

## AB INITIO STUDY OF AMMONIA CLUSTERS: $(\text{NH}_3)_n$ ( $n = 2-6$ )

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### ABSTRACT

Hydrogen bonded neutral clusters of ammonia,  $(\text{NH}_3)_n$  ( $n = 2-6$ ), have been theoretically investigated employing the D95++(d,p) (and wherever necessary, higher) basis sets at the Hartree-Fock (HF) level as well as with second-order Møller-Plesset (MP2) perturbation theory. While the ammonia trimer and tetramer exhibit perfect molecular symmetries and are nonpolar, the pentamer and hexamer both optimize with slight deviations from perfect symmetries and are seen to possess marginal, but nonzero dipole moments. The  $(\text{NH}_3)_n$  linear clusters are seen to be chemically softer than the corresponding cyclic ones.

**Keywords:** *ab initio* calculation, ammonia clusters, Hartree-Fock, Møller-Plesset.

### INTRODUCTION

In recent times, there have been a large number of accurate theoretical as well as experimental investigations on hydrogen bonded molecular clusters of polar molecules such as  $(\text{H}_2\text{O})_n$  ( $n = 2-10$ ) and  $(\text{HF})_n$  ( $n = 2-10$ ), as well as their anions [1-7]. These systems can be probed only by ultrafast dynamical studies employing the sophisticated techniques of femtosecond-pulsed laser spectroscopy [6-7]. On the theoretical side, several accurate methods such as the Møller-Plesset perturbation theory and Coupled Cluster methods with extended basis sets have been used to describe the crucial role of electron correlation in these rather bound neutral as well as anionic clusters [1-5]. As in the case of water and hydrogen fluoride, the ammonia molecule too possesses an electric dipole moment (of around 1.8 Debye), and hence is also expected to polymerize into higher order, (*i.e.*  $n > 2$ ) neutral  $(\text{NH}_3)_n$  clusters by hydrogen bonding, the experimental signature for the existence of which has indeed been observed [8-9].

One, and for its time fairly exhaustive, set of *ab initio* computations for neutral  $(\text{NH}_3)_n$  ( $n = 1-5$ ) polymers had been carried out in 1984 by Hirao *et al.* [10] at the Hartree-Fock level, their best basis set employed being 6-31G\*\*. While Hirao *et al.* obtained decent structures for the  $n \geq 3$  clusters, for the ammonia dimer, their cyclic structure with  $C_{2h}$  symmetry turned out to be more stable than the asymmetric one, a result in contradiction to the two more recent, accurate and independent theoretical

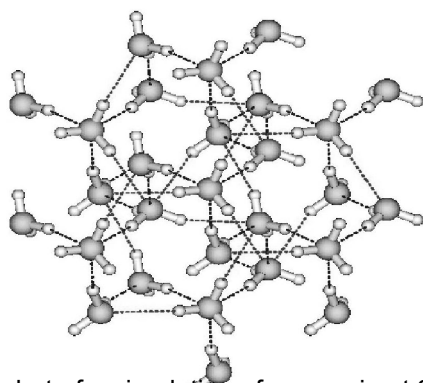
investigations of Zhu and Yang [11] and Cybulski [12], who have demonstrably emphasized incorporation of electron correlation for a proper theoretical description of  $(\text{NH}_3)_2$ . Both the aforementioned conclusions support the experimental findings of Odutola *et al.* [8], who carried out, in 1979, molecular beam electric deflection of ammonia polymers. Odutola *et al.* [8] further conjectured that existence of ammonia polymers larger than the dimer should be compatible only with nonpolar cyclic structures (with zero dipole moment), since they seemed to elude detection by inhomogeneous electric fields. Olthof *et al.* [31] presented a model potential for ammonia dimer derived from the vibrational-rotation tunneling states and further developed a model for monomer inversion in the dimer [14]. The most recent, state-of-the-art computation on the  $(\text{NH}_3)_2$  dimer was performed by Lee and Park [15] at the Hartree-Fock (HF), MP2, and MP4 (single point) levels, who used a series of correlation-consistent basis sets cc-pVXZ ( $X = \text{D, T, Q}$ ) and their augmented versions, strengthen the conclusion [11-14] that the asymmetric  $C_s$  dimer is more stable than the centrosymmetric  $C_{2h}$  one. A 'polarization model' for the  $(\text{NH}_3)_n$  polymers ( $n = 3-6$ ) was proposed by Turner and David [16], who, in line with the nonpolar nature of the clusters for  $n \geq 3$ , were led to planar (for nitrogen atoms) geometries representing the most stable structures. Novaro *et al.* [17] used their so-termed 'bare-minimal' Gaussian basis set for their studies on the trimer  $(\text{NH}_3)_3$ , with several geometrical configurations with rigid, unrelaxed

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monomers, augmented by three-body terms in the intermolecular potential representing numerically small yet physically significant contributions to electron correlation, that were decisive for relative stability. The importance of correlation for a decent representation of the intermolecular potential especially at large distances has been further corroborated by Sadlej *et al.* [18] in their accurate theoretical studies on the  $\text{NH}_3 \cdots \text{H}_2\text{O}$  complex. Thus, in essence, for a correct theoretical description of the neutral  $(\text{NH}_3)_n$  clusters, a proper inclusion of electron correlation is extremely crucial.

Signorelli's group has been studying structural and dynamical properties of a system consisting of 28 ammonia molecules using molecular dynamics (MD) simulations [19]. A snapshot of a typical pure ammonia simulation at *ca.* 300 K is shown in figure 1. The structure of ammonia molecules is dominated by the hydrogen bond interactions and this, naturally, also affects the dynamical properties of ammonia in many ways. One may expect that diffusion of ammonia molecules is rather slow for a molecule as small as ammonia, due to the hydrogen bond network. Indeed, this is the case but one must always bear in mind that the hydrogen bond network is not at all static. Hydrogen bonds are continuously broken and formed in the liquid phase of ammonia. This fluxional behaviour is very important in the analysis of the behaviour of ammonia solvation shells around ions and phenomena such as proton transfer.

For neutral ammonia clusters of large size ( $n \geq 34$ ) model theoretical studies supporting the experimental findings have been reported [20-21]. Further, there are reports on the experimental as well as theoretical investigations on the ionic clusters of ammonia [22-26]. Although studies on molecular complexes formed with neutral ammonia clusters have been reported [27-33], accurate theoretical computations on neutral ammonia clusters (for  $n > 2$ ) seem to be rather scarce. The present work endeavors to eliminate this deficiency through an accurate, *ab initio* theoretical investigation on neutral  $(\text{NH}_3)_n$  clusters ( $2 \leq n \leq 6$ ), at different levels of electron correlation.



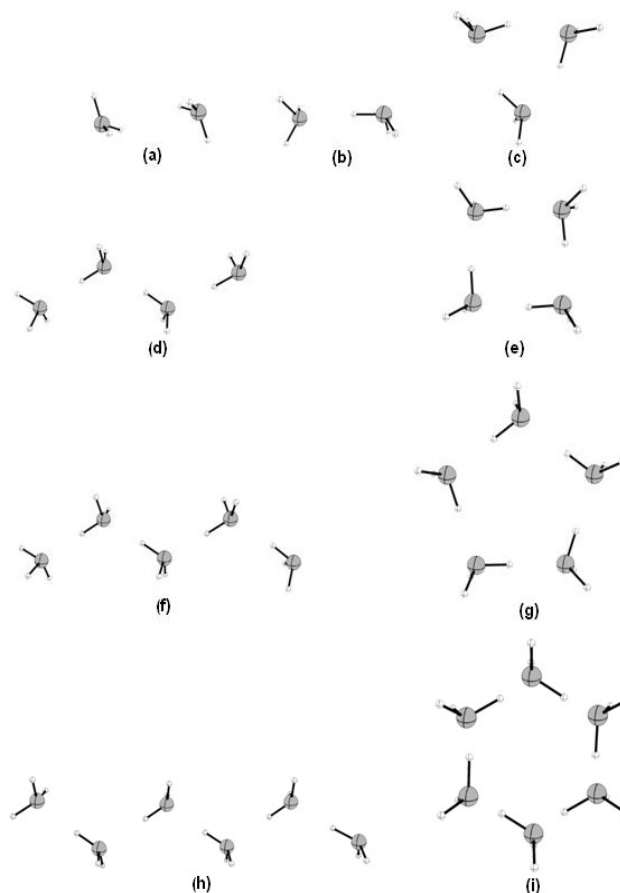
**Figure 1.** Snapshot of a simulation of ammonia at 300 K. The dotted lines represent hydrogen bonds [21]

## COMPUTATIONAL METHODS

The clusters of ammonia from dimer through hexamer (along with an exhaustive search for their corresponding energetically close isomers) were optimized at the RHF and MP2 levels of theory with the D95++(d,p) basis sets as well as higher ones as was found necessary, employing the Gaussian 98W suite of programs [34]. Single point energies have been obtained at the MP3, and MP4 levels using the corresponding MP2 optimized geometries. A set of frequency calculations was further carried out on some clusters at the RHF and MP2 levels to determine which of the conformers of  $(\text{NH}_3)_n$  were truly minimal on the potential energy surface (PES).

## RESULT AND DISCUSSION

The *ab initio* equilibrium structures of the  $(\text{NH}_3)_n$  clusters resulting from the computations carried out as describe above are depicted in Figure 2. The hydrogen bonding is displayed both for the actual minimal-energy structures as well as their energetically close variant.



**Figure 2.** Geometries of ammonia clusters at MP2/D95++(d,p) level

**Table 1.** Relative energies<sup>a</sup> in kcal/mol of ammonia clusters using D95++(d,p) basis set<sup>b</sup>

| Cluster                                         | RHF             | MP2             | MP3    |
|-------------------------------------------------|-----------------|-----------------|--------|
| NH <sub>3</sub> C <sub>3v</sub>                 | 0.0             | 0.0             | 0.0    |
| (NH <sub>3</sub> ) <sub>2</sub> C <sub>2h</sub> | -2.38           | -3.81 (-2.21)   | -3.64  |
| (NH <sub>3</sub> ) <sub>3</sub> C <sub>s</sub>  | -2.51 (-1.16)   | -4.12 (-2.60)   | -3.81  |
| (NH <sub>3</sub> ) <sub>3</sub> C <sub>3h</sub> | -8.34 (-3.7)    | -13.12 (-8.62)  | -12.33 |
| (NH <sub>3</sub> ) <sub>4</sub> C <sub>4h</sub> | -13.15 (-7.04)  | -20.16 (-14.24) | -19.1  |
| (NH <sub>3</sub> ) <sub>4</sub> Lin             | -8.53           | -13.21          | -12.76 |
| (NH <sub>3</sub> ) <sub>5</sub> Cyc             | -15.87 (-9.06)  | -25.37 (-18.20) | -24.23 |
| (NH <sub>3</sub> ) <sub>5</sub> Lin             | -11.74          | -18.19          | -17.36 |
| (NH <sub>3</sub> ) <sub>6</sub> Cyc             | -19.78 (-10.75) | -31.76 (-22.28) | -30.35 |
| (NH <sub>3</sub> ) <sub>6</sub> Lin             | -15.02          | -23.07          | -22.15 |

<sup>a</sup>The energy (in au) values of NH<sub>3</sub> at various levels are: RHF = -56.2011, MP2 = -56.3925, MP3 = -56.4043, MP4 = -56.4067.

<sup>b</sup> Values in parentheses indicate relative energies after inclusion of ZPE at the respective levels

**Table 2.** HOMO-LUMO gap and dipole moments of ammonia clusters at RHF/ D95++(d,p) level geometry

| Cluster                             | Sym                   | HOMO-LUMO gap (eV) | Dipole moment (Debye) <sup>a</sup> |
|-------------------------------------|-----------------------|--------------------|------------------------------------|
| NH <sub>3</sub>                     | C <sub>3v</sub>       | 12.64              | 1.72                               |
| (NH <sub>3</sub> ) <sub>2</sub>     | C <sub>2h</sub>       | 12.52              | 0.00                               |
| (NH <sub>3</sub> ) <sub>3</sub>     | C <sub>s</sub>        | 11.15              | 2.33                               |
| (NH <sub>3</sub> ) <sub>3</sub>     | C <sub>3h</sub>       | 12.22              | 0.00                               |
| (NH <sub>3</sub> ) <sub>4</sub> Cyc | C <sub>4h</sub>       | 11.63              | 0.00                               |
| (NH <sub>3</sub> ) <sub>4</sub> Lin | C <sub>1</sub> Linear | 10.89              | 6.15                               |
| (NH <sub>3</sub> ) <sub>5</sub> Cyc | C <sub>1</sub>        | 11.85              | 0.27                               |
| (NH <sub>3</sub> ) <sub>5</sub> Lin | C <sub>1</sub> Linear | 11.22              | 8.32                               |
| (NH <sub>3</sub> ) <sub>6</sub> Cyc | C <sub>1</sub>        | 11.77              | 1.24                               |
| (NH <sub>3</sub> ) <sub>6</sub> Lin | C <sub>1</sub> Linear | 11.14              | 9.17                               |

<sup>a</sup>At MP2/DZP level

Table 1 gives their relative energies at various levels of theory while Table 2 gives certain other properties of interest like HOMO-LUMO gap and dipole moment. It may be noted that for the dimer, the structure with C<sub>s</sub> symmetry that exhibits a dipole moment of 2.31 Debye is indeed more stable than the centrosymmetric, nonpolar cyclic C<sub>2h</sub> one (Figure 2a and b), in qualitative conformity with the earlier works [11-12,15]. The present work leads to a relative stability of the former over the latter of about 0.067 kcal/mol MP2/ D95++(d,p) level of calculation; this number stabilizes the C<sub>s</sub> over C<sub>2h</sub> by about 2.6 times that is suggested in [15]. This may be attributed to the size of basis set used. However, the qualitative trends are correctly brought out by this basis, which justifies its use for analysis of higher clusters. Further, at MP2/D95++(d,p) and MP2/D95++(2d,2p) levels the C<sub>2h</sub> has one imaginary frequency indicating that only the C<sub>s</sub> dimer exists as a true minimum on the corresponding PES.

Since the work by Odutola *et al.* [8] is suggestive of nonpolar ammonia clusters for  $n = 3-6$ , we looked for symmetric as well as near symmetric clusters. The trimer at both the RHF and MP2 levels optimizes to C<sub>3h</sub> symmetric cyclic structure with apparently no other energetically close PES (local-) minima structures (Figure 2c). Further, the investigations on the tetramer lead two different conformers; the most stable, cyclic C<sub>4h</sub> symmetric structure is found to be stabilized by 4.62

kcal/mol relative to the more spread linear one. Thus, as conjectured by Odutola *et al.* [8] both the trimer and the most stable tetramer indeed do give nonpolar and cyclic ('ring', as in [8]) optimized structures.

The pentamer poses a very intriguing question, since our exhaustive search over the most stable species of (NH<sub>3</sub>)<sub>5</sub> revealed that the optimized equilibrium structure for the pentamer is certainly not one with a perfect C<sub>5h</sub> symmetry, but rather a cyclic non-(nitrogen)-planar one with a dipole moment of a mere 0.27 Debye (Figure 2g). To confirm this, we performed C<sub>5h</sub> symmetry-constrained geometry optimization at both RHF and MP2 levels, using the D95++(d,p) and D95++(2d,2p) basis sets. The vibrational frequencies at these levels show two imaginary frequencies indicating that the C<sub>5h</sub> structure is actually not a minimum on the PES even though it has a zero dipole moment. The relative energies, in kcal/mol, of the pentamer in the two computations turned out to be as follows: for the 'relaxed' computation: -15.87 (RHF) and -25.37 (MP2), while for the 'C<sub>5h</sub>-constrained' computation: -15.6 (RHF) and -23.77 (MP2). Thus, the conjecture of higher ( $n > 2$ ) ammonia clusters being nonpolar appears to be only partly true. In addition, a pentamer with a linear structure (dipole moment -8.32 Debye) is also observed on the PES, as shown in Figure 2f.

We carried out an extensive search on hexamers with near as well as perfect  $C_{6h}$  symmetry. Two structures were obtained, namely linear and cyclic, as depicted in Figure 2h,i, respectively (the corresponding dipole moment being 1.24 and 9.17 Debye). The MP2 relative energies of the cyclic and linear hexamer structures, respectively, are: -31.76 and -23.07 kcal/mol. This emphasizes the fact that the most stable higher-order ammonia clusters with  $n = 5$  and  $6$  are in fact slightly polar; imparting only a partial validity (for  $n = 3$  and  $4$ ) to Odutola *et al.* [8] conjecture of nonpolarity of higher clusters. This scenario therefore reflects a strong need for extremely accurate experiments on neutral ammonia clusters.

It may be noted that for  $n = 4-6$ , the linear species are typically higher in energy by around 5-7 kcal/mol than their most stable, relatively compact counterparts, which signifies a deficiency of hydrogen bonding of two H-bonds. Further, the MP2 and MP4 relative energies are remarkably similar, indicating that MP2 energies are sufficient for obtaining trends. We also have reported the HOMO-LUMO gap values for the species in Table 2, which may be taken to be a measure of hardness [35] in a Koopmans-sense. The HOMO-LUMO gap decrease with increasing clusters size for most stable cyclic structures, indicating enhancement in their chemical softness and hence the chemical reactivity. It may also be noted that the cyclic clusters are indeed more stable than the corresponding linear clusters and exhibit higher HOMO-LUMO gaps (Table 2) which is in accordance with the Hard-Soft Acid-Base principle [35].

Comparison between our *ab initio* calculations and previous MD simulation [19] for structure of ammonia molecules is not comparable since *ab initio* calculations reflect the situation at 0 K and also much too small to be representative for the bulk of a liquid. The MD simulation will provide us with detailed structural and dynamical properties while *ab initio* calculations only provide static structures. However, both methods provide conclusive evidence that the ammonia cluster structures and dynamics are completely dominated by hydrogen bond rearrangement at the global minimum energy structure.

## CONCLUSION

For the dipole-bonded neutral agglomerates of ammonia, the  $(NH_3)_n$  clusters, an accurate representation of electron correlation is indispensable in a proper theoretical treatment. These clusters for  $n = 2-6$  have been studied herein using the D95++ basis sets at the Hartree-Fock level as well as second-(fully optimized), third- and fourth-order (single point) levels of the Møller-Plesset perturbation theory. Different, energetically close (and local minima on the PES) structures to the most stable ones have also been reported. The present study reaffirms the conclusion of

$C_s$  symmetry for the most stable dimer as borne out in the previous works, and further investigates the higher order clusters. While the ammonia trimer and tetramer exhibit perfect molecular symmetries and are nonpolar, in conformity with surmise of the 1979 experiments, the pentamer and the hexamer both optimize with slight deviations from perfect symmetries and are seen to possess marginal, but nonzero dipole moments. The cyclic  $(NH_3)_n$  clusters, become chemically softer with ' $n$ ', as inferred from their Koopmans HOMO-LUMO gaps. It may be remarked that the  $n = 5$  and  $6$  ammonia clusters, with their only marginal dipole moments, may well have eluded the experiments performed 1979, but pose a strong need for accurate experimentation for their detection as well as theoretical computations with a higher basis, for their further corroboration.

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