

a summary of results is pertinent here. Using the POL basis, the GVB results lead to a cis-trans barrier of 66.6 kcal for the ground (N) state of ethylene. This is in good agreement with the experimental activation energy of 65 kcal. The $\pi\pi^*$ triplet (T) state is found to have a minimum in energy for the perpendicular geometry with its minimum lying 1.7 kcal lower than the saddle point in the N state. The T state has a cis-trans barrier of 31.4 kcal.

Cyclopropane and the Trimethylene Biradical

We have reported previously^{24,25} the results of GVB calculations on cyclopropane and the broken-bond trimethylene intermediate involved in the geometrical and structural isomerizations of C_3H_6 . In Figure 12a we note that the orbitals of the C-C bond have essentially sp^4 (82% p) character and are bent outside the ring in agreement with Coulson and Moffitt's earlier VB calculations.²⁶ As the central CCC angle is increased from 60 to 120° the orbitals change continu-

(23) W. J. Hunt, W. A. Goddard III, and T. H. Dunning, Jr., submitted for publication; see also W. J. Hunt, Ph.D. Thesis, California Institute of Technology, Sept 1972; T. H. Dunning, Jr., W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **4**, 147 (1969).

(24) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *J. Amer. Chem. Soc.*, **94**, 638 (1972).

(25) W. A. Goddard III and P. J. Hay, to be published.

(26) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

ously into p orbitals for planar end groups. We found essentially no barrier to ring closure (<1 kcal) for trimethylene and a barrier height of 60.5 kcal in good agreement with the experimental activation energy (64.2 kcal).

General Characteristics of GVB Orbitals

In Table IV we summarize the results of the GVB calculations of hydrocarbons. In addition to the HF and GVB total energies, the overlap $\langle\phi_{ia}|\phi_{ib}\rangle$ and the pair-splitting energy $\Delta\epsilon_i$ (i.e., the energy change due to adding the second natural orbital to the pair) is reported for each pair. To a very good approximation (~ 0.001 hartree), the total improvement in energy in GVB over HF is given by the sum of the pair splitting energies. In Table V we note that improved agreement with experimental heats of reaction is obtained using GVB functions.

Typically for reactions involving breaking of single bonds, GVB accounts for an improvement of 10–12 kcal in ΔH of the reaction (corresponding to about 10–15% of the total bond strength). For multiple bonds, although the pair lowerings are much larger than for single bonds, these are partially offset by pair lowerings in the molecular fragments with the result that total improvements in heats of reaction are 14–40 kcal.

Ab Initio Study of the Hydrogen Bond in $[H_3N-H \cdots NH_3]^+$

Peter Merlet,^{1a} Sigrid D. Peyerimhoff,*^{1a} and Robert J. Buenker^{1b}

Contribution from the Institut für Physikalische Chemie, Johannes Gutenberg Universität, 65 Mainz, Germany, and the Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68508. Received February 11, 1972

Abstract: *Ab initio* SCF calculations with varying flexibility in the basis set are reported for the hydrogen-bonded $[H_3N-H \cdots NH_3]^+$ complex. The calculations indicate that the proton transfer between the two nitrogen nuclei occurs with very little adjustment in the magnitudes of the terminal NH distances and HNH angles but is accompanied by a significant decrease (0.25 bohr) in the NN separation in the course of this exchange. An analysis of the charge distribution calculated for this hydrogen-bonded complex is also undertaken and a treatment of the vibrational structure associated with the proton transfer in this system is discussed.

I. Introduction

It is difficult to overestimate the importance of the hydrogen bond in various chemical and biological processes, particularly those which occur routinely in nature. At the same time, however, it would be rather easy to underestimate the difficulties involved in achieving a reliable theoretical description of this phenomenon; the main reason for this complexity is the fact that the characteristics of a given hydrogen bond depend quite strongly upon the properties of the specific electro-negative centers involved. As a result, even though the typical hydrogen bond produces a relatively small binding energy (generally somewhat less than 10 kcal/

mol), examples of this phenomenon are known with binding energies as great as 50 kcal/mol.²

Most theoretical *a priori* investigations on this general subject have dealt with systems containing oxygen,³

(2) A well-known example is the system $[F-H \cdots F]^-$ which has been studied experimentally by (a) S. A. Horrell and D. H. McDaniel, *J. Amer. Chem. Soc.*, **86**, 4497 (1964); (b) T. C. Waddington, *Trans. Faraday Soc.*, **54**, 25 (1958), while theoretical calculations have been carried out by (c) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 6101 (1970); (d) E. Clementi and A. D. McLean, *J. Chem. Phys.*, **36**, 745 (1962); (e) A. D. McLean and M. Yoshimine, *IBM J. Res. Develop.*, **11**, (1967).

(3) More recent examples in the literature are (a) K. Morokuma and J. R. Winick, *J. Chem. Phys.*, **52**, 1301 (1970); (b) D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *Chem. Phys. Lett.*, **4**, 527 (1970); (c) G. H. F. Diercksen, *Theor. Chim. Acta*, **21**, 335 (1971); (d) G. H. F. Diercksen and W. P. Kraemer, *Chem. Phys. Lett.*, **6**, 419 (1970), for $[F-H \cdots OH]^-$; (e) M. Dreyfus, B. Maigret, and A. Pullman, *Theor. Chim. Acta*, **17**, 109 (1970), for formamide dimer; (f) M. Dreyfus and A. Pullman, *ibid.*, **19**, 20 (1970), for formamide dimer; (g) E. Clementi,

* Address correspondence to Lehrstuhl für Theoretische Chemie, Universität Bonn, 65 Bonn, Germany.

(1) (a) Johannes Gutenberg Universität; (b) University of Nebraska.

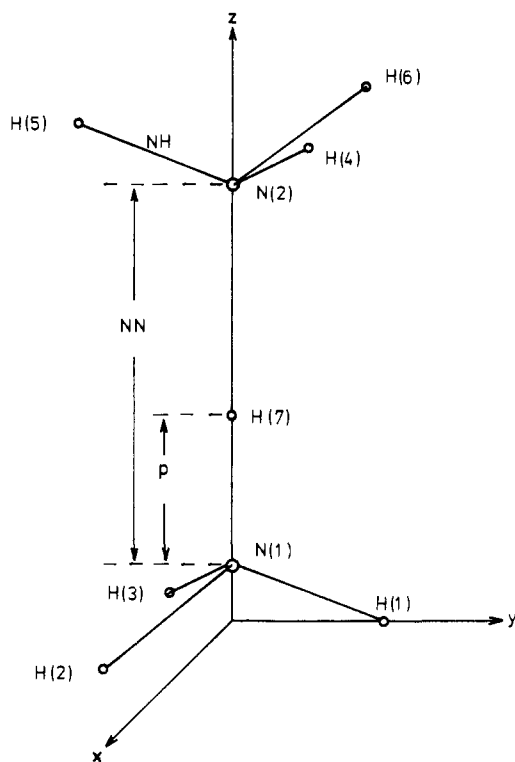


Figure 1. Coordinate system for the $N_2H_7^+$ complex.

particularly with the hydrogen bond in water^{3a-c} and the complex^{2c,4} $[H_2O-H \cdots OH_2]^+$, but it would be unwise to restrict the study of this phenomenon to systems of this type. There is good evidence, for example, that hydrogen bridges occur in ammonia⁵ and that a rather strong bond of this type is possible between a neutral NH_3 molecule, on the one hand, and an ammonium ion, on the other; the resulting $[NH_3-H \cdots NH_3]^+$ complex is isolectronic with the aforementioned water system $[H_2O-H \cdots H_2O]^+$. The existence of such an ammonia complex in the gas phase has been demonstrated by mass spectrometry.⁶ In concentrated solutions of ammonium salts in liquid ammonia a frequency shift⁷ is observed in the NH stretching vibration of NH_4^+ indicating a hydrogen bridge, and X-ray analysis of the system $NH_4Cl \cdot (NH_3)_3$ has shown⁸ that the component ammonium ion can be involved in three separate hydrogen bonds, each corresponding to a different NN nuclear separation ($R_{NN} = 2.8-3.0 \text{ \AA}$).

The present paper concerns itself with this hydrogen bond involving two nitrogen atoms. The calculations to be considered are of the *ab initio* SCF type, so that any differences between nitrogen and oxygen in hydrogen-bonded complexes are described strictly in

J. Mehl, and W. v. Niessen, *J. Chem. Phys.*, **54**, 508 (1971), for hydrogen bonding in guanine-cytosine and in formic acid dimer.

(4) W. P. Kraemer, and G. H. F. Diercksen, *Chem. Phys. Lett.*, **5**, 463 (1970).

(5) See, for example, W. Hamilton and J. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968. An extensive *ab initio* study of the $NH_3 + HCl \rightarrow NH_4Cl$ reaction, in which hydrogen bonding between N and Cl plays a role, has been reported by E. Clementi, *J. Chem. Phys.*, **46**, 3851 (1967); **47**, 2323 (1967); and E. Clementi and J. Gayles, *ibid.*, **47**, 3837 (1967). The hydrogen bond in the similar system NH_3-HF has been treated recently by P. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 4991 (1971).

(6) A. M. Hogg, R. M. Haynes, and P. Kebarle, *ibid.*, **88**, 28 (1966).

(7) J. Corset, P. V. Huang, and J. Lascombe, *Spectrochim. Acta, Part A*, **24**, 2045 (1962).

(8) I. Olovson, *Acta Chem. Scand.*, **14**, 1453 (1960).

terms of distinctions in nuclear charge and in atomic basis sets, the latter being determined by calculations for the individual atoms rather than *in situ*. Attention is given to the influence of the basis set on the theoretical description of the potential surface involved in the proton exchange between the two electronegative centers (in the present case NH_3 molecules), and particular emphasis is placed on the changes which occur in other geometrical quantities such as NN and NH distances during the proton migration. A detailed study of the charge distributions which develop as the proton transfer takes place also proves instructive and an analysis of the vibrational structure resulting from the associated double-well potential is undertaken.

II. Rigid Model Approach

A. Potential Curves for Separation of NH_4^+ and NH_3 . The coordinate system employed for the $N_2H_7^+$ complex is given in Figure 1; the distance between the central proton H(7) and the nucleus N(1) is hereafter referred to as p . Only geometrical configurations in which the central proton and the two nitrogen nuclei are collinear have been considered; the remaining hydrogens are arranged in a staggered conformation (the barrier to internal rotation should be relatively small because of the large NN separation). Both of these geometrical restrictions seem justified from considerations of steric repulsion and should not in themselves lead to any unrealistic conclusions in the theoretical description of this hydrogen-bonded system.

The basis set chosen for the initial series of calculations (hereafter referred to as basis I) consists of groups of gaussian lobe functions representing the nitrogen 1s, 2s, and 2p AO's and the hydrogen 1s function, respectively⁹ (85 individual gaussians, 19 groups); the hydrogen AO's have been optimally scaled to allow for the differences in environment in the neighborhood of a nitrogen atom as opposed to that of a free hydrogen atom ($\eta^2 = 1.9$). This basis set was then used in calculations for both separated molecules NH_3 and NH_4^+ in their experimental equilibrium geometries¹⁰ (NH_3 : C_{3v} symmetry, $R_{NH} = 1.931$ bohrs, $\angle HNH = 108.2^\circ$; NH_4^+ : T_d symmetry, $R_{NH} = 1.99$ bohrs, $\angle HNH = 109.28^\circ$). The ionization potential of NH_3 is calculated to be 10.9 eV as compared with the experimental value¹¹ of 10.15 eV; the proton affinity of ammonia is found to be 223 kcal/mol, also in fairly good agreement with the experimental value¹² of 207 kcal/mol (calculated total energy of NH_3 is -56.1433 hartrees).

The same basis set was then used to obtain a potential curve for the approach of an ammonium ion to a neutral NH_3 molecule along the path indicated in Figure 1. Only the NN distance is thereby allowed to vary while the other geometrical quantities (NH distances and HNH angles) are held fixed at their experimental equilibrium values in the separated reactants. The resulting potential curve (b) is given in Figure 2 and is seen to possess a relatively shallow minimum for $R_{NN} = 5.0$ bohrs (2.646 \AA); the calculated binding energy of the combined system is 25.9 kcal/mol.

(9) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).

(10) (a) K. Kuchitsu, J. P. Guillory, and L. S. Bartell, *ibid.*, **49**, 2488 (1968); R. Moccia, *ibid.*, **40**, 2176 (1964).

(11) G. R. Brantam, D. C. Frost, F. G. Herring, C. A. McDowell, and I. A. Stenhouse, *Chem. Phys. Lett.*, **3**, 581 (1969).

(12) M. A. Hanuey and J. L. Franklin, *J. Chem. Phys.*, **50**, 2028 (1969).

A second series of calculations for the same nuclear configurations has been carried out using a slightly different basis set (basis II) for which the hydrogen 1s function located at H(7) is simply deleted; *i.e.*, H(7) is literally treated as a bare proton. This potential curve (a) is also contained in Figure 2 and is seen to lie substantially higher on the energy scale than that for basis I; average energy differences for corresponding nuclear geometries are in the order of 0.15 hartree (≈ 90 kcal/mol). These results emphasize that the central (migrating) proton is located in a region of fairly high electron density and that the use of basis set II, which does not include a hydrogen 1s function at this center, is not at all likely to produce a realistic description of the hydrogen bonding process.¹³ Despite the importance of the hydrogen 1s function on H(7), the shapes of the two potential curves in Figure 2 are quite similar, however, with R_{NN} values differing by only 0.03 Å (basis II yields the smaller value).

One of the more convenient methods of improving the quality of a contracted or grouped basis set is to decompose various of its members into two or more parts, that is, by allowing the SCF procedure to determine the optimum mixing coefficients between the various components in each of the occupied MO's. Thus in the final calculation the nitrogen 2s as well as 2p AO functions and the 1s AO located at the central hydrogen H(7) have been decomposed into two groups; the other hydrogen 1s functions and the short-range species located at the nitrogen nuclei have been left unaltered. At the same time a primitive $2p_z$ gaussian lobe function has been added at the central proton to allow for a still better representation of the charge density in this region. In standard notation this procedure results in a change from a [3,1|1|1] to a [4,2|1|2,1] basis, although the number of primitive gaussians employed has only been increased by one (the 2p on H(7)).

This basis set (referred to as basis III) leads to a lower value for the proton affinity of NH_3 (218 kcal/mol) than obtained with the more restrictively grouped basis, and consequently to better agreement with the experimental result (207 kcal/mol). The ionization potential of NH_3 is calculated to be 11.2 eV in this treatment, in somewhat worse agreement with experiment than before. The calculated total energy of NH_3 is -56.1650 hartrees, about 0.057 hartree above the Hartree-Fock value;¹⁴ further energy lowerings require the use of d functions on the nitrogen nuclei, for example, and the use of 2p AO's on all the protons, not just on H(7).

From Figure 2 it is seen that the more flexible basis leads to a significantly different description of the NN stretch potential curve (c) for the rigid approach of the NH_4^+ and NH_3 species than the former basis sets. The equilibrium NN distance increases by 0.10 bohr relative to the best value obtained previously, and the binding energy is observed to increase from 25.9 to 32.0 kcal/mol. The reliability of these results is of course subject to question because of the failure to include correlation effects in the theoretical treatment. On the other hand, the fact that the number of electron pairs does not change in this process suggests that such effects

(13) This fact is also indicated by the corresponding expansion coefficient of the H(7) function in the $5a_1$ MO, which is 0.3 in basis I, a relatively high value.

(14) R. G. Body, D. S. McClure, and E. Clementi, *J. Chem. Phys.*, **49**, 4916 (1968).

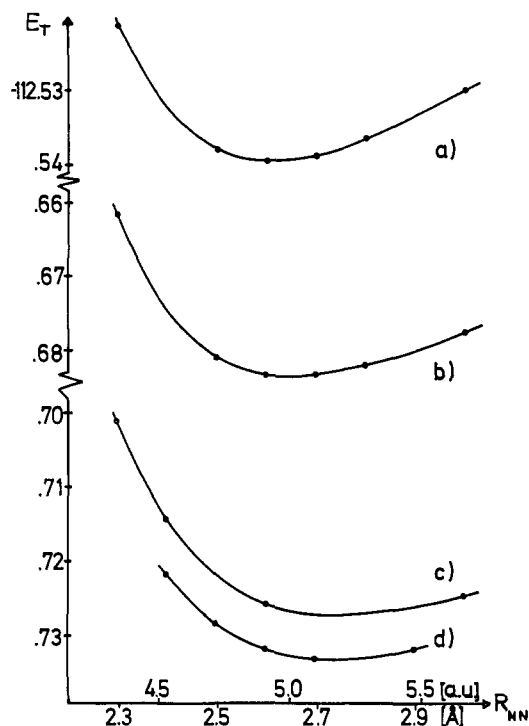


Figure 2. Total energy of the N_2H_7^+ system (in au \equiv hartree) as a function of the distance between the two nitrogen nuclei: (a) rigid model, nonequivalent ligands, basis set II; (b) rigid model, nonequivalent ligands, basis set I; (c) rigid model, nonequivalent ligands, basis set III; (d) less rigid model, equivalent ligands, basis set III.

are relatively unimportant in the present case; this assumption is also supported by analogous calculations of the binding energy of the water dimer¹⁵ and the hydronium ion-water complex.¹⁶ The experimental value for the N_2H_7^+ binding energy is not known, but the present calculated result is consistent with an estimate based on mass spectroscopic investigations of NH_4^+ (ion)- NH_3 (solute) forces, which estimates this figure to be in excess of 20 kcal/mol. It is also consistent with the expectation that the binding energy should increase in the isoelectronic series N_2H_7^+ , O_2H_5^+ , F_2H^- with increasing electronegativity of the heavy atoms; the calculated value of 32 kcal/mol for the first member in this series would agree at least qualitatively with the experimental (D_0) value of 36 kcal/mol¹⁷ for O_2H_5^+ and the two measured values for F_2H^- of 36^{2a} or 58 kcal/mol,^{2b} respectively.

B. Potential Curves for Proton Exchange. In the next series of calculations the central proton is allowed to migrate from the ammonium ion to the NH_3 species for two different NN separations of 4.9134 bohrs (2.6 Å) and 5.6692 bohrs (3.0 Å), corresponding respectively to approximately the equilibrium R_{NN} separation and a value significantly larger. All other NH distances and HNH angles are held constant at their values in NH_4^+ and NH_3 , respectively. All resulting potential curves are expected to be asymmetric because of the different environments assumed at the two nitrogen

(15) The experimental value is 5.0 kcal/mol and is to be compared with the 4.84 kcal/mol value calculated with an extended double- ζ gaussian basis; see ref 3c.

(16) The calculated values are 32.24 kcal/mol (ref 4) and 36.9 kcal/mol (ref 2c) while the experimental result is 36 kcal/mol.

(17) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Amer. Chem. Soc.*, **89**, 6393 (1967).

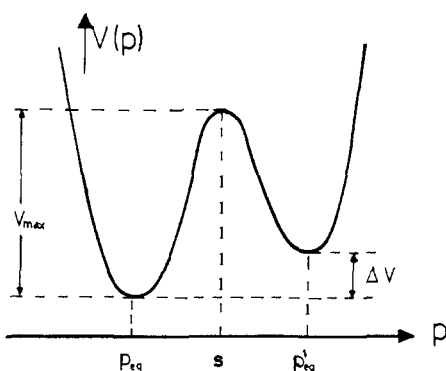


Figure 3. Definition of characteristic parameters for the description of a double-minimum potential curve.

nuclei. Quantitative aspects of the various potential curves are summarized in Table I in terms of values

Table I. Comparison of Several Characteristic Parameters of the Potential Curves for Proton Exchange at Different Values of R_{NN} Obtained on the Basis of the Rigid Model Approach Using Different Basis Sets^a

	$V(p_{eq})$	V_{max}	ΔV	p_{eq}	s	p'_{eq}
$R_{NN} = 4.9134$						
Basis I	-112.6909			2.350	One minimum	
II	-112.5470			2.402	One minimum	
III	-112.7269	0.0023	0.0005	2.095	2.457	2.809
$R_{NN} = 5.6692$						
Basis I	-112.6791	0.0193	0.0052	2.096	2.870	3.555
II	-112.5321	0.0085	0.0010	2.140	2.846	3.517
III	-112.7246	0.0244	0.0008	2.000	2.842	3.641

^a For definition of parameters see Figure 3. All values are given in atomic units (1 au of energy = 1 hartree = 27.21 eV = 627.7 kcal/mol; 1 au of length = 1 bohr = 0.52917 Å).

for certain characteristic parameters defined for a standard double minimum potential curve (Figure 3).

At the smaller NN separation, basis I and basis II indicate only a single potential minimum in contrast to the case for the more flexible basis III which leads to a double potential well at both NN distances; thus basis set composition is quite important for these curves.¹⁸ It is also interesting that the more deficient basis (II) leads to more symmetric curves than basis I: *i.e.*, the shapes of corresponding proton migration potential curves are affected noticeably by the removal of the central hydrogen 1s function, contrary to the results in Figure 2. By far the most significant effect of the larger basis III is the tendency it produces for increased bonding between the proton and either of the heavy atoms. This result can be seen quite clearly by comparing the characteristic parameters of these potential curves in Table I; for both NN distances the value of p_{eq} is decreased relative to the analogous results obtained with basis I or II, while the barrier (V_{max}) is enhanced. Moreover, since the linear spaces spanned by each of the former two basis sets are contained entirely in the linear manifold of the present basis, there is no question that the potential curves of basis III more accurately reflect the experimental situation corresponding to the hydro-

(18) These findings are similar to the results of ref 3g for the dimeric form of formic acid (especially Figures 12 and 13) and support the conclusion reached therein that any basis of less than double- ζ quality may not be reliable enough for the description of hydrogen bonding phenomena.

gen bonding process. Indeed, basis set decompositions of this type have generally led^{19,20} to a decrease in equilibrium separations (and to quite good agreement with experimental data). These results are again a manifestation of the fact that a basis set which is constrained to represent a *molecular environment* with functions which have been optimized solely for the *constituent* atoms is under a significant handicap, simply because the charge distribution in a molecule can be significantly different from that of a free atom.

III. A Less Rigid Model for the Proton Transfer

Thus far it has been possible to distinguish between the two ligands involved in this hydrogen bonding process because different (fixed) bond lengths and HNH angles have been associated with the two nitrogen nuclei, specifically the experimental values of NH_4^+ , on the one hand, and of NH_3 , on the other. In reality the two nitrogen nuclei are indistinguishable and such quantities as NH separations and HNH bond angles must vary gradually between the same sets of limiting values as the proton migration occurs. Since this entire process takes place at *finite* NN separations, however, the limiting values need not and probably do not correspond to those associated with equilibrium NH_4^+ and NH_3 (separated at *infinity*), respectively. Clearly the asymmetry present in the potential curves indicated in Table I has resulted from the failure to account for such gradual changes in the environment of the two nitrogen nuclei and therefore must be considered merely an artifact of the rigid model assumed.

The ideal situation would be to optimize each of the NH distances and HNH angles at every point in the proton transfer between the two heavy nuclei; for practical purposes some restrictions have to be made, however. Since the HNH angles in NH_4^+ and NH_3 are very nearly the same, in what follows a fixed value of 109.28° has been assumed for these quantities for the entire process at both nitrogen nuclei. Also since variations in the NN separation in the course of the proton transfer are small compared to the absolute value of R_{NN} , it has furthermore been assumed that the NH distances are all equal and independent of R_{NN} , at least in the R_{NN} range of interest. The location of H(7) changes considerably and thus calculations employing the extended basis III have been carried out at $R_{NN} = 4.9134$ bohrs (2.6 Å) to investigate its influence on the magnitude of the NH separations. The results (contained in Table II) show that the optimum NH distance is also very nearly independent of the proton separation p (see Figure 1); the optimal value remains very close to 1.905 bohrs for the entire range of p and thus in the remaining calculations to be discussed all six of the terminal NH distances are assumed to be fixed at this value throughout. Small differences in the NH distances and HNH angles undoubtedly do occur in the actual proton transfer, but such changes do not appear to add any significant information to the mechanism of the hydrogen bonding process. The assumption of equivalent environment at the two nitrogen nuclei for the entire proton migration is of course an oversimpli-

(19) R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, *J. Chem. Phys.*, **46**, 2029 (1967).

(20) S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *ibid.*, **45**, 734 (1966); S. D. Peyerimhoff, R. J. Buenker, and J. L. Whitten, *ibid.*, **46**, 1707 (1967).

Table II. Total Energy of $N_2H_7^+$ (Equivalent Ligands at $R_{NN} = 4.9134$ bohrs) for Several Positions p of H(7) and NH Distances^a

p	NH distance				NH' _{opt}	$E(NH'_{opt})$
	1.795	1.891	1.931	1.990		
1.80	-112.7017	-112.7208	-112.7195	-112.7103	1.900	-112.7209
1.90	0.7084	0.7277	0.7270	0.7179	1.905	0.7280
2.00	0.7116	0.7309	0.7303	0.7213	1.906	0.7312
2.10	0.7123	0.7316	0.7311	0.7222	1.907	0.7320
2.20	0.7119	0.7312	0.7306	0.7217	1.906	0.7315
2.30	0.7111	0.7304	0.7298	0.7208	1.906	0.7307
2.40	0.7106	0.7299	0.7293	0.7202	1.906	0.7302
2.457	0.7105	0.7298	0.7292	0.7201	1.906	0.7301

^a The optimal NH distances and corresponding energies are also given. All values are obtained using basis set III (atomic units).

Table III. Characteristic Parameters of the Potential Curves for Proton Exchange at Several Values of R_{NN} Obtained Using Basis Set III and the Less Rigid Model (Equivalent Ligands)^a

Parameter	R_{NN}				
	4.5354	4.7248	4.9134	5.1023	5.4803
V_{max}	0.0	0.0001	0.0019	0.0053	
p_{eq}	2.268	2.192	2.096	2.047	2.031
$V(p_{eq})$	-112.7218	-112.7285	-112.7320	-112.7331	-112.7319
$V(1/2 R_{NN})$	-112.7218	-112.7284	-112.7301	-112.7278	

^a All values are given in atomic units.

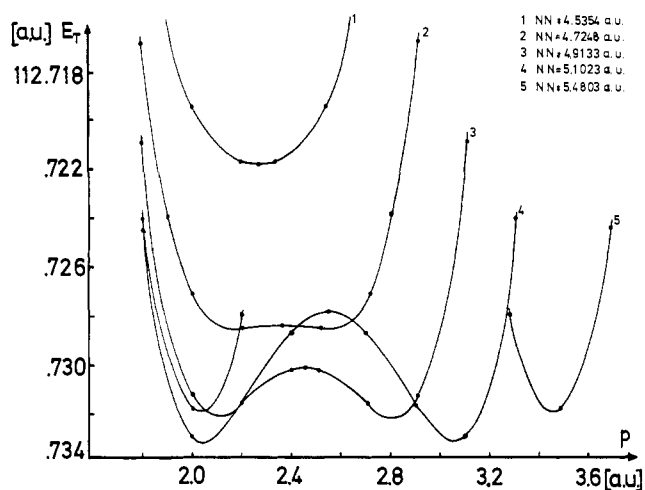


Figure 4. Total energy of the $N_2H_7^+$ system as a function of p at different NN separations. The less rigid model (equivalent ligands) and basis set III are employed.

fication; it ensures a symmetric potential curve for the proton exchange (as long as R_{NN} is held fixed), however, a situation which is demanded by the indistinguishability of the nitrogen nuclei.

In spite of these considerations there is still strong evidence that the proton transfer is accompanied by significant fluctuations in R_{NN} , and thus the total energy of $N_2H_7^+$ has been calculated under the aforementioned assumptions for the structure as a function of both the independent variables R_{NN} and p . The resulting potential curves are contained in Figure 4, from which it can be seen that the double-minimum character of these curves is preserved as R_{NN} decreases well beyond its optimum values (approximately 5.1 bohrs). Characteristic parameters for these data (see Figure 3) are given in Table III, including the total energies for the corresponding minima and maxima. From these data it is possible to construct an optimal NN stretch potential curve (in this case for optimized p at each point for equal and, for all practical purposes, optimized

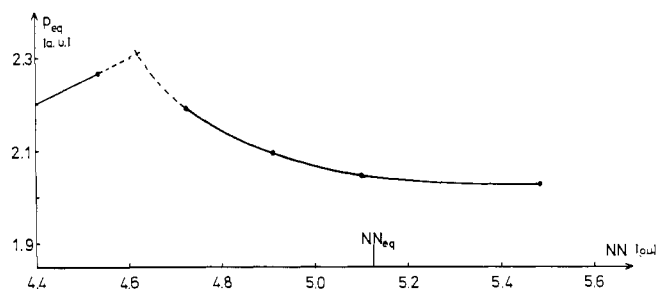


Figure 5. Positions of the double-potential minima p_{eq} (see Figure 3) as a function of the NN distance, derived from the curves in Figure 4.

NH distances), also contained in Figure 2. This curve (d) is seen to lie everywhere lower than any of its counterparts discussed previously, as a result of the NH and p distance optimization. It is also instructive to plot the optimal p value (p_{eq}) as a function of the NN separation, again using the results of Table III (Figure 5). At relatively small values of R_{NN} there is no double minimum potential and thus the optimal p value is simply equal to one-half of R_{NN} , hence the straight-line dependence to the left in the figure. At approximately $R_{NN} = 4.61$ bohrs the situation changes rather suddenly, however, and the optimal value of p starts to decrease with increasing R_{NN} as the double-well potential begins to form. Finally, the absolute minimum in energy is obtained at $R_{NN}(opt) = 5.126$ bohrs, at which point the optimal p value has decreased to $p_{eq}(opt) = 2.044$ bohrs from its maximum value of other 2.3 bohrs. At still larger values of R_{NN} the formation of the separated NH_3 and NH_4^+ species becomes complete and thus p_{eq} does approach its limiting value of the equilibrium NH distances in NH_4^+ (1.99 bohrs); the terminal NH separations must then also adjust to their respective optimal values in the two fragments.

The optimization of the NH, p , and NN distances has produced another increase in the binding energy of $N_2H_7^+$, to 36 kcal/mol. A summary of the various equilibrium quantities is given in Table IV for compari-

Table IV. Comparison of Equilibrium NN Separations and Corresponding Energies, Binding Energies (D_e) and Optimal p Distances Obtained from Several Treatments

Structure	Basis	$-NN_{eq} = R_{NN}(opt)$		$E_T(NN_{eq})$, au	D_e , kcal/mol	$p_{eq}(opt),^a$ au
		au	Å			
Rigid model	II	4.928	2.608	-112.5394		$2.14 < p_{eq} < 2.40$
Rigid model	I	5.000	2.646	-112.6836	-25.9	$2.10 < p_{eq} < 2.35$
Rigid model	III	5.100	2.699	-112.7269	-32.0	$2.00 < p_{eq} < 2.10$
Less rigid model (equivalent ligands)	III	5.126	2.713	-112.7332	-36.0	2.044

^a A thorough optimization has not been carried through in all cases and would require the treatment of more NN distances.

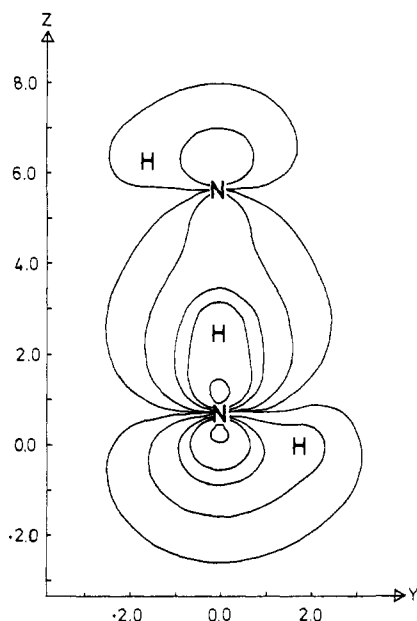


Figure 6. Charge density contours for the $5a_1$ MO. The calculation is carried out with basis set III, the less rigid model (equivalent ligands) at $R_{NN} = 5.1023$ bohrs and $p = 2.00$ bohrs. Contour values are 0.001, 0.01, 0.05, 0.1, 0.3.

son with the corresponding results for different basis sets and different geometrical models for the proton transfer. From the values for the total energy in particular it is obvious that the changes in basis set are the most effective in improving the treatment of this process, while the various geometrical optimizations, though less effective, are still seen to be significant.

As a final remark it should be pointed out that the calculations indicate that the NN distance varies significantly as the proton is transferred between the two nitrogen nuclei. This observation is especially obvious from the fact that the curve in Figure 4 with the lowest potential minimum ($R_{NN} = 5.1023$ bohrs) is not the same as that with the lowest potential maximum ($R_{NN} = 4.9133$ bohrs). On the basis of polynomial fittings for the various NN-stretch potential curves for constant p , it is found that R_{NN} varies from its value of 5.126 bohrs at the lowest minimum (equilibrium) to 4.88 bohrs at the lowest potential maximum in the proton transfer.²¹ This adjustment lowers the barrier to proton exchange by 0.003 hartree (1.9 kcal/mol) compared to the process at fixed R_{NN} and is thus a significant factor in the transfer; the actual barrier is

(21) This distance is obtained specifically by determining the R_{NN} value which leads to the lowest energy under the condition that $p = (1/2)R_{NN}$.

thereby reduced to 2 kcal/mol, only about *half* the value obtained from the calculation with R_{NN} held fixed at its optimal value. This result for the barrier height is smaller than the value for the rotational barrier of ethane, and thus the present calculations indicate very nearly free exchange of the proton between the two nitrogen atoms; somewhat surprisingly, however, it appears that this transfer is accompanied by relatively large variations in the NN separation.

IV. Charge Distribution

The inclusion of a hydrogen 1s function at H(7) in the AO basis set has been shown to be quite important for the description of the hydrogen bond in $[NH_3-H \cdots NH_3]^+$. This function makes by far its greatest contribution to the $5a_1$ MO, whose charge density is plotted in Figure 6. This orbital represents the in-phase addition of the two nonbonding orbitals of the NH_3 ligands, reinforced by the presence of the 1s AO located at the central proton. The $6a_1$ MO, which represents essentially the out-of-phase combination of these two orbitals, would be very nearly isoenergetic with the $5a_1$ without the effect of the central 1s AO; instead, their orbital energy difference in the hydrogen-bonded complex ranges from 0.2 to 0.3 hartree, depending on the relative position of H(7).²² Among all the other occupied MO's of $N_2H_7^+$ only the $3a_1$, essentially a combination of the 2s AO's on both nitrogens, appears to be dependent (although only slightly) upon the description of the central hydrogen atom, so that the $5a_1$ MO seems to be the only species which is responsible for the hydrogen bridge.

One of the more effective means of describing the charge distribution associated with this hydrogen bond involves the use of contour diagrams representing differences in charge density or plots of electron density differences along the line of centers. In the first case to be considered (Figure 7) comparison is made with the free NH_3^+ and NH_3 molecules, respectively. From this diagram it is clear that the approach of the ammonia fragment leads to a decrease in the electron density of its lone pair; this effect is balanced by a pronounced buildup of electronic charge in the neighborhood of the terminal hydrogen atoms of the (former) NH_3^+ ligand. In general there is a tendency to equalize the electronic charge at each of the hydrogen atoms in the complex (compared to those in the separated atoms), brought about in turn by the interaction of the negative end of the NH_3 dipole with the positively charged ammonium ion.

(22) The influence of H(7) on the $6a_1$ MO is negligible; the coefficient of the p_z function located at this center is very small in the expansion of the $6a_1$, in the order of 0.06.

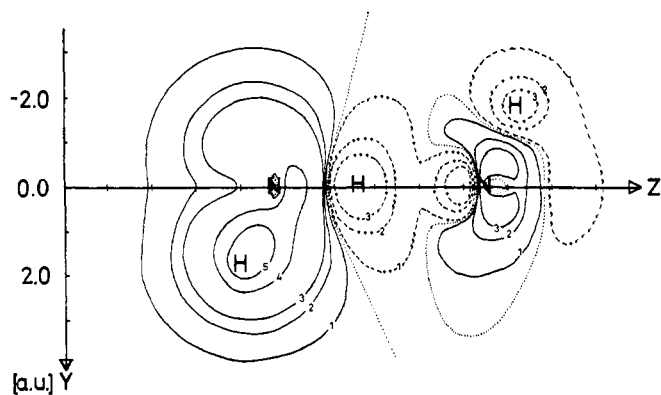


Figure 7. Total charge density contours representing the difference in charge between the $N_2H_7^+$ system and a NH_4^+ and NH_3 system located appropriately. The calculations are carried out with basis set III and for equivalent ligands at $R_{NN} = 5.1023$ bohrs and $p = 2.00$ bohrs. Solid lines indicate an increase, dashed lines a decrease in charge; dotted lines represent no change in electronic charge. Contour values are: 1 \equiv 0.001, 2 \equiv 0.005, 3 \equiv 0.01, 4 \equiv 0.05, 5 \equiv 0.1 (contour lines in the immediate neighborhood of the nuclei are omitted.)

Alternatively the hydrogen-bonded complex may be compared to two neutral NH_3 fragments plus a bare proton, as is done in Figure 8. In this case the changes are much more dramatic, with charge being drawn away from the nearer NH_3 species (N(1) in this case) to the region of the central proton; the charge density of the N(2) lone pair, as in the previous case, is also shifted toward the central H(7) nucleus. Clearly this comparison is less useful because the magnitude of the charge transfer which takes place is so much greater than in the $NH_4^+-NH_3$ case. In both comparisons, however, it is obvious that the redistribution of charge compared to the separated fragments occurs within the entire complex, not just within a small region of it.

V. Vibrational Analysis

The existence of a double-well potential for the proton transfer in the $N_2H_7^+$ complex, as well as for other hydrogen-bonded species, produces a characteristic vibrational structure in the infrared spectrum of this system. A complicating factor in the present case, and perhaps in most hydrogen-bonded complexes, is the observation discussed in section III that the heavy atoms are subject to a significant amount of relative motion as the proton transfer proceeds. Specifically in $N_2H_7^+$ the calculations have indicated a contraction of R_{NN} of 0.25 bohr from its equilibrium value to that corresponding to the top of the potential barrier. The following analysis considers both types of motion simultaneously by treating the system as a linear triatomic molecule, that is, by ignoring any relative motion within either of the NH_3 ligands. This procedure reduces the number of vibrational coordinates²³ to only four, of which two correspond to the degenerate bending vibrations, also not given explicit consideration in the present treatment.

The remaining two coordinates then correspond to the symmetric NN stretch (Q_1) and the antisymmetric proton transfer (Q_3) vibrations, respectively. These

(23) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966; see especially p 153 ff.

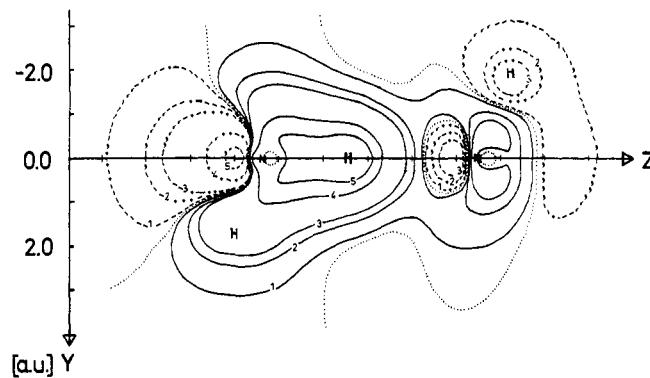


Figure 8. Total charge density contours representing the difference in charge between the $N_2H_7^+$ system and two NH_3 systems and a H^+ , located appropriately. Details are the same as in Figure 7.

(normal) coordinates are defined explicitly in terms of the displacements of the three centers in the z direction (Figure 1) and are denoted by z_1 , z_H , and z_2 , respectively.²³

$$Q_1 = (1/2)(z_2 - z_1)$$

$$Q_3 = - \frac{m_N}{m_H + 2m_N}(z_1 + z_2 - 2z_H)$$

m_H is the mass of the proton and m_N is the mass of the entire NH_3 ligand. The corresponding potential curves and vibrational energy levels can be calculated by using the Born-Oppenheimer approximation and by assuming that the two types of motion are completely separable; the latter restriction ignores any coupling in the two-dimensional motion of these nuclei, an assumption which is of course not entirely justified by the SCF calculations discussed heretofore, but one which is still quite useful.

The single-well potential curve as a function of the normal coordinate Q_1 is then obtained as a polynomial (sixth order) under the condition of Q_3 being held constant at its equilibrium value (at either of the potential minima); the double-well Q_3 potential curve is constructed in an analogous manner. The vibrational wave functions in all cases have been expanded^{24,25} in terms of Hermite polynomials (up to 20 terms in the expansion), a procedure which (together with the polynomial form of the potential curves) allows for an easy evaluation of all necessary matrix elements.²⁴ A tabulation of the resulting frequencies is contained in Table V, together with a comparison of corresponding data for the deuterated complex. The fully symmetric NN stretching mode ν_1 is not infrared active so that comparison with experimental data is difficult; the calculations indicate that its fundamental frequency is relatively small (668 cm^{-1}), reflecting the weakness of the attraction between the two NH_3 ligands.²⁶

The calculated eigenvalues for the antisymmetric ν_3 vibration show the characteristic doubling expected for

(24) E. Heilbronner, H. H. Günthard, and R. Gerdil, *Helv. Chim. Acta*, **39**, 1171 (1956).

(25) E. Heilbronner, H. Rutishauser, and F. Gerson, *ibid.*, **42**, 2286 (1959).

(26) On the other hand, when it is recalled that the fragments are relatively massive and that the nitrogen centers are separated by over 5.0 bohrs, it is clear that the presence of the central proton is capable of producing a significant amount of bonding in the complex.

Table V. Eigenvalues of the Vibrational Wave Function^a

<i>j</i>	Eigenvalues, cm ⁻¹		
	<i>e</i> _{<i>j</i>1}	<i>e</i> _{<i>j</i>3}	<i>e</i> _{<i>j</i>3} ^D
0	334.0	838.1	684.3
1	980.3	1124.9	768.3
2	1579.4	2384.6	1672.8
3	2117.2	3636.0	2330.1
4	2589.8	5184.3	3255.5
5	3042.1	6924.0	4295.6

^a *e*_{*j*1} is the value corresponding to the potential *V*₁. *e*_{*j*3} and *e*_{*j*3}^D are the eigenvalues corresponding to the double-minimum potential *V*₃ of N₂H₇⁺ and *V*₃^D of the deuterated complex [H₃D-D...NH₃]⁺, respectively. All values are with respect to the minima of corresponding curves.

such a double-well potential;^{27,28} the depth of the minima is not great enough, however, to allow for more than one such pair of levels (*ν*₃ = 0, 1, with a splitting of 283 cm⁻¹). The next allowed transitions in the infrared region are 0 → 3 and 1 → 2, respectively, the latter of which is slightly less probable (especially at low temperatures) because of the lower population of the first excited level relative to that of the ground state. The calculated frequencies are 2798 and 1260 cm⁻¹ respectively for N₂H₇⁺ and 1646 and 904 cm⁻¹ for the deuterated species. The larger of these values for N₂H₇⁺ is quite consistent with the absorption band for *ν*₃ found in the infrared spectrum of concentrated solutions of ammonium salts in liquid ammonia and also in solid NH₄Cl·(NH₃)₃

(27) R. L. Somorjai and D. F. Hornig, *J. Chem. Phys.*, **36**, 1980 (1962).

(28) J. Brickmann and H. Zimmermann, *ibid.*, **50**, 1608 (1969).

in the range⁶ of 2400–3200 cm⁻¹. The second absorption band corresponding to the *ν*₃ = 1 → 2 transition should become prominent at higher temperatures in the 1000–1500-cm⁻¹ region of the spectrum, not far from the characteristic ammonia inversion frequency (also an antisymmetric vibration).

Finally, in evaluating these results it should be emphasized that the barrier to proton transfer in the preceding vibrational analysis (for constant *R*_{NN}) is almost twice as large as it is when the effect of simultaneous NN contraction is given explicit consideration. Inclusion of cross-terms in the description of the two-dimensional potential for the nuclear motion can thus be expected to lead to a general decrease in the spacing of the vibrational energy levels associated with the proton transfer, but the actual quantitative effects of such a perturbation have not yet been determined.²⁹

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(29) NOTE ADDED IN PROOF. After the present paper was submitted, it came to our attention that similar study of the proton transfer between NH₄⁺ and NH₃ was carried out by J. J. Delpuech, G. Serratrice, A. Strich, and A. Veillard, *Chem. Commun.*, results submitted for publication.

Properties of Atoms in Molecules.

IV. Atomic Charges in Some Linear Polyatomic Molecules

Peter Politzer* and Patricia H. Reggio

Contribution from the Department of Chemistry,
Louisiana State University in New Orleans, New Orleans, Louisiana 70122.
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Abstract: Atomic charges have been calculated for a number of linear polyatomic molecules, using a recently proposed method which involves integrating the molecular electronic density over regions associated with the individual atoms. The results correlate well with the experimentally observed properties of the molecules; for example, the atomic charges computed for SCN⁻ and OCN⁻ show detailed agreement with the nucleophilic behavior of these ions. For SCN⁻, OCN⁻, SCO, and OCO, the quantities of valence electronic charge in various portions of the molecules, such as the internuclear regions, are also presented, in order to permit a comparative analysis of their electronic structures.

A new definition of atomic charge, based directly upon the total electronic density distribution in a molecule, has recently been proposed.¹ It involves partitioning the space of the molecule into regions associated with the individual atoms, and then integrating the molecular electronic density function over each of these regions. This method has been applied to a group of diatomic and a few polyatomic molecules,

(1) P. Politzer and R. R. Harris, *J. Amer. Chem. Soc.*, **92**, 6451 (1970).

and the calculated charges were shown to be in good agreement with the physical and chemical properties of the molecules.^{1,2}

Results

Atomic charges have now been computed for some additional linear polyatomic molecules, and also for two molecular ions, OCN⁻ and SCN⁻. The ions were treated in the same manner as the molecules; the atomic

(2) P. Politzer, *Theor. Chim. Acta*, **23**, 203 (1971).