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Generation of “unstable” doubly charged metal ion complexes in a laser vaporization cluster source

N.R. Walker, G.A. Grieves, J.B. Jaeger, R.S. Walters, M.A. Duncan*

Department of Chemistry, University of Georgia, Athens, GA 30602-2556, USA

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Abstract

Doubly charged metal ion complexes of the form $M^{2+}(L)_n$ are generated using a laser vaporization cluster source in conjunction with a time-of-flight mass spectrometer. Contrary to expectations, a variety of doubly charged species are produced with this source, including many so-called “unstable” or “metastable” ions in which the metal has a second ionization potential greater than the first ionization potential of the ligand or solvent. The species identified include $Mg^{2+}(CO_2)_n$, $Mg^{2+}(H_2O)$, $Mg^{2+}(Ar)_n$, $Co^{2+}(Ar)_n$, $Co^{2+}(H_2O)$, $Si^{2+}(Ar)_n$ and $Ti^{2+}(CO_2)_n$. This is apparently the first observation by any means of $Co^{2+}(Ar)_n$, $Ti^{2+}(CO_2)_n$ and $Si^{2+}(Ar)_n$. Of the complexes studied, only the “stable” species $Mg^{2+}(Ar)_n$ have been generated previously by laser vaporization. The conditions necessary for the production of these ions are investigated and possible mechanisms for their growth are suggested. Charge-transfer photodissociation is observed for $Co^{2+}(Ar)$ complexes.

Keywords: Metal dications; Photodissociation; Metastable cluster ions; Metal ion solvation

1. Introduction

Studies of singly charged gas phase metal ion–molecular complexes of the form $M^{+}(L)_n$ have greatly contributed to our understanding of the microscopic processes of metal ion solvation and metal–ligand interactions [1–9]. By contrast, gas phase studies of multiply charged metal ion complexes are less common, owing to significant difficulties in their production. However, advances have recently been made with techniques for the production of complexes containing both doubly charged cations [10–18] and anions [19–21]. Complexes of triply charged cations have also been generated [22,23]. The present work describes new applications of a laser vaporization cluster source to the generation of doubly charged metal ion $M^{2+}(L)_n$ complexes. This is the first successful application of this method to the generation of a wide range of multiply charged, metal-containing cluster ions.

As discussed by Schröder and Schwarz [12], the stability of an $M^{2+}(L)_n$ unit is governed by its energetics with respect to charge transfer. When the second ionization potential (IP) of the metal is lower than the first IP of the ligand or solvent species, the $M^{2+}L$ unit is intrinsically stable at all values of the internuclear separation *r* (Fig. 1). A smooth potential connects the separate species at the asymptote with the

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* Corresponding author. Tel.: +1-706-542-1998; fax: +1-706-542-1234.
E-mail address: maduncan@uga.edu (M.A. Duncan).

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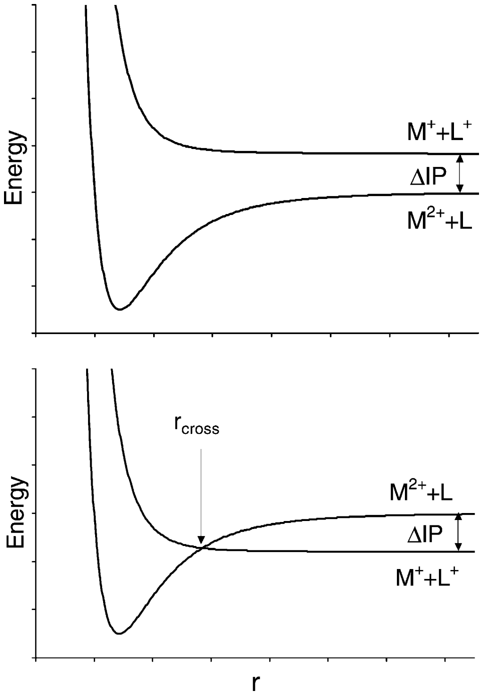

Fig. 1. The schematic potential curves showing the interactions in an intrinsically stable doubly charged metal ion complex (upper frame) and one which is asymptotically unstable (lower frame).

electrostatically bound well. When the second IP of the metal is higher than the first IP of the ligand, however, the doubly charged complex is asymptotically unstable. The potential surface describing the $M^{2+}+L$ species and that for the $M^{+}+L^{+}$ species usually cross at some value r known as the "crossing distance" due to strong attractive forces that come into play on close approach of the doubly charged ion and a polar or polarizable atomic or molecular species. In these circumstances, $M^{2+}L$ may be denoted as either "stable" (Fig. 1) or "metastable" depending on whether the bound portion of the well lies below or above the $M^{+}+L^{+}$ asymptote. Particularly in metastable cases, the barrier to charge transfer may be overcome by collisional excitation during or subsequent to cluster growth and an isolated $M^{2+}L$ unit is highly susceptible to charge transfer-induced fragmentation yielding M^{+} and L^{+} which separate by so-called Coulomb explosion. Because of these energetic considerations, the formation of multiply charged metal ion complexes from separated components is expected to be highly sensitive to the collisional environment where growth occurs. The formation of $M^{2+}L$ complexes with a laser vaporization source has been assumed to be inefficient due to presumptions about cluster growth mechanisms and the high frequency of collisions in this environment. However, there have apparently been few systematic investigations to explore these issues with laser vaporization.

Techniques for generating $M^{2+}(L)_n$ clusters have typically involved either desolvation from the liquid phase or the fragmentation of neutral or singly charged gas-phase units of higher mass. These methods take advantage of the pre-existing environment of the multiply charged metal ion, which is already surrounded by stabilizing ligands at the instant of formation in the gas phase. Kebarle and coworkers established the usefulness of electrospray ionization sources by generating a wide variety of solvated complexes containing multiply charged, alkaline earth metal ions [10,11]. Electrospray sources continue to be used by a variety of groups to study a range of systems and properties [10,13,17,18,24,25]. A limitation of this method is that complexes must be present initially in solution in order to permit their subsequent study, although Posey and coworkers have sought to address this difficulty [17,18]. In an alternative approach, Stace and coworkers have shown that complexes can be produced using a "pick-up" method, in which neutral clusters containing metal ions are doubly ionized within the electron impact source of a mass spectrometer to yield $M^{2+}(L)_n$ species [14–16,26–30]. The pick-up method has recently been applied to perform spectroscopy on size-selected $M^{2+}(L)_n$ species [30]. This method also has limitations: some complexes accessible via electrospray are not easily produced by the pick-up method, and the size of the smallest cluster ions observed with this method does not necessarily indicate the smallest achievable $M^{2+}(L)_n$ unit [13,25,31,32].

Although many singly charged complexes of metal cations have been produced by laser vaporization, there are few reports of multiply charged species. Velegrakis and Luder [33] used laser vaporization to generate $Mg^{2+}(Ar)_n$ clusters. In $Mg^{2+}(Ar)_n$ complexes, $IP(Mg^+) < IP(Ar)$, so the complexes are stable over all values of n. A similar logic applies to the stability of $Ca^{2+}(H_2O)_n$, which have been produced previously by our group and other workers [10,13,34,35]. Data from a further example of this type of multiply charged complex, $Ti^{2+}(CO_2)_n$, are presented below. In addition, data are presented here for several complexes where $IP(M^+) > IP(L)$. This is the first time that species from this second category of asymptotically unstable complexes have been generated by laser vaporization. These include $Mg^{2+}(CO_2)_n$, $Mg^{2+}(H_2O)$, $Co^{2+}(Ar)_n$, $Co^{2+}(H_2O)$ and $Si^{2+}(Ar)_n$. Observation of the $Co^{2+}(H_2O)$ complex is particularly surprising, because the second IP of cobalt is significantly higher than the first IP of water. These results indicate that a wide range of multiply charged complexes can be produced with a laser vaporization source. Possible mechanisms for the formation of the complexes are discussed below.

2. Experimental

$M^{2+}(L)_n$ complexes are generated by laser vaporization in a pulsed nozzle cluster source, using a molecular beam apparatus described previously [1,36]. The fundamental, second harmonic or third harmonic of a Spectra Physics Nd:YAG laser (Quanta Ray INDI 30) are used to vaporize a rotating rod of the sample metal. A repetition rate of 10 Hz and pulse energy of 40–60 mJ/pulse is employed, focused to a spot size of about 1 mm. This pulse energy is significantly higher than that typically used with this same cluster source to produce singly charged metal-containing cluster ions [1].

Pure expansion gases or mixtures containing ligand/solvent molecules are pulsed through the cluster source using a General Valve (Series 9, 1 mm orifice). We employ the so-called “cutaway” configuration of the sample holder, in which the gas expands directly over the sample rod surface rather than flowing through a growth channel. A backing pressure of 40 psig is used. For the solvents which are liquid at room temperature (water, acetonitrile, acetone, THF, benzene, methanol, ethanol), argon is passed through a reservoir to entrain the vapor within the flow prior to supersonic expansion. We use the partial pressures of these liquids at ambient temperature.

The cluster products formed from the source are expanded into vacuum and skimmed into a differentially pumped mass spectrometer chamber. Pulsed extraction plates accelerate the ions from the molecular beam into a reflectron time-of-flight mass spectrometer where they are analyzed by their m/z ratio. Doubly charged cluster ions of mass m have the same m/z ratios as singly charged ions of mass $m/2$ and are consequently transmitted with the same flight time. Based on the time-of-flight alone, therefore, it is sometimes difficult to identify these doubly charged species. However, doubly charged ions of odd-mass have unique flight times and are easily recognized. Likewise, doubly charged ions with multiple isotopomers have half-integer isotope spacings and are also easily recognized. In the studies here, many of the metals employed have multiple isotopes that facilitate mass assignments.

3. Results

3.1. $Mg^{2+}(L)_n$ complexes

This investigation began with the accidental observation of $Mg^{2+}(CO_2)_n$ cluster ions during experiments on singly charged $Mg^+(CO_2)_n$ complexes. In the past, we had observed stable multiply charged complexes (e.g., $Ca^{2+}(H_2O)$ [34]), but this was the first time that we had seen any doubly charged complexes that are asymptotically unstable. Realizing the interest in these species, and the limited previous work in this area with laser vaporization sources, we decided to investigate the generality of the method for a variety of metal ions and ligands. In experiments with magnesium, the ligand species examined included Ar, H_2O, NH_3, CH_3CN, C_4H_8O (THF), CH_3OH, $(CH_3)_2CO$, C_6H_6 and C_2H_5OH. Doubly charged metal (Mg^{2+}) complexes were found to form with Ar or H_2O, but not

Table 1

Complex	IP(M^+)	IP(L)	μ(L)	α(L)	r_{cross} (Å)
$Mg^{2+}(Ar)$	15.03	15.8	–	1.64	–
$Mg^{2+}(CO_2)$	15.03	13.8	–	2.63	11.7
$Mg^{2+}(H_2O)$	15.03	12.6	1.85	1.48	6.2
$Mg^{2+}(CH_3CN)$	15.03	12.2	3.92	4.40	5.9
$Mg^{2+}(C_4H_8O)$	15.03	9.2	1.75	∼9	3.3
$Mg^{2+}(CH_3OH)$	15.03	10.8	1.71	3.23	3.9
$Mg^{2+}((CH_3)_2CO)$	15.03	9.7	2.88	6.39	3.3
$Mg^{2+}(C_2H_5OH)$	15.03	10.5	1.69	5.41	3.8
$Ti^{2+}(CO_2)$	13.57	13.8	–	2.63	–
$Fe^{2+}(Ar)$	16.18	15.8	–	1.64	37.8
$Fe^{2+}(CO_2)$	16.18	13.8	–	2.63	6.1
$Co^{2+}(Ar)$	17.05	15.8	–	1.64	11.6
$Co^{2+}(CO_2)$	17.05	13.8	–	2.63	4.6
$Co^{2+}(H_2O)$	17.05	12.6	1.85	1.48	3.7
$Si^{2+}(Ar)$	16.34	15.8	–	1.64	26.7

with the other ligands. Table 1 provides the ionization energetics for these species and the others discussed below.

Fig. 2 shows the mass spectrum measured for cluster ions of $Mg^{2+}(CO_2)_n$. Because of the isotopes of magnesium (24, 25, 26), the assignment of doubly charged ion peaks is readily made and unambiguous from the half-integer spacings. The doubly charged ions are present at the same time with a distribution of more intense singly charged complexes. The $^{24}Mg^+$ peak is off-scale in the figure, and some of the singly charged complex peaks exhibit broad widths due to space charge effects from the high ion densities. In both the singly and doubly charged complexes, the respective peak intensities are consistent with the naturally-occurring ratio of isotopic abundances. Under these conditions the doubly charged ions have intensities that are within about a factor of 5 of those for the corresponding singly charged ion. The largest signals are obtained from the $n = 1$ and 2 complexes, and the distribution extends out to $n = 5$ or so. However, these signal intensities are sensitive to several instrumental parameters as discussed below.

Extensive studies of the electronic spectroscopy and photodissociation processes of singly charged $Mg^+(CO_2)_n$ complexes have been reported previously by our research group [1,36]. We have recently reported infrared photodissociation spectroscopy for these species that probed their structures [37]. $Mg^{2+}(CO_2)_n$ clusters have been produced previously by other methods, but this is the first time that they

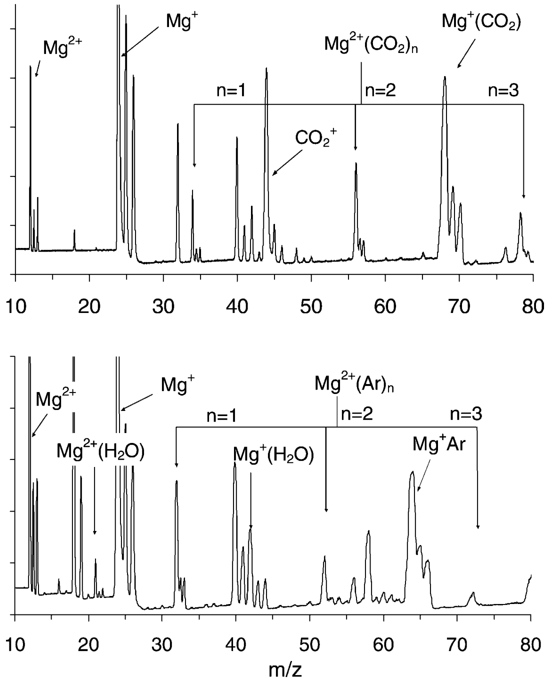

Fig. 2. The mass spectra measured for doubly charged complexes containing magnesium and carbon dioxide, argon and water.

have been made by laser vaporization. Spears et al. [38] studied the likelihood of charge transfer during collisions between Mg^{2+} and CO_2 within a flowing afterglow, and noted the presence of $Mg^{2+}(CO_2)_n$ clusters with $n \leq 6$. Stace and coworkers more recently examined the stability of $Mg^{2+}(CO_2)_n$ clusters as a function of size as part of a larger study of other $Mg^{2+}(L)_n$ systems [14–16].

Fig. 2 also shows a mass spectrum with $Mg^{2+}(Ar)_n$ and $Mg^{2+}(H_2O)$ complexes, again generated with the laser vaporization source. However, unlike the CO_2 complexes above, $Mg^{2+}(H_2O)_n$ clusters with $n > 1$ are not observed. The doubly charged ions are produced with similar conditions to those used for $Mg^{2+}(CO_2)_n$ complexes, and many singly charged complexes are again present in the mass spectrum. As noted above, the $Mg^{2+}(Ar)_n$ complexes are intrinsically stable, but the water complex is asymptotically unstable by about 3 eV. The water complexes can only be made in an expansion of argon. Experiments with a helium expansion gas or with a neon–helium (70–30%) mixture produced no measurable $Mg^{2+}(H_2O)$ signals. The signal levels from $Mg^{2+}(Ar)$ are substantial, and so we tried photodissociation for this ion at 355 nm. However, we were not able to measure any photodissociation from this ion.

The singly charged $Mg^{+}(Ar)_n$ clusters have been studied previously by our research group and electronic spectroscopy was reported for the $n = 1$ complex [39]. Velegrakis and Luder first reported the formation of the doubly charged complexes [33]. Likewise, our group and others have studied the singly charged $Mg^{+}(H_2O)_n$ complexes, and we reported a detailed study of the electronic spectroscopy of the $n = 1$ complex [40]. Doubly charged $Mg^{2+}(H_2O)_n$ clusters have been generated using both electrospray [10] and the "pick-up" method [14], but previous work with laser ablation [40–43] has not reported the analogous doubly charged complexes. The singly charged magnesium–water clusters are well-known to exhibit apparent intracluster reactions. Fuke and coworkers [42,43] showed that $Mg^{+}OH(H_2O)_{n-1}$ clusters are observed in greater abundance than $Mg^{+}(H_2O)_n$ when $5 < n < 15$. In addition, a photoinduced chemical reaction was observed leading to the production of $Mg^{+}OH(H_2O)_n$ ions. The hydration of Mg^{2+} has been extensively studied over the past 10 years. Theoretical work [44–51] has most frequently been directed toward a better understanding of the structure, coordination and solvation number of individual $Mg^{2+}(H_2O)_n$ clusters. Experimental studies [24,51–54] have yielded some quantitative information, such as sequential binding enthalpies [52], and evidence for a degree of chemical rearrangement between molecules in different solvation shells [53]. Collision-induced dissociation of doubly charged $Mg^{2+}(H_2O)_n$ complexes yields evidence for production of $Mg^{+}OH(H_2O)$ [53]. It has been suggested that a salt bridge structure between water molecules in the first and second solvation spheres facilitates proton transfer [53] in these systems.

3.2. $Ti^{2+}(CO_2)_n$

Based on our success in the production of doubly charged complexes of magnesium, we decided to investigate transition metals. We looked at titanium because it has a low second IP, and therefore many doubly charged complexes would be intrinsically stable. As expected, doubly charged complexes are easily made. Fig. 3 (lower trace) shows a mass spectrum in which clusters of $Ti^{2+}(CO_2)_n$ are present. The position of the peaks, the m/z increment separating clusters of different n and isotope abundance ratio of titanium are all consistent with the assignment of $Ti^{2+}(CO_2)_n$. This is the first observation to our knowledge of $Ti^{2+}(CO_2)_n$ clusters generated within a laser vaporization source. This species has $IP(M^{+}) < IP(L)$, so these complexes are stable. We did not investigate many other $Ti^{2+}(L)_n$ complexes because of the numerous mass coincidences that result from the mass of ^{48}Ti.

3.3. $Co^{2+}(L)_n$ complexes

Cobalt has a high second ionization potential (17.08 eV) and therefore its complexes should be difficult to stabilize with respect to charge transfer.

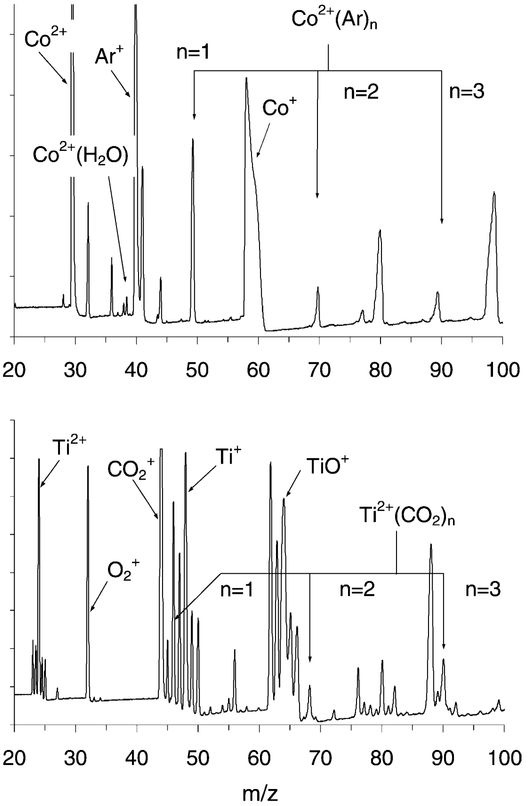

Fig. 3. The mass spectra measured for doubly charged transition metal ion complexes of cobalt and titanium.

The first molecule observed in combination with Co^{2+} was Ar, which was selected owing to the comparatively high first ionization potential of the atom (15.8 eV). The series of $Co^{2+}(Ar)_n$ cluster ions is shown in Fig. 3 (upper). Peaks are observed corresponding to half-integer *m*/*z* ratios of 49.5, 69.5 and 89.5, indicating doubly charged species assigned to $Co^{2+}(Ar)$, $Co^{2+}(Ar)_2$ and $Co^{2+}(Ar)_3$, respectively. Cobalt is mono-isotopic, preventing the confirmation of the assignment with isotope intervals. However, the spectrum contains no other peaks that are transmitted at half-integer *m*/*z* ratios. Singly charged $Co^{+}(Ar)_n$ clusters have been studied previously [55,56], but this is believed to be the first report of the generation of $Co^{2+}(Ar)_n$ clusters.

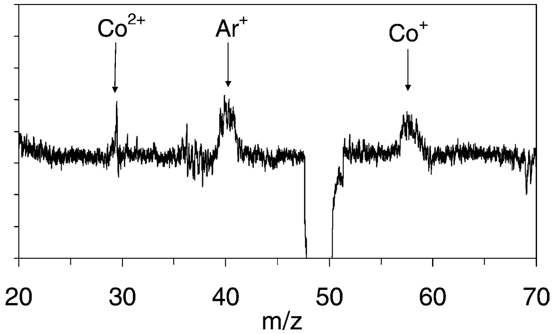

Fig. 4. The photodissociation mass spectrum of $Co^{2+}(Ar)$ at 355 nm. The large negative peak that is offscale indicates the depletion of the parent ion and $m/z = 49.5$, while the positive peaks indicate the photofragments produced.

The identity of $Co^{2+}(Ar)$ was confirmed with mass-selected photodissociation at 355 nm. Fig. 4 shows a difference mass spectrum in which the depletion of the selected parent ion is plotted in the negative direction (shown as a large off-scale peak) and the photofragments are plotted as positive peaks. The fragments observed include Co^{2+}, Ar^{+} and Co^{+}. The latter has an *m*/*z* value that is greater than the parent ion. Apparently, there are low-lying electronic states of the complex that allow some dissociation via the $Co^{2+} + Ar$ channel and some via the charge-transfer $Co^{+} + Ar^{+}$ state. Another possibility is that absorption occurs to the charge transfer state and some branching into these two fragment channels occurs by electron transfer at the curve crossing as the species move apart. The fragment ion masses seen for Co^{+} and Ar^{+} are broader than our typical mass resolution, which would be consistent with some kinetic energy release in the photodissociation process. This behavior is expected for dissociation off the repulsive wall of the $Co^{+} + Ar^{+}$ potential. Also consistent with this picture, the depletion of the parent ion is quite large, as indicated by the negative offscale peak. However, the fragment ions that reach the detector represent a much smaller signal. Loss of fragment ion signal would also be expected if there is kinetic energy release into the fragments.

$Co^{2+}(H_2O)$ is produced using conditions similar to those employed for $Mg^{2+}(H_2O)$. The instrumental parameters are optimized for the observation of the multiply charged species and the signal from Co^{+}

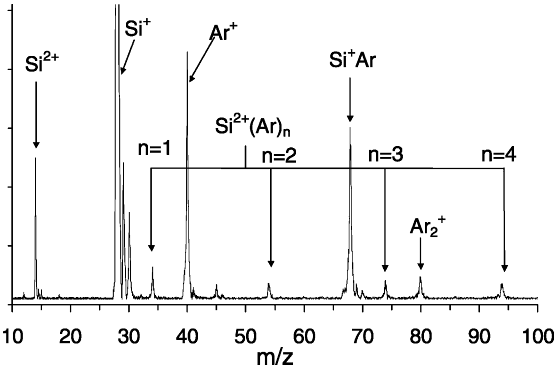

Fig. 5. The mass spectrum of doubly charged silicon–argon complexes.

is broadened by space-charge effects. The presence of a peak situated a half-integer *m*/*z* increment below the position of the peak assigned to $Co^{2+}(H_2O)$ provides confirmation of the assignment (Fig. 3). The signal from $Co^{2+}(H_2O)$ is accompanied by large peaks for the bare Co^{2+} ion and for $Co^{2+}(Ar)_n$ clusters. As in the case for the magnesium–water system, only the $n = 1$ complex is produced, and this complex can only be produced in an argon expansion. $Co^{2+}(H_2O)_n$ clusters have been generated previously by electrospray [10,13,57], and $Co^{2+}(H_2O)_n$ clusters with $n = 4$–7 have been characterized with electronic spectroscopy [57]. The difference between the second ionization potential of the metal and the first ionization potential of the ligand (4.48 eV) is greater in the case of $Co^{2+}(H_2O)$ than in any other M^{2+}–L combination studied during this work.

3.4. $Si^{2+}(Ar)_n$ complexes

Having made several metal complexes, we were interested to see if other related complexes could also be made. Complexes of $Si^{2+}(Ar)_n$ are shown in Fig. 5. Complexes of this species are identified readily and unambiguously within the mass spectra. The increment of 20 *m*/*z* units separating clusters with sequential values of *n* provides confirmation of the assignment. Laser vaporization was used previously by Velegrakis and coworkers [58] to generate $Si^+(Ar)_n$ clusters. However, this group did not present data from $Si^{2+}(Ar)_n$ complexes. Complexes of $Si^{2+}(Ar)_n$ are additional examples of cluster ions in which $IP(M^+) > IP(L)$ and their apparent stability therefore requires further explanation.

3.5. Other complexes

In the course of these survey experiments, several other metal ion ligand systems were also investigated. Small complexes of Fe^{2+} with argon and CO_2 were also apparently made, but mass coincidences precluded a conclusive assignment of these mass peaks. The principal isotopes of iron (^{56}Fe and ^{54}Fe) have even mass and the attachment of these to H_2O, CO_2 and Ar results in units that are also of even mass. Attempts to produce complexes of $Ni^{2+}(Ar)_n$ and $Al^{2+}(Ar)_n$ were also made, using similar conditions to those employed for Mg^{2+} and Co^{2+}. However, no doubly charged complexes were observed for these species.

4. Discussion

As shown here in these survey experiments, a variety of doubly charged metal ion complexes can be produced with laser vaporization. However, as indicated above, not all experiments were successful. As discussed earlier, the stabilization of doubly charged ions like these has required careful control of growth conditions in other sources. It is therefore important to consider how such cluster growth and stabilization is possible in the laser vaporization source. Although our experience so far is limited, we can already draw some conclusions from the results of these initial experiments. The most important variable governing the production of doubly charged metal ion complexes is the vaporization laser power. In other experiments designed to study singly charged ion complexes we typically employ 5–10 mJ/pulse, while these experiments use 40–60 mJ/pulse. The vaporization laser in both cases is focused with a 30 cm lens. The high laser power is believed to produce a hotter plasma with more energetic electron-metal collisions that can promote the higher energy ionization processes. The wavelength of the vaporization laser does not appear to matter so much. In the case of $Mg^{2+}(CO_2)_n$, for example, we have used the fundamental of the Nd:YAG laser (1064 nm), the second (532 nm) and the third harmonic (355) with comparable success. The generation of multiply charged complexes is favored by nozzle gas pulse durations shorter than usual, consistent with less efficient cooling of the complexes. In normal experiments on singly charged ions we use pulse durations of 200–250 μs, while the doubly charged complexes are optimized with pulses closer to 160–200 μs. In addition, the multiply charged species are typically observed within the leading component of a bimodal distribution of cluster ions. They are observed to arrive in the extraction region of the mass spectrometer earlier (by ∼100 μs) than the optimal distribution of singly charged cluster ions, which is typically observed in the apparatus ∼950 μs after the vaporization laser (with an argon backing gas). Apparently at the high laser power employed, the center of the gas pulse is superheated and cluster growth is inefficient here. Regions before and after this center time have metal in them via diffusion from the central vaporization zone. The leading part of the gas pulse spends less time at high pressure, and therefore complexes here experience fewer collisions with the expansion gas on average.

A final issue regarding the vaporization laser is its alignment relative to the gas flow channel that ends at the sample rod surface. We find that ion yields are often enhanced when the laser focus is misaligned slightly away from the gas flow. It is not clear whether this promotes direct ablation of metal as ions or whether it promotes the generation of photoelectrons that can then undergo collisional ionization of neutral metal. However, we find that this alignment procedure is important for the doubly charged ions in the same way that it was in the past for singly charged ions.

We have learned in our previous studies on singly charged complexes that electron–ion recombination is a critical consideration in both the growth and survival of ionized metal complexes. It is well known that recombination is efficient at the low temperatures of these supersonic expansions [59]. Unless we take special precautions, our source produces more neutral clusters than cations. As we have discussed elsewhere [1], to make singly charged metal ion complexes, we adjust the vaporization laser timing relative to the gas pulse so that vaporization occurs near the leading edge of the pulse where the gas density is lower. We believe that the lower gas density provides fewer collisions and a greater electron mobility. Fewer electrons are entrained in the gas flow and less neutralization takes place. Although these mechanistic details are difficult to prove, we find empirically that the timing adjustment of the vaporization laser relative to the gas pulse is critical for good ion yields. We have also found empirically that the addition of a small amount of water vapor to the expansion gas improves the singly charged ion yield, especially for weakly bound complexes (metal–argon or metal–neon) [1]. The mechanism for this appears to be that water acts as an electron scavenger, producing hydroxide ions and clusters, which are indeed observed in the negative ions from the same expansions. We employed these same general conditions to the formation of doubly charged ions. However, the exact vaporization laser timing and the amount of water vapor added varied from one metal to another.

Even with these adjustments of the source, it is still not possible to produce all the doubly charged metal ion complexes that we attempted to make. Some of the other considerations for the growth and stabilization of doubly charged metal ion complexes have been discussed previously by other groups active in this area [12,14–16]. Fig. 1 shows the relevant potential energy curves that govern the stability of these complexes. For so-called "stable" complexes (upper trace), the second IP of the metal is less than the first IP of the ligand, and metal–ligand binding is possible without charge transfer at all internuclear distances. $Mg^{2+}(Ar)_n$ or $Ti^{2+}(CO_2)_n$ complexes fall into this category. For asymptotically unstable complexes, $IP(M^+) > IP(L)$ and the lowest energy potential at long metal–ligand separations is that for the $M^+ + L^+$ species, which has a repulsive interaction. $Mg^{2+}(CO_2)$, $Mg^{2+}(H_2O)$, $Co^{2+}(Ar)$, $Co^{2+}(H_2O)$

and $Si^{2+}(Ar)$ complexes fall into this category. If a doubly charged metal ion approaches a neutral ligand, the $M^{2+} + L$ potential crosses that of $M^+ + L^+$ and charge transfer is possible, leading to dissociation of the complex. It is these complexes that are difficult to form and stabilize. However, at small values of r (internuclear separation), the interaction between M^{2+} and L lies at lower energy than that between M^+ and L^+ owing to the attractive ion-induced dipole interaction. If a complex can be produced on this inner bound portion of the potential, stable or "metastable" complexes can be formed and stabilized. The electrospray [10] source accomplishes this by desolvation of ions already existing in solution, while the "pick-up" method [14–16] accomplishes this using fragmentation or ionization of pre-formed neutral $M(L)_n$ and/or $M(L)_n(Ar)_m$ clusters. The "charge stripping" method [12,32] depends upon the ionization of a given singly charged species following impact with a neutral species. In each case ionization occurs after the complex components are already in close contact with one another. Even growth from separated components may also be possible if charge transfer is inefficient. In a study of the approach of Ti^{2+} to various alkenes by Weisshaar and coworkers [60,61], it was concluded that electron transfer occurred efficiently only when the potential energy surfaces cross at distances below 7 Å. Spears et al. [38] had earlier suggested that the comparatively large value of r_{cross} might account for the extremely slow rate constant measured for charge transfer during collisions between Mg^{2+} and CO_2. Stace and coworkers [14–16] have since used a simple electrostatic model to calculate r_{cross} from the difference in ionization potentials between the metal and ligand, the dipole moment (μ) and polarizability (α) of the ligand. They showed that Mg^{2+} complexes where the potential energy surfaces cross at longer distances have a tendency to be stable at smaller cluster sizes. So, in this previous work, the crossing distance seems to be important for both the growth of doubly charged complexes and their stabilization in environments where many collisions are present.

The formation of multiply charged clusters in the laser vaporization source appears to have less in common with electrospray sources and more features in common with the pick-up source. In every case that doubly charged clusters are produced, there is already a large density of neutral and singly charged complexes present. In the laser vaporization process, a hot plasma is produced and energetic electrons are present from the metal vaporization process. The conditions are more extreme at high laser pulse energies, which are employed here. It thus seems likely that electron impact or Penning ionization of pre-grown neutral or singly ionized clusters could account for the formation of the doubly charged species seen here. Ionization of neutrals or singly charged ions produces the doubly charged species when the ligands are already bound at close range, thus bypassing the opportunity for charge transfer in traversing the curve crossing region. However, as noted before by Stace and coworkers [14–16], there is correlation with the complexes that we can produce and stabilize and the potential curve crossing point. Table 1 shows the crossing distances for each of the complexes studied here, which are calculated according to the model provided by Stace and coworkers [14–16]. The complexes of $Mg^{2+}(CO_2)_n$, $Mg^{2+}(Ar)_n$, $Co^{2+}(Ar)_n$ and $Si^{2+}(Ar)_n$ which we are able to produce all have crossing distances that are greater than 11 Å. This figure is significantly greater than the upper limit suggested by Weisshaar to be necessary for charge transfer to occur. The $M^+(L)_n$ complexes which we were not able to produce (Mg^{2+} with NH_3, CH_3CN, C_4H_8O (THF), CH_3OH, $(CH_3)_2CO$, C_6H_6 and C_2H_5OH; Co^{2+} with CO_2) all have extremely short crossing distances. It makes sense that these complexes are difficult to produce initially or they are hard to stabilize under the collisional environment in our source.

Both $Mg^{2+}(H_2O)$ and $Co^{2+}(H_2O)$ exhibited unusual behavior in that only the $n = 1$ complexes were seen, and it was found that argon expansions are necessary for their formation. These complexes are produced with weaker intensity than $Mg^{2+}(Ar)_n$ and $Co^{2+}(Ar)_n$, which are simultaneously present in the respective mass spectra and it is not possible to form these ions except when the argon complexes are present. Spontaneous dissociative proton transfer has been observed previously in $Ca^{2+}(H_2O)_n$ complexes formed by sequential ligation [35] from bare elemental dications and it is possible that a similar behavior is displayed by both $Co^{2+}(H_2O)_n$ and $Mg^{2+}(H_2O)_n$ here. This process would involve the dissociation of $M^{2+}(H_2O)_n$ to yield $M^+OH(H_2O)_{n-1}$ and H_3O^+, and could only occur when $n > 1$. It is conceivable that such a process destroys larger clusters, leaving only the $n = 1$ complex behind. However, it is also true that the surfaces described by these metal/water reactants cross at much shorter distances than the other $M^{2+}(L)$ complexes observed. A formation mechanism involving sequential ligation would not be consistent with that proposed above for the formation of $Mg^{2+}(CO_2)_n$, $Mg^{2+}(Ar)_n$, $Co^{2+}(Ar)_n$ and $Si^{2+}(Ar)_n$ complexes. An alternative mechanism (see below) is consistent with the data from the various complexes, and would permit the stability of $Co^{2+}(H_2O)_n$ and $Mg^{2+}(H_2O)_n$ to be understood despite short crossing distances.

It is proposed that the water complexes are formed via substitution reactions with existing $M^{2+}(Ar)_n$ complexes. Argon atoms may then be ejected during the subsequent fragmentation of the cluster, yielding $M^{2+}(H_2O)$. No mixed complexes of $M^{2+}(H_2O)(Ar)_n$ or complexes of $M^{2+}(H_2O)_n$ with $n > 1$ are present in either mass spectrum. The intensity of peaks corresponding to $Mg^{2+}(H_2O)$ and $Co^{2+}(H_2O)$ are quite weak and these larger complexes could be present in smaller amounts and not detected with our sensitivity. The formation of $M^{2+}(H_2O)_n$ complexes with $n > 1$ may also be inhibited by the low intensity of $M^{2+}(Ar)_n$ with $n > 4$.

5. Conclusions

Several examples of both stable and asymptotically unstable doubly charged metal ion complexes (and those with silicon) are produced by a laser vaporization cluster source. Examples in this initial survey include $Mg^{2+}(CO_2)_n$, $Mg^{2+}(H_2O)$, $Co^{2+}(Ar)_n$, $Co^{2+}(H_2O)$, $Si^{2+}(Ar)_n$ and $Ti^{2+}(CO_2)_n$ complexes. Plausible mechanisms can explain the cluster growth in this environment, and the growth and stability patterns seen make sense in light of previous ideas (crossing point position) about these complexes. Several complexes are produced that have been seen previously with other sources, and some new complexes are reported for the first time. Argon and CO_2 complexes are formed with several ions, consistent with the relative stability expected for these complexes because of their long range charge-transfer curve crossing points. Water complexes with Mg^{2+} and Co^{2+} are proposed to form by substitution reactions with an existing doubly charged complex of $M^{2+}(Ar)_n$.

The laser vaporization source provides a convenient alternative to other sources that produce multiply charged ions in the gas phase. It is inherently a pulsed source, and so the ions provided come in intense packets suitable for interrogation with pulsed laser spectroscopy (e.g., photodissociation). The intensities of the ion signals seem to be comparable to those provided with other sources. Like the pick-up method, the laser vaporization source provides an advantage over electrospray sources in that complexes with non-solvent ligands (Ar, CO_2, etc.) can be produced. The laser source also provides a more general method with which to obtain clusters from a wide variety of refractory materials. We have found that many variables determine the optimization of this source, but the initial results are promising in that many complexes were produced. Further investigations of this method are clearly warranted for the study of photodissociation spectroscopy, collision-induced dissociation and/or ion–molecule reactions.

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