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Formation of hydrated triply charged metal ions from aqueous solutions using nanodrop mass spectrometry

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Abstract

Forming hydrated clusters containing triply charged metal ions is challenging due to the competing process of dissociation by forming the metal hydroxide with one less net charge and a protonated water molecule. It is demonstrated for the first time that it is possible to form such clusters using a method we call “nanodrop mass spectrometry”. Clusters of the form $[M(H_2O)_n]^{3+}$, where $M = Ce, Eu, \text{ and } La$, are generated using electrospray ionization and are mass analyzed in a Fourier-transform ion cyclotron resonance mass spectrometer with an ion cell cooled to $-140^\circ C$. Clusters containing trivalent La with n ranging from 16 to over 160 can be readily produced. These clusters are stable at this temperature for many seconds, enabling all standard methods to probe structure and reactivity of these unusual species. Photodissociation experiments on extensively hydrated clusters of trivalent lanthanum using resonant infrared radiation indicate that a minimum of 17 water molecules is necessary to stabilize these trivalent clusters under the low-energy ion excitation conditions and long time frame of these experiments. These results indicate that a minimum droplet size of approximately a nanometer is necessary for these trivalent species to survive intact. This suggests that elemental speciation of trivalent metal ions from aqueous solutions should be possible using nanodrop mass spectrometry.

Keywords

Ion solvation; Trivalent metal ions; Ligated trications; Electrospray; Hydration

1. Introduction

Investigating the structure of hydrated ions in the gas phase can provide insight into ionic processes that occur in bulk solution. Clusters containing singly charged metal ions have been formed using several different methods and the structures of these clusters have been investigated in significant detail [1-7]. Formation of hydrated multiply charged ions is more challenging due to competing effects of dissociation aided by Coulomb repulsion of two charged product ions [8-20]. For example, a single water molecule can be readily attached to Ca^{2+} . However, addition of a second water molecule to this cluster results in the formation of the metal hydroxide with one less net charge and a protonated water molecule (reaction (1)) [8,9]:

Similarly, the isolated sulfate dianion is unstable and spontaneously undergoes rapid dissociation by ejection of an electron (reaction (2)) [15-17]:

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Charge separation reactions of this type can prevent the formation of larger, multiply charged clusters by condensing water onto smaller clusters in supersonic expansions.

Both thermospray [21] and electrospray ionization (ESI) [10-14,22-24] have been used to produce hydrated divalent metal ion clusters. Kebarle and coworkers [11-13] first used ESI to form and study a plethora of previously inaccessible, hydrated doubly charged clusters. Clusters, such as $\text{Ca}^{2+}(\text{H}_2\text{O})_n$ [11-13,22-24] and $(\text{SO}_4)^{2-}(\text{H}_2\text{O})_n$ [16-18], that cannot be formed by condensing water onto bare or minimally solvated ions, can be readily formed using ESI. Activation of $\text{M}^{2+}(\text{H}_2\text{O})_n$ clusters can lead to dissociation by two pathways: loss of a neutral water molecule (reaction (3)) or proton transfer to form a singly charged metal hydroxide and a protonated water molecule (reaction (4)) [9-13]:

Similarly, dissociation of $(\text{SO}_4)^{2-}(\text{H}_2\text{O})_n$ can result in either loss of a water molecule (reaction (5)) or intermolecular proton transfer followed by charge separation (reaction (6)) [16-18]:

For large clusters, loss of a neutral water molecule is the favorable process. For smaller clusters, the charge separation reactions become competitive and ultimately dominate as the cluster size decreases. The branching ratio for these two competitive dissociation channels depends on the extent of hydration, the identity of the species, as well as experimental parameters, such as internal energy deposition and observation time. Factors that affect the minimum number of water molecules necessary to stabilize the divalent ions are discussed elsewhere [9,10,14,18].

By comparison to divalent ions, only a limited number of solvated triply charged clusters have been successfully generated. Kebarle and coworkers first reported the observation of solvated, triply charged metal ions in the gas phase in 1990 [19]. Using electrospray ionization, they generated clusters of numerous Group III elements solvated by dimethylsulfoxide (DMSO) and dimethylformamide. Despite operating under conditions where $[\text{M}(\text{H}_2\text{O})_n]^{2+}$ clusters were readily formed for numerous alkaline earth and transition metal ions [11-13], no $[\text{M}(\text{H}_2\text{O})_n]^{3+}$ clusters were produced: charge-reduced species of the form $[\text{M}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$ were observed instead.

Since Kebarle and coworkers' initial report, numerous efforts have been made to generate new $[\text{ML}_n]^{3+}$ clusters and to further understand the formation and solvation of these clusters. Kojima et al. used electrospray and laser spray [25] to generate $[\text{ML}_n]^{3+}$, where M = selected Group III elements and L = DMSO, hexamethylphosphoramide, and selected sugars [26]. Experiments with water/methanol solutions yielded no triply charged clusters solvated by only these protic solvents. More recently, Shvartsburg used electrospray ionization to form clusters of this type, including $[\text{M}(\text{acetonitrile})_n]^{3+}$ [27], $[\text{M}(\text{DMSO})_n]^{3+}$ for selected metals outside of Group III [28], and $[\text{M}(\text{diacetonealcohol})_n]^{3+}$ for selected Group III elements, the only previous report of a triply charged metal in a cluster with a protic solvent [29].

An alternative approach to forming these triply charged clusters has been employed by Stace and coworkers in which ligated, neutral clusters are formed and subsequently ionized by electron impact [20,30]. With this technique, $[\text{HoL}_n]^{3+}$ clusters have been formed where L = acetone or acetonitrile [30], and $[\text{AlL}_n]^{3+}$ clusters were formed where L = DMSO, pyridine,

or acetonitrile [20]. No $[M(H_2O)_n]^{3+}$ clusters were observed for either of these metal ions; in both cases, reduced charge species were formed instead.

Here, electrospray ionization is used to generate substantial yields of triply charged metal ions of Ce, Eu, and La solvated by water. This is the first reported observation of triply charged metal ions solvated by only water. It is shown that maintaining extensively solvated clusters throughout the entire process, from electrospray droplet formation through mass analysis, is essential to successfully generate these species. Clusters of $[M(H_2O)_n]^{3+}$ with as few as 16 water molecules are observed in these experiments. Experiments in which larger hydrated clusters are photodissociated result in no $[M(H_2O)_n]^{3+}$ with $n < 16$, indicating that a minimum of 16 water molecules are necessary to stabilize the trivalent form of the metal ion in these hydrated clusters under the conditions of this experiment.

2. Experimental methods

2.1. Chemicals

Lanthanum(III) chloride heptahydrate and europium(III) chloride hexahydrate were obtained from Aldrich Chemical Company (Milwaukee, WI). The hexahydrate salt of cerium(III) nitrate was obtained from Alfa Aesar (Ward Hill, MA). All chemicals were used without further purification. Electrospray solutions were made to 1.0 mM of the respective metal ion using ultra-pure water (18.2 M Ω and ≤ 4 ppb total organic content) from a Milli-Q Gradient water purification system (Millipore, Billerica, MA).

2.2. Mass spectrometry

All experiments are performed using a home-built Fourier-transform ion cyclotron resonance (FT/ICR) mass spectrometer with a 2.75 T superconducting magnet and an external electrospray ionization source. This instrument and its use to form extensively hydrated clusters of a variety of species have been described in detail elsewhere [18,23,24,31,32]. Additional parameters associated with the ESI interface that play an important role in these experiments are described in more detail below. Ions are formed by nanospray using borosilicate capillaries that have inner diameters of 0.78 mm and have a tip at one end pulled to an inner diameter between 1 and 3 μ m (measured using an optical microscope) using a Flaming-Brown micropipette puller (Sutter Instruments model P-87, Novato, CA). A platinum wire, inserted into the other end of the capillary and in contact with the solution, is used as an electrode. A potential near the onset of electrospray droplet formation (~ 800 V) is applied to this wire. The tip of the borosilicate capillary is placed approximately 1 mm from the orifice of the electrospray interface, a schematic diagram of which is shown in Fig. 1. Charged droplets formed by electrospray are introduced into the interface through an 11.4 cm long stainless steel capillary that has an inner diameter of 500 μ m. This capillary is in thermal contact with a surrounding brass sleeve, stainless steel housing, and a copper block that can be resistively heated. The temperature of the air inside the metal capillary is unknown, but it is almost certainly lower than that of the copper block. The distribution of hydrated ions observed in these experiments is very sensitive to the copper block temperature. Abundant hydrated clusters of the form $[M(H_2O)_n]^{3+}$ were obtained with the copper block at temperatures between 96 and 106 $^{\circ}$ C, whereas negligible abundances of $[M(H_2O)_n]^{3+}$ clusters were observed with the copper block temperature above 120 $^{\circ}$ C.

After exiting from the capillary, the ions pass through two mechanically pumped regions (~ 1.8 and 80 mTorr, respectively). The energy of the collisions that occur in the first mechanically pumped stage can be controlled by varying the potential on the capillary, tube lens, and the first skimmer, which has a 1 mm orifice. Typical potentials on these interface components were 37, 120, and 12 V, respectively ("soft" ESI interface conditions). Ions are

guided through an additional high vacuum pumping stage to the cell using a series of electrostatic ion guides and are accumulated in a cylindrical cell for 8–12 s. To assist in trapping and thermalization of the ions, dry N₂ gas is pulsed into the cell at a pressure of $\sim 10^{-6}$ Torr using a piezoelectric valve. After ion injection, a mechanical shutter is closed to prevent additional ions from entering the cell. Ion detection is done with a the cell pressure $< 10^{-8}$ Torr. The ion cell is surrounded by a copper jacket that can be resistively heated or cooled using liquid nitrogen. This cell is described in more detail elsewhere [24]. To increase the lifetime of the hydrated ions, the cell is cooled to -140 °C using pulses of liquid nitrogen. Data are acquired and analyzed using the modular FT/ICR data acquisition system 'MIDAS' [33].

Infrared multiphoton dissociation (IRMPD) experiments were performed by irradiating the ensemble of clusters present in the cell with ~ 60 mW of light at 3470 cm^{-1} ($\sim 3\text{ cm}^{-1}$ linewidth) generated by an optical parametric oscillator/amplifier (OPO/OPA) system (LaserVision, Bellevue, WA) pumped by the fundamental of an Nd:YAG laser (10 Hz repetition rate, ~ 3.8 W total power, Continuum Surelight I-10, Santa Clara, CA). Photodissociation was initiated after an 8 s pump-down delay using a TTL-triggered mechanical shutter inside the pump laser cavity. This light was aligned with the ion cell using a series of protected silver mirrors enclosed in a positive-pressure, dry nitrogen purge box containing calcium sulfate desiccant (Dri-Rite Co., Blue Island, IL). The light was focused with a 1 m CaF₂ lens placed ~ 75 cm from the center of the ion cell and was introduced into the vacuum chamber through a custom-built, Brewster-angle mounted CaF₂ window. The laser beam profile is $\sim 3\text{ mm} \times 10\text{ mm}$ in the center of the cell corresponding to an approximate fluence of $\sim 2000\text{ W/m}^2$.

3. Results and discussion

3.1. Triply charged metal ions solvated by water

An electrospray mass spectrum of a solution of lanthanum(III) chloride obtained using a copper block temperature of 96 °C and soft interface conditions shows a distribution of extensively hydrated lanthanum ions (Fig. 2). The predominant form of the clusters is $[\text{La}(\text{H}_2\text{O})_n]^{3+}$ with n ranging between 16 and 163. No clusters with $n < 16$ were observed (Fig. 2A), suggesting that at least 16 water molecules are required to solvate and preserve the hydrated 3+ form of the metal ion. The loss of a water molecule is entropically favored over the charge separation reaction for $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ clusters [18]. If the same is true for these hydrated lanthanum clusters, then experiments done on a shorter time frame or where excess energy is added into the clusters may result in enhanced formation of $[\text{La}(\text{H}_2\text{O})_n]^{3+}$ with $n < 16$. A much lower abundance of $[\text{La}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$ clusters are formed with a similar size distribution as $[\text{La}(\text{H}_2\text{O})_n]^{3+}$. Also apparent in this spectrum, and others shown here, is the nodal behavior, suggestive of either shell structures of water around the central metal ion, or perhaps reflecting preferred droplet sizes upon the final Rayleigh fission of larger, highly charged droplets originating from the electrospray ionization process. The size distribution at which these nodes appear can be changed by various experimental parameters, and this phenomenon is currently under investigation.

Similar results are obtained for the other trivalent metal ions investigated here. Electrospray ionization of $\text{Ce}(\text{NO}_3)_3$ results in a rich spectrum containing numerous hydrated species, including $[\text{Ce}(\text{H}_2\text{O})_n]^{3+}$, $[\text{Ce}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$, and $[\text{Ce}(\text{NO}_3)(\text{H}_2\text{O})_n]^{2+}$ (Fig. 3). $[\text{Ce}(\text{H}_2\text{O})_n]^{3+}$ clusters with n ranging from 18 to 88 are observed. The smallest $[\text{Ce}(\text{H}_2\text{O})_n]^{3+}$ cluster ($n = 18$) contains more water molecules than the smallest $[\text{La}(\text{H}_2\text{O})_n]^{3+}$ cluster ($n = 16$), consistent with the smaller ionic radius of Ce versus La.

Electrospray ionization of $\text{Eu}(\text{Cl})_3$ produces distributions of $[\text{Eu}(\text{H}_2\text{O})_n]^{3+}$ ($n = 68\text{--}84$) and $[\text{Eu}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$ ($n = 16\text{--}54$) (Fig. 4). Eu has two isotopes, ^{151}Eu (47.8%) and ^{153}Eu (52.2%) making Eu containing clusters readily identifiable based on the 0.67 and 1.0 m/z spacing of the

two nearly equivalent abundance isotopes for the 3+ and 2+ clusters, respectively. A calculated isotope distribution of $[\text{Eu}(\text{OH})(\text{H}_2\text{O})_{43}]^{2+}$ is inset with Fig. 4. In addition to these hydrated Eu clusters, there appears to be some clusters that contain one or more other molecules in addition to water. The pickup of acetone or other small volatile molecules is often observed under these experimental conditions and this almost certainly results from the presence of these molecules in the background laboratory air. There does not appear to be any significant contribution from $[\text{Eu}(\text{H}_2\text{O})_n]^{2+}$ clusters. Therefore, the charge reduction of $[\text{Eu}(\text{H}_2\text{O})_n]^{3+}$ occurs primarily by hydroxide formation and H_3O^+ loss, and not by direct reduction of the metal ion.

Compared to the electrospray mass spectra obtained for Ce and La, that of Eu exhibits significantly reduced abundances of $[\text{M}(\text{H}_2\text{O})_n]^{3+}$ relative to $[\text{M}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$. The ionic radius of Ce(III) is only slightly smaller than that of La(III), whereas Eu(III) is significantly smaller than the other two lanthanide metals. A comparison of published effective ionic radii [34] indicates that for a given coordination number between 6 and 9, the effective ionic radii of Ce^{3+} and Eu^{3+} are 98.0 ± 0.6 and

$91.9 \pm 0.1\%$ that of La^{3+} , respectively. Due to its smaller ionic radius, the higher charge density on europium should favor dissociation via the charge separation channel over that for the loss of a water mole at higher values of n than those clusters containing Ce or La. Clusters larger than those presented here may preserve greater abundances of $[\text{Eu}(\text{H}_2\text{O})_n]^{3+}$. Periodic trends governing the branching ratio between these two unimolecular dissociation pathways are currently under investigation.

3.2. Minimum stable cluster size

In order to investigate the minimum stable cluster sizes for $[\text{La}(\text{H}_2\text{O})_n]^{3+}$, clusters were irradiated with 3470 cm^{-1} light for 20 s (Fig. 5). This frequency corresponds to the bonded hydrogen stretch region in cationic water clusters [6] and was chosen to yield rapid photodissociation of the extensively hydrated clusters. Irradiating these clusters with light at this wavelength results in significant reduction in the size of the clusters. The initial ion population (Fig. 5A) contains $[\text{La}(\text{H}_2\text{O})_n]^{3+}$, $n = 17\text{--}85$, and $[\text{La}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$, $n = 2\text{--}53$. $[\text{La}(\text{OH})_2(\text{H}_2\text{O})_n]^+$ clusters are not observed. After 20 s of low-power laser irradiation, substantially smaller clusters are formed. The highest observed n for $[\text{La}(\text{H}_2\text{O})_n]^{3+}$ and for $[\text{La}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$ is 65 and 42, respectively. However, the lowest observed size of these two clusters is the same as that found without laser irradiation. In addition, $[\text{La}(\text{OH})_2(\text{H}_2\text{O})_n]^{1+}$ clusters with $n = 9\text{--}21$ are clearly observed. Spectra obtained at $\sim 2.5 \times$ greater laser fluence show smaller average cluster sizes. However, the lowest observed n for $[\text{La}(\text{H}_2\text{O})_n]^{3+}$ and for $[\text{La}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$ are the same (17 and 2, respectively).

These results suggest that 17 water molecules are necessary to stabilize the trivalent form of La under very low-energy excitation conditions and long time frames. The observation of $[\text{La}(\text{H}_2\text{O})_{16}]^{3+}$ in some ESI spectra may be the result of higher energy excitation that may occur in the ESI interface. For $[\text{La}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$, the inability to observe smaller clusters may be due low absorption of radiation at 3470 cm^{-1} . This frequency is strongly absorbed by water molecules that are hydrogen bonded; smaller clusters in which all the water molecules are coordinated directly with the metal ion and do not hydrogen bond to other ligands will not absorb significantly at this wavelength.

It is interesting to note that the largest $[\text{La}(\text{OH})_2(\text{H}_2\text{O})_n]^{1+}$ cluster ($n = 21$) is also observed in spectra obtained at higher laser power. This result indicates that loss of H_3O^+ from $[\text{La}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$ clusters of $n \geq 23$ must occur, suggesting that the onset for the charge separation reaction for $[\text{La}(\text{H}_2\text{O})_n]^{3+}$ may also occur for $n \geq 17$. Future studies of the dissociation of mass

selected clusters will provide additional insight into both the size and energy dependence of cluster dissociation.

3.3. Mechanism of ion formation: solvent evaporation versus condensation

Hydrated ions observed in ESI mass spectra can be formed by condensing water onto bare or minimally solvated ions [31,35], and/or by evaporation of water from more extensively solvated droplets [31]. The former process can result in charge reduction of the analyte or metal ion species via proton transfer to solvent [31,36,37]. The ESI mass spectra of the trivalent hydrated metal ions are very sensitive to source conditions. For example, effects of changing the heater block temperature from 106 to 120 °C on the ESI mass spectra of LaCl_3 in water are shown in Fig. 6A and B, respectively. With the heater block at 106 °C, the abundance of $[\text{La}(\text{H}_2\text{O})_n]^{3+}$ clusters is significantly greater than that for $[\text{La}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$, and 3+ clusters with $n \geq 17$ are observed. In contrast, a small increase in heater block temperature (from 106 to 120 °C) results in $[\text{La}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$ clusters becoming the dominant species. The abundances of $[\text{La}(\text{H}_2\text{O})_n]^{3+}$ clusters are then negligible, despite the fact that $[\text{La}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$ clusters with $n \geq 32$ are observed. In addition, $[\text{La}(\text{OH})_2(\text{H}_2\text{O})_n]^+$ clusters become readily apparent.

With the heater block at a higher temperature (120 °C), an increase in cluster size can be obtained by making conditions in the first expansion region more gentle by decreasing the potential applied to the tube lens from 120 to 110 V (Fig. 6C). The distribution of $[\text{La}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$ clusters is then clearly shifted to higher n . The abundance of $[\text{La}(\text{H}_2\text{O})_n]^{3+}$ clusters is still negligible, despite the fact that the average cluster size is significantly above $n = 16$, the apparent minimum number of water molecules necessary to stabilize $[\text{La}(\text{H}_2\text{O})_n]^{3+}$. The increased clustering obtained under more gentle expansion conditions does not prevent charge reduction processes from occurring. Thus, formation of the $[\text{La}(\text{H}_2\text{O})_n]^{3+}$ depends not just on the number of water molecules that are attached, but also on how these clusters are formed. These results indicate that charge reduction can occur very early in the electrospray ionization interface.

These results may help explain why others, who have reported attempts to form $[\text{M}(\text{H}_2\text{O})_n]^{3+}$, where M is a trivalent metal ion, have been unsuccessful despite forming clusters with more than the minimum number of water molecules necessary to stabilize these clusters. It is essential that the hydrated clusters be formed by solvent evaporation from even larger droplets rather than by condensation of water on bare or minimally solvated ions in the ESI interface.

4. Conclusions

Electrospray ionization has been used to produce trivalent metal ions surrounded by a variety of ligands, but previous attempts to form such ions surrounded by highly protic solvents, like water, have been unsuccessful due to the competing dissociation channel for formation of a metal hydroxide with one less charge and loss of protonated water. We clearly demonstrated that extensively hydrated trivalent metal ions can be readily generated in high abundance, with the number of water molecules attached to the trivalent metal ion ranging from 16 to over 160. Critical to the observation of these species is that these trivalent metal ions remain surrounded by a minimum number of water molecules (about 16 in these experiments) throughout the experiment. This critical cluster size corresponds to a sphere with a diameter of approximately 1 nm. Thus, these trivalent metal ions can be preserved through the electrospray ionization mass spectrometry process by maintaining droplet sizes of at least a nanometer for the duration of the experiment. These results suggest that it may be possible to do elemental speciation analysis on a wide variety of metal ions of 3+ and even higher valence using this nanodrop mass spectrometry method.

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Fig. 1.

Schematic diagram of the electrospray ionization interface used in these experiments. A general description of the FT/ICR mass spectrometer and a detailed description of the cooled ion cell can be found in [32] and [24], respectively.

Fig. 2.

Electrospray mass spectra of a solution LaCl_3 obtained with soft electrospray interface conditions and a copper block temperature of 96°C : (top) complete spectrum, (A) expanded low mass region showing the presence of $[\text{La}(\text{H}_2\text{O})_n]^{3+}$ with as few as 16 water molecules, (B) expanded region centered $\sim 540\text{ m/z}$, and (C) expanded region centered $\sim 940\text{ m/z}$ taken from a separate mass spectrum obtained under identical instrument conditions but using a different excitation waveform and digitizer settings in order to improve signal to noise and resolving power in this region.

Fig. 3.

Electrospray mass spectrum of a solution containing $\text{Ce}(\text{NO}_3)_3$ obtained using soft ESI interface conditions and a copper block temperature of 104°C : (top) complete spectrum showing the presence of $[\text{Ce}(\text{H}_2\text{O})_n]^{3+}$ ($n = 18\text{--}88$), (A) expanded low mass region showing the presence of $[\text{Ce}(\text{H}_2\text{O})_n]^{3+}$ with as few as 18 water molecules, (B) expanded region centered $\sim 300\text{ m/z}$, and (C) expanded region centered $\sim 500\text{ m/z}$.

Fig. 4.

Electrospray mass spectrum of a solution containing EuCl_3 obtained using soft ESI interface conditions and a copper block temperature of 104°C : (top) complete spectrum showing the presence of $[\text{Eu}(\text{H}_2\text{O})_n]^{3+}$ ($n = 68-84$) and (A) expanded region ~ 500 m/z with the calculated isotope distribution of $[\text{Eu}(\text{OH})(\text{H}_2\text{O})_{43}]^{2+}$ displaying all peaks with a relative abundance greater than 1% inset.

Fig. 5. Effects of infrared photodissociation on hydrated clusters of La formed from LaCl_3 solutions with a heater block temperature of 104 °C and soft ESI interface conditions: (A) electrospray mass spectrum and (B) infrared multiphoton dissociation spectra obtained by irradiating all ions generated from electrospray with 3470 cm^{-1} light for 20 s.

Fig. 6.

Electrospray mass spectra of LaCl_3 solutions showing effects of interface heater block temperature and tube lens voltage on cluster formation: (A) spectrum with a copper block temperature of 106 °C and lens element potentials similar to, but not directly comparable to those used in the acquisition of data for Fig. 2, (B) same conditions as (A), but with a copper block temperature of 120 °C, and (C) same conditions as (B) but with the tube lens potential lowered by 10 V.