IR Spectroscopy of Strong H-Bonds

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Gas-Phase Infrared Spectroscopy and Multidimensional Quantum Calculations of the Protonated Ammonia Dimer $N_2H_7^+$**

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The challenge of understanding the unusually high proton conductivity in water and in ice as well as water-mediated proton transfer across biomembranes has triggered considerable work on protonated water networks.[1,2] Important limiting structures in describing these rapidly fluctuating networks are the Zundel ($H_5O_2^+$) and Eigen ($H_9O_4^+$) cations, which are characterized by broad but distinct infrared (IR) absorption spectra in the condensed phase.[3] Interestingly, the infrared signature of the isolated Zundel cation,[4–6] in which a proton is strongly bound and equally shared by two water molecules, has only very recently been fully elucidated.[7] The vibrational frequency of the X···H$^+$···X proton-transfer mode (X = closed-shell atom or molecule) in systems containing strong hydrogen bonds is dramatically red-shifted from the value of the free X–H stretch;[8,9] it often occurs below 1000 cm^{-1}.[10] Until recently, this spectral region has been inaccessible to tunable tabletop lasers, because these lasers were not sufficiently powerful to carry out action spectroscopy on the isolated systems. Theoretical analysis of the resulting band patterns may be even more challenging. The pronounced anharmonic character of such strong hydrogen bonds requires highly accurate, multidimensional quantum treatment of the vibrational-level structure that pushes the limits of current computers.[11]

Strong H-bonds involving ammonia[12] have received much less attention than their water analogues, and their role in ammonia transport proteins that are vital to nitrogen metabolism is just becoming accessible at a molecular level.[13] Gas-phase IR spectroscopy of $N_2H_7^+$, the Zundel cation analogue in protonated ammonia clusters $(NH_4^+)(NH_3)_n$, has to date been restricted to the range above 2600 cm^{-1}.[14] For larger systems ($n = 3$–9), photodissociation spectra at longer wavelengths have been reported using a line-tunable CO_2 laser[15] or a free electron laser.[16,17] These studies have shown that while the $n > 1$ clusters prefer to form an ammonium ion solvated by ammonia molecules, the protonated ammonia dimer is unique in that it adopts a D_{3d} equilibrium geometry, with the excess proton shared equally between two ammonia molecules. Computationally, the structure and spectroscopic characteristics of $(NH_4^+)(NH_3)_n$ clusters have been studied mainly within the harmonic approximation (see references [18,19] and references therein) or using an effective one-dimensional quantum model[20] of the N···H$^+$···N shared-proton stretching vibration in $N_2H_7^+$.

Although isoelectronic to the Zundel cation, $N_2H_7^+$ (see Figure 1 a) presents a conceptually different scenario owing to the differing heights of the classical barriers for proton transfer. Specifically, the shared-proton potential for the

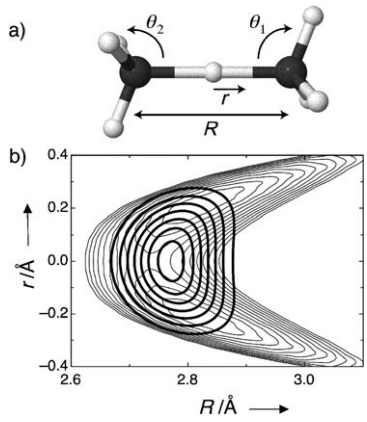

Figure 1. a) Optimized transition-state (TS) geometry of $N_2H_7^+$ with definition of large amplitude coordinates for proton motion *r*, center-of-mass displacements of the terminal ammonia molecules *R*, and their umbrella-type motion θ_1 and θ_2. b) Potential-energy surface (MP2/aug-cc-pVTZ, thin lines) along *r* and *R* (all other coordinates fixed at the TS, contours from 100 to 1100 cm^{-1}) and ground-state vibrational density (thick lines) of the 4D model Hamiltonian projected onto *r* and *R*.

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Zundel cation displays a single minimum at the midpoint between the oxygen atoms, but this arrangement evolves into a double-minimum situation in $N_2H_7^+$ (see Figure 1b), with the minimum-energy structures separated by a 1–3-kcal mol^{-1} barrier, depending on the level of quantum chemistry.[20] This situation leads to a vibrational ground state that is energetically higher than the barrier for proton transfer, thus rendering an analysis in terms of the local minima corresponding to the proton being bound to either of the two NH_3 groups meaningless. Herein, we provide a joint theoretical and experimental study addressing the consequences of this quantum-mechanical symmetrization through the zero-point averaging[21,22] on the IR spectrum in the range of the shared-proton vibrational transitions.

Experimental gas-phase IR spectra of the protonated ammonia dimer are shown in Figure 2a,b; peak positions are listed in Table 1. Both are action spectra, in which the absorption of IR photons is measured indirectly by the mass-selective detection of the photofragment ions (see the Supporting Information). Infrared multiple-photon dissociation (IRMPD) spectra were measured from 560 to 1650 cm^{-1}. These spectra have the advantage that they probe the bare ion, but they require absorption of multiple photons (6–16 photons in the range from 600 to 1700 cm^{-1}) to photodissociate $N_2H_7^+$ to $NH_4^+ + NH_3$ ($D_0 = 9440$ cm^{-1}),[12] thereby complicating theoretical simulation of the band intensities. The infrared vibrational predissociation (IRVPD) spectrum (610 to 2000 cm^{-1}) is complementary in that it probes the corresponding Ar-tagged species, which, because of its much lower dissociation threshold (i.e. lower than the photon energy used in the experiment), reflects the linear absorption spectrum of $N_2H_7^+$·Ar. As such, the IRVPD spectrum is more straightforward to calculate and interpret, but the structure might be perturbed by the Ar "messenger".[6]

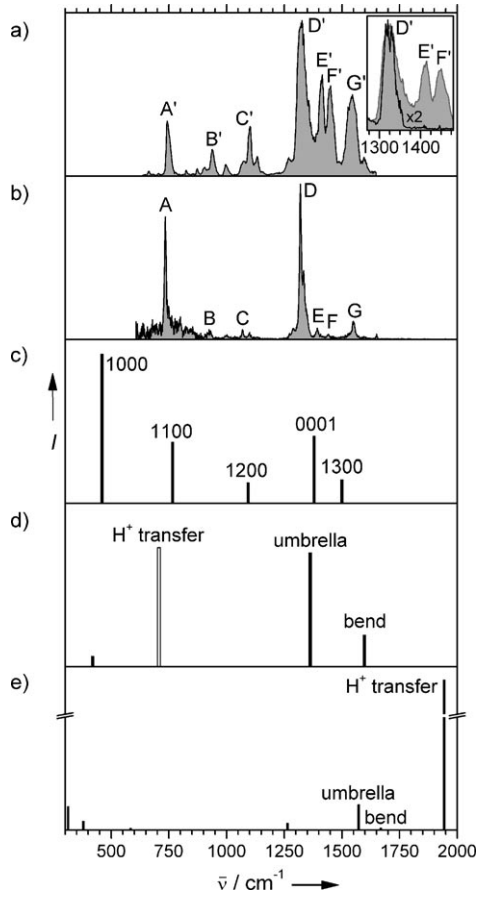

Figure 2. Experimental IR photodissociation (a,b) and calculated linear IR absorption spectra (c–e) of $N_2H_7^+$. a) Experimental gas-phase IRMPD spectrum of $N_2H_7^+$. Capital letters index the prominent peaks for reference in Table 1. The inset shows two IRMPD spectra taken with different laser pulse parameters (see text). b) Experimental IRVPD spectrum of $N_2H_7^+$·Ar. c) Anharmonic spectrum based on the 4D model. d) Harmonic MP2 spectrum at the D_{3d} transition state with the position of the proton-transfer mode from the anharmonic 1D model. e) Harmonic MP2 spectrum at the C_{3v} minimum.

Table 1: Experimental and calculated vibrational frequencies (in cm^{-1}) and intensities for $N_2H_7^+$.[a]

IRMPD		IRVPD		4D Simulation		
Freq.	Int.	Freq.	Int.	Freq.	Int.	Assignment
				464	2.204	Ψ_{1000}
743 (A′)	0.35	734 (A)	0.79	765	0.86	Ψ_{1100}
938 (B′)	0.17	ca. 930 (B)	0.06			
1097 (C′)	0.10	1069 (C)	0.07	1091	0.31	Ψ_{1200}
1325 (D′)	1.00	1320 (D)	1.00	1354	1.00	Ψ_{0001}
1415 (E′)	0.65	1392 (E)	0.07			
1451 (F′)	0.58	1440 (F)	0.03	1485	0.36	Ψ_{1300}
1545 (G′)	0.52	1550 (G)	0.12			

[a] The calculated values are from anharmonic 4D calculations. The states were classified by the quantum numbers *m*, *n*, *k*, and *l*, which refer to the coordinates *r*, *R*, $\theta_s = (\theta_1 + \theta_2)/2$, and $\theta_a = (\theta_1 - \theta_2)/2$, respectively. Intensities were normalized to the strongest peak in the range from 600 to 1700 cm^{-1}.

Both IR spectra show rich vibrational structure in the 600–1700-cm^{-1} region, and most importantly, they display features at similar wavenumbers, thus establishing that the addition of the Ar atom to $N_2H_7^+$ does not polarize the shared proton or distort it significantly from the equilibrium geometry of the bare ion. The two most prominent peaks in the IRVPD spectrum (peaks A and D in Figure 2b) are found at 734 and 1320 cm^{-1}, red-shifted by only 9 and 5 cm^{-1}, respectively, from the positions of bands A′ and D′ (743 and 1325 cm^{-1}) in the IRMPD spectrum. Such red shifts are typical when Ar is used as a messenger species.[6] The relative intensities of the individual peaks are quite different in the two spectra, as expected from the different photodissociation mechanisms,[23] that is, (single-photon) vibrational predissociation versus (multiple-photon) direct dissociation. A more detailed investigation shows that the IRMPD cross section depends nonlinearly on the laser pulse energy (and other parameters). With a macropulse energy of 50 mJ (at 8 μm), only band D′ is observed in the IRMPD spectrum (see inset Figure 2a, black line). Bands A′–C′ and E′–G′ are detected when the macropulse energy is increased to 130 mJ. This protocol yields the gray spectrum shown in Figure 2a, in which the transition D′ is saturated. This behavior complicates the assignment of the IRMPD spectrum based on linear absorption cross sections, and we therefore focus our attention on the IRVPD spectrum.

To assign the vibrational spectra, we performed calculations at two different levels of theory. Common analysis of vibrational spectra makes use of the harmonic approximation for the shape of the potential-energy surface in the vicinity of a minimum, assuming classical nuclei. In the present case, this approach would correspond to a lower symmetric C_{3v} configuration. The harmonic vibrational frequencies and oscillator strengths according to such a normal-mode analysis are shown in Figure 2e. A very intense vibrational transition is predicted at 1943 cm^{-1}, corresponding to motion of the shared proton along the proton-transfer coordinate. Several weaker transitions are calculated at approximately 1600, 1300, and 400 cm^{-1}. The agreement between the C_{3v} harmonic spectrum and either experimental IR spectrum is poor; in particular, the calculations do not reproduce the bands in the 500–1500-cm^{-1} region.

An apparent improvement can be achieved if we compare the experimental data to harmonic frequencies and intensities computed at the D_{3d} structure corresponding to the classical proton-transfer transition state, in which the proton is equally shared by the ammonia molecules (Figure 2d). This procedure recovers physical frequencies and intensities for all but one vibrational mode, the proton-transfer mode. For the position of this mode we therefore use the anharmonic value of Asada et al.,[20] which causes a considerable red shift of the intense 1943-cm^{-1} band in the C_{3v} spectrum down to 707 cm^{-1}. This lower value is actually quite close to the range recently reported for a large number of shared-proton systems involving oxygen atoms,[8] and this spectrum (Figure 2d) now compares rather well with the experimental IRVPD spectrum with regard to the positions of bands A, D, and G. This agreement appears to be fortuitous, however, as a more extensive treatment of the anharmonicities will show that the assignment of band A to the fundamental of the shared-proton mode is incorrect.

A deeper understanding of the spectrum requires a more sophisticated model that takes the anharmonic coupling between multiple modes into consideration. As a full-dimensional treatment of this system is not yet feasible, we performed calculations at reduced dimensionality (see the Supporting Information). Specifically, we have chosen the four coordinates defined in Figure 1a to span four-dimensional (4D) potential-energy and dipole-moment surfaces. Several low-lying vibrational eigenstates of this potential were calculated, and a cut of the 4D ground-state wave function is shown in Figure 1b. It clearly confirms our initial assertion that, in contrast to a classical nuclei prediction, this hydrogen bond is symmetric. The ground-state density reaches a maximum with the proton at the center, consistent with its zero-point energy lying above the barrier.

Using the ground-state wave function as the initial state, matrix elements of the dipole-moment operator were calculated, from which the IR intensities could be obtained. Table 1 reports the excitation frequency of those transitions that have nonzero intensity, and the corresponding spectrum is shown in Figure 2c. Satisfactory agreement with the IRVPD bands is observed. The calculations support our assignment of the most intense band in the IRVPD spectrum (D, 1320 cm^{-1}) to the antisymmetric (out-of-phase) combination of the NH_3 umbrella motions (1354 cm^{-1}). The 4D calculations find the fundamental of the proton-transfer mode not around 700 cm^{-1}, as predicted by the anharmonic 1D model,[20] but considerably lower, at 464 cm^{-1}. Note that this predicted location is below the current experimental observation window, such that the fundamental transition should not have been accessible in the experimental spectra shown in Figure 2a,b. In this scheme, band A, the second-strongest transition in the IRVPD spectrum, corresponds to the 1+1 combination band involving the proton-transfer mode and the symmetric stretching vibration of the ammonia molecules (R in Figure 1a). The 1+2 combination band is predicted at 1091 cm^{-1}, close to band C (1069 cm^{-1}) in the IRVPD spectrum. Such a pronounced coupling between the antisymmetric and symmetric stretching modes is typical for strong hydrogen bonds and has been observed, for example as described in reference [24].

The assignment of the other bands remains tentative. The harmonic transition-state calculations indicate that the bending motion of the shared proton (1598 cm^{-1}) could be responsible for band G (1550 cm^{-1} in the IRVPD spectrum), as it is calculated to lie 236 cm^{-1} above the antisymmetric umbrella mode, which compares well with the gap of 230 cm^{-1} between bands D and G. This degree of freedom was not included in the 4D simulations and therefore does not show up in the 4D IR spectrum. Finally, the less intense band F (1440 cm^{-1}) could be assigned to the 1+3 combination band calculated at 1485 cm^{-1}.

In summary, the 4D anharmonic model agrees satisfactorily with experimental data, thus providing first tentative assignments for the main absorption bands (A, C, D, and G in Figure 2) until a full-dimensional treatment of this system becomes available. The 4D model further predicts the fundamental of the shared proton mode at 464 cm^{-1}, a region that is difficult to access with table-top lasers but can be accessed using radiation from an IR free electron laser. This work will hopefully stimulate new experiments on this prototypical low-barrier hydrogen-bonded system.

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