Infrared Spectroscopy of the $\text{Ti}(\text{H}_2\text{O})\text{Ar}^+$ Ion-Molecule Complex: Electronic State Switching Induced by Argon

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Abstract

Titanium-water complexes are produced by laser vaporization in a pulsed supersonic expansion, mass selected in a time-of-flight spectrometer, and studied with infrared laser photodissociation spectroscopy using argon complex predissociation. Density functional theory calculations provide structures and vibrational spectra for these ions. Spectra in the O–H stretching region indicate that the water is intact in these complexes, even though inserted structures are computed to be more stable. Although the ground state of $\text{Ti}(\text{H}_2\text{O})^+$ is established to be a quartet, that predicted and observed for $\text{Ti}(\text{H}_2\text{O})\text{Ar}^+$ is a doublet. Attachment of argon changes the electronic ground state of this system.

1. Introduction

Metal cation interactions with water provide the basis for much of aqueous solvation chemistry [1]. The molecular details of these interactions have been investigated with mass spectrometry of gas phase ion-molecule complexes [2-13] and with corresponding computational studies [14-19]. Collision-induced dissociation studies have provided cation-water binding energies [8-11], while computational studies provide structures, relative stabilities and predicted spectra for complexes with different numbers of water molecules and different charge states [14-19]. Newer experiments have employed mass-selected photodissociation spectroscopy in both the UV-visible and infrared regions to measure electronic and vibrational patterns, as well as the coordination numbers of solvent spheres around different metal ions [20-46]. In the present report, we use infrared photodissociation spectroscopy to investigate the complexes formed from titanium cations and water.

Infrared photodissociation spectra have been reported previously for several cation-water complexes, including single-water and multiply solvated species in both singly- and doubly-charged states [28-47]. Small complexes with water in the first solvation shell are generally studied with the method of argon or neon atom "tagging," while larger complexes can be studied via the elimination of water. Most mono-hydrated complexes form C_{2v} structures consistent with the favorable charge-dipole interaction. In vibrational spectra, the cation-water interaction shifts the symmetric and antisymmetric O–H stretches to lower frequencies, as the charge polarizes water and shifts electron density away from its highest occupied bonding molecular orbital. This effect is greater for dications, as expected for the stronger charge-dipole interaction [36-39]. The relative intensity of the O–H stretch vibrational bands also change as a result of the cation binding. Both bands have higher computed intensities in metal complexes than for isolated water, and the symmetric stretch gains intensity relative to the antisymmetric stretch because of

the more effective charge oscillation along the molecular axis. In certain $M^+(H_2O)$ complexes, when a single rare gas atom can be used to detect photodissociation, and this atom binds on the C_2 axis of the complex, partially resolved rotational structure can be measured [28,30,34,36,37,43-45]. This is possible because the three heavy atoms (metal, oxygen, rare gas) have their mass on the C_2 axis and only the light hydrogen atoms rotate around this axis. When such rotational structure can be detected, it provides additional insight into the structure of the complex, and the relative intensities of different lines provide its rotational temperature. As shown below, such rotational structure is detected for the titanium-water complex, revealing new details about its electronic structure.

2. Experimental

Titanium-water ion-molecule complexes are produced in a pulsed-nozzle laser vaporization source using methods described previously [30-40]. Mass analysis and selection is accomplished with a specially designed reflectron time-of-flight mass spectrometer. Selected ions are investigated with infrared photodissociation spectroscopy in the O–H stretching region using an infrared optical parametric oscillator/amplifier laser system (OPO/OPA; LaserVision, Inc.) pumped by a Nd:YAG laser (Continuum 8010). Resonant single photon absorption leads to elimination of argon from the $Ti(H_2O)Ar_m^+$ species, provided that the IR photon energy is greater than the argon binding energy. The fragment ion intensity is recorded as a function of the laser frequency using a digital oscilloscope (LeCroy) connected to a PC computer.

Density functional theory (DFT) is employed to investigate the structures and vibrational spectra of the $Ti(H_2O)Ar_m^+$ complexes for comparison to the experiment. These computations use the M06-L functional in the Gaussian09 package and the basis sets was LANL2DZ ECP for

Ti and 6-311++G** for O, H, and Ar. The computed vibrational frequencies are scaled by a factor of 0.959. All quoted energies include zero point corrections.

3. Results and Discussion

Laser vaporization of a titanium rod sample in an expansion containing ambient water vapor produces a mass spectrum containing species of the form $\text{Ti}(\text{H}_2\text{O})_n^+$, similar to those reported previously for other metal-water systems [30-40]. Because the binding energy of water to the metal ion is predicted to be greater than the energy of an infrared photon in the O–H stretching region, we employ the method of argon tagging [30-40]. Inclusion of argon in the expansion produces ions of the form $\text{Ti}(\text{H}_2\text{O})_n\text{Ar}_m^+$. Mass selection of these ions and infrared excitation in the O–H stretching region causes elimination of argon on vibrational resonances, producing vibrational spectra, as described below.

The infrared photodissociation spectrum of $\text{Ti}(\text{H}_2\text{O})\text{Ar}^+$ measured in this way is shown in Figure 1 (top trace). The spectrum contains a single sharp band at 3591 cm^{-1} , and a series of closely spaced features in the $3640\text{--}3710\text{ cm}^{-1}$ region. This spectrum can be compared to the patterns seen previously for several singly hydrated metal ion complexes that have been studied with this same methodology. In cases in which the argon tag atom binds off the C_2 symmetry axis of the $\text{M}^+\text{-OH}_2$ system, only two bands are found corresponding to the symmetric and antisymmetric stretches of water [30-33,35,40]. The resolution of the laser in these experiments is about 1 cm^{-1} , and the rotational constants of these complexes are much smaller than this, giving rise to vibrational bands with unresolved rotational structure. In other cases when there is no argon present, or when it is present and binds on the C_2 symmetry axis leaving only the light hydrogen atoms off this axis, partially resolved K-type sub-band rotational structure can be resolved for the antisymmetric stretch band [28-30,34,36,37,43-45]. At the low temperature

expected for ions produced in this experiment, this sub-band structure usually has three prominent features; the two outer bands are spaced by about 50 cm^{-1} and these are more intense than the central feature because of their 3:1 nuclear spin statistical weighting factors. However, the pattern seen here for the titanium system does not exactly match either of the simple patterns seen previously. Instead, it has symmetric multiplet structure in the higher frequency region reminiscent of the K-type structure, but each line appears to be doubled. Such additional splittings have also been seen previously for transition metal-water complexes which exhibit an unquenched spin-orbit interaction [43-45]. We investigate this further below.

The spectrum of $\text{Ti}(\text{H}_2\text{O})\text{Ar}_2^+$ is shown in Figure 2. It contains a simpler structure of only two bands at 3554 and 3642 cm^{-1} . This is the behavior expected for a di-argon complex with argon atoms located off the C_2 symmetry axis. This causes the A rotational constant to become much smaller and the K-type rotational structure can no longer be resolved. This same kind of behavior has been seen previously for several other metal-water complexes tagged with two rare gas atoms [30,31,33,35]. The pattern of two O–H stretches seen here is consistent with a single isomeric structure with an intact water molecule. The bands here are also shifted about 40 cm^{-1} further to the red than the structure seen for the single-argon complex. This can occur if at least one argon attaches in a position on a hydrogen of water [30,31,33,35].

To investigate the electronic structure of this system, we performed computational studies on the complexes that might be formed from titanium cations and water. The full details of these computations are presented in the Supporting Information for this article. This system has been investigated previously [15], but that work focused on the cation-water complexes without any attached rare gas atoms. Our computations investigate $\text{Ti}(\text{H}_2\text{O})^+$, $\text{Ti}(\text{H}_2\text{O})\text{Ar}^+$ and $\text{Ti}(\text{H}_2\text{O})\text{Ar}_2^+$ complexes at the same level of theory. The structures and relative energies obtained for these systems are shown in Figure 3. We find that an inserted H-Ti-OH^+ complex lies much lower in

energy (-26.8 kcal/mol) than the $\text{Ti}(\text{H}_2\text{O})^+$ ion-molecule complex. Consistent with previous work [15], we also find cation-water complexes with C_{2v} symmetry, with both doublet and quartet electronic states present at low energy. For the $\text{Ti}(\text{H}_2\text{O})^+$ complex, we find that the quartet ($^4\text{B}_2$) state lies at slightly lower energy than the corresponding doublet (+0.77 kcal/mol). In the previous work, Ugalde and coworkers performed a much more extensive study of the $\text{Ti}(\text{H}_2\text{O})^+$ complex using DFT/B3LYP or CASPT2 methods and several different basis sets [15]. They also found a quartet ground state, but it was the $^4\text{B}_1$ state [15]. With every method employed, the quartet state in that study was found to lie > 11 kcal/mol lower than the corresponding doublet state, and their methods accurately reproduced the atomic Ti^+ quartet-doublet splitting. On the basis of this previous work, therefore, it is safe to conclude that the ground state of $\text{Ti}(\text{H}_2\text{O})^+$ without the argon is actually the quartet. The M06-L method employed here finds that the $^2\text{B}_2$ state is only +0.77 kcal/mol higher than the $^4\text{B}_2$, getting the correct order for these states, but much closer energetics. M06-L also underestimates the known atomic quartet-doublet splitting. For $\text{Ti}(\text{H}_2\text{O})\text{Ar}^+$, the argon binds opposite the water, near or on the C_2 axis. The doubly-tagged complexes have two possible isomers, with either both argons attached to the metal or one on the metal and one on an OH of water. In the singly-tagged complexes, the ^2A electronic state is predicted to lie at slightly lower energy (0.48 kcal/mol) than the ^4A , whereas in the doubly-tagged complexes the quartet state lies lower. Considering the issues with M06-L for the spin state energetics, these predicted energies for the tagged complexes cannot be trusted completely.

Comparing these computational results to our experimental spectra, we can rule out any contribution from the inserted species which is predicted to be the global minimum energy structure. This ion would have only a single O–H stretch at high frequency, and it would not have the widely-spaced K structure seen in Figure 1. It is conceivable that such an insertion

reaction does occur, but that it leaves the HTiOH^+ cations formed too warm internally to allow efficient tagging with argon. The argon tag is essential to our measurement, so we would not be able to detect such ions. It is also conceivable that there is a barrier to the insertion reaction, and that under the cold expansion conditions here we trap out an entrance-channel, pre-reactive complex. The lowest energy state for the ion-molecule complex is a quartet, while that for the inserted species is a doublet, so the reaction on the quartet surface is spin-forbidden. Either scenario could explain the missing reaction product, but we cannot distinguish between these two alternatives.

The ions we detect are therefore those with the local-minimum, ion-molecule structure. For both the singly and doubly tagged complexes, we detect the two vibrations expected for the symmetric and antisymmetric stretches of water. These bands for the $\text{Ti}(\text{H}_2\text{O})\text{Ar}^+$ complex are measured at 3591 and 3662 cm^{-1} (we derive the antisymmetric stretch band center from the rotational analysis presented below). These frequencies are lower than those for the corresponding vibrations of the isolated water molecule (3657 and 3756 cm^{-1} [49]) because of the shift induced by the cation binding to water. As discussed previously [30-40], the cation polarizes water, with charge transfer away from the O–H bonds, leading to this frequency reduction. The intensities of these two bands are comparable, in contrast to the much larger antisym:sym intensity ratio seen for the isolated water molecule (6.6:1 from computations). As noted earlier, such an enhancement of the symmetric stretch vibrational band has also been seen previously for other metal ion-water complexes [30-40], because this motion oscillates charge more effectively along the C_2 axis.

Figure 3 shows that the lowest energy structure computed for $\text{Ti}(\text{H}_2\text{O})\text{Ar}_2^+$ has both argons bound to the metal cation in a quartet state. According to DFT, the lowest energy electronic state for this structure is the quartet (^4A); the corresponding doublet state is computed

to lie at +1.8 kcal/mol). A structure with one argon on the metal ion and another on a hydrogen of water is also found, lying higher in energy by +5.1 (doublet) or +5.1 (quartet) kcal/mol. As shown in the theory traces in Figure 2, the structure with argon on an OH leads to a significant red shift in the O–H stretches, like that seen in the experiment. We can therefore safely conclude that the di-argon complex we detect has this kind of structure. The doublet and quartet states of the complex with this structure have energies that are computed to be almost identical. The IR spectra of the complex in these two spin states are also computed to be roughly the same. Therefore, we cannot determine the spin state detected in the experiment. However, the two sharp bands detected suggest that only a single structure and spin state is present.

The partially resolved rotational structure provides a more detailed probe of the geometry and electronic structure of the $\text{Ti}(\text{H}_2\text{O})\text{Ar}^+$ complex. The lower traces of Figure 1 represent the results of simulations of the rotational structure using the program PGOPHER [50]. The simulations are for parallel-type symmetric stretch and perpendicular-type antisymmetric stretch bands, including the 3:1 nuclear spin weighting factors for the $K = \text{even:odd}$ levels, and the appropriate spin-rotation splitting for the doublet and quartet states, respectively. The A rotational constant, the spin-rotation constant ϵ_{aa} , and the temperature are used as adjustable parameters to match the patterns in the spectrum; the B, C constants (whose structure cannot be resolved) are set equal at a value taken from the computed structure. The significance of the spin-rotation interaction here and typical values for the ϵ_{aa} parameter are discussed elsewhere [22,43-45]. A linewidth of 1.0 cm^{-1} is applied to the simulated spectrum to match that observed in the experiment.

It is clear from Figure 1 that the rotational simulation for a doublet ground state complex matches the experimental spectrum nicely, whereas that for the quartet state does not. The parameters used for the simulation are all reasonable for the $\text{Ti}(\text{H}_2\text{O})\text{Ar}^+$ complex. The A

rotational constant is slightly smaller than the corresponding value for the isolated water molecule, and comparable to the values used in previous work [30-40]. It indicates that the H-O-H angle for the water moiety has expanded somewhat compared to its isolated structure. The spin-rotation parameter of -7.0 cm^{-1} is comparable to values used by Metz and coworkers for the hydrated cobalt, nickel, and manganese cation complexes [43-45]. The temperature of 10 K is also reasonable for our supersonic beam expansion conditions. $\text{Ti}(\text{H}_2\text{O})\text{Ar}^+$ is therefore a cation-water ion-molecule complex with a doublet ground state. Even though the quartet state is predicted to lie at only $+0.48\text{ kcal/mol}$, it is apparently not formed to any appreciable degree.

The A rotational constant determined here is smaller than the corresponding value for the isolated water molecule. Two factors can cause this. The hydrogen atoms for the water molecule in the complex can be further away from the C_2 axis than in water, occurring from either an H-O-H bond angle expansion or a lengthening of the OH bonds. Our computational results show that both of these occur to some extent, but we have argued in the past that the former is more important. According to our computations, the H-O-H bond angle in the doublet ground state of $\text{Ti}(\text{H}_2\text{O})\text{Ar}^+$ is 106.5° , compared to the angle of 104.5° for the isolated water molecule. This angle expansion has been detected in previous work on similar complexes, and has been underestimated by theory [21,22]. It is a consequence of polarization of the lone pair electrons away from the water molecule. The O-H bond distance is computed to be $0.967\text{ \AA}$ compared to the value of $0.957\text{ \AA}$ for water. However, another effect that can lower the A constant is any mass from the argon tag atom that lies off the C_2 axis. According to our computed structure for the doublet ground state, the equilibrium position of the argon lies 8.5° off the C_2 axis in the plane of the water molecule, with an equivalent minimum on the opposite side of the axis, and a nearly flat angular potential (see Supporting Information). Vibrational averaging would lead to an effective position of the argon on the C_2 axis, but this mass may

make a slight contribution to the moment of inertia about this axis. Without spectra for multiple additional isotopomers, we therefore cannot determine the exact structure of this complex.

However, if we assume that the O-H bond distance is that computed and assume that the argon does not contribute to the moment of inertia, we derive an experimental estimate for the H-O-H bond angle of 108.9°. We compare this angle to those derived for other metal cation-water complexes in Table 1. The magnesium and calcium complexes were studied via electronic spectroscopy when no tag atom was present, whereas the other systems were studied via tagging making the same assumptions indicated here. H-O-H bond angle expansion appears to be a general feature of cation-water bonding.

According to our present computations, and much previous work at higher levels of theory, the ground state of the $\text{Ti}(\text{H}_2\text{O})^+$ complex is a quartet. According to our experiment, the ground state of the $\text{Ti}(\text{H}_2\text{O})^+\text{Ar}$ complex is unambiguously a doublet. Therefore, the addition of argon to the $\text{Ti}(\text{H}_2\text{O})^+$ complex causes the spin state to change from a quartet to a doublet. It is perhaps not too surprising that such an effect could occur, since the argon here is acting essentially as a weakly bound ligand. Although it is much more weakly bound than the water (the Ti^+-OH_2 bond energy is 48.0 kcal/mol), the metal-argon bond energy is substantial (8.4 kcal/mol). Ligand-electron repulsion, also known as a ligand field effect, is well known to affect the spin states of transition metal complexes. The key consideration is the ligand field splitting compared to the spin-pairing energy. The apparent "switch" in spin states suggested here when the weakly bound argon is added is only possible because the doublet and quartet states lie so close in energy for this system.

4. Conclusions

The $\text{Ti}(\text{H}_2\text{O})\text{Ar}^+$ and $\text{Ti}(\text{H}_2\text{O})\text{Ar}_2^+$ complexes were produced in a laser vaporization cluster source, mass selected in a time-of-flight spectrometer, and studied with infrared photodissociation spectroscopy and computational chemistry. Although an inserted H-Ti-OH^+ complex is predicted to be more stable, the experiment detects a cation-water ion-molecule complex. The equilibrium structure of the complex is predicted to be close to C_{2v} , with a slight off-axis binding for the argon. The spectrum indicates a similar structure, with the H-O-H bond angle expanded slightly compared to that of isolated water. The OH stretches of the complexes are shifted to lower frequency and the symmetric stretch vibrational band is enhanced relative to that in water. Both effects have been seen previously for other cation-water complexes. Although quartet and doublet electronic states are predicted to lie extremely close in energy, the rotationally resolved spectrum indicates that the ground state exists only as a doublet. According to theory, the $\text{Ti}(\text{H}_2\text{O})^+$ complex without the attached argon has a quartet ground state. Surprisingly, the addition of the argon switches the ground electronic state of this system.

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Table 1. The HOH bond angle of various $M^+(H_2O)$ systems

System	HOH Angle (degrees)
H_2O	104.5
$Ti^+(H_2O)$	108.9
$Mg^+(H_2O)$	110.6 ²¹
$Ca^+(H_2O)$	106.8 ²²
$Li^+(H_2O)$	106.3 ³⁴
$Cr^+(H_2O)$	111.9 ³⁶
$Sc^+(H_2O)$	107.1 ³⁷

Figure Captions

Figure 1. The infrared photodissociation spectrum of the $\text{Ti}(\text{H}_2\text{O})\text{Ar}^+$ complex, detected via the elimination of argon (upper trace). The lower traces show simulations of the partially resolved rotational structure for complexes with quartet or doublet ground states, respectively.

Figure 2. The infrared photodissociation spectrum of the $\text{Ti}(\text{H}_2\text{O})\text{Ar}_2^+$ complex, detected via the elimination of argon (upper trace), compared to spectra predicted by theory for doublet versus quartet ground states of two isomeric structures.

Figure 3. Structures predicted by theory for the lowest lying isomers and spin states of titanium-water complexes. Additional structures and their energetics are presented in the Supporting Information.

Figure 1

Figure 2

Figure 3

doublet/quartet
+0.77/+0.0 kcal/mol

doublet/quartet
-26.8/+30.6 kcal/mol

doublet
+0.0 kcal/mol

quartet
+0.48 kcal/mol

doublet/quartet
+5.1/5.1 kcal/mol

doublet/quartet
+1.8/0.0 kcal/mol