sup>1</sup> A <sub>1</sub> '	-55.43767	-56.10482	-56.10600
	C <sub>3v</sub>	<sup>1</sup> A <sub>1</sub>	-55.45542	-56.09829	-56.10669
NH <sub>4</sub> <sup>+</sup>	D <sub>4h</sub>	<sup>1</sup> A <sub>1g</sub>	-55.60535	-56.25233	-56.25349
	T <sub>d</sub>	<sup>1</sup> A <sub>1</sub>	-55.86885	-56.45552	-56.45888
NH <sub>4</sub>	T <sub>d</sub>	<sup>2</sup> A <sub>1</sub>	-55.74335	-56.50104	-56.53286
	C <sub>2v</sub> (Y shape)	<sup>2</sup> B <sub>1</sub>	-55.95740	-56.59854	-56.60284
O <sup>+</sup>		<sup>4</sup> S	-73.51108 <sup>d</sup>	-74.27788 <sup>e</sup>	-74.27788 <sup>e</sup>
O		<sup>1</sup> D	-73.70978 <sup>b,f</sup>	-74.62115 <sup>c,f</sup>	-74.62115 <sup>c,f</sup>
		<sup>3</sup> P	-73.80425 <sup>b</sup>	-74.70548 <sup>c</sup>	-74.70548 <sup>c</sup>
OH <sup>+</sup>	C <sub>∞v</sub>	<sup>1</sup> Δ	-73.95005 <sup>f</sup>	-74.77844 <sup>f</sup>	-74.80371 <sup>f</sup>
	C <sub>∞v</sub>	<sup>3</sup> Σ <sup>-</sup>	-74.04893	-74.87120	-74.87323
OH	C <sub>∞v</sub>	<sup>2</sup> Π	-74.36489	-75.28539	-75.28716
OH <sub>2</sub> <sup>+</sup>	D <sub>∞h</sub>	<sup>2</sup> Π	-74.62450	-75.49163	-75.49268
	C <sub>2v</sub>	<sup>2</sup> A <sub>1</sub>	-74.62473	-75.49034	-75.49268
	C <sub>2v</sub>	<sup>2</sup> B <sub>1</sub>	-74.66974	-75.50855	-75.51285
OH <sub>2</sub>	C <sub>2v</sub>	<sup>1</sup> A <sub>1</sub>	-74.96590	-75.90324	-75.90864
OH <sub>3</sub> <sup>+</sup>	D <sub>3h</sub>	<sup>1</sup> A <sub>1</sub> '	-75.32839	-76.19962	-76.20060
	C <sub>3v</sub>	<sup>1</sup> A <sub>1</sub>	-75.33044	-76.19316	-76.20060
OH <sub>3</sub>	D <sub>3h</sub>	<sup>2</sup> A <sub>1</sub> '	-75.32825	-76.32022	-76.32940
	C <sub>∞v</sub>	<sup>2</sup> Π	-75.48263	-76.41252	-76.41460
	C <sub>s</sub> (planar)	<sup>2</sup> A''	-75.48284	-76.41249	-76.41500
F <sup>+</sup>		<sup>3</sup> P	-97.62160 <sup>d</sup>	-98.70254 <sup>e</sup>	-98.70254 <sup>e</sup>
F		<sup>2</sup> P	-97.98709 <sup>b</sup>	-99.26548 <sup>c</sup>	-99.26548 <sup>c</sup>
FH <sup>+</sup>	C <sub>∞v</sub>	<sup>2</sup> Π	-98.19185	-99.37333	-99.37338
FH	C <sub>∞v</sub>	<sup>1</sup> Σ <sup>+</sup>	-98.57285	-99.88613	-99.88729
FH <sub>2</sub> <sup>+</sup>	C <sub>2v</sub>	<sup>1</sup> A <sub>1</sub>	-98.86411	-100.07469	-100.07787
FH <sub>2</sub>	C <sub>∞v</sub>	<sup>2</sup> Π	-99.10412	-100.39262	-100.39292

<sup>a</sup> Energies quoted in this table are those resulting from termination of the geometry-optimization procedure. In most cases they would not exactly correspond to those calculated using the geometrical parameters (rounded to the nearest 0.001 Å and 0.1° for bond lengths and bond angles, respectively) quoted in the text. Differences are not expected to be greater than 0.0001 au. <sup>b</sup> Energies calculated using optimum atomic exponents of ref 5. <sup>c</sup> Energies calculated using unscaled 4-31G atomic basis functions of ref 6. <sup>d</sup> Energies calculated using optimum atomic ion exponents: M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **51**, 3927 (1969). <sup>e</sup> Energies calculated using optimum valence-shell scaling factors for atomic ions. These are: C<sup>+</sup>, ζ<sub>2</sub>' = 1.022, ζ<sub>2</sub>'' = 1.099; N<sup>+</sup>, ζ<sub>2</sub>' = 1.020, ζ<sub>2</sub>'' = 1.084; O<sup>+</sup>, ζ<sub>2</sub>' = 1.016, ζ<sub>2</sub>'' = 1.085; F<sup>+</sup>, ζ<sub>2</sub>' = 1.015, ζ<sub>2</sub>'' = 1.075. <sup>f</sup> The molecular orbitals were allowed to become complex.

H <sub>2</sub> <sup>+</sup>	[STO-3G] (10) D <sub>∞h</sub> : <sup>2</sup> Σ <sub>g</sub> <sup>+</sup> : AH <sub>1</sub> = 1.061 (1.060)	NH	[STO-3G] (13) C <sub>∞v</sub> : <sup>3</sup> Σ <sup>-</sup> : AH <sub>1</sub> = 1.082 (1.0481)
H <sub>2</sub> <sup>+</sup>	[4-31G] (10) D <sub>∞h</sub> : <sup>2</sup> Σ <sub>g</sub> <sup>+</sup> : AH <sub>1</sub> = 1.041 (1.060)	NH	[4-31G] (13) C <sub>∞v</sub> : <sup>3</sup> Σ <sup>-</sup> : AH <sub>1</sub> = 1.033 (1.0481)
H <sub>2</sub>	[STO-3G] (10) D <sub>∞h</sub> : <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> : AH <sub>1</sub> = 0.712 (0.742)	NH <sub>2</sub> <sup>+</sup>	[STO-3G] C <sub>2v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.101, H <sub>1</sub> AH <sub>2</sub> = 108.1
H <sub>2</sub>	[4-31G] (10) D <sub>∞h</sub> : <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> : AH <sub>1</sub> = 0.730 (0.742)	NH <sub>2</sub> <sup>+</sup>	[4-31G] C <sub>2v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.029, H <sub>1</sub> AH <sub>2</sub> = 116.0
CH <sup>+</sup>	[STO-3G] (10) C <sub>∞v</sub> : <sup>1</sup> Σ <sup>+</sup> : AH <sub>1</sub> = 1.185 (1.131)	NH <sub>2</sub> <sup>+</sup>	[STO-3G] D <sub>∞h</sub> : <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> : AH <sub>1</sub> = 1.079
CH <sup>+</sup>	[4-31G] (10) C <sub>∞v</sub> : <sup>1</sup> Σ <sup>+</sup> : AH <sub>1</sub> = 1.108 (1.131)	NH <sub>2</sub> <sup>+</sup>	[4-31G] D <sub>∞h</sub> : <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> : AH <sub>1</sub> = 1.021
CH	[STO-3G] (10) C <sub>∞v</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 1.143 (1.120)	NH <sub>2</sub> <sup>+</sup>	[STO-3G] C <sub>2v</sub> : <sup>3</sup> B <sub>1</sub> : AH <sub>1</sub> = 1.079, H <sub>1</sub> AH <sub>2</sub> = 147.4
CH	[4-31G] (10) C <sub>∞v</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 1.118 (1.120)	NH <sub>2</sub> <sup>+</sup>	[4-31G] C <sub>2v</sub> : <sup>3</sup> B <sub>1</sub> : AH <sub>1</sub> = 1.020, H <sub>1</sub> AH <sub>2</sub> = 157.5
CH <sub>2</sub> <sup>+</sup>	[STO-3G] D <sub>∞h</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 1.128	NH <sub>2</sub>	[STO-3G] D <sub>∞h</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 0.999
CH <sub>2</sub> <sup>+</sup>	[4-31G] D <sub>∞h</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 1.078	NH <sub>2</sub>	[4-31G] D <sub>∞h</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 0.980
CH <sub>2</sub> <sup>+</sup>	[STO-3G] C <sub>2v</sub> : <sup>2</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.132, H <sub>1</sub> AH <sub>2</sub> = 136.0	NH <sub>2</sub>	[STO-3G] (11) C <sub>2v</sub> : <sup>2</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.015 (1.004), H <sub>1</sub> AH <sub>2</sub> = 131.3 (144)
CH <sub>2</sub> <sup>+</sup>	[4-31G] C <sub>2v</sub> : <sup>2</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.079, H <sub>1</sub> AH <sub>2</sub> = 141.8	NH <sub>2</sub>	[4-31G] (11) C <sub>2v</sub> : <sup>2</sup> A <sub>1</sub> : AH <sub>1</sub> = 0.985 (1.004), H <sub>1</sub> AH <sub>2</sub> = 144.9 (144)
CH <sub>2</sub>	[STO-3G] D <sub>∞h</sub> : <sup>1</sup> Δ: AH <sub>1</sub> = 1.061	NH <sub>2</sub>	[STO-3G] (11) C <sub>2v</sub> : <sup>2</sup> B <sub>1</sub> : AH <sub>1</sub> = 1.058 (1.024), H <sub>1</sub> AH <sub>2</sub> = 100.2 (103.4)
CH <sub>2</sub>	[4-31G] D <sub>∞h</sub> : <sup>1</sup> Δ: AH <sub>1</sub> = 1.055	NH <sub>2</sub>	[4-31G] (11) C <sub>2v</sub> : <sup>2</sup> B <sub>1</sub> : AH <sub>1</sub> = 1.015 (1.024), H <sub>1</sub> AH <sub>2</sub> = 108.3 (103.4)
CH <sub>2</sub>	[STO-3G] (11) C <sub>2v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.123 (1.11), H <sub>1</sub> AH <sub>2</sub> = 100.5 (102.4)	NH <sub>3</sub> <sup>+</sup>	[STO-3G] C <sub>3v</sub> → D <sub>3h</sub> : <sup>2</sup> A <sub>1</sub> → <sup>2</sup> A <sub>2</sub> '': AH <sub>1</sub> = 1.056
CH <sub>2</sub>	[4-31G] (11) C <sub>2v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.100 (1.11), H <sub>1</sub> AH <sub>2</sub> = 105.4 (102.4)	NH <sub>3</sub> <sup>+</sup>	[4-31G] C <sub>3v</sub> → D <sub>3h</sub> : <sup>2</sup> A <sub>1</sub> → <sup>2</sup> A <sub>2</sub> '': AH <sub>1</sub> = 1.010
CH <sub>2</sub>	[STO-3G] D <sub>∞h</sub> : <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> : AH <sub>1</sub> = 1.069	NH <sub>3</sub>	[STO-3G] C <sub>∞v</sub> : <sup>3</sup> Σ <sup>-</sup> : AH <sub>1</sub> = 2.852, AH <sub>2</sub> = 3.565, AH <sub>3</sub> = 1.082, H <sub>1</sub> AH <sub>2</sub> = 0.0, H <sub>1</sub> AH <sub>3</sub> = 180.0
CH <sub>2</sub>	[4-31G] D <sub>∞h</sub> : <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> : AH <sub>1</sub> = 1.061	NH <sub>3</sub>	[4-31G] C <sub>∞v</sub> : <sup>3</sup> Σ <sup>-</sup> : AH <sub>1</sub> = 2.971, AH <sub>2</sub> = 3.701, AH <sub>3</sub> = 1.032, H <sub>1</sub> AH <sub>2</sub> = 0.0, H <sub>1</sub> AH <sub>3</sub> = 180.0
CH <sub>2</sub>	[STO-3G] (12) C <sub>2v</sub> : <sup>3</sup> B <sub>1</sub> : AH <sub>1</sub> = 1.082 (1.078), H <sub>1</sub> AH <sub>2</sub> = 125.5 (136)	NH <sub>3</sub>	[STO-3G] D <sub>3h</sub> : <sup>1</sup> A <sub>1</sub> ': AH <sub>1</sub> = 1.006
CH <sub>2</sub>	[4-31G] (12) C <sub>2v</sub> : <sup>3</sup> B <sub>1</sub> : AH <sub>1</sub> = 1.069 (1.078), H <sub>1</sub> AH <sub>2</sub> = 132.0 (136)	NH <sub>3</sub>	[4-31G] D <sub>3h</sub> : <sup>1</sup> A <sub>1</sub> ': AH <sub>1</sub> = 0.986
CH <sub>3</sub> <sup>+</sup>	[STO-3G] C <sub>3v</sub> → D <sub>3h</sub> : <sup>1</sup> A <sub>1</sub> → <sup>1</sup> A <sub>1</sub> '': AH <sub>1</sub> = 1.120	NH <sub>3</sub>	[STO-3G] (15) C <sub>3v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.033 (1.012), H <sub>1</sub> AH <sub>4</sub> = 104.2 (106.7)
CH <sub>3</sub> <sup>+</sup>	[4-31G] C <sub>3v</sub> → D <sub>3h</sub> : <sup>1</sup> A <sub>1</sub> → <sup>1</sup> A <sub>1</sub> '': AH <sub>1</sub> = 1.076	NH <sub>3</sub>	[4-31G] (15) C <sub>3v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 0.991 (1.012), H <sub>1</sub> AH <sub>4</sub> = 115.8 (106.7)
CH <sub>3</sub>	[STO-3G] (11) D <sub>3h</sub> : <sup>2</sup> A <sub>2</sub> '': AH <sub>1</sub> = 1.078 (1.079)	NH <sub>4</sub> <sup>+</sup>	[STO-3G] D <sub>4h</sub> : <sup>1</sup> A <sub>1g</sub> : AH <sub>4</sub> = 1.057
CH <sub>3</sub>	[STO-3G] (11) C <sub>3v</sub> : <sup>2</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.080 (1.079), H <sub>1</sub> AH <sub>4</sub> = 118.3 (120)	NH <sub>4</sub> <sup>+</sup>	[4-31G] D <sub>4h</sub> : <sup>1</sup> A <sub>1g</sub> : AH <sub>4</sub> = 1.037
CH <sub>3</sub>	[4-31G] (11) C <sub>3v</sub> → D <sub>3h</sub> : <sup>2</sup> A <sub>1</sub> → <sup>2</sup> A <sub>2</sub> '': AH <sub>1</sub> = 1.070 (1.079)	NH <sub>4</sub> <sup>+</sup>	[STO-3G] (16) T <sub>d</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.044 (1.037)
CH <sub>4</sub> <sup>+</sup>	[STO-3G] C <sub>3v</sub> : <sup>2</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.354, AH <sub>3</sub> = 1.108, H <sub>3</sub> AH <sub>4</sub> = 118.8	NH <sub>4</sub> <sup>+</sup>	[4-31G] (16) T <sub>d</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.012 (1.037)
CH <sub>4</sub> <sup>+</sup>	[4-31G] C <sub>3v</sub> : <sup>2</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.427, AH <sub>3</sub> = 1.080, H <sub>3</sub> AH <sub>4</sub> = 119.1	NH <sub>4</sub>	[STO-3G] T <sub>d</sub> : <sup>2</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.197
CH <sub>4</sub> <sup>+</sup>	[STO-3G] C <sub>2v</sub> : <sup>2</sup> B <sub>1</sub> : AH <sub>1</sub> = 1.100, AH <sub>4</sub> = 1.198, H <sub>1</sub> AH <sub>2</sub> = 118.7, H <sub>4</sub> AH <sub>5</sub> = 72.4	NH <sub>4</sub>	[4-31G] T <sub>d</sub> : <sup>2</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.058
CH <sub>4</sub> <sup>+</sup>	[4-31G] C <sub>2v</sub> : <sup>2</sup> B <sub>1</sub> : AH <sub>1</sub> = 1.072, AH <sub>4</sub> = 1.171, H <sub>1</sub> AH <sub>2</sub> = 120.3, H <sub>4</sub> AH <sub>5</sub> = 63.5	NH <sub>4</sub>	[STO-3G] C <sub>s</sub> → C <sub>2v</sub> (Y shape): <sup>2</sup> A' → <sup>2</sup> B <sub>1</sub> : AH <sub>1</sub> = 2.644, AH <sub>2</sub> = 3.358, AH <sub>4</sub> = 1.058, H <sub>4</sub> AH <sub>5</sub> = 100.3
CH <sub>4</sub> <sup>+</sup>	[STO-3G] D <sub>2d</sub> : <sup>2</sup> B <sub>2</sub> : AH <sub>1</sub> = 1.134, H <sub>1</sub> AH <sub>2</sub> = 137.4	NH <sub>4</sub>	[4-31G] C <sub>s</sub> → C <sub>2v</sub> (Y shape): <sup>2</sup> A' → <sup>2</sup> B <sub>1</sub> : AH <sub>1</sub> = 2.868, AH <sub>2</sub> = 3.600, AH <sub>4</sub> = 1.014, H <sub>4</sub> AH <sub>5</sub> = 108.6
CH <sub>4</sub> <sup>+</sup>	[4-31G] D <sub>2d</sub> : <sup>2</sup> B <sub>2</sub> : AH <sub>1</sub> = 1.110, H <sub>1</sub> AH <sub>2</sub> = 140.7	OH <sup>+</sup>	[STO-3G] C <sub>∞v</sub> : <sup>1</sup> Δ: AH <sub>1</sub> = 1.080
CH <sub>4</sub>	[STO-3G] D <sub>4h</sub> : <sup>1</sup> A <sub>1g</sub> : AH <sub>4</sub> = 1.074	OH <sup>+</sup>	[4-31G] C <sub>∞v</sub> : <sup>1</sup> Δ: AH <sub>1</sub> = 1.021
CH <sub>4</sub>	[4-31G] D <sub>4h</sub> : <sup>1</sup> A <sub>1g</sub> : AH <sub>4</sub> = 1.081	OH <sup>+</sup>	[STO-3G] (10) C <sub>∞v</sub> : <sup>3</sup> Σ <sup>-</sup> : AH <sub>1</sub> = 1.084 (1.0289)
CH <sub>4</sub>	[STO-3G] C <sub>s</sub> → C <sub>2v</sub> (Y shape): <sup>3</sup> A'' → <sup>3</sup> B <sub>1</sub> : AH <sub>1</sub> = 3.550, AH <sub>2</sub> = 4.262, AH <sub>4</sub> = 1.082, H <sub>4</sub> AH <sub>5</sub> = 125.6	OH <sup>+</sup>	[4-31G] (10) C <sub>∞v</sub> : <sup>3</sup> Σ <sup>-</sup> : AH <sub>1</sub> = 1.023 (1.0289)
CH <sub>4</sub>	[4-31G] C <sub>s</sub> → C <sub>2v</sub> (Y shape): <sup>3</sup> A'' → <sup>3</sup> B <sub>1</sub> : AH <sub>1</sub> = 3.338, AH <sub>2</sub> = 4.067, AH <sub>4</sub> = 1.069, H <sub>4</sub> AH <sub>5</sub> = 132.1	OH	[STO-3G] (10) C <sub>∞v</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 1.014 (0.9706)
CH <sub>4</sub>	[STO-3G] (13) T <sub>d</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.083 (1.085)	OH	[4-31G] (10) C <sub>∞v</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 0.968 (0.9706)
CH <sub>4</sub>	[4-31G] (13) T <sub>d</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.081 (1.085)	OH <sub>2</sub> <sup>+</sup>	[STO-3G] D <sub>∞h</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 1.014
CH <sub>5</sub> <sup>+</sup>	[STO-3G] D <sub>3h</sub> : <sup>1</sup> A <sub>1</sub> ': AH <sub>1</sub> = 1.114, AH <sub>2</sub> = 1.136	OH <sub>2</sub> <sup>+</sup>	[STO-3G] C <sub>2v</sub> : <sup>2</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.014, H <sub>1</sub> AH <sub>2</sub> = 162.2
CH <sub>5</sub> <sup>+</sup>	[4-31G] D <sub>3h</sub> : <sup>1</sup> A <sub>1</sub> ': AH <sub>1</sub> = 1.100, AH <sub>2</sub> = 1.118	OH <sub>2</sub> <sup>+</sup>	[4-31G] C <sub>2v</sub> → D <sub>∞h</sub> : <sup>2</sup> A <sub>1</sub> → <sup>2</sup> Π: AH <sub>1</sub> = 0.987
CH <sub>5</sub> <sup>+</sup>	[STO-3G] C <sub>4v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.083, AH <sub>4</sub> = 1.139, H <sub>4</sub> AH <sub>5</sub> = 81.2	OH <sub>2</sub> <sup>+</sup>	[STO-3G] C <sub>2v</sub> : <sup>2</sup> B <sub>1</sub> : AH <sub>1</sub> = 1.033, H <sub>1</sub> AH <sub>2</sub> = 109.8
CH <sub>5</sub> <sup>+</sup>	[4-31G] C <sub>4v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 1.071, AH <sub>4</sub> = 1.117, H <sub>4</sub> AH <sub>5</sub> = 81.5	OH <sub>2</sub> <sup>+</sup>	[4-31G] C <sub>2v</sub> : <sup>2</sup> B <sub>1</sub> : AH <sub>1</sub> = 0.991, H <sub>1</sub> AH <sub>2</sub> = 119.9
CH <sub>5</sub> <sup>+</sup>	[STO-3G] C <sub>s</sub> (I): <sup>1</sup> A': AH <sub>1</sub> = 1.367, AH <sub>2</sub> = 1.370, AH <sub>3</sub> = 1.106, AH <sub>4</sub> = 1.098, H <sub>1</sub> AH <sub>2</sub> = 37.2, H <sub>2</sub> AH <sub>3</sub> = 83.8, H <sub>3</sub> AH <sub>4</sub> = 140.0, H <sub>4</sub> AH <sub>5</sub> = 117.7	OH <sub>2</sub>	[STO-3G] (17) C <sub>2v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 0.990 (0.957), H <sub>1</sub> AH <sub>2</sub> = 100.0 (104.5)
CH <sub>5</sub> <sup>+</sup>	[4-31G] C <sub>s</sub> (I): <sup>1</sup> A': AH <sub>1</sub> = 1.241, AH <sub>2</sub> = 1.242, AH <sub>3</sub> = 1.086, AH <sub>4</sub> = 1.077, H <sub>1</sub> AH <sub>2</sub> = 40.1, H <sub>2</sub> AH <sub>3</sub> = 84.8, H <sub>3</sub> AH <sub>4</sub> = 131.6, H <sub>4</sub> AH <sub>5</sub> = 116.2	OH <sub>2</sub>	[4-31G] (17) C <sub>2v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 0.951 (0.957), H <sub>1</sub> AH <sub>2</sub> = 111.2 (104.5)
CH <sub>5</sub> <sup>+</sup>	[STO-3G] C <sub>s</sub> (II): <sup>1</sup> A': AH <sub>1</sub> = 1.095, AH <sub>4</sub> = 1.103, AH <sub>7</sub> = 1.364, H <sub>7</sub> AH <sub>1</sub> = 104.5, H <sub>1</sub> AH <sub>4</sub> = 141.8, H <sub>4</sub> AH <sub>5</sub> = 111.6, H <sub>7</sub> AH <sub>8</sub> = 37.5	OH <sub>3</sub> <sup>+</sup>	[STO-3G] D <sub>3h</sub> : <sup>1</sup> A <sub>1</sub> ': AH <sub>1</sub> = 0.983
CH <sub>5</sub> <sup>+</sup>	[4-31G] C <sub>s</sub> (II): <sup>1</sup> A': AH <sub>1</sub> = 1.074, AH <sub>4</sub> = 1.083, AH <sub>7</sub> = 1.238, H <sub>7</sub> AH <sub>1</sub> = 108.0, H <sub>1</sub> AH <sub>4</sub> = 134.4, H <sub>4</sub> AH <sub>5</sub> = 108.1, H <sub>7</sub> AH <sub>8</sub> = 40.4	OH <sub>3</sub> <sup>+</sup>	[STO-3G] C <sub>3v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 0.990, H <sub>1</sub> AH <sub>4</sub> = 113.9
CH <sub>5</sub>	[STO-3G] D <sub>3h</sub> : <sup>2</sup> A <sub>1</sub> '': AH <sub>1</sub> = 1.085, AH <sub>2</sub> = 1.358	OH <sub>3</sub> <sup>+</sup>	[4-31G] C <sub>3v</sub> → D <sub>3h</sub> : <sup>1</sup> A <sub>1</sub> → <sup>1</sup> A <sub>1</sub> '': AH <sub>1</sub> = 0.964
CH <sub>5</sub>	[4-31G] D <sub>3h</sub> : <sup>2</sup> A <sub>1</sub> '': AH <sub>1</sub> = 1.074, AH <sub>2</sub> = 1.426	OH <sub>3</sub>	[STO-3G] C <sub>3v</sub> → D <sub>3h</sub> : <sup>2</sup> A <sub>1</sub> → <sup>2</sup> A <sub>1</sub> '': AH <sub>1</sub> = 1.145
CH <sub>5</sub>	[STO-3G] C <sub>s</sub> (I) → C <sub>3v</sub> : <sup>2</sup> A' → <sup>2</sup> A <sub>1</sub> : AH <sub>1</sub> = 3.376, AH <sub>2</sub> = 4.088, AH <sub>3</sub> = 1.080, H <sub>2</sub> AH <sub>3</sub> = 97.5, H <sub>3</sub> AH <sub>4</sub> = 118.3	OH <sub>3</sub>	[4-31G] C <sub>3v</sub> → D <sub>3h</sub> : <sup>2</sup> A <sub>1</sub> → <sup>2</sup> A <sub>1</sub> '': AH <sub>1</sub> = 1.056
CH <sub>6</sub>	[4-31G] C <sub>s</sub> (I) → C <sub>3v</sub> : <sup>2</sup> A' → <sup>2</sup> A <sub>1</sub> : AH <sub>1</sub> = 3.202, AH <sub>2</sub> = 3.933, AH <sub>3</sub> = 1.070, H <sub>2</sub> AH <sub>3</sub> = 90.0, H <sub>3</sub> AH <sub>4</sub> = 120.0	OH <sub>3</sub>	[STO-3G] C <sub>s</sub> (planar) → C <sub>∞v</sub> : <sup>2</sup> A' → <sup>2</sup> Π: AH <sub>1</sub> = 2.687, AH <sub>2</sub> = 3.399, AH <sub>3</sub> = 1.014, H <sub>1</sub> AH <sub>2</sub> = 0.0, H <sub>2</sub> AH <sub>3</sub> = 180.0
NH <sup>+</sup>	[STO-3G] C <sub>∞v</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 1.140	OH <sub>3</sub>	[4-31G] C <sub>s</sub> (planar) → C <sub>∞v</sub> : <sup>2</sup> A' → <sup>2</sup> Π: AH <sub>1</sub> = 2.859, AH <sub>2</sub> = 3.590, AH <sub>3</sub> = 0.968, H <sub>1</sub> AH <sub>2</sub> = 0.0, H <sub>2</sub> AH <sub>3</sub> = 180.0
NH <sup>+</sup>	[4-31G] C <sub>∞v</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 1.049	OH <sub>3</sub>	[STO-3G] C <sub>s</sub> (planar): <sup>2</sup> A'': AH <sub>1</sub> = 2.449, AH <sub>2</sub> = 3.160, AH <sub>3</sub> = 1.014, H <sub>1</sub> AH <sub>2</sub> = 1.1, H <sub>2</sub> AH <sub>3</sub> = 110.8
NH <sup>+</sup>	[STO-3G] C <sub>∞v</sub> : <sup>4</sup> Σ <sup>-</sup> : AH <sub>1</sub> = 1.136	OH <sub>3</sub>	[4-31G] C <sub>s</sub> (planar): <sup>2</sup> A'': AH <sub>1</sub> = 2.790, AH <sub>2</sub> = 3.507, AH <sub>3</sub> = 0.968, H <sub>1</sub> AH <sub>2</sub> = 2.5, H <sub>2</sub> AH <sub>3</sub> = 95.3
NH <sup>+</sup>	[4-31G] C <sub>∞v</sub> : <sup>4</sup> Σ <sup>-</sup> : AH <sub>1</sub> = 1.060	FH <sup>+</sup>	[STO-3G] C <sub>∞v</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 1.034
NH	[STO-3G] (14) C <sub>∞v</sub> : <sup>1</sup> Δ: AH <sub>1</sub> = 1.079 (1.0439)	FH <sup>+</sup>	[4-31G] C <sub>∞v</sub> : <sup>2</sup> Π: AH <sub>1</sub> = 1.025
NH	[4-31G] (14) C <sub>∞v</sub> : <sup>1</sup> Δ: AH <sub>1</sub> = 1.029 (1.0439)	FH	[STO-3G] (10) C <sub>∞v</sub> : <sup>1</sup> Σ <sup>+</sup> : AH <sub>1</sub> = 0.956 (0.917)
		FH	[4-31G] (10) C <sub>∞v</sub> : <sup>1</sup> Σ <sup>+</sup> : AH <sub>1</sub> = 0.922 (0.917)
		FH <sub>2</sub> <sup>+</sup>	[STO-3G] C <sub>2v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 0.974, H <sub>1</sub> AH <sub>2</sub> = 112.0
		FH <sub>2</sub> <sup>+</sup>	[4-31G] C <sub>2v</sub> : <sup>1</sup> A <sub>1</sub> : AH <sub>1</sub> = 0.969, H <sub>1</sub> AH <sub>2</sub> = 125.5
		FH <sub>2</sub>	[STO-3G] C <sub>s</sub> → C <sub>∞v</sub> : <sup>2</sup> A' → <sup>2</sup> Π: AH <sub>1</sub> = 2.575, AH <sub>2</sub> = 3.287, H <sub>1</sub> AH <sub>2</sub> = 0.0
		FH <sub>2</sub>	[4-31G] C <sub>s</sub> → C <sub>∞v</sub> : <sup>2</sup> A' → <sup>2</sup> Π: AH <sub>1</sub> = 2.738, AH <sub>2</sub> = 3.467, H <sub>1</sub> AH <sub>2</sub> = 0.0

According to both theoretical calculations, both  ${}^3B_1$  and  ${}^1A_1$  states have bent equilibrium geometries, the singlet having the smaller bond angle. In both theories the triplet state has a lower energy. Experimentally both states are known, the triplet being lower. The theory gives good agreement with experiment for the singlet geometry. For the triplet, early spectroscopic evidence<sup>11</sup> favored a linear structure. However more recent electron spin resonance<sup>20</sup> and spectroscopic work<sup>12</sup> indicates a bent form with a bond angle of about  $136^\circ$ . The present theory and other work<sup>21-23</sup> are clearly consistent with the bent structure.

The energy separation between singlet and triplet forms of  $CH_2$  is not well known experimentally, although there is recent evidence that it is small.<sup>24</sup> The STO-3G and 4-31G bases lead to values of 40 and 37 kcal/mol, but these are probably overestimates, since the correlation correction is expected to be larger for the singlet state where there are more paired electrons.

**$CH_3^+$ ,  $CH_3$ .** We next consider methyl and its cation, which are examples of symmetric triatomic hydrides  $AH_3$  which may exist in a planar ( $D_{3h}$ ) or pyramidal ( $C_{3v}$ ) form. Walsh proposed an energy level diagram<sup>25</sup> for these symmetries in which the ordering in the planar ( $D_{3h}$ ) configuration is

$$1a_1' < 2a_1' < 1e' < 1a_2'' < 3a_1'$$

Here  $1a_1'$  is the central atom inner shell,  $2a_1'$  and  $1e'$  describe the three in-plane AH  $\sigma$  bonds, and  $1a_2''$  is a nonbonding  $2p\pi$  atomic orbital. On bending to the nonplanar  $C_{3v}$  form, the  $1a_2''$  orbital becomes  $a_1$  in symmetry and is lowered in energy by acquisition of s character on the central atom. The ordering in  $C_{3v}$  is then

$$1a_1 < 2a_1 < 1e < 3a_1 < 4a_1$$

According to the Walsh scheme, the bending into a pyramidal form is largely determined by the number of electrons in the  $1a_2'' \rightarrow 3a_1$  molecular orbital. These general features are confirmed for the molecules treated here.

The methyl cation  $CH_3^+$  has no  $\pi$  electrons and is found to be planar with a  $D_{3h}$  electron configuration  $(1a_1')^2(2a_1')^2(1e')^4$ ,  ${}^1A_1'$ . Comparable results are obtained for both basis sets. The methyl radical  $CH_3$  is found to be very slightly bent at the STO-3G level but planar with 4-31G. As we shall find subsequently, STO-3G appears to underestimate bond angles somewhat, so the planar form is probably correct. This is consistent with experimental data.

**$CH_4^+$ ,  $CH_4$ .** Methane has a ground electron configuration and state  $(1a_1)^2(2a_1)^2(1t_2)^4$ ,  ${}^1A_1$  in its  $T_d$  tetrahedral form. Removal of one electron to give  $CH_4^+$  would therefore lead to a degenerate state  $(1a_1)^2(2a_1)^2(1t_2)^3$ ,  ${}^2T_2$ . This will distort into some lower symmetry according to the Jahn-Teller theorem<sup>26,27</sup> to

(20) E. Wasserman, W. J. Kuck, R. S. Hutton, and W. A. Yager, *J. Amer. Chem. Soc.*, **92**, 7491 (1970); R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, **53**, 1280 (1970).

(21) J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969).

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(24) R. W. Carr, Jr., T. W. Eder, and M. G. Topor, *J. Chem. Phys.*, **53**, 4716 (1970).

(25) A. D. Walsh, *J. Chem. Soc.*, 2301 (1953).

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(27) H. A. Jahn, *ibid.*, **164**, 117 (1938).

give a nondegenerate ground state. Two lower symmetries were previously investigated<sup>7</sup> with the STO-3G basis and have now been extended to 4-31G. The first is  $C_{2v}$  in which two pairs of CH bonds, each forming an isosceles  $CH_2$  group, are perpendicular to each other with a common bisector. Within the restrictions implied by this symmetry, two distinct minima were found. One corresponds to opening the bond angles in both groups giving a  $D_{2d}$  structure which approaches a planar form. In the second  $C_{2v}$  structure, one  $CH_2$  angle is opened and the other is closed to a much smaller angle. This corresponds roughly to a complex between  $CH_2^+$  and  $H_2$ . Dissociation from this form to these products requires 34 kcal/mol according to the 4-31G basis. Finally, a  $C_{3v}$  structure was optimized and found to give a  ${}^2A_1$  state with one CH bond lengthened and the other three opened out toward a planar structure. This corresponds roughly to a proton attached to a methyl radical on the three-fold axis. The energy ordering of these structures is predicted to be

$$E(D_{2d}) < E(C_{2v}) < E(C_{3v})$$

in all three types of calculation. However, it should be noted that the energy separation among them is rather small (a spread of about 3 kcal/mol for the 4-31G basis). Similar  $D_{2d}$  and  $C_{3v}$  structures have previously been reported.<sup>28</sup>

The lowest triplet state of neutral  $CH_4$  has an electron configuration  $(1a_1)^2(2a_1)^2(1t_2)^3(3a_1)$  and corresponds to a  ${}^3T_2$  state. This again is expected to distort according to the Jahn-Teller theorem. However, it appears that triplet methane dissociates to  $CH_3 + H$  with both basis sets. Studies were made with  $C_{3v}$  geometry, allowing for one bond to be inequivalent to the other three, but energy minimization leads to complete dissociation. Presumably, there is a weak interaction involving dispersion forces between a methyl radical and a hydrogen atom, but the level of theory used here is insufficient to show such an effect. A local potential minimum in the surface was found for a  $C_{2v}$  structure corresponding to a weak interaction between triplet  $CH_2$  and a hydrogen molecule lying on the  $CH_2$  axis. However, this has a higher total energy than  $CH_3 + H$ .

Methane was also examined in the square-planar ( $D_{4h}$ ) form. In this geometry, the ground state is found to be  $(1a_{1g})^2(2a_{1g})^2(1e_u)^4(1a_{2u})^2$ ,  ${}^1A_{1g}$ . This electron configuration was previously proposed by Monkhorst.<sup>29</sup> The  $a_{2u}$  molecular orbital contains a nonbonding pair of  $\pi$  electrons. The energy of this structure is substantially higher than that of the tetrahedral form (168 kcal/mol with 4-31G) and is, in fact, unstable with respect to dissociation into  $CH_3 + H$ .

**$CH_5^+$ .** Protonated methane has recently been studied theoretically by a number of authors,<sup>30</sup> with the aim of determining the relative energies of several possible structures. In Table II we give energies for the trigonal bipyramid ( $D_{3h}$ ), square pyramid ( $C_{4v}$ ), and the less symmetrical  $C_s(I)$  and  $C_s(II)$  structures. These extend our previously published results.<sup>7</sup> It is ap-

(28) J. Arents and L. C. Allen, *J. Chem. Phys.*, **53**, 73 (1970); R. N. Dixon, *Mol. Phys.*, **20**, 113 (1971).

(29) H. J. Monkhorst, *Chem. Commun.*, 1111 (1968).

(30) V. Dyczmons, V. Staemmler, and W. Kutzelnigg, *Chem. Phys. Lett.*, **5**, 361 (1970).

parent that both basis sets indicate the energy ordering to be

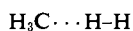
$$E(D_{3h}) > E(C_{4v}) > E(C_s)$$

and that the  $C_s$  structure corresponds approximately to a complex between  $\text{CH}_3$  and  $\text{H}_2^+$  (or  $\text{CH}_3^+$  and  $\text{H}_2$ ). The two long CH bonds in the  $C_s$  structures are found to be rather shorter with the 4-31G basis. Both basis sets give virtually identical energies for  $C_s(\text{I})$  and  $C_s(\text{II})$ , indicating nearly free relative rotation of the  $\text{CH}_3$  and  $\text{H}_2$  parts of the molecule. The energy difference between  $D_{3h}$  and  $C_s(\text{I})$  is found to be 7.2 kcal/mol with the 4-31G basis. These results are similar to those of Dyczmons, Staemmler, and Kutzelnigg,<sup>30</sup> who have used a larger basis set and obtain lower total energies. They also find the  $C_s$  structures to be most stable but obtain a larger separation (14 kcal/mol) between  $D_{3h}$  and  $C_s$ .

**$\text{CH}_5$ .** In considering the possible existence of the  $\text{CH}_5$  neutral molecule, we have to examine calculated energies relative to those of possible separated products. Here the products would be  $\text{CH}_4 + \text{H}$  or  $\text{CH}_3 + \text{H}_2$ . Both basis sets give a lower energy for  $\text{CH}_4 + \text{H}$  (provided that atomic scale factors are used for the separate hydrogen atom). Experimentally, heats of formation of  $\text{CH}_4 + \text{H}$  and  $\text{CH}_3 + \text{H}_2$  are indistinguishably close.

All calculations that we have carried out on  $\text{CH}_5$  give energies higher than  $\text{CH}_4 + \text{H}$ . Starting with a  $C_s$ -( $\text{I}$ ) structure like  $\text{CH}_5^+$  and following the potential surface downwards, one hydrogen was found to detach itself leading to dissociation into  $\text{CH}_4 + \text{H}$ . As with triplet  $\text{CH}_4$ , it is probable that only a weak intermolecular-type complex exists between  $\text{CH}_4$  and  $\text{H}$  and that the level of theory used here is insufficient to allow for such an interaction.

Local minima were found for  $\text{CH}_5$  which represent loose complexes between  $\text{CH}_3$  and  $\text{H}_2$  with both basis sets. These have  $C_{3v}$  symmetry with the hydrogen molecule on the threefold axis



According to the 4-31G basis, the distance between the carbon atom and the nearest hydrogen of  $\text{H}_2$  is 3.2 Å, and the intermolecular attractive energy (relative to  $\text{CH}_3 + \text{H}_2$ ) is 0.22 kcal/mol.

Finally, we have studied the trigonal-bipyramid ( $D_{3h}$ ) structure. With the 4-31G basis, this is found to have a high energy, 50 kcal/mol above  $\text{CH}_4 + \text{H}$ . It is unlikely to play a significant role in the interaction of methane and a hydrogen atom.

**$\text{NH}^+$ ,  $\text{NH}$ .** The  $\text{NH}^+$  ion is isoelectronic with  $\text{CH}$ . We have examined the doublet state  $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)$ ,  ${}^2\Pi$ , and the quartet state  $(1\sigma)^2(2\sigma)^2(3\sigma)(1\pi)^2$ ,  ${}^4\Sigma^-$ . The latter correlates with the ground state of the corresponding united atom ( $\text{O}^+$ ). Both theories predict the quartet state to be lower in energy (the difference being 28 kcal/mol with the 4-31G basis). Experimentally it is known that the doublet is lesser by 1.0 kcal/mol.<sup>31</sup> This failure of the theory emphasizes the difficulty of comparing energies of states of different multiplicity without an adequate treatment of correlation differences. A treatment by Liu and Verhaegen<sup>32</sup> with a larger basis gives similar results. Approaching the

(31) R. Colin and A. E. Douglas, *Can. J. Phys.*, **46**, 61 (1968).

(32) H. P. D. Liu and G. Verhaegen, *J. Chem. Phys.*, **53**, 735 (1970).

Hartree-Fock limit, they find the quartet to be predicted as 18 kcal/mol more stable and attribute the observed reversal to correlation differences.

The neutral  $\text{NH}$  molecule has a lowest energy configuration  $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^2$ . This leads to  ${}^3\Sigma^-$ ,  ${}^1\Delta$ , and  ${}^1\Sigma^+$  states. We have examined the  ${}^3\Sigma^-$  and  ${}^1\Delta$  states, the latter using complex molecular orbitals as were required for the linear form of singlet methylene. Both types of calculation predict that  ${}^3\Sigma^-$  is of lower energy, in agreement with experimental findings.<sup>10</sup> The 4-31G basis gives a separation of 46 kcal/mol between  ${}^3\Sigma^-$  and  ${}^1\Delta$ . Again this is probably too large because the correlation correction will be greater for the singlet state. Experimentally, an upper limit of 37 kcal/mol has been obtained for this separation by Okabe and Lenzi.<sup>33</sup> A fuller treatment by Cade<sup>34</sup> including an estimate of the correlation differences gave 38 kcal/mol.

**$\text{NH}_2^+$ ,  $\text{NH}_2$ .** The amino cation  $\text{NH}_2^+$  is isoelectronic with methylene and it has similar electronic states. The lowest state is predicted to be a bent triplet  ${}^3B_1$ . The theoretical angle is larger than for  $\text{CH}_2$  ( $157^\circ$  with 4-31G), in line with the general prediction of widening angles in cations. The singlet state has a smaller angle ( $116^\circ$  with 4-31G). A bent singlet structure was also found by Peyerimhoff, Buenker and Allen.<sup>35</sup> The theoretical singlet-triplet separation is 59 kcal/mol (4-31G), but, as with  $\text{CH}_2$ , this is probably an overestimate.

The neutral amino radical is an example of a Renner-type<sup>36,37</sup> molecule. In its linear form it has a degenerate ground state with three  $\pi$  electrons,  $(1\sigma_g)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^3$ ,  ${}^2\Pi_u$ . On bending to  $C_{2v}$  symmetry this leads to two states,  $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)$ ,  ${}^2B_1$ , and  $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1)^2$ ,  ${}^2A_1$ . According to the Walsh scheme,<sup>18</sup> the  $3a_1$  molecular orbital lies below  $1b_1$ , so that the  ${}^2B_1$  state will lie lower. This is confirmed by the theoretical studies with both basis sets, which give bent configurations for both states,  ${}^2B_1$  being the more bent and also lower in energy.

The two lowest states of  $\text{NH}_2$  have been the subject of an intensive spectroscopic examination. The results are in reasonable agreement with the theoretical results given here and (for the  ${}^2B_1$  state) by Claxton.<sup>38</sup> Thus, using the 4-31G basis, we obtain values of  $108$  and  $145^\circ$  for the HNH angles in the  ${}^2B_1$  and  ${}^2A_1$  states, compared with the experimental values of  $103$  and  $\sim 144^\circ$ . The theoretical energy separation between the states is 26.5 kcal/mol, to be compared with an experimental value of about 29 kcal/mol. A small potential hump in the upper potential curve (difference between linear  ${}^2\Pi$  and bent  ${}^2A_1$ ) is found theoretically (2.3 kcal/mol).

**$\text{NH}_3^+$ ,  $\text{NH}_3$ .** The ammonia cation  $\text{NH}_3^+$  is found to be planar, with  $D_{3h}$  symmetry, using both basis sets. This result was also obtained by Claxton and Smith.<sup>39a</sup> It is isoelectronic with the methyl radical and has the same configuration  $(1a_1')^2(2a_1')^2(1e')^4(1a_2'')$ ,  ${}^2A_2''$ .

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(34) P. E. Cade, *Can. J. Phys.*, **46**, 1989 (1968).

(35) S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966).

(36) G. Herzberg and E. Teller, *Z. Phys. Chem., Abt. B*, **21**, 410 (1933).

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(38) T. A. Claxton, *Trans. Faraday Soc.*, **66**, 1537 (1970).

(39) (a) T. A. Claxton and N. A. Smith, *ibid.*, **66**, 1825 (1970); (b) J. S. Hyde and E. S. Freeman, *J. Phys. Chem.*, **65**, 1636 (1961); T. Cole, *J. Chem. Phys.*, **35**, 1169 (1961).



It may be noted that the STO-3G basis gives planar  $\text{NH}_3^+$  but slightly nonplanar  $\text{CH}_3$ . This reflects the general trend found in most systems for the valence angles to be larger in cations than in isoelectronic neutral species. The radical ion has an electron spin resonance spectrum which is consistent with a planar structure.<sup>39b</sup> An analysis of the Franck-Condon factors for a vertical transition of pyramidal ammonia to planar  $\text{NH}_3^+$  led Botter and Rosenstock<sup>40</sup> to suggest the NH bond in the ion to be 0.06–0.07 Å shorter than in the parent. This is in disagreement with our findings.

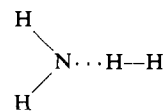
The ammonia molecule is found to be nonplanar with both basis sets. The experimental HNH angle is about 107°, which lies between the theoretical values of 104° (STO-3G) and 116° (4-31G). The 4-31G basis gives a structure which approaches planarity, leading to much too small a value of the inversion barrier (0.4 kcal/mol compared with the experimental value of 5.8 kcal/mol).<sup>41</sup> This deficiency of the extended basis parallels results of Rauk, Allen, and Clementi,<sup>42</sup> who found that inclusion of d functions had an important influence on the calculated barrier.

The lowest triplet state of ammonia was found to have a linear geometry corresponding to a very weak complex (binding energy 0.4 kcal/mol with 4-31G) between NH and  $\text{H}_2$ ,  $\text{HN} \cdots \text{H}-\text{H}$ . No binding was found for the reversed form  $\text{NH} \cdots \text{H}-\text{H}$ . Both basis sets correctly predict the separated products  $\text{NH} + \text{H}_2$  to be more stable than  $\text{NH}_2 + \text{H}$ .

$\text{NH}_4^+$ ,  $\text{NH}_4$ . The ammonium ion  $\text{NH}_4^+$  is isoelectronic with  $\text{CH}_4$  and was considered in tetrahedral ( $T_d$ ) and square-planar ( $D_{4h}$ ) symmetry. The tetrahedral form was found to be much more stable (by 129 kcal/mol with 4-31G), as expected on the basis of experimental and other theoretical work.<sup>43,44</sup>

The neutral  $\text{NH}_4$  system was initially considered with tetrahedral  $T_d$  symmetry. Early theoretical work<sup>45</sup> with a one-center basis of Slater-type functions suggested that this might be stable with respect to  $\text{NH}_3 + \text{H}$ . A later one-center study<sup>46</sup> again suggested that the tetrahedral form is at least a minimum in the potential surface. The computations reported here give much lower total energies and do not support these conclusions. In the first place, the tetrahedral restriction leads to total energies substantially above that of  $\text{NH}_3 + \text{H}$  (44 kcal/mol with the 4-31G basis). Further, the tetrahedral form is found to be a saddle point and not a local potential minimum. On lowering the symmetry to  $C_{3v}$  with one bond inequivalent to the other three, it was found that the energy decreased continuously along the dissociation path to  $\text{NH}_3 + \text{H}$ . In fact, no energy below this limit has been found for  $\text{NH}_4$  with either basis set.

The 4-31G basis predicts that  $\text{NH}_3 + \text{H}$  is slightly more stable than  $\text{NH}_2 + \text{H}_2$  (by about 3 kcal/mol), but experimentally the two energies are equal within quoted errors. A search of the  $\text{NH}_4$  surface in the appropriate region led to a  $C_{2v}$  local minimum approximating to a loose complex



The intermolecular binding (relative to  $\text{NH}_2$  and  $\text{H}_2$ ) is found to be 0.8 kcal/mol. Since the  $\text{NH}_2$  part is in its  ${}^2B_1$  state with two electrons in a  $\sigma$ -type lone pair orbital on nitrogen, this interaction may be considered as a very weak hydrogen bond.

$\text{OH}^+$ ,  $\text{OH}$ . The  $\text{OH}^+$  ion has two  $\pi$  electrons with the configuration  $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^2$ . As with the isoelectronic NH system, the lowest state is found to be the triplet  ${}^3\Sigma^-$ . Again, the STO-3G basis predicts too long a bond length (1.084 Å) while the 4-31G basis gives a value (1.023 Å) in good agreement with experiment (1.029 Å). As for the  $\text{CH}^+$  cation, full valence-shell exponent optimization for  $\text{OH}^+$  with the Slater-type basis gives improved results ( $\zeta_{\text{O}} = 2.35$ ,  $\zeta_{\text{H}} = 1.45$ , and  $R = 1.006$  Å).

The neutral hydroxyl radical is found to have the configuration  $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^3$ ,  ${}^2\Pi$ , in agreement with the experimental assignment.

$\text{OH}_2^+$ ,  $\text{OH}_2$ . The water ground-state results have been reported previously<sup>1,6</sup> and need little comment. The calculated bond angles are both somewhat in error, the STO-3G value being too small and the 4-31G value too large. The STO-3G geometry is close to the full STO result of Pitzer and Merrifield<sup>47</sup> (0.990 Å and 100.3°), while the 4-31G basis gives results similar to the "essentially double zeta quality" calculation of Kollman and Allen<sup>48</sup> (0.965 Å and 110.5°).

The triplet state of water was examined in general  $C_s$  symmetry, but no geometry was found to give a significantly lower energy than the most stable products  $\text{O}({}^3P) + \text{H}_2$ . The most stable form of this system is therefore probably a weak intermolecular complex between O and  $\text{H}_2$ . However, both bases are insufficiently flexible to describe such an interaction. It should be noted that these results are not consistent with the bound triplet state (with respect to  $\text{H}_2 + \text{O}$ ) postulated recently on the basis of electron-scattering experiments.<sup>49</sup>

The highest occupied molecular orbital of water is the  $\pi$ -type ( $1b_1$ ) lone-pair orbital, so that the ground state of the cation  $\text{H}_2\text{O}^+$  is expected to be  $(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)$ ,  ${}^2B_1$ . This is indeed found, but there is an opening of the valence angle by about 10° for each basis set. Some bond lengthening is also indicated. Similar results for the bond angle were found by Krauss.<sup>43</sup>

$\text{H}_2\text{O}^+$  in its linear form is another Renner-type system<sup>36,37</sup> with a  ${}^2\Pi$  ground state, there being three  $\pi$  electrons. On bending, these split into  ${}^2A_1$  and  ${}^2B_1$ , the latter being the lower. The upper ( ${}^2A_1$ ) state was also examined and found to be only slightly bent with the STO-3G basis but linear with the 4-31G basis. Comparison with the corresponding state of  $\text{NH}_2$  again indicates some opening of bond angles in cations compared with isomeric neutral systems.

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(40) R. Botter and H. M. Rosenstock, *Advan. Mass Spectrom.*, **4**, 579 (1968).

(41) J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **36**, 1914 (1962).

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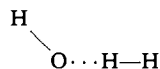
(46) C. E. Melton and H. W. Joy, *ibid.*, **46**, 4275 (1967).



**OH<sub>3</sub><sup>+</sup>, OH<sub>3</sub>.** The oxonium ion H<sub>3</sub>O<sup>+</sup> was examined in C<sub>3v</sub> symmetry and found to be slightly pyramidal for the STO-3G basis (HOH angle of 113.9°), with a small inversion barrier (~1 kcal/mol). However, the extended basis gives a planar D<sub>3h</sub> structure. As with other systems, both basis sets lead to valence angles larger in cations than in the isomeric neutral system (NH<sub>3</sub> in this case). Since the NH<sub>3</sub> inversion barrier is overestimated by the STO-3G basis, it seems probable that the H<sub>3</sub>O<sup>+</sup> structure actually is planar. This agrees with other work including a study with a large Gaussian basis by Moskowitz and Harrison.<sup>50</sup>

The existence of the H<sub>3</sub>O radical as a stable species has been suggested and some one-center theoretical work has lent support.<sup>46,51,52</sup> However, the computations reported here do not lead to a tightly bound species. Initially, H<sub>3</sub>O was examined in C<sub>3v</sub> symmetry and found to become flat (D<sub>3h</sub>), but the energy of this symmetrical form is substantially higher (49 kcal/mol with 4-31G) than H<sub>2</sub>O + H. Further, on lowering the symmetry to a C<sub>2v</sub> planar form with one OH bond longer than the other two, it was found that the D<sub>3h</sub> structure was only a saddle point in the potential surface and that the energy decreased continuously to dissociation into H<sub>2</sub>O + H. This is analogous to the behavior of NH<sub>4</sub>.

The lowest energy was found for a loose complex of a hydroxyl radical and a hydrogen molecule



with the H<sub>2</sub> pointing approximately toward a doubly occupied lone-pair orbital of OH. The binding energy with respect to OH + H<sub>2</sub>, however, is only 0.6 kcal/mol (4-31G) so that this corresponds to a weak hydrogen bond. Actually, this structure is presumably not close to the lowest point of the real potential surface since both basis sets incorrectly predict OH + H<sub>2</sub> to be more stable than H<sub>2</sub>O + H. Using experimental heats of formation, H<sub>2</sub>O + H is 15 kcal/mol more stable, so the most stable form is presumably a complex between H<sub>2</sub>O and H which is not described by these methods (there being insufficient basis functions on hydrogen to allow for atomic polarization).

**FH<sup>+</sup>, FH.** The HF<sup>+</sup> radical ion is isoelectronic with hydroxyl and has the ground-state configuration (1σ)<sup>2</sup>(2σ)<sup>2</sup>(3σ)<sup>2</sup>(1π)<sup>3</sup>, <sup>2</sup>I. The neutral molecule has four π electrons, giving a closed-shell <sup>1</sup>Σ<sub>g</sub><sup>+</sup> state. Both basis sets predict a substantial bond length increase of the order of 0.1 Å on ionization of HF.

**FH<sub>2</sub><sup>+</sup>, FH<sub>2</sub>.** Protonated hydrogen fluoride FH<sub>2</sub><sup>+</sup> is isoelectronic with water and is found to have the same electron configuration in the bent C<sub>2v</sub> form. The bond angle is predicted to be somewhat larger than that of water by both basis sets.

Neutral FH<sub>2</sub> is found to behave like other structures with too many AH bonds. No tightly bound structure is found, the lowest calculated energy corresponding to a weak linear complex between a fluorine atom and a hydrogen molecule (binding energy of 0.4 kcal/mol). However, it should be noted that the theory incorrectly predicts F + H<sub>2</sub> to be more stable than FH

(50) J. W. Moskowitz and M. C. Harrison, *J. Chem. Phys.*, **43**, 3550 (1965).

(51) H. J. Bernstein, *J. Amer. Chem. Soc.*, **85**, 484 (1963).

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+ H, so the real minimum probably corresponds to a weak complex between hydrogen fluoride and a hydrogen atom.

### General Comparisons

In this section, we make a number of overall comparisons with experimental properties for which experimental data are available. Beginning with the geometrical structures, we present in Table III a

**Table III.** Theoretical and Experimental Values for Geometrical Parameters

Molecule	Bond length, Å			Bond angle, deg		
	STO-3G	4-31G	Exptl	STO-3G	4-31G	Exptl
H <sub>2</sub>	0.712	0.730	0.742			
CH	1.143	1.118	1.120			
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	1.123	1.100	1.110	100.5	105.4	102.4
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	1.082	1.069	1.078	125.5	132.0	136
CH <sub>3</sub>	1.080	1.070	1.079	118.3	120.0	120
CH <sub>4</sub>	1.083	1.081	1.085			
NH ( <sup>1</sup> Δ)	1.079	1.029	1.044			
NH ( <sup>3</sup> Σ <sup>-</sup> )	1.082	1.033	1.048			
NH <sub>2</sub> ( <sup>2</sup> A <sub>1</sub> )	1.015	0.985	1.004	131.3	144.9	144
NH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> )	1.058	1.015	1.024	100.2	108.3	103.4
NH <sub>3</sub>	1.033	0.991	1.012	104.2	115.8	106.7
OH	1.014	0.968	0.971			
OH <sub>2</sub>	0.990	0.951	0.957	100.0	111.2	104.5
FH	0.956	0.922	0.917			

list of theoretical and experimental values for lengths and angles in neutral molecules. This indicates that deviations between the sets of numbers are quite systematic. The STO-3G basis gives bond lengths which are mostly too long, with a mean absolute deviation of 0.023 Å for the entries in the table. The 4-31G results are superior, the lengths being too short (except for HF), with a mean absolute deviation of only 0.010 Å. The reproduction of observed bond angles is not as good. The STO-3G basis systematically gives angles which are too small (mean deviation of 5.3°), whereas the 4-31G values are too large (mean deviation of 4.1°). The large overestimation of valence angles in molecules with lone pairs of electrons is clearly one of the most unsatisfactory features of the extended basis set. For the positive ions, there are very few experimental data, but the distances for diatomics AH<sup>+</sup> show similar errors with the 4-31G basis. For the STO-3G basis as noted in the previous section, bond lengths are overestimated because the standard molecular scale factors are inappropriate for ions.

It would be of interest to compare the geometries predicted in this paper with corresponding studies using other basis sets. Unfortunately, other work has involved a variety of different bases only applied in isolated cases. The only fairly complete results are for a large one-center basis set applied to the symmetric ten-electron hydrides CH<sub>4</sub>, NH<sub>4</sub><sup>+</sup>, NH<sub>3</sub>, H<sub>2</sub>O, and HF.<sup>53</sup> These calculations give good geometries which are superior to most of those reported here. This is probably partly due to the inclusion of d and f functions. On the other hand, we have found that the one-center approach is much less effective when applied to AH<sub>n</sub> systems with nonequivalent AH bonds. Also the

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Table IV. Totally Symmetric Stretching and Bending Force Constants

Molecule (state)	$F_{XH}$ , mdyn/Å			$F_{\alpha}$ , mdyn/Å		
	STO-3G	4-31G	Exptl	STO-3G	4-31G	Exptl
H <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	8.9	6.4	5.7 <sup>a</sup>			
CH ( <sup>2</sup> Π)	6.0	4.6	4.5 <sup>a</sup>			
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	6.4	5.3		0.90	0.80	
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	7.4	6.3		0.54	0.43	
CH <sub>3</sub> ( <sup>2</sup> A <sub>2</sub> '')	7.5	6.3			0.11 <sup>b</sup>	0.18 <sup>b</sup>
CH <sub>4</sub> ( <sup>1</sup> A <sub>1</sub> )	7.4	5.9	5.8 <sup>c</sup>			
NH ( <sup>1</sup> Δ)	7.6	6.6	5.6 <sup>a,e</sup>			
NH ( <sup>3</sup> Σ <sup>-</sup> )	7.3	6.2	6.0 <sup>a,e</sup>			
NH <sub>2</sub> ( <sup>2</sup> A <sub>1</sub> )	9.1	8.5		0.60	0.31	
NH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> )	7.8	7.1		1.06	0.77	
NH <sub>3</sub> ( <sup>1</sup> A <sub>1</sub> )	8.4	8.3	7.1 <sup>c</sup>	0.80	0.47	0.53 <sup>c</sup>
OH ( <sup>2</sup> Π)	9.2	8.0	7.8 <sup>a</sup>			
OH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	9.7	9.0	8.4 <sup>d</sup>	1.32	0.86	0.76 <sup>c</sup>
FH ( <sup>1</sup> Σ <sup>+</sup> )	11.3	9.6	9.7 <sup>a</sup>			

<sup>a</sup> Derived from experimental frequencies and anharmonicities quoted in G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950. <sup>b</sup> This force constant refers to the out-of-plane bending (per bond) for planar CH<sub>3</sub> (symmetry D<sub>3h</sub>). The experimental result is due to D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **47**, 5146 (1967). <sup>c</sup> J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, **20**, 523 (1964). <sup>d</sup> J. W. Nibler and G. C. Pimentel, *J. Mol. Spectrosc.*, **26**, 294 (1968). <sup>e</sup> No anharmonic correction applied in absence of data.

Table V. Proton Affinities, Hydrogen Atom Affinities, and Ionization Potentials (kcal/mol)

Molecule	Proton affinity			Hydrogen atom affinity			Ionization potential		
	STO-3G	4-31G	Exptl <sup>a</sup>	STO-3G	4-31G	Exptl <sup>a</sup>	STO-3G	4-31G	Exptl <sup>a</sup>
H	55	53	62	80	80	104	311	313	314
H <sub>2</sub>							336	341	356
C	143	127	138	29	45	81	224	247	260
CH	219	191	175	107	102	103	197	231	257
CH <sub>2</sub>	215	192	198	92	85	111	199	224	240
CH <sub>3</sub>	136	119	125	97	85	103	187	207	227
CH <sub>4</sub>	120	118	118				272	279	292
N	100	80	97	31	36	86	278	319	335
NH	180	160	141	51	57	90	241	269	303
NH <sub>2</sub>	231	205	184	76	83	104	181	210	263
NH <sub>3</sub>	259	221	207				156	191	234
O	154	105	114	41	52	102	184	268	314
OH	191	142	142	67	77	119	198	260	303
OH <sub>2</sub>	229	183	164				186	248	291
F	128	68	86	57	77	136	229	353	402
FH	183	120					239	322	364

<sup>a</sup> Experimental values were calculated from 298°K heats of formation.  $\Delta H_f^\circ$  (298°K) values for CH<sub>2</sub> and CH<sub>2</sub><sup>+</sup> were taken from W. A. Chupka and C. Lipshitz, *J. Chem. Phys.*, **48**, 1109 (1968); all others are from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. L. Herron, and K. Draxl, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS-26, U. S. Government Printing Office, Washington, D. C.

method cannot be effectively extended to larger molecules.

A second set of properties which may be compared with experimental data is the set of totally symmetric force constants. Some of these are obtained in the process of finding the equilibrium geometry. In fact, the final three energies for each independently varied geometrical parameter are fitted by a parabola, the curvature of which gives the force constant. Some such constants for the STO-3G basis were compared with appropriate experimental quantities in ref 1. In Table IV we present a fuller comparison for both basis sets for the symmetric neutral molecules. Again the extended basis set is found to give superior results, being usually within 10% of experimental values. It may be noted that within the sets of CH<sub>n</sub>, NH<sub>n</sub>, OH<sub>n</sub> molecules, the ordering of theoretical force constants is identical with the ordering of both theoretical and experimental bond lengths.

Finally, we can make a number of comparisons of appropriate energy differences with experimental pro-

ton affinities, bond energies, and ionization potentials. These are presented in Table V. It should be noted that the experimental numbers should really be corrected for differences in zero-point vibrational energies, but this cannot be done at present because of lack of data. The comparison brings out some features that have already been noted in our previous hydrocarbon study.<sup>7</sup> For all three properties, results are generally better with the 4-31G basis. Theoretical proton affinities are mostly too high, but the 4-31G basis gives quite good results. Mean absolute errors are 30 and 12 kcal/mol for STO-3G and 4-31G, respectively. For the bond energies (listed as hydrogen atom affinities), results are less satisfactory, particularly for the more polar bonds. The 4-31G bond energies are all too small, reflecting, in large part, the substantial contributions to bond energies of correlation energy differences. Mean absolute errors for bond energies are 38 and 33 kcal/mol. Theoretical ionization potentials are systematically low with both basis sets, the errors being somewhat greater for the molecules with nitrogen, oxygen,

and fluorine. This again is understandable, since the total correlation energy is expected to be larger in a neutral molecule than in the corresponding cation.

## Conclusions

The following general conclusions may be drawn from this work: (1) The molecular orbital configurations and geometrical shapes of the smaller neutral molecules considered are correctly given by the rules formulated by Walsh.<sup>19,25</sup> Most of these results are now confirmed experimentally.<sup>10,11</sup> (2) Positive ions are found to have states and structures which are sim-

ilar to those of the isoelectronic neutral systems. However, some opening out of bond angles is predicted by the theory. (3) The theory indicates that the lowest triplet states of the saturated molecules do not exist as tightly bound species but rather are loose intermolecular complexes between smaller fragments. The same applies to the higher valency compounds  $\text{CH}_5$ ,  $\text{NH}_4$ ,  $\text{H}_3\text{O}$ , and  $\text{H}_2\text{F}$ .

**Acknowledgments.** The initial version of the complex self-consistent-field routines was written by Dr. D. Miller. Useful discussions with Mr. J. B. Lisle are acknowledged. This research was supported in part by National Science Foundation Grant No. GP25617.

# Molecular Orbital Studies on Bifunctional Catalysis of Glucose Mutarotation. The Hydrogen Bond with 2-Pyridone<sup>1</sup>

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**Abstract:** The CNDO/2 MO method was used to study the double hydrogen bond between 2-pyridone and the portion of the glucose molecule involved in the mutarotation reaction. A correction was applied to the energy curve to account for kinetic energy constraints. The calculations indicate that the double hydrogen bond is stronger than the sum of the two separate single hydrogen bonds. The reasons appear to involve electron delocalization and a difference in the number of degrees of freedom of kinetic energy lost per hydrogen bond. In addition, it was found that the electronic rearrangements that characterized the actual ring-opening reaction are initiated with the formation of the hydrogen bond.

The concerted action of two or more functional groups is generally recognized as an important factor in enzyme catalysis. This was first suggested by Swain and Brown<sup>2</sup> on the basis of their study of the mutarotation of tetramethylglucose. In recent years the suggestion has received considerable support from structural and kinetic studies of enzymes. The current investigations are part of an effort to learn more about the basis for the rate enhancement in the model reaction.

A Hückel MO study of a series of bifunctional catalysts<sup>3</sup> led to the conclusion that electronic coupling between the functional groups is an important factor. This is in qualitative agreement with the conclusion reached by Rony<sup>4</sup> on the basis of measurements of activation parameters. Rony<sup>5</sup> later suggested electronic coupling as a generally necessary condition for concerted reactions.

The first stage of the interaction must involve a double hydrogen-bond (H bond) formation between catalyst and substrate. This paper reports the results of molecular orbital calculations, in the CNDO/2 approximation,<sup>6,7</sup> on the hydrogen bonding of glucose

with 2-pyridone. The extended Hückel procedure<sup>8</sup> was also tried but was not suitable.

Cooperativity effects appear to cause a decrease in the lengths of the H bonds and an increase in the stabilizing energy.

## Calculations

Calculations were performed on the IBM 360/75 of the Triangle Universities Computing Center. Intermediate numbers were carried in double precision for all molecular orbital calculations.

(1) **Molecular Orbital Procedure.** The CNDO/2 calculations were performed with QCPE program CNDOTWO.<sup>9</sup> The program was modified to suit local input-output requirements and to facilitate changing dimension statements. A further modification was the use of an eigenvalue subroutine<sup>10</sup> based on the Q-R algorithm.<sup>11</sup> Parameters used were those of Pople and Segal.<sup>7</sup> Except for hydrogen, the orbital exponents were those given by Slater's<sup>12</sup> rules. An exponent of 1.2 was used<sup>13</sup> for hydrogen 1s.

(7) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

(8) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

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(10) D. J. Clyde, E. M. Cramer, and R. J. Sherin, "Multivariate Statistical Programs," Biometrics Laboratory, University of Miami, Miami, Fla., 1966.

(11) See, for example, J. H. Wilkinson, "The Algebraic Eigenvalue Problem," Oxford University Press, London, 1965, Chapter 8.

(12) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

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(2) C. G. Swain and J. F. Brown, Jr., *J. Amer. Chem. Soc.*, **74**, 2538 (1952).

(3) H. J. Gold, *ibid.*, **90**, 3402 (1968).

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