Study of the Structure, Energetics, and Vibrational Properties of Small Ammonia Clusters $(NH_3)_n$ ($n = 2-5$) Using Correlated ab Initio Methods

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Equilibrium geometries, interaction energies, and harmonic frequencies of $(NH_3)_n$ isomers ($n = 2-5$) have been computed using correlated calculations (MP2) in conjunction with Dunning's aug-cc-pVXZ (X = D, T, Q) basis sets and the Counterpoise procedure. Whenever available, literature values for the binding energy and geometry of dimers and trimers agree well with our data. Low lying isomers for $(NH_3)_4$ and $(NH_3)_5$ have been found to have similar binding energies (roughly 16 and 20 kcal/mol for the tetramer and pentamer, respectively), perhaps suggesting the presence of a very smooth energy landscape. Using BSSE corrected forces or freezing the monomer structure to its gas phase geometry have been found to have only a weak impact on the energetic and structural properties of the clusters. The effect of zero-point energy (ZPE) on the relative stability of the clusters has been estimated using harmonic frequencies. The latter also highlighted the presence of vibrational fingerprints for the presence of double acceptor ammonia molecules. Many-body effects for $(NH_3)_n$ isomers ($n = 2-4$) have been investigated to explore the possibility of building a pairwise interaction model for ammonia. In the frame of the work presented, we have found the 3-body effect to account for 10−15% of the total interaction energy, whereas the 4-body effects may be neglected as first approximation.

Introduction

Due to their relevance in many chemical and biological contexts, substantial effort is made in investigating the intermolecular forces between hydrogen bonded molecules. As a consequence, the study of the binding energy and equilibrium geometry of medium-sized water clusters represents one of the most active areas in this field. As a mere indication of the attention paid to these systems, it is worth mentioning that a recent review on the water trimer[1] listed 271 articles dealing with $(H_2O)_3$. A somewhat similar treatment has also been given to hydrogen fluoride clusters, mostly due to the prototypical nature of the H-bond interaction.[2] As a net result of this effort, a general consensus is now emerging on the relative stability of $(H_2O)_n$ and $(HF)_n$ isomers,[3−6] on the effect of the intermolecular vibrational motion,[7] and on several interesting details of cluster dynamics.[8,9] Moreover, this effort has produced a critical mass of data against which it is possible to test the accuracy of the model potentials used in statistical simulations of liquid and solid HF and H_2O.[10−12]

Despite the importance of NH_3 in many fields of science and technology, NH_3 clusters have been subjected to far less scrutiny. In particular, less attention has been paid to the intermolecular interaction between ammonia molecules and to the structure and energetics of its medium sized aggregates, perhaps due to a less peculiar behavior of liquid ammonia when compared to HF and H_2O.

Among the NH_3 clusters, the most studied one is certainly the ammonia dimer. Both experimental and theoretical investigations are available providing information on its properties. An early study by Odutola et al.[13] used electric field deflection. The results obtained in this study on $(NH_3)_n$ ($n = 1-6$) provided evidence for the presence of a dipole moment in NH_3 and its dimer. Successively, Klemperer and co-workers recorded the microwave spectra for $(NH_3)_2$ and several deuterium substituted isotopomers[14,15] finding indications of a vibrationally averaged structure far from the ideal case of linear hydrogen bond. Due to the lack of substantial changes in the spectrum upon isotopic substitution, it was also suggested that the dimer structure was quite rigid. The suggestion of a nonclassical H-bonded structure for the dimer was also supported by its rare gas matrix FTIR spectra.[16] At variance with the idea of a rigid structure, IR predissociation spectra obtained exciting the "umbrella modes" in $(NH_3)_2$[17] provided indications of a tunneling motion exchanging the identity of donor and acceptor molecules.

The controversy raised by these experimental results on $(NH_3)_2$ prompted several theoretical investigations involving ab initio calculations as well as model potentials. Hirao et al.[18] computed the binding energy for clusters up to the pentamer using Hartree−Fock (HF) and the 6-31G* basis set. In contrast, with the experimental suggestions, a substantially linear H-bond was found. This finding were successively revised by more accurate calculations including a description of the dispersion interaction.[19−25] In particular, it was proposed that the C_s minimum energy structure is less linear than predicted by the HF/6-31G* calculations, and that the interchange between hydrogen bond donor and acceptor surmounts a C_{2h} transition state with a very low energy barrier (roughly 7 cm^{-1} [23] or 5.9 cm^{-1} [25]). Besides, the acceptor molecule is free to rotate around its own C_3 axis. These ideas were also supported by the model potential results by Olthof et al.[22] In this study, a model surface was fitted to the $(NH_3)_2$ infrared spectra,[26] and a low barrier was found to separate the two isomeric species. In conclusion, all modern evidence suggests that $(NH_3)_2$ is a hydrogen bonded complex with a nonclassical (i.e., nonlinear) H-bond structure

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with the propensity to easily interchange the donor/acceptor nature of the two molecules.

The situation for the larger clusters appears instead less clear, owing perhaps to a lesser number of investigations carried out so far. On the experimental side, the work by Odutola et al.[13] provided evidence for a very small electric dipole in the larger clusters up to the hexamer, thus posing some constraint on the possible structure of these aggregates. This information was successively used in the interpretation of IR dissociation spectra of $(NH_3)_n$ ($n = 3-6$) by Snels et al.[17] Invoking a cyclic structure for these species, a qualitative explanation of the increasing blue shift in the "umbrella" ν_2 mode of ammonia with the size of the cluster was proposed using a simple electrostatic model. The idea of a cyclic structure for the trimer and tetramer was also supported by the results of the photodissociation experiments carried out by Huisken and Pertsch[27] and by Heijmen et al.[28] However, the broader absorption band obtained from the pentamer in ref 27 seemed to indicate a less rigid structure than the tetramer, perhaps suggesting the possibility that $(NH_3)_5$ may be a fluxional species. Larger species than the hexamer ($n =$ 18, 745, 1040) were studied by Buck et al.,[29] who excited their low energy intermolecular modes with a beam of He atoms. The recorded energy-loss spectra were interpreted on the basis of the ammonia crystal phonons, but direct structural information was not extracted from the experiment data.

Assuming a cyclic geometry, Hirao et al.[18] carried out ab initio geometry optimization for $(NH_3)_n$ ($n = 3-5$). When compared with the experimental results available at the time,[13] the HF/6-31G* results[18] appeared to largely overestimate the binding energy of these clusters, probably due to a lack of basis set superposition error (BSSE) corrections.

A more extensive search for the minimum energy structure of $(NH_3)_n$ ($n = 3-7$) was carried out by Greer et al.[31] using a nonpolarizable model potential calibrated against coupled pair functional results[30] on the ammonia dimer. Whereas the minimum energy structures for the trimer and tetramer were found to be cyclic (as taken by Hirao et al.[18]), the global minimum for $n = 5$ was found to be a distorted pyramid. Also, the hexamer and heptamer featured a complicated tri-dimensional global minima structure. Similar results were obtained by Beu and Buck,[32] who extended the investigation including clusters containing up to 18 ammonia molecules. In this case, a simple "charge plus Lennard-Jones" interaction potential was used, its parameter being calibrated to reproduce the NH_3 crystal sublimation energy and structure by Impey and Klein.[33] The results for $n \geq 5$ suggested that these larger clusters may have the tendency to form 3D isomeric structures very close in energy. In other words, this could hint to the presence of a smooth energy landscape characterized by several low lying local minima. An additional study using a model potential was carried out by Dykstra and Andrews,[34] who employed model potentials including polarization terms to improve on previously used effective pair potentials. Unfortunately, only clusters up to the tetramer were investigated, preventing a more extensive comparison between different interaction models.

As for higher level calculations, only two studies have employed correlated ab initio methods to investigate clusters larger than the ammonia dimer. In the work by Szczesniak et al.,[35] the relative contribution from several components of the total interaction energy in $(NH_3)_3$ was investigated employing symmetry-adapted perturbation theory (SAPT) up to the third order. Interestingly, it was found that for N−N distances in the range of the attractive well, the 3-body effects in the equilateral geometry for $(NH_3)_3$ are roughly 0.7 kcal/mol (i.e., less than 10% of the total interaction energy) and that they are mostly accounted for by the induction and Heitler−London terms at the SCF level. In other words, whereas 3-body effects may be necessary to quantitatively model ammonia clusters and liquid, the contribution of electron correlation to these quantities could be neglected. With a somewhat different purpose, HF/6-31G* and MP2/6-31G* interaction energies and equilibrium geometries for $(NH_3)_n$ ($n = 2-6$) were presented by Kulkarni and Pathak.[36] In their work, two isomeric pentamers and three different hexamers were studied, the results providing evidence that linear species have smaller binding energies than compact ones, as found for neutral and protonated water clusters.[7,37−39] It was also shown that the cyclic structure for the hexamer is lower in energy than a "book"-like one at the MP2/6-31G* level, a conclusion requiring however some caution due to the lack of BSSE correction in the calculations.

As it should be apparent from the above summary, information on ammonia clusters larger than the dimer are somewhat scarce; the lack of consensus even on the minimum energy structure for a cluster as small as the pentamer is a clear indication of this paucity of data. To improve on this situation, high level ab initio calculations on $(NH_3)_n$ ($n \geq 2$) are needed. These theoretical results would be important to obtain a better understanding of the interaction between ammonia molecules and their effects. They would also provide reference data for a new generation of model potentials, perhaps explicitly including many-body effects as available for water and HF.[10−12] Thus, we present a MP2 study of the structure, intermolecular binding energy and harmonic frequencies of $(NH_3)_n$ ($n = 2-5$). Several isomers for each cluster size were optimized, and their interaction energy decomposed in its 2-, 3-, and 4-body contributions. Harmonic frequencies were computed and used to correct for the nuclear zero-point motion.

The outline of the paper is as follows. In section II, we give the details of the procedure used to study the structure and energetics of the $(NH_3)_n$ clusters. Section III describes the results of our calculations and provides a comparison with the available experimental results. Section IV presents our conclusions and a discussion of the possible future work.

Methodology

All of the electronic structure calculations on $(NH_3)_n$ ($n =$ 2−5) were performed using the Gaussian 98 and 03 ab initio packages using Hartree−Fock (HF) and second-order Møller−Plesset perturbation theory (MP2) with frozen core. Although it is well-known that HF has the shortcoming of neglecting dispersion effects and of overestimating dipole moments, we found it to be a useful device in the initial optimization steps for the intermediate clusters ($n = 3$ and 4). Unfortunately, we also found that dispersion provides a crucial contribution to the structural stability of some pentamers, forcing us to adopt an MP2-based optimization strategy in all steps.

Putative structures for possible isomers were obtained from previous literature results (mostly using model interaction potentials[32]) or considering geometrical arrangements likely to have relatively strong H-bonds. In view of the future goal of developing an ab-initio-based interaction potential between rigid ammonia molecules, all of the geometries for $(NH_3)_n$ ($n = 2-4$) were re-optimized keeping the intramolecular ammonia geometry frozen and compared with the fully relaxed species.

Recent work studying the potential energy surface (PES) of the ammonia dimer with the supermolecular approach employed the Dunning's family basis sets aug-cc-pVXZ (X = D,T,Q) and different levels of perturbation theory,[23−25] ensuring that all of the relevant contributions were introduced. It was found that MP2 provides quantitative results for both equilibrium geometry and interaction energies when compared with MP4, suggesting that higher order dispersion components contribute only weakly.[23,25] In this study, a similar recipe was followed, attempting a rough extrapolation of the MP2 interaction energies exploiting the properties of Dunning's basis sets. In addition, the performances of Pople-type triple-ζ basis set family 6-311++G with increasing polarization functions (2d,2p), (3d,3p), and (3df,3pd) were also tested on the smaller clusters with the hope they could provide a less expensive alternative in computing the full ammonia dimer PES. The initial test between the two families of basis sets focused on the calculations of monomer properties influencing intermolecular interactions (dipole and quadrupole moment, polarizability, etc.) and involved a comparison with the available experimental data. Successively, this comparison was extended to the study of $(NH_3)_n$ ($n = 2$ and 3) structures and energetics. As a net result, we found the Dunning's basis sets to provide a more balanced performance with increasing basis set size, so that the latter was chosen to describe $(NH_3)_4$ and $(NH_3)_5$ in our study.

Using the supermolecular approach, interaction energies were computed on the optimized geometries for $(NH_3)_n$ ($n = 2-5$). Basis set superposition error (BSSE), usually responsible for an overestimation of the intermolecular binding energy in clusters, was accounted for by means of the counterpoise correction procedure[40−42] on the optimized structures. To improve our understanding of the intermolecular interactions, additional BSSE-corrected calculations were performed on the relevant monomer combinations to decompose the interaction energies into their *n*-body contributions for the clusters up to the tetramer. The computational strategy for the many body decomposition can be briefly summarized using $(NH_3)_4$ as an example and with the help of the energy decomposition described by the following equation:

$$E(\mathbf{X}_1,\mathbf{X}_2,\mathbf{X}_3,\mathbf{X}_4) = \sum_{i=1}^{4} E^{(1)}(\mathbf{X}_i) + \sum_{i<j=1}^{4} E^{(2)}(\mathbf{X}_i,\mathbf{X}_j) + \sum_{i<j<k=1}^{4} E^{(3)}(\mathbf{X}_i,\mathbf{X}_j,\mathbf{X}_k) + \sum_{i<j<k,l=1}^{4} E^{(4)}(\mathbf{X}_i,\mathbf{X}_j,\mathbf{X}_k,\mathbf{X}_l) \quad (1)$$

where $E(\mathbf{X}_1,\mathbf{X}_2,\mathbf{X}_3,\mathbf{X}_4)$ is the $(NH_3)_4$ interaction energy, $\mathbf{X}_i$ is the position of all the atoms in the *i*th molecule, $E^{(1)}(\mathbf{X}_i)$ is the energy required to distort NH_3 from its gas-phase structure to the one in the complex, $E^{(2)}(\mathbf{X}_i,\mathbf{X}_j)$ is the 2-body interaction between two molecule *i* and *j*, and so on. Thus, given an optimized isomer for the tetramer (either fully relaxed or with the intramolecular structure kept frozen to the experimental gas-phase geometry), single-point calculations were performed taking the monomers in a three member fashion, pairwise fashion, and single monomers to evaluate 3-, 2-, and 1-body (distortion) effects. All of the calculations involving the subclusters were carried out using the CP procedure and the basis set of the subclusters itself to eliminate the BSSE as much as possible. The remaining 4-body effect was obtained as a complement to the total interaction energy value.

To make sure that BSSE has no serious influence on the equilibrium geometries for these weakly bound clusters, BSSE-corrected optimizations were also carried out starting from the uncorrected optimized geometries; this allowed us to explore and compare the BSSE-corrected PES with the uncorrected one.

Harmonic frequencies were computed on the fully relaxed clusters as a way to introduce zero-point energy (ZPE) correction and to study the effects of vibrational motion on their relative stability. We also investigated possible patterns in the N−H frequency shifts of the ammonia aggregates that could be used as a spectroscopic signature of some structural feature.

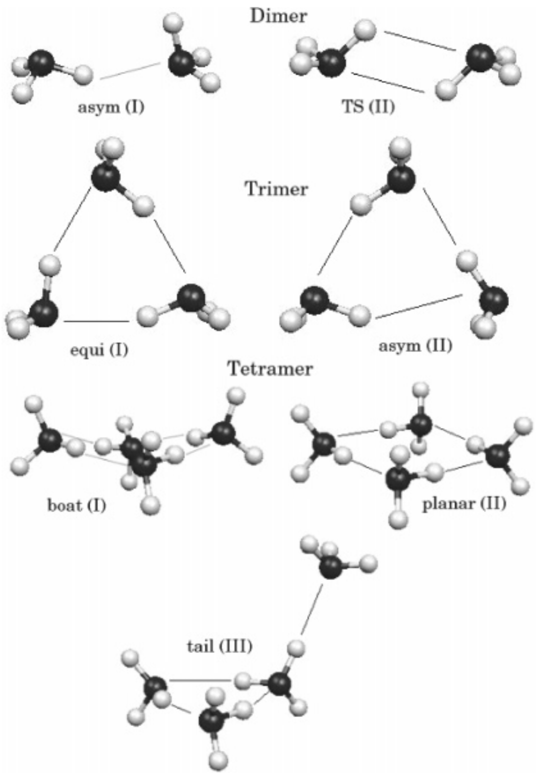

Figure 1. Equilibrium structures for $(NH_3)_n$ ($n = 2-4$) obtained with counterpoise corrected MP2/aug-cc-pVTZ optimizations.

Results

Figures 1 and 2 show the $(NH_3)_n$ ($n = 2-5$) structures obtained at the end of the BSSE corrected optimizations with MP2/aug-cc-pVTZ. Table 1 lists various energetic data (in kcal/mol) for the different isomeric clusters of this work (Figures 1 and 2) and previous ab initio and model potential results.

The meaning of the symbols in Table 1 is the following: BE indicates the (BSSE) uncorrected adiabatic binding energy for an optimized cluster (i.e., computed using the energy of fully relaxed local minima), ZPE is its harmonic zero point energy, BE^{CP} gives its vertically corrected BSSE-free BE, and Opt^{CP} gives the BSSE corrected BE after the structural relaxation on the Counterpoise surface. As mentioned in the methodological section, we have also carried out structural optimizations for $(NH_3)_n$ ($n = 2-4$) at the MP2/aug-cc-pVDZ level constraining the ammonia molecules in their gas-phase structure. According to these results (Supporting Information), the adoption of the frozen intramolecular approximation produces negligible changes from the results of the "fully relaxed" approach for both energy and structure.

For the sake of organization, the structural results are discussed first and separately for every cluster size, with particular emphasis on their energy landscape. Successively, experimental binding energies are compared with the ab initio results and with previous theoretical literature data, and the importance of many-body effects on the total binding energy is examined. Last, harmonic frequencies at the MP2/aug-cc-pVDZ level are discussed, highlighting the connection between specific sets of normal modes and relative frequency shifts from the single molecule results.

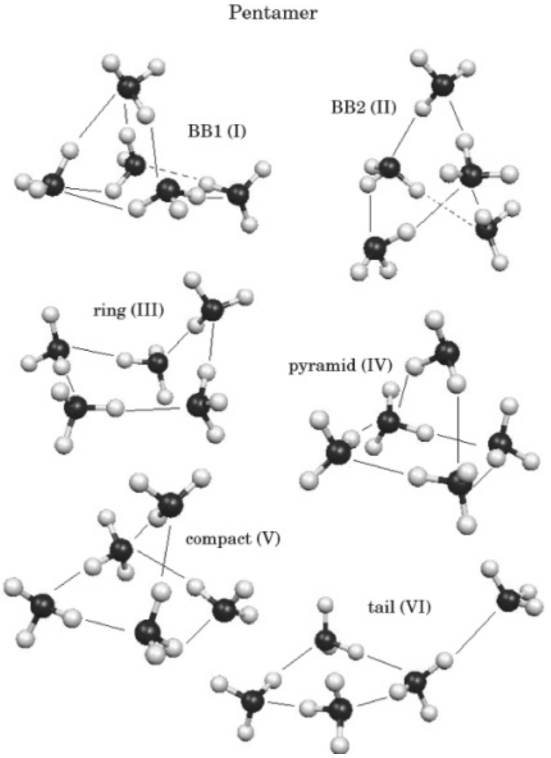

Figure 2. Equilibrium structures for $(NH_3)_5$ obtained with counterpoise corrected MP2/aug-cc-pVTZ optimizations.

Ammonia Dimer. The results for all basis sets support the asymmetric isomer (asym, I) as the most stable one, with the cyclic species (II) being a transition state (TS). These results are in good agreement with the work by Lee and Park.[23] The relative difference between "asym" and TS represents the hydrogen donor−acceptor exchange barrier[23] and amounts to roughly 3 cm^{-1} at the CP-corrected MP2/aug-cc-pVQZ level. As expected, introducing vertical Counterpoise correction on the optimized isomeric geometries reduces the binding energies, but no substantial changes are seen in the relative energy of the two isomers. Similarly, only slight changes are observed after the relaxation on the CP-corrected PES. Besides, we notice that energy results at the MP2/aug-cc-pVTZ level show very good agreement with the one obtained using MP2/aug-cc-pVQZ. Given the fact that MP2 has been already reported to compare well with the more expensive MP4 and Coupled Cluster methods[23] for several atomic basis, the good agreement between basis sets in our calculations suggests that the MP2/aug-cc-pVTZ level may provide an accurate representation for the energetic of the ammonia clusters.

Our best BE value for the asymmetric dimer agrees very well with the most accurate ab initio data available, namely the coupled pair functional (CPF) result provided by Sagarik et al.,[30] the W2 results by Boese et al.,[25] and the local-MP data of Stårling et al.[24] As for the model potential results in Table 1, the BE for the asymmetric dimer obtained by Beu and Buck[32] using the potential developed by Impey and Klein[33] is 2.784 kcal/mol. Although this value underestimates the MP2 BE by roughly 0.3 kcal/mol, we found that the optimized structure is in good agreement with all of the ab initio results. Conversely, the equilibrium structure presented in ref 34 as minimum energy geometry for the dimer does not resemble any of the stationary points reported in the literature or by us. This fact has been already discussed in the literature,[43,44] and it is mainly due to the difficulty, at the time, of parametrizing properly the nonelectric part of the potential model. Nevertheless, the interaction energy for this cluster (2.924 kcal/mol) is only slightly lower than the ab initio values,[34] perhaps suggesting that induction may play a important role in defining the interaction energy.

$(NH_3)_3$. The trimer $(NH_3)_3$ presents the largest differences between the BEs of two local minima (Figure 1) among all of the cluster sizes. As seen in Table 1, all of the calculations on $(NH_3)_3$ predict the most symmetric isomer I (henceforth "equi") to be the most stable structure, with isomer II (asym) lying 3.4−3.7 kcal/mol above isomer I on the BSSE corrected surface. This large energy difference is due to the inverted ammonia in the ring, a feature that also induces a large dipole moment (3.04 D versus 0 D for "equi") in the system. The other correlated ab initio result for the most stable $(NH_3)_3$ in Table 1 is provided by Kulkaum and Pathak.[36] However, their MP2/6-31++G(d,p) result is roughly 2.7 kcal/mol more binding than our best results due to the lack of BSSE correction. Similarly to the dimer case, good quantitative agreement between MP2/aug-cc-pVTZ and MP2/aug-cc-pVQZ results is found.

Concerning the model potential results in Table 1, these come from three previously published studies.[31,32,34] The two structures, also labeled equi, obtained by Beu and Buck[32] and Greer et al.[31] are almost identical to our lowest energy isomer. In both cases, rigid body, pairwise additive potentials were used to calculate BE, the resulting interaction energies agreeing well between themselves. However, these values underestimate by roughly 2 kcal/mol our CP-corrected MP2/aug-cc-pVQZ value, suggesting that the lack of many-body effects in the 2-model potentials may undermine the accuracy of their energy landscape for larger clusters. The remaining model potential result for the trimer was obtained by Dykstra and Andrews.[34] Similarly to the dimer, the geometry for $(NH_3)_3$ in ref 34 shows the three ammonia molecules in the cycle to be rotated by 60° around their C_3 axes when compared to our ab initio "equi" structure.[43,44] Notwithstanding this, the difference in BE between our CP-corrected MP2/aug-cc-pVQZ results and the model potential is only 1 kcal/mol.

$(NH_3)_4$. Three stationary structures (Figure 1) were obtained at the MP2/aug-cc-pVDZ level for the ammonia tetramer. The two most stable isomers (I "boat" and II "planar") have an estimated binding energy of roughly 15.5 kcal/mol at the CP-corrected MP2/aug-cc-pVTZ level. These two species are almost degenerate, the sign and magnitude of their small energy difference depending on the level of the calculations. Their main structural difference is in the value of the torsional angle between the four nitrogens, constrained to lie in the same plane in isomer II. Depending on the calculation level, the latter is either a transition state (at MP2/aug-cc-pVDZ) connecting two equivalent "boat" isomers through a puckering (or a pseudorotation) motion or a minimum (at MP2-aug-cc-pVTZ). The third species, isomer III (tail), lies instead roughly 3 kcal/mol from isomer I. As found for $(NH_3)_2$ and $(NH_3)_3$, the uncorrected results by Kulkarni and Pathak[36] indicate a larger BE for the "boat" structure than our results.

Whereas the "boat" and "planar" isomers have equivalents in the literature,[31,32,34] this is the first time the tail isomer is studied. The latter was built adding an external ammonia molecule to the "equi" $(NH_3)_3$ as a way to explore the trapping of an ammonia molecule outside the ring. In principle, this may happen during the stepwise formation of $(NH_3)_4$ in a dissipating cold environment (e.g., in He droplets[45]), facilitated perhaps by the compact nature of the trimer and its lack of dipole moment. As a consequence of the binding of the external ammonia molecule, we found a change in the ring N−N distances with

TABLE 1: Energy Values for $(NH_3)_n$ ($n = 2-5$), in kcal/mol[j]

	$(NH_3)_n$										
$n = 2$	MaDZ BE	ZPE	BE^{CP}	Opt^{CP}	MaTZ BE	BE^{CP}	Opt^{CP}	MaQZ BE	BE^{CP}	Opt^{CP}	other
asym[a]	3.624	44.777	2.735	2.771	3.287	3.001	3.011	3.220	3.089	3.090	4.03[h]
TS[a]	3.403		2.735	2.756	3.239	2.999	2.999	3.197	3.082	3.082	
asym[b]	3.623		2.737		3.286		3.000	3.219	3.088		2.934[c]
TS[b]	3.403		2.729		3.239		2.995	3.196	3.081		2.925[c]
asym											2.995[d]
TS											2.983[d]
asym											3.090[e]
dimer											2.924[f]
asym					2.784[g]						
$n = 3$											
equi[a]	11.919	69.001	9.242	9.326	10.974	10.067	10.074	10.747	10.334	10.329[i]	13.02[h]
asym[a]	7.827	68.155	5.775	5.886	7.182	6.439	6.453	6.961	6.633	6.633[i]	
equi											8.262[c]
equi											8.439[d]
trimer											9.392[f]
$n = 4$											
boat[a]	18.523	92.244	14.304	14.427	17.002	15.515	15.537				20.12[h]
planar[a]	18.52		14.298	14.426	17.009	15.514	15.535				
tail[a]	15.128	91.442	11.503	11.640	13.786	12.552	12.569				
boat											12.631[c]
planar											12.612[d]
boat											13.098[d]
boat											14.119[f]
$n = 5$											
BB1[a]	23.867	115.445	17.932	18.177	21.377	19.315					16.728[c]
BB2[a]	23.706	115.091	17.886	18.128	20.958	19.077					16.589[c]
ring[a]	23.617	115.287	18.161	18.334	21.287	19.358					25.48[h]
pyramid[a]	24.053	115.608	17.892	18.181	21.388	19.263					
compact[a]	23.705	115.329	17.883	18.127	21.260	19.203					
tail[a]	21.532	114.918	16.359	16.533	18.930	17.286					
BB3											16.587[c]
ring											16.926[d]

[a] This work. [b] Reference 23. [c,d] Reference 32, model potential. Reference 31, model potential. [e,f] Reference 25, W2 result. Reference 34, model potential [g,h] Reference 24, LMP2. [h] Reference 36, MP2/6-31+G* result. [i] CP-corrected MP2/aug-cc-pVQZ using a geometry obtained with a CP-corrected optimization at the MP2/aug-cc-pVTZ level. [j] MaXZ (X=D, T, Q) is a shorthand notation for MP2/aug-cc-pVXZ. BE are the uncorrected values (i.e., still including BSSE error) and ZPE is the harmonic corrections. BE^{CP} indicates the binding energy obtained with a vertical counterpoise (CP) correction and Opt^{CP} gives the results of a full CP-corrected optimization of the cluster. The "other" column collects literature values obtained using both ab initio calculations and model potentials.

respect to the trimer geometry. In particular, the distance between the coordinating molecule and its H-bond donor in the ring is reduced by 0.06 Å, whereas the distance between the same molecule and its H-bond acceptor counterpart is increased by 0.09 Å. Parallel changes are also found for the harmonic frequencies of the hydrogen bonded NH stretches, but we postpone a more complete discussion of this finding to the section devoted to the vibrational features of these clusters.

Similarly to the trimer case, model potential results for the BE of the cyclic structure are provided in refs 31, 32, and 34. Comparing these values with our ab initio data, we notice a worsening of the interaction model performance with respect to the $(NH_3)_3$ case. In particular, the results in refs 32 and 31 underestimate the ab initio BEs by 2.9 and 2.4 kcal/mol, respectively. The model by Dykstra and Andrews[34] performs better, the discrepancy being only 1.4 kcal/mol.

$(NH_3)_5$. As far as $(NH_3)_5$ is concerned, the increasing number of possible isomeric structures (see Figure 2) makes the detailed discussion of the energy landscape quite complicated. However, two observations are easily extracted from the results in Table 1. First, the "tail" isomer is the least stable species, lying roughly 2 kcal/mol above all of the other species due to the lower number of H-bond contacts. Second, the energy ranking for $(NH_3)_5$ is quite compressed and strongly sensitive to the level of treatment. In particular, it is seen that uncorrected results using both aug-cc-pVDZ and aug-cc-pVTZ favor compact species, whereas the CP-corrected values indicate the "ring" isomer as the most stable one, although marginally. As found before, this reversal in energy ranking is due to a different magnitude of the BSSE correction, which is in turn related to the number of H-bond contacts. In our view, this outcome reinforces the suspicion/hypothesis that the energy landscape for the $(NH_3)_5$ isomers is very smooth, similarly to what has been obtained for the water hexamer. It is therefore difficult to indicate a possible global minimum at this stage, and higher level of ab initio theory may be necessary to discriminate among the present isomers.

As far as we know, only a few structures have been proposed as putative global minima for the ammonia pentamer using model potentials. The binding energies of the two 3D structures described in refs 32 and 31 are shown in Table 1. By visual comparison, these structures appear similar to isomer I (obtained optimizing the lowest energy structure from ref 32, henceforth "BB1") and isomers II and IV ("BB2" and "pyramid", respectively). As found before for the smaller clusters, the BEs obtained with model potentials are roughly 2.5 kcal/mol smaller than the ones provided by CP-corrected ab initio calculations.

TABLE 2: Binding (BE) and Vaporization (Δ*E*) Energies for $(NH_3)_n$ ($n = 2-5$), in kcal/mol[a]

n	BE[b]	Δ*E*[b]	Δ*E*[c]	Δ*E*[d]	Δ*E*[e]	Δ*E*[f]
2, asym	3.011(1.651)	1.651	3.090	4.6(5)	≤2.85	2.8
3, equi	10.074(6.197)	4.546	5.637	3.9(5)	2.85 ≤ Δ*E* ≤ 5.72	3.5
4, planar	15.537(10.125)	3.928	4.659	5.2(5)	2.85 ≤ Δ*E* ≤ 5.72	5.1
5, ring	19.358(12.612)	2.487	3.828	3.9(5)		5.1

[a] The first column shows adiabatic and ZPE corrected (between brackets) BEs computed in this work using Counterpoise corrected energies and ZPE at the MP2/aug-cc-pVTZ level. Δ*E* values from this work are computed including ZPE corrections. [b] This work. [c] Reference 31, model potential. [d] Reference 46, thermochemical measurements. [e] Reference 28, photodissociation experiments. [f] Reference 47, ionization treshold measurements.

Many-Body Effects and Comparison with Experiments. Using the results presented in Table 1, it is possible to compare our theoretical prediction with experimentally inferred quantities. This comparison is carried out in Table 2 where we report ZPE-corrected BEs and molecular evaporation energies (Δ*E*), thermochemical data for the formation of $(NH_3)_n$ from $(NH_3)_{n-1}$,[46] as well as data derived from photodissociation of $(NH_3)_n$ into $(NH_3)_{n-1}$ [28] and photoionization[47] studies. We also listed the results by Greer et al.[31] obtained using model potentials without the inclusion of ZPE. All of the incremental energy data from this work have been computed using zero-point energies at the MP2/aug-cc-pVDZ level and CP-corrected results for the electronic energies obtained using the largest affordable basis set and CP corrected optimization (when possible). Whenever multiple isomers were found, we listed only the BE for the one with lowest total energy.

At first glance, we see that ZPE accounts for a 30−40% reduction in the BE for all cluster sizes. Moreover, we found no significant changes in the relative energy ranking upon introduction of the ZPE correction for all $(NH_3)_n$, the only noteworthy result being the slight increase in relative stability of the "ring" pentamer. From Table 2, it is also apparent that less energy is required to evaporate an ammonia molecule from $(NH_3)_5$ than from the trimer and tetramer, a result supported by the less compact structure of the larger cluster.

From the Δ*E* data in Table 2, one notices that there is a reasonable agreement between theoretical values and experimental results, especially taking into account the small magnitude of this quantity and the difficulties in measuring it. In particular, all our values fall in the range indicated in ref 28. There is, however, a relatively large discrepancy between theory and experiments in the case of $(NH_3)_4$ and $(NH_3)_5$. Specifically, the experiments in refs 46 and 47 provide substantially higher evaporation energies than theory, a result that was explained by Greer et al.[31] with the suggestion that the concentration of small clusters was overestimated during the thermochemical experiments due to the variation in ionization probability with cluster size.

Table 3 presents the many body decomposition (eq 1) of the BE for clusters up to the tetramer. For a direct comparison of each order of many-body effects for different cluster sizes, the different contributions (i.e., 2-, 3-, and 4-bodies) have been renormalized dividing by the number of possible sub-clusters (e.g., the total 2-body contribution in a tetramer has been divided by 6, the number of different dimers it contains). Given the small magnitude of four-body effects in the tetramer, higher many-body contributions have not been calculated for the pentamers. From the data shown in Table 3, it seems that 2- and 3-body effects are mandatory for an accurate decomposition of the total BE, whereas the 4-body effect appears to be negligible. This finding is of importance for the task of building a model potential for ammonia, suggesting that one may concentrate only on low order many-body effects. Interestingly, the renormalized 2-body effects decrease with increasing cluster size, the principal reason for this trend being the longer distance, on average, between pairs of ammonia molecules in large clusters.

TABLE 3: Many-Body Contributions to the Binding Energy of $(NH_3)_n$ ($n = 2-4$), in kcal/mol[a]

system	2-body		3 body		4 body
$n = 2$, asym	3.011	3.011			
$n = 2$, sym (TS)	2.999	2.999			
$n = 3$, equi	9.053	3.018	1.142	1.142	
$n = 3$, asym	6.206	2.069	0.369	0.369	
$n = 4$, boat	12.984	2.164	2.632	0.658	0.150
$n = 4$, plane	13.171	2.195	2.441	0.610	0.155
$n = 4$, tail	11.561	1.927	1.150	0.288	0.004

[a] For each *n*-body contribution, the first column presents the total value and the second column shows the total contribution divided by the number of *n*-body moieties in the cluster.

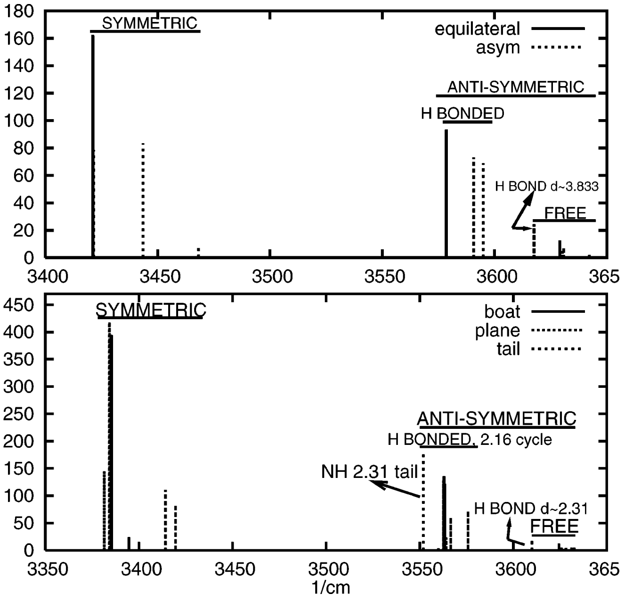

Figure 3. N-H stretching frequencies for $(NH_3)_3$ and $(NH_3)_4$ obtained using MP2/aug-cc-pVDZ. The meaning of the label in the picture is the following: "H BOND d 2.886" indicates a NH bond involved in a H-bond with the two nitrogens at a distance of roughly 3.833 Å; "NH 2.31 tail" indicates the stretching of the NH bond of the ammonia in the ring donating an H-bond to the external NH_3 with an N−H distance of 2.31 Å; "H BOND d 2.31" indicate the stretching of an NH involved in a long H-bond (roughly 2.31. Å long).

Frequencies. Ab initio harmonic frequencies were calculated for ammonia clusters on the fully optimized structures at the MP2/aug-cc-pVDZ level. These were analyzed in order to extract information on the frequency shift for the N−H stretching modes, in an attempt to associate a particular geometrical feature to a range of frequencies.[48] The results of our frequency calculations for the N−H stretches are shown in Figures 3−5 for the trimers, tetramers, and pentamers; the complete set of data is given as Supporting Information.

As a first comment, we mention that all NH stretch frequencies are seen to decrease upon increasing the cluster size, a common feature present in several H-bonded clusters. Although somewhat difficult to quantify due to the complicated dependency on the aggregate geometry, we notice that the average frequency of antisymmetric stretches decreases by roughly 20 cm^{-1} going from the trimer to the tetramers and by roughly

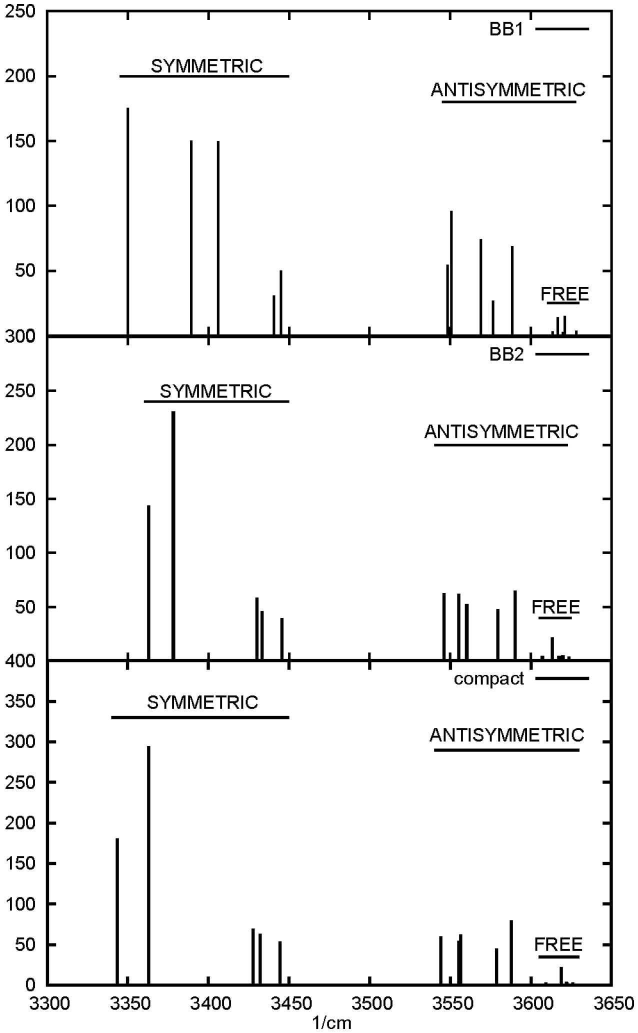

Figure 4. N-H stretching frequencies for the BB1, BB2, and compact isomers of $(NH_3)_5$ obtained using MP2/aug-cc-pVDZ.

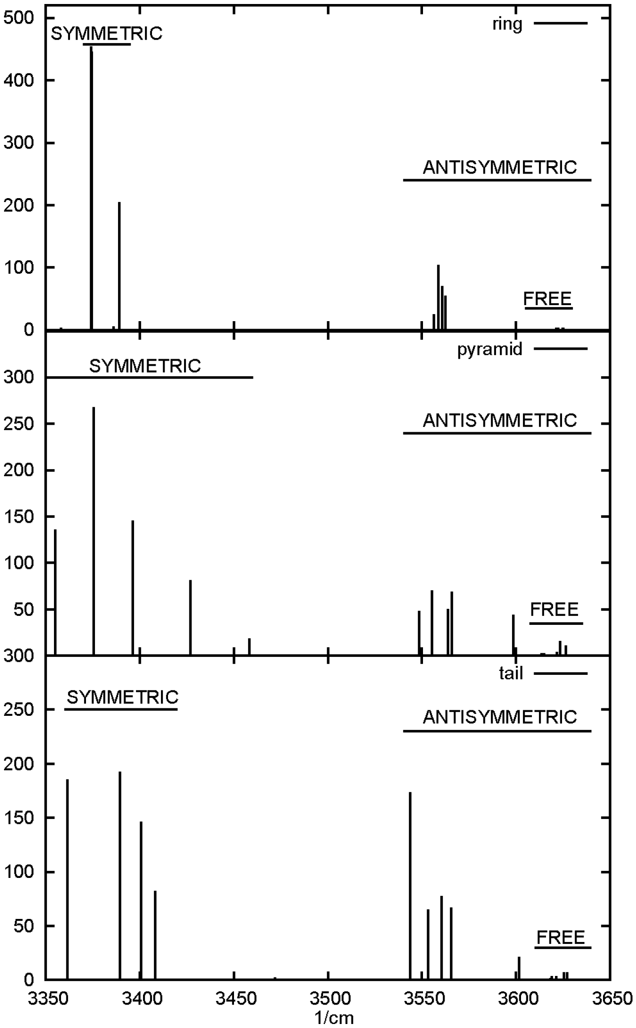

Figure 5. N-H stretching frequencies for the ring, pyramid, and tail isomers of $(NH_3)_5$ obtained using MP2/aug-cc-pVDZ.

5−10 cm^{-1} from tetramers to pentamers. In the case of symmetric stretches, the frequency shifts are found to be larger: roughly 50 cm^{-1} going from the trimer to tetramers and roughly 10−20 cm^{-1} from tetramers to pentamers.

Our analysis also highlighted the presence of two additional overlapping trends, one of which is the common occurrence of a lower frequency (roughly 100−120 cm^{-1}) for the symmetric stretches when compared with antisymmetric ones. Moreover, free H atoms are always found to participate only in antisymmetric stretches, vibrating at higher frequencies (roughly 40−50 cm^{-1}) than H-bonded ones. In the case of antisymmetric H-bonded NH stretches, we also found a clear dependency of the frequency on the H-bond length (i.e., the N−H···N distance), with the NH involved in long H-bonds (above 2.24 Å) showing a higher frequency (20−40 cm^{-1}) than short H-bonded ones. According to our optimized structures, these long H-bonds are present when an ammonia molecule acts as double donor or double acceptor, a feature shown only by our cage-like and "tail" structures. Thus, the presence of the vibrational signature for these long H-bonds could be used as an indication of the transition from a planar ring-like structure to a 3D one or for the presence of "docked" ammonia molecules outside a cycle.

An energetic ordering similar to the one found for antisymmetric stretches is also found for the symmetric vibrations. Once again, low-frequency values are associated with atoms involved in short N−H···N bonds, whereas high values are representative of symmetric stretches involving atoms implicated in long N−H···N bonds for a particular isomer.

Discussion and Conclusions

In this work, a high level ab initio study of the structure and energetics for the ammonia clusters $(NH_3)_n$ ($n = 2-5$) has been presented. The calculations, carried out using MP2 and the family of basis sets aug-cc-pVXZ (X = D, T, Q), suggest that the tetramer and the pentamer have several almost degenerate isomers and hint at the possibility of a smooth energy landscape. This picture is not modified by the introduction of zero-point motion corrections, at least within the framework of the harmonic approximation. The latter, as shown previously for the neutral water clusters, may not be sufficient for a satisfactory treatment of the effects of quantum motion in "floppy" aggregates, so that more accurate quantum treatments appear to be required. The presence of small energy differences between isomers also suggest the possibility of their fast interconversion, at least between the most stable species for each cluster size. This, however, needs to be properly investigated extracting conversion pathways from molecular dynamics simulations and localizing the relevant transition states with ab initio techniques.

The isomeric structures obtained in this work are in good agreement with the general suggestion derived from experiments that clusters containg more than 2 ammonia molecules should have small dipole moments. The only exception to this rule is represented by species (trimer asym, tetramer and pentamer tails) lying 3−4 kcal/mol above the most stable structure. The latter may be formed during the stepwise addition of NH_3 to smaller clusters in He droplet and remain trapped in a local minimum due the ultracold condition of formation.

Although in reasonable agreement with experimental results, our theoretical calculations tend to suggest lower binding energies and evaporation energies than experimental data. At the present stage, it is not possible to indicate clearly the origin of these small discrepancies, the lack of higher order excitation in our ab initio method being the most probable cause. However, previous works on the ammonia dimer presented evidence suggesting that triple and quadruple excitations, as included in the MP4 method, do not play an important role in defining the electronic binding energy for the cluster. In this situation, perhaps, an experimental reinvestigation of binding energies seems warranted.

Comparing our ab initio results for the interaction energy with model potential ones highlighted important shortcomings in the description of the energetics for small ammonia clusters provided by the latter. In particular, literature model potentials have the tendency to underestimate binding energy, despite their good performance in predicting the structure of local minima on the potential energy surface. We interpret this finding as a clear indication that better models are needed, perhaps also including an explicit treatment of the molecular polarization in the cluster environment as suggested by the improved results in ref 34. In this respect, the many-body decomposition of the interaction energy provided in Table 3 seems to imply that an adequate treatment of three-body effects is necessary, and that one may dispense with the inclusion of higher order effects, at least for relatively small clusters. Work along this lines is already underway in our laboratory.

A natural comparison to the systems studied in this work is provided by the neutral water clusters. The latter presents larger binding energies and stronger hydrogen bond than ammonia clusters due to stronger polarization (and acidic nature) of the OH bonds. Despite these fundamental differences in molecular shape and electronic structure, the energy differences between isomers in these two families of clusters are quite similar (see, for instance, ref 41 for data on the water clusters), so that one may expect the ammonia clusters to present a behavior somewhat similar to the one of water aggregates. In particular, we would expect to find different isomers formed when using different conditions for cluster formation.

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Supporting Information Available: Optimized geometries, total and CP-corrected MP2 energies, and vibrational frequencies for the optimized clusters discussed in the text; complete reference for ref 27. This material is available free of charge via the Internet at http://pubs.acs.org.

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