

# Structure of ammonia clusters from $n=3$ to 18

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Optimized structures and bonding energies have been calculated for ammonia clusters from  $n=3$  to  $n=18$  using a pairwise additive model potential. The trimer and tetramer are stable cyclic configurations. From the pentamer onward the structures are three dimensional with an increasing tendency to amorphous behavior. The exceptions are the heptamer with a  $C_s$  axis, the hexadecamer with a central atom, and the very stable and completely symmetric dodecamer with the  $D_{6h}$  point group. Here each ammonia molecule is bound by two covalent and two hydrogen bonds. In general, the coordination number increases from 2.0 for the rings over 4.0 for  $n=12$  to 4.2 for  $n=18$ . The structures agree where available with previously obtained results for a more elaborate potential.

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## I. INTRODUCTION

Ammonia is one of the most important solvent molecules that is able to form hydrogen bonded networks. In contrast to the behavior of water or methanol, the smallest entity, the dimer, does not develop a linear hydrogen bond. A first indication of this behavior was discovered by the group of Klemperer, who interpreted their results of a microwave experiment as evidence for a cyclic dimer structure.<sup>1</sup> After ten years of intensive research and many other experimental results, Olthof *et al.*<sup>2,3</sup> proposed a model potential that was partly fit to the data and could explain all of them. The dimer turned out to perform a rather floppy motion over a very low barrier between two equivalent minimum positions with the proton donor and acceptor interchanged. The behavior of the solid phase of these three hydrogen bonded molecules is again different. The methanol crystal is built of hydrogen bonded chains of molecules with coordination number two and with adjacent chains pointing in opposite directions. Ice forms the famous fourfold coordinated hexagonal lattice with a tetrahedral arrangement of the two hydrogen and the two covalent bonds. Ammonia condenses into a cubic lattice with six nearest neighbors, three of which are hydrogen and three are covalently bound.<sup>4</sup> Now it is extremely interesting to explore the structures of the larger clusters and compare them with those of water and methanol. There are only a few calculations available, essentially for small clusters. Greer *et al.* calculated the structure of ammonia clusters from dimer to heptamer<sup>5</sup> using a pairwise-additive potential obtained by the coupled pair functional method in an *ab initio* configuration interaction scheme.<sup>6</sup> Dykstra and Andrews used a molecular mechanics approach to determine structures from dimer to tetramer.<sup>7</sup> The trimer was extensively studied by Szczyński *et al.* using the Møller–Plesset perturbation theory.<sup>8</sup> Here also the question of the role of three-body forces was addressed.

In this contribution we present calculations of the structure of ammonia clusters from  $n=3$ –18. In order to cover this size range, we use a relatively simple model potential,<sup>9</sup> which has recently proved to reproduce reasonably well the properties of the liquid.<sup>10</sup> For small clusters sizes, the calculated structures agree well with those available in the literature, which are obtained by much more sophisticated and reliable *ab initio* methods.<sup>8,5</sup> Based on these results, in a subsequent paper we will calculate the vibrational frequencies, which can directly be used for comparison with available experimental data<sup>11</sup> and as guideline for future experiments.

The paper is organized as follows. In Sec. II we briefly describe the potential model. In Sec. III we report the results of the structural properties of the ammonia clusters and compare them with those obtained for water and methanol. In Sec. IV we conclude with a discussion of our results.

## II. POTENTIAL MODEL

The  $\text{NH}_3$ – $\text{NH}_3$  intermolecular potential used in our structure calculation is the simple site–site model of Impey and Klein.<sup>9</sup> Therein, the  $\text{NH}_3$  monomer is considered rigid and its geometry is defined by the nitrogen-hydrogen distance,  $r_{\text{NH}}=1.0124 \text{ \AA}$ , and the angle between the N–H bonds and the  $C_3$  axis of the molecule (pointing away from the H atoms),  $\theta_{\text{HNC}_3}=112.13^\circ$ .

This potential features electrostatic and Lennard-Jones interactions. The electrostatic interaction is modeled by four interaction sites on each molecule: three sites with partial charge  $q_{\text{H}}=0.462e$  located at the H atoms, and a site with a charge  $-3q_{\text{H}}$  located on the  $C_3$  axis,  $0.156 \text{ \AA}$  from the N atom toward the H atoms. Lennard-Jones interactions are modeled only between the N atoms by a 12-6 potential with parameters  $\sigma=3.4 \text{ \AA}$  and  $\epsilon/k_B=140 \text{ K}$ . The described potential was extensively used by Diraison *et al.*<sup>10</sup> in molecular dynamics simulations of liquid ammonia and reproduces the x-ray and neutron diffraction data satisfactorily. We assume here that this effective two-body potential is pairwise additive and describes correctly the clusters. This question was

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TABLE I. Calculated binding energies (in kJ/mol) for  $(\text{NH}_3)_n$  clusters. For each cluster size  $n=2-18$ , the three lowest isomers are being considered.  $E^*$  are the results for Greer *et al.* (Ref. 5).

| $n$ | $E_a$   | $E_b$   | $E_c$   | $E^*$   |
|-----|---------|---------|---------|---------|
| 2   | -11.65  | -11.53  | -10.67  | -12.93  |
| 3   | -34.57  | -25.14  | -24.01  | -35.31  |
| 4   | -52.85  | -52.77  | -52.67  | -54.80  |
| 5   | -69.99  | -69.41  | -69.40  | -70.82  |
| 6   | -95.03  | -92.12  | -91.94  | -95.13  |
| 7   | -118.16 | -116.54 | -116.06 | -119.45 |
| 8   | -142.84 | -142.77 | -140.64 |         |
| 9   | -165.25 | -164.70 | -163.96 |         |
| 10  | -190.84 | -189.25 | -187.31 |         |
| 11  | -214.42 | -212.82 | -212.01 |         |
| 12  | -244.52 | -237.03 | -237.02 |         |
| 13  | -263.59 | -262.11 | -261.35 |         |
| 14  | -289.09 | -288.32 | -288.16 |         |
| 15  | -313.60 | -312.67 | -312.54 |         |
| 16  | -341.18 | -341.01 | -339.45 |         |
| 17  | -366.13 | -365.86 | -364.41 |         |
| 18  | -392.48 | -391.00 | -389.98 |         |

addressed in detail in Ref. 8, where the contributions of non-additive effects were studied for the ammonia trimer using *ab initio* methods. Although the contribution of three-body forces is 9.6% of the total energy, the minimum geometry was not changed. This gives us some confidence that our results will be a realistic description of the larger clusters as well.

### III. RESULTS AND DISCUSSION

The equilibrium structure calculations basically imply minimizing the total interaction energy of the cluster, considered as being composed of rigid molecules. To determine local minima on the potential energy surface, the positions and orientations of all molecules (specified by the Cartesian coordinates of their mass centers and by Euler angles) are optimized without constraints, starting from random initial configurations. Typically, several thousands of minimizations are necessary to yield the global minimum for a particular cluster size and we have performed roughly as many thousands of minimizations as given by the cluster size.

The results of our calculations are summarized in Table I for the energetics and in Figs. 1–4 for the structures. Table I contains the binding energies of the three lowest lying isomers for each cluster size. They compare well with those obtained by Greer *et al.*,<sup>5</sup> which are available for  $n=3-7$  and that are also presented in Table I. The calculations are based on a fit to a very reliable two-body potential, resulted from an *ab initio* configuration calculation by means of the coupled pair method.<sup>6</sup> While the bonding energy of the dimer,  $E = -11.65$  kJ/mol, is relatively close to the values obtained in the *ab initio* calculation of Sagarik *et al.* ( $-12.96$  kJ/mol)<sup>6</sup> and by the best fit model potential of Olthof *et al.* ( $-12.19$  kJ/mol),<sup>2</sup> the geometry, displayed in Fig. 1, is too close to a linear hydrogen bond as compared to the optimized results of Ref. 2. Here the angles formed by the  $C_3$  axes of the molecules and the positive direction of the N–N axis are  $\theta_1 = 40^\circ$  and  $\theta_2 = 95^\circ$ , while the present calculation

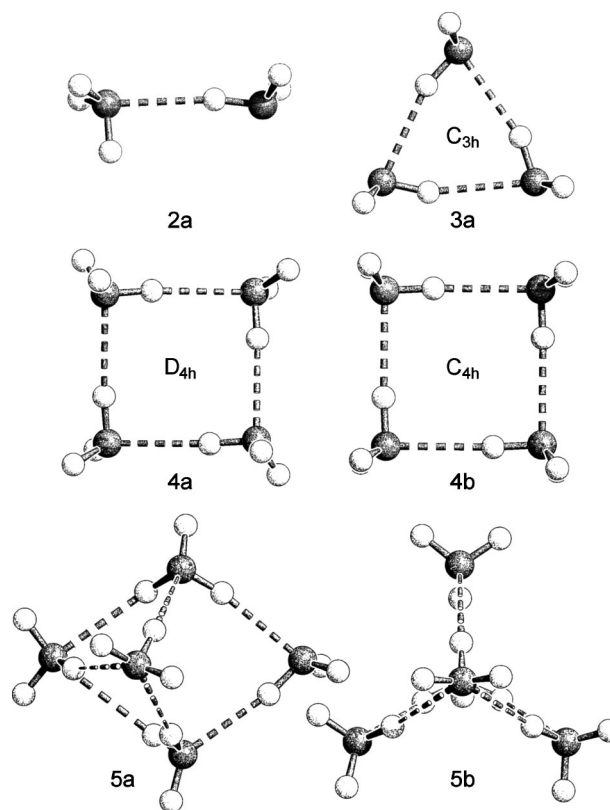


FIG. 1. The energetically most stable ammonia dimer and trimer structures and the two energetically most stable tetramer and pentamer configurations.

gives  $\theta_1 = 27^\circ$  and  $\theta_2 = 74^\circ$ . The corresponding distances between the N atoms are  $R_{\text{NN}} = 3.255 \text{ \AA}$  as compared to  $3.330 \text{ \AA}$  (Sagarik *et al.*)<sup>6</sup> and  $3.354 \text{ \AA}$  (Olthof *et al.*)<sup>2</sup>.

The trimer is a planar ring with three hydrogen bonds, in which each molecule acts both as a proton donor and acceptor. It obeys the  $C_{3h}$  point group. The N–N distance is  $R_{\text{NN}} = 3.255 \text{ \AA}$  in fair agreement with the values of Szcześniak *et al.*<sup>8</sup> ( $3.30 \text{ \AA}$ ) and of Greer *et al.*<sup>5</sup> ( $3.33 \text{ \AA}$ ), who evidenced the same symmetry of the trimer. The angle between the H–N bond involved in the bonding of two molecules and the corresponding N–N direction is  $\theta_{\text{HNN}} = 12.3^\circ$ . This is again in close agreement with the *ab initio* calculations of Ref. 8 ( $\theta_{\text{HNN}} = 15^\circ$ ). Regarding the energy, we find  $E = -34.57$  kJ/mol, as compared to  $-35.58$  kJ/mol (Ref. 8) and  $-35.31$  kJ/mol (Ref. 5).

The three lowest configurations found for the tetramer have planar or nearly planar cyclic structures, similar to the one of the trimer. In agreement with the calculations of Greer *et al.*<sup>5</sup> and in slight disagreement with those of Ref. 12, the lowest-energy configuration does not have planar  $C_{4h}$  symmetry, but nearly planar  $D_{4h}$  symmetry (configuration 4a of Fig. 1, with the mass centers of the molecules displaced by about  $0.4 \text{ \AA}$  alternatively on one and the other side of the symmetry plane). The N–N distance  $R_{\text{NN}} = 3.226 \text{ \AA}$  is of the same order as for the dimer and the trimer and close to the value obtained by Greer *et al.* ( $3.30 \text{ \AA}$ ), while the angle between the H–N bond involved in the bonding of two molecules and the corresponding N–N direction,  $\theta_{\text{HNN}} = 3.0^\circ$ , is smaller than for the trimer. The bonding energy is  $E = -52.85$  kJ/mol and, as can be seen from Table I, the energy

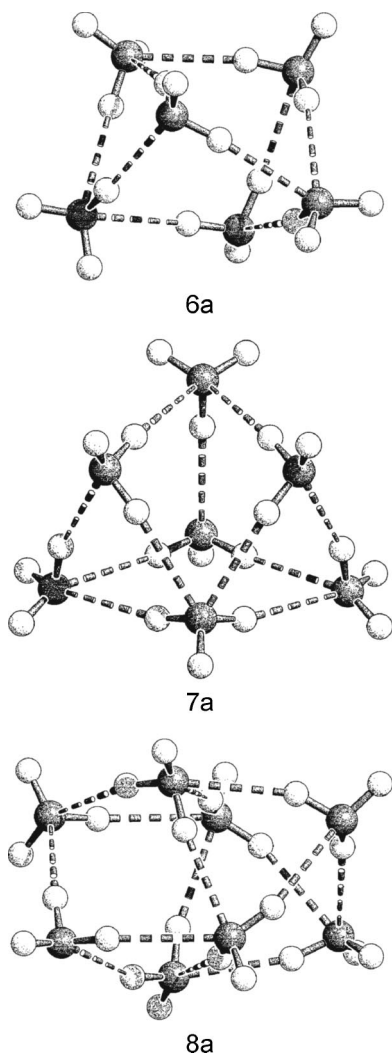


FIG. 2. The energetically most stable ammonia hexamer, heptamer, and octamer configurations.

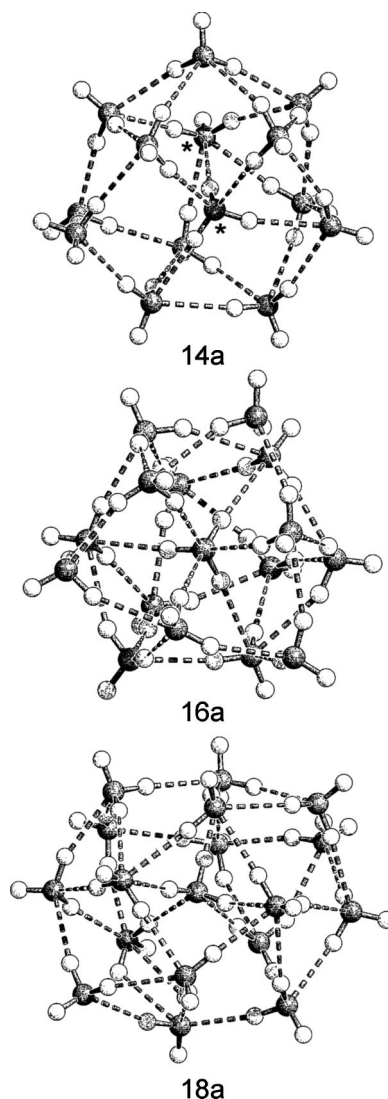


FIG. 4. The energetically most stable ammonia cluster for  $n=14$ , 16, and 18. The two central molecules for  $n=14$  are marked by asterisks.

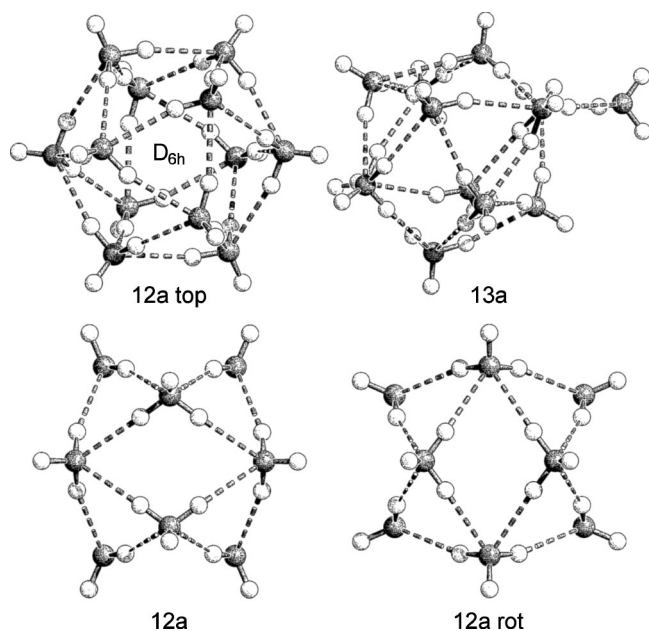


FIG. 3. The energetically most stable ammonia clusters for  $n=12$  in three different views and  $n=13$ .

differences between the first three configurations is just of the order of 0.1 kJ/mol. The second lowest isomer of the tetramer has perfectly planar  $C_{4h}$  symmetry, with  $R_{NN} = 3.227 \text{ \AA}$ , very close to the value for the lowest tetramer, but with reduced  $\theta_{HNN} = 2.1^\circ$ .

The results for the trimer and tetramer are in nice qualitative agreement with the conclusions of Pertsch and Huisken.<sup>11</sup> By comparing their measurement of the umbrella mode of size-selected ammonia trimers and tetramers in a predissociation experiment with the results of Snels *et al.*,<sup>13</sup> who did not observe dissociation of these clusters with their low-power laser, Pertsch and Huisken concluded that more than one infrared photon of 12.5 kJ/mol is necessary for the dissociation to take place and that the clusters are probably cyclic, such that two bonds have to be broken. In a later experiment by Heijmen *et al.*,<sup>14</sup> the fact that two photons are necessary for the dissociation was confirmed by using two lasers for the excitation. Our results for the dissociation energies are in line with these conclusions. While for the dimer with 11.5 kJ/mol one photon is indeed sufficient, the corresponding energies for the trimer and tetramer are 22.9 and

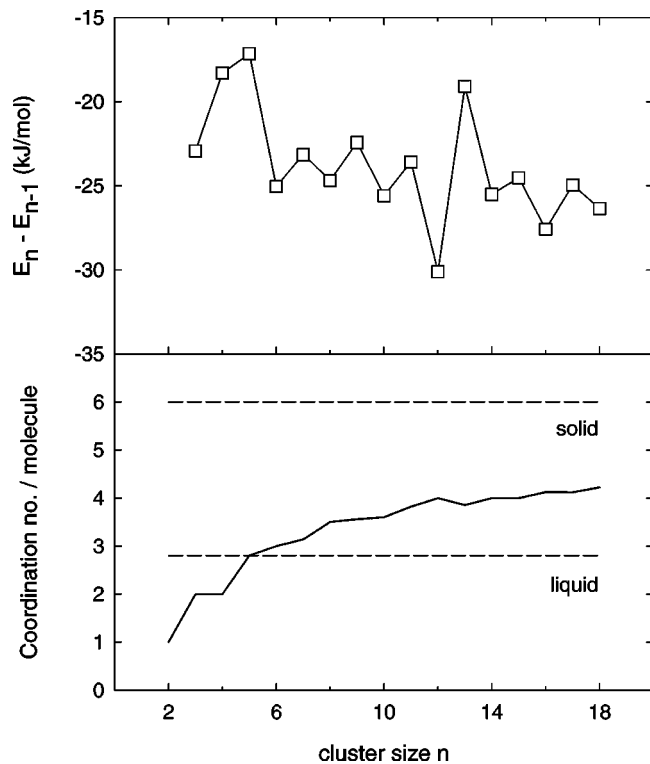


FIG. 5. Incremental binding energies (upper panel) and coordination number (lower panel) as a function of cluster size.

18.3 kJ/mol, respectively, which cannot be reached by one photon of the CO<sub>2</sub> laser. Here the incremental bonding energies  $\Delta E = E_n - E_{n-1}$  have to be used as lower bounds. They are plotted in the upper panel of Fig. 5 and show a relative minimum for the trimer.

The pentamer is the first cluster with a three-dimensional structure and four threefold coordinated molecules. The coordination properties of the component molecules for the various cluster sizes may be extracted from Tables II and III. Our most stable configuration has no well-defined symmetry, in complete agreement with the results of Ref. 5 and opposed to Ref. 12, where it is predicted to have  $C_{5h}$  symmetry. The N–N distances resulted from our calculations cover a range between 3.211 and 5.237 Å. The loss of symmetry and the distribution of the N–H distances as compared to its predecessors is also reflected by the much larger number of predicted IR spectral lines, as will be discussed in the second paper. The second lowest-energy pentamer isomer has a

quite similar binding energy, but a completely different geometrical arrangement as is also shown in Fig. 1.

Analogously to the pentamer, the hexamer has no symmetry but is stronger bound, as indicated by the much larger incremental energy  $\Delta E$  and the narrower distribution of N–H distances (see Table II, Figs. 2 and 5). This trend continues from size  $n=7$  up to  $n=11$ . The involved clusters exhibit a sort of amorphous behavior with a broad distribution of N–H distances. The number of fourfold coordinated molecules increases from one for the heptamer to nine for the undecamer ( $n=11$ ); see Fig. 2 and Tables II and III. The heptamer has  $C_s$  symmetry, again in complete agreement with the findings of Greer *et al.*<sup>5</sup>

One of the most remarkable of the investigated ammonia clusters is in many respects the lowest-energy dodecamer ( $n=12$ ), which is, in fact, the first cluster to show a regular cage structure. It is shown in Fig. 3 under three different angles, such that all molecules and bonds are visible. The top view emphasizes its  $D_{6h}$  symmetry, with a  $C_3$  axis and a median reflection plane coinciding with the plane of the figure. Under this angle, the dodecamer appears to be composed of four reciprocally rotated triangular rings perpendicular to the  $C_3$  axis and disposed symmetrically about the midplane. However, the two inner triangles are not formed by nearest neighbors.

The two lower views of the dodecamer in Fig. 3 are rotated with respect to one another by 90° and the upper view is, in fact, taken perpendicularly to one of the formed triangles. The structure is thus seen to have, in addition to the already mentioned symmetry elements, three reciprocally orthogonal  $C_2$  axes and as many reciprocally orthogonal reflection planes. All bond lengths are equal to  $R_{NN} = 3.296$  Å, very close to the solid state value of 3.3 Å.

The dodecamer can be actually regarded as an intermediate stage toward the solid state ammonia. In the solid state the lone pair of any nitrogen is bonded to the three nearest neighbors, while the corresponding three H atoms are, in turn, bonded to the N atoms of three nearest neighboring molecules. Thus, each molecule is hydrogen bonded to six nearest neighbors. In the obtained dodecamer, the lone pair of any nitrogen is bonded to only two nearest neighbors, while only two of its H atoms are bonded to neighboring N atoms. Thus, each molecule is fourfold coordinated. The fact that each molecule has one free H–N bond and two H–N bonds involved in the cohesion of the dodecamer, such that all H–N bonds can be grouped in two equivalence classes,

TABLE II. Character of the N–H bonds and coordination properties of ammonia clusters. Columns 2–8 give the number of bonds with the indicated properties.

| Size | DA  | DDA | DAA | 3-fold | 4-fold | Total/2 | Per molecule | dist./Å     | Comment   |
|------|-----|-----|-----|--------|--------|---------|--------------|-------------|-----------|
| 2    | 1   | ... | ... | ...    | ...    | 1       | 1.00         | 2.25        | floppy    |
| 3    | 3   | ... | ... | ...    | ...    | 3       | 2.00         | 2.276       | cyclic    |
| 4    | 4   | ... | ... | ...    | ...    | 4       | 2.00         | 2.216       | cyclic    |
| 5a   | 1   | 2   | 2   | 4      | ...    | 7       | 2.80         | 2.223–2.618 | cage      |
| 5b   | 3   | 1   | 1   | 2      | ...    | 6       | 2.40         | 2.198–2.301 | bipyramid |
| 6    | ... | 3   | 3   | 6      | ...    | 9       | 3.00         | 2.230–2.413 | cage      |
| 7    | ... | 3   | 3   | 6      | 1      | 11      | 3.14         | 2.212–2.387 | cage      |
| 8    | ... | 2   | 2   | 4      | 4      | 14      | 3.50         | 2.262–2.359 | amorphous |

TABLE III. Character of the N–H bonds and coordination properties in the ammonia clusters. Columns 2–8 give the number of bonds with the indicated properties.

| Size | 2-fold | 3-fold | 4-fold | 5-fold | 6-fold | Total/2 | Per molecule | dist./Å     | Comment      |
|------|--------|--------|--------|--------|--------|---------|--------------|-------------|--------------|
| 9    | ...    | 4      | 5      | ...    | ...    | 16      | 3.56         | 2.192–2.574 | amorphous    |
| 10   | ...    | 4      | 6      | ...    | ...    | 18      | 3.60         | 2.260–2.403 | amorphous    |
| 11   | ...    | 2      | 9      | ...    | ...    | 21      | 3.82         | 2.270–2.556 | amorphous    |
| 12   | ...    | 0      | 12     | ...    | ...    | 24      | 4.00         | 2.310       | cage         |
| 13   | 1      | 0      | 12     | ...    | ...    | 25      | 3.85         | 2.260–2.356 | (12+1) cage  |
| 14   | ...    | 2      | 10     | 2      | ...    | 28      | 4.00         | 2.175–2.673 | central axis |
| 15   | ...    | 4      | 8      | 2      | 1      | 30      | 4.00         | 2.220–2.479 | central mol  |
| 16   | ...    | 3      | 9      | 3      | 1      | 33      | 4.13         | 2.250–2.481 | central mol  |
| 17   | ...    | 3      | 9      | 5      | ...    | 35      | 4.12         | 2.157–2.677 | amorphous    |
| 18   | ...    | 3      | 8      | 7      | ...    | 38      | 4.22         | 2.170–2.690 | amorphous    |

has a decisive impact on the (very simple) structure of the calculated IR spectrum, as will be argued in the forthcoming paper.

The next larger cluster, with  $n = 13$ , can be viewed as the very stable dodecamer with one molecule attached to it (see Fig. 3). The higher sizes, from  $n = 14$ –18, are characterized by amorphous arrangements of molecules with different coordination numbers, ranging from three to six with a maximum at four. Three of these structures are presented in Fig. 4. The cluster  $n = 14$  shows the first two fivefold coordinated molecules, which define the central axis marked by asterisks. The size  $n = 16$  has a central atom, which is sixfold coordinated and thus a bit more stable than the neighboring ones. The cluster  $n = 18$  is simply amorphous, without any central molecule.

The general behavior discussed so far is also reflected in the incremental energy differences and the average coordination number of the investigated clusters, which are shown in Fig. 5. The most stable energetic configurations are the trimer and the dodecamer. Not surprisingly, these are indeed very symmetric structures. In contrast, the pentamer and the 13-mer have the lowest relative binding energies, both containing a molecule attached to an already very stable structure, the tetramer ring and the dodecamer, respectively. The rest of the clusters exhibit a similar behavior with a slight even–odd alternation and a somewhat larger stability for  $n = 16$ .

The average coordination number increases from 2 for the trimer and tetramer, over 3 for the hexamer, to 4 for the decamer. For the larger clusters it then slowly increases to 4.2. This is quite far from the value 6 for the solid (certainly a consequence of the many surface molecules in this size range), but still larger than the value for the liquid yielded by simulations.<sup>10</sup>

If we compare the transition from cyclic structures to three-dimensional cages for different hydrogen bonded systems, the key parameter turns out to be the number of available bonds. For methanol with one hydrogen bond per molecule, the ring structure pertains to the nonamer.<sup>15</sup> For water with two hydrogen bonds, the transition occurs between the pentamer and the hexamer.<sup>16</sup> For ammonia with three hydro-

gen bonds, it already takes place between the tetramer and the pentamer. For hydrazine with four possible candidates for hydrogen bonds, the first three-dimensional structure is already found for the tetramer.<sup>17</sup>

In conclusion, we note that, aside from the quite symmetric cyclic trimer and tetramer, the most remarkable structure is the dodecamer with  $D_{6h}$  symmetry. All 12 molecules are in an equivalent position with the same N–N distance and two hydrogen and two covalent bonds. The coordination number increases from  $n = 3$  to  $n = 18$  from 2.0 to 4.2. It is larger than that of the liquid but does not reach the value 6.0 of the solid.

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