The Dissociation Energy, Electronic and Vibrational Spectroscopy of Co\(^+\)(H\(_2\)O) and its Isotopomers

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Abstract: The electronic spectra of Co\(^+\)(H\(_2\)O), Co\(^+\)(HOD) and Co\(^+\)(D\(_2\)O) have been measured from 13500 cm\(^{-1}\) to 18400 cm\(^{-1}\) using photodissociation spectroscopy. Transitions to four excited electronic states with vibrational and partially resolved rotational structure are observed. Each electronic transition has an extended progression in the metal-ligand stretch, and the absolute vibrational quantum numbering is assigned by comparing isotopic shifts between Co\(^+\)(H\(_2\)\(_{16}\)O) and Co\(^+\)(H\(_2\)\(_{18}\)O). For the low-lying excited electronic states, the first transition detected is to \(v_3'=1\). Extrapolation from this data allows the Co\(^+\)-(H\(_2\)O) binding energy to be determined as \(D_0(0 \text{ K})(\text{Co}^+\text{-H}_2\text{O})=13730\pm90 \text{ cm}^{-1}(164.2\pm1.1 \text{ kJ/mol})\). The photodissociation spectrum shows well-resolved \(K_a\) band structure due to rotation about the Co-O axis. This permits determination of the spin rotation constants \(\epsilon''=-6 \text{ cm}^{-1}\) and \(\epsilon'=4 \text{ cm}^{-1}\) and the excited state rotational constant \(A'=14.5 \text{ cm}^{-1}\) for the 15872 cm\(^{-1}\) band. However, the \(K_a\) rotational structure depends on \(v_3'\), making the rotational constants unreliable. From the nuclear spin statistics of the rotational structure, the ground state is assigned as \(^3\!B_1\). The electronic transitions observed are from the Co\(^+\)(H\(_2\)O) ground state (which correlates to the \(^3\!F, \ 3d^8\) ground state of Co\(^+\)) to excited states which correlate to Co\(^+\) (\(^3\!F, \ 3d^74s\) and \(^3\!P, \ 3d^8\)). These excited states of Co\(^+\) interact less strongly with water than the ground state. As a result, the excited states are less tightly bound and have a longer metal-ligand bond than the ground state. Calculations at the CCSD(T)/aug-cc-pVTZ level predict that binding to Co\(^+\) increases the H-O-H angle in water from 104.1\(^{\circ}\) to 106.8\(^{\circ}\), as the metal removes electron density from the oxygen lone pairs. The O-H stretching frequencies of the ground states of Co\(^+\)(H\(_2\)O) and Co\(^+\)(HOD) were measured by combining IR excitation with visible photodissociation in a double resonance experiment. In Co\(^+\)(H\(_2\)O) the O-H symmetric stretch is \(v_1'=3609.7 \text{ cm}^{-1}\); the antisymmetric stretch is \(v_5'=3679.5 \text{ cm}^{-1}\). These values are 47 and 76 cm\(^{-1}\), respectively lower than those in bare H\(_2\)O. In Co\(^+\)(HOD) the O-H stretch is observed at 3650 cm\(^{-1}\), a red shift of 57 cm\(^{-1}\) relative to bare HOD.

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I. INTRODUCTION

The importance of metal-water interactions in solvation, catalysis and biology has inspired numerous experimental and computational investigations of metal ion-water complexes. Gas-phase studies allow for direct examination of the intrinsic interactions between metal ions and solvent molecules, including their dependence on the ions’ charge and electron configuration and the metal-ligand bond’s effect on solvent structure.\(^1\) The binding energies of water molecules to first-row transition metal cations \(M^+\) were first measured by Magnera, David and Michl\(^2\) and Marinelli and Squires\(^3\) using collision-induced dissociation (CID) in a triple-quadrupole mass spectrometer and were later refined in a guided-ion beam (GIB) measurement by Dalleska, Honma, Sunderlin and Armentrout.\(^4\)

The \(\text{Co}^+(\text{H}_2\text{O})\) complex is of particular interest because \(\text{Co}^+\) binds strongly to ligands, providing insight into metal-ligand interactions. This is illustrated by the measured \(\text{Co}^+\)-H\(_2\)O bond dissociation energies: 155±12 kJ/mol,\(^2\) 168±16 kJ/mol,\(^3\) and 161±7 kJ/mol.\(^4\) This strong non-covalent interaction is due to the cobalt ion’s has a 3d\(^8\) (\(^3\)F\(_4\)) ground state.\(^5\) Metal cations with 3d\(^n\) electronic configurations bind more strongly than those with 3d\(^{n-1}\) 4s\(^1\) configurations, as the 3d orbital is smaller than the 4s, which allows the metal to get closer to the ligand. Unlike the s orbitals, the d orbitals are directional, so the fully occupied orbitals point away from the ligand, reducing metal-ligand repulsion. One potential implication of this strong bond is the recent proposal that cobalt ion-water interactions are the key to efficient \(\text{Co}^{2+}/\text{Co}^+\) reduction in the cobalamin (vitamin B\(_{12}\)) cofactor of methyltransferases.\(^6\)
There have been several studies of the electronic spectra of M\(^+\)(H\(_2\)O)\(_n\) complexes. This includes studies of hydrated alkaline earth cations Mg\(^+\)(H\(_2\)O)\(_7\), Ca\(^+\)(H\(_2\)O)\(_8\) and Sr\(^+\)(H\(_2\)O)\(_9\) and transition metal cations V\(^+\)(H\(_2\)O)\(_{10}\), Ni\(^+\)(H\(_2\)O)\(_{11}\) and Zn\(^+\)(H\(_2\)O)\(_{12}\). Poisson et al. studied photolysis of Co\(^+\)(H\(_2\)O)\(_n\) (n=1-10) at 532, 355 and 266 nm, but observed no photodissociation of Co\(^+\)(H\(_2\)O).\(^{13}\) In studies of hydrated Co(II) cluster ions, our group measured the electronic spectra of Co\(^{2+}\)(H\(_2\)O)\(_n\) (n=4-7) in the visible via photodissociation,\(^{14}\) and Donald et al. photoexcited M\(^{2+}\)(H\(_2\)O)\(_n\) (M=Mn, Fe, Co, Cu; n=19-124) at 193 and 248 nm to determine H\(_2\)O ligand binding energies for these large clusters.\(^{15}\)

In addition, Brucat and coworkers measured electronic spectra of Co\(^+\)(L) complexes for L=Ar, Kr, Xe, CO\(_2\),\(^{16}\) and N\(_2\).\(^{18}\) Duncan and coworkers recently measured the electronic spectrum of Co\(^+\)(Ne).\(^{19}\) The photodissociation spectra of these complexes extend throughout the visible, with vibrationally- and, often, rotationally-resolved transitions to several excited states. The spectra are similar, as they are due to metal-centered transitions between states arising from the d\(^8\) (\(^3\)F\(_4\)) Co\(^+\) ground state and states correlated to d\(^7\)s (\(^3\)F) and d\(^8\) (\(^3\)P) excited states of Co\(^+\). Analysis of the spectra reveals metal-ligand bond lengths, excited state vibrational frequencies, and diabatic dissociation energies for the ground and excited electronic states.

Vibrational spectra of several transition metal M\(^+\)(H\(_2\)O)\(_n\) have been measured in the O-H stretching region. These spectra elucidate the cation’s effect on the ligands’ bonds and, for larger clusters, reveal hydrogen-bonding networks. Duncan and coworkers have used argon tagging to measure vibrational spectra of M\(^+\)(H\(_2\)O) (M= Sc,\(^{20}\) V,\(^{21}\) Cr,\(^{22}\) Mn,\(^{23}\) Fe,\(^{24}\) Ni,\(^{25}\) Cu\(^{26}\)) and M\(^{2+}\)(H\(_2\)O) (M= Sc,\(^{20}\) V,\(^{27}\) Cr,\(^{22}\) Mn,\(^{23}\)) in the O-H
stretching region. The vibrational spectrum of Co\(^{+}\)(H\(_2\)O) has not been previously published, although Furukawa et al. measured the photodissociation spectra of Co\(^{+}\)(H\(_2\)O)\(_n\) (n=4-6) in the O-H stretching region.\(^{28}\) O'Brien and Williams also used vibrational spectra of solvated, multiply charged ions M\(^{2+}\)(H\(_2\)O)\(_n\) (M=Mn, Fe, Co, Ni, Cu, Zn; n=5-8) in the O-H stretching region to determine the coordination number of the metal ion.\(^{29}\)

Several groups have also calculated the structure and binding energies of Co\(^{+}\)(H\(_2\)O).\(^{30}\) The Co\(^{+}\)(H\(_2\)O) complex is calculated to be planar, with C\(_{2v}\) symmetry. However, the calculations predict four low-lying electronic states whose energies are so similar that the ground state depends on the level of theory.

Electronic spectroscopy of M\(^{+}\)(H\(_2\)O) potentially allows one the ability to measure bond dissociation energies, vibrational levels of excited states, excited state dissociation energies, and in some cases rotational structure, which can be used to determine the geometries of the ground and excited electronic states. Vibrational spectra of M\(^{+}\)(H\(_2\)O) reveal how metal ions affects bonds in the H\(_2\)O ligand. Our group used photodissociation spectroscopy and vibrationally mediated photodissociation (VMP) to measure the electronic spectrum and O-H stretching frequencies of Ni\(^{+}\)(H\(_2\)O).\(^{11}\) The current experiments extend this work to the Co\(^{+}\)(H\(_2\)O) complex and its isotopomers.

II. EXPERIMENTAL METHODS

The experiments are performed utilizing a home-built laser ablation source dual time-of-flight reflectron mass spectrometer, which is described in detail elsewhere.\(^{31}\) Cobalt ions are produced through the ablation of a cobalt rod by the 532 nm second
harmonic of a pulsed Nd:YAG laser operating at 15 mJ/pulse at a repetition rate of 20 Hz. The Co$^+$ interacts with a gas mix of 0.1-0.4% H$_2$O seeded in helium at 30 psi backing pressure introduced through a pulsed piezoelectric valve to form Co$^+$(H$_2$O). Ions expand into vacuum and cool, forming a supersonic molecular beam with a rotational temperature of ~15 K. The ion beam is skinned, extracted into the time-of-flight mass spectrometer, accelerated, and re-referenced to ground potential. Ions are mass selected and are dissociated with a laser at the turning point of the reflectron. Parent and fragment molecules are reaccelerated and are mass analyzed in the second time-of-flight stage. Ions are measured at a microchannel plate detector. The resulting signal is amplified, collected on a digital oscilloscope or a gated integrator, and recorded using a LabView-based program. By taking the ratio of the amount of fragments to parents and laser power as a function of laser wavelength we obtain the photodissociation spectrum.

For electronic spectroscopy studies, a wavelength range of 543-740 nm (13511-18431 cm$^{-1}$) was scanned with a Continuum ND6000 dye laser at a line width of 0.1 cm$^{-1}$ using a variety of laser dyes. A multipass mirror arrangement$^{32}$ allows the laser to make approximately 11 passes through the ion cloud, enhancing the dissociation yield. To avoid damaging the mirrors, the dye laser is attenuated to <10 mJ per pulse. The infrared studies use a Laser Vision IR OPO/OPA tunable from 2200 cm$^{-1}$ to >4000 cm$^{-1}$. This laser is also multi-passed and produces approximately 10 mJ per pulse near 3600 cm$^{-1}$, with a line width of approximately 1.8 cm$^{-1}$. The dye laser wavelength is calibrated using the optogalvanic spectrum of neon; the IR laser is calibrated using the absorption spectrum of water vapor. The spectra of Co$^+$(HOD), Co$^+$(D$_2$O) and Co$^+$(H$_2$^{18}O) were also measured to aid in analyzing and assigning the spectrum. They were produced using a
H$_2$O/D$_2$O mixture, pure D$_2$O, and H$_2^{18}$O (Cambridge Isotope Labs) in the carrier gas respectively.

The computational studies used the Gaussian 09 suite of programs. The geometries, relative energies and vibrational frequencies of low-lying states of Co$^+(\text{H}_2\text{O})$ were calculated with the B3LYP and BHandHLYP hybrid density functionals with the 6-311++G(3df,p) basis set. Higher-lying excited states were calculated using time-dependent density functional theory (TD-DFT). In addition, the geometries and relative energies of low-lying states of Co$^+(\text{H}_2\text{O})$ were calculated at the CCSD(T)/aug-cc-pVTZ level, as was the Co-O stretch potential.

III. RESULTS AND DISCUSSION

A. Electronic Spectroscopy

Photodissociation studies of Co$^+(\text{H}_2\text{O})$ and its isotopomers Co$^+(\text{HOD})$, Co$^+(\text{D}_2\text{O})$ and Co$^+(\text{H}_2^{18}\text{O})$ were carried out from 13500 cm$^{-1}$ to 18400 cm$^{-1}$. In this wavelength region, only one active dissociation channel, cobalt cation + water, is observed. This is not surprising, as production of CoOH$^+$ + H from Co$^+(\text{H}_2\text{O})$ is endothermic by 360 kJ/mol, requiring wavelengths below 332 nm. The electronic spectrum was thus obtained by monitoring the Co$^+$ fragment from photolysis of Co$^+(\text{H}_2\text{O})$ and its isotopomers. The photodissociation spectrum is structured with well-resolved vibrational features and partially resolved rotational structure as illustrated in Figure 1.

The electronic spectrum is similar to those of other Co$^+(\text{L})$ (L=Ne, Ar, Kr, Xe, CO$_2$) complexes, which show transitions to several excited electronic states, with long progressions in the metal-ligand stretch. Here, a number of the vibrational
features are single, sharp peaks, while others are multiplets (typically triplets). This is similar to rotational structure observed in the electronic spectra of Mg\(^+(H_2O)\),\(^{7b-d}\) Ca\(^+(H_2O)\),\(^5\) Ni\(^+(H_2O)\)\(^{11}\) and Zn\(^+(H_2O)\).\(^{12}\) These molecules are near-prolate tops. Rotation about the M-O bond (the \(a\) axis) has a small moment of inertia (only the hydrogen atoms are off axis), and hence a large \(A\) rotational constant of \(\sim 14\ \text{cm}^{-1}\). The \(B\) and \(C\) rotational constants are similar and much smaller (\(\sim 0.25\ \text{cm}^{-1}\), depending on the metal and the M-O bond length). The sharp single peaks such as the one at 13964 cm\(^{-1}\) in Figure 1 are due to parallel bands, \(\Delta K_a=0\). Perpendicular bands, which have \(\Delta K_a=\pm 1\), lead to several peaks spaced by \(\sim 30\ \text{cm}^{-1}\), (as is observed near 13808 cm\(^{-1}\) for Co\(^+(H_2O)\)) as several initial \(K_a\) states are populated even at the \(\sim 15K\) rotational temperature. This allows us to distinguish four different vibrational progressions, two of which are parallel bands (labeled \(B\) and \(D\)) while the other two are perpendicular bands (labeled \(A\) and \(C\)). In order to determine whether these are due to four different electronic states or to combinations of vibrations, and to assign the vibration progressions, we measured spectra of isotopomers and calculated the geometries, rotational constants and vibrational frequencies of the ground and several excited states of Co\(^+(H_2O)\).

The nature of the ground state of Co\(^+(H_2O)\) has been the subject of several studies. Early calculations by Rosi and Bauschlicher using the modified coupled-pair functional method showed that interaction of ground state Co\(^+\) (\(d^8, 3F\)) with \(H_2O\) leads to four low-lying states.\(^{30a}\) Rosi and Bauschlicher orient the molecule so that it lies in the \(xz\) plane. However, using a standard axis system in which the molecule is in the \(yz\) plane, with the Co-O bond along the \(z\) axis, the \(b_1\) and \(b_2\) orbitals are reversed from
those of Rosi and Bauschlicher. For consistency, all orbitals and states have been converted to standard notation. Rosi and Bauschlicher predict the ground state to be $^3\text{B}_1$, with the nearly degenerate $^3\text{A}_2$ and $^3\text{A}_1$ states 245 cm$^{-1}$ higher in energy and the $^3\text{B}_2$ state at 630 cm$^{-1}$. The results of several calculations, which generally predict a $^3\text{B}_1$ or $^3\text{A}_2$ ground state, are summarized in table 1.

The geometry of each of the four low-lying states of Co$^+$(H$_2$O) was optimized at the B3LYP/6-311++G(3df,p), BHHandHLYP/6-311++G(3df,p), and CCSD(T)/aug-cc-pVTZ level. In each case, the $^3\text{B}_1$, $^3\text{A}_2$ and $^3\text{A}_1$ states are nearly degenerate. The $^3\text{B}_2$ state lies somewhat higher in energy and distorts from $C_{2v}$ to $C_s$ symmetry by out-of-plane hydrogen bending. The ground state was calculated to be the $^3\text{A}_2$ state with B3LYP and BHHandHLYP and $^3\text{B}_1$ with CCSD(T). As will be discussed later, the experiments determine the ground state to be $^3\text{B}_1$. Molecular orbitals for the $^3\text{B}_1$ state are shown in figure 2. In $C_{2v}$ symmetry, the 3d orbitals on Co$^+$ lead to $3d\sigma(z^2)$ and $3d\delta(x^2-y^2)$ with $a_1$ symmetry, $3d\delta(xy)$ with $a_2$ symmetry, $3d\pi(xz)$ with $b_1$ symmetry, and $3d\pi(yz)$ with $b_2$ symmetry. In the $^3\text{B}_1$ state, the $3d\sigma(z^2)$ and $3d\delta(x^2-y^2)$ orbitals mix. One hole is in this mixed, $a_1$ orbital, and the second hole is in the $3d\pi(xz)$ orbital. This mixing was also observed by Rosi and Bauschlicher.

The Co$^+$(H$_2$O) molecule has six vibrations, whose calculated values are shown in Table 2. The three high-frequency vibrations are essentially perturbed H$_2$O vibrations. There are also three low-frequency vibrations: the Co-O stretch and two H$_2$O hindered rotations (bends). Five of the six vibrations primarily correspond to motion of the hydrogen atoms. Thus, substitution of deuterium for hydrogen should lead to large isotopic shifts in these frequencies, while the Co-O stretch should show only a small H/D
isotopic shift. Experimentally, each band (A-D) consists of a series of peaks separated by \( \sim 320 \text{ cm}^{-1} \). This spacing decreases slightly at higher energy due to vibrational anharmonicity. Upon deuteration, the peak spacing decreases only slightly. Therefore, the observed vibrations are assigned to a progression in the Co-O stretch (\( v_3' \)) and each band (A-D) corresponds to a transition to a different electronic state.

The first peak observed in the photodissociation spectrum is not necessarily the transition to \( v'=0 \), as this transition might lie below the dissociation energy. Therefore, the origin band, and so the vibrational quantum numbering, is not clear from the \( \text{Co}^+(\text{H}_2\text{O}) \) spectrum, but can be determined using isotope shifts. For an electronic transition between two Morse oscillators, the shift is given by

\[
\Delta E_{iso} = \omega_{e_3'} (1 - \rho_3) v_3' - \omega_{e x e_3'} (1 - \rho_3^2) (v_3') (v_3' + 1) + \Delta T_{00} \quad (1)
\]

where \( \omega_{e_3}' \) and \( \omega_{e x e_3}' \) are the upper state frequency and anharmonicity, \( \Delta E_{iso} \) is the difference in the \( v_3' \rightarrow v_3''=0 \) transition energy between the light (L) and heavy (H) isotopomers, \( \rho_3 = \sqrt{\mu_3^L / \mu_3^H} \) and \( \Delta T_{00} \) is the difference in the origin transition between the two isotopomers.

In principle, in order to determine the quantum numbering of the transitions, the observed energy shift can be used between any two of \( \text{Co}^+(\text{H}_2\text{O}), \text{Co}^+(\text{HOD}), \) and \( \text{Co}^+(\text{D}_2\text{O}) \). However, hydrogen-to-deuterium substitution leads to two complications. The first is that it significantly changes the \( A \) rotational constant and thus the appearance of the perpendicular bands. Rotational simulations of each vibrational feature would thus be required to determine the isotope shift. The second difficulty is that H/D substitution
leads to large frequency shifts in five of the six vibrations. If the frequencies of these vibrations change upon electronic excitation, it will lead to a shift in the zero point energy (and hence in $T_{00}$) upon deuteration. It is difficult to quantify this effect, as only one of these vibrational frequencies ($v_5''$) is measured. Clearly, isotopic substitution at Co or O is preferable. Cobalt-59 is the only stable isotope. So, isotopic shifts were measured using $H_2^{18}O$. This has two advantages: $H_2^{18}O$ does not affect the $A$ rotational constant, and the shift in the zero point energy is small. Lessen et al. also used $^{18}O$ substitution to assign the vibrational quantum numbering in $V^+(H_2O)$.

Figure 3 shows the observed shift from $Co^+(H_2^{16}O)$ to $Co^+(H_2^{18}O)$ for the first three peaks in each of the four electronic states. For the higher-energy bands, C and D, the observed shifts lie along the solid line, indicating that the first observed peak is due to the $v_3'=0 \leftrightarrow v_3''=0$ transition. However, for the low-energy bands, A and B, the shifts lie along the upper, dashed line, so the first peak observed is due to the $v_3'=1 \leftrightarrow v_3''=0$ transition. Once the quantum numbers have been assigned, the Co-O stretching frequencies and anharmonicities in each excited electronic state can be calculated. The results are summarized in Table 2. All of the excited states have similar Co-O stretching frequencies of $v_3 \approx 325$ cm$^{-1}$. This is substantially lower than the calculated CCSD(T)/aug-cc-pVTZ value for the ground state: $v_3''=400$ cm$^{-1}$.

The lowest energy at which $Co^+(H_2O)$ photodissociates is the $v_3'=1, K_a'=0 \leftrightarrow v_3''=0, K_a''=1$ transition of band A at 13808 cm$^{-1}$. This gives an upper limit to the $Co^+-H_2O$ bond strength (corrected for the rotational energy in $K_a''=1$, approximately 8 cm$^{-1}$) of $D_0(Co^+-H_2O) \leq 13816$ cm$^{-1}$. Transitions to $v_3'=0$ are not observed for bands A and B, implying that they lie below the dissociation energy. The bond strength's lower limit is estimated from
the observed $v'_3=1-5$ transitions in band B extrapolated to $v'_3=0$ at 13640 cm$^{-1}$. Combining the upper and lower limits gives $D_0(0K)(\text{Co}^+\text{-H}_2\text{O})=13730\pm90$ cm$^{-1}$ = 164.2$\pm$1.1 kJ/mol. This is in agreement with the values reported earlier: 155$\pm$12 kJ/mol, $^2$ 168$\pm$16 kJ/mol $^3$ and 161$\pm$7 kJ/mol. $^4$

The relative intensities in each $v'_3$ vibrational progression reflect the change in the Co-O bond length following electronic excitation. These intensities are calculated by solving the one-dimensional Schrödinger Equation along the Co-O stretch coordinate. Here the molecule is treated as a pseudo diatomic, with the H$_2$O as a single “atom” with mass 18 amu. To determine $\Delta r_{\text{Co-O}}$ from the experimental intensities the ground electronic state is modeled as a Morse oscillator with the CCSD(T) vibrational frequency and experimental dissociation energy. For each excited state, a Morse oscillator with the experimental frequency and anharmonicity is used, and $\Delta r_{\text{Co-O}}$ is adjusted until the best match is found between the calculated and measured intensities. This corresponds to a change in the metal-ligand bond length $\Delta r_{\text{Co-O}}$ of 0.14 to 0.19 Å, depending on the excited state. Although this analysis does not identify the sign of $\Delta r_{\text{Co-O}}$, it is clear from the rotational structure (discussed below) that the bond length increases upon electronic excitation.

The excited states of $\text{Co}^+(\text{H}_2\text{O})$ accessed in this study correlate to electronically excited $\text{Co}^{++}+\text{H}_2\text{O}$. The excited states involved are identified by estimating the diabatic dissociation energy of each excited state. Treating the Co$^+$-H$_2$O stretch as a Morse oscillator,

$$D_e = \frac{v_3^2}{4 x_3} \quad (2)$$
where $\nu_3$ and $x_3$ are the Co-O stretching frequency and anharmonicity. The resulting values are shown in Table 2. The calculated dissociation energies have large uncertainties due to errors in anharmonicity. It would be more accurate to determine the excited state dissociation limits using a LeRoy-Bernstein plot which properly accounts for the long-range Co$^+$-H$_2$O interactions. This approach has been used to measure very precise bond strengths for Co$^+$-rare gas complexes.$^{16a, 16c, 19}$ Unfortunately, this method is not applicable as vibrational levels sufficiently close to the dissociation limit are not observed. The energy of the excited state of Co$^+$ is estimated using equation 3 and solving for $\Delta E(Co^+)$.  

$$D'_0 = D''_0 + \Delta E(Co^{\ast\ast}) - T_{00} \quad (3)$$

where $D''_0$ and $D'_0$ are dissociation energies for the ground and excited electronic state, $\Delta E(Co^\ast)$ is the energy difference between Co$^+$ and (Co$^\ast$)$^\ast$ and $T_{00}$ is the origin band for the transition in the molecule. Using $D''_0 = 13730$ cm$^{-1}$, the $D'_0$ values were calculated and are listed in Table 2. The resulting $\Delta E(Co^{\ast\ast})$ are sufficiently accurate to identify the triplet excited electronic state of Co$^+$ to which each excited state of Co$^+$($H_2O$) correlates, but not the spin-orbit state. States A and B correlate to Co$^+$ $^3F_J$ (3d$^7$4s) at 9813-11322 cm$^{-1}$, while the C and D states correlate to $^3P_J$ (3d$^8$) at 13261-13593 cm$^{-1}$. If the parallel and perpendicular bands correspond to transitions from the ground state of Co$^+$($H_2O$) (which correlates to the $^3F_4$ ground state of Co$^+$) to excited states with even $\Delta J$ and odd $\Delta J$ respectively, then we can assign the spin-orbit state to which each excited state correlates, and estimate $D'_0$ using equation 2, with the known $\Delta E(Co^{\ast\ast})$. These results are summarized in Table 2. Morse potential curves for the ground and excited states of
Co\(^+\)(H\(_2\)O) observed in this study are shown in figure 4. The excited states are bound by \(\sim 10000\) cm\(^{-1}\), or about 75% of the ground state binding energy. This is consistent with the decreased Co-O stretching frequency and increased Co-O bond length upon electronic excitation.

These results are similar to those observed in electronic photodissociation studies of Ni\(^+\)(H\(_2\)O) by our group and of Co\(^+\)(L) complexes by Brucat, Duncan and coworkers. In the Ni\(^+\)(H\(_2\)O) study, transitions from the \(^2\)A\(_1\) ground state of Ni\(^+\)(H\(_2\)O), which correlates to the \(^2\)D (3d\(^9\)) ground state of Ni\(^+\), to the nearly degenerate \(^2\)A\(_1\) and \(^2\)A\(_2\) ground states, which correlate to the \(^2\)F (3d\(^8\)4s) excited state of Ni\(^+\) are observed. Each band contains a long progression in the Ni-O stretch, as the Ni-O bond lengthens by 0.20 Å upon electronic excitation. The diabatic bond strength of the excited states is also \(\sim 78\)% that of the ground state.\(^{11}\) The electronic spectra of Co\(^+\)(L) (L=Ne,\(^{19}\) Ar,\(^{16a, b}\) Kr, Xe,\(^{16c}\) CO\(_2\)\(^{17}\) and N\(_2\)\(^{18}\)) all show transitions to excited states in the visible with extended progressions in the M-L stretch. The observed excited states correlate to Co\(^+\) \(^3\)F (3d\(^7\)4s) and \(^3\)P (3d\(^8\)). In addition, Brucat and coworkers observed weak transitions to singlet states which correlate to Co\(^+\) \(^1\)D (3d\(^8\)).\(^{16c}\) For many Co\(^+\)(RG) complexes, vibrational structure is observed up to the diabatic dissociation limit, which allows for the determination of very accurate bond strengths. The Co\(^+\)-RG bond strengths range from 930 cm\(^{-1}\) for Co\(^+\)(Ne) to 7700 cm\(^{-1}\) for Co\(^+\)(Xe). Diabatic binding energies of excited states which correlate to 3d\(^8\) states are smaller than those of the ground state, while those of states which correlate to 3d\(^7\)4s states are even smaller. These photodissociation spectra typically show well-resolved rotational structure, from which bond lengths have been determined.
Time dependent density functional theory calculations were carried out in order to characterize the electronic excitations which lead to the observed excited states of Co⁺(H₂O). These calculations used the BHandHLYP functional with the 6-311++G(3df,p) basis set. This particular functional was selected because it predicts excitation energies of bare M⁺ much more accurately than other popular functionals (e.g., B3LYP), as we have discussed in detail in our studies of V⁺(OCO) and Ni⁺(H₂O).¹¹,³⁵ Potential curves of the ground and excited triplet states of Co⁺(H₂O) are shown in figure 5. At each value of $r_{\text{Co-O}}$ the geometry of the rest of the molecule is fixed at its equilibrium value. Several excited states are predicted in the energy range observed in the photodissociation spectrum. All of the bands in this region are calculated to be weak, with integrated oscillator strengths of $f<0.0010$. This is consistent with the low signal levels observed.

Band A is likely due to the $2^3\text{A}_2 \leftrightarrow \text{X}, 3\text{B}_1$ transition, which is predicted to be a perpendicular band, with a calculated $T_e=11700$ cm⁻¹. The primary excitation is $4b_1, 3d\pi \leftrightarrow 1a_2, 3d\delta$. Band B is tentatively assigned to the $2^3\text{B}_2 \leftrightarrow \text{X}, 3\text{B}_1$ transition ($4b_1, 3d\pi \leftrightarrow 4b_2, 3d\pi$), with a calculated $T_e=12000$ cm⁻¹. Though this transition is symmetry forbidden, it could be observed due to vibronic coupling or to a magnetic dipole transition and is expected to show parallel band structure. This is observed in the $1\text{A}_2 \leftrightarrow \text{X}, 1\text{A}_1$ band of H₂CS.³⁶ Band C is assigned to the perpendicular $3^3\text{A}_2 \leftrightarrow \text{X}, 3\text{B}_1$ transition ($11a_1, 4s\sigma \leftrightarrow 4b_2, 3d\pi$), with a calculated $T_e=16700$ cm⁻¹. Band D is likely due to the $3^3\text{B}_1 \leftrightarrow \text{X}, 3\text{B}_1$ (primarily $11a_1, 4s\sigma \leftrightarrow 9a_1, 3d\delta+3d\sigma$) transition, with a calculated $T_e=14400$ cm⁻¹, although the symmetry forbidden $3^3\text{B}_2 \leftrightarrow \text{X}, 3\text{B}_1$ (primarily $11a_1, 4s\sigma \leftrightarrow 1a_2, 3d\delta$) transition, with a calculated $T_e=16500$ cm⁻¹ is also a possibility.
B. Electronic Spectroscopy: Rotational Structure

Rotational structure in the electronic transitions can give information about the geometry of the molecule, as well as the symmetry of the ground and excited states. As previously mentioned, the four electronic bands of Co\(^+\)(H\(_2\)O) show two types of rotational structure. Each vibrational transition in bands A and C (fig. 2) is a multiplet, consisting of several peaks spaced by about 30 cm\(^{-1}\). This spacing is significantly smaller in Co\(^+\)(HOD) and even smaller in Co\(^+\)(D\(_2\)O). Bands B and D consist of single, sharp vibrational peaks. Analogous structure is also observed in electronic bands of M\(^+\)(H\(_2\)O) (M=Mg,\(^{7b-d}\) Ca,\(^8\) Zn,\(^{12}\) Ni\(^{11}\)). For Ni\(^+\)(H\(_2\)O) the A” and B”\(\approx\)C” rotational constants are approximately 13.8 cm\(^{-1}\) and 0.30 cm\(^{-1}\), respectively,\(^{11}\) and similar values are expected for Co\(^+\)(H\(_2\)O). The rotational Hamiltonian for open-shell M\(^+\)(H\(_2\)O) can be expressed as the sum of a purely rotational and a spin-rotation term:\(^{37}\)

\[
H = H_{rot} + H_{sr} \quad (4)
\]

with

\[
H_{rot} = AN_a^2 + BN_b^2 + CN_c^2 \quad (5)
\]

\[
H_{sr} = \frac{1}{2} \sum_{\alpha=a,b,c} \sum_{\beta=a,b,c} \varepsilon_{\alpha,\beta} (N_{\alpha}S_{\beta} + S_{\beta}N_{\alpha}) \quad (6)
\]

where \(N\) is the rotational angular momentum, \(S\) is the spin angular momentum, \(A\), \(B\), and \(C\) are the rotational constants, and \(\varepsilon_{\alpha,\beta}\) are the components of the spin-rotation tensor in the inertial axis system \((a,b,c)\). For a prolate near-symmetric top, the eigenvalues of \(H_{rot}\) are given by
where $J$ is the total rotational angular momentum quantum number, $K_a$ is the quantum number for rotation along the $a$ axis (the Co-O bond in our molecule), and $\bar{B} = \frac{1}{2}(B + C)$ For a symmetric prolate top, $A > B$ and $B=C$. The $A$ rotational constant is inversely proportional to the moment of inertia for rotation about the $a$ axis. It thus depends on the H-O-H bond angle and the O-H bond length and is strongly affected by deuterium substitution. The multiplet bands ($A$ and $C$) are perpendicular transitions with selection rules $\Delta K_a=\pm 1$ and $\Delta J=0$, $\pm 1$.38 The triplets observed for Co$^+(H_2O)$ are due to transitions from $K_a''=0$ to $K_a'=1$ and from $K_a''=1$ to $K_a'=0$ and 2. The sharp bands $B$ and $D$ are parallel transitions with selection rules $\Delta K_a=0$ and $\Delta J=0$, $\pm 1$ for $K_a\neq 0$ and $\Delta K_a=0$ and $\Delta J=\pm 1$ for $K_a=0$. Transitions are observed from $K_a''=0$ to $K_a'=0$ and from $K_a''=1$ to $K_a'=1$. These transitions overlap as the $A$ constants are similar for the two electronic states, resulting in a single peak rather than a multiplet. Because individual J lines are not resolved in the photodissociation spectra of Co$^+(H_2O)$ and its isotopomers, the perpendicular transitions are more useful for determining rotational constants.

Figure 6 shows the $v_3'=2\leftrightarrow v_3''=0$ transition in the perpendicular band $C$ for Co$^+(H_2O)$, Co$^+(HOD)$ and Co$^+(D_2O)$, highlighting the partially resolved rotational structure. The three major peaks are labeled by the $K_a$ quantum numbers. Spin-rotation and J interaction determines the structure within each peak. The relative intensities of peaks arising from $K_a''=0$ and 1 allows one to ascertain the lower state of the electronic transitions. These intensities are determined by the overall wavefunction, a product of vibrational, rotational, electronic and nuclear wavefunctions:

$$\psi_{\text{tot}} = \psi_{\text{vib}} \psi_{\text{rot}} \psi_{\text{elec}} \psi_{\text{nucl}}$$
where \( \psi_{\text{tot}} \) must be ODD to satisfy conservation principles. The vibrational wavefunction \( \psi_{\text{vib}} \) is EVEN for the ground state and for any \( a_1 \) vibration. The rotational wavefunction \( \psi_{\text{rot}} \) is EVEN if \( K_a'' \) is even, and ODD if \( K_a'' \) is odd. At the \( \sim 15K \) temperature, \( \text{Co}^+\,(\text{H}_2\text{O}) \) molecules cool to \( K_a''=0 \) and 1. Cooling states with \( K_a''=1 \) to \( K_a''=0 \) is very inefficient, as it requires changing nuclear spin. If \( \text{Co}^+(\text{H}_2\text{O}) \) has \( C_{2v} \) symmetry, the two protons are equivalent, and there are 3 symmetric (EVEN) states in \( \Psi_{\text{nucl}} \) and 1 antisymmetric (ODD) state. For \( \text{Co}^+(\text{D}_2\text{O}) \), the EVEN:ODD ratio is 1:2. Thus, if \( \psi_{\text{elec}} \) is EVEN, the spectra should show enhanced intensity for odd \( K_a'' \) for \( \text{Co}^+(\text{H}_2\text{O}) \) and for even \( K_a'' \) for \( \text{Co}^+(\text{D}_2\text{O}) \). This is what is observed in electronic spectra of \( M^+(\text{H}_2\text{O}) \) \((M=\text{Mg},^{7b,\text{d}}\text{Ca},^8\text{Zn},^{12}\text{Ni}^{11})\), all of which have a \( ^2A_1 \) ground state. However, the spectra in figure 6 show enhanced intensity for \( K_a''=0 \) for \( \text{Co}^+(\text{H}_2\text{O}) \) and for \( K_a''=1 \) for \( \text{Co}^+(\text{D}_2\text{O}) \), indicating that states with \( K_a''=0 \) have ODD overall spatial symmetry. This same intensity pattern is observed throughout the perpendicular bands \( \text{A} \) and \( \text{C} \). In the parallel bands, transitions from \( K_a''=0 \) and 1 overlap, making intensity comparisons difficult. In \( C_{2v} \) the electronic wavefunction is symmetrical (EVEN) for rotational about the \( C_2 \) axis (the \( a \) axis) for states with \( A \) symmetry and is antisymmetrical (ODD) for states with \( B \) symmetry. The observed intensities indicate that the lower state involved has \( \psi_{\text{elec}} \) ODD and thus has \( B_1 \) or \( B_2 \) symmetry. Calculations predict that the ground state of \( \text{Co}^+(\text{H}_2\text{O}) \) is \( ^3B_1 \) or \( ^3A_2 \) (table 1), with a low-lying \( ^3A_1 \) state. The \( ^3B_2 \) state is somewhat higher in energy and is often calculated to distort to \( C_s \) symmetry. Thus, based on the calculations and experimental intensities, \( \text{Co}^+(\text{H}_2\text{O}) \) has \( C_{2v} \) symmetry and the lower electronic state in the perpendicular transitions is a \( ^3B_1 \) state. This state appears to be the ground state of
Co⁺(H₂O), as the relative intensities of bands A-D do not depend on the conditions in the ion source (and hence its temperature).

The rotational structure in the spectra of Co⁺(H₂O), Co⁺(HOD) and Co⁺(D₂O) was simulated using the *spfit* and *spcat* programs. Figure 6 shows simulated spectra, and the fit parameters are listed in table 4. Fits to the spectra indicate a Lorentzian linewidth of 1 cm⁻¹, which likely reflects the excited state lifetime. The modest spectral resolution precludes detailed analysis of the J structure. In addition, although the spin-rotation interaction parameter, $\epsilon$, has components along all three rotational axes, $\epsilon_{aa}$ will dominate as the A rotational constant is much larger than B=C. Therefore, in the analysis, all other components of $\epsilon$ are assumed to be zero. To further constrain the fits, the ground state rotational constants are set to their calculated values. Based on the calculated CCSD(T)/aug-cc-pVTZ ground state geometry, Co⁺(H₂O) is a near-prolate top with rotational constants $A_e=13.93$ cm⁻¹, $B_e=0.292$ cm⁻¹ and $C_e=0.286$ cm⁻¹. To correct these rotational constants for zero-point displacement, an anharmonic frequency calculation was carried out. Because this is not available for CCSD(T) in *Gaussian09*, they were carried out at the BHandHLYP/6-311++G(3df,p) level, and the difference between the zero-point corrected and equilibrium rotational constants is added to the CCSD(T) equilibrium rotational constants, giving $A_0^{''}=13.74$ cm⁻¹, $B_0^{''}=0.289$ cm⁻¹ and $C_0^{''}=0.283$ cm⁻¹. The simulations are moderately sensitive to the change in $B$ and $C$ on electronic excitation, and clearly indicate that the Co-O bond lengthens ($\Delta B<0$). Due to the modest spectral resolution, $\Delta r_{\text{Co-O}}$ from the vibrational intensities is substantially more precise than $\Delta r_{\text{Co-O}}$ derived from rotational analysis of $\Delta B$. The vibrational analysis
gives $\Delta r_{\text{Co-O}}=0.19\pm0.02$ Å. For Co$^+$($\text{H}_2\text{O}$), this implies $\Delta B=-0.044$ cm$^{-1}$ which is the value used in the fit.

Two factors contribute to the spin-rotation parameter $\epsilon$: coupling of the electron spin to the magnetic field due to molecular rotation and second-order interaction between the spin-orbit coupling and the Coriolis interaction.$^{37b}$ The second term dominates. In atomic Co$^+$, the spin-orbit splitting is 697 cm$^{-1}$ for the $^3\text{F}$ ($3d^9$) ground state, 657 cm$^{-1}$ for the $^3\text{F}$ ($3d^84s^1$) excited state and 89 cm$^{-1}$ for the $^3\text{P}$ ($3d^8$) excited state. The large atomic spin-orbit coupling leads to fairly large spin-rotation constants. Including $\epsilon_{aa}$ modifies the energies given by equation 7. A perturbation treatment shows that it introduces an additional term proportional to $\epsilon_{aa}K_a\Sigma$, where $\Sigma=0,\pm1$ is the projection of the spin angular momentum onto the $a$ axis. This leads to broadening in peaks with $K_a>0$. It also produces a term proportional to $K_a^2$, which affects the apparent $A$ rotational constant.$^{8b,40}$ For Co$^+$($\text{H}_2\text{O}$), we determine $\epsilon''_{aa}=-6$ cm$^{-1}$. The effect of this parameter is most clearly seen in the width of the $K_a'=0\leftrightarrow K_a''=1$ peak. For the upper state, $\epsilon'_{aa}=4$ cm$^{-1}$, which leads to the broad structure in the $K_a'=2\leftrightarrow K_a''=1$ peak. The value of $\epsilon''_{aa}$ is half that in Ni$^+$(H$_2$O).

In the absence of spin-rotation interaction, equation 7 predicts that the $K_a'=0\leftrightarrow K_a''=1$ and $K_a'=2\leftrightarrow K_a''=1$ transitions are separated by $4A'$. As noted above, $\epsilon'_{aa}$ modifies this spacing. So, once $\epsilon'_{aa}$ has been fit, $A'$ can be determined. Excitation of the Co-O stretch $\nu_3'$ should reduce the $B$ and $C$ rotational constants, but should have little effect on the $A$ rotational constant. This is confirmed by the anharmonic frequency calculations. However, comparison of the rotational structure of peaks in band $C$ with
$v_3' = 0$ to 5 (figure S1) shows that the spacing between the $K_a' = 0 \leftrightarrow K_a'' = 1$ and $K_a' = 2 \leftrightarrow K_a'' = 1$ peaks drops monotonically from 85 cm$^{-1}$ for $v_3' = 0$ to 53 cm$^{-1}$ for $v_3' = 5$. The widths of the peaks don’t change significantly, suggesting that $\epsilon_{\alpha\alpha}$ doesn’t depend on $v_3'$. Fitting the spectra thus requires unphysically large values of $A' \approx 21$ cm$^{-1}$ for $v_3' = 0$ and rather low $A' \approx 13$ cm$^{-1}$ for $v_3' = 5$. A similar apparent reduction of $A'$ with increased Co-O stretch excitation is observed for band A. The A and B states are almost degenerate, as are the C and D states. Interactions between these states could lead to perturbations in the rotational structure that depend strongly on the excitation energy. As a result of this perturbation, we are unable to use the rotational structure to determine the excited state geometry.

C. Vibrational Spectroscopy

A key question is how the presence of the metal ion affects the bonding in the water ligand. One way to address this question is to measure the vibrations of the ligand. Our calculations predict that binding to Co$^+$ reduces the water O-H stretching frequencies by $\sim 50$ cm$^{-1}$ for the symmetric stretch, $\sim 80$ cm$^{-1}$ for the antisymmetric stretch, and $\sim 20$ cm$^{-1}$ for the bend (table 1). Comparable red shifts in the O-H stretches have been observed in spectra of other transition metal M$^+$ (H$_2$O) complexes.$^{11, 20-26}$

Measuring vibrational spectra of small, tightly-bound ions using photodissociation is challenging. Breaking the strong Co$^+$-H$_2$O bond requires four photons in the O-H stretching region. This high bond strength and the small size of the molecule make infrared multiple photon dissociation (IRMPD) very inefficient. Spectra of several
M⁺(H₂O) have been measured via photodissociation of argon tagged M⁺(H₂O)(Ar)ₓ complexes, where absorption of light by the O-H chromophore eventually leads to loss of the weakly bound argon.²⁰-²⁶ Calculations predict that the presence of the argon usually only leads to small shifts in the O-H stretching frequencies. However, the argon does change the rotational structure. A particular concern in Co⁺(H₂O) is that the energies of the ³B₁, ³A₁ and ³A₂ states are so similar that binding to argon could actually change the ground state! Because Co⁺(H₂O) has a structured electronic photodissociation spectrum, vibrationally mediated photodissociation (VMP) is used to measure its vibrational spectrum. In this two laser double-resonance technique, parent molecules are dissociated using a fixed wavelength (from a dye laser) in the visible region while an infrared laser, firing 30 ns before, scans through the wavelength region of interest. When the IR laser is in resonance with a vibrational transition, molecules will be vibrationally excited, which leaves less population in the ground vibrational level. As the photodissociation laser is set to a wavelength where vibrationally cold molecules absorb, but vibrationally excited molecules do not (or absorb only weakly), the vibrational excitation leads to less photodissociation. Hence a vibrational spectrum is obtained by monitoring the depletion or “dip” of the fragment signal. We have used this technique to measure the O-H stretching vibrations of Ni⁺(H₂O).¹¹

Figure 7 shows vibrational spectra of the O-H stretching region of Co⁺(H₂O) measured using VMP. The spectrum in the top panel was obtained with the photodissociation laser set to the 16215 cm⁻¹ (ν₃′=1, Kₐ′=1) ← X ³B₁ (ν₃″=0, Kₐ″=0) transition. This double-resonance experiment only probes vibrational transitions with Kₐ″=0. The O-H symmetric stretch vibration is a parallel transition, (ΔKₐ=0), and the (0,0)
transition is observed at 3610 cm$^{-1}$. The O-H antisymmetric stretch vibration $\nu_5$ is a perpendicular transition, ($\Delta K_a=\pm 1$); exciting the intense (1,0) transition at 3693 cm$^{-1}$ leads to >40% depletion of the photofragment signal. Similar vibrational spectra are observed when exciting other electronic transitions with $K_a''=0$. The lower spectrum was obtained with the photodissociation laser set to the 16253 cm$^{-1}$ ($v_3'=1$, $K_a'=2$) $\leftrightarrow X^3\Sigma_1$ ($v_3''=0$, $K_a''=1$) transition. The observed transitions all have $K_a''=1$. The symmetric stretch (1,1) transition is also observed at 3610 cm$^{-1}$, while the antisymmetric stretch leads to two absorptions, (0,1) at 3670 cm$^{-1}$ and (2,1) at 3713 cm$^{-1}$.

In principle, vibrational spectra can also be measured in an enhancement experiment in which the visible laser is set to a wavelength at which vibrationally excited molecules selectively absorb. We have used this method to measure vibrational spectra of $V^+(OCO)$, with greatly improved signal-to-noise over the depletion experiment.$^{41}$ In order to find the absorption of the vibrationally excited molecules the IR laser is first set to an absorption and the visible laser is scanned. The difference between the resulting spectrum and one with the IR laser blocked gives the photodissociation spectrum of vibrationally excited molecules. For small molecules such as $V^+(OCO)$ this often has well-defined peaks. In the present study, the IR laser was set to 3693 cm$^{-1}$ as the visible laser scanned the low-energy region of bands A and B. Unfortunately, the resulting vibrationally mediated photodissociation spectrum is broad, with no sharp features. This persists for other IR bands shown in figure 7, and when scanning the visible laser over bands C and D as well. The vibrationally mediated photodissociation spectrum of $Ni^+(H_2O)$ is also mostly non-resonant, although one moderately intense peak is observed.$^{11}$ For larger species, the vibrationally excited molecules often show a broad
photodissociation spectrum due to efficient intramolecular vibrational relaxation (IVR). However, IVR should be slow in a molecule as small as Co\(^+\)(H\(_2\)O) due to the low vibrational density of states near 3700 cm\(^{-1}\). One possible mechanism for state mixing is via coupling to one of the many low-lying electronic states.

The vibrational spectra were simulated using the *spfit* and *spcat* programs, and the results are shown in figure 7 and summarized in Table 4. The simulations use a temperature of 15 K and assume that the visible laser overlaps all of the thermally populated J states so the double resonance experiment selects states with specific K\(_a\)" but does not select J". For the ground state, the same calculated rotational constants were used as for the electronic spectrum. Anharmonic frequency calculations at the BHandHLYP level predict rotational constants for the ground and excited vibrational states. The change in rotational constants upon vibrational excitation (\(\Delta A=0.13\) cm\(^{-1}\), \(\Delta B=\Delta C=0\) for \(v_1\) and \(v_5\)) was then used in the spectral simulations. The spin-rotation parameter \(\epsilon_{aa}\) was assumed to be the same for the ground and vibrationally excited states. For the ground electronic state, the previously determined \(\epsilon_{aa}=-6\pm1\) cm\(^{-1}\) gives a good fit to the vibrational and electronic spectra. The O-H symmetric stretch frequency is \(v_1=3609.7\pm1\) cm\(^{-1}\) and the O-H antisymmetric stretch is \(v_1=3679.5\pm2\) cm\(^{-1}\). Binding to Co\(^+\) thus leads to red shifts of 47 and 76 cm\(^{-1}\) in the symmetric and antisymmetric stretching frequencies, respectively. For Co\(^+\)(HOD) we measure an O-H stretching frequency of 3650 cm\(^{-1}\), a red shift of 57 cm\(^{-1}\) compared to bare HOD. The Co\(^+\)(HOD) vibrational spectrum and fit are in figure S2. When Co\(^+\) binds to H\(_2\)O, it removes electron density from the oxygen, which slightly weakens the O-H bonds. Therefore, we observe a red shift in the O-H stretching frequencies.
The red shifts are slightly larger than those observed in Ni\textsuperscript{+}(H\textsubscript{2}O),\textsuperscript{11} 40 cm\textsuperscript{-1} and 68 cm\textsuperscript{-1}. Furukawa et al. measured IR spectra of Co\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{n} (n=4-6) in the O-H stretching region via photodissociation spectroscopy.\textsuperscript{28} Their spectra show that all the ions are three coordinate and are fairly hot, so the sharpest spectrum obtained is of the tagged cluster Co\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{4}(N\textsubscript{2}). This ion has IR absorptions at 3430, 3530 cm\textsuperscript{-1} due to H-bonded OH groups and at 3620 and 3710 cm\textsuperscript{-1} due to free OH groups. The free-OH stretches are less red-shifted than in Co\textsuperscript{+}(H\textsubscript{2}O), as each water molecule donates less electron density to the cation in the cluster.

IV. SUMMARY AND CONCLUSIONS

The electronic spectra of Co\textsuperscript{+}(H\textsubscript{2}O), Co\textsuperscript{+}(HOD) and Co\textsuperscript{+}(D\textsubscript{2}O) were measured from 13500 cm\textsuperscript{-1} to 18400 cm\textsuperscript{-1} using photodissociation spectroscopy. They show transitions to four excited electronic states, with long progressions in the Co-O stretch and partially resolved rotational structure. The absolute vibrational quantum numbering is assigned by comparing isotopic shifts between Co\textsuperscript{+}(H\textsubscript{2})\textsuperscript{16}O) and Co\textsuperscript{+}(H\textsubscript{2})\textsuperscript{18}O). For the two low-lying excited electronic states, the first transition observed is to v\textsubscript{3}'=1. This allows the Co\textsuperscript{+}- (H\textsubscript{2}O) binding energy to be bracketed as D\textsubscript{0}(0 K) (Co\textsuperscript{+}-H\textsubscript{2}O)=13730±90 cm\textsuperscript{-1} (164.2±1.1 kJ/mol). The ground state is assigned as \textsuperscript{3}B\textsubscript{1} based on the nuclear spin statistics of the K\textsubscript{a} rotational structure. The vibrational spectrum of Co\textsuperscript{+}(H\textsubscript{2}O) in the O-H stretching region was measured using photodissociation. The O-H stretches are observed at v\textsubscript{1}=3609.7 cm\textsuperscript{-1} for the symmetric stretch and v\textsubscript{5}=3679.5 cm\textsuperscript{-1} for the antisymmetric stretch. This corresponds to a 47 cm\textsuperscript{-1} red shift for the symmetric stretch and 76 cm\textsuperscript{-1} red shift for the antisymmetric stretch, relative to bare H\textsubscript{2}O.
V. ACKNOWLEDGEMENTS

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Supporting Information Available: overlapped photodissociation spectrum of Co$^+$(H$_2$O), highlighting the rotational structure in band C with $v_3$=0 to 5 (Figure S1) and vibrational spectrum of Co$^+$(HOD) in the O-H stretching region (Figure S2).
References

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<td></td>
<td>$^3A_2$</td>
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<td></td>
<td>$^3B_1$</td>
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<td></td>
<td>$^3B_2$</td>
<td>1.992</td>
<td></td>
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<td>944</td>
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<td>MR-SDCI(+Q) (Ref. 30e)</td>
<td>$^3A_1$</td>
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<td></td>
<td></td>
<td>35</td>
<td>$3dz^2, 3dxy$</td>
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<td>$^3A_2$</td>
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<td>0.967</td>
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<td>$^3B_1$</td>
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<td></td>
<td>$^3B_2$</td>
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<td></td>
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<td>105</td>
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<tr>
<td>CCSD(T)/aug-cc-pVTZ (This work)</td>
<td>$^3A_1$</td>
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<td>0.964</td>
<td>106.7</td>
<td>39</td>
<td>$3d\sigma(z^2), 3d\delta(x^2-y^2)$</td>
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<tr>
<td></td>
<td>$^3A_2$</td>
<td>1.9996</td>
<td>0.964</td>
<td>106.8</td>
<td>25</td>
<td>$3d\sigma(z^2), 3d\delta(xy)$</td>
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<td>$^3B_1$</td>
<td>1.9705</td>
<td>0.965</td>
<td>106.8</td>
<td>0</td>
<td>$[3d\delta(x^2-y^2), 3d\pi(xz)] + [3d\sigma(z^2), 3d\pi(xz)]$</td>
</tr>
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<td>$^3B_2$</td>
<td>1.9115</td>
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</table>

**Table 1.** Calculated energies and geometries of low-lying states of Co$^+$(H$_2$O)
Table 2. Experimental and calculated vibrational frequencies of Co\(^+\)(H\(_2\)O) and Co\(^+\)(D\(_2\)O). The frequencies at the BH\(\text{an}d\)HLYP/6-311++G(3df,p) level are scaled by 0.92. By binding to Co\(^+\), the symmetric and antisymmetric stretches of H\(_2\)O red shift by 47 and 76 cm\(^{-1}\), respectively.

<table>
<thead>
<tr>
<th>Vibrational Symmetry</th>
<th>Mode ((v_i))</th>
<th>Description</th>
<th>Frequency (cm(^{-1})) BH(\text{an}d)HLYP</th>
<th>Frequency (cm(^{-1})) BH(\text{an}d)HLYP</th>
<th>Frequency (cm(^{-1})) Experimental</th>
<th>Co(^+)(H(_2)O)</th>
<th>Co(^+)(D(_2)O)</th>
<th>H(_2)O</th>
<th>D(_2)O</th>
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</thead>
<tbody>
<tr>
<td>a(_1)</td>
<td>1</td>
<td>H-O-H symmetric stretch</td>
<td>3604</td>
<td>2626</td>
<td>3609.7 ± 1</td>
<td>3657</td>
<td>2671</td>
<td></td>
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<tr>
<td></td>
<td>2</td>
<td>H-O-H bend</td>
<td>1575</td>
<td>1169</td>
<td>1595</td>
<td>1178</td>
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<td></td>
<td></td>
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<tr>
<td></td>
<td>3</td>
<td>Co-O stretch</td>
<td>354</td>
<td>343</td>
<td>-</td>
<td>-</td>
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<tr>
<td>b(_1)</td>
<td>4</td>
<td>Out-of-plane bend</td>
<td>318</td>
<td>246</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
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<tr>
<td>b(_2)</td>
<td>5</td>
<td>H-O-H antisymmetric stretch</td>
<td>3674</td>
<td>2725</td>
<td>3679.5 ± 2</td>
<td>3756</td>
<td>2788</td>
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<td></td>
<td>6</td>
<td>In-plane bend</td>
<td>538</td>
<td>405</td>
<td>-</td>
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</table>
Table 3. Spectroscopic constants, dissociation energies and equilibrium bond lengths for the ground and excited states of Co\(^ {3+} \)(H\(_2\)O). Term values \( T_{00} \), excited state frequencies \( \nu_3 \) and anharmonicities \( x_3 \) for the Co-O stretch are determined from the photodissociation spectrum. The values in parentheses are assigned by extrapolating the spectra. Morse dissociation energies \( D_0 \) are calculated using equation 2 with the experimental frequencies and anharmonicities and corrected for zero-point energy. Experimental \( D_0 \) are calculated from dissociation to the Co\(^ {3+} \) atomic state shown. The ground state frequency is calculated at the CCSD(T)/aug-cc-pVTZ level and the anharmonicity determined using the experimental dissociation energy.
<table>
<thead>
<tr>
<th>Co$^+$ (H$_2$O) (cm$^{-1}$)</th>
<th>$^3$B$_1$ Ground State ($v^a=0$)</th>
<th>State C ($v_3'=2$)</th>
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<tbody>
<tr>
<td>A</td>
<td>13.74$^a$</td>
<td>14.5</td>
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<tr>
<td>B</td>
<td>0.289$^a$</td>
<td>0.245</td>
</tr>
<tr>
<td>C</td>
<td>0.283$^a$</td>
<td>0.241</td>
</tr>
<tr>
<td>$\epsilon_{aa}$</td>
<td>-6 ± 1</td>
<td>4 ± 1</td>
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<tr>
<td>Co$^+$ (D$_2$O)</td>
<td></td>
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</tr>
<tr>
<td>A</td>
<td>6.87$^a$</td>
<td>7.3</td>
</tr>
<tr>
<td>B</td>
<td>0.252$^a$</td>
<td>0.212</td>
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<tr>
<td>C</td>
<td>0.243$^a$</td>
<td>0.203</td>
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<tr>
<td>$\epsilon_{aa}$</td>
<td>-3 ± 1</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>Co$^+$ (HOD)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>9.56$^a$</td>
<td>9.95</td>
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<tr>
<td>B</td>
<td>0.272$^a$</td>
<td>0.228</td>
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<tr>
<td>C</td>
<td>0.264$^a$</td>
<td>0.224</td>
</tr>
<tr>
<td>$\epsilon_{aa}$</td>
<td>-3.5 ± 1</td>
<td>3 ± 1</td>
</tr>
</tbody>
</table>

Table 4. Rotational constants for Co$^+$ (H$_2$O) and isotopomers. Excited state values are for the $v_3'=2$ band of electronic state C. $^a$) Calculated at the CCSD(T)/aug-cc-pVTZ level.
Figure captions

**Figure 1.** Photodissociation spectra of the Co⁺(H₂O), Co⁺(HOD) and Co⁺(D₂O) complexes from 13500 to 18400 cm⁻¹. The combs indicate the Co-water stretch quantum number v₃’ in each of the four electronic states observed.

**Figure 2.** Molecular orbital diagram and orbital occupancy of Co⁺(H₂O) X, 3B₁.

**Figure 3.** Assignment of the cobalt-water stretch vibrational quantum numbering for the four electronic states observed in the photodissociation spectrum of Co⁺(H₂O). Experimental shifts of Co⁺(H₂¹⁶O) vs. Co⁺(H₂¹⁸O) are compared to values calculated assuming the first peak observed is due to v₃’=1←v₃”=0 (dashed line), v₃’=0←v₃”=0 (solid line), and to v₃’=0←v₃”=1 (dotted line). The four electronic states are labeled as in Figure 1.

**Figure 4.** Potential energy curves of the ground and excited electronic states of Co⁺(H₂O) along the Co-O stretch based on experiment. The inset shows an expanded view of the excited states in the region near the dissociation limit.

**Figure 5.** Calculated potential energy curves for triplet states of Co⁺(H₂O) along the Co-O stretch. Excited states are calculated using TD-DFT at the BHandHLYP/6-311++G(3df,p) level.

**Figure 6.** Partially resolved rotational spectra of the Band C (v₃’=2) ← X 3B₁ (v₃”=0) band of Co⁺(H₂O) (top), Co⁺(HOD) (middle) and Co⁺(D₂O) (bottom) showing the ΔKₐ=±1 features characteristic of a perpendicular transition. The simulated spectra are also shown, using the spectroscopic parameters in Table 3, a rotational temperature of 15 K and a Lorentzian linewidth of 1 cm⁻¹.

**Figure 7.** Vibrational spectra of Co⁺(H₂O) in the O-H stretching region. The spectra are obtained by vibrationally mediated photodissociation, monitoring depletion in the Co⁺ photofragment produced by irradiation of the (v₃’=1, Kₐ’=1) ← X 3B₁ (v₃”=0, Kₐ”=0) transition at 16215 cm⁻¹ (top) and (v₃’=1, Kₐ’=2) ← X 3B₁ (v₃”=0, Kₐ”=1) transition at 16253 cm⁻¹ (bottom). IR absorption removes molecules from v”=0, leading to a 15-45% reduction in the fragment yield. Simulated spectra are also shown, using the spectroscopic parameters in Table 4. Vertical bars denote the positions of the symmetric and antisymmetric stretches in bare H₂O.
Figure 1
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure for graphical abstract
Figure S1. Overlapped photodissociation spectrum of Co(H_2O), highlighting the rotational structure in band C with v_3'=0 to 5. The spacing between the (0,1) and (2,1) transitions drops with increasing Co-O stretch quantum number, which indicates a reduction in the excited state A’ rotational constants.
Figure S2. Vibrational spectrum of Co$^+$ (HOD) in the O-H stretching region. The spectrum is obtained by vibrationally mediated photodissociation, monitoring depletion in the Co$^+$ photofragment produced by irradiation of the band C ($v_3' = 4$, $K_a' = 1$) $\leftrightarrow$ X $^3\text{B}_1$ ($v_3'' = 0$, $K_a'' = 0$) transition at 17139 cm$^{-1}$. The simulated spectrum (shown in black) contains both parallel (shown in green) and perpendicular (shown in red) contributions. The simulation uses the following parameters, all in cm$^{-1}$: $v_0=3650$, $A''=9.56$, $B''=0.272$, $C''=0.264$, $\epsilon''_{aa}=-3.5$; $A'=9.46$, $B'=0.272$, $C'=0.264$, $\epsilon'_{aa}=-3.5$. Only $v_0$ and $\epsilon''_{aa} = \epsilon'_{aa}$ are adjusted in the fit. Rotational constants $A_e$, $B_e$ and $C_e$ are from the CCSD(T)/aug-cc-pVTZ geometry are corrected by the change in the rotational constant due to zero point (to get ground state constants) and to OH stretch excitation (to get upper state constants) using anharmonic frequency calculations at the BHandHLYP/6-311++G(3df,p) level.