Electric Deflection of Middle-Size Ammonia Clusters Containing (e⁻, Na⁺) Pairs

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ABSTRACT: Effective polarizabilities of $Na(NH_3)_n$ ($n = 8-27$) clusters were measured by electric deflection as a function of the particle size. A significant field-induced shift of the beam intensity profile without the occurrence of broadening revealed that the clusters behave as liquidlike polar objects in the conditions of the experiment (cluster temperatures were estimated in the range of $110-145$ K). Most of the cluster polarity is attributed to the spontaneous promotion of the alkali atom valence electron to a diffuse state stabilized by the cluster solvent field, with the consequent formation of (e⁻, Na⁺) pairs. The average modulus of the dipole of Na−NH₃ clusters, μ_0, was determined using the Langevin-Debye theory, and the data was compared with previous measurements obtained for Na−H₂O clusters. Sodium-doped ammonia clusters exhibit much larger μ_0 values and a step size dependence which is not present when the solvent is water. This evidence suggests that while the (e⁻, Na⁺) structure is rather compact in $Na(H_2O)_n$ clusters and remains almost unchanged during the solvation process, in $Na(NH_3)_n$ the unpaired electron abandons the proximity of the Na⁺ ion and gradually extends and occupies new solvent shells.
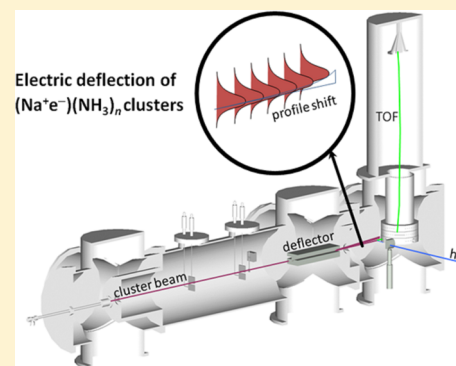
INTRODUCTION

It is well-known that clusters formed by one sodium atom embedded in a small number n of polar hydrogen-bonding molecules, such as H_2O or NH_3, favor the spontaneous promotion of the alkali atom valence electron to a diffuse state stabilized by the cluster solvent field. The (e⁻, Na⁺) moiety formed in the cluster has attracted a great interest in the past four decades, mainly because of its relation with the solvated electron,[1,2] a fundamental issue in physical chemistry. It is possible to conceive the (e⁻, Na⁺) structure as a one-center delocalized electron surrounding the first solvation shell of the alkali cation[3] as well as a two-center solvated electron in the vicinity of the solvated cation[4] forming a solvent-separated ion pair (SSIP) or even a contact ion pair (CIP). Recently, it was shown in detail for $Na(H_2O)_{n\leq6}$[5] and $Na(NH_3)_{n\leq6}$[6] that as the number of solvent molecules increases a one-center geometry is gradually replaced by different two-center geometries in which the Na⁺ can be situated either on the surface or in the interior of the cluster. Two-center (e⁻, Na⁺) pairs do not exclusively form in clusters but also in liquid solvents as, for instance, the (e⁻, Na⁺) contact pairs found in tetrahydrofuran.[7]

Primary experimental evidence on the system relied strongly on seminal mass-selective photoionization studies done on sodium-doped water and ammonia clusters,[8,9] which were more recently extended to clusters having other hydrogen-bonding solvents, for example, alcohols.[10,11] As a result of these experiments, it was immediately observed that the size dependence of the ionization potential (IP) of $Na(NH_3)_n$ clusters was different from that of Na−water or Na−alcohol clusters.

Experiments performed on small $Na(Sv)_n$ clusters, where Sv represents a solvent molecule like water or small alcohols, give the expected behavior which consists of a progressive reduction of the measured IP with the cluster size due to the solvation-induced charge separation and the delocalization of the unpaired electron in the cluster. However, once the first solvation shell of Na⁺ is completed ($n = 4$ for water and $n = 6$ for methanol and ethanol), the cluster size dependence of the IP changes abruptly. When the solvent molecules in the cluster surpasses the maximum coordination number of Na⁺ and the buildup of a second solvation shell begins, ionization energies become almost invariant with n[8−11] (∼3.17 eV for $Na(H_2O)_{n>4}$, ∼3.19 eV for $Na(CH_3OH)_{n>6}$, and ∼3.07 eV for $Na(CH_3CH_2OH)_{n>6}$), and these values approximately match respectively the measured vertical binding energies of solvated electrons in liquid water,[12,13] methanol,[12,14] and ethanol.[12,14] A similar behavior was also observed in aqueous clusters with other alkali metals.[15,16]

It is not easy to explain the abrupt change in the rate of variation of the IPs with n in Na−water or Na−alcohol clusters. It was suggested[3] that the leveling off of the IP values occurs because both e⁻−Na⁺ and (long-range) e⁻−Sv energies compensate each other once the first solvation shell is completed, although the same effect was interpreted[10,11,17] as a consequence of an autoionization process that follows the initial excitation to a high Rydberg-like state in which the

amount of relaxation energy released only depends on the size of the first solvation shell of Na^+.

The aforementioned behavior is not followed by Na–ammonia clusters. Here, the tendency of the cluster IPs to decrease with n extends far beyond the closing of the first solvation shell to finally become close to the low threshold energy for photoelectron emission of liquid ammonia (about 1.45 eV, according to a recent reevaluation[18] of earlier experimental data[19,20]) when the amount of NH_3 molecules in the cluster is large enough.[18,21] Moreover, a detailed analysis of the (IP vs n) dependence revealed the existence of steps like, for instance, the clear plateau observed for $Na(NH_3)_n$ clusters in the size range defined by $n = 10-17$.[9,18] It has been proposed[18] that this substructure might be related with the closing of solvation shells around the diffuse electron and the cation.

Unfortunately, the implications derived from the evolution of the measured IPs with n and with the type of solvent do not necessarily provide a complete description of the solvation structure. One reason for this is that the measured ionization threshold does not only depend on the electronic and geometric structures of the neutral state of the cluster but also on how they change after the removal of the electron (to give an ionic state) and the occurrence of solvent reorganization.[17]

Recently, we employed a new strategy to explore the nature of middle-size $Na(H_2O)_n$ clusters beyond the first solvation shell ($n = 6-33$)[22] which involves the measurement of the electric susceptibility of the particles, χ, as a function of n. The electric susceptibility is often referred to as an effective polarizability, α_{eff}.[23] The experiment was done using a well-known procedure[24−26] called electric deflection (ED) based on quantifying the deflection angle of a highly collimated beam of clusters in a static electric field gradient. We found that the presence of (e^-, Na^+) species in water clusters produces a marked enhancement of α_{eff} above the values measured with the same technique for pure water clusters[23] with equal number of solvent molecules. The size dependence of α_{eff} in Na–water clusters is characterized by a simple monotonous increase, without any evidence of a progressive building up of the solvent structure.

In the present study, we applied the same experimental procedure to determine the effective polarizability of sodium–ammonia clusters, $Na(NH_3)_n$ with $n = 8-27$, and the measurements were supplemented with ab initio calculations of permanent dipole moments and electronic polarizabilities, α_{el}, done on selected structures with $n \leq 11$. The work was motivated by the following questions: (1) will the distinct behavior of sodium-doped ammonia clusters, revealed by their IPs, be also discernible in α_{eff} measurements and (2) will this property allow us to understand the change that occurs in the electronic or geometric structures when the solvent is ammonia instead of water?

With all this in mind, the results have been interpreted qualitatively in terms of the relative influence of the solvent interactions, namely, how the H-bonding network is comparatively distorted and how the molecules reorient to accommodate the cation–electron pair. Finally, we have explored the possibility of observing an indication of the closing of solvation shells by analyzing the size dependence of the measured α_{eff}.

■ METHODS

The molecular beam apparatus used to carry out the experiments has been described in detail elsewhere.[22,27] Here, we will present a brief summary of the main components of the machine and give a short explanation of the ED technique used to determine the effective polarizability of the particles. Sodium-doped ammonia clusters were prepared using a pick-up arrangement[18,28] in which, first, $(NH_3)_n$ clusters are generated by a pulsed supersonic expansion of a 5% NH_3–He gaseous mixture at a pressure of 1 bar, and after that, attachment of one sodium atom occurs as the clusters pass through a collision cell having about 8×10^{-4} mbar of sodium vapor. The use of one-photon (340 nm) ionization time-of-flight mass spectrometry allowed us to quantify the intensity of $Na(NH_3)_n$ clusters in the beam selectively to the number of solvent molecules n. We limited this study to middle-size clusters with $n = 8-27$ ($n \approx 20$ at the maximum of the size distribution) for which the intensity was good enough to perform the ED experiments.

Before getting to the deflector region of constant electric field gradient, the cluster beam was collimated to 200 μm along the deflection coordinate z; this requirement ensures a good resolution in measuring the deflection angle. The configuration of the deflection electrodes used to establish the inhomogeneous electric field is well-known,[24] being the z-components of the electric field, F_z, and the field gradient, $\nabla_z F$, both proportional to the applied voltage, V. We used in the experiments electric field strengths up to $F_z = 8.1$ kV/mm, which corresponds to a gradient $\nabla_z F = 2.0$ kV/mm^2; these values are lower than those previously used in our study of sodium–water clusters[22] because of the higher effective polarizability of the sodium–ammonia system. Mass selective field-on (and field-off) intensity profiles, ϕ, were recorded against the coordinate z for $Na(NH_3)_n$ clusters about half a meter downstream from the deflector, 2 mm prior to the entrance of the mass spectrometer. At this point, the beam was probed at different positions by translating the spot of an ionization laser in 80 μm steps along the z-coordinate. This was achieved by translating a cylindrical lens which was mounted on a precision linear stage, outside of the vacuum chamber. For a given mass channel, the intensity profile in absence of the field exhibits a Gaussian shape (filled squares in Figure 1), the width of which is essentially determined by the extent of collimation and the photoionization laser spot size. On the other hand, when the collimation slits are fully open, the intensity shows no
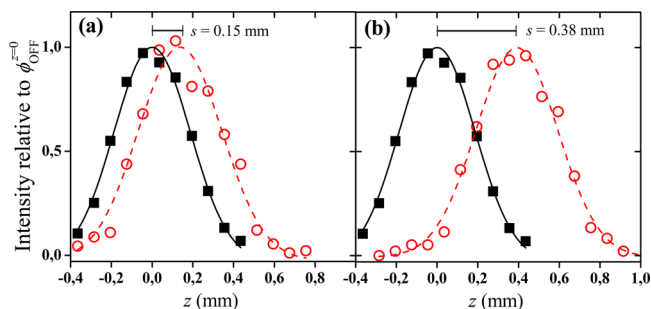

Figure 1. Shift s of the intensity profile maximum of $Na(NH_3)_{17}$ by effect of the inhomogeneous electric field. Squares, field-off profile; open circles, field-on profile. Left panel (a): $V = 7.5$ kV ($F_z = 5.1$ kV/mm, $\nabla F_z = 1.25$ kV/mm^2). Right panel (b): $V = 12.0$ kV ($F_z = 8.1$ kV/mm, $\nabla F_z = 2.0$ kV/mm^2).

dependence on z within ±1.5 mm from the beam center;[27] this implies that the efficiency of ion collection and the mass analysis are insensitive to the position of the particle along z, and consequently, no distortions are introduced in the shape of the recorded profiles.

A frequency-doubled Nd:YAG pumped dye laser (1 mJ/pulse and a wavelength of 340 nm) provides the light used to generate the photoions. Although the photon energy exceeds the ionization potential of $Na(NH_3)_n$ clusters,[9] it is known from photoelectron spectroscopy experiments[29] that most of the excess energy involved in the process is removed by the photoelectron, with the amount of internal energy left in the cluster ion lower than the binding energy among ammonia molecules (≈0.3 eV). As a consequence of that, we assumed that dissociation would hardly occur during photoionization, ensuring the right assignment of cluster sizes.

The procedure used to determine the propagation speed of the clusters, v_y, was successfully applied previously to other systems.[22,27] All the experiments were carried out close to the front of the supersonic beam pulse where a very small velocity spread was found and v_y showed no size dependence to our experimental resolution. The measured value for v_y was 1480 ± 43 m/s.

In the conditions of the experiment, we will show that the ED technique reveals the polar and nonrigid character of $Na(NH_3)_n$ clusters, which resemble the behavior of the sodium−water system studied previously. In the presence of the field, the clusters behave as polarizable bodies that deviate toward higher fields ($z > 0$) by the same amount,[23] producing a global shift of the intensity profile (open circles in Figure 1), indicated by s. For a cluster of mass m propagating with a speed v_y, the average effective polarizability is obtained from the measurement of s according to the equation

$$s = \frac{C}{mv_y^2}\alpha_{\text{eff}}F_z\nabla_z F = \frac{C'}{mv_y^2}\alpha_{\text{eff}}V^2 \qquad (1)$$

where C and C' are known apparatus constants. Beam profile shifts without broadening were previously observed in relatively large molecules,[30,31] complexes,[32] and molecular clusters[22,23] that go through fluctuations and isomerizations during the experiment time scale; in such cases, the system's structure is referred to as floppy or even liquidlike.

Using the Langevin-Debye equation,[33] α_{eff} can be written as a function of the particle electronic polarizability and an orientational term along the field direction, according to

$$\alpha_{\text{eff}} = \alpha_{\text{el}} + \frac{\langle\mu_0^2\rangle}{3k_{\text{B}}T} \qquad (2)$$

The orientational polarizability, represented by the second term of eq 2, is originated in the partial alignment of the cluster dipole (the modulus of which is indicated μ_0) and results from the canonical ensemble average of the dipole projection along the electric field's axis at the internal temperature of the cluster, T. Low-barrier intracluster modes available in nonrigid clusters generally make this mechanism the dominant contribution to α_{eff}.

Permanent dipoles and electronic polarizabilities of selected isomers of clusters $Na(H_2O)_n$, $n = 1-6$, and $Na(NH_3)_n$, $n = 1-6$ and $n = 8-11$, were calculated using the GAUSSIAN 98 package,[34] by performing density functional theory[35] (DFT) computations at the BP86 level employing the Sadlej[36] and the 6-311++G** basis sets, which are known to provide accurate

polarizability values. The same approach was previously used to evaluate the electric properties of the clusters $Na(H_2O)_8$ and $Na(H_2O)_{20}$.[22]

■ RESULTS AND DISCUSSION

In Figure 1, we display the change in the intensity profile of a representative cluster, $Na(NH_3)_{17}$, by effect of the inhomogeneous electric field, for two different field strengths. The significant shift of the intensity profile maximum toward the high-field region without the occurrence of broadening reveals that the cluster behaves as a nonrigid polar object.[32] Gaussian fitting was found to represent adequately the measured profiles, both in the absence (ϕ_{OFF}) and in the presence of the field (ϕ_{ON}), with the shift $s = \phi_{\text{ON}}^{\text{max}} - \phi_{\text{OFF}}^{\text{max}}$. For each mass channel, s showed a linear dependence with the square of the deflection voltage, in accordance with eq 1, which gives us experimental access to α_{eff} from the line slope. Errors attributed to the (s vs V^2) fitting procedure, and the measurement of the beam velocity and the apparatus constant C', allow us to determine α_{eff} within ±70 Å^3.

The size dependence of the experimental effective polarizability of $Na(NH_3)_n$ clusters is shown in the right panel of Figure 2 (filled squares); α_{eff} increases rapidly with the size of
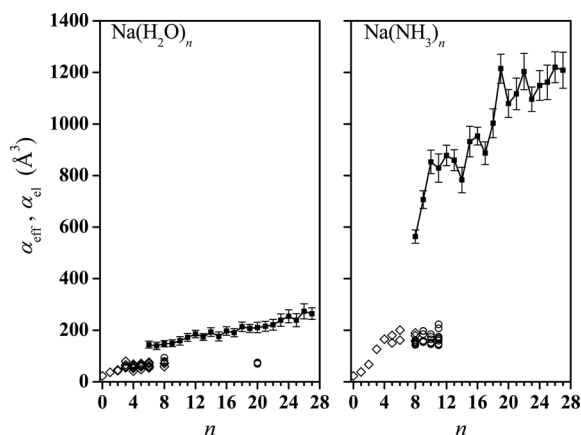

Figure 2. Electric properties of $Na(H_2O)_n$[22] and $Na(NH_3)_n$ clusters (this work) as a function of n. Experimental effective polarizability (α_{eff}): filled squares. Computed electronic polarizability (α_{el}): open diamonds and open circles. Errors bars were derived by propagating errors corresponding to the determination of the (s vs V^2) slope, v_y, and C'. Open diamond optimized structures are from refs 38 (Na−H$_2$O isomers) and 37 (Na−NH$_3$ isomers). Open circle optimized structures are from refs 39 (Na−H$_2$O isomers) and 17 (Na−NH$_3$ isomers).

the cluster, reaching a value of about 1200 Å^3 for $n = 27$. For comparison, we included in the left panel earlier measurements[22] done for $Na(H_2O)_n$ clusters (filled squares) in which α_{eff} values remain below 300 Å^3, for the same size range, and show a smaller slope. The fact that a much larger polarizability is found in $Na(NH_3)_n$ clusters may be due to two reasons: (1) the screening of the (e^-, Na^+) local electric field is weaker when the solvent is ammonia, giving rise to larger dipole moments, and (2) a larger delocalization of the electronic charge occurs in Na−NH$_3$ structures. To understand how these two effects comparatively contribute to α_{eff}, we have performed single-point DFT calculations of α_{el} on optimized structures (several isomers) determined for $Na(NH_3)_n$ by Hashimoto and Daigoku ($n = 1-6$)[37] and Gao and Liu ($n = 8-11$)[17] and for

$Na(H_2O)_n$ by Schulz et al. ($n = 1-8$)[38] and Buck et al. ($n = 8$, 20).[39]

Calculated electronic polarizabilities are included in Figure 2 as open diamonds and circles. The smaller value ($\alpha_{el} = 22.81$ Å^3) corresponds to the isolated sodium atom ($n = 0$), in good agreement with the experimental result.[40] The calculations show that α_{el} becomes rapidly larger with the number of solvent molecules in the cluster up to $n = 4$ or 5 and then tends to stabilize. The sharp increase of α_{el} observed in clusters $Na(NH_3)_4$ or $Na(NH_3)_5$ can be explained by the closing of the first solvation shell around the sodium atom and by considering the evidence[6] that at this point the unpaired 3s electron spreads beyond the vicinity of the Na atom and interacts with the coordination NH_3 molecules. For $n \geq 5$, the electronic polarizability of $Na(NH_3)_n$ clusters (averaged for the available isomers) levels off at values of about 170 Å^3, evidencing basically a highly delocalized wave function for the unpaired electron that is poorly sensitive to the amount of NH_3 molecules in the cluster. On the other hand, in the case of Na–H_2O clusters, α_{el} exhibits a less significant increase with n adopting values of about 75 Å^3 once the first solvation shell is complete. The smaller electronic polarizability observed for aqueous clusters is in agreement with previous calculations[37] where it was shown that the distribution of the 3s unpaired electron is more compact in $Na(H_2O)_n$ than in $Na(NH_3)_n$ for $n \geq 4$.

In spite of the large electronic polarizabilities of $Na(H_2O)_n$ and $Na(NH_3)_n$ clusters, it becomes clear from Figure 2 that this contribution to the measurable effective polarizability is minor and that the orientational term in eq 2 governs the electric susceptibility of the particles in the electric field. Consequently, the magnitude of the instantaneous cluster dipole will have a dominant influence on α_{eff}, meaning that μ_0 will be markedly larger for $Na(NH_3)_n$ than for $Na(H_2O)_n$ with the same cluster size.

If the temperature is known, eq 2 gives us access to the fluctuation-averaged cluster dipoles by assuming that $\alpha_{el} = 170$ Å^3 for $n \geq 12$. How can we estimate T in the conditions of the experiment? Bearing in mind that the temperature of clusters formed in a pick-up source depends primarily on evaporative cooling, it is possible to estimate T with the help of the evaporative ensemble theory.[41] In particular, we have used the equation

$$\gamma \cong \frac{\Delta E_{evap}(n)}{k_B T} \tag{3}$$

which is essentially a scaling law (validated by the theory) between the temperature of the evaporating cluster and the energy loss per evaporation, $\Delta E_{evap}(n)$, associated in our case with the process $Na(NH_3)_n \rightarrow Na(NH_3)_{n-1} + NH_3$. It has been shown[41] that the parameter γ in eq 3, known as Gspann parameter, is almost independent of the cluster size and composition but exhibits a weak dependence with the time since the evaporation process began. On a typical experimental time scale of tens of microseconds, the most frequently value used for γ is 23.5 ± 1.5;[42] however, we have corrected this value to account for the longer time scale of our ED experiment (source-to-deflector time-of-flight = 1.2×10^{-3} s) resulting in $\gamma = 28.3$. Experimental $\Delta E_{evap}(n)$ values for Na–ammonia clusters are only accessible for $n \leq 6$[29] and show no clear dependence on the cluster size. By introducing the value of ΔE_{evap} ($n = 6$) in eq 3, it comes out that $T = 145$ K; this

temperature is more easily attributed to the smaller clusters of the studied series than to the larger ones. One can expect that as soon as n increases and the evaporating NH_3 molecule becomes distant from the (e^-, Na^+) moiety, ΔE_{evap} of $Na(NH_3)_n$ clusters will finally converge toward that of the $(NH_3)_n$ clusters. A temperature of 110 K corresponds to this situation, where ΔE_{evap} was taken from calculations made on $(NH_3)_n$ clusters up to $n = 18$.[43] Consequently, it seems reasonable to assume that the temperature of the whole series of clusters will lie within the range of 110–145 K. The middle point of this temperature range was used to evaluate μ_0 in terms of eq 2, and an uncertainty of ± 18 K was propagated to compute the error bars in Figure 3. We believe that such
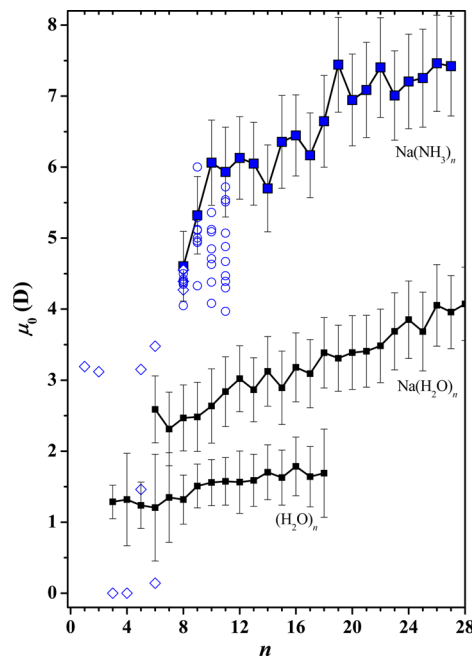

Figure 3. Size dependence of cluster dipole moments derived from eq 2 by using α_{eff} values from the ED measurements: $Na(NH_3)_n$, this work ($T = 128$ K, $\alpha_{el} = 170$ Å^3); $Na(H_2O)_n$, from ref 22 ($T = 200$ K, $\alpha_{el} = 75$ Å^3); $(H_2O)_n$, from ref 23 ($T = 200$ K, α_{el} from ref 44). Open diamonds and circles: μ_0 calculated for optimized structures of $Na(NH_3)_n$ from refs 37 and 17, respectively. Errors bars were derived by propagating the error assigned to α_{eff} and the uncertainty of T.

representation of the data captures the relevant features of the (μ_0 vs n) dependence, even though we could not include in the calculation the exact temperature distribution within clusters.

The resulting μ_0 values of liquidlike $Na(NH_3)_n$, $n = 8-27$, are plotted in Figure 3 (filled symbols) including for comparison previous ED measurements for nonrigid $Na(H_2O)_n$[22] and $(H_2O)_n$.[23] For all the clusters, the data reveal that the tendency of μ_0 is to increase with the cluster size. This observation can be explained by considering that the overall dipole orientation caused by intracluster motion is favored when the number of molecules in the cluster is larger. A closer examination of the data in Figure 3 shows that while the (μ_0 vs n) increase for aqueous aggregates is approximately constant, two sharp increments of more than 1 D become visible for $Na(NH_3)_n$ clusters with $n = 8-10$ and $17-19$, apparently associated with the partial shell closing of ammonia molecules (see below). The

steps are distinguished in spite of the large error bars partly originated in the uncertainty of T.

Definitely, the most remarkable feature that comes out from the data in Figure 3 is the large dipole moment found for Na−NH$_3$ clusters in comparison to that found for the aqueous homologues. Before going to this, we focus our attention to the difference in polarity between Na(H$_2$O)$_n$ and (H$_2$O)$_n$ clusters, $\Delta\mu_0 = \mu_0 \left[Na(H_2O)_n \right] - \mu_0 \left[(H_2O)_n \right] \approx 1$ D within the studied size range. This very low $\Delta\mu_0$ value implies that the charge separation inherent to the (e$^-$, Na$^+$) pair is very efficiently shielded by the water structure. Moreover, the fact that $\Delta\mu_0$ is almost independent of the cluster size can be taken as an indication that very few water molecules are enough to stabilize the (e$^-$, Na$^+$) pair, forming a rather compact moiety in which the average separation between the Na$^+$ ion and the center of the odd electron distribution becomes insensitive to further hydration in the cluster. This compact solvation structure is likely to occur in water so as to minimize the disruption of the strong hydrogen bond network.

On the other hand, the larger μ_0 values found for Na(NH$_3$)$_n$ clusters are consistent with a less compact (e$^-$, Na$^+$) structure in which the unpaired electron gradually abandons the proximity of the Na$^+$ ion as the cluster becomes larger. In other words, the electron is pushed away from the Na$^+$ first solvation shell and the system adopts the characteristics of a solvent-separated ion pair in which the electron and the sodium ion are separated and shielded dielectrically by the solvating ammonia molecules. This structure has been previously referred to[18] as a two-center interior state, also for Na(NH$_3$)$_n$ clusters. The formation of SSIPs in ammonia would be favored by the relatively small contribution of the NH$_3$−NH$_3$ H-bonding energy to the stabilization of the cluster, which is dominated by the Na$^+$−NH$_3$ interactions.

Open symbols in Figure 3 represent μ_0 values computed using DFT for optimized Na(NH$_3$)$_n$ structures from refs 37 (diamonds) and 17 (circles). However, it is not straightforward to compare the dipole moments calculated for such 0 K geometries with those determined by ED for melted clusters. On the one hand, the calculations reveal that solidlike clusters exhibit dipole moments that are strongly dependent on the geometries of the dominant isomers. For example, clusters with n = 3, 4, and 6 (corresponding to isomers NaA3a, NaA4a, and NaA6a of ref 37) are highly symmetric and exhibit $\mu_0 \approx 0$, while other geometries with n = 1, 2, 5, 6 (isomer NaA6b[37]) as well as several isomers of larger clusters with n = 8−11[17] are less symmetric and the resulting overall dipoles are larger. On the other hand, μ_0 values of liquidlike clusters as those measured in the experiment cannot be associated with a single structure but to an average of multiple low-barrier conformations which interconvert among each other during the time scale of the ED experiment (hundreds of microseconds). As shown in Figure 3, fluctuation averaged dipole moments of liquidlike Na(NH$_3$)$_n$ clusters lie above the values calculated for rigid isomers with the same cluster size. This behavior can be attributed to the frequent existence of disordered polar structures along the dynamics of liquidlike clusters.

As it was mentioned before, an interesting feature in the (α_{eff} vs n), and also (μ_0 vs n), dependence of liquidlike Na(NH$_3$)$_n$ clusters is the appearance of two sharp steps at n = 8−10 and 17−19, with α_{eff} less sensitive to the cluster size in the ranges n = 10−17 and n = 17−27. Size dependence of the ionization potential, measured earlier[9,18,29] for the same clusters, exhibits a very similar step pattern as shown comparatively in Figure 4.
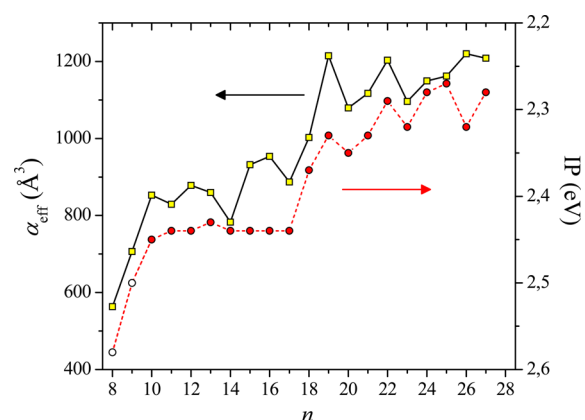

Figure 4. Size dependence of the effective polarizability (left axis, this work) and the vertical ionization potential (right axis, open circles, refs 9, 29; filled circles, ref 18) of Na(NH$_3$)$_n$ clusters.

Both properties, namely, IPs (circles, right axis) and α_{eff} ED data (squares, left axis), give the same variation when plotted against the cluster size. However, because ED experiments are performed on neutral particles, the explanation for why α_{eff} steps are present in Na(NH$_3$)$_n$ clusters and absent in Na(H$_2$O)$_n$ clusters is apparently not related with the ionization process or the characteristics of the ion state but with structural differences in the ground state.

We attribute the α_{eff} steps appearing at n = 8−10 and 17−19 to an increase in the cluster average dipole moment appearing with the building up of a new solvent shell. When the number of NH$_3$ molecules in the new shell is large enough to stabilize the unpaired electron, the mean e$^-$−Na$^+$ distance becomes larger and μ_0 increases. Further addition of NH$_3$ molecules in the same shell will not significantly increase the cluster dipole until occupation of the following solvent shell. According to this description, and considering that a minimum of four NH$_3$ molecules is required for the closing of the first solvation shell of Na$^+$ in ammonia clusters,[6,45] apparently six additional NH$_3$ molecules are required to stabilize the unpaired electron beyond the Na$^+$(NH$_3$)$_4$ solvate. For $n \geq 10$, the electron and the sodium ion become completely separated and dielectrically shielded by the solvating ammonia molecules, forming a solvent-separated (e$^-$, Na$^+$) pair. The next step starting at n = 17 is compatible with the closing of the second solvation shell of Na$^+$ for n = 16 found previously by IP studies,[29] allowing the electron to extend to the third solvent shell for $n \geq 17$. On the other hand, the absence of α_{eff} steps in Na(H$_2$O)$_n$ clusters is in agreement with the existence of a compact and stable (e$^-$, Na$^+$) moiety which, as discussed before, would essentially remain unaltered as the number of NH$_3$ molecules in the cluster increases.

■ CONCLUSIONS

Effective polarizabilities of quasi-liquid Na(NH$_3$)$_n$ (n = 8−27) clusters formed in a pick-up source by reaction between a (NH$_3$)$_n$ cluster and a Na atom were measured by electric deflection as a function of the particle size. Even though an important electronic contribution to α_{eff} comes out in the calculations performed on Na(NH$_3$)$_n$ clusters, as a consequence of the promotion of the sodium 3s electron to a diffuse state stabilized by interactions with NH$_3$ molecules, the dominant polarization mechanism relies on the tendency of the cluster dipole to align with the external electric field.

The strong increase of the overall cluster dipole with n observed for $Na(NH_3)_n$ has been explained in terms of the formation of solvent-separated (e^-, Na^+) pairs in which the center of the odd electron distribution gradually separates from the Na^+ ion when the number of NH_3 molecules in the cluster increases. This scenario is supported by the appearance of steps in the $(\mu_0$ vs $n)$ dependence that become visible each time the unpaired electron can have access to a new solvent shell, thereby intensifying the $e^-{-}Na^+$ charge separation. Our data points out that at least six additional NH_3 molecules are required to stabilize the unpaired electron in the second solvation shell beyond the $Na^+(NH_3)_4$ solvate, allowing the electron to extend to a third shell in clusters with at least 17 NH_3 molecules. The formation of SSIPs in $Na{-}NH_3$ clusters would be favored by the small contribution of the $NH_3{-}NH_3$ H-bonding energy to the stabilization of the cluster, dominated by the $Na^+{-}NH_3$ interactions.

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Notes
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