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Cluster ion studies of Ho^{2+} and Ho^{3+} solvation in the gas phase

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Abstract

An attempt has been made to prepare triply charged ions of holmium in association with a range of solvent clusters. Neutral atoms of holmium are generated in the gas phase using an effusive oven and are crossed with a beam consisting of solvent/argon clusters. Collisions between the holmium atoms and the clusters lead to the formation of neutral metal–solvent complexes. Ionisation by electron impact in the source of a high resolution mass spectrometer enables measurements to be undertaken on the intensities and fragmentation patterns of the resultant ions as a function of size. Only singly and doubly charged complexes are observed when water and methanol are used as solvents. Stable triply charged complexes are formed with the solvents acetone and acetonitrile, and intensity measurements suggest the preferred coordination number in both cases is 6. Measurements following the collisional activation of the holmium/acetonitrile complexes show evidence of chemical reactivity. (Int J Mass Spectrom 188 (1999) 113–119) © 1999 Elsevier Science B.V.

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1. Introduction

Recent success in our laboratory toward the production of intense beams of gas phase cluster ions comprising of a doubly charged metal ion, M^{2+}, solvated by a variable number of ligand molecules, L_n [1–5], has prompted an investigation into the feasibility of using the cluster beam pick-up technique to generate triply charged clusters of the type $[ML_n]^{3+}$. Such ions were first studied in the gas phase by Kebarle and co-workers [6] using an electrospray ion source with triple quadrupole mass spectrometric detection. It was observed that triply charged clusters could be produced via the electrospray of M^{3+} salts with dipolar aprotic solvents, namely dimethylsulfoxide (DMSO) or dimethylformamide (DMF), for a series of metal ions, M = yttrium, lanthanum, cerium, neodymium or samarium. Ion abundances for the $[ML_n]^{3+}$ species were low however, thus making quantitative determinations of ion/ligand bond energies by ion equilibria [7,8] or threshold collision-induced dissociation [9] methods more difficult than is the case for doubly charged ions. No triply charged hydrates, $[M(H_2O)_n]^{3+}$, were observed by Kebarle and co-workers [6], even under “mild” electrospray conditions where in previous work [7,8], M^{2+} salts had led to abundant hydrates of the form $M(H_2O)_n^{2+}$. Species observed using M^{3+} salts were always in the form of the charge reduced variant, $MOH(H_2O)_n^{2+}$.

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Dedicated to Brian Green for his many innovative contributions to mass spectrometry instrument development and for his tireless help in teaching us how to take advantage of them.

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Other research groups [10,11] have also studied the electrospray of trivalent metal salt solutions. The primary motivation behind their work [10,11] was to determine whether there is a correlation between the distribution of ions in an electrospray mass spectrum and the distribution of ions in the bulk solution. If such a correlation exists, electrospray may be used as a reliable elemental speciation technique. In agreement with Kebarle and co-workers [6], Cheng et al. [10] found that with protic solvents, such as H_2O and CH_3OH, only the charge reduced, solvent derived oxide species were observed in the mass spectra. Again it was found that only the aprotic solvents, DMSO and CH_3CN, were capable of preserving the expected solution phase charge state of the metal ions and produce $[ML_n]^{3+}$ clusters as their principal species. The difference in species produced is ascribed to the presence or absence of labile protons, and hence the relative propensity for metal–solvent–oxide formation, in these two classes of solvent.

Stewart and Horlick performed an extensive study of the electrospray mass spectra of lanthanide metal salt solutions [11]. Again, no $[ML_n]^{3+}$ clusters were observed in protic solvents. Their study involved monitoring, via a cone voltage fragmentation technique, the declustering processes taking place in the production of bare metal and molecular ions from solvated ions. The relative intensities of M^{2+}, M^+, and MO^+ species in the declustered mass spectra for metals at the beginning of the lanthanide series (light M) were found to be different to those for heavier metals toward the end of the series. This observation was interpreted in terms of the chemical and physical properties of the metal and solvent system, namely trends in the difference in ionisation potential between metal, $IP(M^{2+})$, and solvent, IP(L), and the ease with which the metal ion will form an oxide [11].

It is notable that no doubly charged species (ML^{2+}) that did not contain the metal–solvent–oxide unit or metal–counter–ion unit were reported in any of the above electrospray studies of lanthanide metal salt solutions. Such ions are not expected to be present in large concentrations in bulk solution, although Eu^{2+}(aq), Yb^{2+}(aq), and Sm^{2+}(aq) are metastable [12]. Perhaps in accord with this enhanced stability, clusters of the form $Eu(H_2O)_n^{2+}$ and $Eu(CH_3OH)_n^{2+}$ have been observed recently in an electrospray study by Woodward and co-workers [13] using solvent doped nebulising and drying gases. These species show interesting cluster size distributions characterised by a switch in intensity ratio between the solvent–metal ion clusters, e.g. $Eu(CH_3OH)_n^{2+}$, and the solvent–metal–oxide derived clusters, e.g. $EuOCH_3(CH_3OH)_n^{2+}$. Similar switching in intensity has been observed in studies of the singly charged alkaline earth analogues of these systems, incorporating magnesium, calcium and strontium, by ourselves [3,4] and others [14–17].

In this article we report the results of attempts to investigate the feasibility of using the pick-up technique [1–5] to produce cluster ions of the form $[Ho(L)_n]^{3+}$, where L is either acetone, acetonitrile, methanol, or water.

2. Experimental

Argon as a carrier gas was passed through a reservoir containing a solvent in its liquid state, and the gas/vapour mixture was allowed to undergo supersonic expansion through a pulsed conical nozzle, with a backing pressure of typically 30 psi. The resulting solvent/argon cluster beam passed through a skimmer 2 cm downstream, before entering the “pick-up” region. Holmium vapour was generated by using a commercial Knudsen effusion cell operated at 1250 °C, which resulted in a partial pressure of metal atoms of approximately 10^{-2} Torr immediately above the cell. Previous work [1–5] has shown this to be the optimum partial pressure range for the efficient production of mixed solvent/metal clusters. A shutter at the exit of the effusion cell is used to confirm the identity of clusters containing holmium. Where a survey is performed of the relative intensities of parent ions of a given series, the difference is taken between the signal intensity with the shutter open and closed. This treatment acknowledges and removes the contribution of any background that is not dependent on material originating in the effusion cell.

Crossing the region above the effusion cell, some

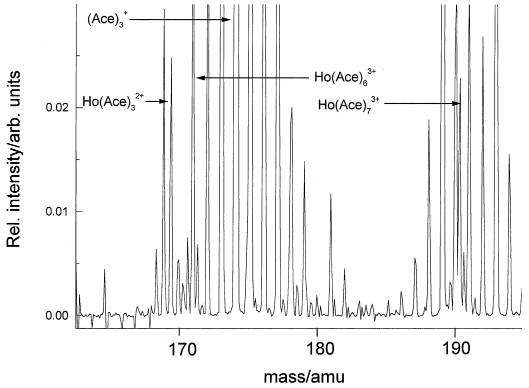

Fig. 1. Section of a mass spectrum recorded following the ionisation of mixed clusters of holmium with acetone.

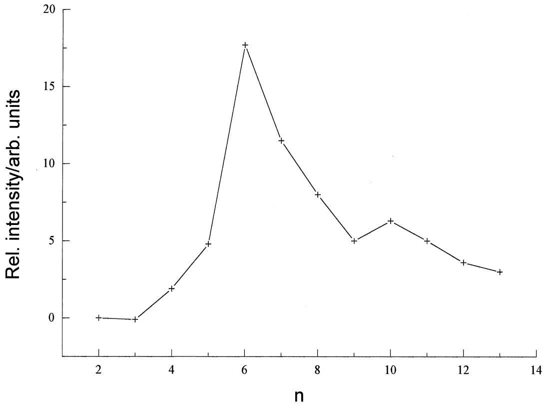

Fig. 2. Relative intensities of $[Ho(CH_3COCH_3)_n]^{3+}$ cluster ions plotted as a function of n.

of the mixed solvent/argon clusters pick up an atom of holmium, simultaneously ejecting many of the argon atoms in order to disperse excess energy. Again, previous work [1–5] has shown that the presence of argon is crucial to the success of the pick-up process. Approximately 70 cm downstream from the skimmer, the neutral clusters of $Ho(L)_n$ pass into the ion source of a VG ZAB-E high resolution mass spectrometer, where they are ionised by 100 eV electron impact. The mass spectrometer has reverse geometry, which means that ions pass through a magnetic sector and an electrostatic analyser (ESA) prior to detection at a Daly scintillation detector. Experiments on collisional activation are facilitated by the presence of a gas cell in the field-free region between the magnet and the ESA. When referenced to the mass increments separating singly charged ions, doubly and triply charged species appear in the mass spectra at half integer and one-third integer intervals, respectively.

3. Results and discussion

3.1. Acetone (CH_3COCH_3)

A short section of a mass spectrum recorded for the holmium/acetone/argon system is shown in Fig. 1. As can be seen, there are many peaks that correspond to ions that do not contain holmium, which are a consequence of the presence of acetone and mixed argon/acetone clusters in the beam; a feature of the experiment that is necessary for success of the pick up process. Holmium readily forms both doubly and triply charged complexes with acetone. Of the two triply charged ions identified in Fig. 1, $[Ho(CH_3COCH_3)_6]^{3+}$ is coincident with the position of a singly charged species, but $[Ho(CH_3COCH_3)_7]^{3+}$ is not. Also present are doubly charged ions of the form $[Ho(CH_3COCH_3)_n]^{2+}$, and a further series of ions that can be attributed to doubly charged mixed clusters of $[Ho(CH_3COCH_3)_n(H_2O)]^{2+}$, and are probably formed as a result of the trace presence of water within the apparatus.

The relative intensities of the triply charged ions $[Ho(CH_3COCH_3)_n]^{3+}$ are shown in Fig. 2. For most values of n the ions occur at one-third integer mass units (and therefore where there is a negligible contribution from singly charged ions in the background), when n is a multiple of 3, the ions of interest are coincident with singly charged species. Taking the difference between the signal observed when the shutter is open and shut ensures that any contribution from singly charged species does not affect the data.

The distribution of ion intensities shows a pronounced maximum at $n = 6$, and ions were observed to be stable at values of n as low as 2. The lower limit

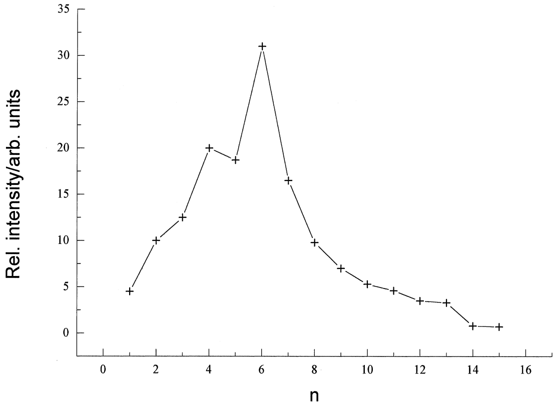

Fig. 3. Relative intensities of $[Ho(CH_3COCH_3)_n]^{2+}$ cluster ions plotted as a function of *n*.

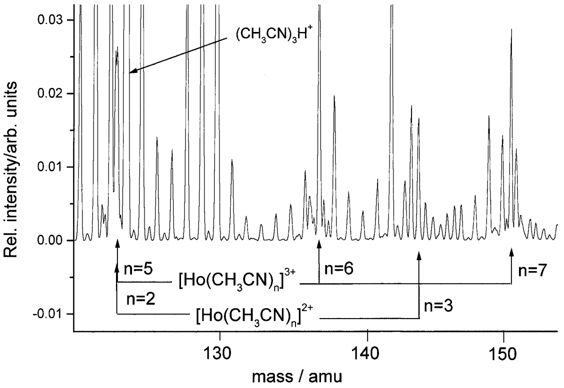

Fig. 4. Section of a mass spectrum recorded following the ionisation of mixed clusters of holmium with acetonitrile.

is determined by the ability of the solvent molecules to stabilise the triple charge on the metal ion against charge transfer. The ionisation energy (IE) of Ho^{2+} is 23.0 eV, which is significantly larger than that of acetone (9.70 eV). Hence, a single acetone molecule in the presence of the metal ion will induce charge transfer, but as the number of solvent molecules increases, the complex as a whole becomes stabilised through electron donation from the ligands. The existence of a maximum in the intensity distribution could be linked to the completion of a stable solvation shell, and a solvation shell of six molecules for Ho^{3+} would be consistent with measurements from other, condensed phase, studies on lanthanide ions [18]. The relative intensities of $[Ho(CH_3COCH_3)_n]^{2+}$ clusters were also monitored as a function of n, and the results are shown in Fig. 3. All ions of the series were easily distinguished because their odd mass means that they appear at half integer positions relative to any singly charged ions in the mass spectrum. A peak in the intensity distribution was observed at $n = 6$, but there is also a less pronounced peak at $n = 4$.

Of additional interest is the presence in Fig. 3 of an ion of measurable intensity when $n = 1$, which is quite an unusual feature in doubly charged systems [1–9]. It indicates that one acetone molecule is sufficient to stabilise a double charge on the holmium (IE of $Ho^+ = 11.80$ eV) thus reducing the propensity to charge transfer and coulomb explosion. Obviously, the comparatively low second ionisation energy of holmium makes an important contribution to this observation.

3.2. Acetonitrile (CH_3CN)

A short section of a mass spectrum obtained for the $Ho/Ar/CH_3CN$ system is shown in Fig. 4. The system yields stable doubly and triply charged ions of holmium with acetonitrile, and these are indicated in the mass spectrum. Once again, there are coincidences between singly charged ions and both doubly and triply charged species. Where the complex is doubly charged, coincidences occur at odd n. For triply charged ions, coincidences occur where n is a multiple of 3. A complicating feature of the mass spectrum is the close proximity of many doubly and triply charged ions. As indicated in Fig. 4, $[Ho(CH_3CN)_5]^{3+}$ and $[Ho(CH_3CN)_2]^{2+}$ are separated by just 0.2 m/z. The high number of coincidences complicates the acquisition of a detailed parent ion intensity distribution as a function of cluster size. However, an inspection of Fig. 4, certainly suggests that $[Ho(CH_3CN)_6]^{3+}$ is the largest of the triply charged ions shown, which would be consistent with earlier results shown for acetone.

Selected $[Ho(CH_3CN)_n]^{3+}$ ions were subjected to collisional activation and the consequences were ana-

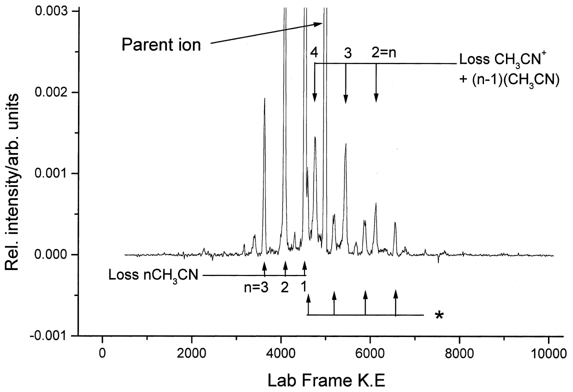

Fig. 5. MIKE scan recorded following the collisional activation of $[Ho(CH_3CN)_7]^{3+}$ using air as the collision gas at a pressure of 10^{-6} mbar. Fragments corresponding the loss of nCH_3CN or $(n - 1)CH_3CN + CH_3CN^+$ are labeled. Fragments labeled with an asterisk correspond to the additional loss of either HCN or CN.

lysed using the MIKE technique [19]. A typical result for $[Ho(CH_3CN)_7]^{3+}$ is shown in Fig. 5, where two separate processes give rise to a major fraction of the fragments seen. These are (1) the loss of up to four neutral molecules, leaving triply charged fragment ions and (2) charge transfer to give CH_3CN^+ which is then lost from the parent ion, accompanied by between one and three neutral molecules to leave a doubly charged metal ion. The latter process (Coulomb explosion) causes the resultant fragments to have a large kinetic energy spread (and therefore a broader peak shape). Also present in Fig. 5, are a further series of peaks due to Coulomb explosion, but where charge transfer is accompanied by a chemical reaction (this series of ions is denoted by an asterisk in Fig. 5). The calculated mass identifies the ejected fragment as either CN, or HCN; unfortunately the width of the peak is sufficient to embrace both these possibilities. Neither neutral loss makes a significant contribution to the fragmentation pattern of isolated CH_3CN^+ in a typical mass spectrum; however, the fragment could be the product of an internal ion–molecule reaction that takes place prior to charge separation. The only other reactions identified thus far in these experiments have involved Mg^{2+} and Sr^{2+} in association with primary alcohols [1,3,4].

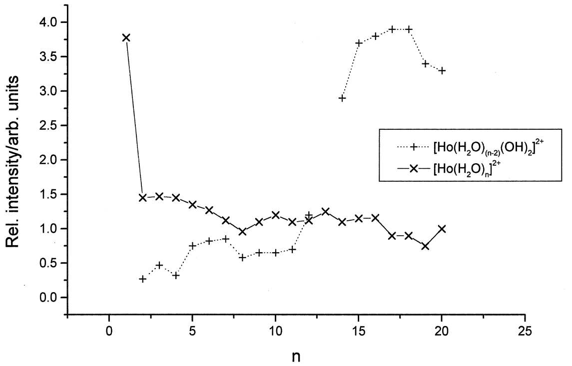

Fig. 6. Relative intensities of $[Ho(H_2O)_n]^{2+}$ and $[Ho(H_2O)_{n-2}](OH)_2]^{2+}$ plotted as a function of n.

3.3. Water (H_2O)

The characteristics of doubly charged complexes of holmium with water were also studied, and experiments undertaken in order to establish whether triply charged complexes of holmium could be formed using water as a ligand. From the mass spectra, it was possible to identify doubly charged clusters of the form $[Ho(H_2O)_n]^{2+}$. Mass coincidence with singly charged ions precluded the study of $[Ho(OH)(H_2O)_{n-1}]^{2+}$ species directly, but ions corresponding to $[Ho(OH)_2(H_2O)_{n-2}]^{2+}$ and $[Ho(OH)_4(H_2O)_{n-4}]^{2+}$ were also observed, and found to have comparable intensities to the hydrated species. Unfortunately, triply charged cluster ions of the form $[Ho(H_2O)_n]^{3+}$ were difficult to identify in the mass spectra, possibly because they are all coincident with singly charged ions of one-third their mass. To circumvent this problem, D_2O was used in a separate series of experiments, and these results are discussed here.

The recorded intensities of the doubly charged clusters $[Ho(H_2O)_n]^{2+}$ and $[Ho(OH)_2(H_2O)_{n-2}]^{2+}$ are plotted in Fig. 6 a function of n. As with the results presented for acetone, it is interesting to note that an intense ion corresponding to $[Ho(H_2O)]^{2+}$ was observed; however, in this case the probability of charge transfer is very low because the ionisation energy of H_2O (12.61 eV) is larger than that of Ho^+. With the exception of $n = 1$, the intensities of the

$[Ho(H_2O)_n]^{2+}$ ions shown in Fig. 6 remain approximately constant, however, those of the doubly dehydrogenated ion increase abruptly between $n = 11$ and $n = 14$; unfortunately data could not be recorded for the ion at $n = 13$. Previous observations on Mg^+/H_2O complexes [14–16] have attributed changes in intensity between $Mg(H_2O)_n^+$ and $MgOH(H_2O)_{n-1}^+$ as n increases, to the enhanced stability of Mg^+–OH compared with Mg^+–H_2O. The transition being driven by a combination of Mg–OH bond energy and progressive solvation [14–16].

3.4. Deuterium dioxide (D_2O)

By carefully conditioning the expansion nozzle and inlet system with D_2O, it was possible to generate mixed clusters of holmium and deuterium oxide, with minimal interference from H/D exchange on the surfaces of the apparatus. Use of the heavier isotope avoided the mass coincidences experienced using H_2O, thus facilitating the search for triply charged complexes. However, the recorded mass spectra just confirmed the results for doubly charged ions containing water, and showed no evidence of triply charged $[Ho(D_2O)_n]^{3+}$ clusters.

3.5. Methanol (CH_3OH)

The recorded mass spectra for holmium/methanol cluster ions showed evidence of peaks corresponding to $[Ho(CH_3OH)_n]^{2+}$, and $[Ho(OCH_3)_2(CH_3OH)_{n-2}]^{2+}$ but no triply charged complexes were apparent in any of the spectra. A survey of the relative intensities of the $[Ho(CH_3OH)_n]^{2+}$ and $[Ho(OCH_3)_2(CH_3OH)_{n-2}]^{2+}$ cluster ions is shown in Fig. 7. Because of a mass coincidence, it was not possible to identify peaks corresponding to the singly dehydrogenated species, $[Ho(OCH_3)(CH_3OH)_{n-1}]^{2+}$, for any value of n. The pattern in Fig. 7 shows an overall trend of increasing signal intensity in the $[Ho(CH_3OH)_n]^{2+}$ ions. There appears to be additional structure associated with an alternation in the relative intensities of both series of ions, which depends on whether Ho^{2+} has an odd or an even number of solvating methanol molecules. The data imply that, once a threshold is crossed at $n = 4$, an even number of ligands creates a more stable structure than an odd number. It is quite possible that the primary solvation shell consists of four molecules, and that once formed, additional methanol molecules are then hydrogen bonded to the underlying structure. For reasons, as yet unexplained, the data would suggest that the addition of pairs of methanol molecules to such a unit is favoured over single entities.

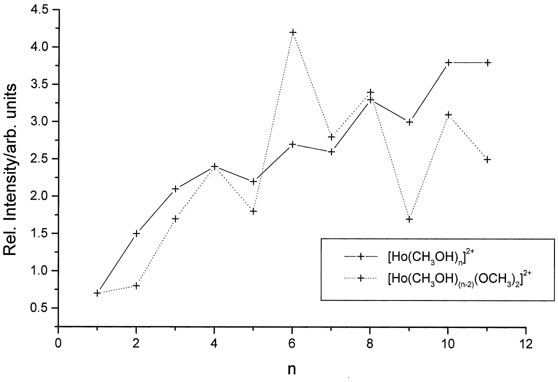

Fig. 7. Relative intensities of $[Ho(CH_3OH)_n]^{2+}$ and $[Ho(CH_3OH)_{n-2}(OCH_3)_2]^{2+}$ plotted as a function of n.

3.6. Ammonia

Ammonia was investigated as a possible solvent for multiply charged holmium ions; however, no evidence of either doubly or triply charged complexes could be found.

4. Conclusion

We have attempted to use the pick-up technique to generate solvent complexes containing Ho^{3+}. As observed in earlier experiments on lanthanides by Kebarle and co-workers [6], only aprotic solvents appear capable of preserving the triple charge on the metal ion. The presence of water and methanol as solvents resulted in production of the charge-reduced variants, $HoOH(L_n)^{2+}$ and $HoOCH_3(L_n')^{2+}$, respectively. The fact that two very different preparative methods yield similar observations would suggest that charge reduction is an intrinsic property of the solvated clusters. It appears that high oxidation states have to be stabilised by ligands that form strong bonds with the metal ion. Both water and methanol are relatively poor electron donors, and when coordinated to a cation with a high oxidation state, the latter polarises the electron density on the oxygen atom to a point where the O–H bond is significantly weakened. A thermodynamic rationale of the process has been presented by Kebarle and co-workers [7].

Triply charged complexes of holmium were produced using acetone and acetonitrile as solvents. In the case of acetone, complexes of the form $[Ho(CH_3COCH_3)_n]^{3+}$ showed evidence of the formation of a stable solvation shell at $n = 6$, and acetonitrile would appear to exhibit a similar trend. The collisional activation of $[Ho(CH_3CN)_n]^{3+}$ clusters produced evidence of a chemical reaction which may result from an internal ion molecule process prior to charge separation.

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