INFRARED MULTIPHOTON DISSOCIATION SPECTRA OF PROTON-BRIDGED CATIONIC SPECIES

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Here we demonstrate the application of the FTICR/IRMPD technique (described in the previous talk) on the spectroscopy of some organic molecules containing a proton bound between two oxygen atoms. There has been considerable interest in this type of system concerning the question of whether the proton is shared equally between the oxygen atoms, or covalently bound to one and hydrogen-bonded to the other. Our results provide experimental evidence supporting the case for a shared or "bridging" proton.

IRMPD spectra are presented for 3 proton-bridged species: protonated methyl ether dimer $(C_2H_6O)_2H^+$, protonated ethyl ether dimer $(C_4H_{10}O)_2H^+$, and protonated diglyme $C_6H_{14}O_3H^+$, which has an intramolecular proton bridge. The spectra are qualitatively similar, showing several strong absorptions between 6 and 13 $\mu$m. Geometries and vibrational frequencies calculated at the B3LYP/aug-cc-VDZ level are also presented. In all cases, the calculations show that the proton prefers a "bridging" position between two oxygen atoms. In the methyl ether dimer, the proton is in a truly symmetric location, with both $OH^+$ bond lengths equal at 1.25 $\AA$. The calculated vibrational frequencies agree quite well with the experimental spectra, confirming our assignment of these spectra to proton-bridged species.

Analysis of the vibrational modes shows that two strong bands appearing around 750 $\mathrm{cm}^{-1}$and 1000 $\mathrm{cm}^{-1}$contain significant $OH^+$ stretching character of the bound proton. This motion is strongly coupled to the heavy atom motion in the molecules, which explains the dramatic redshift from the region around 3000 $\mathrm{cm}^{-1}$, where an OH stretching mode would typically be expected to appear. In fact, comparable calculations for species where the proton is bound to a single oxygen atom show strong bands *only* near 3000 $\mathrm{cm}^{-1}$, and *not* in the region where the experimental spectra are observed. This further supports the conclusion that the observed spectra arise from species with a "proton-bridge" between the oxygen atoms.