THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2005, *109,* 1487−1490
Published on Web 02/08/2005

Fundamental Excitations of the Shared Proton in the $H_3O_2^-$ and $H_5O_2^+$ Complexes

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Received: December 22, 2004; In Final Form: January 21, 2005

We exploit recent advances in argon predissociation spectroscopy to record the spectroscopic signature of the shared proton oscillations in the $H_3O_2^-$ system and compare the resulting spectrum with that of the $H_5O_2^+$ ion taken under similar conditions. Very intense $1 \leftarrow 0$ transitions are observed below 1100 cm^{-1} in both cases and are surprisingly sharp, with the 697 cm^{-1} transition in $H_3O_2^-$ being among the lowest in energy of any shared proton system measured to date. The assignments of the three fundamental transitions associated with the three-dimensional confinement of the shared proton in $H_3O_2^-$ are carried out with full-dimensional (DMC) calculations to treat this strongly anharmonic vibrational problem.

Understanding the essential molecular physics responsible for the anomalously high mobility of protons in water is an important challenge for contemporary aqueous chemistry.[1−8] Water-mediated “proton wires,” for example, are routinely invoked to explain charge transport across cell membranes and the primary charge-separation step in photosynthesis.[9−11] The elementary proton-transfer event is thought[2,8] to be driven by fluctuations in the liquid that lead to a transient contraction of the inter-oxygen distance. This contraction, in turn, causes the H-bond between a water molecule and the charge defect to evolve into a three-center, two-electron covalent bond. Of the two fundamental structures involved in the proton-transfer process (i.e., the isolated $H_3O_2^-$ and $H_5O_2^+$ ions), the anionic $H_3O_2^-$ complex is especially interesting because it involves a strong low-barrier hydrogen bond (LBHB) − a phenomenon often introduced to explain the surprisingly high rates of some enzyme-catalyzed reactions.[12−14] In this letter, we explore the quantum nature of the shared proton in a spectroscopic comparison of the elementary systems $H_3O_2^-$ and $H_5O_2^+$.

Because of their central role in aqueous charge transport, the $H_3O_2^-$ and $H_5O_2^+$ ions have been extensively investigated with electronic structure theory,[15−22] and both display stable configurations where one hydrogen atom resides between the two oxygen atoms (e.g., $[H_2O\cdots H\cdots OH_2]^+$ and $[HO\cdots H\cdots OH]^-$). Experimental evidence for this arrangement has been provided by analysis of the pattern of high energy OH stretching vibrations associated with the spectator OH groups.[23,24,28] To explore how the quantum nature of these proton-bound systems affects their properties at finite temperature, Parrinello and co-workers[2] carried out path integral calculations that explicitly included quantum effects. They found that the bridging proton in $H_5O_2^+$ behaves in a classical manner, in the sense that the quantum-averaged structure appears similar to that anticipated from thermal fluctuations of the atoms moving classically in the molecular force field. The $H_3O_2^-$ system, on the other hand, represents a more interesting case in that it is predicted to be dominated by quantum zero-point motion, even at room temperature.[2] Our goal in this work is to identify the fundamental transition associated with oscillation of the shared proton along the H-bond axis of the $H_3O_2^-$ ion. The character and breadth of the bands derived from this elementary excitation are of particular interest, as these features encode the extent to which the shared proton motion couples to the overall molecular framework.

The calculated structure of the $H_3O_2^-$ ion is indicated in Figure 1. Note that this asymmetric arrangement involves a single ionic H-bond between the hydroxide ion and the water molecule, an extreme variation of the binding motif observed previously in many $X^-\cdot H_2O$ complexes.[25] Also shown (Figure 1) is a potential energy curve[21] describing the displacement of the shared proton with the oxygen atoms fixed at their separation in the global minimum structure. The barrier in the resulting double minimum surface is approximately 130 cm^{-1} (0.016 eV).

In the usual treatment of strong H-bonds,[26] three transitions appear in the low energy (<1500 cm^{-1}) region of the infrared spectrum, where two of these are associated mostly with displacement of the hydrogen atom perpendicular to the H-bond axis (denoted $BH_\perp$) while one intense band arises from oscillation along the H-bonding axis, denoted $BH_\parallel$. Of course, the infrared spectroscopic signatures of such $O\cdots H^+\cdots O$ systems have been studied for decades in condensed media, and the resulting broad, intense low-frequency features are often assigned to motions of the shared proton (i.e., “*D*” bands”).[26] We

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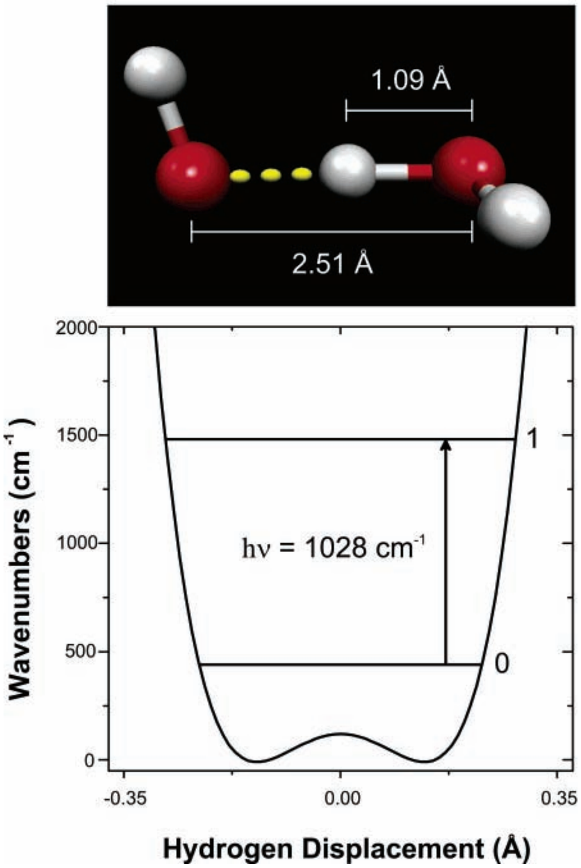

Figure 1. (TOP) Calculated structure (MP2/aug-cc-pVDZ) of the $H_3O_2^-$ complex showing the asymmetric, single ionic H-bonded motif. (BOTTOM) Potential energy surface governing the motion of the shared proton between the fixed oxygen atoms previously calculated by Samson and Klopper [ref 21]. The vibrational levels were obtained by numerically solving the one-dimensional Schrodinger equation, which leads to the predicted shared proton fundamental of 1028 cm^{-1}.

are interested in identifying the intrinsic location of this intense $BH_{||}$ band in the spectrum of isolated $H_3O_2^-$.

Calculations of the vibrational levels associated with the motion of the shared proton in $H_3O_2^-$ have yielded widely varying results. Early estimates of its $BH_{||}$ transition energy were provided by the harmonic frequencies at the global minimum,[19,20,27] which pointed to values in the 1400−1600 cm^{-1} range depending on the level of theory. Later, Klopper[21] carried out a numerical integration of the one-dimensional Schrodinger equation for the potential (Figure 1) and arrived at a much lower value of 1028 cm^{-1}. Both methods indicate that this complex displays a much larger red-shift than any previously studied $X^-{\cdot}H_2O$ cluster, consistent with the high basicity of the hydroxide ion.[25] Interestingly, the solution to the one-dimensional potential places the zero-point level above the barrier as indicated in Figure 1.[21] It is important to recognize, however, that this elementary treatment only allows for the motion of a single particle, while it is clear that the two spectator hydrogen atoms in fact adiabatically track the displacement of the shared proton.[16] As a result, the multidimensional nature of this small system presents a surprisingly difficult theoretical challenge at the very limit of current theoretical methods.

On the experimental side, Price et al. reported the $H_3O_2^-$ vibrational spectrum in the OH stretching region[24] and found a single sharp feature at 3653 cm^{-1}, lying between that associated with the bare hydroxide ion (3555 cm^{-1})[29] and the usual location (∼3700 cm^{-1}) of a nonbonded OH stretch. This demonstrated that the complex was effectively symmetrical with respect to the OH groups, which was rationalized in the context of the expected vibrational averaging due to the high amplitude zero-point motion of the shared proton. Two weaker transitions at 3100 and 3380 cm^{-1} were tentatively assigned to the $2 \leftarrow 0$ overtone transition of the $BH_{||}$ mode, which was calculated[19] to be heavily mixed with the intramolecular bending mode in the harmonic frequency calculations. Subsequently, however, Bowman and co-workers[16] treated the anharmonic vibrational problem using sophisticated vibrational self-consistent field (VSCF) methods and concluded that the shared proton oscillation would occur even lower in energy than anticipated by the earlier estimates and would be strongly coupled to the internal rotation of the spectator OH groups. This approach placed the $BH_{||}$ value in the 820−860 cm^{-1} range, casting doubt on the overtone assignments in the high-energy spectra. Further complicating the situation, McCoy and Bowman have very recently revisited these VSCF calculations and concluded that the $BH_{||}$ fundamental may in fact occur as low as 650 cm^{-1}.[30] For comparison, the reaction path version of Multimode yields a value of 741 cm^{-1} on the same surface.[31]

Despite the substantial theoretical uncertainty over its exact location, there is general agreement that the $BH_{||}$ fundamental in $H_3O_2^-$ should be readily identified as one of the most intense transitions ever recorded in the 600−900 cm^{-1} range. While large scale free electron lasers (FEL) have traditionally been the only intense sources of such low energy photons, very recent advances in nonlinear mixing technology[32] now allow access to this region with much more modest instrumentation, albeit with much lower power. Moreover, the tabletop laser systems are readily interfaced with argon predissociation spectroscopy, which requires much less power than the multiphoton dissociation approach adopted in the FEL studies.

Spectra were obtained using the Yale double focusing, tandem time-of-flight photodissociation spectrometer described in detail elsewhere.[33] Infrared absorptions were detected using the "messenger" method,[34,35] where a weakly bound rare gas atom is attached to the ion of interest and then isolated for interaction with the laser using a mass spectrometer. Photon absorption is monitored by mass loss upon argon evaporation. Laser excitation in the energy range 600−1900 cm^{-1} was provided through three stages of parametric conversion using a Laser Vision KTP/KTA/$AgGaSe_2$ optical parametric oscillator/amplifier. This study is essentially a tabletop variation of a similar argon predissociation study of the $BrHBr^-$ anion recently carried out using a large-scale free electron laser.[36]

Figure 2 compares the $H_3O_2^-{\cdot}Ar$ and $H_5O_2^+{\cdot}Ar$ predissociation spectra in the 600−1900 cm^{-1} region. The most intense bands in the $H_5O_2^+{\cdot}Ar$ spectrum at 1085 and 1770 cm^{-1} have been recently reported[37] and assigned to the $BH_{||}$ fundamental and the asymmetric superposition of the intramolecular bends on the two flanking water molecules, respectively. The higher energy band is broader, and the bond displacements associated with this vibrational assignment indicate that the bends are strongly correlated with the motion of the shared proton. The spectrum in Figure 2A extends the scan range over that reported earlier down to 600 cm^{-1} and reveals weaker vibrational structure in the 900−1000 cm^{-1} range. Most important for this work, there are no additional, intense low energy bands, and the strong transitions observed earlier are therefore definitively assigned to $BH_{||}$ activity in the $H_5O_2^+$ system. The lower energy bands labeled α in Figure 2A are strongly dependent upon the number of attached argon atoms, and their origin is not clear at this time.

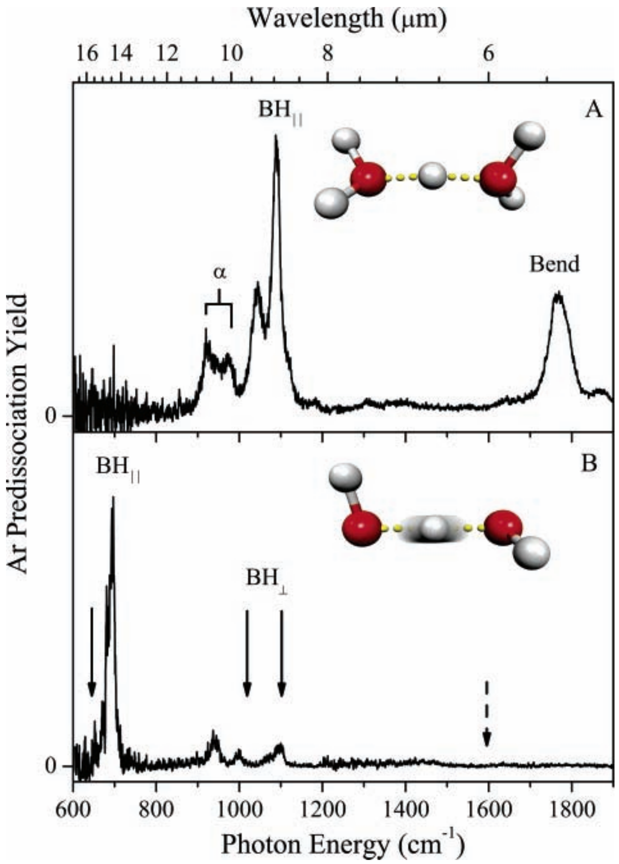

Figure 2. Argon predissociation spectra of the (A) $H_5O_2^+$ and (B) $H_3O_2^-$ complexes in the 600−1900 cm^{-1} (16.7−5.3 μm) region. The narrow, intense features denoted $BH_{||}$ in each spectrum correspond to the fundamental transition (1 ← 0) of the shared proton parallel to the H-bond axis. The broad sub-structure labeled α in (A) has been determined to be largely argon dependent (see text), while the more intense feature denoted Bend corresponds to a combination band involving excitation of the terminal water bends and the shared proton motion. In (B), the less intense features labeled $BH_\perp$ largely correspond to motion of the shared proton perpendicular to the H-bond axis. The solid arrows indicate the predicted locations of the parallel and perpendicular transitions for the bridging hydrogen obtained using full dimensionality calculations (DMC) as described in the text. The dashed arrow in (B) marks the fundamental for the bending mode (ν_2) of the isolated water monomer [ref 40].

The $H_3O_2^-\cdot Ar$ spectrum is presented in Figure 2B, and it is dominated by a very strong band at 697 cm^{-1}, far below the bands displayed by the cationic system. To put the intensity of the 697 cm^{-1} feature in context, this band exhibits a transition moment that is approximately 1000 times larger than that associated with excitation of the free OH stretches in this complex. Consequently, it is very likely that this feature arises from the $BH_{||}$ fundamental, and it is indeed quite close to the 645 cm^{-1} value we obtain using fixed-node diffusion Monte Carlo[38,39] with the potential surface of Huang et al.[16] In these diffusion Monte Carlo simulations, the wave function is forced to change sign when the shared proton passes through the plane perpendicular to the O−O axis, intersecting the axis at the midpoint of the vector between the two oxygen atoms. It is of interest that there is no significant activity in the vicinity of the HOH bending vibration in the isolated water molecule[40] (dashed arrow in Figure 2B), providing further evidence that the independent fabric of the water molecule is lost in the (vibrationally averaged) [HO···H···OH]$^-$ structure. The calculations that accurately predicted the $BH_{||}$ band also provide the assignment for the weaker 1090 cm^{-1} band reported earlier[30] primarily to the perpendicular oscillation of the shared proton ($BH_\perp$) relative to the heavy atom axis. The other $BH_\perp$ mode was predicted by fixed-node diffusion Monte Carlo simulations in which the wave function changes sign when it passes through a plane that contains the O−O axis and bisects the HOOH torsion angle. It is expected to occur at ∼1020 cm^{-1}, supporting the assignment of one of the remaining weaker bands (at 940 and 995 cm^{-1}) to this motion. Thus, the three vibrations that characterize the three-dimensional confinement of the shared proton are encoded in the spectra in an exceptionally simple fashion.

While the strong $BH_{||}$ band in the $H_3O_2^-\cdot Ar$ spectrum was anticipated, the observation that its spectrum is much simpler than those of either the $BrHBr^-$ or $H_5O_2^+$ clusters is surprising. Both of these strongly bound systems are thought to occur with a single minimum potential function describing the displacement of the shared proton in an overall symmetrical arrangement.[2,36] Nonetheless, the features in the $H_5O_2^+$ spectrum are rather complex, with multiplet sub-structure and strong mixing between the shared proton stretch and the bending motion of the two water molecules. In addition, the $BrHBr^-$ spectrum[36] displayed a very strong progression involving the Br−Br stretch in combination with the shared proton fundamental. Note that this progression is present in the argon matrix spectrum[41] of $BrHBr^-$, but it is somewhat suppressed. As such, it would be useful to obtain the $H_3O_2^-$ matrix spectrum to clarify the role of the rare-gas perturbation on the linear spectrum. Both these effects act to dilute the oscillator strength associated with the proton motion. On the other hand, although calculations suggest that the $H_3O_2^-$ system is intrinsically quantum in nature, the $BH_{||}$ band in the isolated $H_3O_2^-$ spectrum is relatively narrow ($\Delta\nu_{\mathrm{fwhm}} = 21$ cm^{-1}), and it appears with very little clutter from combination bands. This result does not follow the trend displayed by the $X^-\cdot H_2O$ series (X = halide), where soft mode activity becomes increasingly pronounced in the spectra of the smaller halides.[25] The simple appearance of the spectrum is also interesting in the context of the red-shifted bands associated with strong H-bonds, where it is almost universally accepted that the more red-shifted bands appear with increasing bandwidths.[42] Thus, although one generally observes very poorly resolved features when these occur in the neighborhood of 1000 cm^{-1} in the bulk, the $H_3O_2^-$ $BH_{||}$ band is among the sharpest we have observed of any anion−water complex. We therefore conclude that such broadening, which may well occur in aqueous hydroxide, is not driven by intrinsic intracluster vibrational mode coupling.

Acknowledgment. M.A.J. and A.B.M. thank the National Science Foundation for generous support of this work under grants 0111245 and 0200968, respectively. We also thank Professor J. M. Bowman for many useful discussions on these systems and for providing us with the potential surface for $H_3O_2^-$.

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