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# SCF MO LCGO Studies on Hydrogen Bonding: The System $NH_3 \cdot H_2O$

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The energy hypersurface of the system $NH_3 \cdot H_2O$ is investigated for a number of different internuclear geometries. In the minimum energy structure involving a linear hydrogen bond, $NH_3$ acts as proton acceptor. The binding energy of the system is calculated to be 6.28 kcal/mole and the bond distance $d$(NO) to be 3.07Å. The potential energy curve of the inversion of the hydrogenbonded $NH_3$ is computed and discussed.

Die Energiehyperflächen des $NH_3 \cdot H_2O$-Systems wurden für eine Anzahl von verschiedenen geometrischen Anordnungen untersucht. Im Falle der Struktur minimaler Energie wird eine lineare Wasserstoffbindung gebildet, $NH_3$ wirkt als Protonakzeptor. Die Berechnungen ergeben eine Bindungsenergie des Systems von 6,28 kcal/Mol und einen NO-Abstand von 3,07 Å. Außerdem wurde die Potentialkurve für die Inversion des über eine Wasserstoffbrücke gebundenen $NH_3$ berechnet und diskutiert.

The object of the present investigation is to study hydrogen bonding in the mixed ammonia-water dimer using an extended gaussian basis set, especially to get some information on the interaction in ammonia-water systems. It is well known from chemistry that ammonia is a stronger base (proton acceptor) than water. Therefore it is of particular interest to analyze the relative proton donor/acceptor strengths of the two molecular fragments in the hydrogen bonded system. No experimental results are available so far on the equilibrium geometry and on the hydrogen bonding energy of the mixed dimer and both semiempirical [1] and *ab initio* investigations [2] have been performed only recently. On the other hand, the inversion barrier of a single ammonia has been studied quite extensively experimentally [3] as well as theoretically [4]. As will be shown the ammonia-water dimer is relatively stable and it might well be possible to observe it in the vapour phase. In this connection it is of some interest to study the potential energy curve of the $NH_3$– inversion in the most stable geometrical structure of the system $NH_3 \cdot H_2O$.

The SCF wavefunctions and energies have been calculated using Roothaan's SCF MO LCGO method [5]. The calculations are carried out on an IBM 360/91 computer using the program system IBMOL/VERSION IV [6], modified by one of the authors (G.D.) [7], and by a test release of the program system MUNICH [8]. The molecular orbitals are expanded in a set of gaussian orbitals

$$\eta = x^l y^m z^n \exp(-\alpha r^2)$$

(unnormalized) which are contracted to reduce the number of linear parameters. The basis sets used in the present calculations consist of (11.7.1)-functions at the nitrogen and oxygen atoms, contracted to {5.4.1}-functions, and of (6.1)-functions at each hydrogen atom, contracted to {3.1}-functions [14]. The exponents $\alpha$ and the contraction coefficients are taken from the literature [9]. The exponents of the $d$-type polarization functions at the nitrogen and at the oxygen atom, and of the $p$-type polarization functions at the hydrogen atoms have been optimized by SCF-calculations on ammonia and water, resp., ($\alpha(d_N) = 0.75$, $\alpha(d_O) = 1.00$, $\alpha(p_H) = 0.75$).

The results obtained for the two subsystems ammonia and water using the basis sets described above are in good agreement with those of other extended basis set calculations [10, 4]. The data for the water molecule have been reported previously [11]. For the ammonia molecule in its experimental geometry ($d(\mathrm{NH}) = 1.91054$ a.u., $\sphericalangle$ (HNH) = 106.7° [12]) the total SCF energy is computed to be $E^{\mathrm{SCF}}(\mathrm{NH}_3) = -56.21220$ a.u. The corresponding values for the theoretical equilibrium geometry are calculated to be (using a parabola approximation around the experimental geometry values with the increments $\Delta d = 0.1$ a.u., and $\Delta \sphericalangle = 5°$): $d(\mathrm{NH}) = 1.90$ a.u., $\sphericalangle$ (HNH) = 107.2°, and $E^{\mathrm{SCF}}(\mathrm{NH}_3) = -56.21230$ a.u. For the planar geometry of ammonia ($\sphericalangle$ (HNH) = 120°) the total energy has been computed to be $E^{\mathrm{SCF}}(\mathrm{NH}_3) = -56.20279$ a.u. for a bond length of $d(\mathrm{NH}) = 1.91054$ (exp. pyramidal), and to be $E^{\mathrm{SCF}}(\mathrm{NH}_3) = -56.20420$ a.u. for the theoretical equilibrium bond length of $d(\mathrm{NH}) = 1.87$ a.u. (parabola approximation). From the SCF energies of the two theoretically determined equilibrium structures the height of the inversion barrier in the ammonia molecule is computed to be $E = 5.08$ kcal/mole [7]. From experimental measurements this energy barrier was found to be 5.81 kcal/mole [3]. In the most accurate single determinant SCF MO study on the $\mathrm{NH}_3$ molecule reported so far [4], in which a more extended gaussian basis set has been used, the following geometrical parameters for the pyramidal structure have been obtained: $d(\mathrm{NH}) = 1.890$ a.u. $\sphericalangle$ (HNH) = 107.2° giving an SCF energy of $E^{\mathrm{SCF}}(\mathrm{NH}_3)_{\mathrm{pyr}} = -56.22191$ a.u., while for the planar structure with $d(\mathrm{NH}) = 1.860$ a.u. an SCF energy of $E^{\mathrm{SCF}}(\mathrm{NH}_3)_{\mathrm{plan}} = -56.21382$ a.u. has been calculated. The height of the $\mathrm{NH}_3$-inversion barrier deduced from these energy values was found to be 5.08 kcal/mole, in agreement mit the theoretical value given above.

By a comparison of the results obtained for the monomers, $H_2O$ and $NH_3$, with the corresponding experimental data it may be concluded that the basis set used in the present investigation provides a sufficient flexibility to calculate the equilibrium geometries and inversion barriers to a satisfactory accuracy also for the mixed dimer system.

The investigations have been restricted to two structures, both with linear hydrogen bonds between the molecular fragments $NH_3$ and $H_2O$, which are best characterized by their proton acceptor/donor properties: In structure A the $NH_3$ molecule acts as a proton acceptor and the $H_2O$ molecule as a proton donor and in structure B the opposite is the case. The different geometrical configurations within the two main structures A and B of the mixed dimer discussed here will be described as follows: In all the three configurations A1, A2, A3 derived from structure A (Fig. 1) the nuclei H ... N ... H ... O ... H define a symmetry plane of the system, with the H-atoms at the two ends in "*trans*"-position. While the water molecule is always considered in its experimental geometry, the configurations A1, A2, and A3 differ in the various arrangements assumed for the $NH_3$

molecule: in structure A1 the ammonia molecule is treated in its experimental geometry, too, with the H-atoms pointing away from the water molecule. In structure A2, the ammonia molecule is considered in its planar geometry and the theoretical value is used for the bond distance $d$(NH), and finally in structure A3, the ammonia molecule is again treated in its experimental geometry, but this time with the H-atoms facing the water molecule. For the three geometries A1, A2, and A3 the bond distance $d$(NO) has been varied over a wide range.

In addition, geometrical configurations of structure A have been studied with intermediate angles $\sphericalangle$ (HNH). For all these angles the bond length $d$(NH) used is determined by linear interpolation between the values of the experimental pyramidal and the theoretical planar geometry of the ammonia molecule. For each angle two internuclear separations $d$(NO) have been studied: The minimum energy value $d$(NO) of structure A1, and a value determined by linear interpolation from the minimum energy values $d$(NO) of structures A1, A2, and A3, respectively. Similarly in the two geometrical configurations B1 and B2 derived from structure B (Fig. 2) the nuclei N ... H ... O ... H define the symmetry plane of the mixed

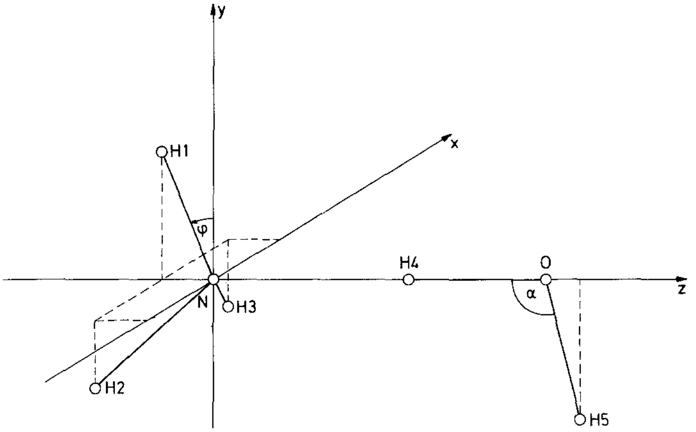

Fig. 1. Coordinate system for $H_3N$–HOH with $NH_3$ acting as proton acceptor (structure A)

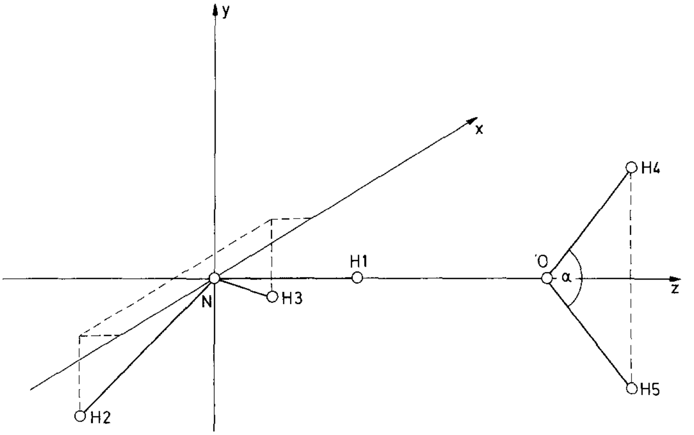

Fig. 2. Coordinate system for $H_2NH$–$OH_2$ with $NH_3$ acting as proton donor (structure B)

dimer, and in addition the hydrogen atoms not involved in hydrogen bonding and the associated nitrogen- and oxygen atom define two planes which are perpendicular to each other. In structure B1 the two subsystems ammonia and water are treated in their experimental geometry, while in structure B2 the ammonia molecule is considered in its planar geometry and the theoretical value

Table 1. Total SCF energies for the system $NH_3$–$H_2O$ in different geometrical configurations (A) and (B)

| | $d$(NO) | $d$(NH) | $\varphi$ | $E^{SCF}$ |
|---|---|---|---|---|
| *Configuration* (A), Fig. 1. | | | | |
| 1(A1) | 10.0 | 1.910537 | 22.13° | −132.26587 |
| 2 | 8.0 | | | −132.26837 |
| 3 | 6.5 | | | −132.27264 |
| 4 | 6.0 | | | −132.27397 |
| 5 | 5.75 | | | −132.27418 |
| 6 | 5.5 | | | −132.27372 |
| 7 | 5.0 | | | −132.26863 |
| 8 | 4.5 | | | −132.25061 |
| 9(A2) | 6.75 | 1.87 | 0° | −132.26134 |
| 10 | 6.25 | | | −132.26210 |
| 11 | 5.75 | | | −132.26166 |
| 12 | 5.25 | | | −132.25772 |
| 13(A3) | 10.0 | 1.910537 | −22.13° | −132.26383 |
| 14 | 8.5 | | | −132.26413 |
| 15 | 7.75 | | | −132.26442 |
| 16 | 7.25 | | | −132.26456 |
| 17 | 6.75 | | | −132.26444 |
| 18 | 6.5 | | | −132.26412 |
| 19 | 6.25 | | | −132.26346 |
| 20 | 5.75 | | | −132.26031 |
| 21 | 5.847 | 1.901378 | 17.13° | −132.27300 |
| 22 | 6.083 | 1.87916 | 5° | −132.26440 |
| 23 | 5.75 | | | −132.26421 |
| 24 | 6.422 | | − 5° | −132.26154 |
| 25 | 5.75 | | | −132.26067 |
| 26 | 6.664 | 1.88832 | −10° | −132.26257 |
| 27 | 5.75 | | | −132.26104 |
| 28 | 7.008 | 1.901378 | −17.13° | −132.26468 |
| 29 | 5.75 | | | −132.26182 |
| 30 | 7.492 | 1.919696 | −27.13° | −132.26097 |
| *Configuration* (B), Fig. 2 | | | | |
| 1(B1) | 10.0 | 1.910537 | – | −132.26505 |
| 2 | 8.0 | | | −132.26616 |
| 3 | 6.75 | | | −132.26756 |
| 4 | 6.25 | | | −132.26788 |
| 5 | 6.0 | | | −132.26767 |
| 6 | 5.0 | | | −132.25673 |
| 7(B2) | 6.5 | 1.87 | – | −132.25970 |
| 8 | 6.25 | | | −132.25991 |
| 9 | 6.0 | | | −132.25990 |
| 10 | 5.75 | | | −132.25948 |

All values in atomic units.

Table 2. Binding energies and equilibrium distances of some neutral hydrogen bonded molecules calculated using an [11s7p1d/6s1p] basis set

| System | $d$(AB) [a.u.] | Binding energy | [kcal/mole] |
|---|---|---|---|
| $H_3N$-HOH (A1) | 5.797 | 6.28 | |
| $H_3N$-HOH (A2) ($NH_3$ planar) | 6.183 | 3.72[a] | |
| $NH_3$-HOH (A3) ($NH_3$ inverted pyramid) | 7.23 | 0.23 | |
| $H_2NH$-$OH_2$ (B1) | 6.34 | 2.33 | |
| $H_2NH$-$OH_2$ (B2) ($NH_3$ planar) | 6.14 | 2.35[a] | |
| $H_2O$-HOH | 5.67 | 4.83 | [10] |
| HF-HF | 5.50 | 4.5 | [13] |

[a] The binding energy refers to a water molecule in its experimental geometry and a *planar* $NH_3$ molecule at infinite separation.

has been used for the bond distance $d$(NH). For both structures B1 and B2 the variation of the bond length $d$(NO) has been studied over a wide range.

The total SCF-energies for all points on the hypersurface investigated are listed in Table 1. The binding energies for the more important structures of the mixed dimer $NH_3 \cdot H_2O$ and for some homomolecular dimers are compiled in Table 2. The potential energy curves for the variation of the distance $d$(NO) are displayed in Fig. 3 for the five structures described above.

It has been found by these investigations, that the three structures A1, B1, and A3 of the mixed dimer $NH_3 \cdot H_2O$ are all stable against dissociation into the molecular fragments $NH_3$ and $H_2O$. The minimum energy geometry is determined to be structure A1, with the ammonia molecule acting as the proton acceptor. The hydrogen bond energy (dimerisation energy) of this structure has been calculated to be B = 6.28 kcal/mol and the associated intersystem separation is computed to be $d$(NO) = 5.78 a.u. Both values may be compared to those found in an earlier investigation using a somewhat smaller basis set: $B$ = 5.8 kcal/mole, $d$(NO) = 5.896 a.u. [2]. As it was expected from chemical experience, the structure B1 with the water molecule as the proton acceptor is less stable than A1. The binding energy obtained in this case is only about $B$ = 2.32 kcal/mole (intersystem separation approximately $d$(NO) = 6.25 a.u. ~ 3.31Å). The corresponding results reported in the literature [2] are: $B$ = 2.3 kcal/mole and $d$(NO) = 3.41 Å.

For the homomolecular dimers of the constituting subsystems $NH_3$ and $H_2O$ the following dimerisation energies have been computed: $B((H_2O)_2)$ = 4.83 kcal/mole [10], and $B((NH_3)_2)$ = 2.71 kcal/mole [2] (which might be slightly less accurate being calculated with a somewhat smaller basis set). From a comparison of these values it is concluded that in ammonia–water systems, mixed dimers of structure A1 or possibly higher mixed polymers should be predominant because of their greater hydrogen bonding energy compared to the homomolecular polymers. This would at least be expected to be true for water – ammonia mixtures in the gas phase, where only smaller clusters occur as a result of the high thermal energy. The situation in solutions is apparently much more complex and no predictions can be made at the present stage for that case.

It can be seen from Fig. 3 that for equivalent geometries (pyramidal or planar) of the ammonia molecule the total energy of the mixed dimer is lower for structure

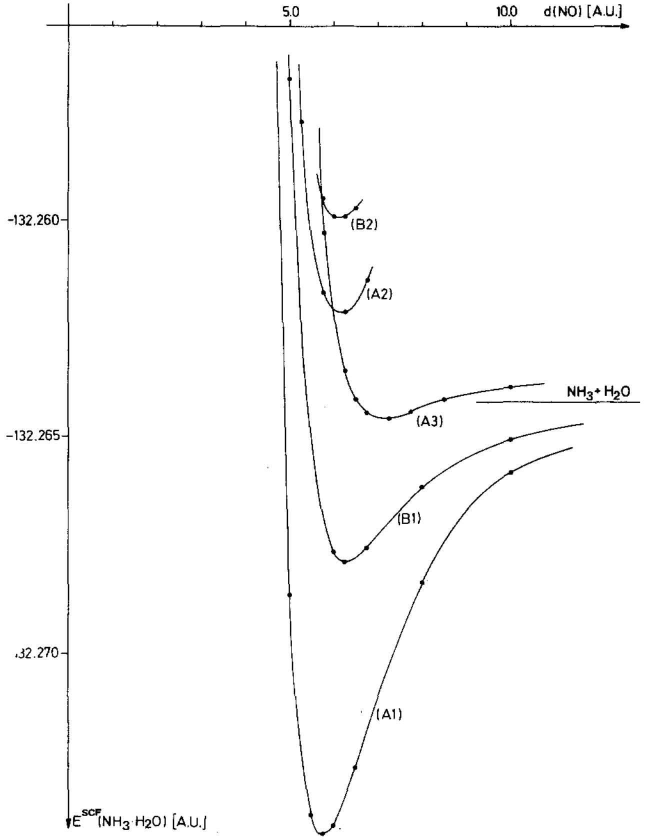

Fig. 3. Energy curves for a variation of the intersystem distance *d*(NO) for different structures of $NH_3 \cdot H_2O$; (A1): $H_3N$-HOH; (A2): $H_3N$-HOH ($NH_3$ planar); (A3): $NH_3$-HOH ($NH_3$ inverted pyramid; (B1): $H_2NH$-$OH_2$; (B2): $H_2NH$-$OH_2$ ($NH_3$ planar)

A than for structure B for all intersystem separations *d*(NO) investigated. This is well in accordance with the general chemical experience that ammonia is a stronger proton acceptor (base) than water. This result is supported by SCF-calculations on the protonated water and ammonia molecules: $OH_3^+$ and $NH_4^+$. The corresponding binding energies of the added proton are found to be quite different: $B(H_3O^+) = 173.05$ kcal/mole, $B(NH_4^+) = 215.84$ kcal/mole.

The potential energy curve of structure A3 is analyzed in some more detail: In this geometrical arrangement both subsystems ammonia and water are acting simultaniously as proton acceptor and donor. Because four hydrogen nuclei are "crowded" in a rather small region of space in this structure it was expected that the repulsion between the four hydrogen atoms might lead to an overall repulsion of the two subsystems for all intersystem separations *d*(NO). Therefore it was somewhat surprising to find that in a small region about an intersystem separation of *d*(NO = 7.23 a.u. the mixed dimer can stabilize even in this structure although with the rather small dimerisation energy of 0.23 kcal/mole. This result will change

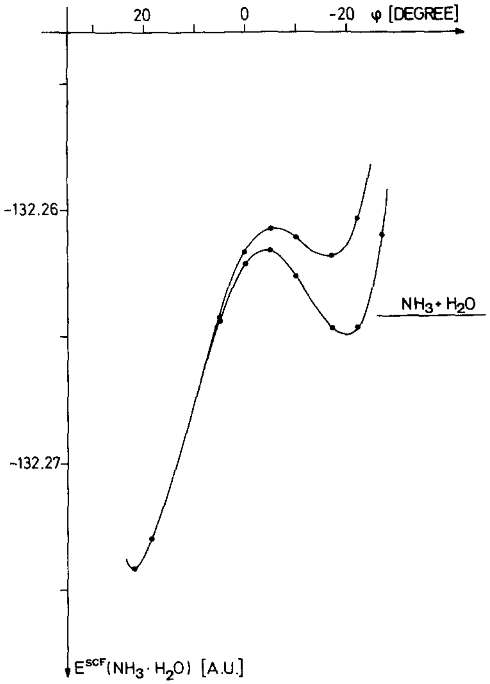

Fig. 4. Energy curve for the ammonia inversion (variation of the angle ∢ (HNH)) in structure A; upper curve *d*(NO) constant; lower curve *d*(NO) linearly interpolated

quantitatively if correlation energy is taken into account, but it is expected to be qualitatively correct because a rather flexible basis set is employed in the present calculations.

Two potential energy curves have been calculated for the inversion of a hydrogen bonded ammonia in the dimer $NH_3 \cdot H_2O$ in structure A and are shown in Fig. 4. The upper curve is calculated with a fixed NO-distance taken from the most stable structure A1 ($d(NO) = 5.75$ a.u.), and the lower curve is calculated with (linearly) interpolated NO-distances, as described above. Unsymmetrical double minimum potentials have been obtained for this inversion. Both energy barriers are well above the energy of the infinitely separated subsystems by 2.2 kcal/mole and 1.6 kcal/mole, respectively. The same is true for the upper minimum of the upper energy curve which is unstable against a dissociation into the subsystems by 1.5 kcal/mole. Only the upper minimum of the lower potential energy curve seems to be stable against a dissociation into the subsystems with a very small binding energy of about $B = 0.4$ kcal/mole. The height of the barrier of the two potential energy curves with respect to the two minima has been calculated to be: 8.5 kcal/mole and 0.7 kcal/mole for the upper curve, and 7.9 kcal/mole and 2.0 kcal/mole for the lower curve, respectively. As a result of the perturbation caused by the attached water molecule and the resulting charge shift produced by the hydrogen bond formation it is not the geometrical configuration A2 (with a planar $NH_3$ fragment and $\varphi = 0$) which represents the maximum point of the inversion barrier. As can be seen in Fig. 4 both maxima are slightly shifted to negative $\varphi$-values (for a definition of $\varphi$ see Fig. 1).

The experimental curve for the inversion is expected to be somewhat between the potential energy curves discussed above. Because of the high frequency of the inversion compared to the vibration of the two subsystems relative to each other, it is expected that the experimental curve is nearer to the upper theoretical curve. From the present results, without a more quantitative investigation of the individual vibrations, no definite prediction can be made on whether an inversion of a hydrogenbonded ammonia should be observable, or whether such an inversion leads instantly to a dissociation into the subsystems.

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