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A low-energy CAD study of the ions $\text{MOH}(\text{H}_2\text{O})^+$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) and $[\text{M}(\text{H}_2\text{O}_2)]^+$ ($\text{M} = \text{Cr}, \text{Fe}, \text{La}, \text{Pr}$)

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Abstract

The ions $[\text{MOH}(\text{H}_2\text{O})]^+$ ($\text{M} = \text{divalent Mn, Co, Ni, Cu, Zn}$) and $[\text{M}, \text{O}_2, \text{H}_2]^+$ ($\text{M} = \text{trivalent Cr, Fe, La, Pr}$) have been formed using an electrospray technique from aqueous solutions of metal salts. Their low-energy, collisionally activated dissociations have been studied in a triple sector instrument. At the lowest collision energies, $[\text{MOH}(\text{H}_2\text{O})]^+$ ($\text{M} = \text{Co, Mn, Ni,}$) dissociates by loss of water, but with increasing energy loss of OH and formation of $[\text{M}(\text{H}_2\text{O})]^+$ becomes the major reaction. This behavior correlates more with M^+OH than with $\text{M}^+\text{—OH}_2$ bond energies. $[\text{ZnOH}(\text{H}_2\text{O})]^+$ dissociates only to $[\text{ZnOH}]^+$ at all available collision energies, which is inconsistent with published relative bond energies. $[\text{CuOH}(\text{H}_2\text{O})]^+$ dissociates to $[\text{Cu}(\text{H}_2\text{O})]^+$ and OH at low collision energy, but $[\text{CuOH}]^+$ becomes slightly greater in yield at high energy, implying that, in $[\text{CuOH}(\text{H}_2\text{O})]^+$, $\text{D}(\text{Cu}^+\text{—OH})$ is less than $\text{D}(\text{Cu}^+\text{—OH}_2)$. The dissociation spectra of $[\text{M}, \text{O}_2, \text{H}_2]^+$ ($\text{M} = \text{Cr, Fe,}$) which may be $[\text{M}(\text{OH})_2]^+$, show only loss of water at low collision energy, yielding MO^+ , but with increasing collision energy simple bond scission yields $[\text{MOH}]^+$ as the major product. $[\text{M}, \text{O}_2, \text{H}_2]^+$ ($\text{M} = \text{La, Pr}$) shows the same behavior, but the threshold energy for the appearance of MOH^+ is much higher, consistent with the considerably higher $\text{M}^+\text{—O}$ bond energy. (Int J Mass Spectrom 202 (2000) 251–259) © 2000 Elsevier Science B.V.

Keywords: Collisionally activated dissociation; Metal complexes; Hydrates; Hydroxides; Oxides

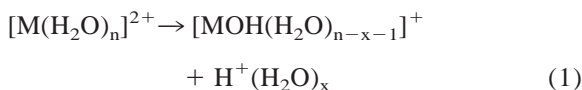
1. Introduction

The study of hydrated metal ions $[\text{M}(\text{H}_2\text{O})_n]^{m+}$ in the gas phase received tremendous attention after the introduction of the electrospray technique, because such ions cannot be formed by the sequential addition of water molecules to the bare metal ions. The formation and properties of singly and doubly charged metal hydrates have been investigated [1–8]. Theoretical calculations on the structures and hydration energies of metal cations have provided complementary informa-

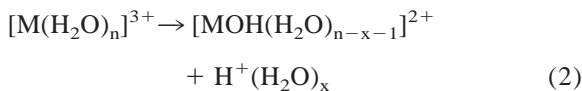
tion [9–11]. $[\text{M}(\text{H}_2\text{O})_n]^+$ ions with $n = 0, 1, 2, \dots$ are readily obtained by the electrospray technique from aqueous solutions of alkali metal salts and $[\text{M}(\text{H}_2\text{O})_n]^{2+}$ ions are readily obtained from aqueous solutions of alkaline earth and some transition metal salts. There is, however, a tendency for the hydrates of the divalent transition metal ions to be unstable if n is small when formation of the singly charged, hydrated metal hydroxide, $[\text{MOH}(\text{H}_2\text{O})_{n-1}]^+$, becomes competitive with the formation of $[\text{M}(\text{H}_2\text{O})_n]^{2+}$ [4]. Collisionally activated dissociation (CAD) of $[\text{M}(\text{H}_2\text{O})_n]^{2+}$, either in the interface region of the electrospray source or in a collision cell after

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ion extraction, leads to charge reduction by interligand proton transfer followed by loss of $\text{H}^+(\text{H}_2\text{O})_x$ [Eq. (1)].



Attempts have been made, so far unsuccessfully, to form triply charged hydrates $[\text{M}(\text{H}_2\text{O})_n]^{3+}$ in the gas phase by electrospray [2] or by the pick-up technique in which argon/water/metal atom clusters are ionized by an electron beam [11]. The fact that no $[\text{M}(\text{H}_2\text{O})_n]^{3+}$ ions have been observed implies that, due to the very high third ionization energies of all metal ions, the $[\text{M}(\text{H}_2\text{O})_n]^{3+}$ ions, which are present in aqueous solution, are unstable and spontaneously react via interligand proton transfer when transferred to the gas phase. The major ions seen in the electrospray spectra are the doubly charged hydrates of the metal hydroxides formed by interligand proton transfer [Eq. (2)]. If sufficiently large solvent shells containing a single metal ion could be formed, then gas-phase $[\text{M}(\text{H}_2\text{O})_n]^{3+}$ ions should be observable. How large such a shell must be is at present not known.



In this article we report on an investigation of the collisionally activated dissociation of singly charged, metal-containing ions $[\text{MOH}(\text{H}_2\text{O})]^+$ formed in an electrospray source from aqueous solutions containing first-row transition metal ions, $\text{M}^{2+}(\text{aq})$. CAD of $[\text{MOH}(\text{H}_2\text{O})]^+$ could lead to the loss of either OH or H_2O , forming $[\text{MOH}]^+$ or $[\text{M}(\text{H}_2\text{O})]^+$ respectively. Which neutral is preferentially lost for a given metal should depend on the relative strengths of binding of the two ligands, OH and H_2O , in the precursor ion. This property varies significantly across the first row of the transition metal series [12, 13]. We also investigated the electrospray spectra of aqueous solutions of some trivalent metal ions from the first row transition metal series and the actinide series. No $[\text{M}(\text{H}_2\text{O})_n]^{3+}$ ions were observable nor was any ion obtainable corresponding to $[\text{MOH}(\text{H}_2\text{O})]^+$. However, a singly charged ion with empirical formula $[\text{M}_2\text{O}_2\text{H}_2]^+$ was obtained for all the metals studied,

and we report on its collisionally activated dissociation. The results are interpreted in terms of the known, but limited, thermochemistry of metal hydroxide and oxide ions.

2. Experimental

Electrospray spectra were obtained using a triple sector mass spectrometer (quadrupole/hexapole/quadrupole, Quattro, FISIONS, UK) in the manner that has been described previously [7, 14, 15]. Aqueous solutions (1×10^{-3} M) of di- and trivalent metal salts were infused using a syringe pump at a flow rate of $5 \mu\text{L min}^{-1}$. The capillary, counter electrode and cone potentials were varied for each solution to obtain sufficient intensity of the particular ion of interest. The capillary potential was $\sim +2.5$ kV and the counter electrode potential was $\sim +100$ V. In-source CAD was accomplished using the electric field in the intermediate pressure region of the source between the cone and the grounded skimmer [16]. The required field in this region was relatively high (≥ 30 V cm^{-1}) to obtain the singly charged ions of interest with workable intensity from solutions of trivalent metal salts compared with that (~ 20 – 30 V cm^{-1}) needed to obtain the required singly charged ions from divalent metal salts. The temperature of the desolvation chamber, through which dry nitrogen flowed, was 80°C .

CAD spectra were obtained using argon as the target gas at pressures in the collision cell sufficient to decrease the incident ion intensity by no more than 10%. The energy of these ions was determined by their initial energy gained in the expansion through the pinhole in the cone plus that gained due to the difference in potential between the grounded skimmer and the collision cell (called E_{Lab}), which was electrically floated in the range -5 to -40 V with respect to ground.

The metal salts, which were sulfates, nitrates, or chlorides of reagent grade quality, were dissolved in deionized water to give metal ion concentrations of 1.0×10^{-3} M.

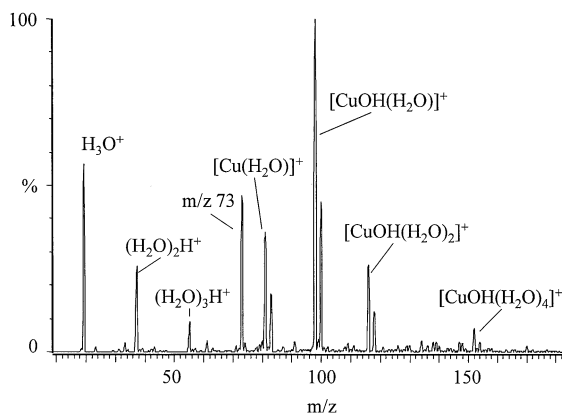


Fig. 1. Electrospray mass spectrum obtained from a 1.0×10^{-3} M aqueous solution of CuSO_4 ; cone potential +20 V.

3. Results

The use of a very low field between cone and grounded skimmer allows the observation of doubly charged hydrated ions of all the divalent transition metals used in this study, as has been described previously for cupric ions [7]. When the field is increased, the doubly charged ions disappear and are replaced by singly charged ions. Figure 1 shows a mass spectrum obtained from an aqueous cupric sulfate solution using a cone potential of +20V. The major ions, in addition to those due to the hydrated proton, are from the series $[\text{CuOH}(\text{H}_2\text{O})_n]^+$ ($n = 1-5$). (Throughout this article the m/z of any metal-containing ion will always refer to the one containing the metal isotope of highest natural abundance.) The peak due to $[\text{CuOH}(\text{H}_2\text{O})_4]^+$ (m/z 152) is anomalously large compared to the adjacent $[\text{CuOH}(\text{H}_2\text{O})_3]^+$ (m/z 134) suggesting that this four-coordinate complex is especially stable. It is to be noted that little if any $[\text{CuOH}]^+$ (m/z 80) is present but that $[\text{Cu}(\text{H}_2\text{O})]^+$ (m/z 81) is present in good yield. The peak at m/z 73 in the spectrum is composed of both $\text{H}^+(\text{H}_2\text{O})_5$ and protonated tetrahydrofuran, the latter from tetrahydrofuran absorbed in and adsorbed on the surfaces of the sample introduction system.

The electrospray mass spectrum shown in Figure 2 was obtained with an aqueous solution of $\text{La}_2(\text{SO}_4)_3$. A diligent search, varying the ion source parameters over as wide a range as possible, provided no evidence for the formation of hydrated La^{3+} . Similarly, no $[\text{Pr}(\text{H}_2\text{O})_n]^{3+}$

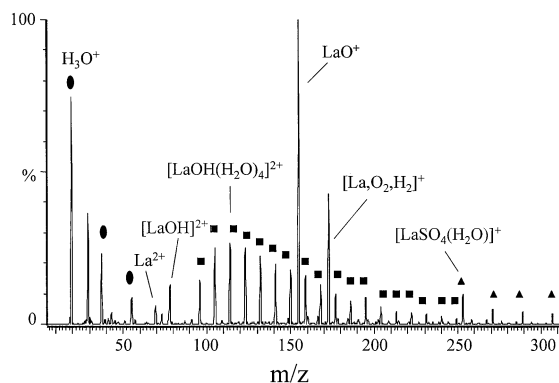


Fig. 2. Electrospray mass spectrum obtained from a 1.0×10^{-3} M aqueous solution of $\text{La}_2(\text{SO}_4)_3$; cone potential +78V. The three ion series are \bullet $(\text{H}_2\text{O})_n\text{H}^+$; \blacksquare $[\text{LaOH}(\text{H}_2\text{O})_n]^{2+}$; \blacktriangle $[\text{LaSO}_4(\text{H}_2\text{O})_n]^+$.

was observed when aqueous solutions of $\text{Pr}(\text{NO}_3)_3$ were examined. The ion series $[\text{LaOH}(\text{H}_2\text{O})_n]^{2+}$ in Figure 2 has n values ranging from 0 (m/z 78) to 19 (m/z 249), the high limit of the scanned range. $[\text{LaOH}(\text{H}_2\text{O})]^{2+}$ (m/z 87) is present, but with very low relative intensity, and it is notable that $[\text{LaOH}]^{2+}$ is present in much higher yield. A similar, very low relative intensity of $[\text{PrOH}(\text{H}_2\text{O})]^{2+}$ was observed in the electrospray spectrum of $\text{Pr}_2(\text{SO}_4)_3$. The peaks at m/z 235 and m/z 253 constitute the commencement of a series of hydrates containing lanthanum together with the sulfate anion. m/z 235, which has a very low intensity, is $[\text{LaSO}_4]^+$ and m/z 253 is $[\text{LaSO}_4(\text{H}_2\text{O})]^+$. Higher hydrates of $[\text{LaSO}_4]^+$ are present under the same experimental conditions.

$[\text{MOH}(\text{H}_2\text{O})]^+$ ions were obtained from electro-sprayed aqueous solutions containing Mn(II), Co(II), Ni(II), Cu(II), or Zn(II) salts by judicious choices of cone potential. In dealing with electrospray spectra of aqueous solutions, there is always the possibility that both singly and doubly charged ions might have the same mass-to-charge ratios. Since the CAD spectra of doubly charged ions generally show some product ions that are singly charged and often of higher m/z than the precursor ions, this characteristic was used as a check on the purity of all ions subject to collisionally activated decomposition. Aqueous solutions of Fe(II) salts were the only systems in which there was evidence for both singly and doubly charged ions at the same m/z value. $[\text{FeOH}(\text{H}_2\text{O})]^+$ occurs at m/z 91, as does $[\text{Fe}(\text{H}_2\text{O})_7]^{2+}$ and the CAD spectrum of m/z 91,

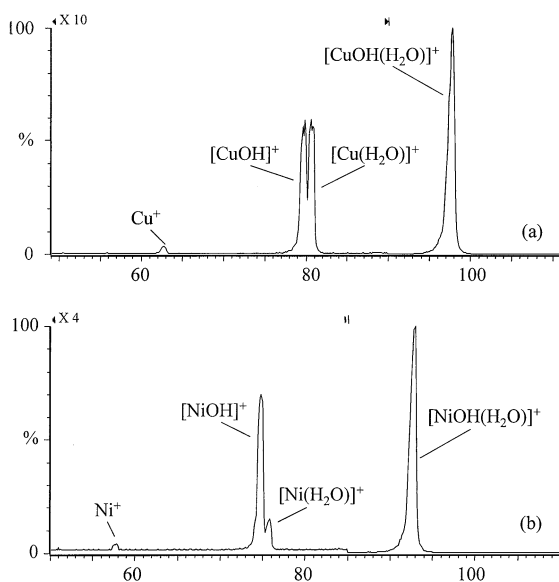


Fig. 3. The CAD spectra of (a) m/z 98, $[\text{CuOH}(\text{H}_2\text{O})]^+$, $E_{\text{Lab}} = 20$ eV; (b) m/z 93, $[\text{NiOH}(\text{H}_2\text{O})]^+$; $E_{\text{Lab}} = 20$ eV.

under some source conditions, showed product ions at m/z values 127, 109, 82 and 64 attributable to, respectively, $[\text{FeOH}(\text{H}_2\text{O})_3]^+$, $[\text{FeOH}(\text{H}_2\text{O})_2]^+$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_4]^{2+}$. At cone potentials of around +12 V, m/z 91 appeared to be composed mainly of $[\text{Fe}(\text{H}_2\text{O})_7]^{2+}$, while when the potential was 71 V, the ion appeared to be mainly $[\text{FeOH}(\text{H}_2\text{O})]^+$. However, both at low and at high cone potentials, m/z 73, corresponding to both $[\text{Fe}(\text{H}_2\text{O})_5]^{2+}$ from $[\text{Fe}(\text{H}_2\text{O})_7]^{2+}$ and $[\text{Fe}(\text{OH})]^+$ from $[\text{FeOH}(\text{H}_2\text{O})]^+$, was the major product ion in the CAD spectra. CAD experiments with m/z 91 obtained from aqueous Fe(II) salts were therefore not pursued.

Typical CAD spectra are shown in Figure 3. Figure 3a shows the spectrum obtained for the decomposition of $[\text{CuOH}(\text{H}_2\text{O})]^+$, m/z 98, at 20 eV laboratory energy and the CAD spectrum in Figure 3b shows the decomposition of $[\text{NiOH}(\text{H}_2\text{O})]^+$ at the same energy. The major product ions in both figures are $[\text{MOH}]^+$ and $[\text{M}(\text{H}_2\text{O})]^+$; there are also very small peaks due to M^+ . The relative intensities of all these product ions, and the analogous ones for $\text{M} = \text{Co}, \text{Mn}$, changed with change of collision energy in the manner shown in Figure 4. $[\text{ZnOH}(\text{H}_2\text{O})]^+$ yielded only one major product ion, $[\text{MOH}]^+$, at all collision energies. No $[\text{Zn}(\text{H}_2\text{O})]^+$ was observed but a very small yield of Zn^+ did appear at

collision energies above 20 eV. In Figure 5 are shown the variations in relative intensities of the CAD product ions from the higher hydrate of copper, $[\text{CuOH}(\text{H}_2\text{O})_2]^+$ $[\text{MOH}(\text{H}_2\text{O})]^+$ ions could not be produced from solutions containing Cr(III), Fe(III), La(III), or Pr(III) salts. CAD of the major doubly charged ions, $[\text{MOH}(\text{H}_2\text{O})_n]^{2+}$, in the electrospray spectra resulted in the loss of water molecules with no loss of charge, as described previously [2] and also in charge reduction giving mainly two metal-containing products, MO^+ and $[\text{M}, \text{O}_2, \text{H}_2]^+$. These two ions are prominent in the electrospray spectrum of aqueous $\text{La}_2(\text{SO}_4)_3$ shown in Figure 2, which was obtained with the high cone potential of 78 V. A typical CAD spectrum obtained with $[\text{PrOH}(\text{H}_2\text{O})_2]^{2+}$ as precursor ion is shown in Figure 6. Singly charged ions of m/z corresponding to $[\text{M}, \text{H}_2, \text{O}_2]^+$ were obtainable from solutions of each of the triply charged cations, and their CAD spectra were obtained as functions of collision energy. $[\text{Fe}, \text{H}_2, \text{O}_2]^+$, in addition to being obtainable from solutions of Fe(III) salts, was also produced by electrospraying aqueous solutions of Fe(II) salts. With cone voltages lower than 20 V, $[\text{Fe}, \text{H}_2, \text{O}_2]^{2+}$ was found to be coincident with the isobaric ion $[\text{Fe}(\text{H}_2\text{O})_7]^{2+}$, and a CAD spectrum composed of products from both ions was observed. However, when the cone potential was greater than 30 V, no ions attributable to $[\text{Fe}(\text{H}_2\text{O})_7]^{2+}$ were observed. With this condition, the CAD spectra of $[\text{Fe}, \text{H}_2, \text{O}_2]^+$ obtained with ions from Fe(II) and Fe(III) solutions were identical, as was the variation of product ion intensities with changes in collision energy.

Figures 7a and 7b show, respectively, the CAD spectra of $[\text{Cr}, \text{O}_2, \text{H}_2]^+$ and $[\text{Fe}, \text{O}_2, \text{H}_2]^+$, while Figures 8a and 8b show the relative intensities of the product ions from these two precursor ions as functions of collision energy.

4. Discussion

4.1. Dissociation of $[\text{MOH}(\text{H}_2\text{O})]^+$

$[\text{MOH}(\text{H}_2\text{O})]^+$ ions formed from solutions of the divalent metal cations, Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} , are collisionally decomposed by two pathways:

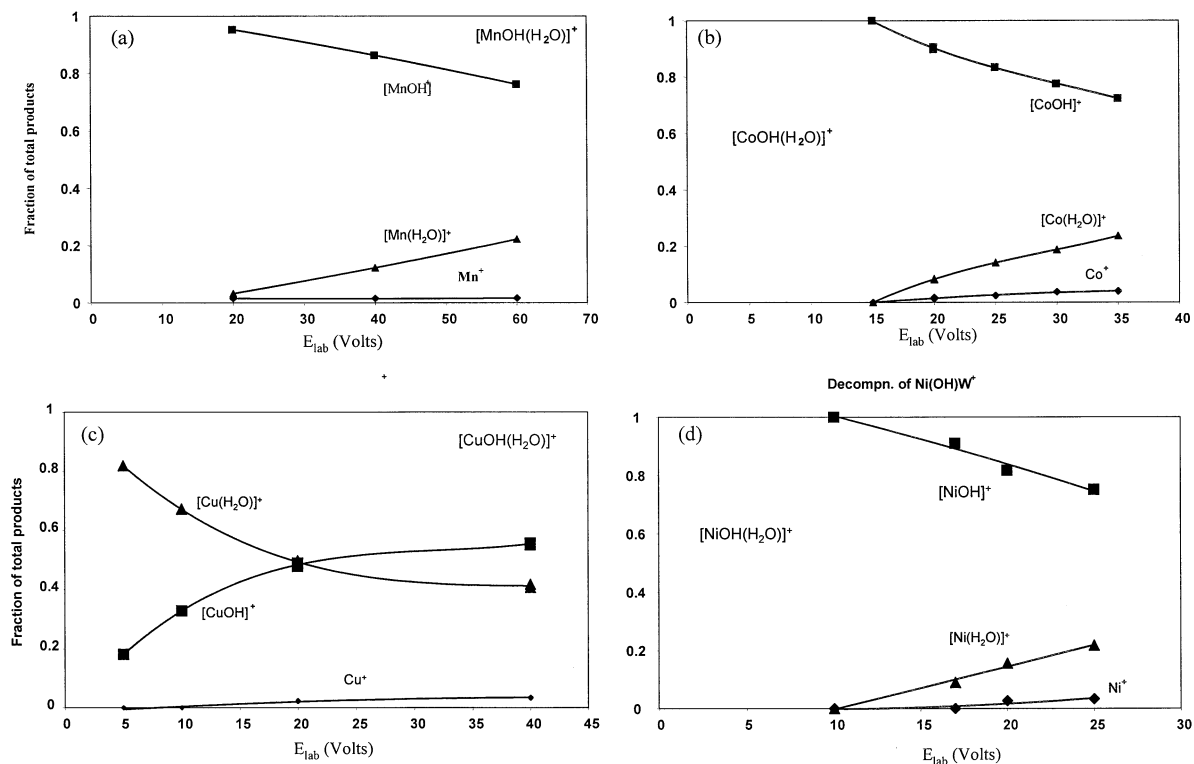


Fig. 4. The variations of fractional product ion yields from $[\text{MOH}(\text{H}_2\text{O})]^+$ ($M =$ (a) Mn, (b) Co, (c) Cu, (d) In) as functions of precursor ion energy.

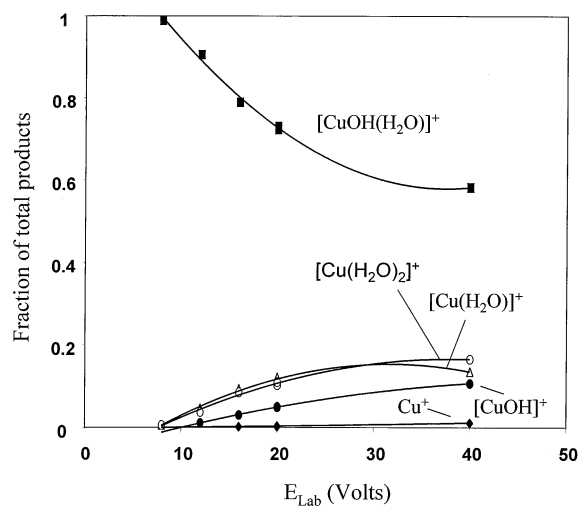
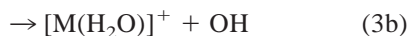


Fig. 5. The variations of fractional product ion yields from $[\text{CuOH}(\text{H}_2\text{O})_2]^+$ as functions of precursor ion energy.

The first reaction leads to the $M(\text{II})$ hydroxide ion by loss of water, while the second leads to loss of hydroxyl and formation of the monovalent metal hydrate. The latter statement assumes that $[\text{M}(\text{H}_2\text{O})]^+$ is as written and is not $[\text{H}-\text{M}-\text{OH}]^+$. Magnera and

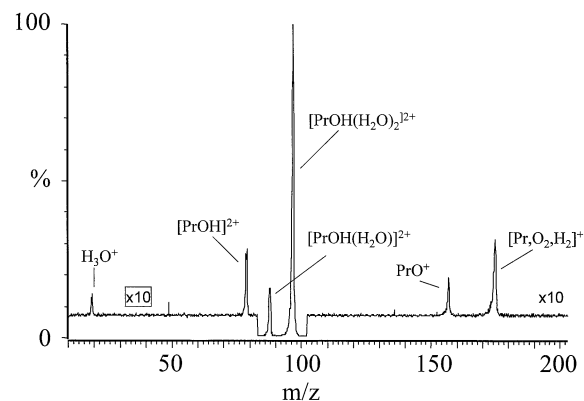


Fig. 6. The CAD spectrum of m/z 97, $[\text{PrOH}(\text{H}_2\text{O})_2]^{2+}$; $E_{\text{Lab}} = 40$ eV.

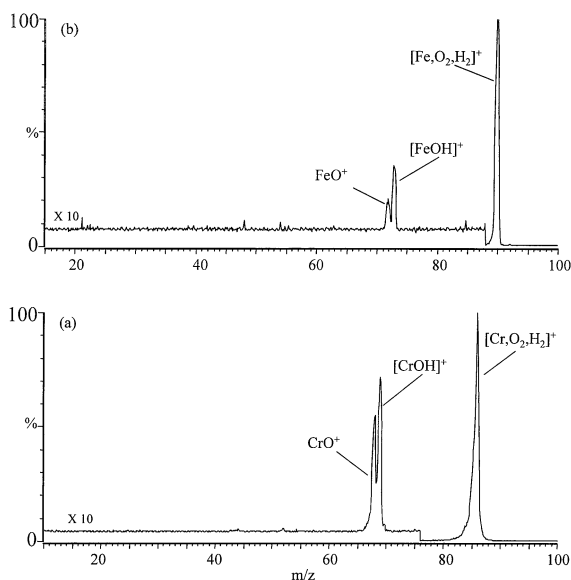


Fig. 7. The CAD spectra of: (a) m/z 86, $[\text{Cr},\text{O}_2,\text{H}_2]^+$, $E_{\text{Lab}} = 40$ eV; (b) m/z 90, $[\text{Fe},\text{O}_2,\text{H}_2]^+$, $E_{\text{Lab}} = 24$ eV.

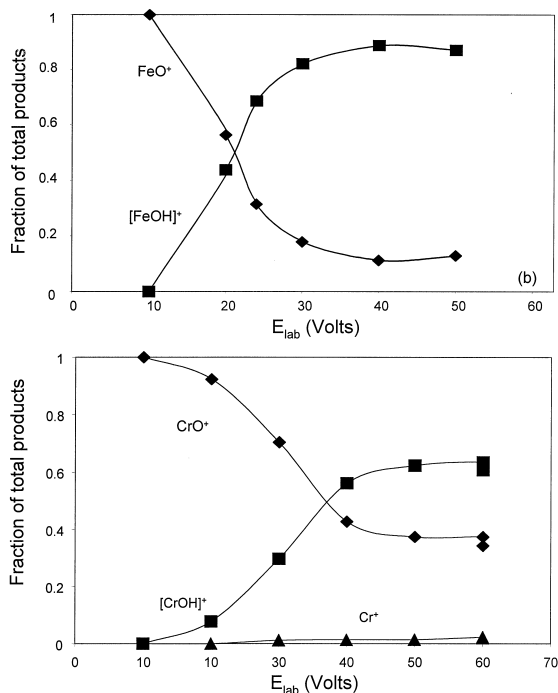


Fig. 8. The variations with precursor ion energy of fractional product ion yields from (a) $[\text{Cr},\text{O}_2,\text{H}_2]^+$, $E_{\text{Lab}} = 40$ eV and (b) $[\text{Fe},\text{O}_2,\text{H}_2]^+$, $E_{\text{Lab}} = 25$ eV.

coworkers have discussed the structure of $[\text{M}(\text{H}_2\text{O})]^+$ in the light of their studies of the dissociations of $[\text{MOH}(\text{H}_2\text{O})]^+$ and $[\text{M}(\text{H}_2\text{O})_n]^+$, which were obtained by fast atom sputtering of hydrated metal salts and frosted metal plates [13]. They concluded that since their measured water binding energies for several first-row transition metal cations were in strong disagreement with values calculated using their measured $\text{M}^+—\text{OH}$ bond energies and known $\text{M}^+—\text{H}$ bond energies, the structures of most of the ions were the simple hydrates. From the general trend observed, it was concluded that $[\text{M},\text{O},\text{H}_2]^+$ for mostly all but the early transition metals should be metal ion hydrates. This argument by Magnera and coworkers depends on the additivity of bond energies, assuming that the individual $\text{M}^+—\text{H}$ and $\text{M}^+—\text{OH}$ bond energies are independent of the presence of other ligands. Interestingly, their experimental method produced $[\text{Cu}(\text{H}_2\text{O})_n]^+$ but did not produce $[\text{CuOH}(\text{H}_2\text{O})]^+$ from frosted copper plates [12], and they therefore could not obtain a measure of the $\text{Cu}^+—\text{OH}$ bond energy. This implies that all the ions produced in the sputtering experiments were initially the singly charged metal cations that were then hydrated before entering the gas phase.

The branching ratio for the collisionally activated decomposition of $[\text{MOH}(\text{H}_2\text{O})]^+$ [Eq. (3a,b)] is dependent on the collision energy as illustrated in Figure 4. At low collision energy the only product for $\text{M} = \text{Mn}, \text{Co}, \text{Ni}$ and Zn is $[\text{MOH}]^+$. Increasing collision energy leads to the formation of Zn^+ from $[\text{ZnOH}(\text{H}_2\text{O})]^+$ but no $[\text{Zn}(\text{H}_2\text{O})]^+$ is observed, whereas each of the $[\text{MOH}(\text{H}_2\text{O})]^+$ ions containing $\text{Mn}, \text{Co},$ or Ni yields $[\text{M}(\text{H}_2\text{O})]^+$ in increasing relative yield with increasing energy. The threshold for the appearance of $[\text{M}(\text{H}_2\text{O})]^+$ appears to increase in the order $\text{Ni} < \text{Co} < \text{Mn}$ and, at any laboratory collision energy, the fractional amount of $[\text{M}(\text{H}_2\text{O})]^+$ increases in the order $\text{Ni} < \text{Co} < \text{Mn}$. This is in keeping with the change in the ratio of measured bond strengths $D(\text{M}^+—\text{OH})/D(\text{M}^+—\text{OH}_2)$ shown in Table 1, which follows the order $\text{Ni} < \text{Co} < \text{Mn}$. Although the strength of the $\text{M}^+—\text{OH}_2$ bond shows only a small change with increase of atomic number, the strength of the $\text{M}^+—\text{OH}$ bond changes by a factor of two from

Table 1.
Bond strengths (kJ mol⁻¹) of M—OH⁺ and M—OH₂⁺

M	M—OH ⁺ ^a	M—OH ₂ ⁺ ^a	M—OH ₂ ⁺ ^b
Mn	343	136,111 ^c	134.2
Co	302	155,168 ^c	152.6
Ni	177	153,166 ^c	170.1
Cu	—	146	157.8
Zn	127	163	137.2

^a T. F. Magnera, D. E. David, J. Michl, *J. Am. Chem. Soc.* 111 (1989) 4100.

^b Theoretical results from E. Magnusson and N. W. Moriarty, *Inorg. Chem.* 35 (1966) 5711.

^c P. J. Marinelli and R. R. Squires, *J. Am. Chem. Soc.* 111 (1989) 4101.

Ni to Mn. The theoretical M⁺—OH₂ bond strengths obtained by Magnusson and Moriarty [17] shown in column 4 of Table 1 are in reasonable agreement with the experimental values and show the same small trends. Magnera and coworkers obtained D(Zn⁺—OH) = 127 kJ mol⁻¹ and D(Zn⁺—OH₂) = 163 kJ mol⁻¹, which, assuming bond additivity, would imply that the preferred low-energy dissociation of [ZnOH(H₂O)]⁺ should be to [Zn(H₂O)]⁺. However, the exclusive product observed in the present work is [ZnOH]⁺. Our findings for zinc are therefore not consistent with the experimental bond energies found by Magnera and coworkers, even after allowing for the approximation of bond energy additivity.

The collisionally activated decomposition of [CuOH(H₂O)]⁺ is different from that of any of the other transition metals in this study in that at low collision energy the hydrated cation [Cu(H₂O)]⁺ is the major product at low collision energy. With increasing collision energy, loss of water rather than hydroxyl becomes more important and, at laboratory energies above 20 eV, [CuOH]⁺ is the most abundant product. This implies that D((H₂O)Cu⁺—OH) is less than D(HOCu⁺—OH₂) which would follow the trend in Table 1 of decreasing D(M⁺—OH) with increasing atomic number, while at the same time D(M⁺—OH₂) shows no such trend. It is to be noted that in their sputtering experiments Magnera and coworkers found that copper alone, of all the transition metals studied, did not yield an [M(OH)H₂O]⁺ ion [12]. Instead, only [Cu(H₂O)_n]⁺ ions were observed. As seen in

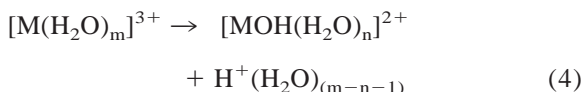
Figure 5, when the more highly hydrated ion [CuOH(H₂O)₂]⁺ is collisionally activated, the only product at low collision energy is due to loss of H₂O leading to [CuOH(H₂O)]⁺. The next products to appear as the collision energy is increased are [Cu(H₂O)₂]⁺ and [Cu(H₂O)]⁺. Loss of OH in competition with loss of H₂O is possible even when two H₂O are present. The binding energy of the second water molecule in [Cu(H₂O)₂]⁺ is equal to or slightly higher than the first [13]. The product ions [CuOH]⁺ and Cu⁺ appear only at the higher energies. These observations imply that the M—OH bond strengths in [MOH(H₂O)_n]⁺ (M = Mn, Co, Ni and Zn) are greater than those of M—OH₂ and that the reverse is the case for M = Cu.

The decomposition of [MOH(H₂O)]⁺ to [MOH]⁺ does not involve a lowering of the oxidation state of M, whereas the decomposition to [M(H₂O)]⁺ involves the reduction from M(II) to M(I). This latter process will be energetically favored by a large difference between the first and second ionization energies of M, which is observed since the difference increases in the order of increasing atomic number (i.e. Mn, 8.21 eV; Co, 9.20 eV; Ni, 10.53 eV; Cu, 12.57 eV). The only exception to such an order is Zn, which has a difference of 8.57 eV between its first and second ionization energies but was found to decompose solely to [ZnOH]⁺ over the experimental range of collision energy. Zn, having a closed d-shell, is usually not regarded as being a transition element, so that its nonconformity is not unexpected. However it is to be noted that the difference in ionization energies is one of the lowest of the group and so its behavior is not wholly inconsistent with the above trend.

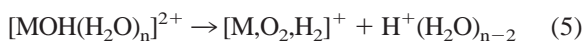
4.2. Dissociation of [M₂O₂H₂]⁺

No triply charged hydrates {[M(H₂O)_n]³⁺} were obtained by the electrospray technique in the present work (M = La, Pr) or in a previous study (M = Sc, Y, La, Ce, Nd, Sm, Co)[2]. The [MOH(H₂O)_n]²⁺ ions, which are observed in electrospray spectra, result from interligand proton transfer [Eq. (4)], which occurs either during the process by which the tripositive aqueous ions are transferred from solution to the

gas phase or by collisionally activated dissociation in the low pressure interface region of the ion source. Decreasing the field to a nominal value of 0 V in this latter region was to no avail in careful but fruitless searches for $[\text{M}(\text{H}_2\text{O})_n]^{3+}$.



The $[\text{MOH}(\text{H}_2\text{O})_n]^{2+}$ ions produced by electro-spray can be further charge-reduced in a second interligand proton transfer by appropriately increasing the cone voltage to produce first $[\text{M},\text{O}_2,\text{H}_2]^+$ and then MO^+ :

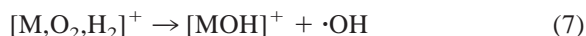


The spectrum in Figure 2 was obtained from a 1.0×10^{-3} M aqueous solution of $\text{La}_2(\text{SO}_4)_3$ with a cone voltage of 78 V. There is a series of ions of the general formula $[\text{LaOH}(\text{H}_2\text{O})_n]^{2+}$ with n ranging from 2 to 26, the latter occurring at the limit of the scan range. It is to be noted that it was found to be impossible, no matter how electrode potentials were varied, to produce $[\text{MOH}(\text{H}_2\text{O})]^{2+}$ in the electrospray source using aqueous solutions of the trivalent cations Cr^{3+} , Fe^{3+} , La^{3+} and Pr^{3+} . Electron transfer from ligand to metal centre cannot therefore compete with inter-ligand proton transfer in the charge reduction process involving $[\text{MOH}(\text{H}_2\text{O})_n]^{2+}$.

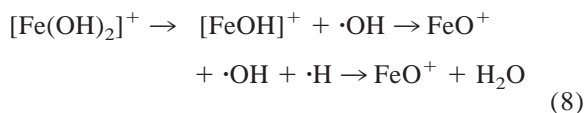
The decomposition of $[\text{MOH}(\text{H}_2\text{O})_n]^{2+}$ according to Eqs. (5) and (6) could also be carried out in the collision cell. However, MO^+ , the singly charged oxide in which the metal has oxidation number of +3, could not be collisionally decomposed with the collision energies available in either the source or the collision cell. This is in keeping with the high metal–oxygen bond energies of MO^+ : 316, 322, 799 and 869 kJ mol^{-1} respectively for FeO^+ , CrO^+ , PrO^+ and LaO^+ [18,19].

The structure of $[\text{M},\text{H}_2,\text{O}_2]^+$ could be either $[\text{M}(\text{OH})_2]^+$ or $[\text{MO}(\text{H}_2\text{O})]^+$, in both of which the metal is in the +3 oxidation state. The CAD results strongly suggest that the structure is $[\text{M}(\text{OH})_2]^+$. MO^+ is the sole product for all the metals studied at low collision energy, but with increasing energy

$[\text{MOH}]^+$ ($\text{M} = \text{Cr}, \text{Fe}$) appears and becomes the major ion at high energy (Figures 7 and 8).



The formation of the oxide ion from the dihydroxide ion is a rearrangement reaction that will be entropically favored over $\text{M}-\text{OH}$ scission at low internal ion energy if both processes have not too dissimilar activation energy requirements. Murad [20] has obtained $D_0^0(\text{FeO}^+ - \text{H}) = 453 \pm 19 \text{ kJ mol}^{-1}$ and $D_0^0(\text{Fe}^+ - \text{OH}) = 318 \pm 19 \text{ kJ mol}^{-1}$, which allows a rough estimate to be made of the relative energy requirements for the two competing reactions [Eqs. (6) and (7)]. Since no thermodynamic data is available for the bond energy of the second hydroxide in $\text{Fe}(\text{OH})_2$, if we make the approximation that the $\text{Fe}^+ - \text{OH}$ bonds are independent of each other and have bond energies equal to that measured for $\text{Fe}-\text{OH}^+$, then the sequence shown in Eq. (8) may be used to analyze the rearrangement reaction and obtain an approximate value for the enthalpy change for the reaction leading to loss of water.



The first and second steps are endothermic by, respectively, 318 and 453 kJ mol^{-1} , and the combination of the hydrogen atom and hydroxyl radical is exothermic by 499 kJ mol^{-1} . The overall endothermicity of 272 kJ mol^{-1} is less than the endothermicity of 318 kJ mol^{-1} for the direct loss of hydroxyl. Even if we acknowledge that crude approximations have been made, this analysis suggests that on energetic grounds the rearrangement reaction of Eq. (8) is favored for $[\text{Fe}(\text{OH})_2]^+$ at low collision energy but the higher energy, more entropically favored, simple scission reaction of Eq. (7) will take precedence at the higher collision energies. The same analysis for $[\text{Cr}(\text{OH})_2]^+$ using 311 kJ mol^{-1} and 376 kJ mol^{-1} [13] yields an endothermicity of 188 kJ mol^{-1} for the rearrangement reaction to form oxide and water; this value is comparable with 311 kJ mol^{-1} for the loss of a hydroxide group. Again, oxide formation should be favored over hydroxyl loss, as is observed.

Evidence for competition between formation of MO^+ and $[\text{MOH}]^+$ was observed in the CAD spectra of $[\text{M}, \text{O}_2, \text{H}_2]^+$ ($\text{M} = \text{La}, \text{Pr}$) at collision energies above 30 eV, MO^+ being the sole product at all energies below this value. For example, the product ratio $[\text{MOH}^+]/[\text{MO}^+]$ from the CAD of $[\text{La}, \text{O}_2, \text{H}_2]^+$ was 0.03 at 36 eV and 0.16 at 44 eV. The higher energy thresholds for loss of OH from $[\text{M}, \text{O}_2, \text{H}_2]^+$ ($\text{M} = \text{La}, \text{Pr}$) must be associated with much higher $\text{M}^+ - \text{O}$ binding energies for the lanthanides than for those of the transition metals. The enthalpies of dissociation, $\text{MO}^+ \rightarrow \text{M}^+ + \text{O}$, for Fe and La, calculated from available thermodynamic data [19] are, respectively, 316 and 869 kJ mol^{-1} . Lack of appropriate thermodynamic data precludes a comparison of $\text{D}(\text{M}^+ - \text{OH})$ and $\text{D}(\text{MO}^+ - \text{H})$ for these actinide metals. The data for the first-row transition metals shows an inverse relationship between $\text{D}(\text{MO}^+ - \text{H})$ and $\text{D}(\text{M}^+ - \text{O})$, a high $\text{D}(\text{M}^+ - \text{O})$ being associated with a low $\text{D}(\text{MO}^+ - \text{H})$. [13] If the same holds true for the actinides, then their very high $\text{D}(\text{M}^+ - \text{O})$ values will favor MO^+ formation until much higher internal energies than required for the trivalent transition metals, as observed.

5. Conclusions

Hydrated, doubly charged transition metal cations $[\text{M}(\text{H}_2\text{O})_n]^{2+}$, when collisionally activated lose water ligands with no loss of charge until the number of water ligands becomes small when interligand proton transfer and dissociation leads to the singly charged hydrated hydroxide, $[\text{MOH}(\text{H}_2\text{O})_n]^+$. The lowest hydrate, $[\text{MOH}(\text{H}_2\text{O})]^+$, decomposes by loss of either OH or H_2O . For $\text{M} = \text{Mn}, \text{Co}, \text{Ni}$ and Zn , H_2O is lost preferentially at low collision energies consistent with the higher $\text{M}-\text{OH}$ than H_2O binding energies. By contrast, the copper-containing ion loses hydroxide, which is consistent with the relative binding energies of OH and H_2O . At higher collision energies, the $[\text{MOH}(\text{H}_2\text{O})]^+$ ions of all the metals except zinc show competitive loss of OH and H_2O . $[\text{ZnOH}(\text{H}_2\text{O})]^+$ dissociates by loss of H_2O at all the available collision

energies, even though the reported dissociation energy of $[\text{Zn}-\text{OH}]^+$ is less than that of $[\text{Zn}-\text{OH}_2]^+$. No $[\text{M}(\text{H}_2\text{O})_n]^{3+}$ ions could be produced from M^{3+} ions of transition metals (Fe, Cr, La) or the actinide Pr. The ions are charge-reduced in the electrospray process by interligand transfer to $[\text{MOH}(\text{H}_2\text{O})_n]^{2+}$. When collisionally excited they produce the singly charged ion $[\text{M}, \text{O}_2, \text{H}_2]^+$, which is most probably $[\text{M}(\text{OH})_2]^+$. At low collision energy, this ion decomposes by a rearrangement process to MO^+ and H_2O . At higher energy, loss of OH becomes competitive. This competition occurs at much higher energy with La and Pr than with Fe and Cr, which is consistent with their much higher $\text{M}-\text{O}$ bond energies.

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