Infrared Spectrum of the Protonated Water Dimer in the Gas Phase

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The frequency-dependent gas-phase infrared multiple photon dissociation (IRMPD) spectrum for the proton-bound dimer of water is reported. The present spectrum is shown to be only in fair agreement with a spectrum reported in an earlier communication but is in agreement with spectra predicted by theoretical means. Two different possible assignments of the observed infrared bands are provided. The first is based on the harmonic oscillator approximation from density functional theory calculations, and a second is based on a quantum four-dimensional model calculation of anharmonic frequencies and intensities. Both calculated spectra agree fairly well, but the density functional calculation assignments are in better agreement. This is expected despite the anharmonic nature of the asymmetric stretch due to the flat potential energy surface associated with this mode.

The proton-bound dimer of water (Figure 1) and larger protonated water clusters are of considerable importance both because of the interest in proton mobility from a biochemical point of view as well as the interest in the strong hydrogen bonding that takes place in these clusters. A normal hydrogen bond is on the order of $10-20$ kJ mol^{-1}, whereas the proton-bound water dimer is bound by some 130 kJ mol^{-1}.[1] Many theoretical studies of protonated water clusters have been conducted in the past.[2-7] Experimentally, the vibration−rotation spectrum has been observed for $H_5O_2^+$ and $H_9O_4^+$ in the OH stretching region ($3550-3850$ cm^{-1}) using infrared multiple-photon dissociation spectroscopy (IRMPD).[8] Much more recently, the gas-phase vibrational spectrum of the proton-bound water dimer was measured by observing IRMPD in an ion trap using the free-electron laser for infrared experiments (FELIX) in The Netherlands.[9] The $H_5O_2^+$ ions were formed with an electrospray source and transferred to a linear radio frequency hexapole ion trap at 100 K where the ions were exposed to high intensity and tunable infrared light from the FEL and the dissociation products were monitored.

In the present work, we present an infrared spectrum for the proton-bound water dimer also determined by observing IRMPD using a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer (MICRA,[10] a mobile ion cyclotron resonance analyzer), coupled to the FEL in Orsay, France (CLIO). The FTICR is based on the use of a permanent magnet, which is an assembly composed of two Halbach[11] cylinders producing a nominal magnetic field of 1.25 T. The ICR cell presents an open geometry derived from a cubic cell ($20 \times 20 \times 20$ mm^3) where the excitation electrodes have been replaced by two
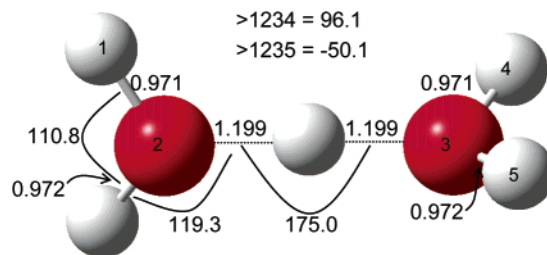

>1234 = 96.1
>1235 = -50.1

Figure 1. B3LYP/6-31+G** structure of the proton-bound water dimer.

tunnels made of four interconnected electrodes. Gases are introduced through the combination of a leak valve and followed by a pulsed three-way valve that directs the gas flow either to the mass spectrometer or to the pump of the gas inlet system.

The FEL at CLIO (Centre Laser Infrarouge d'Orsay),[12] a European facility in France, provides highly intense IR radiation from $3-120$ μm. This FEL consists of a linear accelerator followed by an ondulator placed in an optical cavity. For a given electron energy, which can be tuned from 10 to 50 MeV, a continuous scanning of the wavelength over a spectral range of $\Delta\lambda/\lambda = 2.5$ is obtained by scanning the ondulator gap. In the present study, the electron energy was 42 MeV, giving access to the wavenumber range from 700 to 1900 cm^{-1}. The IR laser wavelength was scanned by steps of $\sim$6 cm^{-1}, which is smaller than the laser bandwidth which is about $0.3-0.5\%$ of the spectral wavelength. The laser wavelength and its bandwidth are monitored with a monochromator associated with a spiricon. The FEL output consists of 8-μs macropulses at a frequency of 25 Hz. Each macropulse is composed of a train of 500 micropulses about 2 ps in duration. The mean IR power over the spectral domain used was $\sim$500 mW, corresponding to
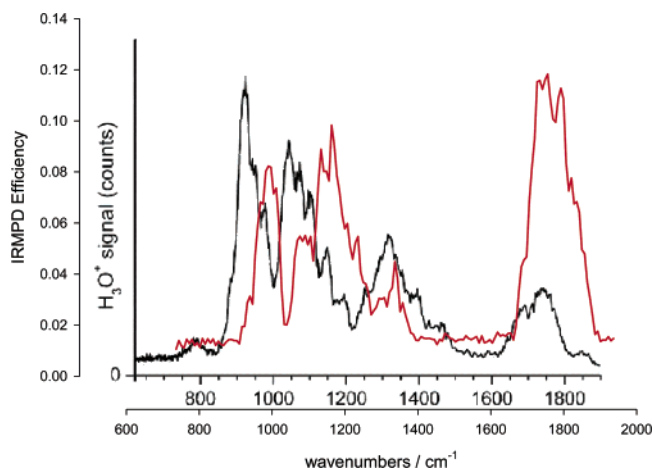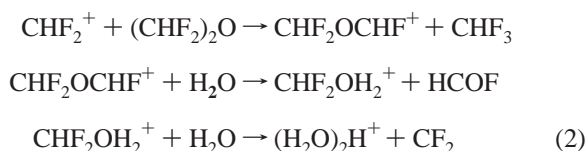
Figure 2. Comparison of the experimental infrared spectrum of $H_5O_2^+$ obtained in the present work (red) and that reported by Asmis et al. (ref 9, black).

Figure 3. Comparison of the experimental infrared spectrum of $H_5O_2^+$ with that predicted by B3LYP/6-31+G** calculations.

macropulses of 20 mJ and micropulses of 40 μJ. The infrared beam is focused on the middle of the FTICR cell with a 1-m focal length mirror. The laser beam dimension in the middle of the cell is smaller than the ion cloud (the beam waist diameter is close to 200 μm for a laser wavelength of 5 μm), but provided the irradiation time is long enough—1.5 s in the present experiments based on a reasonable efficiency of dissociation—all of the ions can interact with the laser beam. For each wavelength, the experimental sequence is repeated between one and eight times in order to average the mass spectrum. The IRMPD efficiency is defined as

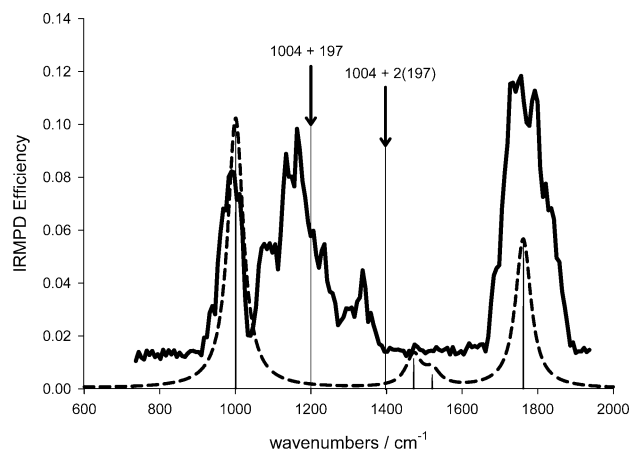$$-\log\left(\frac{I_{parent}}{I_{parent} + \sum_i I_{fragment(i)}}\right) \quad (1)$$

and is plotted as a function of the IR laser wavenumber to obtain the IRMPD spectrum of the parent ion.

Proton-bound water dimers were prepared by the method of Clair and McMahon[13] involving the bimolecular reaction sequence given in eq 2 occurring in gas-phase mixtures of $(CHF_2)_2O$ and H_2O.

$$CHF_2^+ + (CHF_2)_2O \rightarrow CHF_2OCHF^+ + CHF_3$$

$$CHF_2OCHF^+ + H_2O \rightarrow CHF_2OH_2^+ + HCOF$$

$$CHF_2OH_2^+ + H_2O \rightarrow (H_2O)_2H^+ + CF_2 \quad (2)$$

Sufficient collisions occur that it is expected that the proton-bound dimers are thermalized to room temperature (298 K), and indeed association equilibrium studies have been conducted using this method to produce proton-bound dimers.[14]

In Figure 2, a comparison of the present infrared spectrum (in red) with the spectrum of Asmis et al. (in black) is shown. In the Asmis et al. experiments, ions were mass selected and accumulated in a linear hexadecapole ion trap (100 K) and collisionally cooled with helium buffer gas prior to irradiation with the FEL. To construct their infrared spectrum, only the fragment ion H_3O^+ was monitored, whereas in the present experiments, both the fragment and parent ion are monitored simultaneously. Although there are four main features in both spectra, they are clearly quite different. The two low-frequency bands appear at higher frequency in the present spectrum compared to those in the spectrum of Asmis et al. The ions

stored in the ICR cell are approximately 200 K higher in temperature than that reported in the apparatus of Asmis et al. If the temperature were the source of the difference in the spectra, then it would be expected that broadening of the features would occur rather than a complete shift to some 70-cm^{-1} higher frequency. Another possibility for the disagreement is that there are isomers of $H_5O_2^+$, other than the proton-bound dimer, that are accessible at the higher temperatures of the present experiment. However, a search for other isomers was unsuccessful. At this point, we are unable to determine the source of the discrepancy between the present infrared spectrum and that obtained by Asmis et al. However, we do note that on the basis of both methods of assigning the experimental bands presented below the positions of the absorptions agree with the present spectra.

A first set of assignments may be arrived at on the basis of the harmonic oscillator model. Density functional optimizations and frequency calculations were performed at the B3LYP/6-31+G** level and basis set.[15] For most modes, the harmonic approximation can be used with scaling factors yielding satisfactory agreement with experimental frequencies. However, in the present case, the proton lies in a very broad potential, and it has been predicted that modes associated with the motion of this central proton will not be adequately described by the harmonic approximation. In Figure 3, a comparison of the present experimental spectrum with the predicted spectrum is presented. There is very good agreement between the bands centered at 990 and 1756 cm^{-1}, which are assigned to the O−H−O asymmetric stretch and the H_2O bend, respectively. There is not, however, a normal mode predicted to be centered at 1163 or 1337 cm^{-1} as observed in the experimental spectrum. There is a mode, though, predicted to occur at 197 cm^{-1} that is associated with the mutual rotation of the H_2O moieties about the O−O axis. This mode is a purely symmetric mode that can combine with the O−H−O asymmetric stretch. The two bands, then, at 1163 and 1337 cm^{-1} might be assigned to combination bands composed of one or two quanta, respectively, of the 197-cm^{-1} band and the O−H−O asymmetric stretch. It should be noted that in infrared spectra obtained by IRMPD it is not possible to compare intensities of bands with great confidence (as in absorption spectroscopy) because of the complex nature of the IRMPD process. Very strong combination bands for proton-bound dimers of rare gases[16] and halides[17] have been observed previously in rare-gas matrices and in the gas phase. It should also be noted that simple harmonic oscillator approximation calculations have been shown to provide very unsatisfactory agreement with matrix isolation data for the

TABLE 1: Comparison of Experimental and Theoretical Infrared Bands (cm^{-1})

experiment[a]	harmonic B3LYP/6-31+G**[a]		quantum 4D model[b]		Asmis et al. experiment[c]
	value	assignment	value	assignment	
	618	O−H−O$_{sym}$ str	587	O−H−O$_{sym}$ str	
990	1004	O−H−O$_{as}$ str	968	OHO$_x$ bend	921
			1026	OHO$_y$ bend	1043
1163	1201	O−H−O$_{as}$ str + H$_2$O rot	1158	O−H−O$_{as}$ str	1317
1337	1398	O−H−O$_{as}$ str + 2(H$_2$O rot)			
1756	1763	H$_2$O bend	1671	O−H−O$_{as+sym}$ str	
					1741[e]

a This work. *b* Reference 7. *c* Assignments based on the quantum 4D model.[9] *d* Not assigned in ref 9. *e* Asmis et al. assign this band to the H$_2$O bend.
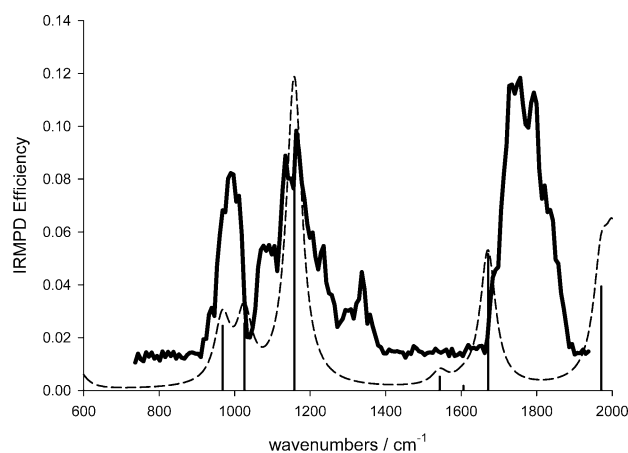
Figure 4. Comparison of the experimental infrared spectrum of H$_5$O$_2^+$ with that predicted by the quantum 4D model of Vener et al.[7]

asymmetric stretch of proton-bound dimers of rare gases isolated in rare-gas matrixes. However, it was suggested[18] and later verified[19] that the disagreement between the calculations and the experimental values for Ar$_2$H$^+$ could be due to the neglect of the rest of the rare-gas matrix, and the species observed is better described as a proton in a flattened octahedral hole (i.e., Ar$_6$H$^+$). Very good agreement has been observed for alcohol and ether proton-bound dimers and the B3LYP/6-31+G** calculations, which will be part of a forthcoming article.[20]

Another set of calculations for the infrared spectrum of H$_5$O$_2^+$ also deserves discussion. Vener et al. performed quantum 4D model calculations, and their predicted spectrum is compared to the present experimental spectrum in Figure 4. There is good agreement but only in the vicinity of the observed absorptions centered at 990 and 1163 cm^{-1}. These absorptions are assigned to the OHO bends, and the O−H−O asymmetric stretch, respectively (Table 1). There is also agreement, although less satisfactory, between the experimental band centered at 1756 cm^{-1} and the predicted one at 1671 cm^{-1}. This band, which is predicted to have reasonable intensity, was ignored by Asmis et al., and their band at 1741 cm^{-1} was assigned to the H$_2$O bend as predicted by the harmonic model. One problem with the assignments based on the quantum 4D calculations is that the band centered at 1337 cm^{-1} has no assignment but may be due to ignoring some of the low-frequency modes (below 500 cm^{-1}) in this model that may combine with the asymmetric stretch to produce combination bands.

In summary, there appears to be a discrepancy between the present infrared spectrum for the proton-bound water dimer and the spectrum acquired recently by Asmis et al. The CLIO spectrum can be adequately described by assignments based on the harmonic oscillator approach despite the caveats that have previously been proposed to be associated with harmonic frequencies. The quantum 4D model of Vener et al. can also

be used to describe the experimental spectrum, although with very different assignments of the modes. Only through comparisons of more experimental and theoretical spectra will insight be provided, thus resolving whether the harmonic oscillator approximation calculations are adequate or anharmonic calculations such as the quantum 4D model are necessary to describe these proton-bound dimers properly.

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