Solvation of the $Cl^-{\cdot}H_2O$ Complex in CCl_4 Clusters: The Effect of Solvent-Mediated Charge Redistribution on the Ionic H-Bond

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The OH stretching bands associated with the ionic H-bond in the $Cl^-{\cdot}H_2O$ complex are found to dramatically shift toward higher energy upon complexation with carbon tetrachloride molecules in a size selected photofragmentation study of the $Cl^-{\cdot}H_2O{\cdot}(CCl_4)_n$, $1 \leq n \leq 5$, clusters. The large sequential shifts (80−100 cm^{-1}/CCl_4) associated with addition of the first few molecules effectively "tune" the OH stretch $\upsilon = 1$ level through a Fermi resonance with the $\upsilon = 2$ level of the intramolecular bending vibration. By the addition of the fifth molecule, the large red-shift displayed by the bare complex (577 cm^{-1} relative to isolated water) is reduced by a factor of 2. We discuss the origin of these effects in the context of charge redistrubition from chloride to the surrounding solvent molecules.

I. Introduction

Many recent developments in mass-selected spectroscopy [1−3] have lead to a new understanding of the structures and intramolecular distortions in ion−molecule complexes. When a water molecule binds to a halide ion to form the $X^-{\cdot}H_2O$ ion−molecule complex, the resulting asymmetric, or single ionic H-bonded (IHB) structure displays a characteristic spectral pattern in the mid infrared region.[4−7] The OH stretching modes, which are strongly coupled in the isolated water molecule, adopt local character in the $X^-{\cdot}H_2O$ complexes. Although the weaker free OH band (OH_{Free}) is insensitive to the anion, the band arising from the OH bound the ion (OH_{IHB}) dominates the spectrum and is generally shifted hundreds of wavenumbers below the OH_{Free} transition in a manner strongly correlated with the binding energies of the complexes.[8] The $Cl^-{\cdot}H_2O$ case has captured particular theoretical attention, where many groups have reported both the ab initio structure as well as the vibrational spectrum arising from motion on this potential surface.[9−18]

In considering the qualitative origin of the strong red-shifts in the OH_{IHB} stretching modes, Martinez and Lisy[19] have pointed out that much (80%) of the shift in $Cl^-{\cdot}CH_3OH$ can be recovered by replacing the Cl^- ion with a (unit) point charge, highlighting the role of electrostatics. More recently, Thompson and Hynes[17] have explored the $X^-{\cdot}H_2O$ series (X = F, Cl, Br, I), and concluded that, in addition to the electrostatic effect, about 40% of the shift in $Cl^-{\cdot}H_2O$ arises from charge-transfer to the water molecule. In their approach, the extent of charge-transfer was estimated by fitting the ab initio generated shape of the OH stretching potential surface to a model involving mixing between two diabatic states (i.e., $Cl^-{\cdot}H_2O$ and $HCl{\cdot}OH^-$). In this paper, we follow how the energy of the OH_{IHB} fundamental is affected when $Cl^-{\cdot}H_2O$ is sequentially solvated by CCl_4 molecules, which are nonpolar but very polarizable species. This is accomplished by acquiring mid infrared predissociation spectra of the mass-selected $Cl^-{\cdot}H_2O{\cdot}(CCl_4)_n$ cluster ions in the OH stretching region (3000−3800 cm^{-1}). We discuss the observed shifts in the context of intracluster charge redistribution involving both water and carbon tetrachloride.

II. Experimental Section

Spectra are obtained using the Yale tandem time-of-flight photofragmentation spectrometer described previously.[20] The $Cl^-{\cdot}H_2O{\cdot}(CCl_4)_n$ cluster ions are prepared using our two-valve ion source[21] in which trace CCl_4 and Ar are expanded through the primary supersonic nozzle, whereas water vapor is entrained into the expansion using a second valve whose low-pressure flow is directed just outside the nozzle. The expanding mixture is ionized by a 1 keV electron beam counterpropagating with the axis of the supersonic flow. Infrared photons in the 2500−3800 cm^{-1} range are generated with a KTP/KTA-based optical parametric oscillator/amplifier (LaserVision), which delivers about 5 mJ/pulse in a bandwidth of about 2 cm^{-1}. Because the $X^-{\cdot}H_2O$ complexes are typically bound by more than the energy of the OH stretching fundamentals, the spectrum of the bare chloride hydrate was estimated using an argon variant of the 'messenger' technique pioneered by Okumura and Lee[22]

$$Cl^-{\cdot}H_2O{\cdot}Ar_n + h\nu \rightarrow Cl^-{\cdot}H_2O{\cdot}Ar_{n-m} + m\mathrm{Ar} \qquad (1)$$

The weakly bound argon atoms have the advantages that they quench the complex near its equilibrium geometry as well as enable detection of its mid infrared spectrum in a linear regime. The larger argon clusters display an asymptotic loss of 5 argon atoms upon excitation in the 3200 cm^{-1} region. In the $Cl^-{\cdot}H_2O{\cdot}(CCl_4)_n$ clusters studied here, excitation in the mid-IR is sufficient to induce predissociation

$$Cl^-{\cdot}H_2O{\cdot}(CCl_4)_n + h\nu \rightarrow Cl^-{\cdot}H_2O{\cdot}(CCl_4)_{n-1} + CCl_4 \qquad (2)$$

where loss of one CCl_4 monomer is the dominant decay channel in each case. Hiraoka[23] has recently measured the binding energy of the $Cl^-{\cdot}CCl_4$ complex to be about 14 kcal/mol (~4600 cm^{-1}), indicating that we are likely measuring the spectra of species containing internal excitation on the order of 1500 cm^{-1}. Unfortunately, we have not been able to prepare sufficiently large quantities of the argon solvated $Cl^-{\cdot}H_2O{\cdot}(CCl_4)_n$ clusters to acquire their spectra for comparison.

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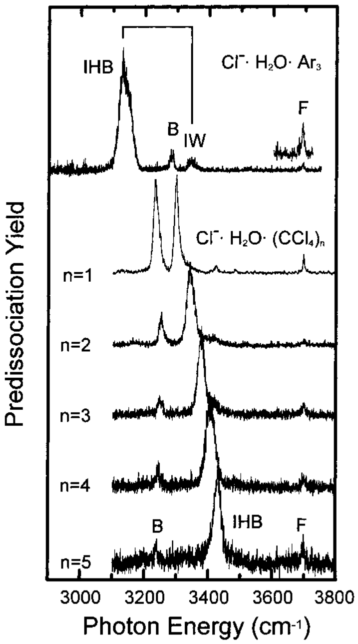

Figure 1. Vibrational predissociation spectra of $Cl^- \cdot H_2O \cdot Ar_3$ and $Cl^- \cdot H_2O \cdot (CCl_4)_n$, $n = 1-5$. The band assignments are ionic hydrogen-bonded OH stretch (IHB), intramolecular water bending overtone (B), ion-water stretch soft mode (IW), and free OH stretch (F).

III. Results and Discussion

IIIA. Appearance of the Spectra. The mid-IR spectra of the $Cl^- \cdot H_2O \cdot (CCl_4)_n$ clusters are presented in Figure 1. We remark that the $Cl^- \cdot H_2O \cdot CCl_4$ system has been studied previously by Okumura and co-workers,[24] who reported the relatively strong feature corresponding to the free OH at about 3700 cm^{-1} in their first report of the asymmetric nature of the $Cl^- \cdot H_2O$ complex. The complete spectrum in Figure 1 (i.e., including the OH_{IHB} region) illustrates that the CCl_4 molecule causes a very significant perturbation of the $Cl^- \cdot H_2O$ spectrum as evidenced by the differences in the top two traces in Figure 1. Note that the $Cl^- \cdot H_2O \cdot CCl_4$ complex is unique in that it displays a much more pronounced free OH feature than the other CCl_4 complexes, or indeed any of the other halide-water clusters we have studied.

Several effects are immediately apparant from the qualitative appearance of the spectra. First, the OH_{IHB} band is dramatically shifted to higher energy with each additional CCl_4 molecule. This is an interesting result, since the much more weakly bound argon solvated $Cl^- \cdot H_2O$ clusters display a red-shift at the early stages of solvation before evolving into a weak blue-shift for $n \geq 3$. Second, the bands remain relatively sharp despite the large incremental shift (and residual internal energy), with widths typically smaller than those found in the argon complexes. Third, as the OH_{IHB} blue-shifts, it evolves first into a strong doublet before emerging on the high energy side of a weaker feature, which is much less shifted by increasing numbers of CCl_4 molecules. The band in combination with the OH_{IHB} involving the ion−water stretching soft mode (IW) is found to follow the shift in the OH_{IHB} but fall off in intensity as the band evolves toward higher energy. The energy of the ion−water stretch (in the OH_{IHB} vibrationally excited state) is reduced from 210 to 188 cm^{-1} upon addition of the first CCl_4 solvent molecule.

IIIB. Spectra of the $Cl^- \cdot HDO \cdot CCl_4$ Isotopmer and Comparison with $Br^- \cdot H_2O$. The strongly size-dependent doubling of the OH_{IHB} band is reminiscent of an earlier study from our group[5] in which we followed the vibrational spectra through the $X^- \cdot H_2O$ (X = Cl, Br, I) series. The OH_{IHB} fundamental incrementally shifts to lower energies with smaller halides, and as this occurs, the OH_{IHB} ($v = 1$) level was suggested to "cross" the $v = 2$ level of the intramolecular bend (denoted B in Figure 1). This relative insensitivity of the bending level to the ion is expected since the bending displacement can be carried by free OH motion even as the other hydrogen becomes increasingly anchored to the ion. In the $X^- \cdot H_2O$ series, $Br^- \cdot H_2O$ also displays an almost equal intensity doublet in the OH_{IHB} range as indicated in Figure 2c, which is suprisingly similar to the OH_{IHB} band in the $Cl^- \cdot H_2O \cdot CCl_4$ spectrum reproduced in Figure 2a. Note first that the splitting between the doublets is very similar in each case (66 cm^{-1} in $Cl^- \cdot H_2O \cdot CCl_4$ vs 60 cm^{-1} in $Br^- \cdot H_2O \cdot Ar_3$), indicating that a similar mechanism is at play in both systems. This doubling is characteristic of an accidental degeneracy between two unperturbed (zero order) states when only one such state carries oscillator strength from the common ground state. The splitting between these equal intensity peaks therefore provides a direct determination of the matrix element (H_{Fermi}) for this Fermi resonance interaction, yielding a value on the order of 30 cm^{-1}.

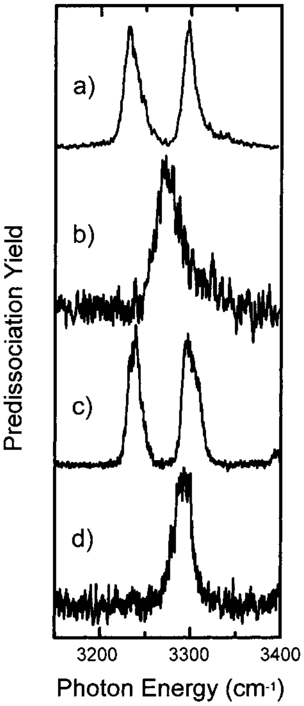

Figure 2. Isotopically labeled vibrational predissociation spectra of the $Cl^- \cdot CCl_4$ and Br^- monohydrates indicating the collapse of the doublet upon isotopic substitution: (a) $Cl^- \cdot H_2O \cdot CCl_4$, (b) $Cl^- \cdot HDO \cdot CCl_4$, (c) $Br^- \cdot H_2O \cdot Ar$,[8] and (d) $Br^- \cdot HDO \cdot Ar$.[8]

To challenge the Fermi resonant (diad) model for the doublet in the $Cl^- \cdot H_2O \cdot CCl_4$ and $Br^- \cdot H_2O \cdot Ar$ systems, we have also recorded spectra of the $Cl^- \cdot HDO \cdot CCl_4$ and $Br^- \cdot HDO \cdot Ar$[8] isotopic variations with the results displayed in Figure 2b and 2d, respectively. The collapse of the doublets upon isotopic substitution is readily explained by the two-state coupling model. In the asymmetric structure, the $Cl^- \cdot HDO$ moiety occurs in two isomeric forms according to whether the H or D atom is bound to the ion. Because the motion of the two hydrogen atoms is largely decoupled, the HDO form with the H attached to the ion displays its OH_{IHB} band very close to the position in the $X^- \cdot H_2O$ complex, whereas the frequency of the bending mode in HDO (1402 cm^{-1}) is significantly lower than that in H_2O (1595 cm^{-1}) and is not strongly shifted upon complex formation. This has the effect of lowering the $2 \leftarrow 0$ bending overtone

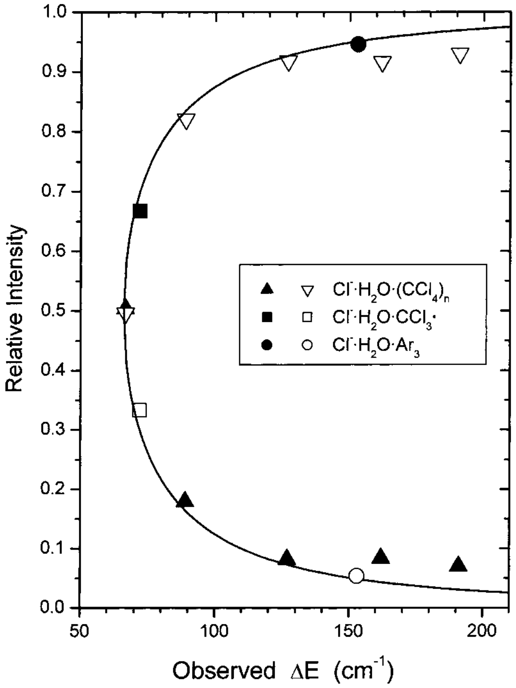

Figure 3. Relative intensities of the nominally IHB and bend overtone bands as a function of the observed splitting (ΔE) between them. Symbols denote the bands in $Cl^-{\cdot}H_2O{\cdot}Ar_3$ (circles), $Cl^-{\cdot}H_2O{\cdot}(CCl_4)_n$, $n = 1-5$ (triangles), and $Cl^-{\cdot}H_2O{\cdot}CCl_3{\cdot}$ (squares). Solid symbols refer to the band appearing at lower energy for a given species, while the hollow symbols refer to the companion band at higher energy. The branching ratio, calculated using eqs 4 and 5 with $H_{\text{Fermi}} = 33$ cm^{-1}, is displayed by the solid line.

transition and revealing the unperturbed location of the OH_{IHB} $v=1$ level in the HDO complexes.

Note that the HDO OH_{IHB} band does not appear exactly in the center of the H_2O IHB/B doublet since there is a small residual coupling between the OH/OD oscillators in both HDO and H_2O complexes. In HDO, this coupling would act to raise the level of the strongly red-shifted OH_{IHB} as its companion OD_{Free} level lies lower in energy, whereas the OH_{Free} lies above the OH_{IHB} in the H_2O isotopomer, and would act to lower the energy of the OH_{IHB} $v=1$ level.

IIIC. Analysis of the Fermi Resonance Interaction with a Two-State Model. In Figure 3, we explore how the relative intensities of the two coupled bands depend on their separation in the $Cl^-{\cdot}H_2O{\cdot}(CCl_4)_n$ series as well as the $Cl^-{\cdot}H_2O{\cdot}CCl_3{\cdot}$ ion−radical complex, which will be discussed in detail elsewhere. The data clearly fall on a universal curve, where the two bands occur with equal intensity as the splitting approaches 66 cm^{-1}. To understand the relative intensities of the diad displayed in Figure 3, we have constructed a simple model of the interaction using a fixed matrix element in a 2 × 2 deperturbation scheme. In the case where the transition moment to the bend overtone is much smaller than that to the IHB, the intensity branching can be traced to the coefficients describing the expansion of the observed states in an unperturbed basis consisting of the stretch (|IHB⟩) and the overtone of the bend (|B⟩) zero-order states

$$|1\rangle = c_1^{IHB}\,|IHB\rangle + c_1^{B}\,|B\rangle \tag{3a}$$

$$|2\rangle = c_2^{IHB}\,|IHB\rangle + c_2^{B}\,|B\rangle \tag{3b}$$

The expansion coefficients are given by

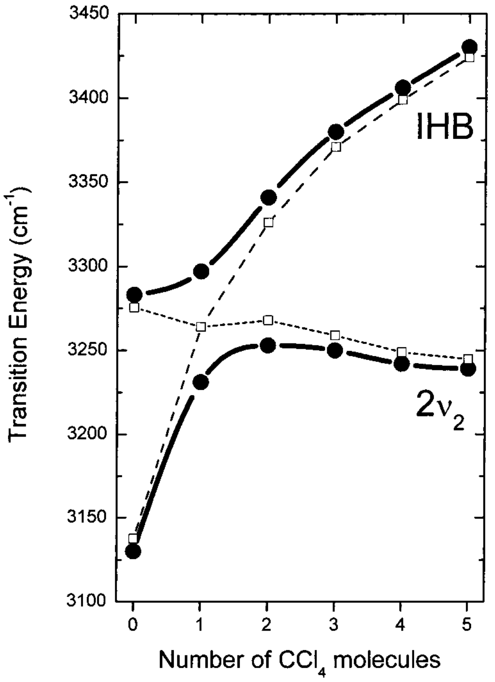

Figure 4. Observed band positions (●) and deperturbed band origins (□) for the coupled IHB and bend overtone ($2\nu_2$) transitions using $H_{\text{Fermi}} = 33$ cm^{-1}. The solvent effectively tunes the two levels through an avoided crossing at $n = 1$.

$$|c_1^{IHB}|^2 = \frac{\Delta_i^2}{\Delta_i^2 + H_{\text{Fermi}}^2} \tag{4}$$

where Δ_i denotes the shift displayed by a zero-order state in response to the interaction matrix element, H_{Fermi}, and is related to the observed separation between the states, $\Delta E = E_2 - E_1$, as follows

$$\Delta_i = \frac{\Delta E - \sqrt{\Delta E^2 - 4H_{\text{Fermi}}^2}}{2} \tag{5}$$

In this "bright state" model, the transition moment to the mixed state is partitioned according to $|c_i^{IHB}|^2$. The solid line in Figure 3 displays the calculated relative intensities with a constant matrix element of 33 cm^{-1}, clearly capturing the essential physics of the situation. This is important because it provides a general propensity rule for evaluating the behavior of the bend/stretch mixing in the $Cl^-{\cdot}H_2O$ subcluster when exposed to very different local environments.

The success of this simple model in recovering the intensity branching between the mixed states enables us to use the 2 × 2 deperturbation scheme to extract the unperturbed locations of the B and IHB levels with increasing CCl_4 solvation. These are displayed in Figure 4, where the squares connected by the dashed lines indicate the deperturbed level positions for the two modes. Interestingly, the IHB level is shifting smoothly toward higher energy upon solvation, whereas the bend overtone ($2\nu_2$) shows a smaller sequential shift in the *opposite* direction. This parallels the trend observed in the $X^-{\cdot}H_2O$ (X = Cl, Br, I) study[5] where the bending overtone also shifts to lower energy as the ion−water bond weakens (and the OH_{IHB} blue-shifts) in the series Cl→Br→I.

This effect, where the CCl_4 molecules "tune" the IHB and B levels through a Fermi resonance interaction, is a more dramatic example of the solvent-induced intramolecular coupling we reported earlier[25] in the $I^- \cdot HCOOH \cdot Ar_n$ ($n = 1-4$) series. In that case, argon solvation selectively red-shifts the OH_{IHB} and its combination bands with respect to a nearby C−H mode, again causing a solvent-dependent doubling of the dominant band.

IIID. Remarks on the Origin of the Shifts and Widths of the IHB Band Envelopes. The relative sharpness of the OH_{IHB} bands in the $Cl^- \cdot H_2O \cdot (CCl_4)_n$ clusters with increasing solvation is qualitatively different than the behavior recently reported[6] for the argon complexes of $Cl^- \cdot H_2O$ as well as the related $I^- \cdot ROH$ (ROH = MeOH, EtOH, *I*-PrOH) systems.[26] Some of this breadth is apparent in the spectrum of the $Cl^- \cdot H_2O \cdot Ar_3$ cluster shown in the top trace of Figure 1. The alcohols displayed a particularly clear pattern where the OH_{IHB} bands develop many distinct peaks, with the number of peaks initially growing in direct proportion to the number of attached argon atoms. For a given number of argon atoms, peaks associated with smaller argon clusters remain in the spectrum, whereas a new peak emerges with each additional argon atom, displaying a roughly additive red-shift based on earlier band positions. This behavior was interpreted in a model where many isomers were inferred to coexist in the ion ensemble and differ according to the proximity of the argon atom to the OH group. Some sites apparently yield a red-shift in the OH_{IHB} position while other, presumably more remote sites contribute a much smaller blue-shift. Thus, a particular peak within the mutliplet directly reflects the number of argons located in the red-shifting class of binding sites. With the behavior of the argon clusters in mind, the evolution of the OH_{IHB} band shapes in the $Cl^- \cdot H_2O \cdot (CCl_4)_n$ spectra is remarkable. The band blue-shifts by very large steps with each additional CCl_4 and yet remains sharp, with no trace of the features displayed by the smaller clusters at a given size.

To understand the qualitative trends displayed by the $Cl^- \cdot H_2O \cdot (CCl_4)_n$ clusters, it is useful to recall the recent work of Thompson and Hynes,[17] in which they concluded that OH_{IHB} shift in $Cl^- \cdot H_2O$ was about equally due to electrostatics and charge-transfer. The latter was traced to mixing between the ground state and the $HCl \cdot OH^-$ (diabatic) excited state. It is clear that both effects would lead to a blue-shift upon complexation with a highly polarizable solvent molecule. For example, a nearby CCl_4 molecule would act to lower the local electric field in vicinity of the water molecule and relax the OH_{IHB} back toward the unperturbed free OH. Similarly, a CCl_4 molecule attached to Cl^- would cause strong differential solvation of the charge-localized $Cl^- \cdot H_2O$ and $HCl \cdot OH^-$ diabatic states. The increased separation would then decrease the extent of charge-transfer at the ground state configuration, again leading to a blue-shift. What is puzzling about the observed spectra, however, is that both these effects should be strongly dependent on the position of the CCl_4 molecule relative to the water, and the $Cl^- \cdot H_2O \cdot CCl_4$ ensemble used in this study was not cooled with argon and therefore possessed modest internal excitation (~1500 cm^{-1}). The heterogeneous collection of instantaneous $H_2O-Cl^- -CCl_4$ angles in our ion ensemble would, by the above arguements, yield diffuse bands with widths at least on the order of the sequential solvation shift (as was observed in $Cl^- \cdot H_2O \cdot Ar_n$ and $I^- \cdot ROH \cdot Ar_n$ systems). We therefore seek an alternative explanation for the shift which would not necessarily lead to broadening upon modest internal excitation.

Aside from their relative polarizabilities, a major difference between Ar and CCl_4 is that the latter can accommodate some excess electron density via charge-transfer to the LUMO based on the network of low lying σ^* orbitals antibonding between carbon and chlorine. This binding motif is well-known in the "front side" complexes such as $Cl^- \cdot BrCH_3$, which are calculated to exist and involve considerable charge redistribution to the methyl halide.[27,28] Very recently, Hiraoka and co-workers have carried out calculations[23] on the $Cl^- \cdot (CCl_4)_n$ clusters and found that the single contact geometry is preferred (as opposed to binding in the pocket as in the $Cl^- \cdot CH_3Br$ Sn2 entrance channel complex). Moreover, these authors conclude that the $Cl^- \cdot (CCl_4)_n$ complexes are stabilized by considerable charge-transfer from Cl^- to the surrounding CCl_4 molecules. This was evidenced by elongation of the C−Cl bonds as the excess electron penetrates into the σ^*-based LUMO. In light of these findings, it is reasonable to expect this charge delocalization to affect the binding of a water molecule to the ion.

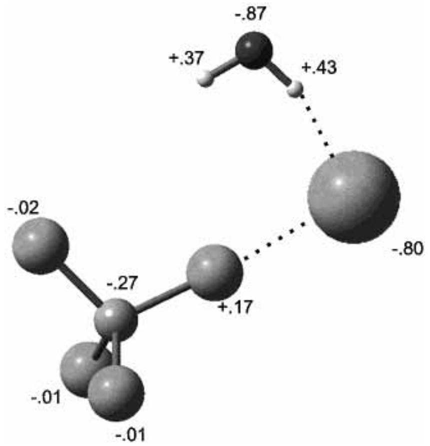

Figure 5. Geometry of the $Cl^- \cdot H_2O \cdot CCl_4$ cluster calculated at the MP2/Lanl2dz level together with the extracted Mulliken charges on the atoms.

To our knowledge, high level calculations have not yet been reported for the $Cl^- \cdot CCl_4 \cdot H_2O$ complexes, and so we have carried out preliminary electronic structure calculations at the modest MP2/Lanl2dz level[29] to explore the likely structure of the cluster and general aspects of intra-cluster charge-transfer. The resulting minimum energy structure is displayed in Figure 5, where the CCl_4 molecule is found to reside next to the water molecule, on the same side of the ion. This structure is interesting in light of the unusually strong OH_{Free} feature displayed by this complex in Figure 1 ($n = 1$). We note that the observed transition energy of this feature (3695 cm^{-1}) is not perturbed from the usual position of the free OH in the halide hydrates, however, so the mechanism of the intensity enhancement is not immediately obvious.

Also included in the structure shown in Figure 5 are the Mulliken charges extracted from the ab initio calculation. The charge on the water molecule is only -0.07 compared to -0.14 on the CCl_4 framework, indicating that the CT to carbon tetrachloride is dominating the CT to water. In this context, we suggest that the OH_{IHB} is relaxing back toward its position in the bare water molecule in response to a smaller excess charge density on the chloride. This amounts to a kind of competitive charge redistribution mechanism in which water accommodates some of the excess charge when it is the only solvent present, but this process is suppressed when the charge redistibution is more efficient to a third body, in this case CCl_4. This mechanism of charge delocalization depends primarily on the proximity of CCl_4 to the ion, but not as much on the relative separation between the H_2O and CCl_4, which would explain why the bands remain sharp even when these species are likely to be mobile under our experimental conditions.

The competitive charge redistribution scheme also provides a qualitative explanation for the additivity of the shift displayed in Figure 4 since, as pointed out earlier by Hiraoka et al.,[23] each additional CCl_4 molecule can continue to relieve some of the excess charge on the Cl^{-}. We also note that the ion−water stretching soft mode (IW in Figure 1) was observed to weaken upon addition of the first CCl_4 (from 210 to 188 cm^{-1}), as would be expected if the smaller charge density leads to a weakening of the ion−water bond.

IV. Summary

We have recorded the infrared predissociation spectra of the $Cl^{-}\cdot H_2O\cdot(CCl_4)_n$, $n = 0-5$, clusters which display a remarkable sequential blue-shift in the frequency of the ion-bound OH stretching mode upon solvation while remaining relatively sharp. The fact that this shift primarily involves the OH_{IHB} stretch leads to a situation where the OH_{IHB} $v = 1$ level is effectively "tuned" through a Fermi resonance interaction with the $v = 2$ level of the intramolecular bend. A simple 2×2 deperturbation analysis revealed a matrix element of 33 cm^{-1} for the interaction. We interpret the general behavior of this system in the context of charge redistribution within the cluster such that the CCl_4 molecules relieve some the excess charge on the Cl^{-} ion, which in turn weakens the ionic H-bond to the water molecule upon solvation.

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