Electronic spectroscopy and photodissociation dynamics of Co^{2+}–methanol clusters: $Co^{2+}(CH_3OH)_n$ (n = 4–7)

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Solvated cluster ions $Co^{2+}(CH_3OH)_n$ (n = 4–7) have been produced by electrospray and studied using photofragment spectroscopy. There are notable differences between the photodissociation spectra of these complexes and the analogous water complexes. $Co^{2+}(CH_3OH)_6$ absorbs significantly more strongly than $Co^{2+}(H_2O)_6$. The photodissociation spectra of $Co^{2+}(CH_3OH)_n$ (n = 4, 5 and 6) are very similar, which suggests that they share the $Co^{2+}(CH_3OH)_4$ chromophore, with additional solvent molecules in the second shell. In contrast, our earlier studies indicate that $Co^{2+}(H_2O)_6$ is six coordinate, and its spectrum is significantly different from that of $Co^{2+}(H_2O)_4$. The larger clusters $Co^{2+}(CH_3OH)_n$ (n = 5–7) dissociate by simple loss of one or more solvent molecules. Larger clusters tend to lose more solvent molecules, especially at higher photon energies. As with the corresponding water cluster, $Co^{2+}(CH_3OH)_4$ photodissociates by proton transfer through a salt-bridge intermediate. This is accompanied by a modest kinetic energy release of 170 kJ mol^{-1} and occurs with a lifetime of 145 ns.

Introduction

Because of the strong interactions between ions and solvent molecules, the properties of microsolvated ions—gas-phase ions surrounded by a few solvent molecules—depend strongly on the number and type of solvent molecule, leading to interesting and unique reactivity, structure and spectroscopy.[1] This is especially true of small, multiply charged ions such as transition metal M^{2+}.[2] An interesting situation occurs for some cluster ions in which competing molecular forces lead to a different geometry than in the condensed phase. For example, aqueous Cu(II) is six coordinate, with two long metal–ligand bonds due to Jahn–Teller distortion.[3] On the other hand, experiments[4–6] and calculations[7] suggest that $Cu^{2+}(H_2O)_n$ clusters (n = 4–8) are four coordinate, with the additional water molecules in the second solvation shell, hydrogen bonding to inner shell water molecules rather than binding directly to the metal. We have previously studied the spectroscopy and photodissociation dynamics of $Ni^{2+}(H_2O)_n$ and $Co^{2+}(H_2O)_n$ (n = 4–7), which are six coordinate for $n \geq 6$.[8–10] Here we extended those studies to the methanol clusters $Co^{2+}(CH_3OH)_n$ to explore how a change in the solvent affects the structure, spectroscopy and dissociation dynamics of the cluster. Some preliminary results on $Co^{2+}(CH_3OH)_n$ were included in a recent review.[2]

In aqueous solution, Co(II) is six coordinate, and EXAFS studies show that Co(II) is also six coordinate in methanol solution. The cobalt–oxygen bond lengths are also similar to those in aqueous solution.[11] Although both methanol and water coordinate to cations through oxygen donation, methanol is less symmetrical, has more degrees of freedom and is somewhat bulkier. Methanol also has a smaller dielectric constant than water (ε = 33.1 *vs.* 80.4). As a result, in solution, the absorption spectrum of methanolic Co^{2+} is similar to that of the aqueous ion, but is red-shifted to λ_{max} = 525 nm and is slightly more intense (ε = 7.2 M^{-1} cm^{-1}).

There have been significantly fewer studies of Co^{2+}–methanol clusters than of Co^{2+}–water clusters. In an early study by Agnes and Horlick,[12] $Co^{2+}(CH_3OH)_n$ clusters with n = 4–12 were generated to demonstrate the utility of electrospray mass spectrometry as a tool for elemental analysis. Kohler and Leary[13] studied $M^{2+}(solvent)_n$ species for several transition metal ions, including Co^{2+}, with various organic solvents. They produced $Co^{2+}(CH_3OH)_n$ with n = 4–7 and examined the collision induced dissociation (CID) of $Co^{2+}(CH_3OH)_4$. Low energy (10 eV) CID primarily leads to proton transfer, forming $H^+(CH_3OH)$ and hydride transfer, forming CoH^+.

Rulísek and Havlas have carried out calculations at several levels of theory on $Co^{2+}(H_2O)_6$ complexes in which one of the water molecules is replaced by another solvent molecule.[14] Replacing a water molecule by methanol is calculated to be exothermic by 16 kJ mol^{-1}. The Co–O bond length is 2.15 Å for methanol, slightly shorter than the 2.16 Å calculated for water. Methanol substitution changes the electronic excitation energy of the cluster only slightly.

In this paper, we examine the absorption properties of isolated $Co^{2+}(CH_3OH)_n$ (n = 4–7) clusters and compare them to the corresponding $Co^{2+}(H_2O)_n$ clusters. In addition to size and solvent effects upon absorption properties, photodissociation dynamics are discussed in terms of dissociation channels, kinetic energy release (KER) and lifetimes.

Experimental

Methods used to prepare and study the $Co^{2+}(CH_3OH)_n$ clusters will be described briefly; a detailed description of the electrospray ion source and reflectron time-of-flight photofragment spectrometer can be found in our earlier studies of $Ni^{2+}(H_2O)_n$ and $Co^{2+}(H_2O)_n$ clusters.[8,9] In general, operating conditions for methanol clusters are more gentle than for the corresponding aqueous species. Cluster ions are produced by flowing a 1–5 × 10^{-4} M solution of CoCl$_2$ in high-purity methanol at 0.4 ml h^{-1} through a hypodermic needle held at ~4 kV. If mixed water : methanol solutions are used, the resulting ions are enriched in methanol, consistent with calculations[14] which predict that methanol binds more strongly to Co^{2+} than water. Ions are produced at atmospheric pressure and enter a chamber held at ~1 Torr through a heated (50 °C) desolvation tube held between 0 and 100 V. Higher voltages enhance production of smaller clusters. The ions pass through

a skimmer, into a chamber at 5×10^{-4} Torr, where an octopole ion guide transports them into an rf ion trap. This trap couples the continuous electrospray source to the inherently pulsed time-of-flight mass spectrometer.[2,15,16] The ions are acquired in the trap for 49 ms, during which they are thermalized to 298 K by collisions with added helium buffer gas and residual air. This allows for a better comparison of the observed spectra to that of the bulk solutions. Ions are ejected from the trap, accelerated to 1800 V and re-referenced to ground potential. Following a field-free region, ions enter the reflectron. At the turning point of the reflectron, ions are irradiated by the unfocused output of a pulsed dye laser pumped by the second or third harmonic of a Nd : YAG laser. The fragments pass through a second field-free region to a microchannel plate detector. Photodissociation pathways are determined from difference spectra—the difference between time-of-flight spectra with the laser blocked and unblocked. Photodissociation cross sections are measured by integrating the area under fragment peaks in the difference spectrum, dividing by the area under the parent peak, and normalizing to laser fluence. Uncertainties in the absolute cross sections are estimated at 50% and are due to laser beam nonuniformity and uncertainty in the overlap between the laser and ion beams.

Results and discussion

Cluster ions $Co^{2+}(CH_3OH)_n$ ($n = 4$ to 12) have been observed, and the photodissociation spectra of clusters with $n = 4$–7 have been recorded from ${\sim}14\,000$ to ${\sim}20\,000$ cm^{-1}. The photodissociation spectrum of a molecule will mirror its absorption spectrum if absorption of light always leads to dissociation. Bond strengths in these clusters have not yet been measured. However, blackbody infrared radiation dissociation studies[17] show that the binding energy of the sixth water molecule in $Ni^{2+}(H_2O)_6$ is 8400 cm^{-1}. The $Co^{2+}(CH_3OH)_6$ cluster should have a similar bond strength, as the bonding is primarily electrostatic. Because the photon energies used significantly exceed this value, absorption should lead to dissociation. For clusters with $n > 4$ photodissociation occurs by loss of one or more solvent molecules; $Co^{2+}(CH_3OH)_4$ photodissociates by proton transfer. Photodissociation dynamics will be discussed after the photodissociation spectra.

Photodissociation spectra

Fig. 1 compares the photodissociation spectra of the $Co^{2+}(H_2O)_6$ and $Co^{2+}(CH_3OH)_6$ clusters to the absorption spectra of Co(II) in water and methanol solution. The spectra shown are the total photodissociatio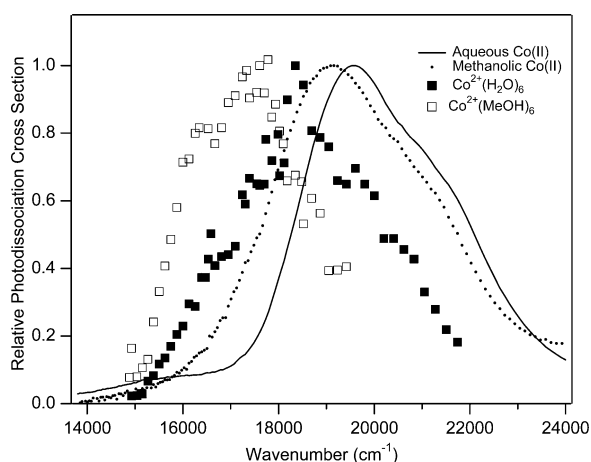n spectra, with all dissociation pathways included. Focusing first on the results in water, in aqueous solution Co^{2+} is surrounded by an inner solvation shell of six water molecules, which leads to a nearly octahedral $Co^{2+}(H_2O)_6$ species.[3] The solvent molecules split the degenerate atomic 3d orbitals into molecular e_g and t_{2g} orbitals. The traditional view is that the absorption spectrum of aqueous Co(II) in the visible is due to transitions between these orbitals. These transitions are weak, with $\varepsilon_{max} = 4.6$ M^{-1} cm^{-1} at $\lambda_{max} = 515$ nm. Because d–d transitions are symmetry forbidden in any structure containing a center of inversion, including octahedral complexes, their intensity is thought to be due to vibronic coupling.[18–20] The photodissociation spectrum of the $Co^{2+}(H_2O)_6$ cluster shows a distinct likeness to the absorption spectrum of aqueous Co(II), as would be expected if $Co^{2+}(H_2O)_{6(aq)}$ is the chromophore in aqueous solution. Based on the similarity between the solution and gas phase spectra and the strength of the cluster absorption, our earlier study of $Co^{2+}(H_2O)_n$ clusters[9] concluded that $Co^{2+}(H_2O)_6$ is the chromophore in the solution spectra of aqueous cobalt(II). This agrees with variable-temperature solution studies[21,22] and recent vibronic coupling calculations[2] on $Co^{2+}(H_2O)_6$ and refutes the suggestion[23,24] that a strongly absorbing minor species such as $Co^{2+}(H_2O)_5$ is responsible for the spectrum.

The absorption spectra of Co(II) in water and methanol are similar, as expected, and the methanol spectrum is red shifted. The reason for this shift becomes apparent when one considers that the corresponding transition ($^4P \leftarrow {}^4F$) in bare Co^{2+} would lie at 14 561 cm^{-1}. The blue shift of the solution spectra indicates that the ground state is solvated more strongly than the excited state. This blue shift is greater for water than for methanol, as it has a higher dielectric constant. The photodissociation spectrum of the $Co^{2+}(CH_3OH)_6$ cluster is broader than that of $Co^{2+}(H_2O)_6$ and is slightly asymmetrical. Both gas phase spectra are red shifted from solution. The size of the shift is slightly larger for the methanol (1800 cm^{-1}) than for the water cluster (1500 cm^{-1}), with the methanol cluster peak occurring at 17 330 cm^{-1}. The red shift of the cluster absorptions means that the second solvent shell contributes significantly to the solvation of Co^{2+} in solution, and the red shift is reduced when solvent molecules are added to the second solvation shell, as we find for $Co^{2+}(H_2O)_7$.[9] The absorptions of the gas phase clusters are almost as broad as those in solution. This is partly due to unresolved vibronic structure, but a contributing factor is also that the clusters have been thermalized to ${\sim}300$ K by collisions in the ion trap. This allows for a better comparison with solution spectra, but it does mean that the $Co^{2+}(CH_3OH)_6$ clusters start with an average of ${\sim}4000$ cm^{-1} vibrational energy. We are installing a liquid nitrogen cooled ion trap in our second generation electrospray instrument.[2,25,26] Cooling the ions to ${\sim}80$ K will reduce the vibrational energy to ${\sim}300$ cm^{-1} and should sharpen features in the photodissociation spectrum.

The d–d absorption bands of Co(II) in solution are quite weak, with maximum extinction coefficients $\varepsilon = 5$ M^{-1} cm^{-1} in water and 7.2 M^{-1} cm^{-1} in methanol. As the d–d transition is symmetry forbidden, these species are only modest chromophores compared to those with an allowed transition, which typically have $\varepsilon \approx 10\,000$ M^{-1} cm^{-1}. We observe somewhat higher photodissociation cross sections for the gas-phase clusters: $\sigma = 6 \times 10^{-20}$ cm^2 ($\varepsilon = 37$ M^{-1} cm^{-1}) for $Co^{2+}(H_2O)_6$ and $\sigma = 2 \times 10^{-19}$ cm^2 ($\varepsilon = 120$ M^{-1} cm^{-1}) for $Co^{2+}(CH_3OH)_6$. As mentioned earlier, errors in the *absolute* cross sections are estimated at 50% due to laser beam nonuniformity and uncertainty in the overlap of the laser and ion beams. However, *relative* cross sections are significantly more precise, and repeated measurements show that the photodissociation cross section of $Co^{2+}(CH_3OH)_6$ is significantly higher than that of $Co^{2+}(H_2O)_6$. One possible explanation is that the larger size and lower symmetry of methanol lead to a less symmetrical

Fig. 1 Total photodissociation spectra of $Co^{2+}(H_2O)_6$ and $Co^{2+}(CH_3OH)_6$ along with the corresponding solution spectra. The gas phase spectra are red shifted from solution by 1500 cm^{-1} (water) and 1800 cm^{-1} (methanol). For comparison, the J-weighted average of the $^4P \leftarrow {}^4F$ transition in the bare dication is at 14 561 cm^{-1}.
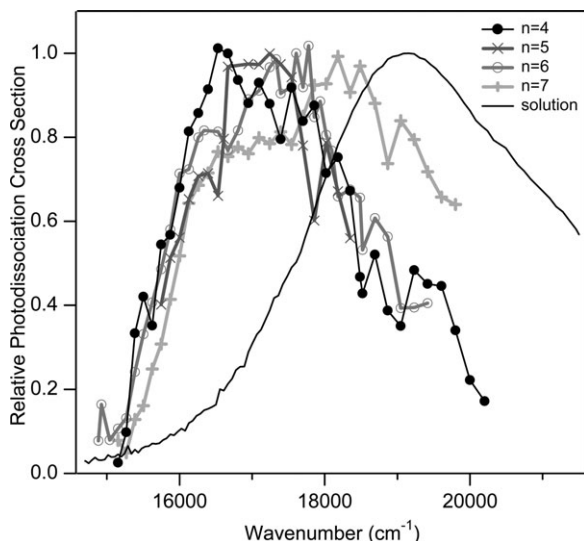
Fig. 2 Comparison of total photodissociation spectra of Co^{2+} $(CH_3OH)_n$ ($n = 4$–7), along with the solution spectrum of Co(II) in methanol.

Fig. 3 Photodissociation spectra of $Co^{2+}(H_2O)_4$ and $Co^{2+}(CH_3OH)_4$ along with the aqueous solution spectrum of $Co^{2+}(H_2O)_4$ obtained by Swaddle and Fabes (Ref. 21). The gas phase spectra are red shifted ~ 1200 cm^{-1} from the aqueous absorption spectrum, as indicated by the dotted line.

local environment around the metal. This could certainly account for the small difference between the absorption of Co(II) in water and methanol solution, but it probably does not account for the large differences between methanol and water clusters. Another possibility is that $Co^{2+}(CH_3OH)_6$ is not six coordinate, but rather is four coordinate, with two solvent molecules in the second solvent shell. Four coordinate tetrahedral Co(II) complexes absorb much more strongly than octahedral complexes, with $\varepsilon \approx 100$–1000 M^{-1} cm^{-1}, and, in solution, Co(II) shifts from octahedral to tetrahedral coordination with bulkier solvents and increased temperature.[11,21]

Fig. 2 highlights the evolution of the photodissociation spectra of $Co^{2+}(CH_3OH)_n$ with cluster size. Overall, the $n = 4$, 5 and 6 spectra are similar, but the $n = 7$ spectrum is much broader, with two peaks. The spectra will be discussed in turn.

The smallest cluster studied, $Co^{2+}(CH_3OH)_4$ is also the strongest chromophore. Fig. 3 compares the gas phase spectra of $Co^{2+}(CH_3OH)_4$ and $Co^{2+}(H_2O)_4$ to the aqueous $Co^{2+}(H_2O)_4$ spectrum obtained by Swaddle and Fabes.[21] They observed $Co^{2+}(H_2O)_4$ in very high temperature (up to 625 K) aqueous solutions and obtained its spectrum by subtracting the contribution from $Co^{2+}(H_2O)_6$. The photodissociation spectra of the two clusters are very similar, with the water cluster red shifted 1200 cm^{-1} from the solution spectrum, and the methanol cluster red shifted a further 300 cm^{-1}, with a maximum at 16 530 cm^{-1}. Both species have a shoulder at higher energy. The cross sections at the major peaks are 2.5×10^{-19} cm^2 ($\varepsilon = 150$ M^{-1} cm^{-1}) for $Co^{2+}(H_2O)_4$ and 4.8×10^{-19} cm^2 ($\varepsilon = 290$ M^{-1} cm^{-1}) for $Co^{2+}(CH_3OH)_4$. The $n = 4$ clusters are the strongest chromophores of the clusters studied, with extinction coefficients typical of tetrahedral complexes.

In our earlier studies, we did not observe photodissociation of $Co^{2+}(H_2O)_5$ or $Ni^{2+}(H_2O)_5$ over the 15 000 cm^{-1} to 22 000 cm^{-1} range investigated.[8,9] Only small quantities of the pentahydrate clusters could be produced, making their study difficult. In contrast, although $Co^{2+}(CH_3OH)_5$ is the least abundant of the methanol clusters studied, it was found to dissociate and the total photodissociation spectrum is shown in Fig. 2. The cluster has a single, relatively narrow peak with a maximum photodissociation cross section of $\sigma = 1.1 \times 10^{-19}$ cm^2 ($\varepsilon = 70$ M^{-1} cm^{-1}) at 17 240 cm^{-1}. Fig. 2 also shows that $Co^{2+}(CH_3OH)_6$ has a similar photodissociation spectrum (and similar cross section, $\sigma = 2 \times 10^{-19}$ cm^2) to the smaller $n = 4$ and 5 clusters. If the $n = 7$ cluster were simply the $n = 6$ cluster with an outer-shell solvent molecule, then their photodissociation spectra would be very similar. This is what we observe for
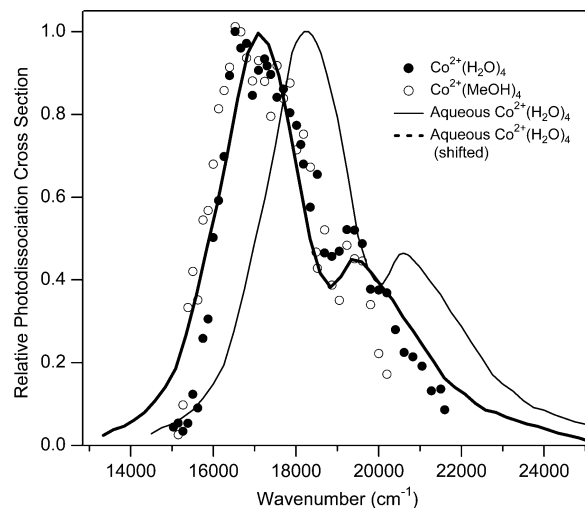
the water clusters, with $Co^{2+}(H_2O)_7$ shifted 150 cm^{-1} to higher energy of $Co^{2+}(H_2O)_6$, towards the solution spectrum.[9] In contrast, the spectrum of $Co^{2+}(CH_3OH)_7$ is broader than that of $Co^{2+}(CH_3OH)_6$, and shifted 850 cm^{-1} towards the solution spectrum with a photodissociation cross section of 1×10^{-19} cm^2 ($\varepsilon = 60$ M^{-1} cm^{-1}) at 18 180 cm^{-1}.

The similarities in the photodissociation spectra of $Co^{2+}(CH_3OH)_n$ with $n = 4$, 5 and 6 suggest that they have a common chromophore, $Co^{2+}(CH_3OH)_4$. So, in the gas phase, $Co^{2+}(CH_3OH)_6$ exists as a four coordinate structure, with two solvent molecules in the second solvation shell, perhaps in equilibrium with a more weakly absorbing six coordinate structure. The differences between the spectrum of $Co^{2+}(CH_3OH)_7$ and the other clusters suggests that its spectrum is due to a six coordinate structure (with one second shell solvent molecule). In solution, the additional solvent molecules further shift the equilibrium towards the observed six coordinate structure.

Experiments by Stace and coworkers reveal similar behavior for Mn^{2+} clusters with water, methanol and larger alcohols.[27] Neutral metal–solvent clusters formed in a pick-up source are ionized by electron impact. In each case Mn^{2+}(solvent)$_4$ is the most abundant ion produced. Collision induced dissociation of larger clusters also tends to form Mn^{2+}(solvent)$_4$, especially for the alcohols. This implies that this cluster is particularly stable. Density functional calculations predict that the lowest energy structure for $Mn^{2+}(CH_3OH)_6$ has four inner shell and two outer shell solvent molecules.[27] These calculations predict that $Mn^{2+}(H_2O)_6$ is also four coordinate, while the experiments do not provide a definite answer on this point.

In aqueous and methanolic solution, Mn^{2+} and Co^{2+} are both six coordinate.[3,11] These structures are, however, not static, as the rate of exchange of inner shell and bulk water molecules is $> 10^6$ s^{-1}.[3] For the late first row transition metals this exchange is by a dissociative mechanism through a transient five coordinate intermediate.[28] However, these intermediates are sufficiently short-lived that the experiments show that, on average, these metal ions are six coordinate in solution. The most likely explanation for gas-phase clusters such as $Co^{2+}(CH_3OH)_6$ being four coordinate while Co^{2+} in methanol solution is six coordinate is that hydrogen bonding to the outer solvation shells stabilizes the six coordinate structure more than the four coordinate. This view is supported by *ab initio* (MP2) calculations on Zn^{2+} clusters with water. For $Zn^{2+}(H_2O)_6$, the four, five and six coordinate structures lie

within 4 kJ mol^{-1} of each other. However, for Zn^{2+}(H$_2$O)$_{12}$ the six coordinate structure is 28 kJ mol^{-1} more stable than the four coordinate structure.[29]

Photodissociation dynamics

There are many pathways the clusters studied can follow when photodissociating. In the larger clusters ($n = 5$–7) dissociation simply occurs by the loss of one or more solvent molecules, with the number of solvent molecules lost depending on the cluster size and photon energy. Co^{2+}(CH$_3$OH)$_5$ photodissociates by losing one methanol across the entire region studied. In Co^{2+}(CH$_3$OH)$_6$ there is competition between the loss of one and two solvent molecules, as shown in Fig. 4. At low photon energies the photoexcited clusters have insufficient energy to lose the second solvent molecule, or this loss occurs after the molecules leave the reflectron (about 3 μs). The competition between loss of one and two solvent molecules thus depends on the binding energies of the sixth and fifth methanol molecules. However, initial vibrational energy in the thermal clusters contributes significantly to the total internal energy of the photoexcited clusters. This thermal vibrational energy is about 4000 cm^{-1}, with a broad distribution (FWHM of 3000 cm^{-1}). As a result, the transition between loss of one and loss of two solvent molecules is broad, giving little information on the thermodynamics. Cooling the ions to ∼80 K will result in much lower thermal energies (∼300 cm^{-1}) and should lead to a sharper transition. The largest clusters studied, Co^{2+}(CH$_3$OH)$_7$ primarily photodissociate by losing two solvent molecules. Loss of one methanol molecule is 30% at 16 000 cm^{-1} and drops with increasing energy; small amounts of loss of three methanol molecules are also observed.

In our earlier work, we observed interesting dynamics in the photodissociation of Co^{2+}(H$_2$O)$_4$ and Ni^{2+}(H$_2$O)$_4$. Loss of one solvent molecule is a very minor channel; dissociation occurs primarily by proton transfer:[8,9]

$$\text{Co}^{2+}(\text{H}_2\text{O})_4 + h\nu \rightarrow \text{CoOH}^+(\text{H}_2\text{O})_2 + \text{H}_3\text{O}^+ \qquad (1)$$

For the corresponding methanol cluster, photodissociation also involves proton transfer:

$$\begin{aligned}\text{Co}^{2+}(\text{CH}_3\text{OH})_4 + h\nu &\rightarrow \text{CoOCH}_3{}^+(\text{CH}_3\text{OH})_2 \\ &\quad + \text{H}^+(\text{CH}_3\text{OH}) \end{aligned} \qquad (2)$$

In low energy CID of Co^{2+}(CH$_3$OH)$_4$, Kohler and Leary also observe proton transfer as a major channel but observe

Fig. 5 Time-of-flight spectra of H$_3$O$^+$ produced by 570 nm photodissociation of Co^{2+}(H$_2$O)$_4$ (top) and H$^+$(CH$_3$OH) produced by photodissociation of Co^{2+}(CH$_3$OH)$_4$ at 545 nm (bottom), taken under low field conditions. The solid lines are simulations with total kinetic energy release (KER) of 110 kJ mol^{-1} and 170 kJ mol^{-1}, respectively. Tailing in the H$^+$(CH$_3$OH) spectrum indicates a dissociation lifetime $\tau = 145$ ns.

several minor channels, including hydride transfer to form CoH$^+$.[13]

Due to Coulomb repulsion between the two fragments, reactions (1) and (2) should lead to substantial kinetic energy release (KER). Fig. 5 shows the time-of-flight profiles of the H$_3$O$^+$ and H$^+$(CH$_3$OH) fragments. The photodissociation laser's polarization was parallel to the ion flight path. Spectra taken at perpendicular laser polarization show no systematic difference, indicating that there is no laser polarization dependence in photodissociation of Co^{2+}(H$_2$O)$_4$ and Co^{2+}(CH$_3$OH)$_4$. No polarization dependence should be observed in photodissociation of (a) a tetrahedral molecule or (b) a molecule with a dissociation lifetime greater than its rotational period and in which several rotational states are photoexcited.[30] Co^{2+}(H$_2$O)$_4$ and Co^{2+}(CH$_3$OH)$_4$ likely fulfil both conditions. Ions which dissociate with kinetic energy release towards the detector arrive at early times and ions which dissociate away from the detector arrive late. Ions whose KER is perpendicular to the flight path miss the detector, leading to the dip in the center of each spectrum. The spectra shown were taken under low field (108 V cm^{-1}) conditions in the reflectron, where KER will split the peaks more than under normal high field (205 V cm^{-1}) conditions. The figure also shows a simulation of the fragment time-of-flight profile.[8,31,32] The simulation is generated by convoluting a histogram of calculated fragment flight times with an instrument response function. The histogram is produced by starting parent ions at a range of positions in the extraction region of the time-of-flight mass spectrometer, using simple electrostatics to calculate their positions and velocities in the reflectron when the photodissociation laser is fired, then calculating the total flight times of resulting fragment ions to the detector, including kinetic energy release, dissociation anisotropy, dissociation rate, and the finite size of the detector. The small shoulders at flight times of 110 ns and 220 ns are due to ringing caused by imperfect impedance matching. For H$_3$O$^+$, the total KER of 110 kJ mol^{-1} corresponds to 48% of the available energy.[9] For H$^+$(CH$_3$OH), a total KER of 170 kJ mol^{-1} is found to best fit the TOF profile. In addition, the tailing in the H$^+$(CH$_3$OH) peak reflects the lifetime of the photoexcited Co^{2+}(CH$_3$OH)$_4$. A dissociative lifetime of 145 ns is obtained from the simulation. Lack of tailing for Co^{2+}(H$_2$O)$_4$ indicates a dissociative lifetime below 30 ns.

The modest kinetic energy releases suggest that the positive charges are well separated at the transition state for proton transfer. This is supported by calculations by Beyer[10,33] which
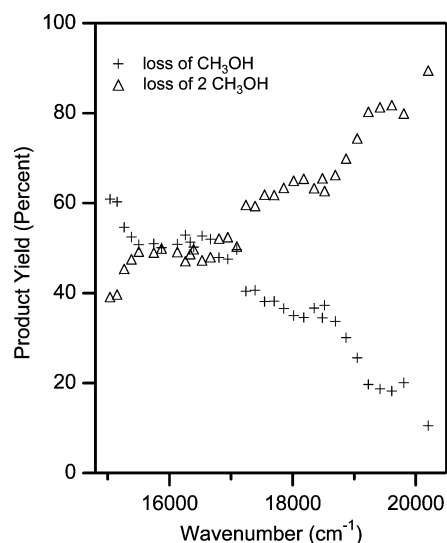

Fig. 4 Competition between loss of one and two methanol molecules in photodissociation of Co^{2+}(CH$_3$OH)$_6$ as a function of photon energy.

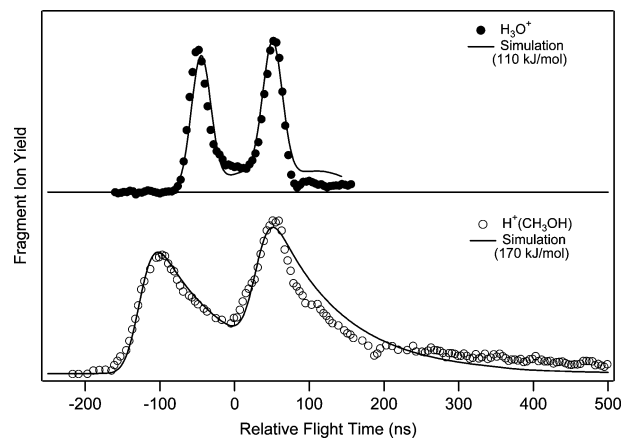predict a salt-bridge mechanism for photodissociation of $Co^{2+}(H_2O)_4$. In this mechanism one of the four inner-shell waters moves to the outer shell, then abstracts a proton (forming a $M^{2+}\cdots OH^-\cdots H_3O^+$ salt bridge) and departs. The salt-bridge transition state is calculated to lie 166 kJ mol^{-1} above the products, consistent with our experimentally determined KER of 110 ± 20 kJ mol^{-1}, as some of the remaining energy could go into internal energy of the products. The higher KER observed for $Co^{2+}(CH_3OH)_4$ dissociation suggests that its transition state lies further above the products. This higher barrier, as well as additional vibrational degrees of freedom in the methanol complex, likely cause it to dissociate more slowly than $Co^{2+}(H_2O)_4$.

Conclusions

Photofragment spectroscopy has been used to measure the photodissociation spectra of $Co^{2+}(CH_3OH)_n$ ($n = 4$–7) clusters produced by electrospray. We observe a notable difference between the photodissociation spectra of methanol and water complexes. $Co^{2+}(CH_3OH)_6$ absorbs significantly more strongly than $Co^{2+}(H_2O)_6$, and similarities between the photodissociation spectrum of $Co^{2+}(CH_3OH)_6$ and the smaller clusters suggest that clusters with a four coordinate geometry (and two outer-shell solvent molecules) contribute to its spectrum. In contrast, our earlier studies indicate that $Co^{2+}(H_2O)_6$ is six coordinate, and its spectrum is quite different from that of $Co^{2+}(H_2O)_4$. The larger clusters $Co^{2+}(CH_3OH)_n$ ($n = 5$–7) dissociate by simple loss of solvent molecules, with more solvent molecules being lost for larger clusters and at higher photon energies. $Co^{2+}(CH_3OH)_4$ dissociates by proton transfer, as does the analogous water cluster. The observed products and kinetic energy release support a salt-bridge dissociation mechanism. Dissociation of the methanol complex leads to higher kinetic energy release, and a significantly longer lifetime, than for the water complex, suggesting that the methanol complex has a higher barrier to dissociation.

Acknowledgements

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