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Excess Electrons Bound to Small Ammonia Clusters

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Dipole-bound anions of small water clusters $(H_2O)_N^-$ ($N \geq 2$) are well-known from experiment and theory. In contrast, the smallest ammonia cluster anion detected so far is the 13-mer $(NH_3)_{13}^-$. Here dipole-bound states of small ammonia clusters $(NH_3)_N^-$ ($N = 2, 3, 4$) are investigated using coupled-cluster ab initio methods. The trimer is found to be the smallest ammonia cluster able to form a dipole bound state, and its vertical detachment energy is predicted to be 27 meV, somewhat smaller than that of the water dimer. For the ammonia tetramer dipole-bound states with triple-acceptor monmers are identified akin to the well-studied double-acceptor binding motif of water cluster anions. Moreover, a $(NH_3)_6^-$ hexamer that has been considered as a model for a cavity-bound state is examined. Ab initio results for this system challenge the notion that an electron localized in an ammonia cavity can be thought of as a delocalized radical anion.

I. Introduction

Single ammonia or water molecules cannot bind an excess electron, since both have neither empty low-lying valence orbitals nor dipole moments sufficient for forming dipole-bound states.[1−3] Nevertheless, clusters of ammonia or water molecules can bind excess electrons, and today there is a wealth of information about these species including mass spectrometric intensities [4−7] and photoelectron spectra,[8−12] and for many water clusters even vibrational spectra have been observed (e.g., refs 13−15).

One of the remarkable differences between ammonia and water cluster anions is that water clusters as small as as the dimer $(H_2O)_2^-$ are readily observed while small ammonia cluster anions are far less abundant. In the early mass spectrometric experiments the smallest $(NH_3)_N^-$ clusters detected were in the $N \approx 35$ range,[6,7] a finding in line with simulations that suggested that only ammonia clusters larger than $N \approx 32$ could bind excess electrons with a substantial binding energy.[16,17] Yet in recent experiments,[12] which employed an ion source with more efficient cooling, $(NH_3)_N^-$ clusters down to the 13-mer where detected. Photoelectron spectra were measured for $N = 20$, 30, 40, 50, and 60, and while the 50-mer and 60-mer spectra show only one broad peak, the spectra of the smaller clusters suggest the presence of at least two isomers similar to their water cluster analogues.[10] In particular, the photoelectron spectrum of the 20-mer $(NH_3)_{20}^-$ shows peaks close to 0.35 and 0.6 eV, respectively, clearly demonstrating that cluster anions in this size range do still have substantial electron binding energies.

On the water side, the observation of very small water cluster anions prompted an enormous amount of ongoing theoretical work (see ref 2 for a review and, e.g., refs 15 and ,18−22 for recent studies). All small water clusters anions (at least up to the 15-mer) bind their excess electron in a dipole-bound (surface) state;[19,23] that is, the water monomers form a cluster with a sufficiently large dipole moment ($> \approx 3$ D) and the excess electron occupies a very diffuse orbital localized in the direction of the dipole vector off the nuclear framework. Owing to the large correlation effects typical for dipole-bound states,[2,20,21,24−26] reliable ab initio calculations require large basis sets and methods that include electron correlation beyond second-order perturbation theory making the investigation of clusters as small as $(H_2O)_7^-$ a formidable challenge. Yet, ab initio studies have elucidated local electron binding motifs of small clusters that have recently been shown to persist in much larger cluster anions,[19,27] and ab initio results provide guidance in the development of reliable atomistic models (e.g., refs 28 and 29) that enabled the study of larger species and finite temperature effects.[19,22,23]

In contrast, until recently only large ammonia cluster anions had been observed, and most theoretical work focused on modeling extended systems (ref. 30 gives a detailed account of this field). There are only three ab initio studies on small clusterlike systems,[30−32] and these studies focus on models for the ammoniated electron. Accordingly the considered clusters are custom-built arrangements of ammonia monomers forming a cavity, and the basis sets are chosen so as to confine the electron within the cavity. Moreover, in none of these studies higher-order electron correlation effects are considered.

Here electron binding properties of small ammonia cluster anions $(NH_3)_N^-$ ($N = 2, 3, 4$) and a hexamer $(NH_3)_6^-$ cavity model are investigated. Similar to water clusters, the only way in which small ammonia clusters might be able to bind an excess electron is by forming dipole-bound states. Thus, the question of whether small ammonia cluster anions exist comes down to whether ammonia clusters do form isomers with sufficiently large dipole moments. Different isomers of the dimer, trimer, and tetramer are considered, and the electron binding energies of these isomers are computed using high-level ab initio methods. Also similar to water clusters, the most stable neutral ammonia clusters have low dipole moments. With very few exceptions the attached electron stabilizes high-dipole isomers of water clusters substantially, and the second question to be considered is how high-dipole ammonia cluster isomers compare energetically with the most stable neutral clusters. Finally, one of the model cavity clusters is investigated. For this system the first question considered is whether this arrangement can actually bind an electron, and the second question pertains to the spatial

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distribution of the excess electron, in particular to how much electron density is localized close to the nitrogen atoms.

II. Computational Details

Computational methods for investigating electron attachment to ammonia cluster need to fulfill two requirements. In the first place, ammonia−ammonia interactions (H-bonds and dispersion) need to be described, and in the second place, electron attachment to a closed-shell system into nonvalence orbitals needs to be described. The first requirement is satisfied using second-order Møller−Plesset perturbation theory (MP2) and basis sets such as the augmented correlation-consistent double-ζ set (aug-cc-pVDZ) or better. To address the second requirement, additional basis functions with exponents far smaller than those of standard diffuse functions are needed, and in many cases electron correlation beyond second order is crucial to compute reliable electron binding energies.[2,25,26]

Here the aug-cc-pVDZ set is used for geometry optimizations of neutral clusters, and for anion clusters additional sets of diffuse functions are placed on one nitrogen atom close to the positive end of the molecular dipole. The exponents of the additional functions are chosen as an even-tempered series starting from the smallest exponent in the valence basis set. For s- and p-type functions, the scaling factor is $10^{1/2}$, for d-type functions, it is 4. In the next section convergence of this basis set with respect to adding diffuse functions is described in detail, and convergence with respect to the valence basis set is tested using the corresponding tripe-ζ set (aug-cc-pVTZ). Moreover, in section 3.3 the 6−31++G* and 6−31++G** split valence basis sets[33] are employed for comparison to earlier work. To compute the electron binding energy, several methods were used. First, the electron bonding energy was computed indirectly as the difference between the total energies of neutral and anion using so-called Δ-methods. The methods employed are self-consistent field (SCF), MP2, coupled-cluster with single and double substitutions (CCSD), and CCSD with noniterative triple substitutions (CCSD(T)). Second, the electron binding energy was computed directly, using Koopmans's theorem (KT) approximation, a Dyson equation based second-order Green's function method (ADC(2)),[34] and the equation-of-motion coupled-cluster (EOM-CCSD) method.[35] Core electrons were not frozen in any of the calculations.

Almost all calculations were performed with the Mainz−Austin−Budapest version of the Aces II program,[36] for the ADC(2) calculations a home-written code was used that requires the transformed integrals from the MOLCAS package version 6.[37]

III. Ab Initio Results

The smallest ammonia cluster, the dimer $(NH_3)_2$, is highly unlikely to bind an electron. In the first place, the lowest energy structure of the neutral, which shows a single hydrogen bond, has only a dipole moment of 2.6 D (CCSD(T)/aug-cc-pVDZ), and even if the two monomers were perfectly aligned, the resulting dipole would not significantly exceed 3 D. Thus, the fixed-nuclei electron binding energy is expected to be very small ($<$1 meV). In the second place, the ammonia dimer exhibits a very small barrier for a H-bond donor−acceptor exchange motion inverting its dipole moment.[38,39] Thus, nuclear motion, either in the form of a donor−acceptor exchange or in the form of an overall rotation, is expected to rapidly shake-off any dipole-bound electron.[40]

A. Trimer. The water trimer with the largest electron binding energy is a chain isomer with the central water monomer accepting two H-bonds. This double-acceptor motif is in fact the prominent motif present in the majority of small observed water cluster anions.[13,27] The analogue $(NH_3)_3^-$ ammonia isomer is a minimum on the potential surface of the neutral cluster,[41] yet in stark contrast to the water cluster, the dipole moment of the ammonia trimer is only about 1 D as the dipoles of the donating monomers counteract the dipole of the accepting ammonia molecule. Thus the double-acceptor ammonia trimer cannot bind an excess electron.

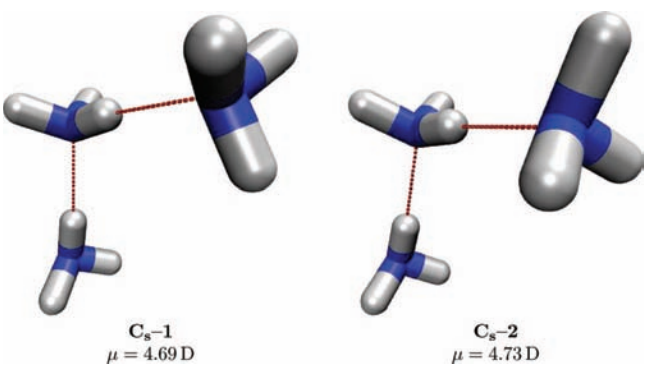
C_s−1 $\mu = 4.69$ D
C_s−2 $\mu = 4.73$ D

Figure 1. Structures of two ammonia trimer anion $(NH_3)_3^-$ conformations and dipole moments of the associated neutral frameworks. The **C_s−1** conformer in the left-hand panel is a minimum, the **C_s−2** conformer in the right-hand panel is a transition state. The clusters have been optimized using the MP2 method and the aug-cc-pVDZ+(5s5p) basis set, and the dipole moments have been computed from the MP2 density of the neutrals.

There is however another $(NH_3)_3^-$ chain isomer that consists of a H-bond donor monomer at the tail, a donor−acceptor monomer in the central position, and an H-bond acceptor monomer at the head; two conformations of this trimer anion are shown in Figure 1. **C_s−1** is a minimum on the anion's potential energy surface and **C_s−2** is a transition state for rotation of the head ammonia monomer. The corresponding stationary points on the potential surface of the neutral are higher-order transition states, and starting geometry optimization of the neutral at the anion geometry without symmetry constraints leads to the zero-dipole C_{3h} symmetrical ring structure that represents the global minimum of the neutral.[39]

The chain trimer **C_s−1** is the smallest ammonia cluster with a sizable dipole moment, and in the following its vertical electron detachment energy (VDE) is computed with different methods to investigate basis set and electron correlation influence in this fundamental system. It turns out that **C_s−1** forms a typical dipole-bound state that follows essentially the same trends as dipole-bound states of small water cluster anions.[2] The distribution of the excess electron is very diffuse (Figure 2), and thus the valence basis set needs to be augmented with functions having much smaller exponents than standard diffuse functions (cf. ref 26). Starting with the aug-cc-pVDZ basis set and systematically adding sp-sets of increasingly diffuse functions (exponent ratios of $10^{1/2}$), see section II) centered on the N atom of the head ammonia monomer shows that five sp sets (smallest exponents of 0.000194) are needed for full convergence and that four sp sets should be sufficient for most purposes. Additional diffuse d-type functions (exponent ratio of 4) increase the computed VDE by a few percent, but the absolute changes are less than 1 meV.

Regarding the valence basis set, Table 1 shows that SCF and MP2 VDEs change very little when going from the double-ζ to the triple-ζ basis set, but that higher-order correlation effects converge much slower. This is a well-known general behavior, and for more strongly bound anions this effect will be much

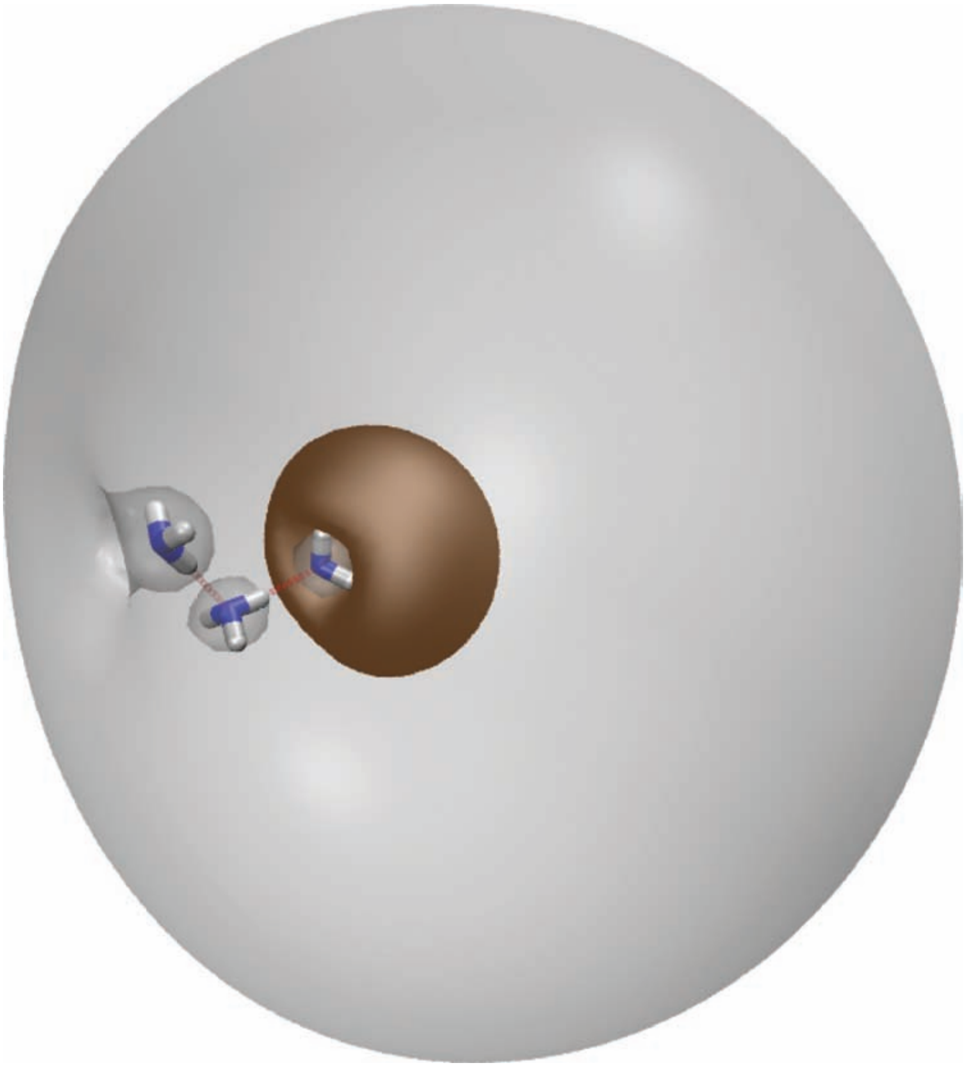

Figure 2. Distribution of the excess electron bound to the trimer $(NH_3)_3^-$, $\mathbf{C}_s\mathbf{-1}$. The density is computed from a natural orbital of the EOM-CCSD density. The two iso-surfaces shown enclose 80% (gray) and 11% (orange) of the electron density.

TABLE 1: Electron Binding Energy of the $(NH_3)_3^-$ Trimer Anion C_s−1 (cf. Figure 1) Computed Using Different Methods and Basis Sets[a]

	aug-cc-pVDZ+(5s5p2d)	aug-cc-pVTZ+(5s5p2d)
KT	6.9	6.8
Δ SCF	7.3	7.1
Δ MP2	13.3	13.3
Δ CCSD	23.7	24.3
Δ CCSD(T)	26.9	27.8
EOM-CCSD	25.9	
ADC(2)	24.2	26.4

[a] All results in meV.

stronger. In other words, while for this weakly bound anion results obtained with a double-ζ valence basis set are close to convergence, for more strongly bound anions triple-ζ or even quadruple-ζ valence sets will be need to achieve the same level of precision.

Similar to the basis set dependence, the correlation dependence also resembles that of the water dimer.[2] The electron binding energy can be analyzed in terms of contributions due to electrostatic, polarization, dispersion, and higher-order correlation interactions between excess electron and the valence electrons of the neutral cluster.[24,25] With KT, only electrostatic effects are included, and only about 25% of the electron binding energy are recovered (Table 1). Polarization effects included at the Δ SCF level contribute very little, while dispersion included at the MP2 level makes a sizable contribution of about 22%. At the Δ CCSD(T) level, presumably the most accurate method used, the VDE is predicted to be 27 meV, and thus, more than 50% of the electron binding energy is due to higher-order correlation effects. Clearly, for the ammonia trimer higher-order correlation effects are absolutely crucial. Interestingly, both the second-order Dyson approach and the EOM-CCSD method give results in fair agreement with the Δ CCSD(T) value. These two methods do not require a Hartree−Fock wave function of the anion as a starting point, and in particular the former method can be applied to far larger systems than CCSD(T).

The correlation dependence as extracted from the contributions to the electron binding energies is reflected in the distribution of the excess electron (Figure 3). The lowest unoccupied orbital from an SCF calculation for the neutral cluster is very diffuse and the iso-surface enclosing 90% of the density has a diameter in excess of 60 Å. Dispersion effects increase the binding energy, and one would expect the density associated with the excess electron to contract considerably. Of course, in a MP2 or coupled-cluster calculation, there is no single orbital describing the excess electron, but there is a many body wave function. Nevertheless, for the dipole-bound systems considered here, one can readily identify a natural orbital of

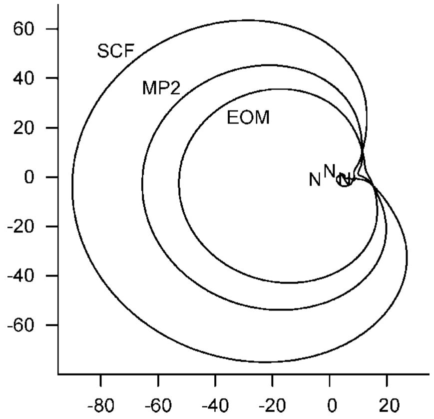

Figure 3. Correlation dependence of the excess electron distribution of trimer $(NH_3)_3^-$ $\mathbf{C}_s\mathbf{-1}$. Displayed are contours in the symmetry plane of the cluster that enclose 90% of the density associated with the excess electron as obtained from the Hartree−Fock LUMO, the natural orbitals of the MP2 density, and the natural orbital of the EOM-CCSD density. The shown MP2 and EOM-CCSD natural orbitals have occupation numbers close to 1 and can easily be distinguished from orbitals describing valence density. The contour values associated with 90% of the density are 3.2×10^{-4}, 5.0×10^{-4}, and 6.7×10^{-4} bohr$^{-1.5}$, respectively. The position of the N atoms close to the origin is indicated, and the length units are bohr.

the MP2 or of the EOM-CCSD density that describes the density associated with the excess electron and shows an occupation number very close to 1 (>0.98). These orbitals do indeed become more compact consistent with the computed electron binding energies (Figure 3). Note that in an EOM-CCSD calculation the many body wave functions is a strong mixture of several configurations, but the natural orbitals have nevertheless occupation numbers close to either 2, 1, or 0. Thus, in principle, there is a one-determinant wave function that describes the dipole-bound states well, yet it is not the Hartree−Fock determinant.

Having established the vertical electron detachment energy of the chainlike trimer anion, let us now consider its stability with respect to the most stable neutral structure. Computing the energy difference between the two neutral structures using MP2, and the VDE of the chain using CCSD(T), the neutral C_{3h} trimer $(NH_3)_3$ is 159 meV lower in energy than $\mathbf{C}_s\mathbf{-1}$, and this value is reduced to 64 meV (1.5 kcal/mol) when zero-point corrections computed at the MP2 level are taken into account. Thus, the anion is predicted to be unstable with respect to adiabatic electron loss, but the energy difference is small. To explore the possibility of dynamical electron loss more, a path connecting the geometry of $\mathbf{C}_s\mathbf{-1}$ and the C_{3h} structure of the neutral was considered that was obtained from a Newton−Raphson energy minimization of the neutral started at the geometry of anion $\mathbf{C}_s\mathbf{-1}$. Along this path the energy of the anion shows a barrier of about 15 meV (120 cm^{-1}), and shortly after crossing the barrier it becomes unstable to electron loss (VDE computed using the EOM-CCSD method). The height of this barrier does not seem large, yet the vibrational frequencies of the anion associated with this motion are considerably smaller (15 and 25 cm^{-1}), and consequently there will be several vibrational levels of the anion living behind this barrier. Thus, the ammonia trimer anion $\mathbf{C}_s\mathbf{-1}$ is predicted to be a metastable species that can decay by electron loss concerted with rearrangement into a ring structure, yet this process will most probably be suppressed by extremely unfavorable Franck−Condon factors.

In summary, the ammonia trimer anion $\mathbf{C}_s\mathbf{-1}$ is predicted to play a role comparable to that of the water dimer. It is the smallest ammonia cluster with a sizable dipole moment and therefore a sizable electron binding energy of about 28 meV. For both the water dimer and the ammonia trimer the presence of an excess electron creates a “new” minimum; that is, the excess electron stabilizes a high dipole moment configuration of the neutral framework that does not correspond to a minimum on the potential surface of the neutral. While electrostatic effects make a large contribution to the electron binding energies of both systems, higher-order electron-correlation effects contribute most. The main difference is that for the water dimer the anion and the most stable neutral structure are essentially isoenergetic, whereas for the ammonia trimer the chainlike anion is higher in energy than the ring-shaped neutral. Yet several low-lying vibrational states of $\mathbf{C}_s\mathbf{-1}$ are predicted to be long-lived.

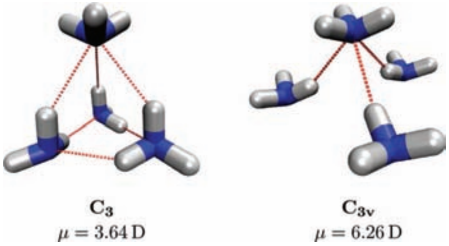

Figure 4. Structures and dipole moments of two ammonia tetramers $(NH_3)_4$. The clusters have been optimized using the MP2 method and the aug-cc-pVDZ basis, and the dipole moments have been computed from the MP2 density.

TABLE 2: Vertical Electron Affinity (VEA) of the $(NH_3)_4$ Ammonia Tetramers C_3 and C_{3v} (cf. Figure 4) Computed Using Different Methods and the aug-cc-pVDZ+(5s5p) Basis Sets[a]

	C_3		C_{3v}
	VEA	VDE	VEA
KT	1.7	2.9	31.3
Δ SCF	1.9	3.2	34.3
Δ MP2	5.7	7.9	56.9
Δ CCSD	17.2	21.3	87.4
Δ CCSD(T)	20.6	25.3	96.0

[a] For the $\mathbf{C_3}$ isomer the vertical electron detachment energy (VDE) is also shown. All results in meV.

B. Tetramer. Whereas the ammonia dimer and trimer form only isomers with small dipole moments, two isomers of the tetramer, $\mathbf{C_3}$ and $\mathbf{C_{3v}}$ shown in Figure 4, which have been identified previously,[41] should have large dipoles. These two ammonia clusters both have one monomer that accepts three H-bonds, a structural motif closely analogous with the double-acceptor monomer of many water cluster anions, and indeed, at the MP2 level large dipole moments of 3.6 D for the $\mathbf{C_3}$ isomer and 6.3 D for the $\mathbf{C_{3v}}$ are predicted. Energetically both triple-acceptor isomers are fairly high in energy lying 164 meV (3.78 kcal/mol) ($\mathbf{C_3}$) and 267 meV (6.16 kcal/mol) ($\mathbf{C_{3v}}$) above the C_{4h} symmetrical global minimum of the ammonia tetramer.[41] Thus, similar to the chain trimer, both isomers can be expected to form dipole-bound states, yet both anions can also be expected to be metastable with respect to the C_{4h} $(NH_3)_4$ isomer.

Vertical electron attachment energies (VAE) of the two triple acceptor clusters, $\mathbf{C_3}$ and $\mathbf{C_{3v}}$, have been computed using different theoretical methods, and the results are listed in Table 2. Higher-order correlation effects contribute again most to the electron binding energies, yet with increasing dipole moment electrostatic effects and dispersion slowly gain more weight. At the CCSD(T) level the $\mathbf{C_3}$ isomer has a VAE of 20.6 meV, while the $\mathbf{C_{3v}}$ isomer has a much larger VAE of 96.0 meV reflecting its substantially larger dipole.

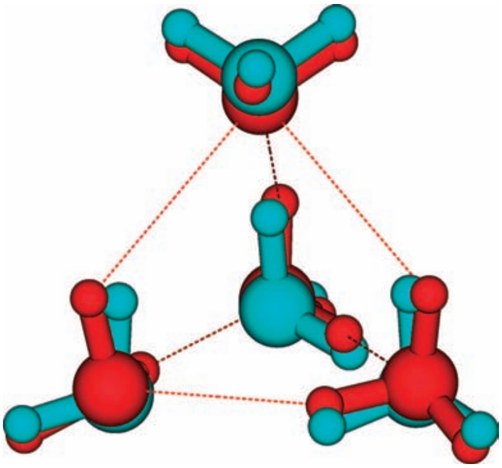

Figure 5. Superimposed structures of the neutral tetramer **C_3** (red) and its anion $(NH_3)_4^-$ (blue).

Since the high-dipole structures correspond to minima on the potential energy surface of neutral $(NH_3)_4$, attachment of an excess electron is not expected to have a major influence on the geometries of **C_3** and **C_{3v}**. Optimizing the geometry of the **C_3** anion does indeed change the structure only very little as can be seen from the superimposed minimum energy structures of the neutral and the anion in Figure 5. Nevertheless, the computed VDE of the optimized structure of the anion (25.3 meV) is significantly larger than the VAE of the neutral (20.6 meV). Thus, both triple acceptor tetramers **C_3** and **C_{3v}** are predicted to form long-lived dipole-bound anions with substantial VDEs. Both anions are predicted to be only metastable with respect to the most stable neutral $(NH_3)_4$ isomer and a free electron, yet owing to associated minima on the potential energy surface of the neutral, the anions **C_3** and **C_{3v}** are expected to be less fragile than **C_s−1**.

C. Hexamer Cage Model. In this section a S_6 symmetrical arrangement of six NH_3 monomers (Figure 6) is studied. This arrangement has been put forward as a cavity model for the ammoniated electron in ref 30 (structure **10**; geometrical parameters were taken from Table 1 of ref 30). Note that similar model systems have been considered in refs[31] and[32] and that this structure is neither a minimum nor a stationary point on the potential energy surface of the hexamer cluster. In contrast to the earlier findings,[31,32] the results presented in ref 30 suggest that a large portion of the excess electron resides in the frontier orbitals of the nitrogen atoms and that the ammoniated electron can be understood as a "multimer radical anion".

Here we investigate an excess electron attached to the $(NH_3)_6$ cage model using the EOM-CCSD method and a variety of basis sets, which are all combinations of a valence basis set centered at the H and N atoms, and an auxiliary basis set located at the center of symmetry. We started with the 6−31++G* valence basis and the 6−31++G* set of chlorine as an auxiliary basis since this is the basis set used in ref 30. However, most functions of the chlorine 6−31++G* basis set are optimized for electrons with large kinetic energies, whereas an excess electron bound to an ammonia cluster is expected to have a very small kinetic energy. Thus, the chlorine basis was replaced with a 2s2p2d set that was then systematically augmented by further spd sets of more diffuse functions until the VDE was converged (the largest exponents for all angular momenta were 0.1; an even-tempered series of exponents with a scaling factor of 3.5 is used). In addition, the larger valence basis sets 6−31++G** and aug-cc-pVDZ were employed with the converged auxiliary basis.

The first question we consider is whether the S_6 structure can actually bind an excess electron, and the EOM-CCSD results for the different basis sets are listed in Table 3. Using just the 6−31++G* chlorine basis or the 2s2p2d set at the center of the cavity yields no or extremely weak binding, respectively. Only if two more diffuse spd sets are added to the auxiliary set does the electron binding energy converge to about 117 meV, and with the more flexible aug-cc-pVDZ valence set, the VDE is 142 meV.

The distribution of the excess electron as obtained from the EOM-CCSD natural orbital (occupation number 0.98) is shown in Figure 6. The maximum of the excess electron's density is clearly at the center of the cavity, but only about 20% of the density is localized within the cavity, and the iso-surface enclosing 80% of the density has a diameter far larger than that of the cavity or that of the whole model cluster. In other words, the model cavity arrangement binds an electron, but for the largest part the electron is not in the cavity. Thus, as pointed out in ref 32, if the goal is to model an excess electron localized within a cavity, an artificial confinement as provided, e.g., by a compact basis set, is needed. Yet, this also implies a dramatic basis set dependence of all computed properties of the charge distribution.[32]

Second, the question of how much of the excess electron is localized close to the ammonia monomers and more specifically on the N atoms is considered. This question is addressed by integrating the density of the excess electron within the covalent radius of the N atoms (taken as 0.71 Å) and integrating the density within the van der Waals volume of the NH_3 monomers (defined by the volume enclosed in the van der Waals radii of the atoms, taken as 1.3 Å for H and 1.55 Å for N). The results are shown in Table 3. By use of a converged basis set, about 3% of the excess electron's density is localized within the covalent radii of the 6 N atoms, i.e., about half a percent for each N atom, and about 12% of the density is enclosed within the van der Waals volume of the 6 NH_3 monomers, i.e., about 2% per monomer. Using a basis set confining the excess electron within the cavity yields somewhat larger values of about 0.8% on each N atom and 3% in the van der Waals volume of each monomer.

These values are much smaller than those suggested in ref 30. The density of the excess electron as obtained from the correlated EOM-CCSD ab initio method suggests that the excess electron behaves similar to a dipole-bound electron. Only a small portion of the excess electron's density is localized on or close to the molecular framework, and this portion represents essentially so-called orthogonality tails, i.e., results from the requirement that the orbital of the excess electron needs to be orthogonal on all occupied valence orbitals.

Let us at this point briefly comment on the results reported in ref 30 that suggested a radical anion character of the ammonia hexamer anion. In comparison with the methods used in this paper, there are two major differences. In the first place, in ref 30 Kohn−Sham density functional theory with the Becke−Lee−Yang−Parr functional was employed. This functional is well-known to suffer from incomplete cancelation of the self-interaction leading to a wrong asymptotic potential for an excess electron and, therefore, to a qualitatively wrong description of anions,[42,43] in particular of diffuse anions[42] and anions where one electron is added to a closed shell.[44] In the second place, the analysis in ref 30 is based on the computed spin density. As discussed in ref 32, an excess electron localized close to an ammonia monomer will cause a spin-dependent polarization of the valence electrons generating a significant spin density at

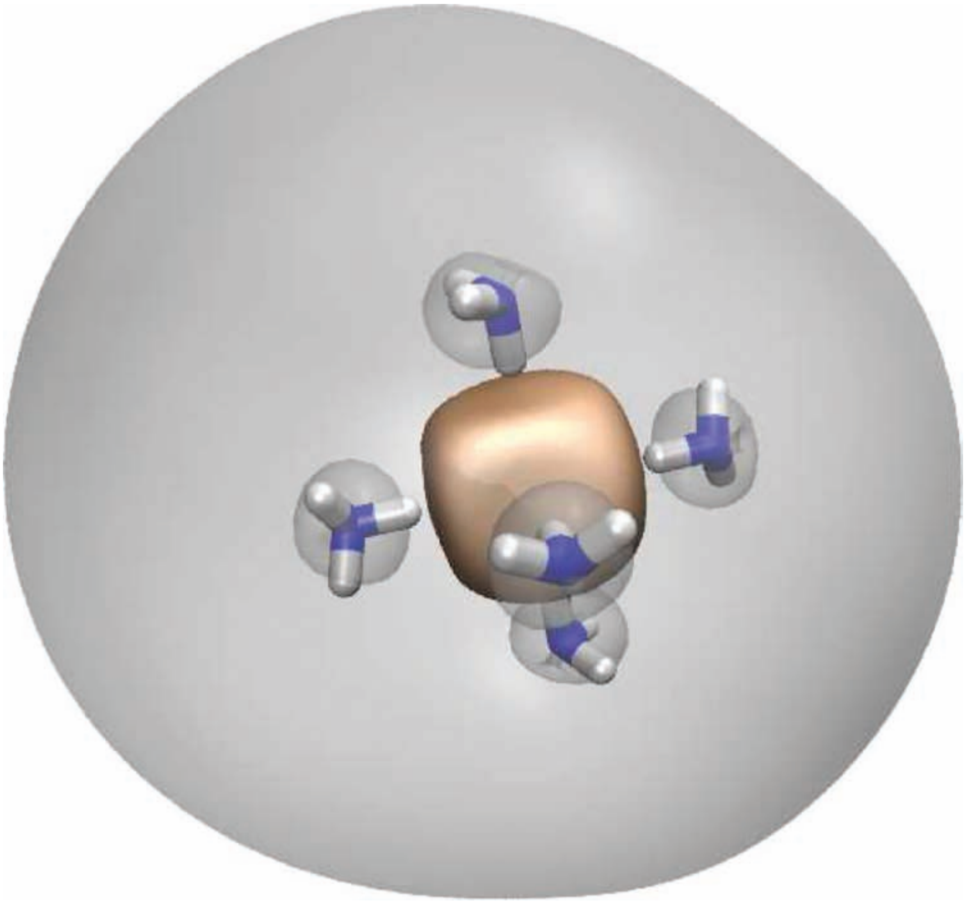

Figure 6. Distribution of the excess electron bound to 6 NH_3 monomers in a cavity model arrangement. The density is computed from a natural orbital of the EOM-CCSD density. The two iso-surfaces shown enclose 80% (gray) and 19% (orange) of the electron density.

TABLE 3: Electron Binding Energy and Density Analysis of an $(NH_3)_6$ Model Cavity (Figure 6)[a]

valence basis	basis at symmetry center	VDE (meV)	% density within *N* covalent radius	% density within NH_3 van der Waals volume
6−31++G*	Cl:6−31+G*	<0	4.9	18
6−31++G*	2s2p2d	0.17	4.9	18
6−31++G*	3s3p3d	92.7	3.7	13
6−31++G*	4s4p4d	117.5	3.0	11
6−31++G*	5s5p5d	117.6		
6−31++G**	4s4p4d	126.1		
aug-cc-pVDZ	4s4p4d	141.6	3.3	12

[a] The VDE has been computed using the EOM-CCSD method and the basis set indicated. The two other columns have been computed from the natural orbital of the EOM density associated with the excess electron (occupation numbers >0.98). The percentages of the excess electron density localized within the covalent radii of the 6 N-atoms and within the van der Waals volume of the 6 NH_3 monomers are shown.

the nuclear positions. Thus, a large spin density on an atom does not automatically suggest a large population of the excess electron, and unravelling spin density into a contribution due to spin polarization and a contribution due to the excess electron is not straightforward.

IV. Conclusions

The electron binding properties of small ammonia clusters $(NH_3)_N^-$ ($N = 2, 3, 4$) and one $(NH_3)_6^-$ cavity model cluster have been studied using couple-cluster ab initio methods. Small ammonia clusters resemble small water clusters in that both can form dipole-bound anions with similar electron binding energies; however, ammonia cluster anions are found to be less stable with respect to the global minimum of the respective neutral cluster and are predicted to be metastable yet long-lived.

An ammonia molecule is slightly more polarizable than a water molecule; however, it has a significantly smaller dipole moment and, therefore, somewhat larger ammonia clusters are needed to form dipole-bound states with similar electron binding energies. In fact, for the very small clusters there is almost a one-to-one correspondence between the $(NH_3)_N^-$ and the $(H_2O)_{N-1}^-$ anions: Both the ammonia dimer and the water monomer have dipole moments in excess of the critical 1.65 D,[45] yet both cannot bind an electron if nuclear motion is taken into account.[40] Both the ammonia trimer and the water dimer form dipole-bound states with electron binding energies in the order of 30 meV, and for both anions the attachment of an excess electron creates a new minimal energy structure; that is, in both cases the structure of the anion does not correspond to a minimum on the potential energy surface of the neutral cluster. Finally, the water trimer is the smallest cluster to exhibit the prominent double-acceptor binding motif, and the ammonia tetramer is the smallest cluster to form anions with a triple-acceptor monomer, a binding motif that can be expected to be present in larger ammonia cluster anions.

All dipole-bound ammonia cluster anions identified are unstable with respect to adiabatic electron loss, that is, with respect to the global minimum of the neutral cluster and a free electron. Long lifetimes are nevertheless predicted, since the relevant structures are far from each other, and the barriers to regions in nuclear coordinate space where the electron becomes unbound are expected to be substantially higher than the corresponding vibrational frequencies of the cluster anion. Owing to this metastability observing these small ammonia cluster anions might be a great challenge (cf. the observation of the water tetramer anion $(H_2O)_4^-$ [13]). However, increasing the backing pressure in the ion source brought the smallest observed cluster down from the 35-mer to the 13-mer, and tagging the clusters with rare gas atoms has certainly the potential to push this number further down. In any event, the ab initio presented structures and energies are valuable input parameters for model development or model validation.

Finally, a ammonia hexamer put forward as a model for a cavity-bound electron was examined. On the one hand, the ab initio results make the well-known problems[32] of using small clusters as models for solvated electrons explicit; namely, in order to model an electron within a cavity, one needs an artificial confinement such as a compact basis set, since most of density associated with the excess electron is not in the model cavity if converged basis sets are used. On the other hand, the analysis of the distribution of the excess electron as obtained from EOM-CCSD calculations shows that only a small portion of the electron is localized within the van der Waals volume of the ammonia monomers, regardless of the basis set employed. Thus the ab initio results do not support the notion that ammonia cluster anions can be understood as radical anions.[30]

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