Cluster size specific chemistry: deuterium atom pickup in Sr\(^+\) solvated by ammonia

David C. Sperry, James I. Lee, James M. Farrar

Department of Chemistry, University of Rochester, Rochester, NY 14627-0216, USA

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Abstract

We report on recent experimental evidence for deuterium atom pickup in metal ion–polar solvent clusters. Mass spectral analysis shows the existence of species that correspond to the empirical formula Sr\(^+\)(ND\(_x\))\(_{3-x}\), where \(x\) is as large as 4 for clusters in the size range \(n = 10–15\). Photodissociation spectra of several of these clusters indicate that their structures are very different from the purely ammoniated analogs, Sr\(^+\)(ND\(_3\)). Based on deuterium scavenging data and absorption spectra, we propose the formation of SrD\(^\text{3+}\) to account for one of the excess deuteriums, and the existence of solvated ND\(_4\) to account for additional deuterium atoms in the cluster.

1. Introduction

Clusters are a unique form of matter, intermediate to isolated gas-phase molecules and condensed media. These small aggregates of molecules and atoms are free to exhibit properties distinct from either the gas or condensed phases. Much attention has been focused on determining the structure and electronic properties of small and medium-sized clusters. Castleman’s group has used a unique form of mixed cluster formation to provide experimental evidence for the structure of protonated water clusters and protonated water–methanol clusters [1–3]. By ‘capping’ the non-hydrogen-bonded surface hydrogen atoms of the cluster with triethylamine added to the seed mixture, the resulting mass spectra were interpreted as providing evidence for a clathrate structure. Scavenger techniques have also been used to determine structure and reactivity. Johnson and collaborators [4,5] reported on reactions of neutral electron scavengers with (H\(_2\)O)\(_n^+\), arguing that an electron transfer mechanism explains the formation of solvated charge transfer products.

Spectroscopic techniques have been used extensively to understand the structures of solutions as modeled by cluster systems [6–12]. Metal ions solvated by ammonia are interesting, as metal–ammonia solutions are particularly well-studied examples of solvated electron systems at low metal concentrations. In this Letter we present results of studies on monovalent strontium ion solvated by ammonia. The data exhibit the formation of a new chemical species that incorporates multiple deuterium atoms into the purely ammoniated cluster within a specific range of cluster sizes. In this study, we have employed our usual technique of mass spectrometry coupled with photodissociation spectroscopy, but have also added reactivity studies to gain insight into the nature of these unique species.
2. Experimental

We have reported on the experimental apparatus employed for these studies previously [7]. Therefore, only a brief description of the experimental procedure and details specific to this system will be reported here.

A distribution of parent clusters is produced when a supersonic expansion of neat NH$_3$/ND$_3$ is expanded through a pulsed valve into a cloud of Sr$^+$ ions generated by laser vaporization of a rotating strontium disk. The clusters thus formed drift into a vacuum chamber that defines the extraction region of a Wiley–McLaren time-of-flight mass spectrometer. The chamber pressure in the source region with the reagent gas on is typically $1 \times 10^{-5}$ Torr. A port in the source chamber allows the optional introduction of a steady stream of gas (neat NO or He) that can interact with the clusters after their formation but before extraction. The relative gas concentration can be monitored via the chamber pressure. The clusters are then accelerated down the flight tube to a space focus point. At an appropriate delay, collimated light from an optical parametric oscillator transversely intersects the mass separated beam. Spectra of all clusters were probed with a Nd:YAG (Spectra-Physics GCR-190) pumped singly-resonant optical parametric oscillator (Spectra-Physics MOPO-730). The laser beam diameter is 5 mm, and the energy is attenuated to 1 mJ/pulse throughout all experiments.

The products of the photodissociation process are mass separated by a reflectron mass spectrometer. The ion signal is collected by microchannel plates, digitized by a transient recorder, and stored on a computer. We obtain a dissociation spectrum by integrating each of the peaks arising from the dissociation process and normalizing to beam flux at a series of wavelengths. The total dissociation spectrum, produced by summing all daughter peaks, is equated with the total absorption cross-section.

3. Results

The cluster size distribution of solvated metal ion clusters produced with a laser vaporization source can be altered by varying the operating conditions of the pulsed source (i.e., backing pressure, timing, laser fluence). In previous work from our laboratory, we have placed emphasis on the formation of small clusters, in order to build up an understanding of their structures from the singly-solvated species up through clusters with six solvent molecules [6,7]. In the present case, we examine the behavior of larger clusters, and to assist the discussion, we show a mass spectrum for Sr$^+$(NH$_3$)$_n$, with $n$ ranging from 1 to 22 in Fig. 1. Under low-resolution conditions, the mass spectrum is striking because it shows a very clear intensity distribution with three distinct envelopes: the first group of peaks corresponds to the local maximum that peaks at $n = 6$; a second distribution of clusters, with a local maximum at $n = 13$ appears; and a third group of clusters with a maximum occurring at $n = 20$ is also readily apparent in this mass spectrum. This pattern in the mass spectrum is suggestive of a shell structure in the clusters, with shell closings occurring at 6, 13, and 20 solvent molecules. The data we present in this Letter, however, show that the clusters in the second cluster group have dramatically different structure, electronic properties, and chemical reactivity compared.

![Fig. 1. Low-resolution mass spectrum showing the intrinsic intensity distribution of Sr$^+$(ND$_3$)$_n$ formed in our source. The inset is a scan with conditions optimized for resolution of $n = 6$ showing the natural Sr isotope distribution.](image-url)
to those in the first cluster group. Thus, we believe that the interpretation of the overall intensity distribution is more subtle, and an accurate description must account for the structural differences between the cluster groups. In the inset of Fig. 1, one can see the mass spectral lines for smaller clusters show the characteristic triplet structure associated with the three most abundant isotopes of strontium: $^{86}$Sr, $^{87}$Sr, and $^{88}$Sr. While the resolution in Fig. 1 is less than optimal, there is evidence of peak broadening in the larger cluster groups, indicating the presence of unresolved structure in the mass spectrum.

In order to understand the cluster mass distribution more fully, we optimized the focusing conditions for the heavier clusters and carried out these experiments with ND$_3$, to reduce the likelihood for mass coincidences. A close look at the mass spectrum for the solvent number range $n=12-14$ is shown in Fig. 2. It is immediately clear from the mass spectrum that additional masses begin to appear in this group of heavier clusters. Furthermore, deuterium substitution shows that the clusters are incorporating deuterium atoms in excess of the number that a cluster of the stoichiometry Sr$^{+}$(ND$_3$)$_n$ would have. In Fig. 2, we assign the masses, extrapolating from the known constant of proportionality between mass and time in the smaller clusters, out to the second and third groups of mass lines. The graph shows the mass assignments corresponding to Sr$^{+}$(ND$_3$)$_n$D$_x$, with $x=0-4$, indicating clearly the propensity for the larger clusters to incorporate up to four additional deuterium atoms. Numerous repetitions of the mass spectrum, both with NH$_3$ and ND$_3$, confirm the assignments of the multiplicity of mass spectral lines as arising from the incorporation of excess hydrogen atoms in ‘conventional’ clusters. These mass assignments lead to the firm conclusion that we are observing a qualitatively new cluster species given symbolically by the formula Sr$^{+}$(ND$_3$)$_x$. For $n$ in the range from 10 to 15, i.e., the second cluster group, $x$ is as large as 4.

The intensities of many of these cluster ions are sufficiently large that we can measure photodissociation spectra by our usual techniques. As we have reported previously, the dissociation spectra for Sr$^{+}$(NH$_3$)$_n$ show a monotonic red shift with increasing cluster size [7]. In more recent work, we have found the absorption maximum appears to approach an asymptotic value of $\sim 6200$ cm$^{-1}$ for large clusters in the group where $n \leq 9$, which will be reported in a future paper. Qualitatively, this red shift is consistent with the increasing volume for
delocalization of the single metal-centered valence electron on Sr$^+$ as the solvation number increases. A representative set of absorption spectra for clusters in the second cluster group is shown in Fig. 3. The spectra have several interesting features. Each of the extra-deuterium containing clusters has a strong, broad absorption band around 11 000 cm$^{-1}$, and a much weaker absorption band at 18 000 cm$^{-1}$. Both bands shift 3000 cm$^{-1}$ higher in energy as $x$ varies from 1 to 3. Clusters containing at least two additional deuterium atoms (i.e., $x \geq 2$) have an absorption band peaking at 6200 cm$^{-1}$. The clusters containing only one extra deuterium, $x = 1$, do not exhibit this low-energy absorption feature. These same trends in absorption profile have been observed for other cluster species of similar size. It appears that the $x = 2, 3$ species have a chromophore that is absent in the $x = 1$ species. Thus we expect that the first deuterium atom is added to the cluster in a location distinct from the second and third. The position of the extra deuterium atom within the cluster could dramatically affect the reactivity of the cluster.

We have used a deuterium scavenging technique, which allows NO gas to react with the entire cluster distribution before the extraction pulse for mass analysis. The resultant mass spectrum shows the cluster distribution after reaction with a given concentration of NO. Nitric oxide is an odd-electron molecule and can therefore effectively scavenge radical species selectively compared to a closed-shell atom such as helium. Fig. 4a shows a representative set of mass spectra with varying concentrations of NO. In the lowermost mass profile, peaks from Sr$^+(\text{ND}_3)D_x$, $x = 0–4$, are clearly visible for $n = 12–14$. This spectrum was taken without adding...
nitric oxide to the source chamber; it represents the inherent cluster intensity distribution formed in our source. The chamber pressure under these conditions is $1 \times 10^{-5}$ Torr. The mass spectrum directly above was taken after adding enough NO to the source chamber to raise its pressure to $7 \times 10^{-5}$ Torr. The peaks corresponding to $x = 2-4$ have clearly lost intensity relative to the peaks corresponding to $x = 1$ for the $n = 13$ cluster group. Because of lower parent cluster intensity the quenching is not as obvious in the $n = 12, 14$ cluster groups; it is, however, still present. The next two traces show mass spectra at higher NO concentrations. It is evident that as the concentration of scavenger gas is increased, nitric oxide preferentially reacts with species containing two or more excess deuterium atoms. At higher scavenger concentrations the entire mass spectrum is quenched. The overall reduction of signal intensity is a result of the interference of the background of nitric oxide with the efficiency of the extraction process in the instrument. This effect can also be observed when using an unreactive gas in the source chamber such as helium. Fig. 4b shows a similar experiment using He instead of NO. The lowermost trace shows the intrinsic mass distribution of the $n = 12, 13, 14$ clusters present with no reactant gas. The two spectra above this trace show the same clusters after the addition of He into the source chamber. The intrinsic mass distribution in the beam is persistent, independent of He concentration. The overall intensity is depleted as a result of the inefficient extraction as in the NO case.

The results of the scavenging experiment coupled with the electronic spectroscopy clearly show that the \(\text{Sr}^+ (\text{ND}_3)_x\) \(D_y\) \((x \geq 2)\) are chemically distinct from the \(x = 1\) species. The heavier species are more reactive with a deuterium scavenging molecule than those containing only one extra deuterium. Furthermore, the second and third additional deuterium atoms in the cluster appear to create a chromophore that is not present in the species containing a single excess deuterium atom.

4. Discussion

Extra deuterium atoms could conceivably be incorporated into clusters by a mechanism that would involve intra-cluster reactions eliminating \(\cdot \text{ND}_2\) or other stable or metastable species from a larger cluster. In fact, intra-cluster reactions have been shown to break covalent bonds in the solvent in many cases, such as \(\text{Mg}^+(\text{H}_2\text{O})_n\) [13–15], \(\text{Ca}^+(\text{H}_2\text{O})_n\) [12,14], \(\text{Mg}^+(\text{CH}_3\text{OH})_n\) [16], and \(\text{M}^+(\text{CH}_3\text{OH})_n\) \((\text{M} = \text{Mg, Ca, Sr, Ba})\) [17]. Given the presence of extra deuteriums in the cluster, we have considered the energetics of deuterium atom transfer and charge transfer in the cluster. Possible configurations include the deuterium bound in the solvent as a neutral \(\text{Sr}^+(\text{ND}_3)_x\) \(\text{ND}_y\) or cationic \(\text{Sr}(\text{ND}_3)_x\) \(\text{ND}_y^+\) species, or the deuterium bound to the metal in either a neutral \(\text{SrD}(\text{ND}_3)_x\) \(\text{ND}_y\) or charged \(\text{SrD}^+(\text{ND}_3)_x\) \(\text{ND}_y\) species. Thermodynamic Born cycle calculations indicate that the latter metal deuteride ion species is the lowest-energy configuration. Data for a Born cycle calculation are not complete, but reasonable estimates of solvation enthalpies and bond energies can be made from data available in the literature.

Alkaline-earth metal hydride ions, despite being stable species, have received relatively little attention. Only a few reports of the ground state properties of \(\text{SrH}^+\) exist [18–22]. The hydrogen is bound by \(\sim 2\) eV [19,21], while the electron affinity (5.58 eV [18]) is very close to that of the metal ion, \(\text{Sr}^+\). Experimental determinations of the electronic properties exist only for \(\text{MgH}^+\) [23], while some theoretical predictions on the general electronic structure were made by Schilling et al. [19].

Since no electronic information is available for \(\text{SrH}^+\), we turn to the isoelectronic \(\text{RbH}\) molecule. Properties of low-lying electronic states of the alkal hydrides were compiled by Stwalley et al. [24]. The \(\text{A}^1\Sigma^+\) state of \(\text{RbH}\) lies $\sim 18\,000$ cm$^{-1}$ above the \(\text{X}^1\Sigma^+\) ground state. This transition energy is in the region of the two highest energy bands in the spectrum of \(\text{Sr}^+(\text{ND}_3)_x\) \(\text{D}_y\). We believe it is reasonable to attribute the transitions at 11 000 and 18 000 cm$^{-1}$ to a solvated \(\text{SrD}^+\) chromophore. These bands shift to higher energy with the addition of deuterium atoms probably as a result of a solvent reorganization which removes ligands from the local solvation environment of the metal deuteride to accommodate the extra deuteriums.

Based on Born thermodynamic cycle calculations, a second additional deuterium atom incorporated into
the lowest-energy feature in the spectrum of transition for a solvated species. The I.P. of increases its lifetime. The radical enhances the metastability, i.e. greatly ms before detection. We speculate that solvation of apparatus, clusters exist for durations approaching 1 metastable lifetime by several fold [30,31]. In our - of the free radical was estimated to be \(\text{eV} \pm \text{eV} \) [25] compared to 5.58 eV for SrH. This fact indicates that the positive charge would prefer to be associated with \(\text{ND}_x\). This is most likely not the case, however, since the preferable solvation enthalpy of \(\text{SrD}^+\) would outweigh the 1 eV gain from the charge transfer. The same energetic arguments apply to the third additional deuterium atom; it can exist as a neutral \(\text{ND}_3\) radical as well.

The hypervalent ammonium radical has received much attention. Many experimental and theoretical probes of the structure and energetics exist in the literature. The absorption spectrum was first identified by Herzberg [26] and named after Schuler who was among those who first observed it. The Schüler band of the isolated \(\text{ND}_3\) radical \((\sim 17200 \text{ cm}^{-1})\) has been assigned to the transition between the 3p \(^2\text{F}_2\) state and 3s \(^2\text{A}_1\) ground state [27]. The lifetime of the free radical was estimated to be \(< 150 \text{ ns} \) [28] while the fully deuterated analog has a much longer lifetime \((> 10 \mu\text{s})\) [27–29]. However, ammoniation of the \(\text{NH}_4^+\) radical has been shown to increase the metastable lifetime by several fold [30,31]. In our apparatus, clusters exist for durations approaching 1 ms before detection. We speculate that solvation of the radical enhances the metastability, i.e. greatly increases its lifetime.

While the isolated \(\text{ND}_x\) species has been studied spectroscopically, no data exist on the 3p \(\rightarrow\) 3s like transition of a solvated species. The I.P. of \(\text{NH}_4^+(\text{NH}_3)_n\) was determined by Fuke et al. [32] to decrease approximately linearly with \(n^{-1/3}\) and extrapolates to the bulk photoelectric threshold limit. This is similar to results seen in solvated alkali metals [33]. As has been suggested previously [26], the ammonium radical should bear electronic similarities to the isoelectronic sodium atom. The 3p \(\rightarrow\) 3s splitting in the solvated radical may track similarly to other solvated one-electron systems. We propose that the solvated \(\text{ND}_x\) radical has a 3p \(\rightarrow\) 3s like transition at \(\sim 6000 \text{ cm}^{-1}\), which coincides with the lowest-energy feature in the spectrum of \(\text{Sr}^+(\text{ND}_x)_2\text{D}_x\), \(x = 2,3\). The approximate doubling in intensity of this band between \(x = 2\) and \(x = 3\) could then be explained by the existence of an additional identical \(\text{ND}_3\) absorber.

Kassab and collaborator have proposed a bubble structure for the solvated \(\text{ND}_3\) radical [34,35]. This model accounts for the repulsive character of the hypervalent electron. The reactivity data shown in Fig. 4 are consistent with this picture. We believe that the Rydberg electron in the radical forces the \(\text{ND}_3\) to exist on the surface of the cluster. Thus, the weakly bound deuterium atom is highly reactive with a hydrogen scavenger like nitric oxide. The first deuterium atom incorporated into the cluster is more tightly bound in the strontium deuteride ion and is therefore not as reactive as the second and third.

5. Conclusions

We have shown the existence of unique chemical species in metal-centered polar solvent clusters corresponding to the empirical formula \(\text{Sr}^+(\text{ND}_x)_2\text{D}_x\), where \(x\) is a large as 4 for clusters in the size range \(n = 10–15\). Photodissociation spectra obtained for several clusters show three distinct features: two bands at \(\sim 11 \text{ 000 cm}^{-1}\) and \(\sim 18 \text{ 000 cm}^{-1}\) present in all clusters, and a low-energy band at \(6200 \text{ cm}^{-1}\), present only in clusters with at least two additional deuterium atoms. Deuterium scavenging studies show that clusters containing at least two excess deuterium atoms \((x \geq 2)\) are more reactive with nitric oxide than clusters containing a single excess deuterium atom. We propose the formation of \(\text{SrD}^+\) to account for one of the excess deuteriums and attribute the two high-energy absorption features \((\sim 11000\text{ and }\sim 18000 \text{ cm}^{-1})\) to this chromophore. We argue the existence of solvated \(\text{ND}_x\) to account for additional deuterium atoms in clusters where \(x \geq 2\) and assign the low-energy feature in our spectra \((6200 \text{ cm}^{-1})\) to the 3p \(\rightarrow\) 3s like transition of the solvated ammonium radical.

References
