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Infrared Spectroscopy of $Cr^+(H_2O)$ and $Cr^{2+}(H_2O)$: The Role of Charge in Cation Hydration

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Singly and doubly charged chromium−water ion−molecule complexes are produced by laser vaporization in a pulsed-nozzle cluster source. These species are detected and mass-selected in a specially designed time-of-flight mass spectrometer. Vibrational spectroscopy is measured for these complexes in the O−H stretching region using infrared photodissociation spectroscopy and the method of rare gas atom predissociation. Infrared excitation is not able to break the ion−water bonds in these systems, but it leads to elimination of argon, providing an efficient mechanism for detecting the spectrum. The O−H stretches for both singly and doubly charged complexes are shifted to frequencies lower than those for the free water molecule, and the intensity of the symmetric stretch band is strongly enhanced relative to the asymmetric stretch. Partially resolved rotational structure for both complexes shows that the H−O−H bond angle is greater than it is in the free water molecule. These polarization-induced effects are enhanced in the doubly charged ion relative to its singly charged analog.

Introduction

The solvation of metal cations by water is not only one of the most fundamental aspects of chemistry in solution[1–3] but also an area in which detailed molecular level understanding is lacking. Measurements in solution are highly averaged over the ensemble of configurations present, and it is therefore difficult to derive a specific picture of the structural motifs and forces at play. Gas phase complexes of hydrated cations have been produced in mass spectrometers for many years to explore the fundamental interactions in these systems.[4–18] Cation−water bonding energies have been determined,[4–14] and various theoretical approaches have been applied to these systems.[19–38] However, it has been quite difficult to measure the structures of cation−water complexes to test the predictions of theory. Electronic spectroscopy has been applied to these systems,[39–48] and new infrared spectroscopy measurements have been reported.[49–52] However, experiments to date have been limited largely to singly charged ions that can be produced more efficiently in the gas phase.[39–47,49–51] In recent developments, new ion sources have made it possible to produce multiply charged complexes for mass spectrometry,[11–18] and some spectroscopy measurements have been reported.[48,52] In the present work, we present infrared measurements on monohydrated chromium ion complexes in which the cation is either singly or doubly charged. A comparison of the spectra and structures derived for these systems investigates the role of charge in cation solvation.

Most of the available experiments on cation-water complexes have examined singly charged ions because these systems are easier to produce in the gas phase.[4–18,39–47,49–51] Both equilibrium measurements and collision induced dissociation have been employed to determine the binding energies of these systems.[4–14] Many singly charged alkali and main group metal cation−water systems have bond energies in the range 20−30 kcal/mol,[4,5,8,9] consistent with the dominance of electrostatic interactions, whereas transition metal complexes have added covalent character with greater bond energies.[6–8,10] Multiply charged ion complexes generally have stronger bonding than corresponding singly charged species.[11–14] Electronic spectroscopy has been described by our group and others for cation−water complexes using mass-selected photodissociation measurements.[39–48] The singly charged ions of the group II metals (Mg^+, Ca^+, Sr^+, etc.) were the focus of these studies because the single valence electron of these cations gives rise to strongly allowed electronic transitions at low energy.[40–42] For certain metals with low ionization potentials, ZEKE photoelectron spectroscopy has been able to probe the ground-state vibrations of cation-water complexes.[46,47] Infrared photodissociation spectroscopy of hydrated alkali cations was first described by Lisy and coworkers.[49] More recently, our research group has employed the laser vaporization cluster source and extended IR photodissociation studies to a number of singly charged main group (Li^+, Al^+, Mg^+) and transition metal (Fe^+, V^+, Ni^+, Cu^+, Co^+) cation−water complexes.[50] In smaller systems, we used the method of rare gas tagging[50,53–56] to enhance the dissociation efficiency. Larger complexes were studied by the elimination of weakly bound second-sphere molecules, allowing a view of progressive solvation.[50f] Many theoretical studies have focused on these singly charged cation−water systems to complement the available experiments.[19–30,49,50]

Multiply charged cation−water complexes are more difficult to produce in the gas phase, requiring new ion sources and special conditions.[11–18,48,52] The critical problem in these systems is their intrinsic stability with respect to charge transfer. In the asymptotic limit, many complexes between a doubly charged cation and a water molecule are "unstable" because the second

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ionization energy of the metal atom is greater than the first ionization energy of water (12.6 eV).[57] A similar problem affects higher metal charge states. However, as discussed in recent articles,[11–18] complexes that are asymptotically unstable may in fact be stabilized by the strong Coulombic attraction that dominates at short bonding distances. The critical consideration is how the ions are produced relative to the location of the curve crossing between the $M^{2+} + H_2O$ and $M^+ + H_2O^+$ potentials. The most general way to make multiply charged ions in the gas phase is with electrospray ionization,[11,14,15,18] beginning with $M^{n+}(H_2O)_n$ species in solution, which are then desolvated. Other sources have been demonstrated by several groups.[12,13,16,17] Velegrakis and co-workers,[16] and more recently our laboratory,[17] have shown how laser vaporization can produce multiply charged systems, including some that are asymptotically unstable. However, all of these methods produce ion densities lower than those available for singly charged complexes, and so spectroscopic measurements on these systems are challenging. Metz and co-workers have described electronic spectroscopy of doubly charged transition metal ion complexes generated from an electrospray source.[48] Stace and co-workers have also measured electronic spectra for dication complexes using their oven-beam production method.[12h] Most recently, Williams and co-workers have obtained infrared spectroscopy on doubly charged calcium and copper ion complexes with water, also produced by electrospray.[52] In the present work, we find that laser vaporization is able to produce both singly charged and doubly charged chromium-water complexes with good efficiency, even though the dication is asymptotically unstable. We obtain infrared photodissociation spectroscopy for both of these systems using rare gas tagging, and are able to compare the effects of charge on cation hydration.

Experimental Section

Cation−water complexes of the form $Cr^{n+}(H_2O)Ar_m$ for these experiments are produced in a pulsed-nozzle laser vaporization cluster source, as described previously.[50] The vaporization laser power and timing with respect to the gas pulse are key variables in optimizing singly versus doubly charged complexes. Mixed complexes with argon that are needed for the rare gas tagging experiments are produced by using argon as the expansion gas. Clusters produced in the source chamber are collimated by a skimmer and then proceed to a pulsed reflectron time-of-flight mass spectrometer located in a differentially pumped chamber. In this instrument, different configurations allow sampling of the full mass spectrum or the isolation of ions with specific mass/charge ratios. Selected ion complexes are investigated with IR photodissociation spectroscopy in the O−H stretching region with an optical parametric oscillator/amplifier laser system (OPO/OPA; LaserVision, Inc.) pumped by a Nd:YAG laser (Continuum 8010). Excitation occurs in the turning region of the reflectron field, where ion optics and laser pulse timing are adjusted to obtain optimized spatial and temporal overlap between the laser and the ion beam. The fragment ions resulting from laser photodissociation correspond to the elimination of argon from selected parent ions containing one metal cation, one water molecule, and one or more argon atoms. The fragment ion intensity is recorded as a function of the infrared laser frequency using a digital oscilloscope (LeCroy) connected to a PC computer via an GPIB interface.

Density functional theory was used to compute the structures, energetics and spectra of the $Cr^+(H_2O)Ar_n$ and $Cr^{2+}(H_2O)Ar_n$ complexes for comparison to the experiment using the B3LYP functional in the Gaussian 03W package and the 6-311+G(d,p) basis set.[58] The computed vibrational frequencies were scaled by a factor of 0.96, which is the recommended value for the B3LYP/6-311+G(d,p) method. Full details about the DFT computations are given in the Supporting Information for this paper.

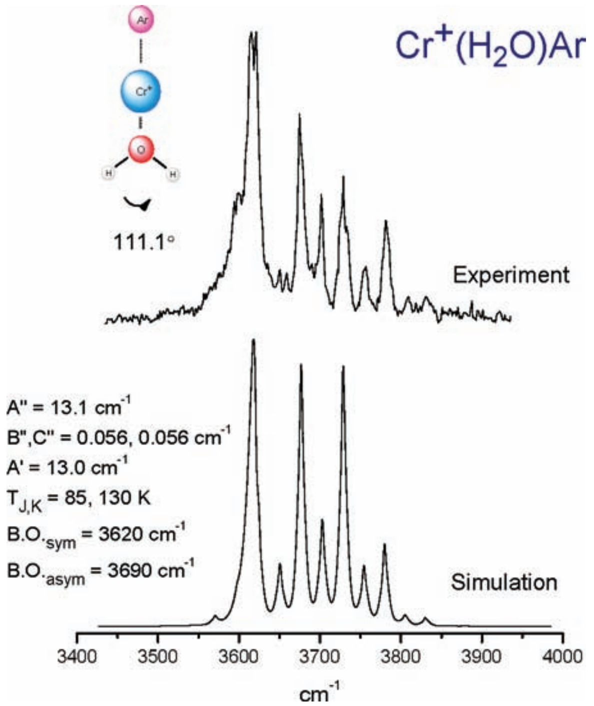

Figure 1. Infrared photodissociation spectrum of $Cr^+(H_2O)Ar$ in the O−H stretching region. The experimental spectrum (upper trace) is compared to a simulation (lower) of the rotational structure expected for the C_{2v} structure shown in the inset.

Results and Discussion

Singly charged chromium−water cation complexes are produced efficiently by our laser vaporization source using conditions like those we have described for other cation-water systems.[50] A mass spectrum is presented in the Supporting Information. The $Cr^+−(H_2O)$ binding energy (1.34 eV; 30.9 kcal/mol; 10800 cm^{-1})[8b] is higher than the infrared excitation energy in the O−H stretching region (~3700 cm^{-1}). Therefore, photodissociation is not possible with single-photon excitation, and multiphoton excitation is not efficient with the laser pulse energies available (5−10 mJ/pulse, unfocused). External water molecules in larger clusters would have lower binding energies (e.g., the hydrogen bond energy of water dimer is ~5 kcal/mol or 1750 cm^{-1}),[59] allowing one-photon dissociation. However, in the present study on monohydrated systems, we must use argon tagging[50,53–56] to make photodissociation more efficient. The measured binding energy of diatomic Cr^+Ar is 2338 cm^{-1} (6.68 kcal/mol)[60] and we compute the argon binding in $Cr^+(H_2O)−Ar$ to be 7.1 kcal/mol (2480 cm^{-1}). Therefore, $Cr^+(H_2O)Ar$ should dissociate by argon elimination when it is excited in the O−H stretch region, and we find experimentally that this is the case.

Figure 1 shows the IR photodissociation spectrum measured for $Cr^+(H_2O)Ar$ in the O−H stretching region, obtained by mass selecting this ion and monitoring the appearance of the $Cr^+(H_2O)$ fragment. There are several peaks in the 3500−3800 cm^{-1} region of the spectrum, where the symmetric and asymmetric O−H stretches of water (3657 and 3756 cm^{-1} for the free molecule) are expected.[61] As we have shown previ-

TABLE 1: O−H Stretch Vibrational Frequencies (cm^{-1}) Computed and Measured for the $Cr^{n+}(H_2O)$ Complexes Studied Here[a]

complex	theory sym/asym	experiment sym/asym	I_a/I_s
$Cr^+(H_2O)$	3624 (143)/3696 (233)		
$Cr^+(H_2O)Ar$	3628 (145)/3700 (228)	3620/3690	1.1
$Cr^+(H_2O)Ar_2$	3631 (139)/3703 (224)	3621/3687	1.2
$Cr^{2+}(H_2O)$	3460 (378)/3506 (403)		
$Cr^{2+}(H_2O)Ar$	3454 (429)/3507 (409)		
$Cr^{2+}(H_2O)Ar_2$	3486 (417)/3539 (368)		
$Cr^{2+}(H_2O)Ar_3$	3515 (360)/3572 (341)	3512/−	0.8
$Cr^{2+}(H_2O)Ar_4$	3528 (308)/3587 (315)	3531/3586	1.4
$Cr^{2+}(H_2O)Ar_5$	3539 (308)/3600 (296)	3546/−	2.7
$Cr^{2+}(H_2O)Ar_6$	3351 (1133)/3580 (290)	3380/3578	0.4

[a] Computed intensities (km/mol) are in parentheses. The intensity ratio of the experimental asymmetric and symmetric stretch bands (I_a/I_s) is determined by the integrated peak area.

ously,[50] these peaks arise from the two vibrational bands and their partially resolved rotational structure. The inset shows the geometry calculated with density functional theory for this complex. It has C_{2v} symmetry with the argon binding to the metal ion opposite the water. This is the same qualitative structure that we have found for other cation−water−argon complexes,[50] and therefore the interpretation of this spectrum is straightforward. The broader band near 3600 arises from the symmetric O−H stretch of the water molecule. This is a parallel-type vibrational band with partially resolved rotational structure along its contour. The lines in the 3650−3850 cm^{-1} range are assigned to the K-type rotational sub-bands of the perpendicular-type asymmetric stretch. The A rotational constant for this system should have a value near 13−14 cm^{-1} because only the light hydrogen atom masses lie off the C_2 axis and can contribute to this moment of inertia. This large A value gives rise to the widely spaced rotational structure. To confirm this assignment, we have simulated the rotational structure of these vibrational bands, as shown in the lower spectrum of the figure, using the program *AsyRotWin*.[65] The simulation includes the nuclear spin statistical weights for the ortho−para (odd:even = 3:1) values of K. A rotational temperature of about 130 K reproduces the main features of the spectrum. The widely spaced structure, the alternating line intensities, and the acceptable fit from the simulation confirm that the complex has C_{2v} symmetry with water close to its free-molecule structure. The band centers for the two vibrations are at 3620 and 3690 cm^{-1}. As another test, we have also measured the spectrum for $Cr^+(H_2O)$ tagged with two argons (see Supporting Information). Because this complex has heavy atoms off the C_2 axis, its A value is much smaller, and the widely spaced rotational structure is no longer detected. Only two main bands are seen for this complex at 3621 and 3687 cm^{-1}, which are essentially at the same position as the band centers for the monoargon complex. We tried to measure the spectrum for the deuterated complex, but the argon binding is apparently greater than the energy of the O−D stretch near 2700 cm^{-1}, and we could not detect dissociation there. These band positions are compared to the predictions of DFT in Table 1.

The vibrational bands found here for the $Cr^+(H_2O)Ar_{1,2}$ complexes are shifted to frequencies lower than those in the free water molecule. The red shifts for the monoargon complex are 37 and 66 cm^{-1} for the symmetric and asymmetric stretches, respectively, similar to those we have seen previously for the corresponding V^+, Fe^+, Ni^+, Cu^+ and Co^+ complexes.[50b,c,f,h] Li^+ complexes with water had smaller O−H red shifts.[50g] The red shift occurs because the highest occupied molecular orbitals on water have partial bonding character, and polarization of the electrons in these orbitals toward the metal ion removes density from the O−H bonds. This weakens the bonds and lowers the frequencies. The shift is greater for the asymmetric stretch, as noted previously.[50b] This polarization affect is very similar to the well-known σ-donation that occurs for transition metal−carbonyl complexes.[62,63] As in those systems, some π-back bonding is also possible for these water complexes.[50b] As shown in Table 1, these measured frequency shifts are reproduced nicely by our DFT calculations.

An additional aspect of these vibrational bands is the relative intensities of the symmetric and asymmetric stretches. In the isolated water molecule, the ratio of line intensities I_a/I_s is about 18.[64] However, in many cation−water systems, this ratio is much smaller, approaching unity.[49,50] The present $Cr^+(H_2O)$ spectrum has an integrated band intensity ratio of $I_a/I_s = 1.1$. This effect is attributed to a change in IR oscillator strength, resulting from the dynamic polarization of the water molecule by the cation, which is very different for the two vibrations. The IR intensity is of course related to the dipole derivative as the molecule vibrates. In the symmetric stretch, the parallel-type vibration has concerted motion of both hydrogens along the C_2 axis, toward and away from the cation, thus effectively modulating the charge induction and amplifying the dynamic dipole. In the asymmetric stretch, the off-axis motion of the perpendicular-type vibration is less effective in this regard. The net result is that the symmetric stretch gains intensity relative to the asymmetric stretch in these complexes. This pattern is also predicted by theory. For the free water molecule, we compute IR intensities of 9 (sym) and 57 (asym) km/mol, versus 143/233 km/mol for $Cr^+(H_2O)$ and 145/228 km/mol for $Cr^+(H_2O)Ar$. As seen from these values, cation binding induces a significant gain in intensity for *both* vibrations, but the advantage goes to the symmetric stretch. According to the calculations, argon does not influence these intensities significantly.

The rotational structure of the $Cr^+(H_2O)Ar$ spectrum provides a probe of the geometry of this complex. As we have discussed,[41,50] the value of the A constant is determined by the distance of the hydrogen atoms away from the C_2 axis, which is in turn related to the O−H bond distance and the H−O−H angle. Unfortunately, a single A value is insufficient to determine these two geometric parameters independently. To proceed, we recognize that the change in O−H bond distance for the water upon binding to the metal ion is not as great as the change in the H−O−H bond angle. This expectation is confirmed in the computed structure (see Supporting Information). If we therefore fix the O−H bond distance at the value computed, we can use the measured A constant to estimate the H−O−H angle. This analysis leads to the conclusion that the H−O−H angle in $Cr^+(H_2O)Ar$ is 111.1°. This angle can be compared to the value in the free water molecule, which is 104.7°, indicating that the H−O−H bonding angle of water has expanded significantly upon complexation to Cr^+. Our computed values for this angle in H_2O and $Cr^+(H_2O)$ are 105.1° and 107.2°, which also indicate some H−O−H expansion. We have documented this behavior previously for water complexes with Mg^+, Ca^+, V^+ and Li^+.[41a,b,50b,g] This analysis also assumes that the metal and argon atoms remain fixed on the C_2 axis and do not contribute significantly to the A constant. This is another oversimplification, as we have recently discussed for the $V^+(H_2O)Ar$ system.[66] A full anharmonic computational study of that complex showed that vibrational averaging in the bending potential contaminates the A value, *effectively* contributing 2−3° to the H−O−H angle

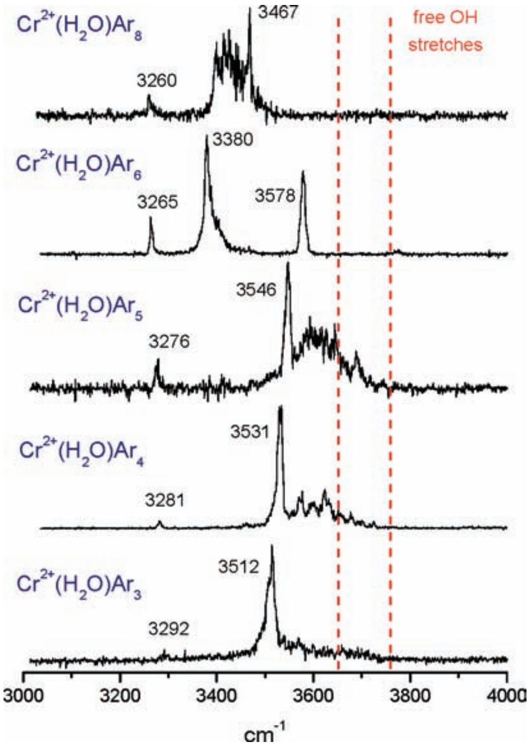

Figure 2. Infrared photodissociation spectrum of $Cr^{2+}(H_2O)Ar_n$ complexes in the O−H stretching region.

expansion. The masses and binding energies here are similar to those in the vanadium system, and so it is reasonable that a similar effect occurs here. Because the apparent angle expansion is greater than the likely vibrational averaging contribution, it is safe to assume that a significant amount of H−O−H angle expansion actually does occur. The bend vibrational averaging may explain in part why the apparent angle expansion is greater than computed. H−O−H angle expansion is also understandable as a result of the cation polarization of the water. When the cation binds to and polarizes the lone pairs toward it, the hydrogens can relax toward a more open angle. In addition to the red shifts and intensity changes in the O−H stretch bands, this angle expansion seems to be another general feature of cation binding to water.

By variation of the vaporization laser intensity and its timing relative to the gas pulse, we are able to make $Cr^{2+}(H_2O)Ar_n$ complexes with reasonably good efficiency (see mass spectrum in Supporting Information). We have discussed previously the likely mechanism of dication cluster production in our source regarding $Co^{2+}(H_2O)$ complexes.[17] The second ionization potential of Cr is 16.5 eV and the first IP of water is 12.6 eV, so therefore $Cr^{2+}(H_2O)$ is asymptotically unstable with respect to charge transfer. We calculate the $Cr^{2+}-(H_2O)$ binding energy to be 75.6 kcal/mol, and so we again must use argon tagging to accomplish photodissociation in this system. The binding energy of argon to Cr^{2+} is not known, but we compute it to be 37.3, 18.7, 13.2, 7.0, 6.0, and 3.3 kcal/mol (13050, 6540, 4617, 2450, 2100 and 1150 cm^{-1}) in the $Cr^{2+}(H_2O)Ar_n$ complexes for $n = 1-6$. Roughly consistent with these energetics, which are not expected to be quantitative, we begin to detect fragmentation of $Cr^{2+}(H_2O)Ar_n$ in the O−H stretching region at $n \geq 3$. The elimination of argon is recognized to come from a doubly charged ion by the apparent mass loss of 20 amu.

Figure 2 shows the IR photodissociation spectra for $Cr^{2+}(H_2O)Ar_n$ ($n = 3-6,8$) complexes. The signal levels here, which vary noticeably for different cluster sizes, depend on the amount of each ion produced and its relative dissociation efficiency. The IRPD spectra all contain structure that appears mostly to the red of the symmetric and asymmetric stretches in free water (marked with dashed red lines). The $n = 3-5$ complexes each have a single main band, with broader structure toward higher frequency. The $n = 6$ complex has two main bands and a slightly weaker one a little further red than the 3280 feature for $n = 4$ and 5. The $n = 8$ spectrum has all of its structure even further to the red. These complexes also all have a weak band near 3260−3290 cm^{-1}. We have computed structures and vibrational frequencies for these complexes (see Supporting Information and Table 1). These calculations find that the argon atoms in the smaller complexes bind directly to the cation like the water up to the complex $Cr^{2+}(H_2O)Ar_5$, which has a completed coordination of six ligands. After this, additional argons bind on the O−H of water. The spectra measured are consistent with this picture of the coordination.

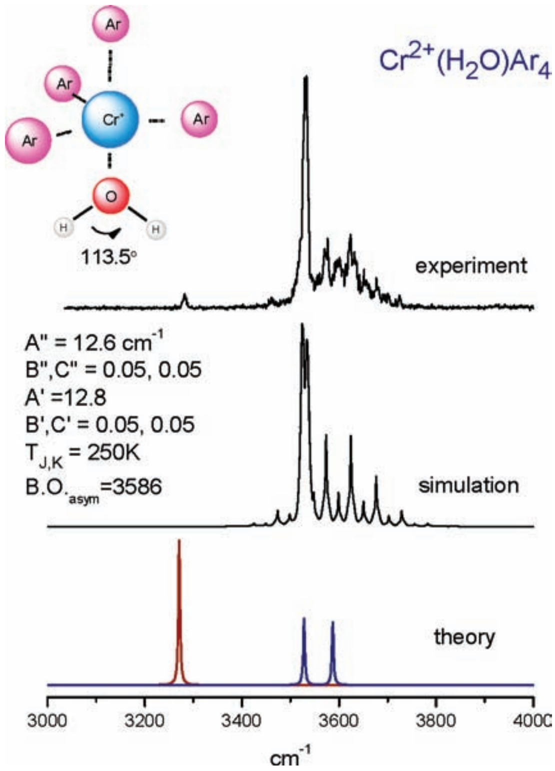

Figure 3. Infrared photodissociation spectrum of $Cr^{2+}(H_2O)Ar_4$ in the O−H stretching region. The experimental spectrum (upper trace) is compared to a simulation (middle trace) of the rotational structure expected for the geometry shown in the inset. The lower trace shows the vibrations predicted by theory (band origins only) for the symmetric and asymmetric stretches of the unreacted complex (blue line) and the insertion product (dark red line) with its hydroxide stretch. As indicated, the hydroxide stretch in an insertion product has a greater IR intensity, and therefore small amounts of this isomer could give a detectable signal.

The $n = 3$ complex is calculated to have symmetric and asymmetric stretches at 3515 and 3572 cm^{-1} with roughly equal intensities. However, we detect only one clear band at 3512 cm^{-1}, with additional broad, ill-defined intensity extending over the 3520−3700 cm^{-1} region. A similar pattern of one sharp band and broad structure to the blue is also found for the $n = 4$ and 5 complexes. Figure 3 shows an expanded view of this structure for the $n = 4$ complex, where its origin becomes apparent. Although this structure is not intense or particularly sharp, it is recognizable as the same kind of rotational profile seen in Figure 1 for the asymmetric stretch of the singly charged complex. The simulated spectrum in Figure 3 provides a reasonable fit to the structure, and as shown in the inset, the rotational constants derived from this correspond to a reasonable geometry for the water moiety. Additionally, the band origin derived from this analysis (3586 cm^{-1}) compares reasonably well with the computed position for the asymmetric stretch (3572 cm^{-1}). However, the A rotational constants employed here do not correspond to the whole complex with argon atom masses; they correspond *just to the water molecule*, which is apparently rotating internally with respect to the rest of the complex. Such internal rotation of water in its complexes has been seen previously.[67–69] It is only possible if the angular potential has no significant barriers. To check this, we have carried out computational scans of the radial potential with DFT (see Supporting Information). Again, this is not expected to be quantitative, but we find barriers to internal rotation of the water of only about 0.3 kcal/mol. It then seems reasonable that internal rotation could be the source of the structure for the $n = 4$ complex. The $n = 3$ and 5 complexes have broad signal in the same frequency range, but with no resolved structure. A potential scan of the $n = 3$ complex shows that it has similar low barriers to internal rotation. We therefore assign those broad bands to unresolved rotational structure for the respective asymmetric stretching bands for those complexes.

Having assigned the broad structure for the $n = 3-5$ complexes to the asymmetric stretch bands, the remaining sharp bands are naturally assigned to the symmetric stretches of each complex. As shown in Figure 2 and Table 1, the measured positions for each of these bands are quite close to their predicted positions, confirming this assignment. With these assignments, we can compare the band positions and relative intensities for these complexes to those of the corresponding singly charged complexes. Additional data for this comparison is provided in Table 1 for the dication complexes whose spectra are computed but not measured. As shown, both the symmetric and asymmetric stretch bands for all the doubly charged complexes are predicted and measured (where possible) to be shifted to the red by much more than those of the singly charged complexes. Theory shows that the red shift is greatest for the $Cr^{2+}(H_2O)$ complex, and then it is gradually less as argon atoms are added to the complex. Even when the binding interaction is distributed to many argon atoms, however, the red shift for the dication complex is still greater than that for the monocation species. The red shift is associated with polarization of the water molecule that removes part of its bonding electron density, and so it is understandable that this effect is greater for the dication.

Similar reasoning applies to the relative intensities of the symmetric and asymmetric stretch vibrations. Compared to the singly charged complexes, both vibrations are computed to have much greater absolute intensities. In part, these greater IR intensities make it possible for us to measure these spectra from the small amounts of parent ions produced. Also as noted for the singly charged complex, the symmetric stretches here mostly have greater intensities than the asymmetric stretches. Table 1 lists the ratios I_a/I_s for the mono- and dication species. As shown, the dications generally have comparable or smaller I_a/I_s values than the monocations. Again, the absolute intensities and the intensity ratios both arise from the dynamic polarization of the vibrating water molecule, and these are both enhanced significantly in the doubly charged complexes.

In addition to red-shifted bands and enhanced band intensities, we also noted for the singly charged complex the expansion of the H−O−H angle induced by the cation binding to water. Although we do not have as clear a picture of this for the dication, we can use the rotational structure for the $n = 4$ complex to estimate the structure of the water in this system. The same caveats apply here as before, and it is also not clear what effect the additional argons have. The argon binding to the dication is quite strong, and this could cause additional inductive effects that we cannot account for completely here. Nevertheless, the rotational constants for the dication complex are A', $A'' = 12.8$, 12.6 cm^{-1}, which are both significantly smaller than those for the singly charged complex. Applying the same logic used before, we derive an H−O−H bond angle of about 113.5°, which is greater than the angle in the monocation complex (111.1°) and significantly greater than the value for free water (104.7°). Again, the stronger polarization of the dication amplifies the effects seen before.

The $n = 6$ complex provides an additional observation supporting the assignments of these spectra. The $n = 5$ species is computed to have a complete coordination of six ligands, with one water and five argons. The $n = 6$ complex is then predicted to have one external argon, which binds to the O−H of water. This binding site has been seen previously as a favorable isomer in other cation-water-argon complexes.[50ce] Here, the implications for this predicted isomer are striking: both the symmetric and asymmetric stretches get an additional red shift and even more IR intensity. Additionally, because the argon goes on the water, the internal rotation should be quenched, eliminating the broadening from rotational structure, and allowing the asymmetric stretch to be seen as a sharp band. Consistent with these predictions, the $n = 6$ spectrum has two sharp vibrational bands at just about the positions predicted, confirming that the cation coordination is six (one water + five argons). The $n = 8$ complex should have three external argons, probably binding with unspecific isomeric structures in the vicinity of the O−H's of water, and these likely give rise to additional red shifting. The broad spectrum seen for that complex is consistent with overlapping spectra for several isomeric species.

A final aspect of these spectra is the small band seen for each complex much farther to the red than any of the other bands discussed yet. The very weak feature at 3292 cm^{-1} for the $n = 3$ complex gradually grows in intensity and shifts to 3281, 3276, 3265 and 3260 for the $n = 4, 5, 6, 8$ complexes. This band is approximately where the overtone of the water bending mode (1595 cm^{-1} for the free molecule) would be found, but the bend is computed to lie at 1616 cm^{-1} for $Cr^{2+}(H_2O)$ and to shift gradually to lower frequency for the argon tagged complexes. Therefore, although we cannot rule this out completely, a bend overtone assignment does not seem to fit here. Hotbands or other conceivable combination bands also do not seem likely, given the cold conditions and the strong computed intensities of the other bands measured. Anharmonic computations in the future may be able to provide further insight into these possibilities. However, another intriguing possibility is that this band could be assigned to small amounts of reaction products in these complexes. In particular, inserted isomers having the $H-Cr^{3+}$-$(OH^-)Ar_n$ structure would have the same apparent mass as nonreacted species, but instead of the O−H stretches there would be a *hydroxide stretch* vibration in this region. We have examined this possibility computationally, and $H-Cr^{3+}(OH^-)$ is a stable structure with a predicted intense hydroxide O−H stretch at 3271 cm^{-1} (see Figure 3). This is exactly the range of the bands seen, and therefore it seems that we do indeed have a small amount of hydroxide isomer present. The +3 oxidation state implied by this structure is known for chromium, and therefore this is a plausible assignment for the minor bands seen.

Conclusions

Singly and doubly charged complexes of chromium with water are produced by laser vaporization in a pulsed nozzle source. The yield of singly charged ions is much greater than that for the corresponding doubly charged species, but both can be produced with attached argon, size-selected, and studied with infrared photodissociation spectroscopy. Spectra for both complexes in the O−H stretching region provide an appealing picture of cation−water interactions at the molecular level. Polarization of water by metal ions leads to red-shifted O−H stretches, enhanced IR absorption intensities and expansion of the H−O−H angle. These effects have been seen previously for singly charged complexes but are now also documented for doubly charged systems. Perhaps not surprisingly, the additional charge greatly enhances each of these polarization effects in the dications. Patterns in the spectra confirm that the dication coordination is six (one water + five argons). Evidence is also presented for insertion chemistry, leading to the detection of a hydroxide band in what is essentially a triply charged chromium complex. Additional studies like these are underway in our laboratory to explore other details of metal ion solvation by water.

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Supporting Information Available: Full details of the DFT and ab initio computations done in support of the spectroscopy here, including the structures, energetics and vibrational frequencies for each of the structures considered as well as the mass spectrum and IR-PD spectrrum. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Burgess, J. *Metal Ions in Solution*; John Wiley and Sons: New York, 1978.

(2) Burgess, J. *Ions in Solution*; Horwood Publishing: Chichester, U.K., 1999.

(3) Richens, D. T. *The Chemistry of Aqua Ions*; John Wiley: Chichester, U.K., 1997.

(4) (a) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445. (b) Nielsen, S. B.; Masella, M.; Kebarle, P. *J. Phys. Chem. A* **1999**, *103*, 9891.

(5) (a) Tang, I. N.; Lian, M. S.; Castleman, A. W., Jr *J. Chem. Phys.* **1976**, *65*, 4022. (b) Märk, T. D.; Peterson, K. I.; Castleman, A. W., Jr *Nature* **1980**, *285*, 392. (c) Holland, P. M.; Castleman, A. W., Jr *J. Chem. Phys.* **1982**, *76*, 4195. (d) Harms, A. C.; Khanna, S. N.; Chen, A. B.; Castleman, A. W., Jr *J. Chem. Phys.* **1994**, *100*, 3540.

(6) (a) Magnera, T. F.; David, D. E.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 4100. (b) Magnera, T. F.; David, D. E.; Stulik, D.; Orth, R. G.; Jonkman, H. T.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 5036.

(7) Marinelli, P. J.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 4101.

(8) (a) Clemmer, D. E.; Chen, Y. M.; Aristov, N.; Armentrout, P. B. *J. Phys. Chem.* **1994**, *98*, 7538. (b) Dalleska, N. F.; Honma, K.; Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 3519. (c) Dalleska, N. F.; Tjelta, B. L.; Armentrout, P. B. *J. Phys. Chem.* **1994**, *98*, 4191. (d) Rodgers, M. T.; Armentrout, P. B. *J. Phys. Chem. A* **1997**, *101*, 1238.

(9) (a) Beyer, M.; Berg, C.; Gorlitzer, H. W.; Schindler, T.; Achatz, U.; Albert, G.; Niedner-Schatteburg, G.; Bondybey, V. E. *J. Am. Chem. Soc.* **1996**, *118*, 7386. (b) Berg, C.; Beyer, M.; Achatz, U.; Joos, S.; Niedner-Schatteburg, G.; Bondybey, V. E. *Chem. Phys.* **1998**, *239*, 379. (c) Beyer, M.; Williams, E. R.; Bondybey, V. E. *J. Am. Chem. Soc.* **1999**, *121*, 1565. (d) Fox, B. S.; Balteanu, I.; Balaj, O. P.; Liu, H. C.; Beyer, M. K.; Bondybey, V. E. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2224.

(10) (a) Dukan, L.; del Fabbro, L.; Pradel, P.; Sublemontier, O.; Mestdagh, J. M.; Visticot, J. P. *Eur. Phys. J. D* **1998**, *3*, 257. (b) Poisson, L.; Pradel, P.; Lepetit, F.; Reau, F.; Mestdagh, J. M.; Visticot, J. P. *Eur. Phys. J. D* **2001**, *14*, 89. (c) Poisson, L.; Lepetit, F.; Mestdagh, J. M.; Visticot, J. P. *J. Phys. Chem. A* **2002**, *106*, 5455. (d) Poisson, L.; Dukan, L.; Sublemontier, O.; Lepetit, F.; Reau, F.; Pradel, P.; Mestdagh, J. M.; Visticot, J. P. *Int. J. Mass Spectrom.* **2002**, *220*, 111. (e) le Caer, S.; Heninger, M.; Maitre, P.; Mestdagh, H. *Rapid Commun. Mass Spectrom.* **2003**, *17*, 351.

(11) (a) Jayaweera, P.; Blades, A. T.; Ikonomou, M. G.; Kebarle, P. *J. Am. Chem. Soc.* **1990**, *112*, 2452. (b) Blades, A. T.; Jayaweera, P.; Ikonomou, M. G.; Kebarle, P. *Int. J. Mass Spectrom. Ion Processes* **1990**, *102*, 251. (c) Peschke, M.; Blades, A. T.; Kebarle, P. *J. Phys. Chem. A* **1998**, *102*, 9978. (d) Peschke, M.; Blades, A. T.; Kebarle, P. *Int. J. Mass Spec.* **1999**, *185*, 685. (e) Peschke, M.; Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **2000**, *122*, 10440.

(12) (a) Stace, A. J.; Walker, N. R.; Firth, S. *J. Am. Chem. Soc.* **1997**, *119*, 10239. (b) Walker, N. R.; Firth, S.; Stace, A. J. *Chem. Phys. Lett.* **1998**, *292*, 125. (c) Walker, N.; Dobson, M. P.; Wright, R. R.; Barran, P. E.; Murrell, J. N.; Stace, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 11138. (d) Stace, A. J. *J. Phys. Chem. A* **2002**, *106*, 7993. (e) Cox, H.; Akibo-Betts, G.; Wright, R. R.; Walker, N. R.; Curtis, S.; Duncombe, B.; Stace, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 233. (f) Wu, G.; Chapman, D.; Stace, A. *Int. J. Mass Spectrom.* **2007**, *262*, 211. (g) Duncombe, B. J.; Duale, K.; Buchanan-Smith, A.; Stace, A. J. *J. Phys. Chem.* **2007**, *111*, 5158. (h) Guan, J.; Puskar, L.; Esplugas, R. O.; Cox, H.; Stace, A. J. *J. Chem. Phys.* **2007**, *127*, 064311.

(13) (a) Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **1999**, *103*, 7385. (b) Schröder, D.; Schwarz, H.; Wu, J. L.; Wesdemiotis, C. *Chem. Phys. Lett.* **2001**, *343*, 258.

(14) (a) Beyer, M.; Williams, E. R.; Bondybey, V. E. *J. Am. Chem. Soc.* **1999**, *121*, 1565. (b) Rodriquez-Cruz, S. E.; Jockusch, R. A.; Williams, E. R. *J. Am. Chem. Soc.* **1999**, *121*, 1986. (c) Rodriguez-Cruz, S. E.; Klassen, J. S.; Williams, E. R. *J. Am. Soc. Mass Spectrom.* **1999**, *10*, 958. (d) Rodriguez-Cruz, S. E.; Jockusch, R. A.; Williams, E. R. *J. Am. Chem. Soc.* **1999**, *121*, 8898. (e) Wong, R. L.; Paech, K.; Williams, E. R. *Int. J. Mass Spectrom.* **2004**, *232*, 59. (f) Bush, M. F.; Saykally, R. J.; Williams, E. R. *Int. J. Mass Spectrom.* **2006**, *253*, 256. (g) Leib, R. D.; Donald, W. A.; Bush, M. F.; O'Brien, J. T.; Williams, E. R. *J. Am. Chem. Soc.* **2007**, *129*, 4894. (h) Leib, R. D.; Donald, W. A.; Bush, M. F.; O'Brien, J. T.; Williams, E. R. *J. Am. Soc. Mass. Spectrom.* **2007**, *18*, 1217.

(15) Shvartsburg, A. A.; Siu, K. W. M. *J. Am. Chem. Soc.* **2001**, *123*, 10071.

(16) Velegrakis, M.; Lueder, C. *Chem. Phys. Lett.* **1994**, *223*, 139.

(17) Walker, N. R.; Grieves, G. A.; Jaeger, J. B.; Walters, R. S.; Duncan, M. A. *Int. J. Mass Spectrom.* **2003**, *228*, 285.

(18) (a) Shi, T.; Orlova, G.; Guo, J.; Bohme, D. K.; Hopkinson, A. C.; Siu, K. W. M. *J. Am. Chem. Soc.* **2004**, *126*, 7975. (b) Shi, T.; Zhao, J.; Hopkinson, A. C.; Siu, K. W. M. *J. Phys. Chem. B* **2005**, *109*, 10590.

(19) (a) Rosi, M.; Bauschlicher, C. W. *J. Chem. Phys.* **1989**, *90*, 7264. (b) Rosi, M.; Bauschlicher, C. W. *J. Chem. Phys.* **1990**, *92*, 1876. (c) Bauschlicher, C. W.; Langhoff, S. R.; Partridge, H. *J. Chem. Phys.* **1991**, *94*, 2068. (d) Bauschlicher, C. W.; Partridge, H. *J. Phys. Chem.* **1991**, *95*, 9694. (e) Bauschlicher, C. W.; Sodupe, M.; Partridge, H. *J. Chem. Phys.* **1992**, *96*, 4453. (f) Sodupe, M.; Bauschlicher, C. W. *Chem. Phys. Lett.* **1993**, *212*, 624. (g) Ricca, A.; Bauschlicher, C. W. *J. Phys. Chem.* **1995**, *99*, 9003. (h) Ricca, A.; Bauschlicher, C. W. *J. Phys. Chem. A* **2002**, *106*, 3219.

(20) (a) Hrusak, J.; Stockigt, D.; Schwarz, H. *Chem. Phys. Lett.* **1994**, *221*, 518. (b) Hrusak, J.; Schröder, D.; Schwarz, H. *Chem. Phys. Lett.* **1994**, *225*, 416.

(21) (a) Irigoras, A.; Fowler, J. E.; Ugalde, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 574. (b) Irigoras, A.; Fowler, J. E.; Ugalde, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 8549. (c) Irigoras, A.; Elizalde, O.; Silanes, I.; Fowler, J. E.; Ugalde, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 114.

(22) (a) Watanabe, H.; Iwata, S. *J. Phys. Chem. A* **1997**, *101*, 487. (b) Watanabe, H.; Iwata, S. *J. Chem. Phys.* **1998**, *108*, 10078. (c) Watanabe, H.; Iwata, S.; Hashimoto, K.; Misaizu, F.; Fuke, K. *J. Am. Chem. Soc.* **1995**, *117*, 755.

(23) (a) Reinhard, B. M.; Niedner-Schatteburg, G. *J. Phys. Chem. A* **2002**, *106*, 7988. (b) Reinhard, B. M.; Niedner-Schatteburg, G. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1471. (c) Reinhard, B. M.; Niedner-Schatteburg, G. *J. Chem. Phys.* **2003**, *118*, 3571.

(24) Bock, C. W.; Markham, G. D.; Katz, A. K.; Glusker, J. P. *Inorg. Chem.* **2003**, *42*, 1538.

(25) Adamo, C.; Lelj, F. *THEOCHEM* **1997**, *389*, 83.

(26) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(27) Feller, D.; Glendening, E. D.; de Jong, W. A. *J. Chem. Phys.* **1999**, *110*, 1475.

(28) Lee, E. C.; Lee, H. M.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2003**, *119*, 7725.

(29) Taylor, M. S.; Muntean, F.; Lineberger, W. C.; McCoy, A. B. *J. Chem. Phys.* **2004**, *121*, 5688.

(30) Gourlaouen, C.; Piquemal, J-P.; Saue, T. Parisel, O. *J. Comput. Chem.* **2005**, *27*, 142.

(31) Kasalova, V.; Allen, W. D.; Schaefer, H. F., III; Pillai, E. D.; Duncan, M. A. *J. Phys. Chem. A* **2007**, *111*, 7599.

(32) Davy, R. D.; Hall, M. B. *Inorg. Chem* **1988**, *27*, 1417.

(33) Akesson, R.; Petterson, L. G. M. *Chem. Phys.* **1994**, *184*, 85.

(34) Bu, Y.; Song, X.; Liu, C. *J. Mol. Struct. (THEOCHEM)* **1999**, *489*, 141.

(35) (a) Trachtman, M.; Markham, G. D.; Glusker, J. P.; George, P.; Bock, C. W. *Inorg. Chem.* **1998**, *37*, 4421. (b) Markham, G. D.; Glusker, J. P.; Bock, C. W. *J. Phys. Chem. B* **2002**, *106*, 5118. (c) George, P.; Glusker, J. P.; Markham, G. D.; Trachtman, M.; Bock, C. W. *Mol. Phys.* **2003**, *101*, 2451.

(36) El-Nahas, A. M. *Chem. Phys. Lett.* **2001**, *345*, 325.

(37) Ducere, J-M.; Goursot, A.; Berthomieu, D. *J. Phys. Chem. A* **2005**, *109*, 400.

(38) Han, J.-G.; Morales, J. A. *THEOCHEM* **2005**, *756*, 55.

(39) Lessen, D. E.; Asher, R. L.; Brucat, P. J. *J. Chem. Phys.* **1990**, *93*, 6102.

(40) Shen, M. H.; Farrar, J. M. *J. Chem. Phys.* **1991**, *94*, 3322.

(41) (a) Willey, K. F.; Yeh, C. S.; Robbins, D. L.; Pilgrim, J. S.; Duncan, M. A. *J. Chem. Phys.* **1992**, *97*, 8886. (b) Yeh, C. S.; Pilgrim, J. S.; Willey, K. F.; Robbins, D. L.; Duncan, M. A. *Int. Rev. Phys. Chem.* **1994**, *13*, 231. (c) Scurlock, C. T.; Pullins, S. H.; Reddic, J. E.; Duncan, M. A. *J. Chem. Phys.* **1996**, *104*, 4591. (d) Duncan, M. A. *Annu. Rev. Phys. Chem.* **1997**, *48*, 69. (e) Duncan, M. A. *Int. J. Mass Spectrom.* **2000**, *200*, 545.

(42) (a) Misaizu, F.; Sanekata, M.; Tsukamoto, K.; Fuke, K.; Iwata, S. *J. Phys. Chem.* **1992**, *96*, 8259. (b) Misaizu, F.; Sanekata, M.; Fuke, K.; Iwata, S. *J. Chem. Phys.* **1994**, *100*, 1161. (c) Misaizu, F.; Tsukamato, K.; Sanekata, M.; Fuke, K. *Laser Chem.* **1995**, *15*, 195. (d) Sanekata, M.; Misaizu, F.; Fuke, K.; Iwata, S.; Hashimoto, K. *J. Am. Chem. Soc.* **1995**, *117*, 747. (e) Sanekata, M.; Misaizu, F.; Fuke, K. *J. Chem. Phys.* **1996**, *104*, 9768.

(43) Thompson, C. J.; Aguirre, F.; Husband, J.; Metz, R. B. *J. Phys. Chem. A* **2000**, *104*, 9901.

(44) (a) Muntean, F.; Taylor, M. S.; McCoy, A. B.; Lineberger, W. C. *J. Chem. Phys.* **2004**, *121*, 5676. (b) Sandford, T.; Andrews, D.; Rathbone, J.; Taylor, M.; Muntean, F.; Thompson, M.; McCoy, A. B.; Parson, R.; Lineberger, W. C. *Faraday Discuss.* **2004**, *127*, 383.

(45) Abate, Y.; Kleiber, P. D. *J. Chem. Phys.* **2005**, *122*, 084305.

(46) Wang, K. H.; Rodham, D. A.; McKoy, V.; Blake, G. A. *J. Chem. Phys.* **1998**, *108*, 4817.

(47) Agreiter, J. K.; Knight, A. M.; Duncan, M. A. *Chem. Phys. Lett.* **1999**, *313*, 162.

(48) (a) Thompson, C. J.; Husband, J.; Aguirre, F.; Metz, R. B. *J. Phys. Chem. A* **2000**, *104*, 8155. (b) Faherty, K. P.; Thompson, C. J.; Aguirre, J. M.; Metz, R. B. *J. Phys. Chem. A* **2001**, *105*, 10054. (c) Beyer, M. K.; Metz, R. B. *J. Phys. Chem. A* **2003**, *107*, 1760. (d) Metz, R. B. *Int. J. Mass. Spectrom.* **2004**, *235*, 131.

(49) (a) Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1996**, *105*, 2938. (b) Lisy, J. M. *Int. Rev. Phys. Chem.* **1997**, *16*, 267. (c) Cabarcos, O. M.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1998**, *108*, 5151. (d) Cabarcos, O. M.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1999**, *110*, 8429. (e) Vaden, T. D.; Forinash, B.; Lisy, J. M. *J. Chem. Phys.* **2002**, *117*, 4628. (f) Patwari, G. N.; Lisy, J. M. *J. Chem. Phys.* **2003**, *118*, 8555. (g) Vaden, T. D.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **2004**, *121*, 3102.

(50) (a) Duncan, M. A. *Int. Rev. Phys. Chem.* **2003**, *22*, 407. (b) Walker, N. R.; Walters, R. S.; Pillai, E. D.; Duncan, M. A. *J. Chem. Phys.* **2003**, *119*, 10471. (c) Walters, R. S.; Duncan, M. A. *Aust. J. Chem.* **2004**, *57*, 1145. (d) Walker, N. R.; Walters, R. S.; Duncan, M. A. *New J. Chem.* **2005**, *29*, 1495. (e) Walker, N. R.; Walters, R. S.; Tsai, M. K.; Jordan, K. D.; Duncan, M. A. *J. Phys. Chem. A* **2005**, *109*, 7057. (f) Walters, R. S.; Pillai, E. D.; Duncan, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 16599. (g) Vaden, T. D.; Lisy, J. M.; Carnegie, P. D.; Pillai, E. D.; Duncan, M. A. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3078. (h) Carnegie, P. D.; Duncan, M. A.,to be submitted.

(51) (a) Inokuchi, Y.; Ohshimo, K.; Misaizu, F.; Nishi, N. *J. Phys. Chem. A* **2004**, *108*, 5034. (b) Inokuchi, Y.; Ohshimo, K.; Misaizu, F.; Nishi, N. *Chem. Phys. Lett.* **2004**, *390*, 140. (c) Iino, T.; Ohashi, K.; Mune, Y.; Inokuchi, Y.; Judai, K.; Nishi, N.; Sekiya, H. *Chem. Phys. Lett.* **2006**, *427*, 24. (d) Iino, T.; Ohashi, K.; Inoue, K.; Judai, K.; Nishi, N.; Sekiya, H. *J. Chem. Phys.* **2007**, *126*, 194302.

(52) (a) Bush, M. F.; Saykally, R. J.; Williams, E. R. *ChemPhysChem* **2007**, *8*, 2245. (b) O'Brien, J. T.; Williams, E. R. *J. Phys. Chem. A* , . in press.

(53) (a) Yeh, L. I.; Okumura, M.; Myers, J. D.; Price, J. M.; Lee, Y. T. *J. Chem. Phys.* **1989**, *91*, 7319–7330. (b) Okumura, M.; Yeh, L. I.; Myers, J. D.; Lee, Y. T. *J. Phys. Chem.* **1990**, *94*, 3416.

(54) Ebata, T.; Fujii, A.; Mikami, N. *Int. Rev. Phys. Chem.* **1998**, *17*, 331.

(55) Bieske, E. J.; Dopfer, O. *Chem. Rev.* **2000**, *100*, 3963.

(56) Robertson, W. H.; Johnson, M. A. *Annu. Rev. Phys. Chem.* **2003**, *54*, 173.

(57) Hunter, E. P.; Lias, S. G. NIST Chemistry WebBook, NIST Standard Reference Database Number 69, February, 2008 (http://webbook.nist.gov/chemistry/).

(58) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A. M.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyata, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.02; Gaussian, Inc.: Pittsburgh, PA, 2003.

(59) Lui, K.; Cruzan, J. D.; Saykally, R. J. *Science* **1996**, *271*, 929.

(60) Lessen, D. E.; Asher, R. L.; Brucat, P. J. *Chem. Phys. Lett.* **1991**, *177*, 380.

(61) Shimanouchi, T. Molecular Vibrational Frequencies. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 20899, February 2008 (http://webbook.nist.gov).

(62) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordinated Compounds*, 5th ed.; John Wiley: New York, 1997; Vol. B.

(63) Frenking, G.; Frohlich, N. *Chem. Rev.* **2000**, *100*, 717.

(64) Galabov, B.; Yamaguchi, Y.; Remington, R. B.; Schaefer, H. F. *J. Phys. Chem. A* **2002**, *106*, 819.

(65) Judge, R. H.; Clouthier, D. J. *Comput. Phys. Commun.* **2001**, *135*, 293.

(66) Kasalova, V.; Allen, W. D.; Schaefer, H. F.; Pillai, E. D.; Duncan, M. A. *J. Phys. Chem. A* **2007**, *111*, 7599.

(67) Gotch, A. J.; Zwier, T. S. *J. Chem. Phys.* **1992**, *96*, 3388.

(68) Susuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A.; Blake, G. A. *Science* **1992**, *257*, 942.

(69) Berden, G.; Meerts, W. L.; Schmitt, M.; Kleinermanns, K. *J. Chem. Phys.* **1996**, *104*, 972.

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