Probing the Vibrations of Shared, OH+O-Bound Protons in the Gas Phase

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Hydrogen bonding plays a crucial role in a wide range of important chemical and biological phenomena, from the solvent properties of water to the structures of proteins and DNA.[1] Hydrogen bonds are typically categorized by strength according to the separation between the heavy atoms that share the proton (r_{AB}). Long distances ($r_{AB} > 2.8$ Å) correspond to weak hydrogen bonds, where the proton is localized in one side of a double well potential. In the intermediate regime ($2.8 > r_{AB} > 2.5$ Å), the barrier between the wells is decreased so that it is comparable with the zero-point energy, and at the shortest distances ($r_{AB} < 2.5$ Å), the proton occupies a symmetric position between the heteroatoms in a single well potential.[2] Shorter, stronger hydrogen bonds falling in the latter two categories are involved in enzymatic catalysis[3] and are also important for proton transfer mechanisms, such as in biological "proton pumps"[4,5] and for proton exchange in acidic and basic aqueous solutions.[6]

Infrared spectroscopy has long been used as a tool for characterization of strong hydrogen bonds in condensed phases.[7–9] Until recently, it was not possible to obtain the corresponding gas-phase data by similar methods (that is, direct absorption), due to the inherent difficulties in getting sufficiently high ion densities. The advent of widely tunable, high fluence sources in the mid-infrared, such as free electron lasers (FELs) and optical parametric oscillators (OPOs), has allowed gas-phase ion spectroscopy of strongly bound ions via infrared

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multiple photon dissociation (IRMPD).[10–13] In a recent IRMPD study, Asmis and co-workers obtained the first spectra for the protonated water dimer ($H_5O_2^+$), the quintessential example of a strong hydrogen bond, in the region corresponding to direct excitation of the vibrational modes of the bound proton between 600 and 1900 cm^{-1}.[14] It was expected that the vibrational potential of the symmetric OHO moiety in $H_5O_2^+$ would be quite flat and anharmonic, making spectral predictions based on harmonic calculations unreliable.[15–17] However, even more sophisticated computational techniques failed to obtain agreement with the observed spectra, leaving the assignment of the experimental spectrum somewhat in doubt,[14,16–18] and making it clear that more experimental work is called for. In this work we report IRMPD spectra directly probing strong, OHO hydrogen bonds in other systems: the protonated dimers of dimethyl and diethyl ether [denoted ($Me_2O)_2H^+$ and ($Et_2O)_2H^+$], and protonated diglyme [1,1′-oxybis(2-methoxyethane)]. These spectra share an intriguing similarity with the $H_5O_2^+$ spectrum, suggesting that this type of OHO "proton bridge" may have a spectral signature in this region of the infrared. It should be noted that two of these systems [($Et_2O)_2H^+$[19] and protonated diglyme[20]] have been investigated previously using IRMPD, but those studies were limited to the region around 10 μm accessible to CO_2 lasers.

Shown in Figure 1a–c are the IRMPD spectra of the protonated methyl and ethyl ether dimers as well as of protonated diglyme. All of the spectra are qualitatively similar, although
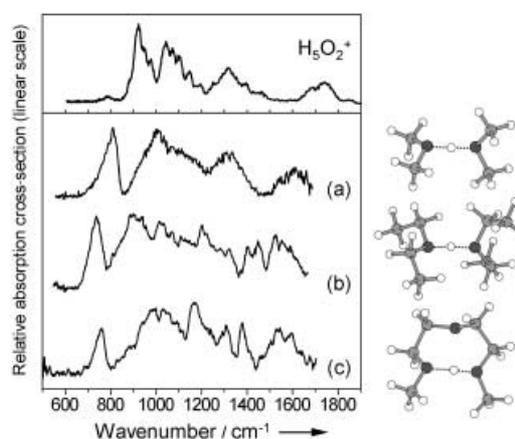

Figure 1. IRMPD spectra of gas-phase species with bridging protons, along with calculated structures (MP2/cc-pVDZ): a) ($Me_2O)_2H^+$ b) ($Et_2O)_2H^+$ c) protonated diglyme. The upper panel shows the IRMPD spectrum of protonated water dimer ($H_5O_2^+$) reproduced from raw data, provided to us by K. R. Asmis (ref. [14]).

the complexity clearly increases with the size of the systems, as expected. All three spectra show a well-separated peak at low frequency (700–850 cm^{-1}), as well as a strong band between 900–1000 cm^{-1}, and a weaker band around 1500–1600 cm^{-1}. The significance of these conserved spectral features can further be appreciated by comparison with the spectrum of $H_5O_2^+$,[21] shown in the upper panel of Figure 1. The similarity in the band-spacings and relative intensities is strik-

ing, particularly in comparison to the $(Me_2O)_2H^+$ spectrum. There is also an interesting trend in the spectra of the proton-bound dimers ($H_5O_2^+$, $(Me_2O)_2H^+$ and $(Et_2O)_2H^+$), where the main bands show an increasing red shift with increasing mass of the monomer units. The general similarity of the four spectra in Figure 1 suggests that a particular structural motif is common to all of these systems, and a natural candidate is the OHO proton bridge. It should be noted that, although the observed bands are broad, the ions are not internally hot, since they are resident in the trap for several seconds prior to photodissociation, which should give them ample time to cool via spontaneous emission.[22] Furthermore, the linewidths are comparable to those observed for the $H_5O_2^+$ experiment, for which the ion trap was cooled to 100 K.[14] Thus it seems likely that the observed broadening is caused by some dynamic effect, which is perhaps exacerbated by the IRMPD mechanism.[10]

Ab initio geometry optimizations and frequency calculations (MP2/cc-pVDZ)[23,24] were performed for these systems as well, producing the calculated structures shown adjacent to the spectra in Figure 1. The $(Me_2O)_2H^+$ and $(Et_2O)_2H^+$ structures are quite analogous to the $H_5O_2^+$ structure,[15] having symmetric OHO subunits [$r_{OH} = 1.193$ Å and 1.201 Å for $(Me_2O)_2H^+$ and $(Et_2O)_2H^+$, respectively]. The case of protonated diglyme is somewhat more complicated, since the lowest energy stable structure possesses a double well potential with an asymmetric OHO subunit (OH bond lengths of 1.312 and 1.119 Å). However, there is also a transition state[24] with a symmetric OHO moiety ($r_{OH} = 1.199$ Å) that is only ≈ 0.2 eV higher in energy, and this has important ramifications for the vibrational spectrum, as discussed below. In any case, even in the minimum, both of the OH bond lengths are significantly larger than expected for a proton–oxygen bond (≈ 0.95 Å), indicating that there is significant "sharing" of the proton between the O atoms. Finally, the O–O separation in all of these systems, including $H_5O_2^+$,[15] is ≈ 2.4 Å, placing them well within the strong, single well regime. Tables of frequencies covering all of the bound proton modes are available in the Supporting Information.

Normally, one would now just present the results of the frequency calculations to compare with the experimental spectra, however the aforementioned difficulties encountered with $H_5O_2^+$ make clear the potential problems that may be encountered with these proton-bound systems. Nonetheless, the only methods available to us for the larger systems considered here are harmonic frequencies from ab initio calculations, so we will present them, but use caution in their interpretation. Figure 2a and 2b show the results of the frequency calculations (unscaled) for $(Me_2O)_2H^+$ and $(Et_2O)_2H^+$. The calculated frequencies are indicated by the stick spectra, and the smooth curve shows a convolution of the calculated lines with a Gaussian shape. The agreement with the experiment is surprisingly good in both cases, and is certainly much better than for $H_5O_2^+$ using harmonic methods.[15] An examination of the calculated normal modes reveals that there is significant mixing of the OHO vibrations with those in the monomer units, but it is still possible to identify those that have strong OHO character. First, the two lowest frequency bands in both spectra
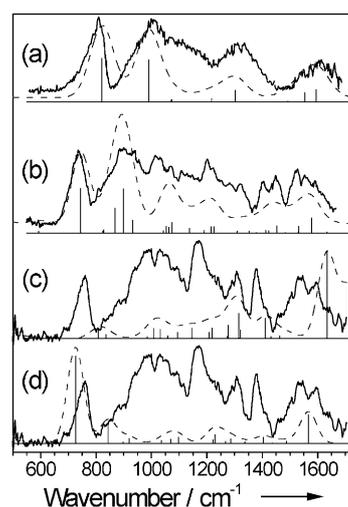

Figure 2. Comparison of experimental (——) and calculated spectra (-----) for a) $(Me_2O)_2H^+$, b) $(Et_2O)_2H^+$, c) lowest energy structure for protonated diglyme and d) symmetric transition-state structure for protonated diglyme. The stick spectra are the (unscaled) calculated frequencies and intensities, and the dashed lines were generated by convolution with Gaussian functions of widths (FWHM) of 90 cm^{-1} for $(Me_2O)_2H^+$ and 70 cm^{-1} for the other spectra.

(750–820 and 900–1100 cm^{-1}), which are also the most intense (up to 2000 km mol^{-1}), contain extensive asymmetric OHO stretching character, mixed with the symmetric CO stretching and HCO bending motions of the monomer units. The highest frequency bands (1500–1600 cm^{-1}) correspond to the OHO bending, this time mixed with the HCH bending motions. The strong bands in between these limits have more complicated descriptions, but still involve significant OHO motion coupled to other vibrations in the ether molecules.

As mentioned above, protonated diglyme is a somewhat more complicated system than the proton-bound ether dimers. Figure 2c and 2d show the spectra of the minimum and symmetric transition-state structures of protonated diglyme, respectively. Clearly, neither calculation gives a satisfactory match to the experiment, but the asymmetric OHO-stretching mode of the symmetric structure at 726 cm^{-1} does match quite well with the experiment, and may have particular significance, as discussed below. Since the symmetric structure is only 0.216 eV higher in energy, it may be accessible to the system at the experimental temperature of ≈ 300 K, in which case one would expect features of both structures to be reflected in the observed spectrum.

Now that we have obtained the harmonic normal modes, the question still remains of their relevance to the assignment of the experimental spectra. Some insight can be gained by analogy with the recent theoretical work on $H_5O_2^+$, which takes into account the anharmonic shifts and couplings between all 15 vibrational modes and is the most sophisticated treatment to-date.[18] There it was observed that the OHO asymmetric stretching mode was shifted only 27 cm^{-1} from the harmonic prediction, whereas the bending modes showed a more dramatic effect, shifting by ≈ 120 cm^{-1}.[18] Based on this result, one might expect the harmonic prediction of the

asymmetric stretches for the current proton-bound systems to be accurate as well, in which case there is a consistent trend in all of the spectra that the lowest frequency bands correspond to the OHO asymmetric stretch. Of course, this assignment is only tentative and preliminary, since the mode coupling in the ether systems is undoubtedly quite different than for $H_5O_2^+$. The question of mode coupling also complicates the interpretation of the aforementioned mass-dependent red shifts of the dimer systems; we simply note here that this shift appears to be more pronounced for the lines we have tentatively assigned to the modes of the bound proton.

Given the similarity between the spectra presented here and the $H_5O_2^+$ spectra, it seems clear that there may be a gas-phase "spectroscopic signature" of a proton involved in a strong hydrogen bond between two equivalent oxygen atoms. The fact that there are features conserved between the spectra of $H_5O_2^+$ and protonated diglyme, which contains an intramolecular bound proton, speaks to the robustness of this putative "signature". Future experiments are planned to study similar systems, for example, protonated dimers of ketones, alcohols, carboxylic acids, in order to further test this hypothesis. This work also opens possibilities for a vast array of related experiments, including examining systems with heterogeneously bound protons (for example, O—H$^+$—N), deuteration effects, and larger, biologically relevant species. One aspect of the current results that is particularly encouraging for potential application of this technique to complex biological systems is the large intensities associated with the OHO modes, which will help them stand out against a background that will almost certainly be quite congested.

Experimental Section

The experimental apparatus is one of a new breed of spectrometer combining tunable, high fluence IR sources for IRMPD with the versatility of Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) for creation and manipulation of gas-phase ions.[25,26] The details of the experimental apparatus will be presented in a future publication.[27] Briefly, the FT-ICR setup consists of a 4.7 Tesla superconducting magnet (Cryomagnetics) and a home-built ICR cell and vacuum system, controlled by a PC using the MIDAS hardware/software interface (NHFML).[28] The infrared light is provided by the free electron laser for infrared experiments (FELIX),[29] and the laser is coupled through a zinc selenide window, making two passes through the center of the ICR cell using weakly focusing (f = 50 cm) copper mirrors.

Gaseous methyl ether (99.5%) and the ambient vapor over liquid samples of ethyl ether (99+ %) and diglyme (99+ %) were introduced into the vacuum chamber via a leak valve. All chemicals were purchased from Sigma-Aldrich and used without further purification, except for a freeze-pump-thaw cycle on the liquid samples to remove dissolved gases. Gas-phase species ($\approx 10^{-7}$ torr) are ionized in situ inside the ICR trap by electron impact (30–70 eV). The species of interest are formed by ion–molecule reactions with background gas during a reaction period of 3–5 s, and then isolated by ejecting undesired species from the ICR cell using a stored waveform inverse Fourier transform (SWIFT) pulse.[30] Immediately thereafter, the parent species are irradiated with pulses from FELIX, and a standard FTICR excitation/detection scheme is done to de-termine the extent of photofragmentation. The IRMPD spectra are generated by plotting the ratio of the fragment to total ion (fragment + parent) peak height as a function of the wavelength of FELIX. The photofragment channels for $(Me_2O)_2H^+$ and $(Et_2O)_2H^+$ were $m/z = 47$ and 75, corresponding to the protonated monomers (Me_2OH^+ and Et_2OH^+), respectively. The photofragment channel for protonated diglyme was $m/z = 103$, corresponding to loss of methanol. A linear correction was also applied to account for power variations in FELIX (see ref. [11]).

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