Structure of Water

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Infrared Spectroscopy and Ab Initio Theory of Isolated $H_5O_2^+$: From Buckets of Water to the Schrödinger Equation and Back

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ab initio calculations · protons · theoretical chemistry · vibrational spectroscopy · water

The Acidic Proton in Bulk Water

Over 200 years ago,[1a] at a time when the terms atom and molecule were not yet well defined, and the term ion was still unknown, Theodor von Grotthuss realized that the electric conductivity of liquid water within a galvanic cell arises from a structural diffusion of charges hopping stepwise along a molecular chain:

"Das *Charakteristische* dieser Theorie besteht darin, *daß die Elemente der Wasseratome selbst entgegengesetzte electrische Zustände annehmen*, wodurch ein wechselseitiger *Molecular-Austausch*,…, in der ganzen zwischen den Polen befindlichen Reihe von Wasseratomen Statt finden muß."[1b]

Michael Faraday explicitly confirmed Grotthuss' theory of electrolysis as a starting point for the development of this own concept of the electric field.[1c] He also helped to establish the so-called Grotthuss mechanism. Subsequent researchers, such as Hückel, Eyring, Bernal, Fowler, and Wannier, have each helped to established a more detailed picture of proton pseudodiffusion along hydrogen bonds, and they have attempted further more elaborate interpretations.[2] It was Manfred Eigen who succeeded in finding the structural interpretation of the hydrated proton as a hydrated H_3O^+ ion,[3,4] only to see himself immediately questioned by Georg Zundel, who postulated a symmetric doubly hydrated proton, namely a symmetric $H_5O_2^+$ structure.[5] Subsequent IR spectroscopic investigations of solutions revealed in part extremely broad and quasicontinuous bands, which did not allow any definite prediction on the presumed proton delocalization.[6] For a long time, neither experiments nor ab initio calculations could decide the conflict. Instead, either Eigen cations or Zundel cations were predicted depending on the surroundings and on the method of investigation or on the level of calculation.[7–10]

Only through the availability of the significantly enhanced computer power was it possible to utilize new theoretical methods, such as Car–Parrinello molecular dynamics (CPMD), which obtains classical trajectories from quantum mechanical forces. The application of this technique to ensembles of up to 32 water molecules plus an extra proton enabled a qualitative view on the complicated behavior of the hydrated proton to be obtained for the first time.[2,11–13] It was found that the extra proton is bound some of the time by just one water molecule (asymmetrically solvated) and some of the time by two (symmetrically solvated). From the point of view of quantum mechanics it is more appropriate to speak about an extended wave packet which contains Eigen and Zundel structures as limiting cases, but not as separate structures. In particular, there would be no well-defined transition state between such limiting structures. New bulk-phase experiments point towards an equilibrium among these two limiting cases as well.[10] At about the same time, and largely independently, it was proposed from fundamental considerations that thermal fluctuations in the second solvation shell of the cation were the rate-limiting step in proton pseudodiffusion, which results in the rearrangement of hydrogen bonds.[14–17] In this respect the description of the Grotthuss mechanism in liquid water is now beyond dispute. Largely qualitiative interpretations still prevail however for proton transfer in and between complex organic compounds with large proton polarizabilities.[6]

Microsolvated Protons as Isolated Gas-Phase Clusters

Until recently, the situation looked quite different for the proton dynamics in isolated nanosolvates, that is, in gas-phase clusters $H^+(H_2O)_n$ with few water molecules. Ultrafast spectroscopy is unsuitable for direct observation, as it is much too invasive. Instead, infrared spectroscopy of vibrational eigenstates has established itself as the method of choice, after it was shown that infrared-induced evaporation of a single or a few water molecules off an isolated cluster ion may serve as an indirect measure for the IR absorption.[18] Until recently this kind of consequence spectroscopy in the gas phase was applied only to free O–H stretching vibrations, as the corresponding laser technique for the mid-IR range (1000–2000 cm^{-1}) was not available. Nonetheless, the investigation of clusters with $n = 5–8$ yielded indirect evidence for symmetric Zundel structures when symmetric hydration

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prevailed, and for (predominantly) asymmetric Eigen structures when asymmetric hydration prevailed.[19] Several conceivable isomerization pathways were postulated, which, in close analogy to the findings from the condensed phase, imply a breaking of hydrogen bonds in the second solvation shell.[20] Ab initio investigations, especially of the cluster $H^+(H_2O)_7$, showed that two-dimensional Zundel-like structures and three-dimensional Eigen-like structures are degenerate. However, only the theoretically predicted Zundel-like structures can be brought into agreement with the experimentally determined IR spectra.[19,21] The experimental and theoretical investigation of so-called "magic" cluster sizes (as for example, $n=21$) have been covered in the literature[22,23] and will not be discussed here.

The Naked Zundel Cation $H_5O_2^+$

The first IR spectra of isolated $H_5O_2^+$ were not very informative, as they were obtained from clusters with high internal temperatures.[18,24,22] Subsequent use of the two European free electron lasers (FEL) extended the explorable range of the spectrum below 1000 cm^{-1}. Several new, albeit broad, bands were found in the mid-IR region, and the spectra only partially agreed with each other.[25,26] In contrast, the aggregates of protonated water clusters having a single, weakly bound argon or neon atom are cold, and may be generated by supersonic jet expansion. Moreover, they are well-suited to predissociation (by boiling off the noble gas chaperon) through single photon IR absorption. The fragmentation intensities then provide indirect information about the IR absorption of the actual water cluster ions—provided that the perturbation of the adatoms remains small or at least estimable. However, the very first spectra of isolated $H_5O_2^+$ were recorded with H_2 as messenger, which at the time showed that the aggregation of H_2 has a significant influence on the hydrogen bond that was difficult to interpret.[27] The experimental breakthrough came with the production of cold noble gas adducts in pulsed supersonic expansion and the generation of long-wave IR radiation[28] with a laser-pumped optical parametric oscillator (OPO) with multistage frequency conversion.[29–31] The new spectra cover all of the fingerprint region, and they contain sharp bands. Most remarkable is a strong doublet, which does not have an obvious explanation, with two sharp bands at 928 and 1047 cm^{-1},[30] thus split by 120 cm^{-1}. A similar doublet is found in the "hot" FEL spectra of naked $H_5O_2^+$ as well.[25,26] As the doublet arises upon both neon and argon tagging,[29–31] the latter leading to shifted duplication of the doublet, it can be seen as a genuine feature of the $H_5O_2^+$ ion itself. An additional single band in the cold tagging spectra somewhat below 1800 cm^{-1} is readily interpreted as a bending vibration and provides for consistency of the data rather than for any further puzzle.

Alone on the basis of the "hot" spectra, theoreticians took up the quest for an interpretation of the long-wave absorption bands, which was further intensified through the publication of the new and sharp doublet bands. Vibrational self-consistent-field (VSCF) calculations on pointwise-calculated ab initio potential hypersurfaces was applied repeatedly to model $H_5O_2^+$, although only pairwise coupling of normal modes was considered. The proton-transfer vibration was found to be an isolated band at 1209 cm^{-1}[32] or 1223 cm^{-1}.[29] The experimental doublet structure could not be reproduced by this approach. Similar results originated from an ab initio molecular dynamics (MD) simulation, where an isolated single band was also found at around 1000 cm^{-1}.[33a] The strong temperature broadening could however be modeled as observed for the first time.

The same study[33a] was the first to work on the problem of electrical and mechanical anharmonicities in IR spectroscopy (see Figure 1), and provided explicit treatment for four seemingly important stretching and bending vibrations of

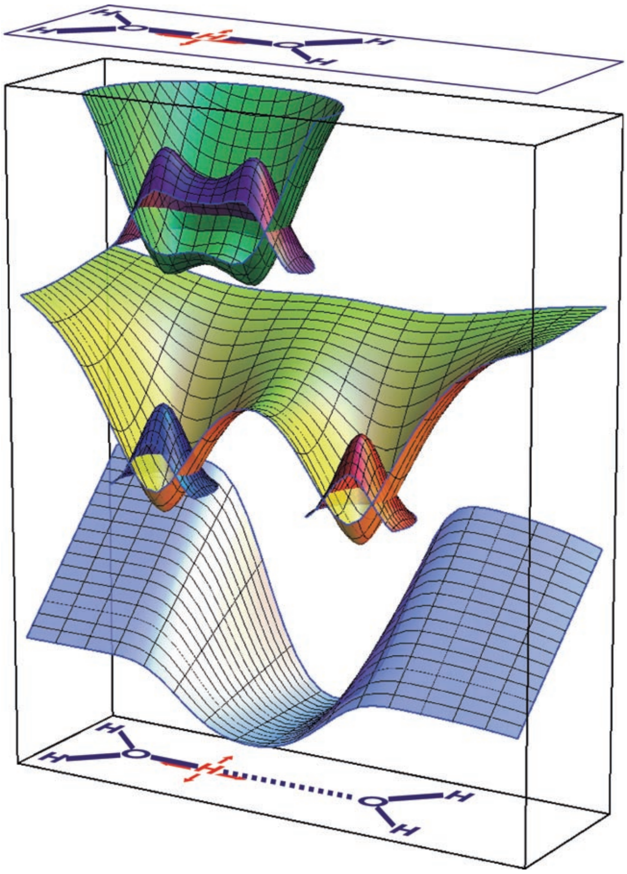

Figure 1. Potential energy wells for the vibration of a proton (shown with red arrows) parallel or perpendicular to the axis between two water molecules. They vary from "large" to "small" O–O distances (yellow and green surfaces, vertically offset). The proton either stays with one of the two water molecules (bottom face of the figure; in reality twisted and tilted with respect to each other) and indicated by the wave function on the yellow surface (Eigen cation, H_3O^+), or is delocalized between the two water molecules (green surface, Zundel cation, with a smaller O–O distance). Potential wells are displayed as two-dimensional cuts through the actual 15-dimensional ($3N-6$) potential hypersurface, which exhibits considerable mechanical anharmonicity (depending on the O–O distance) and which could be determined only by extensive ab initio calculations.[34] Vibrational excited states are not shown. To determine reliable IR intensities, the dipole moment has to be taken as a 15-dimensional hypersurface as well,[34] and is shown as a two-dimensional cut (blue surface, qualitative only) that brings with it a considerable amount of electric anharmonicity.

$H_5O_2^+$ (mechanical anharmonicity). Furthermore, for the first time the actual dependence of the molecular dipole moment of these vibrations was calculated beyond the linear dipole approximation, thus creating a multidimensional dipole moment hypersurface (electrical anharmonicity). Together, both types of anharmonicity combine to give the transition frequencies and intensities. The three bands that resulted at 968, 1026, and 1158 cm^{-1} obviously still disagreed with the experimentally determined doublet. What went wrong? Fermi resonances with overtones of further, not yet considered bending modes were postulated but remained a speculation—it would provide at best further bands. What was missing was the complete progression of the electronic potential and of the dipole moment as a function of all of the $3N-6$ internal degrees of freedom. The limited quantum chemical level of those calculations at that time does not completely give rise to the discrepancy that remained to be explained.[33b]

Vibrational Dynamics in 15 Dimensions

J. Bowman and co-workers fitted 15-dimensional hypersurfaces for the potential energy and for the dipole moment from altogether 50000 (!) single ab initio points at CCSD(T) level with large basis sets (aug-cc-pVTZ) and by utilizing analytic polynomial fits with 8000 coefficients.[34] Alone through this extensive project, $H_5O_2^+$ was able to be extremely well characterized as an isolated ion. IR bands and vibrational spectra do not arise directly from this endeavor however, as none of the aforementioned methods is capable of directly using such hypersurfaces.

At this point, H.-D. Meyer and co-workers started their investigations and utilized the two 15 dimentional hypersurfaces to predict the IR spectra of isolated $H_5O_2^+$.[37–39] Throughout the last two decades, beginning from a cooperation with L. Cederbaum and co-workers, they had developed a new method to model vibrational dynamics.[35,36a] With higher computing power becoming available they treated increasingly larger molecular systems.[36b] The novel approach is called multiconfigurational time-dependent Hartree (MCTDH). It sets up the time-dependent Schrödinger equation for the nuclear motion in all dimensions (here: 15). The total wave function to be determined is represented by a linear combination of products of suitable single particle functions. The expansion coefficients and single particle functions are then simultaneously determined through variational optimization, which allows a very efficient representation of the total wave function. After having performed a sufficient propagation in time, the stationary vibrational eigenstates and their energies are then projected. It is important to note that the full dimensionality of the problem is covered without restrictions, that no restrictions with respect to mode coupling apply, and that coverage of anharmonicities of any desired size can be done as no harmonic approximation is used at any point. The IR intensities of possible transitions between the "exact" vibrational levels arose from transition dipole moments that in turn stem from the "exact" dipole moment hypersurface integrated explicitly over all 15 dimensions. Thus a meaningful prediction of the IR spectrum was expected from this elaborate approach. Indeed, as can be seen in Figure 2[37] the calculated spectrum is by and large identical to the experimental IR spectrum of $H_5O_2^+$. In particular, the mysterious doublet at 1000 cm^{-1} is predicted correctly for the first time, and the bending mode at 1800 cm^{-1} is predicted in any event. This conceptual breakthrough in the modeling of an almost soul-destroying system becomes even more meaningful once the contributing vibrational modes are analyzed. In fact, the doublet does indeed arise from the Fermi resonance of the proton transfer vibration with a combination band that comprises of a single quantum of the symmetric O–O stretching vibration with three quanta of the H–O–H wagging motion. Consequently this is a fourth-order coupling of five quanta in three different modes—partly in overtones. With the benefit of hindsight it is obvious why all the approximate approaches failed to miss this answer to the problem. The ab initio -MD- and CPMD-simulations could not get the right prediction either; in contrast to MCTDH, these methods neglect the considerable extension of the vibrational wave packet (with simultaneous Eigen and Zundel contributions) by approximating it as a classical point in space. Even VSCF had to fail, as it considers coupling of modes only up to first order (pairwise) whereas in this case up to five quanta couple (which is fourth order)!

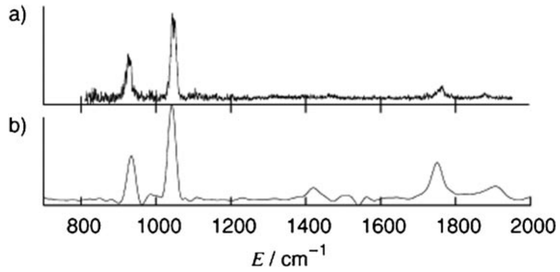

Figure 2. a) Experimental IR spectrum of $H_5O_2^+\cdot Ne$; b) simulation. Reproduced from ref. [37].

It remains to answer the question: Was it worth the gigantic effort? At this point we encounter a surprise. The naked $H_5O_2^+$ transfers its "hydrated" proton from one water molecule to the next in a way which is very much the same that one has predicted for a fully hydrated (asymmetric) $H_5O_2^+$ ion. The H_3O^+ core is almost planar and accordingly coordinates three water molecules through hydrogen bonding in a trigonal-planar arrangement. The molecular planes of the solvating water molecules are slightly tilted with respect to the hydrogen bond; in effect the water molecules of the first solvation shell, together with those of the second solvation shell, coordinate in a rather pyramidal arrangement. Upon migration of the extra proton from one water molecule to the another, the donating H_2O and the accepting H_2O have to swap their preferred geometry, which makes them tilt with respect to each other—a movement that is represented in the IR spectra by the three quanta of the soft and low energy wagging mode. In addition, the activation barrier for the proton transfer lowers by interim relaxation of the O–O distance, which is promoted by the corresponding vibrational mode, as observed in the IR spectra. In total the found combination of five quanta in three different vibrational eigenmodes describes quite precisely the reaction coordinate of the proton transfer in a naked $H_5O_2^+$ ion as well as in a fully hydrated $H_5O_2^+$ cation, which should be perhaps be more appropriately called an Eigen–Zundel cation.

The elucidation of proton-transfer dynamics in acidic aqueous media was begun over 200 years ago. With the highlighted studies it was possible to close one more decisive gap on the way from the Schrödinger equation towards the measurable and visible phenomena occuring "in a bucket of water". Modern and innovative instruments of experimental physical chemistry and of computational theoretical chemistry were well coordinated and used systematically in exemplary international cooperation.

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