Characterization of gas-phase HCl-H₂O clusters using pulsed infrared cavity ringdown spectroscopy

Alex J. Huneycutt^{*a}, Ross J. Stickland^b, Fredrik Hellberg^c, Richard J. Saykally^a

^aDept. of Chemistry, UC Berkeley; ^bCardiff University, Wales; ^cUniversity of Stockholm, Sweden

1. Abstract

Using the Berkeley medium-resolution pulsed cavity ringdown spectrometer we have observed the HCl stretch spectrum of the HCl-H₂O dimer and DCI stretch mode of the completely deuterated analog. The shifts from the free HCl stretch are consistent with theory and Ar matrix isolation work. Rotational structure was obtained for the deuterated cluster and spectroscopic constants for both chlorine isotopomers determined. Cluster number densities were determined to be slightly lower than found for the pure water dimer under similar conditions.

Keywords: Cavity Ringdown, CRLAS, acid clusters, HClH₂O

2. Introduction

The solvation of HCl is thought to play an important role in the generation of Cl₂ and HOCl in the atmosphere through heterogeneous reaction with ClONO₂ on the ice surface of polar stratospheric clouds (PSCs). These species are subsequently photolyzed to generate Cl atoms, which induce chain reactions that destroy ozone. The PSCs catalyze the otherwise slow formation of Cl₂ and HOCl¹. An accurate determination of the contribution of PSCs to the chlorine-ozone destruction cycle requires a detailed knowledge of the HCl-water interactions which leads to Cl₂ and HOCl production.

Previous IR absorption experiments have attempted to determine the degree of solvation and ionization of HCl deposited on thin films of ice at temperatures below 200 K at several acid-water ratios². These experiments used the HCl stretch as a probe to study local environment and relative concentrations of HCl adsorbed on ice films. Conclusive assignment of the undissociated HCl stretch proved difficult due to the proximity of the H₃O⁺ stretching mode frequency to that of the HCl stretching mode frequency of the HCl-H₂O, as determined by matrix isolation spectroscopy.

HCl molecules adsorbed on the ice surface may be expected to interact with more than one water molecule; the HCl stretching frequency is expected to shift significantly with different degrees of interaction³. The magnitude of the shifts can be estimated from those observed for HCl-(H₂O)_n, n < 5 clusters. Matrix isolation results and ab initio predictions for such clusters provide contradictory results for the HCl frequency shift when more than two water molecules are involved. Packer used Moller-Plesset theory to determine the shift for the one water adduct which within 5 cm⁻¹ the value observed in Ar matrices, whereas for the three water adduct the predicted shift was 346 cm⁻¹ lower than that determined from Ar matrix spectroscopy^{3,4}.

The predicted values of the stretching frequency are often hundreds of wavenumbers different from experimentally determined values. Most methods used assume harmonic potentials, whereas the real potential surface of weak hydrogen bonded complexes is significantly anharmonic. However, assuming that the degree of anharmonicity does not change significantly and the matrix perturbation is small, the predicted frequency shifts from HCl to HCl-(H₂O)_n should be consistent with the shifts observed in the matrix isolation studies. The lack of agreement between theory and experiment thus calls into question the assignments from the matrix isolation studies and complicates the assignment of spectral features to undissociated HCl in systems that mimic PSC conditions. Hence, obtaining accurate experimentally determined band frequencies of the clusters is important for assigning the HCl and ice spectra.

Unambiguous assignment is possible using rotationally resolved gas phase spectroscopy which eliminates not only assignment ambiguity but also matrix induced perturbations. We have used a pulsed infrared cavity ringdown spectrometer in conjunction with a pulsed slit-source molecular beam to characterize the HCl stretch of the HCl-H₂O and DCI-D₂O adducts in the gas phase for the first time. The deuterated adduct was rotationally resolved whereas the protonated adduct was not, given the current resolution of 0.04 cm⁻¹. The fundamental frequencies for the HCl stretch

mode of the protonated and deuterated adducts was determined along with the ground and excited vibrational state rotational constants for the deuterated adduct.

3. Experimental

The rotational-vibrational spectra of the HCl-H₂O adduct was obtained using the Berkeley Infrared Cavity Ringdown Spectrometer which has been described in detail elsewhere⁵. The cavity ringdown technique utilizes a cavity formed by high reflectivity mirrors ($R \sim 0.9999$) into which a light pulse is injected. The intensity of the light exiting the cavity is monitored using a LN₂-cooled InSb detector. The signal is amplified, digitized and averaged (20 shots/wavelength). It is then fit to a single first-order exponential decay. The cavity round trip time divided by the decay constant gives the total per-pass cavity losses as a function of wavelength. Tunable infrared radiation is generated by Raman shifting a Nd:YAG pumped dye laser. The dye laser output is focused into a 3.5 m multipass Herriot cell filled with 200 psi H₂ gas. The input light is Stokes shifted by the Stimulated Raman Scattering process to produce, after three sequential shifts, tunable infrared radiation throughout the mid-IR with a bandwidth of ~ 0.04 cm⁻¹.

The HCl-H₂O clusters were produced by bubbling helium through concentrated hydrochloric acid and expanding the vapor into a vacuum chamber using a 1.6" supersonic slit source. With a pulse rate of 50Hz, a He line pressure of 20 psi and a chamber pressure maintained at 200 mTorr, the source is known to produce clusters with 5-10 K rotational temperatures.

4. Results

HCl(H₂O)_n and (H₂O)_{n+1} clusters have similar structure and hydrogen bond strengths up to at least $n = 3$, after which dissociation of the acid into the ion pair is predicted to occur for the acid clusters^{3, 7}. The similar structures and hydrogen bond strengths of the acid and pure water clusters gives rise to similar vibrational modes. These features allow useful comparison between the pure water clusters and the less well characterized acid-water clusters. Similarities between pure water and acid clusters are apparent from the structures illustrated in Figure 1. In the dimer, HCl replaces the donor molecule of the pure H₂O cluster and results in a slightly stronger hydrogen bond than is present in (H₂O)₂ [Packer, 1995 #5]. Figure 2 gives the theoretical binding energies (D_e) for the clusters with $n = 0-3$.

Fig. 1: The structures of small water and acid clusters.

TABLE 1: Theoretical Binding Energies^a for (H₂O)_{n+1} and HCl(H₂O)_n, $n = 1-3$

	MP2/6-31g(2dp)	MP2/Poll ^b	B3LYP ^c	MP2/aug-cc-pVDZ ^d
(H ₂ O) ₂	19.16	18.08		18.4
HClH ₂ O	21.97	20.57	27.6	
(H ₂ O) ₃	59.5			58.2
HCl(H ₂ O) ₂	51.27	50.95	66.1	
(H ₂ O) ₄	102.88			101.7
HCl(H ₂ O) ₃	89.07		120.1	

^a D_e in kJ/mol for (H₂O)_{n+1} $\rightarrow$ H₂O + (H₂O)_n and HCl(H₂O)_n $\rightarrow$ HCl + (H₂O)_n.

^bref 3.

^cref 7.

^dref 6.

The binding energy (D_e) in the acid dimer is almost 14% greater than for the pure water dimer at the highest level of theory with which they are both treated, MP2/Poll. The difference in energy between the pure and acid water cluster is due to changes in strength for the H-Cl, O--H-Cl and O-H--Cl bonds. A substantial portion of this is because the Cl acceptor hydrogen bond in O-H--Cl is a much weaker interaction than the O acceptor O-H--O interaction. A comparison of the D_e values calculated at the MP2/6-31g(2dp) level is given in and Figure 2.

The change in strength of the HCl covalent bond can be followed readily by noting changes in bond length. With increasing solvation, the covalent HCl bond is substantially weakened by two effects. First, the interaction with the water to which it was hydrogen bonded in the dimer becomes stronger as that water also becomes a hydrogen bond donor to the additional water molecules. Second, the Cl electron density interacts with hydrogen atoms on the additional molecules (O-H--Cl), which shifts electron density away from its internal axis, weakening the covalent HCl bond. At the MP2/6-31g(2dp) level the HCl bond length increases from the isolated molecule by 1.3% upon forming the dimer, 2.5 % for the two water cluster and 4.1% for the three water cluster. By the addition of a fourth water, the dissociated ion pair becomes the most stable product according to theory^{3, 7}.

Experimentally the easiest way to monitor the effect of increasing cluster size is by analysis of the cluster size dependent spectral shifts of the vibrational modes. This has been carried out previously by our group for pure water clusters in the

intramolecular vibrational mode regions using cavity ringdown spectroscopy^{5, 8, 9}. A comparison of the theoretical predictions for intramolecular vibrations shows that the perturbation to the H_2O hydrogen bond acceptor internal modes is of similar magnitude for the acid and pure water dimers. The donor molecules are different in the acid and pure water clusters, but the H-bond acceptor modes are expected to be nearly identical between the clusters. Table 3 gives the theoretical predictions and experimental values for these modes. The CCVSF predicted acceptor symmetric and antisymmetric stretch modes for $(H_2O)_2$ are redshifted from the corresponding modes in isolated H_2O by 1.2% and 1.9% respectively whereas the acceptor bend mode is blueshifted by 1.1%¹⁰. The corresponding modes in $HClH_2O$ are shifted by -1.2%, -0.9% and 0.9% respectively where the negative indicates a redshift¹¹.

Fig. 2: Dissociation energy (D_e) in kJ mol^{-1} calculated using MP2/6-31g(2dp) level theory for the following processes, $HCl(H_2O)_n \rightarrow HCl + (H_2O)_n$ and $(H_2O)_{n+1} \rightarrow H_2O + (H_2O)_n$. From ref 3.

TABLE 2: Experimental and Theoretical Vibrational Frequencies (cm^{-1}) for select modes in $HCl(H_2O)_{0-3}$ and $(H_2O)_2$

method	HCl		HClH ₂ O			HCl• (H ₂ O) ₂	HCl• (H ₂ O) ₃	(H ₂ O) ₂		
	ν_{HCl}	ν_1^{a}	ν_2	ν_3	ν_{HCl}	ν_{HCl}	ν_{HCl}	ν_1	ν_2	ν_3
Gas phase ^b	2885				2723			3600	1601	3745
Ar matrix ^c		3629		3721	2659	2390	2500			
Ar matrix ^d		3631	1590		2664			3634	1594	
B3LYP ^e	2939				2626	2245	1740			
MP2/Poll ^f	2982	3791	1645	3918	2709	2394		3799	1648	3925
MP2/6-31g(2dp) ^f	3068	3839	1660	3971	2841	2615	2341	3844	1662	3975
CCVSF ^g	2949	3647	1561	3762	2709			3647	1564	3724

^a ν_1 is the accp sym OH stretch, ν_2 is the accept bend, ν_3 is the accept sym OH stretch.

^bThis work and ref 16.

^cref 4.

^dref 12.

^eref 7.

^fref 3.

[§]ref 10 and ref 11.

The similarities are useful in that the $(\text{H}_2\text{O})_{n+1}$ provides a good starting point for understanding and predicting properties for $\text{HCl}(\text{H}_2\text{O})_n$. On the other hand the pure clusters are present at much higher concentrations than HClH_2O in the molecular beam expansion. This means that the spectral bands from acid containing species might well be obscured by those from pure water clusters. This can be appreciated from the spectrum of the OH stretching region in a pure water expansion under typical operating conditions (see Figure 3). However, the acid clusters do have strong HCl stretch modes that lie well outside of the region of any pure H_2O cluster band. Predicted value of the HCl stretch frequency in these types of clusters is very dependent on the method of calculation as indicated in Table 2.

Fig. 3: H_2O cluster OH stretch spectrum. The solid line is the OH stretch spectrum of a pure H_2O expansion under typical operating conditions. Markers indicate the predicted location of the OH stretch bands in $\text{HCl}(\text{H}_2\text{O})_n$ clusters (ref 15).

Our work represents the first characterization of the gas phase vibrational spectra of a small acid-water cluster. We observed the HCl stretch mode of the HClH_2O cluster. The band is not rotationally resolved but does have a profile consistent with an A-type band of a near prolate rotor. The spectrum is given in Figure 4. The band origin at 2723 cm^{-1} is consistent with the theoretical predictions given in Table 2. The band origin obtained by Ar matrix techniques is redshifted from the gas phase value by 59 cm^{-1} .

Conformation that the band was carried by a single cluster, HClH_2O , as opposed to overlapping bands from different size clusters was achieved by varying the acid concentration in the molecular beam. The He carrier gas that passed through the acid bubbler was seeded through a needle valve into a pure He flow supplying the molecular beam source. The needle valve insured that the acid/water vapor partial pressure was maintained low enough that ice production in the molecular beam expansion was avoided. By changing the bubbler line pressure, the acid concentration in the molecular beam could be varied in a linear fashion.

If the peaks in an unresolved band change intensity at different rates with respect to concentration in the molecular beam, they are

Fig. 4: HClH_2O cluster HCl stretch spectrum. The simulated spectra correspond to the ^{35}Cl and ^{37}Cl isotopomers with a 3:1 intensity ratio. A temperature of 6 K was used and the isotopomer shift was estimated to be equal to that of free HCl, 2.1 cm^{-1} . Ground state spectroscopic constants are from ref 15.

likely due to different carriers. An analysis using intensity variation with concentration was used for spectral carrier cluster size determination in the OH stretching region for pure water clusters¹³. This technique was used for the HClH_2O spectra as well. Figure 5 gives the spectra with the bubbler line He gas pressure at 25, 30 and 35 psi. The triangles indicate the points whose intensity variation was graphed in Figure 6. The increase in intensity with acid vapor concentration is nearly linear at all the points. The intensity-versus-pressure slope in the linear concentration regime for the pure water dimer compared to the trimer at similar pressures shows that the trimer concentration increases 4.2 times faster than the dimer¹³. Excluding point 1, the largest ratio in slopes is 1.8 with all peaks falling within 30% of the mean. The weak shoulder at point 1 increases more slowly but is still within 2.5 times the slope of the fastest peak. This indicates that the different features of the band likely originate from clusters with the same concentration dependence which would not be expected for different size acid clusters.

Fig. 5: HClH_2O signal intensity as a function of $[\text{HCl}]$ and $[\text{H}_2\text{O}]$ in the molecular beam as controlled by acid-bubbler line backing pressure.

Fig. 6: Signal intensity as a function of bubbler line backing pressure for points indicated in figure 5. Slope for each point is given in ppm/psi.

Due to the proximity of this feature to that predicted for the HCl stretch of the dimer and the observed band assigned to it from Ar matrix work and the concentration variation work which indicates that the band has a single carrier, the assignment to the HCl stretch of the HClH_2O cluster appears correct. The band shape also appears consistent with what one would expect from an A-type transition in a prolate rotor like HClH_2O .

The microwave spectrum of a variety of isotopes of HClH_2O has been analyzed by Legon and coworkers^{14, 15}. The rotational spectra give accurate ground state spectroscopic constants for different isotopes of the dimer. A simulated spectrum given in Figure 4 was generated using these ground state constants and estimates for the upper state constants with a 6 K rotational temperature.

The estimated increase in upper state spectroscopic constants was based on upper and lower state differences in the rotationally resolved water dimer acceptor antisymmetric stretch spectrum¹⁶. The HCl stretch band was unresolved at a resolution of 0.04 cm^{-1} . Unlike the rotationally resolved water dimer antisymmetric stretch mode which couples relatively weakly with the hydrogen bond dissociative coordinate, the HCl stretch mode lies along the intermolecular axis. It couples very strongly to the dissociative mode giving rise to short-lived predissociative upper states and a lifetime broadened spectrum. The donor OH stretch spectrum in the pure water dimer which is analogous to the HCl stretch was not rotationally resolved with experimental resolution of $3 \times 10^{-4} \text{ cm}^{-1}$ ¹⁶. Incidentally, no other stretch mode exhibited sufficient rotational resolution for an accurate determination of upper state rotational constants for the water dimer. This is due to line broadening from decreased lifetimes of the excited state with increased coupling to the dissociative coordinate, the hydrogen bond. Thus, the water dimer acceptor antisymmetric stretch provided the best estimates for upper-state rotational constant decreases. They were chosen to be 0.2% smaller than the lower state constants for the simulated spectrum.

The two stick spectra in Figure 4 correspond to the HCl stretch for HClH_2O with two isotopes of Cl. The intensity difference reflects the 3:1 natural abundance ratio. The 2.1 cm^{-1} shift to lower frequency for the ^{37}Cl cluster reflects the shift of the HCl stretch for gas phase HCl molecules. Due to the presence of the additional water molecule

and the associated hydrogen-bond, the shift would be expected to be slightly less than that for the free HCl. Shifts only slightly smaller than those of free HCl were observed in HCl-DCI clusters by Schuder and Nesbitt¹⁷.

Since the HCl stretch mode lies along the internuclear axis and the HClH₂O cluster has an asymmetry parameter of <-0.999, the spectrum was simulated for an A-type transition in a prolate top. A rotational temperature of 6 K was used for the spectrum. 6-8 K is typical for temperatures obtained from rotationally resolved spectra under the present operating conditions.

The number density for these clusters can be calculated using ab initio estimates for the IR intensities. Chaban gives 625 km/mol for the intensity of the HCl stretch in the dimer¹¹. Integration of the band shown in Figure 4 gives a cluster density of $1.1 \times 10^{12} \text{ cm}^{-3}$. This value compares favorably with pure water dimer concentrations of $5 \times 10^{12} \text{ cm}^{-3}$ obtained under similar conditions¹³. Interestingly, the water trimer was observed to have slightly larger concentrations under typical experimental conditions, $7 \times 10^{12} \text{ cm}^{-3}$. The larger abundance of trimer species as well as an increased IR intensity should improve our chances of detecting HCl(H₂O)₂. As yet we have not observed this cluster.

Fig. 7: DCID₂O cluster DCl stretch spectrum. The upper trace is a typical low resolution spectrum (0.2 cm⁻¹); the lower trace is a high resolution spectrum (0.04 cm⁻¹). A rotational temperature of 6 K was determined from the from intensity variation in the high resolution spectrum. The band origins for the partially overlapping ³⁵Cl and ³⁷Cl isotopomers are 2.9 cm⁻¹ apart. This is nearly the value for the free DCl, 3.0 cm⁻¹.

In addition to the HCl stretch of the HClH₂O cluster, the deuterated analog has been observed. The DCl stretch of the DCID₂O cluster has been observed with rotational resolution at 1976 cm⁻¹. The spectrum is given in Figure 7. The upper trace is a low resolution (0.2 cm⁻¹) spectrum and the lower trace is a higher resolution (0.04 cm⁻¹) spectrum. The structure present in the low resolution spectrum of DCID₂O is absent in the low resolution HClH₂O spectrum (compare with figure 4). Unlike the DCID₂O spectra, the high resolution spectrum of HClH₂O did not reveal any resolvable features. This is similar to the H₂O cluster spectra of all modes in all clusters except the dimer acceptor symmetric and antisymmetric stretch and to a lesser extent the donor free stretch. The difference in upper state lifetimes is significant for D₂O as compared to H₂O dimers. In the D₂O system even the donor bonded OD stretch which is coupled most strongly to the dissociative mode has a rotationally resolved spectrum. This difference is attributed to the difference in upper state lifetimes deduced from the spectral linewidth for D₂O and an estimated linewidth of 0.2 cm⁻¹ for H₂O. This gives a predissociative lifetime of ~ 80 ps for the excited donor bonded OH stretch of (H₂O)₂ and about 40 times greater than that for the comparable mode in the deuterated cluster⁸. A similar effect is expected for the acid clusters.

The shift of the DCl stretch in DCID₂O from the isolated DCl is consistent with the shift observed for the protonated clusters. The hydrogen bonded D₂O shifts the stretch from 2091 cm⁻¹ to 1976 cm⁻¹, a redshift of 115 cm⁻¹. This is a much larger than the 39 cm⁻¹ shift from the ν_1 band in D₂O observed for the donor bonded stretch in (D₂O)₂. The HCl shift of the HClH₂O cluster is redshifted from the isolated HCl by 162 cm⁻¹ and the donor bonded OH stretch in (H₂O)₂ is shifted from the ν_1 mode of the monomer by 127 cm⁻¹.

Table 4 compares the band origins observed in Ar matrix work with the gas phase values of the pure water and acid dimer. The matrix effects are to redshift the bands with a greater shift observed for protonated species than deuterated species with the exception of the donor-bonded OH stretch of (H₂O)₂.

TABLE 4: Matrix isolation shifts of modes in small acid and pure water clusters and their constituent species.

	H ₂ O	D ₂ O	HCl	DCl	(H ₂ O) ₂	(D ₂ O) ₂	HClH ₂ O	DCID ₂ O
Method	ν_1	ν_1	ν_{HCl}	ν_{DCl}	$\nu_{\text{db}}^{\text{a}}$	$\nu_{\text{db}}^{\text{a}}$	ν_{HCl}	ν_{DCl}
Gas Phase ^b	3657	2671	2885	2091	3530	2632	2723	1976
Ar Matrix ^c	3639	2659		2075-8	3575	2615	2664	1930
Shift	18	12		13-16	-45	17	59	46

^a ν_{db} is the donor bonded stretch.

^bThis work and ref 16.

^cref 12 and ref 4.

The spectral shift of the two Cl isotope bands is consistent with the shift observed in the free DCl spectrum. The ³⁷Cl band is 2.9 cm⁻¹ to lower frequency than the ³⁵Cl band in the DCID₂O cluster. For free DCl the isotope shift is 3.0 cm⁻¹. This is consistent with the idea that the hydrogen bond weakly interacts with the DCl covalent bond with stronger interactions resulting in smaller shifts. In Figure 4 the isotope shift for the HClH₂O cluster was assumed to be equal to that of the free HCl (2.1 cm⁻¹), this seems valid given the deuterated cluster results.

Determination of the spectral constants for the DCID₂O spectrum was done by fitting the peak wavelengths in Figure 6 to a pseudodiatomic energy level expression

$$\nu = \nu_o + \bar{B}'J(J+1) - D'J^2(J+1)^2 - \bar{B}''J(J+1) + D''J^2(J+1)^2 \quad (1)$$

where $\bar{B} = (B + C)/2$. The ground state parameters were those determined from microwave spectroscopy¹⁵ and D' was fixed at the lower state value. Since only the P and unresolved Q branch of the ³⁷Cl isotopomer were seen, the upper state constants could not be determined from combination differences. The spectroscopic constants for D³⁵ClD₂O and D³⁷ClD₂O are equal to the ground state values of $\bar{B}' = 0.118$ and 0.116 cm⁻¹ respectively within the uncertainty of the measurement of peak position. With increased sensitivity or number density more precise values for the upper state constants can be determined.

The number density for the DCID₂O clusters was determined from the integrated band strength of the low resolution spectrum. Assuming that the IR intensity is the same as for the protonated cluster, the number density is 8.7×10^{11} cm⁻³. Although slightly lower, this value is consistent with that calculated for the HClH₂O cluster and can probably be improved sufficiently to obtain better values for upper state spectroscopic constants.

4. CONCLUSIONS

This work represents the first detection of the HClH₂O and DCID₂O clusters in the gas phase using vibrational spectroscopy. Although these values are consistent with those determined by matrix isolation spectroscopy, the unambiguous determination of band origins from gas phase measurement for the larger clusters is crucial for analysis of the ice and HCl spectra as well as improved understanding of the fundamental aspects of the solvation process for strong acids. We are currently attempting to detect the HCl stretch as well as the OH stretch modes of the larger acid clusters and the deuterated analogs. Given the increase in IR intensity with increasing cluster size and the larger number densities expected for the two and three water acid clusters based on results of our pure water spectra, detection of these clusters should be possible.

5. ACKNOWLEDGMENTS

This work was supported by the Air Force Office of Scientific Research and the National Science Foundation.

6. REFERENCES

1. M. J. Molina, T.-L. Tso, L. T. Molina and F. C.-Y. Wang, "Antarctic Stratospheric Chemistry of Chlorine Nitrate, Hydrogen Chloride, and Ice: Release of Active Chlorine", *Science*, **238**, 1253-1257, 1987
2. L. Delzeit, B. Rowland and J. P. Devlin, "Infrared Spectra of HCl Complexed/Ionized in Amorphous Hydrates and at Ice Surfaces in the 15-90K Range", *The Journal of Physical Chemistry*, **97**, 10312-10318, 1993
3. M. J. Packer and D. C. Clary, "Interaction of HCl with Water Clusters: (H₂O)_nHCl, n=1-3", *The Journal of Physical Chemistry*, **99**, 14323-14333, 1995
4. C. Amirand and D. Maillard, "Spectrum and Structure of Water-Rich Water-Hydracid Complexes from Matrix Isolation Spectroscopy: Evidence for Proton Transfer", *The Journal of Molecular Structure*, **176**, 181-201, 1988
5. J. B. Paul, R. A. Provencal and R. J. Saykally, "Characterization of the (D₂O)₂ Hydrogen-Bond-Acceptor Antisymmetric Stretch by IR Cavity Ringdown Laser Absorption Spectroscopy", *The Journal of Physical Chemistry A*, **102**, 3279-3283, 1998
6. S. S. Xantheas, "Ab initio studies of cyclic water clusters (H₂O)_n, n=1-6. III. Comparison of density functional with MP2 results", *The Journal of Chemical Physics*, **102**, 4505-4517, 1995
7. S. Re, Y. Osamura, Y. Suzuki and H. F. I. Schaefer, "Structures and stability of hydrated clusters of hydrogen chloride, HCl(H₂O)_n, n=1-5", *The Journal of Chemical Physics*, **109**, 973-977, 1998
8. J. B. Paul, R. A. Provencal, C. Chapo, A. Pettersson and R. J. Saykally, "Infrared Cavity Ringdown Spectroscopy of Water Clusters: O-D Stretching Bands", *The Journal of Chemical Physics*, **109**, 10201, 1998
9. J. B. Paul, R. A. Provencal, C. Chapo, K. Roth, R. Casaes and R. J. Saykally, "Infrared Cavity Ringdown Spectroscopy of the Water Cluster Bending Vibrations", *The Journal of Physical Chemistry A*, **103**, 2972-2974, 1999
10. G. M. Chaban, J. O. Jung and R. B. Gerber, "Anharmonic Vibrational Spectroscopy of Hydrogen-Bonded Systems Directly Computed from ab Initio Potential Surfaces: (H₂O)_n, n = 2, 3; Cl-(H₂O)_n, n = 1, 2; H⁺(H₂O)_n, n=1, 2; H₂O-CH₃OH", *The Journal of Physical Chemistry A*, **104**, 2772-2779, 2000
11. G. M. Chaban, R. B. Gerber and K. C. Janda, "Transition from Hydrogen Bonding to Ionization in (HCl)_n(NH₃)_n and (HCl)_n(H₂O)_n clusters: Consequences for Anharmonic Vibrational Spectroscopy", *The Journal of Physical Chemistry A*, **105**, 8323-8332, 2001
12. G. P. Ayers and A. D. E. Pullin, "The i.r. spectra of matrix isolated water species-II. The characterisation of non-rotating monomer water species in an argon matrix by xenon doping: the matrix isolated spectra of H₂O.HCl and (CH₃)₂O.H₂O as model compounds for water dimer spectra", *Spectrochimica Acta.*, **32**, 1641-1650, 1976
13. J. B. Paul, C. P. Collier, R. J. Saykally, J. J. Scherer and A. O'Keefe, "Direct Measurement of Water Cluster Concentrations by Infrared Cavity Ringdown Laser Absorption Spectroscopy", *The Journal of Physical Chemistry A*, **101**, 5211-5214, 1997
14. A. C. Legon and L. C. Willoughby, "Identification and Molecular Geometry of a Weakly Bound Dimer (H₂O, HCl) in the Gas Phase by Rotational Spectroscopy", *Chemical Physics Letters*, **95**, 449-452, 1983
15. Z. Kisiel, B. A. Pietrewicz, P. W. Fowler, A. C. Legon and E. Steiner, "Rotational Spectra of the Less Common Isotopomers, Electric Dipole Moment and the Double Minimum Inversion Potential for H₂O...HCl", *The Journal of Physical Chemistry, A*, **104**, 6970-6978, 2000
16. Z. S. Huang and R. E. Miller, "High-resolution near-infrared spectroscopy of water dimer", *The Journal of Chemical Physics*, **91**, 6613-6631, 1989
17. M. D. Schuder and D. J. Nesbitt, "High resolution near infrared spectroscopy of HCl-DCI and DCI-HCl: Relative binding energies, isomer interconversion rates, and mode specific vibrational predissociation", *The Journal of Chemical Physics*, **100**, 7250-7266, 1994