Vibrational Predissociation of the HCl–(H₂O)₃ Tetramer

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ABSTRACT: The vibrational predissociation of the HCl–(H₂O)₃ tetramer, the largest HCl–(H₂O)ₙ cluster for which HCl is not predicted to be ionized, is reported. This work focuses on the predissociation pathway giving rise to H₂O + HCl–(H₂O)₂ following IR laser excitation of the H-bonded OH stretch fundamental. H₂O fragments are monitored state selectively by 2+1 resonance-enhanced multiphoton ionization (REMPI) combined with time-of-flight mass spectrometry (TOF-MS). Velocity map images of H₂O in selected rotational levels are used to determine translational energy distributions from which the internal energy distributions in the pair-correlated cofragments are derived. From the maximum translational energy release, the bond dissociation energy, D₀ = 2400 ± 100 cm⁻¹, is determined for the investigated channel. The energy distributions in the fragments are broad, encompassing the entire range of allowed states. The importance of cooperative (nonpairwise) interactions is discussed.

The interaction of HCl with water is of fundamental interest as a prototype of acid solvation. The ability of polar solvents to stabilize ions in solution is well-known; however, the energetics, dynamics, and mechanisms of this process have not been completely elucidated yet at the molecular level. Beyond fundamental interest, the solvation of HCl on polar stratospheric clouds creates an activated form of chlorine in the upper atmosphere that is expected to play an important role in the ozone depletion cycle. The study presented here describes the first results on the VP of the HCl–(H₂O)₃ tetramer, the largest cluster for which ionization of HCl is not expected. Theoretical studies conclude that the optimized geometry HCl–(H₂O)₃ is cyclic, as shown in Scheme 1, and the strength of the H-bonds is expected to decrease in the order α, β, γ, δ.

Following excitation of the H-bonded OH stretch fundamental, only two dissociation pathways are possible (Scheme 2): Pathways 1 and 2 yield HCl–(H₂O)₂ + H₂O and HCl + (H₂O)₃.

Scheme 1. Structure of HCl–(H₂O)₃ Tetramer

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Scheme 2. Energetically Allowed Pathways for Dissociation of HCl–(H₂O)₃

Figure 1. IR action spectrum (red) obtained by monitoring the H₂O photofragment in Jₖ,Kₖ = 3₂,1. The black line shows the background from H₂O monomers. The raw data are shown in lighter color, and bold lines show the data with three-point smoothing.

Figure 2. The 2 + 1 REMPI spectra of H₂O via the Ĉ ¹B₁(000) ← Ĥ ¹A₁(000) transition. (Top) The “IR On” spectrum (red) was obtained by exciting the H-bonded OH stretch of HCl–(H₂O)₃ at 3550 cm⁻¹ and the “IR Off” spectrum (black) by recording the background. The arrows mark the following Jₖ,Kₖ transitions: (a) 7₁,₇ ← 7₁,₆, (b) 2₀,₂ ← 3₂,₀, (c) 4₀,₁/₁₁,₄ ← 5₀,₅/₅₁,₅, and (d) 2₀,₁ ← 2₂₁. Assignments are based on the simulated spectrum (300 K) created in PGOPHER (bottom).

Figure 3 shows center-of-mass (c.m.) translational energy (Eₜ) distributions derived from the images. Conservation of energy respectively. By selectively monitoring H₂O fragments after VP, Pathway 1 was isolated for the present study, and the bond dissociation energy and distribution of energy in the products were determined.

Experimental results most relevant to the present study include: (1) the VP dynamics of the HCl–H₂O dimer, and (2) the observation of a large shift in the dipole moments of DCl–(H₂O)ₙ, between n = 5 and 6. This latest work indicates a change in the structure that is characteristic of acid solvation, but the observations are open to other interpretations as well. Other spectroscopic investigations address infrared signatures of the observations are open to other interpretations as well. Other spectroscopic investigations address infrared signatures of the structures of the HCl–(H₂O)ₙ.

Characterization of the fundamental OH stretch region was crucial for our studies as it allowed for tagging HCl–(H₂O)₃ while at the same time inducing dissociation. Zischang et al. have shown that based on experimental observations and ab initio calculations, several transitions are likely associated with the H-bonded OH stretch fundamentals of HCl–(H₂O)₃ in helium nanodroplets: 3560.1, 3546.8, 3476.2, and 3438.5 cm⁻¹. We have obtained IR action spectra in a supersonic molecular beam (helium carrier gas) in the range of 3520–3655 cm⁻¹ by monitoring state-selected H₂O fragments (Jₖ,a,Kₖ = 2₂,1, 3₂,1, 5₀,₅/₅₁,₅) by 2 + 1 REMPI. Our results show several peaks whose intensities vary with the HCl/H₂O ratio in the expansion. On the basis of our measured pressure and concentration dependencies of the action spectra and comparisons with previous spectroscopic work, we assign the intense broad peak observed at 3530–3555 cm⁻¹ to excitation of the H-bonded OH stretch fundamental of HCl–(H₂O)₃. This is most likely analogous to the 3546.8 cm⁻¹ peak observed in the helium droplet study [see the Supporting Information for a detailed discussion of the justification of our assignment and comparisons of our action spectra with previous results]. VP was induced by pulsed laser excitation in this band at 3550 cm⁻¹, which has minimum overlap with other HCl/H₂O mixed clusters and pure water clusters.

Figure 1 shows a representative spectrum obtained by detecting H₂O(Jₖ,a,Kₖ = 3₂,1) in the region of 3520–3560 cm⁻¹. Similar action spectra were observed by detecting HCl(J′) states, albeit with higher background from larger clusters and lower signal-to-noise ratio.

A photofragment yield spectrum was obtained by exciting HCl–(H₂O)₃ at 3550 cm⁻¹ and scanning the UV laser frequency in the region of the ĈB₃(000) ← X′A₁(000) H₂O transition. Figure 2 displays the 2 + 1 REMPI spectrum of H₂O fragments and the background spectrum of water monomers. Fast predissociation in the Ĉ state and spectral congestion limit the state-selective detection of H₂O. The highest isolated rotational state detected in our study was Jₖ,a,Kₖ = 7₁,₆ (704 cm⁻¹), which sets an upper limit to D₉ at approximately 2850 cm⁻¹ for Pathway 1. A more accurate value is obtained by Velocity Map Imaging (VMI). By careful selection of the UV wavelength, the action spectra were observed by detecting HCl(H₂O)₃ at 3560.1, 3546.8, 3476.2, and 3438.5 cm⁻¹.
can be used to determine the dissociation energy and the pair-correlated rovibrational fragment distributions in the form

\[ h\nu_{\text{IR}} + E_{\text{int}}(\text{HCl}-(\text{H}_2\text{O})_2) = D_0 + E_T + E_{\text{rot}}(\text{H}_2\text{O}) + E_{\text{vib,rot}}(\text{HCl}-(\text{H}_2\text{O})_2) \]

(1)

Here, \( h\nu_{\text{IR}} \) is the excitation energy of the H-bonded OH stretch of \( \text{HCl}-(\text{H}_2\text{O})_2 \), \( E_{\text{int}}(\text{HCl}-(\text{H}_2\text{O})_2) \) is the cluster’s internal energy, \( E_{\text{int}}(\text{H}_2\text{O}) \) is the energy of the monitored \( \text{H}_2\text{O}(J_{\text{rot}},K_{\text{rot}}) \) level, and \( E_{\text{vib,rot}}(\text{HCl}-(\text{H}_2\text{O})_2) \) is the rovibrational energy of the cofragment. The internal energy of the parent cluster was estimated from the rotational temperature of the \( \text{H}_2\text{O} \) monomers in the molecular beam to be 10 ± 5 cm\(^{-1}\). By monitoring a specific \( E_{\text{int}}(\text{H}_2\text{O}) \) level, the remaining energy \( (E_{\text{avail}}) \) must be distributed between the internal energy of the cofragment and \( E_T \).

\[ E_{\text{avail}} = h\nu_{\text{IR}} + E_{\text{int}}(\text{HCl}-(\text{H}_2\text{O})_2) - D_0 - E_{\text{rot}}(\text{H}_2\text{O}) \]

\[ = E_T + E_{\text{vib,rot}}(\text{HCl}-(\text{H}_2\text{O})_2) \]

(2)

Note that the energetically allowed internal states of \( \text{HCl}-(\text{H}_2\text{O})_2 \) are pair-correlated with the individual \( \text{H}_2\text{O}(J_{\text{rot}},K_{\text{rot}}) \) fragment being monitored. As expected, due to the large density of states of \( \text{HCl}-(\text{H}_2\text{O})_2 \), the \( E_T \) distributions are broad, encompassing all of the energetically allowed states, and do not display reproducible structures. At the end point of each image (indicated by the arrows in Figure 3), all of the excess energy is in \( E_T \). This allows the determination of \( D_0 \) for Pathway 1.

The maximum values of \( E_T \) determined from images of the three \( \text{H}_2\text{O}(J_{\text{rot}},K_{\text{rot}}) \) levels indicated in Figure 3 give \( D_0 = 2400 ± 100 \) cm\(^{-1}\). The uncertainty stems mainly from the inaccuracies inherent in using the maximum observed \( E_T \) to determine \( D_0 \) in the absence of reproducible peaks or features in the \( E_T \) distributions. Minor contributions to the error derive from uncertainties in \( E_{\text{av}}(\text{HCl}-(\text{H}_2\text{O})_2) \) and the calibration of the IR wavelength (see the Supporting Information).

Comparison with previous experimental work on the VP of \( \text{HCl}-(\text{H}_2\text{O})_2 \), \( \text{H}_2\text{O}_2 \), and \( \text{HCl} \) can add to our understanding of H-bonding and cooperativity in these mixed clusters. Assuming that none of the H-bonds in the cyclic tetramer have become weaker than the corresponding bonds in \( \text{H}_2\text{O}_2 \) and \( \text{HCl}-(\text{H}_2\text{O})_2 \), the weakest bond in the cluster should be \( \text{O}--\text{H} \cdots \text{Cl} \) (b). It is then reasonable that, as in \( \text{H}_2\text{O}_2 \) and \( \text{HCl} \), the quantum of the stretch vibration is transferred to the \( \text{HCl}-(\text{H}_2\text{O})_2 \) ring. VP proceeds by first breaking the \( \text{O}--\text{H} \cdots \text{Cl} \) H-bond, forming the chain isomer of the tetramer. In analogy with other cases of small H-bonded dimers and trimers, no barrier is expected in the VP. Subsequently, after further vibrational energy redistribution in the chain isomer, a second bond breaks, releasing \( \text{H}_2\text{O} \) in Pathway 1. The binding energy of the \( \text{O}--\text{H} \cdots \text{Cl} \) H-bond in the tetramer has not been determined but is expected to be much smaller than the other H-bonds. [It is probably between the values for the \( \text{H}_2\text{O} \) dimer (431 cm\(^{-1}\)) and \( \text{HCl} \) (1334 cm\(^{-1}\)).] Clearly, the sum of this bond energy and that of the \( \text{H}_2\text{O}--\text{H}_2\text{O} \) in the dimer (1105 ± 10 cm\(^{-1}\)) is smaller than the measured \( D_0 \) value for the mixed tetramer, indicating a significant contribution from cooperativity (nonpairwise interactions) to the bonding. In comparison, in the \( \text{H}_2\text{O}_3 \) and \( \text{HCl}_3 \) trimers, it was shown that ~19 and ~22%, respectively, of their \( D_0 \) values derive from nonpairwise interactions. Cooperativity is best evaluated by calculations that separate the contributions of two-, three-, and higher multibody interactions to the binding strength. However, it is generally accepted that interactions higher than three-body add only minor contributions to the binding, and therefore, it is reasonable that for small \( \text{HCl}/\text{H}_2\text{O} \) cyclic clusters cooperativity would contribute on the order of 20% to the binding strength. What we do not see so far, however, are any signs of incipient fragmentation, and the cluster seems to behave in a similar way to the trimers of water and HCl.

In summary, VP of the \( \text{HCl}-(\text{H}_2\text{O})_3 \) cluster to yield \( \text{H}_2\text{O} + \text{HCl}-(\text{H}_2\text{O})_2 \) fragments following excitation of the H-bonded OH stretch fundamental is reported for the first time. This cluster is not expected to lead to acid ionization, and indeed, both neutral \( \text{H}_2\text{O} \) and \( \text{HCl} \) products have been detected by REMPI following VP. VMI was used to determine \( D_0 = 2400 ± 100 \) cm\(^{-1}\) for the \( \text{H}_2\text{O} + \text{HCl}-(\text{H}_2\text{O})_2 \) pathway. The rotational energy distributions in the \( \text{H}_2\text{O} \) and \( \text{HCl}-(\text{H}_2\text{O})_2 \) fragments are broad and encompass all of the internal states allowed by energy conservation. Cooperativity contributions appear to be significant and of the same order of magnitude as those reported before in theoretical and experimental studies of the water and \( \text{HCl} \) trimers. Experiments to observe Pathway 2 are currently underway in our lab. Hopefully, the present results will lead to more theoretical work on the vibrational assignments and VP mechanisms of these mixed clusters.
METHODS

The experimental procedures are similar to those employed in previous work on smaller H-bonded clusters. The mixed HCl/H$_2$O clusters were formed in supersonic expansion through a 0.5 mm orifice of a pulsed valve (~150 μs opening time). The sample concentration and backing pressure were optimized for maximum signal of the HCl(H$_2$O)$_3$ tetramer at 0.6% H$_2$O and 2% HCl (99.995%) in ~2 atm of helium (99.999%). At these concentrations, signals from pure water clusters and from clusters with higher HCl/H$_2$O ratios were minimized (see the Supporting Information for details). The mixture was introduced into a high-vacuum chamber maintained at a base pressure of ~3.0 × 10$^{-8}$ Torr.

The skimmed molecular beam was intersected at right angles by two anticollinear laser beams. Focused IR laser radiation (OPO/OPA system, ~3.5 mJ/pulse; 20 cm lens, 0.4 cm$^{-1}$ bandwidth) was used to excite the OH stretch of the cluster, and focused UV radiation (0.1–0.4 mJ/pulse; 20 cm lens) was used to probe H$_2$O fragments. The IR frequency was calibrated using a simulated REMPI spectrum of H$_2$O. The velocity (m/s) of the detected H$_2$O$^+$ ions was calibrated using a simulated REMPI spectrum of H$_2$O.

Two modes of detection were used to collect data: (i) TOF-MS for spectroscopic investigations and (ii) VMI for $E_T$ distributions. In “IR On” signal was collected when firing the IR laser ~70 ns before the UV laser, whereas in “IR Off”, it was fired ~2 μs after the UV laser. The laser conditions (timing, focusing, power) were optimized to enhance the signal from HCl(H$_2$O)$_3$ while minimizing signals from other clusters.

The VMI arrangement has been described previously. It consists of a four-electrode ion acceleration assembly, a 60 cm field-free drift tube, and a microchannel (MCP) detector coupled to a phosphor screen that is monitored by a CCD camera. The two-dimensional projections were reconstructed using the BASEX method. The velocity (m/s) of the detected H$_2$O$^+$ fragments was proportional to 3.67 times the number of pixels on our detector.

Reducing the UV power eliminated signals from multiphoton UV processes, and background H$_2$O monomer signals were minimized by cryopumping with a coldfinger liquid nitrogen trap. Minimizing the IR-dependent background from higher clusters was crucial for our VMI results. Background images at 10 Hz.

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