

FEATURE ARTICLE

HCl Hydrates as Model Systems for Protonated Water

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Ab initio molecular dynamics simulations are presented of vibrational dynamics and spectra of crystal HCl hydrates. Depending on the composition, the hydrates include distinct protonated water forms, which in their equilibrium structures approximate either the Eigen ion $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ (in the hexahydrate) or the Zundel $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ ion (in the di- and trihydrate). Thus, the hydrates offer the opportunity to study spectra and dynamics of distinct species of protonated water trapped in a semirigid solvating environment. The experimentally measured spectra are reproduced quite well by BLYP/DZVP-level calculations employing Fourier transform of the system dipole. The large overall width (800–1000 cm^{-1}) of structured proton bands reflects a broad range of solvating environments generated by crystal vibrations. The aqueous HCl solution was also examined in search of an objective criterion for separating the contributions of “Zundel-like” and “Eigen-like” protonated forms. It is suggested that no such criterion exists since distributions of proton-related structural properties appear continuous and unimodal. Dipole derivatives with respect to OH and $\text{O}\cdots\text{H}^+$ stretches in water and protonated water were also investigated to advance the understanding of the corresponding IR intensities. The effects of H bonding and solvation on the intensities were analyzed with the help of the Wannier centers’ representation of electron density.

I. Introduction

Protonated water is of basic importance in aqueous physics and chemistry. Two forms were suggested originally for hydrated protons, an “Eigen complex”^{1,2} $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ and a “Zundel ion”^{3,4} $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$. In the first, the proton is localized on a single water molecule, and in the second, it is shared by two water molecules. Dynamical aspects of a solvated proton have also attracted considerable interest, particularly in connection with the anomalously high electrical conductivity of acids; the conductivity is associated with proton hopping between water molecules. Theoretical studies showed that the proton hopping is driven by fluctuations of the protonated water solvation shell.^{5–7} Introduction of computer simulation techniques applicable to proton-transfer systems advanced significantly the atomic-level understanding of the hydrated proton; the techniques include ab initio molecular dynamics^{7,8} and the empirical valence bond (EVB) approach.^{9–12} For recent reviews of pertinent computational studies, see, for example, refs 13

and 14. One of the major conclusions has been that the two limiting forms of protonated water are not mutually exclusive, as thought originally; rather, protonated water dynamics includes continuous interconversion in the structural range limited by the two forms, which is driven by coupling to the motions of the surrounding water molecules. Quantum mechanical effects were shown to enhance proton delocalization.¹⁵ Citing ref 13: “Eigen and Zundel complexes should only be looked upon as limiting cases or caricatures, loosely speaking, similar to the concept of resonance structures used to describe conjugated Π -systems in terms of Lewis bonding.”

Nevertheless, one may gain considerable insight by trapping and observing protonated water close to either of the limiting forms and perhaps also in intermediate stages of proton sharing. To this end, spectroscopic studies have been pursued of isolated gaseous hydronium¹⁶ H_3O^+ and Zundel^{17–19} $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ ions and of protonated water clusters^{20–22}; for example, the protonated water tetramer was shown to adopt the Eigen structure with the hydronium ion at the center,²⁰ while the

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Andrey Dubrovskiy was a graduate student of the Moscow University, visiting at the Hebrew University, while contributing to the present manuscript.

Fawzi Mohamed received his diploma in Computational Science and Engineering at ETH Zürich in 2000. After having worked for 1 year in the private sector, he completed his Ph.D. studies with M. Parrinello at the ETH Zürich (Ph.D. degree awarded in 2006). He worked at the Scuola Normale in Pisa for 1 year. At present, he is pursuing postdoctoral studies with J. Sauer at the Humboldt University. He was recently awarded the Humboldt fellowship. His research interests include ab initio simulations, QM/MM, water, oxides, and method development.

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J. Paul Devlin was born on the dry high plains of Colorado in 1935. He received a B.S. degree from Regis College in Denver in 1956 and completed a Ph.D. in Chemistry at Kansas State University in 1960 with Clarence Hisatsune. He became an assistant professor at Oklahoma State University after a year in the spectroscopy group of Bryce Crawford and John Overend at the University of Minnesota. He moved through the ranks to professor emeritus at Oklahoma State while directing research in vibrational spectroscopy of condensed-phase systems. For the past 25 years, that research has focused on H-bonded solids, with particular emphasis on ice and the various classes of solid-state hydrates. For the past 15 years, the experimental studies have evolved jointly with the computational studies of V. Buch.

protonated hexamer was shown to have a ground state corresponding to the fully hydrated Zundel ion.²¹

An alternative approach to isolate and observe the different protonated water states, which is employed in the present study, is to trap these states in solid phases. Acid hydrates provide convenient model systems for this purpose. In particular, HCl hydrates have been characterized in the past by X-ray diffraction and, depending on composition, were proposed to include protonated water either in the hydronium or in the Zundel form. On the basis of X-ray determinations of structures, the following formulas were proposed for the different hydrates: for the monohydrate,²³ (H₃O⁺)(Cl⁻); for the dihydrate,²⁴ (H₂O···H⁺···OH₂)(Cl⁻); for the trihydrate,²⁵ (H₂O···H⁺···OH₂)(H₂O)(Cl⁻); and for the hexahydrate,²⁶ (H₃O⁺)(H₂O)₅(Cl⁻) (the cation in the latter structure corresponds to the Eigen form, i.e., a hydronium cation fully solvated by three water molecules). Thus, these systems offer a unique opportunity to investigate spectroscopy and vibrational dynamics of individual protonated water forms in a crystal environment. The infrared (IR) spectra of the different HCl hydrate crystals are shown in Figure 1. Note the significant differences between the respective spectra and, in particular, the presence of broad and intense features in the 1000–1700 cm⁻¹ range in the case of the di- and trihydrate and their absence in the case of the mono- and hexahydrate, which suggests that these features are signatures of proton sharing. Absorption bands in this regime were also observed in the gaseous Zundel ion spectra.^{17–19} Our spectroscopic studies of mixed acid–ether and acid–methanol crystals also demonstrated features in this regime, which were assigned to proton-sharing configurations with the help of computational modeling.^{27–29} Related peaks were observed and assigned in inelastic neutron scattering studies of the HClO₄ dihydrate.³⁰

The aim of this article is an understanding of HCl hydrate spectra, with an emphasis on the vibrational dynamics and spectroscopy of protonated water. The computational tool used in the analysis is QUICKSTEP, a Gaussian based ab initio molecular dynamics code which is a part of the CP2K package.^{31,32} A series of studies on the HCl monohydrate was already published,^{33–35} as well as preliminary results on isotopic effects in the dihydrate;³⁶ these results will be briefly summarized in section IV. New results are presented for the di-, tri-, and hexahydrate. Furthermore, effort is made to apply the insights gained from the hydrate studies to proton solvation and spectroscopy in the aqueous HCl solution. Our analysis shows that the Zundel ion is, in fact, a “cartoon-like” idealization even in the trihydrate crystal, whose equilibrium structure includes nearly perfect Zundel forms, as fluctuations in the solvating environment induced by crystal librations are sufficient to induce proton preference for either side of the H₂O···H⁺···OH₂ unit. (The preferred side alternates in accord with the temporary solvation shell structure.)

Past computational studies of the HCl hydrate systems included modeling of the monohydrate, dihydrate, and trihydrate³⁷ using Car–Parrinello molecular dynamics (CPMD) and Car–Parrinello path integral molecular dynamics CP-PIMD and another more recent CPMD study of these systems.³⁸ These studies provided valuable information on structural and dynamic properties of the hydrates; more detailed comparison with the present results will be presented in the respective sections below. The above studies did not focus however on IR absorption spectra and their connection to proton dynamics, which is the main topic of the present study. Another series of studies employing DFT in conjunction with normal-mode

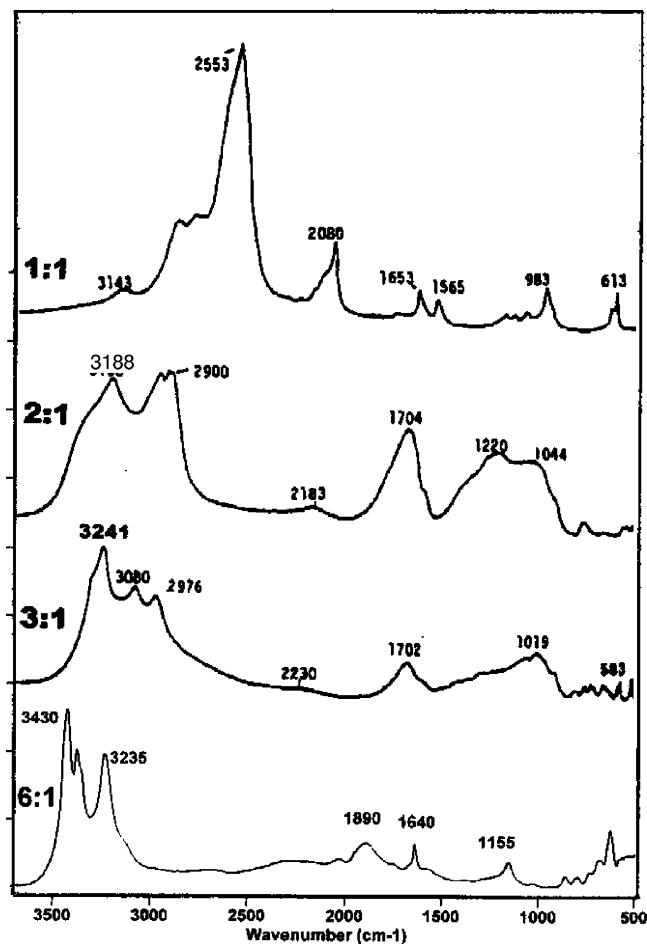


Figure 1. Experimental spectra of crystalline HCl hydrates at 80 K; from top to bottom: mono-, di-, tri-, and hexahydrate. The top three spectra are from ref 27.

analysis addressed IR spectroscopy of the trihydrate and the hexahydrate.^{39–41} While these studies generated some useful assignments, the authors of ref 41 themselves pointed out the difficulties associated with the use of the harmonic approximation for the highly anharmonic protonated water systems. Normal-mode analysis is not sufficient for studying the broad bands characteristic of such systems.

Ab initio dynamics is uniquely suited for that purpose. First, the Born–Oppenheimer potential energy surface obtained at every step allows for a unified first-principle description of proton-containing systems in all possible solvation states. Second, the system dipole function can be obtained at a modest computational overhead and can be used to obtain anharmonic IR spectra via dipole–dipole correlation functions.^{42–49} Third, convenient qualitative analysis of the spectra can be carried out with the help of Wannier functions.^{43,44,49} Specifically, for the purpose of calculation of the system dipole, the valence electron pairs are assigned to geometric centers (“Wannier centers”) of localized orbitals, obtained by transformation of the electronic wave function. In the closed-shell systems of our interest, the Wannier centers can be easily associated, according to their location, with OH bonds and lone pairs of oxygen and of halide ions. One can then use the discretized “location” of the electron pairs as represented by the Wannier centers to elucidate contributions of different parts of the system to the spectrum. See ref 49 for a recent elegant discussion of the use of Wannier centers in the study and analysis of spectra of water and acid solutions. The Wannier centers are used here to elucidate the influence of hydrogen bonding and the solvation environment

on the dipole derivatives with respect to the OH and $\text{O}\cdots\text{H}^+$ stretch in water and protonated-water-containing systems. Analysis is presented of the physical reasons for the dramatic increase in the OH stretch intensity of water upon hydrogen bonding, which has been noted in numerous past studies; see, for example, refs 50 and 51. A very large integrated intensity observed for the $\text{O}\cdots\text{H}^+$ stretch⁴ is also discussed.

At this point, one may contrast the broad but structured hydrate spectra of our interest (Figure 1) with the infrared spectrum of an aqueous acid solution. The acid contributes to the solution spectrum an intense, somewhat structured, continuum (“Zundel continuum”^{4,52}) extending from the water OH stretch band above 3000 cm^{-1} down to the water libration band below 900 cm^{-1} . This continuum reflects the continuous interconversion between the proton states; the more Zundel-like and the hydronium-like configurations are expected to dominate the low and the high end of the continuum, respectively.⁵³ The original analysis of this continuum by Zundel⁴ was based on a simple model in which the proton in the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit is continuously “polarized” by a fluctuating electric field which reflects the dynamic solvation coordinates. Zundel envisaged a quantum mechanical double-well system, with a nearly degenerate pair of lowest symmetric and antisymmetric states separated by small tunneling splitting; in this model, the proton can be easily toggled between the two sides of the well by the electric field perturbation. Later computational studies showed that tunneling does not play an important role in proton dynamics in solution as the computed barrier height in the free-energy profile is only about $k_B T$; when quantum zero-point energy effects are included, the barrier becomes very small indeed.¹⁵ However, the crucial role of proton coupling to the solvation shell dynamics proposed by Zundel stood the test of time and will be discussed further below in connection with hydrate and solution spectroscopy. For the past efforts on computational analysis of the Zundel continuum in the spectra of liquid acid solutions, see refs 53–55; the pertinent results are summarized briefly in section VIIIA. For the debate on the percentage of “Zundel-like” and “Eigen-like” ion forms in solution, see, for example, refs 13, 14, 55–59, and the references therein. Further, more-detailed discussion of past acid solution studies pertaining to these topics will be given in section VIII.

The article is organized as follows. In section II, computational details are given. In section III, OH and $\text{O}\cdots\text{H}^+$ infrared stretch intensities are analyzed with the help of the Wannier centers for H_2O in the gas phase, the gaseous dimer, and the liquid phase, and for the Zundel ion in the gas phase, the HCl dihydrate, and the acid solution. Sections IV–VII address structure and spectroscopy of the different hydrates. In section VIII, connection is made to the aqueous HCl solution. The results are summarized in section IX.

II. Computational Details

The chief computational tool of this study is the CP2K/QUICKSTEP on-the-fly code,^{31,32} which is used for structure minimization, ab initio molecular dynamics (MD) simulation, and calculation of infrared (IR) spectra.

QUICKSTEP is an implementation of the recently developed Gaussian plane wave method, which is based on the Kohn–Sham formulation of density functional theory (DFT).³² The Kohn–Sham orbitals are expanded using a linear combination of atom-centered Gaussian-type orbital functions. The electronic charge density is described using an auxiliary basis set of plane waves. Energies and forces corresponding to the Born–

Oppenheimer surface are calculated for each MD step using the Gaussian DZVP basis set, the exchange-correlation functional of Becke, Lee, Yang, and Parr (BLYP),⁶⁰ and the atomic pseudopotentials of the Goedecker, Teter, and Hutter type.⁶¹ Time steps of 1 fs were employed.

Recently, applications of on-the-fly dynamics to computations of IR spectra of molecular systems have been gaining popularity; for examples, see refs 46–49. The spectra can be obtained from the Fourier transform of the dipole–dipole correlation function. Computation of the system dipole was implemented in QUICKSTEP following ideas outlined in refs 42–45. More details on the implementation are given in ref 33. Briefly, the system dipole is represented as a sum of contributions of nuclei and of Wannier centers representing the “average” locations of electron pairs. To locate the Wannier centers, extended molecular orbitals of the electronic wave function are first transformed to localized orbitals; geometric averages over the latter correspond to the Wannier centers.^{43,44} This means that a point charge is associated with each valence electron pair. The computation is somewhat complicated by periodic boundaries; Berry phase approach is used (see ref 45 for a review) to obtain the total dipole of the periodic system, as a function of time. For classical nuclear dynamics, the IR absorption intensity of radiation at frequency ω polarized in the j direction ($j = x, y, z$) is proportional to the Fourier transform of the thermally averaged dipole–dipole correlation function

$$I_j = \text{const} \cdot \omega \int_{-\infty}^{\infty} \langle D_j(0)D_j(t) \rangle \exp(-i\omega t) dt \quad (1)$$

In the case of the expensive on-the-fly simulations, proper averaging over numerous trajectories is difficult. A single trajectory, typically of the duration of several picoseconds (ps), yields three Cartesian components of the system dipole, as a function of time, for $0 \leq t \leq T$. To obtain maximum information from this trajectory, we adopted the following approximation.³³ $D_j(t)$ was treated as a periodic function of time, with a period of T . The integral in the formula for I_j was taken from $-T/2$ to $T/2$ and was averaged over the values obtained while taking different points along the trajectory as the time origin. In this way, at least the dependence on the initial phase of the oscillations at $t = 0$ was eliminated. Within this scheme, one obtains the following while applying a quantum correction to the vibration amplitude^{33,49,62}

$$I_j = \text{const}' \cdot \omega^2 \left| \int_{-T/2}^{T/2} D_j(t) \exp(-i\omega t) dt \right|^2 \quad (2)$$

The spectrum was averaged over the three polarization directions.

In the on-the-fly simulations of the HCl hydrate crystals, the starting points corresponded to molecular structures derived from X-ray experiments,^{23–26} which were reinitialized using QUICKSTEP. Unfortunately, the QUICKSTEP code allows only orthorhombic unit cells. Among the four different hydrates, only the hexahydrate has an orthorhombic unit cell. The rhombohedral unit cell of the monohydrate, with one formula unit per unit cell, was expanded to an orthorhombic cell of dimensions $9.693 \times 8.394 \times 8.784$ Å, with 12 formula units. For the di- and trihydrate, with monoclinic unit cells, such an expansion could be carried out only approximately. That is, the unit cell was multiplied to generate an expanded cell which approximates an orthorhombic shape and which still has dimensions accessible to on-the-fly simulations. The angles of the expanded cell were readjusted to 90°; the angle adjustment was $\sim 2^\circ$ for both crystals. This approximation is supported by reasonable agree-

TABLE 1: Dipole Derivatives μ' with Respect to H Displacement along a OH or OH⁺ Bond, in Debye/Å, for Various Systems; See Section III for Further Explanation

system	μ' BLYP/DZVP	MP2/aug-cc-pVTZ
H ₂ O	0.61	0.46
(H ₂ O) ₂ , proton donor OH	2.66	2.86
OH ⁺ of isolated Zundel ion	9.15	9.40
edge OH of isolated Zundel ion	2.14	
OH ⁺ of H ₂ O⋯H ⁺ ⋯OH ₂ in dihydrate	11.38	
edge OH of H ₂ O⋯H ⁺ ⋯OH ₂ in dihydrate	7.60	
OH ⁺ of H ₂ O⋯H ⁺ ⋯OH ₂ in solution	10.61	
edge OH of H ₂ O⋯H ⁺ ⋯OH ₂ in solution	7.28	
H ₂ O in solution	4.53, 3.12	

ment between the computed and the experimental IR spectra and between the structural properties of the models and the ones derived from the X-ray diffraction. The simulations of the dihydrate employed a cell with 28 formula units, of dimension $15.897 \times 12.055 \times 11.486$ Å. The simulations of the trihydrate employed a cell with eight formula units, of dimension $7.584 \times 10.154 \times 11.084$ Å. For the hexahydrate, the periodic box dimension used for calculation of spectra was $12.6604 \times 6.4528 \times 17.8979$ Å, corresponding to two formula units; some test calculations of structural properties were also carried out on a larger box, $12.6604 \times 12.9056 \times 17.8979$ Å. Simulations of liquid water employed 64 water molecules in a cubic box of a linear dimension of 12.4138 Å. In simulations of HCl solutions, one to four water molecules were replaced by HCl. The duration of the trajectories was typically several picoseconds. For the hydrate solids, the average temperature of the simulations was in the 100–150 K range. In the liquid-phase simulations, the temperature was in the 301–307 K range. Further details on each simulation are given in the respective sections and/or in the figure captions.

The modest level of electronic structure calculations selected for the present study (BLYP/DZVP) was determined by the need to calculate electronic energy and structure at each MD time step. Judging from the comparison to experiment, the results are rather better than expected. It appears that significant cancellation of errors takes place; the errors are due to the BLYP approximation, the limited basis set, and the classical treatment of the nuclear dynamics. For example, the calculated diffusion constant of liquid water at an average temperature of 307 K is 2.4×10^{-5} cm²/sec; the experimental value at 308 K is 2.9×10^{-5} cm²/sec.⁶³ On the other hand, past ab initio simulations of water on the BLYP/QZV2P level yielded a diffusion constant which is four times too low.⁶⁴

To advance the understanding of the IR spectra, dipole derivatives μ' were investigated with respect to O⋯H stretch and analyzed with the help of Wannier centers for the following systems: the water monomer, the water dimer, the gaseous Zundel ion, the H₂O⋯H⁺⋯OH₂ unit in the HCl dihydrate, and protonated water in aqueous solution. For the sake of consistency, all of these calculations were carried out on the same BLYP/DZVP level. However, for the smaller systems, μ' values were also double checked on the MP2/aug-cc-pVTZ level. Table 1 shows the resulting μ' values calculated with BLYP/DZVP and with MP2 for the gaseous water, for the water dimer (with respect to the proton-donor OH stretch), and for the O⋯H⁺ stretch in the Zundel ion. It was judged that this level of agreement is reasonable for qualitative analysis employing Wannier centers calculated with BLYP/DZVP.

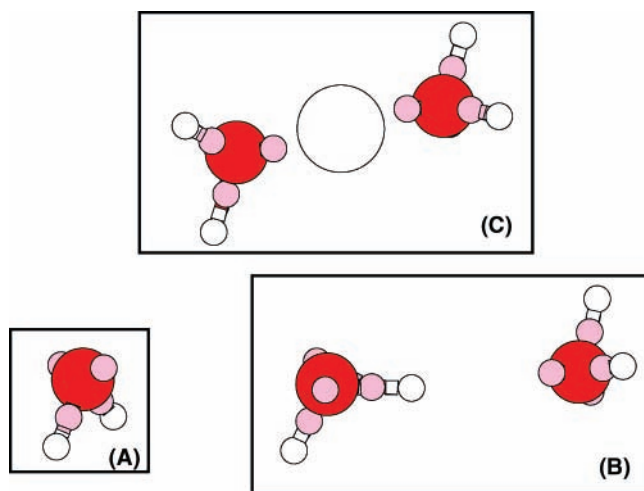


Figure 2. Minimum-energy configurations of the isolated water monomer (A), water dimer (B), and Zundel ion $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$; BLYP/DZVP-level calculation. The large red, small white, and small pink circles denote the O and H atoms and the Wannier centers, respectively. The large white circle in (C) denotes H^+ in the Zundel ion. The Wannier centers represent the “average location” of the valence electron pairs for the purpose of the dipole moment calculation.^{43,44}

III. Understanding Dipole Derivatives with Respect to the OH and $\text{O}\cdots\text{H}^+$ Stretch with the Help of the Wannier Centers

The aim of the present section is to understand qualitatively the intensities of the infrared OH and $\text{O}\cdots\text{H}^+$ stretch bands (which dominate the spectra of the systems of present interest) and their responses to intermolecular bonding. This section explains why hydrogen bonding dramatically increases the OH stretch intensity and why the $\text{O}\cdots\text{H}^+$ stretch band of the protonated dimer in the gas phase and in the condensed phases is unusually intense. As noted above, the analysis is carried out with the help of Wannier centers. In the calculation of the system dipole, Wannier centers can be viewed as discretized “locations” of valence electron pairs.^{43,44,49} Thus, it is enlightening to analyze dipole derivatives with respect to vibrational coordinates in terms of displacements of Wannier centers, which are associated with nuclear vibrations. The numerical results are summarized in Table 1. (For the past effort in this direction with application to the water dimer, see ref 67; that study employed a different “charge–charge flux overlap” analysis and assigned changes in the dipole derivative upon hydrogen bonding to charge transfer and polarization effects.)

Consider first the water monomer. At the present level of the calculation, the OH distance and angle at the minimum energy configuration are 0.983 Å and 102.6°, and the molecular dipole is 2.14 Debye (the reported experimental values, from the compilation in ref 65, are 0.957–0.959 Å, 103.9–105.0°, and 1.855 Debye). The location of the four Wannier centers (Figure 2A) is in accord with chemical intuition. The two “lone pair” centers (W_{lp}) are at a distance of 0.31 Å from the O atoms. The “bonding electron pairs” (W_b) are near the middles of the respective OH bonds, 0.54 Å from the O atom, slightly (0.1 Å) closer to H than to O. The angles formed by the Wannier centers are $W_b\cdots\text{O}\cdots W_b = 101^\circ$, $W_b\cdots\text{O}\cdots W_{lp} = 108^\circ$, and $W_{lp}\cdots\text{O}\cdots W_{lp} = 122^\circ$. Thus, the four “electron pairs” as represented by the Wannier centers adopt an approximately tetrahedral arrangement.

The dipole derivative μ' with respect to OH bond stretching is now considered for the water monomer. The derivative was calculated by displacing a H atom along one of the OH bonds

by ± 0.05 Å and by calculating the corresponding molecular dipole change.⁶⁶ If it were possible to move the H atom without displacing the electronic cloud, $\mu' = 4.80$ Debye/Å would be obtained. In reality, the dipole derivative is ~ 8 times smaller ($\mu' = 0.61$ Debye/Å) since the displaced atom “drags” behind it the electronic cloud. In particular, upon H atom displacement, the nearby bonding electron pair center W_b is displaced in the same direction. Although the displacement of the latter electron pair center is only 1/3 of that of the H atom, it carries double the charge with an opposite sign, thus reducing significantly the change in the total dipole. One may note that the contribution of other electron pairs toward the reduction of μ' is nonnegligible; if this contribution were neglected, μ' would be 2.6 times larger.

It is known that H bonding results in significant increase of the dipole derivative with respect to the OH stretch. To analyze this effect, the water dimer is now considered (Figure 2B). As intuitively expected, the proton-donor OH bond points approximately toward one of the acceptor lone pair Wannier centers. As a result of bonding, this lone pair center is pulled away from its O atom. (The $W_{lp}\cdots\text{O}$ distance is 0.33 Å, 0.02 Å larger than that for the monomer.) On the other hand, the bonding pair Wannier center of the donor OH moves 0.02 Å toward its O atom and away from H, a result which can be readily rationalized by electronic repulsion.

As the donor OH is stretched, its bonding electron pair center follows the H atom to a lesser extent than that in the monomer (24 rather than 34% of the H displacement), apparently due to the electrostatic repulsion from the acceptor lone pair. On the other hand, the acceptor lone pair is displaced slightly toward the approaching H atom, amplifying the change in the dipole. Therefore, now, the dipole derivative with respect to the bonding H displacement is much larger than that in the monomer, -2.66 Debye/Å, 55% of the value which would be obtained solely from the “bare” proton displacement. The effects of the electronic clouds of the two dimer molecules on the dipole derivative cancel to a significant extent since the H atom drags the electronic cloud of the acceptor toward it and the electronic cloud of the donor behind it. If we consider the μ' component along the donor OH bond (which is equal to 2.59 Debye/Å and amounts to 97% of the total μ'), the different contributions can be written as 4.8 Debye/Å from “bare” proton displacement minus 3.10 Debye/Å from the donor electronic cloud plus 0.89 Debye/Å from the acceptor electronic cloud.

An isolated Zundel ion is then considered (Figure 2C). The asymmetric stretch of the central proton corresponds to an unusually intense IR absorption, as demonstrated in the past by calculations^{36,68,69} and by experiment.^{17–19} In accord with chemical intuition, the central proton is bonded to each O atom via one of its lone pairs. At equilibrium, the $W_{lp}\cdots\text{O}$ distance is 0.43 Å, significantly larger than the values for either the water monomer (0.31 Å) or the water dimer (0.33 Å).

Displacement of the central Zundel proton results in a dipole change along the $\text{O}\cdots\text{H}$ direction. The corresponding dipole derivative with respect to proton displacement $\mu' = 9.15$ Debye/Å is nearly two times larger than the value which would be obtained from “bare” proton displacement! This large amplification is due to the concurrent electron-cloud displacement. Three-quarters of the amplification is due to the electron pairs of the two O atoms, which form the bond to the central proton. As the proton moves toward one of the lone pairs, the corresponding $\text{H}^+\cdots\text{O}$ bond is strengthened, and the electron pair is displaced toward the proton, amplifying the dipole. At the same time, the second $\text{H}^+\cdots\text{O}$ bond is stretched and

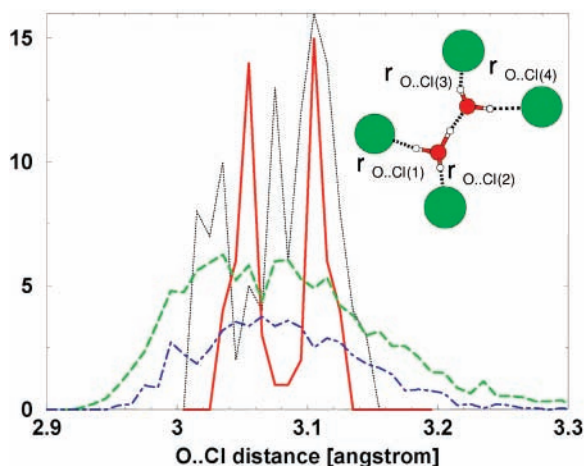


Figure 3. The inset displays a solvated $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit in the crystal dihydrate structure. Cl, O, and H correspond to large green, small red, and small white circles, respectively. The black dotted curve represents the computed distribution of the near-neighbor $\text{O}\cdots\text{Cl}$ distances $r_{\text{O}\cdots\text{Cl}(i)}$, $i = 1, 4$ (see inset), averaged over a 1.8 ps trajectory of the crystal dihydrate at an average temperature of 120 K. The red solid curve represents the distribution of averages $\langle r_j \rangle$, $j = 1, 2$ of the two near-neighbor $\text{O}\cdots\text{Cl}$ distances of the different water molecules ($r_1 = 0.5(r_{\text{O}\cdots\text{Cl}(1)} + r_{\text{O}\cdots\text{Cl}(2)})$, ($r_2 = 0.5(r_{\text{O}\cdots\text{Cl}(3)} + r_{\text{O}\cdots\text{Cl}(4)})$); this bimodal distribution demonstrates the asymmetry of the average solvation environment of the two ends of the “semi-hydronium” unit. The green dashed and blue dot-dashed curves represent the same two distributions as the two previous ones for the distances averaged over 0.1 ps sections of the trajectory rather than over the entire trajectory. Note that the latter distributions are not bimodal.

weakened, resulting in electron pair displacement toward its oxygen and away from the central proton, an effect which doubles the μ' amplification.

The dipole derivative with respect to the edge water OH stretch in the Zundel ion is 2.14 Debye/Å, significantly smaller than the derivative with respect to the central proton but still 3.5 times larger than the value for the isolated water monomer. The displaced proton of OH now “drags” behind it only the lone pair of the corresponding OH bond rather than the entire H_2O electronic cloud, as in the case of the monomer.

The dipole derivatives in the crystal HCl dihydrate are now considered (at the minimum-energy configuration). The calculated dipole derivative with respect to the $\text{O}\cdots\text{H}^+$ stretch in the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit is even larger than that in the gaseous Zundel ion, 11.38 Debye/Å. The contribution of the protonated dimer unit itself, 9.44 Debye/Å, is similar to that of the gaseous Zundel ion discussed above. Most (86%) of the amplification with respect to the gas phase is due to the electrons of the four near-neighbor Cl^- ions, which solvate the protonated dimer unit. As discussed in the next section, the unit is somewhat asymmetric, with the central proton closer by 0.17 Å (at minimum) to one of the neighboring O atoms than to the other. Interestingly, the contribution to the μ' amplification of chloride ions adjacent to the less well solvated $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ (Cl(3) and Cl(4) in the inset of Figure 3) edge is somewhat larger ($\sim 20\%$) than that of the chloride ions at the better-solvated edge (Cl(1) and Cl(2) in the inset of Figure 3).

The dipole derivative with respect to OH stretch of the (better-solvated) water at the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit edge is also large, 7.60 Debye/Å. Interestingly, slightly more than half of this value is due to the electrons of the near-neighbor chloride. That is, displacement of the proton toward Cl^- or away from it affects strongly the electrons of the polarizable anion, resulting in the calculated μ' amplification.

Finally, we consider an acid solution with two fully ionized HCl molecules and 62 water molecules in a cubic box of dimension 12.4138 Å. A configuration was selected from an ab initio molecular dynamics run at a mean temperature of 321 K. In this configuration, one of the cations approached a Zundel-like configuration, with an $\text{O}\cdots\text{O}$ distance of 2.46 Å and the two $\text{O}\cdots\text{H}^+$ distances of 1.13 and 1.34 Å, respectively. The change of the system dipole was calculated upon displacing the proton along the shorter $\text{O}\cdots\text{H}^+$ vector (which is nearly collinear with the $\text{O}\cdots\text{O}$ vector, with an $\text{O}\cdots\text{H}^+\cdots\text{O}$ angle of 166°). The corresponding dipole derivative was again very large, 10.61 Debye/Å, and similar to the dihydrate value. Again, the amplification with respect to the bare proton value originated predominantly from the electrons of the two water molecules comprising the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit. The respective contributions to μ' can be written as the bare proton value of 4.8 Debye/Å plus 1.66 Debye/Å from the electrons of the water molecule nearer to the proton plus 2.67 Debye/Å from the electrons of the second water molecule plus 0.57 Debye/Å from four near-neighbor water molecules and a chloride ion that are adjacent to the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit plus 0.91 Debye/Å from the remaining solution. It is of interest to note that the water molecule more weakly bound to the proton in the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit contributes more to μ' than the more strongly bound molecule. However, unlike the case of the dihydrate, most of the μ' amplification beyond the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit does not originate from the adjacent solvating molecules; rather, it appears to be a cumulative long-range response of the solution electrons.

The dipole derivative was also examined with respect to one of the edge OH bonds of the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit in solution, of length 1.05 Å. The resulting μ' value is 7.28 Debye/Å. The contribution from the water molecule containing the OH is close to the bare proton value; the reduction due to its electrons is modest. The amplification of μ' with respect to the bare proton value is due predominantly to the electrons of the water molecule to which OH is H-bonded; the contribution of these electrons to μ' is 2.08 Debye/Å.

Finally, dipole derivatives were calculated with respect to two OH bonds of the four-coordinated water molecules selected from the solution. The corresponding dipole derivatives were 4.53 and 3.12 Debye/Å. The larger dipole derivative is associated with the shorter hydrogen bond (the corresponding $\text{O}\cdots\text{O}$ distances to the acceptor water molecules are 2.82 and 2.91 Å). The contributions of the entire water molecule with all of its electrons to the two dipole derivatives are 2.76 and 2.10 Debye/Å, indicating $\sim 50\%$ μ' reduction by electrons with respect to the bare proton value. Most of the additional contribution to μ' (1.10 and 0.75 Debye/Å) originates from the electrons of the acceptor water molecule to which the OH is bonded. The μ' amplification by the proton-acceptor electrons is similar to the one obtained in the water dimer.

Summarizing, the dipole derivative μ' with respect to the proton displacement in the OH and $\text{O}\cdots\text{H}^+$ bonds can be either reduced or amplified with respect to the bare-proton displacement by the concurrent displacements of the electronic cloud. In the case of H-bonded OH, the electron pair toward which the proton is displaced moves in the opposite direction, amplifying the dipole derivative. The bonding electron pair of the OH follows the displacement of the proton, thus reducing the μ' value. In the case of the Zundel ion, the electron clouds of both water molecules move in the opposite direction from the proton displacement, resulting in the very large dipole derivative.

Structures and IR spectra of the different HCl hydrates will be now discussed in detail.

IV. Monohydrate: Summary of Results

X-ray investigation of the monohydrate²³ revealed a structure composed of H_3O^+ and Cl^- . X-ray diffraction patterns indicated hexagonal sheets of Cl^- in a periodic arrangement. The data were interpreted initially in terms of a ferroelectric structure with each H_3O^+ straddling three Cl^- ions in a sheet. However, this structure corresponds to a single orientation of the hydronium, while the X-ray data indicated an element of disorder corresponding to two possible orientations for the hydronium ions. The experimentalists interpreted the results in terms of a disordered structure in which three-coordinated hydronium ions can bond to Cl^- sheets from either side. Later computational studies^{37,38} demonstrated instability of the suggested disordered structure.

The HCl monohydrate structure was addressed by us in a recent study.³³ Alternative molecular arrangements were explored. The study included searches for possible crystal structures, calculations of their X-ray diffraction patterns, and on-the-fly simulations of their IR spectra.

Searches for alternative crystal structures yielded a number of antiferroelectric models, with a Cl^- frame similar to that derived from X-ray diffraction. Still, the best agreement between the computations and the experimental data (the diffraction patterns and the IR spectra) was obtained for the original ferroelectric structure, which thus appears to be the dominant component of the crystal. The presence of distinct hydronium orientations is attributed to the presence of ferroelectric domains whose dipoles cancel one another. Such domains commonly occur in ferroelectric substances. In the absence of domains, one would obtain a ferroelectric solid enclosed by positively and negatively charged surfaces. The surface charges would generate a macroscopic electric field within the solid, which would substantially raise the energy of the material.⁷⁰ It was shown that different domains can be accommodated in a continuous Cl^- frame at a modest energy cost. One of the antiferroelectric models appears to serve as a transition structure between the different domains.

In addition, an on-the-fly study revealed strikingly anharmonic vibrational dynamics of the monohydrate system.³⁴ The measured FTIR spectrum, displayed in Figure 1, is dominated by an intense OH stretch band that peaks at 2553 cm^{-1} with accompanying high-frequency sub-bands. This band complex could be reproduced quite well by the on-the-fly simulation. The calculation shows that the band does not reflect the vibrational density of frequencies. It was found that the peak originates from specific sections of an anharmonic trajectory involving hydronium ions and lattice vibrations. Lattice motions are an order of magnitude slower than the OH stretch vibrations. The OH stretch intensity and frequency vary as a function of intermolecular configurations probed by the lattice motion. The observed infrared OH stretch peak originates predominantly from those hydronium ions which happen to oscillate in the direction of one of the neighboring Cl^- ions, along the bisector of the respective $\text{Cl}^- \cdots \text{Cl}^- \cdots \text{Cl}^-$ angle; when the corresponding $\text{O} \cdots \text{Cl}$ distance is close to the minimum, the OH bond nearest to Cl^- acquires a large oscillating dipole in conjunction with a low vibration frequency, resulting in the observed 2553 cm^{-1} feature.

Finally, the amorphous analogue of the HCl monohydrate crystal was explored both experimentally and computationally.³⁵ The composition of amorphous hydrates with a HCl/ H_2O ratio

close to 1 was shown to depend strongly on experimental preparation conditions, as evidenced by the variability of the spectra. Low temperature, $\sim 15\text{ K}$, deposits obtained in the presence of excess HCl appear to be largely molecular. Heating to $\sim 100\text{ K}$ results in a largely ionic solid dominated by H_3O^+ and Cl^- ions, which includes, however, a significant fraction of unreacted molecules; the corresponding spectrum is remarkably similar to that of the crystal monohydrate. This is in contrast to the nominally 1:1 HCl/ H_2O deposit, whose spectrum is quite distinct, and indicates enrichment in Zundel ions. Direct 1:1 deposition appears to result in a solid which is deficient in HCl; that is, the resulting HCl/ H_2O ratio is less than 1.

V. Crystal HCl Dihydrate

The crystal dihydrate structure, derived from X-ray diffraction, was described as composed of Zundel units, solvated by chloride ions,²⁴ with an $\text{O} \cdots \text{O}$ distance of 2.41 \AA . The location of heavy atoms (Cl, O) derived from X-ray diffraction is expected to be much more reliable than that of the H atoms.

The computed near-neighbor $\text{O} \cdots \text{O}$ distance was 2.44 \AA for both the minimum energy structure and the trajectory average; this value is somewhat larger than the X-ray value but similar to the one obtained in the CPMD study of Sillanpaa and Laasonen (2.45 \AA).³⁸ However the protonated water dimer unit in our model structure is clearly asymmetric and can be described as "semi-Zundel". The central proton is closer by 0.17 \AA (at minimum), or 0.13 \AA (average over trajectory), to one of the neighboring O atoms than to the other. This result is qualitatively consistent with the asymmetry of the solvating environment of the protonated water dimer unit. The near-neighbor $\text{O} \cdots \text{Cl}$ distances derived from X-ray diffraction for the more strongly and more weakly solvated H_2O were 3.04 and 3.06 \AA and 3.09 and 3.10 \AA , respectively. The computed distribution of near-neighbor $\text{O} \cdots \text{Cl}$ distances, averaged over the trajectory, appears consistent with the diffraction experiment; the distribution is multimodal due to presence of geometrically inequivalent $\text{O} \cdots \text{Cl}$ distances in the finite duration trajectory and includes peaks ranging from 3.02 to 3.10 \AA (Figure 3, dotted). The asymmetry of solvation of the two water molecules is seen more clearly from the distribution of averages of the two near-neighbor $\text{O} \cdots \text{Cl}$ distances of the different water molecules; as seen in Figure 3 (solid curve), this distribution is clearly bimodal. However, the solvation environment of each $\text{H}_2\text{O} \cdots \text{H}^+ \cdots \text{OH}_2$ unit is not static but rather undergoes continuous modulation due to lattice vibrations, the fact which, as explained below, has a rather dramatic effect on the spectrum. Thus, for example, the distribution of mean $\text{O} \cdots \text{Cl}$ distances, averaged over 100 consecutive MD steps rather than over the entire 1.8 ps trajectory, is much broader and unimodal (Figure 3, dashed and dot-dashed lines).

The computed IR spectrum of the dihydrate is shown in Figure 4A. The major features in the computed spectrum have experimental counterparts; the computed spectrum has some extra structure with respect to experiment, presumably due to the limited duration of the trajectory and the absence of quantum nuclear effects. The band at $\sim 3000\text{ cm}^{-1}$ originates from the OH stretch of the two sides of the $\text{H}_2\text{O} \cdots \text{H}^+ \cdots \text{OH}_2$ unit; the high- and the low-frequency ends of the band originate from the more weakly and more strongly solvated H_2O , respectively. The calculation overestimates the intensity ratio of the low- and high-frequency sub-bands of this feature. The intense features below 2100 cm^{-1} , which are absent in the monohydrate, originate from the central proton of the $\text{H}_2\text{O} \cdots \text{H}^+ \cdots \text{OH}_2$ unit. The integrated intensity ratio of the OH stretch and the proton

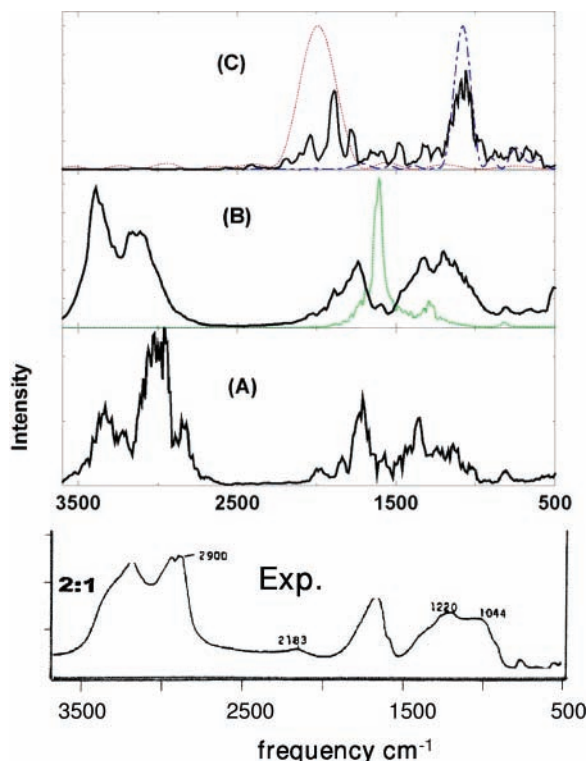


Figure 4. Bottom panel: Experimental spectrum of the crystal HCl dihydrate, same as that in Figure 1. (A) Spectrum of the dihydrate, calculated from the Fourier transform of the system dipole for an 8 ps trajectory at an average temperature of 154 K. (B) The black solid curve represents an average Fourier transform of all of the OH bonds. For the center O···H⁺ distance of the H₂O···H⁺···OH₂ unit, that distance which is shorter at equilibrium was used. The green dotted curve represents the average Fourier transform of all of the HOH angles at the two sides of the protonated dimer units. (C) The black solid curve represents the Fourier transform of the O···H⁺ distance for one of the H₂O···H⁺···OH₂ units, as shown in Figure 5, top. The red dotted and blue dot-dashed curves represent Fourier transforms of trajectory sections marked “bottom” and “top”, respectively, in Figure 5. The spectra were calculated with 10 cm⁻¹ resolution. The solid-line spectra were subsequently averaged over 50 cm⁻¹ intervals.

band complex is only 1.6, despite the fact that there are four times more OH bonds than protons. In this system, the shape of the O···H stretch density of frequencies (i.e., the average Fourier transform of all of the OH bonds, Figure 4B) is fairly similar to the dipole spectrum (Figure 4A). The experimental gross structure of the proton band complex, a feature at ~1700 cm⁻¹, and a broad band below 1500 cm⁻¹ is reproduced qualitatively by the calculation. The origin of the two proton features is now considered. Past studies of the gaseous Zundel ion suggest assignment of the low-frequency band to the asymmetric proton stretch, and the ~1700 cm⁻¹ feature is assigned to water bending, with the intensity amplified by coupling to the central proton motion.⁶⁸ However, analysis of on-the-fly trajectories indicates that the dynamics of the protonated dimer unit in our condensed-phase system differs considerably from that of the gaseous Zundel ion.

The top panel of Figure 5 shows a sample trajectory of a central proton in a H₂O···H⁺···OH₂ unit. In sections of the trajectory, the shorter of the two O···H⁺ distances oscillates around 1.1 Å, and the longer one oscillates around 1.35 Å. During these sections (such as the one marked “bottom”), the protonated water dimer can be described as containing a distorted hydronium ion, connected via a strong hydrogen bond to a water molecule. During other sections of the trajectories (such as the one marked “top” in Figure 5), the proton is

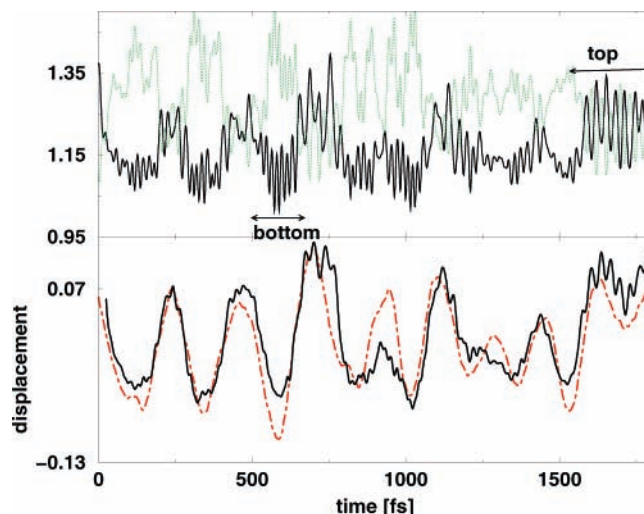


Figure 5. Top panel: time dependence of the two O···H⁺ distances (in Å) for one of the protons in the dihydrate. Bottom panel: The solid curve represents the O···H⁺ distance, which is shorter on average than the black curve of the top panel, averaged over fast oscillations. Bottom panel: The dot-dashed curve represents the asymmetric O···Cl stretch coordinate r_{asy} for the same H₂O···H⁺···OH₂ unit; $r_{\text{asy}} = (r_{\text{O}\cdots\text{Cl}(1)} + r_{\text{O}\cdots\text{Cl}(2)}) - (r_{\text{O}\cdots\text{Cl}(3)} + r_{\text{O}\cdots\text{Cl}(4)})$, where the indices 1 and 2 refer to the near-neighbor distances for the hydronium-like edge of the unit and 3 and 4 refer to the near-neighbor distances for the water-like edge (see inset of Figure 3). The two bottom plots were shifted with respect to each other to emphasize the correlation.

transferred toward the midpoint of the dimer unit, which then resembles a symmetric Zundel ion; during the latter sections, the frequency of O···H⁺ stretch is relatively low; see the Fourier transforms of the O···H⁺ distance in the “top” and “bottom” trajectory sections, shown in Figure 4C.

It is seen in Figure 5 that the proton motion occurs on two time scales. Fast oscillations take place around a temporary “equilibrium distance” r_{eq} , which fluctuates on a much longer time scale of a few hundred femtoseconds (fs). The fluctuations of r_{eq} are strongly coupled to the fluctuations of the solvating environment, most notably, to the asymmetric lattice vibration $r_{\text{asy}} = (r_{\text{O}\cdots\text{Cl}(1)} + r_{\text{O}\cdots\text{Cl}(2)}) - (r_{\text{O}\cdots\text{Cl}(3)} + r_{\text{O}\cdots\text{Cl}(4)})$, where the indices 1 and 2 refer to near-neighbor O···Cl distances for the hydronium-like edge of the unit and 3 and 4 refer to near-neighbor distances for the water-like edge. The trajectory of r_{asy} is displayed in Figure 5 (dot-dashed curve in the bottom panel), together with r_{eq} (solid curve); the correlation between the two is apparent. The frequency of the r_{asy} lattice vibration is ~145 cm⁻¹. For other protonated dimer units, one observes similar trajectories, with preferential proton bonding to one of the O atoms and occasional periods of more egalitarian proton sharing. Sometimes, one observes full proton transfer to the other O atom, but these events are relatively brief and infrequent.

In other words, the proton spectrum reflects the dynamics of the solvating environment. In the limit of an asymmetric environment, in which one end of the protonated dimer is much nearer to its solvating chloride ions than the other, the dimer resembles a H-bonded hydronium–water pair and absorbs infrared radiation at ~1700 cm⁻¹. In the other limit, temporary “symmetrization” of the solvating environment takes place; the proton is displaced toward the center of the unit, which becomes Zundel-like, and absorbs strongly in the 1000–1100 cm⁻¹ regime. The broad range of the solvation states spanned by these two limits is reflected by the large width of the proton band.

In both the experimental and the computed dihydrate spectrum, the proton band complex below 2100 cm⁻¹ can be

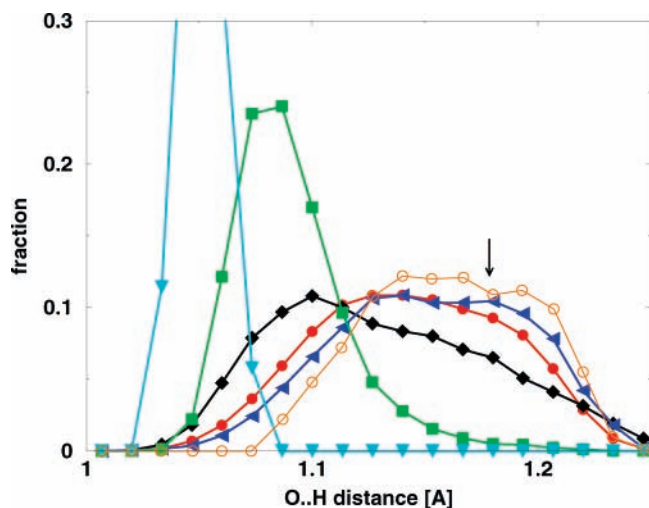


Figure 6. Distribution of the $\text{O}\cdots\text{H}^+$ distances. Definition of the distances: The triangle left and filled circle represent the distance between O and the central proton of the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit in the trihydrate and the dihydrate, respectively. The shorter of the two distances was used. The triangle down, the square, and the diamond represent the longest OH distance of the H_3O^+ unit in the monohydrate, hexahydrate, and water, respectively. The large peak of the monohydrate was truncated to emphasize the remaining plots. In the aqueous solution, the proton was assigned to the instantaneously near-neighbor H_2O molecule (see text for further explanation) from a 7 ps simulation of a solution of 1 HCl in 63 water molecules at an average temperature of 301 K. All distributions are from instantaneous configurations along the trajectories. The exception is the curve for the trihydrate with unfilled circles, which is a distribution of averages of the $\text{O}\cdots\text{H}^+$ distances over consecutive 30 fs stretches of the trajectory, on the order of the vibrational period of the central proton. The arrow is explained in section VIII B.

described as a broad doublet with substructure (Figure 4). The origin of the doublet is of some interest since, as seen in Figure 6, the distribution of $r(\text{O}\cdots\text{H}^+)$ distances in the dihydrate is broad but unimodal. Thus, when integrated over the simulation, the distribution of proton states appears continuous rather than bimodal. The apparent explanation of the two distinct features in the proton spectrum can be obtained by noting that the Fourier transform of the bending coordinate of water at the edges of the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ units peaks at the “hole” in the proton band at $\sim 1600\text{ cm}^{-1}$. Thus, rather than viewing the proton band as a doublet, one should view it as a single broad band originating from the H^+ asymmetric stretch, with an “Evans’s hole”^{71,72} in the middle, originating from the bending. The physical situation corresponds to a vibrational excitation (in our case, an asymmetric proton stretch of the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ units) associated with a broad frequency range and a large dipole derivative. Within the corresponding bandwidth, another vibrational mode (in our case, water bending) is associated with a much narrower frequency span and a much smaller dipole derivative. Coupling results in compound vibrational excitations. In the vicinity of the bending frequency, the excited states are dominated by the “dark” bending contribution, while the stretch-dominated states are pushed to higher and lower frequencies by the coupling. The result is low excitation intensity in the vicinity of the bending frequency, and an “Evans’s hole” appears in the spectrum.

Additional insight into proton correlation with the fluctuating solvation environment is presented in Figure 7. The top panels show contour plots of instantaneous values of $r(\text{O}\cdots\text{H}^+)$ against the asymmetric solvation coordinate r_{asy} (left, top) and against $r_{\text{O}\cdots\text{O}}$ (right, top). Both plots display some correlation, which however appears somewhat more pronounced for r_{asy} than for

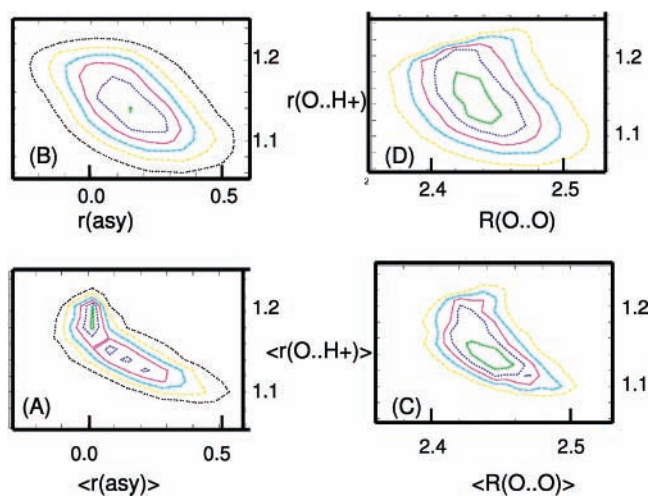


Figure 7. Correlation diagrams of system coordinates in the dihydrate, obtained from all configurations of an 8 ps trajectory at an average temperature of 154 K. All coordinates are in angstrom units. Top panels: contour plots of instantaneous values of $r(\text{O}\cdots\text{H}^+)$ against the asymmetric solvation coordinate r_{asy} (B) and against $r_{\text{O}\cdots\text{O}}$ (D). For each $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ configuration, the shorter $r(\text{O}\cdots\text{H}^+)$ distance was used. Bottom panels display similar contour plots but with coordinate values averaged over consecutive 30 fs stretches of the trajectory (on the order of the proton oscillation period); thus, correlations of the “temporary equilibrium distance” $r_{\text{av}} = \langle r(\text{O}\cdots\text{H}^+) \rangle$ are examined; $r_{\text{asy}} = (r_{\text{O}\cdots\text{Cl}(1)} + r_{\text{O}\cdots\text{Cl}(2)}) - (r_{\text{O}\cdots\text{Cl}(3)} + r_{\text{O}\cdots\text{Cl}(4)})$, where the indices 1 and 2 refer to the near-neighbor distances for the hydronium-like edge of the unit and 3 and 4 refer to the near-neighbor distances for the water-like edge (see inset of Figure 3). The two bottom plots were shifted and rescaled with respect to each other to emphasize the correlation. Contour range, spacing: (A) 0.006–0.036, 0.006; (B) 0.003–0.018, 0.003; (C) 0.0038–0.019, 0.0038; (D) 0.002–0.01, 0.002.

$r_{\text{O}\cdots\text{O}}$. The distributions maximize at values near the minimum-energy configuration. The bottom panels display similar contour plots but with coordinate values averaged over consecutive 30 fs stretches of a trajectory (on the order of the proton oscillation period); thus, structural correlations of the “temporary equilibrium distance” of $r(\text{O}\cdots\text{H}^+)$ are examined. The bottom-left panel is of particular interest. Unlike the top panel, the distribution does not display a maximum at the asymmetric minimum-energy $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ configuration; rather, it maximizes at the symmetric Zundel-like configuration, with a substantial tail toward hydronium-like configurations.

One may note that the asymmetric character of the protonated water dimer obtained in the present study is more pronounced than that obtained in the CPMD study of ref 38. There, the average difference in the two near-neighbor $\text{O}\cdots\text{H}^+$ distances was only $\sim 0.04\text{ \AA}$ rather than 0.13 \AA , as obtained here. We do not know the reason for that difference; some of the deviation may be due to our use of a slightly distorted crystal structure in order to fit the model into an orthorhombic simulation box (see Computational Details). However, the reasonable agreement between computed and measured IR spectra (Figure 4) suggests that the present results are at least qualitatively correct. Also, a distribution of $\text{O}\cdots\text{Cl}^-$ distances computed here appears consistent with X-ray data (see above), and the asymmetry of the Cl^- solvation shell (which was also derived from X-ray diffraction) is the reason for the average asymmetry of the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit. Reference 38 employed a different on-the-fly code, with an expanded experimental unit cell containing 8 and 16 formula units. The dipole spectrum was not calculated in that study; their reported (isotopically shifted)

proton power spectrum for the deuterated system includes a doublet below 2100 cm^{-1} similar to the one shown in Figure 4B.

One aspect of the dihydrate spectroscopy—the isotopic substitution effect—was already examined by us in a past publication.³⁶ Analysis of experimental IR spectra as a function of the H/D ratio showed that the central position in the protonated dimer is occupied preferentially by H rather than by D. A similar effect was reported in ref 30 for another acid hydrate system. Computational analysis employing diffusion Monte Carlo, in fact, demonstrated a H preference for the central position in the gaseous Zundel ion. A similar demonstration in the dihydrate system would require inclusion of nuclear quantum mechanical effects, for example via path integral Monte Carlo simulation.^{13,37} Such studies will be pursued in the future and will be applied additionally to the analysis of isotopic substitution effects on the OH stretch band of the different hydrates. The OH stretch bands of the dihydrate and of the other hydrates as well are structured due to the presence of inequivalent lattice sites, and isotopic fractionation at the different sites was already demonstrated spectroscopically (using the dependence of the sub-band intensities on the H/D ratio³⁶).

VI. HCL Trihydrate

X-ray study of this crystal revealed chains with protonated dimer units $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ interspersed by water molecules.²⁵ The protonated dimer was described as a Zundel ion with a short O \cdots O distance of 2.43 Å. At each end of $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$, water donates a hydrogen that bonds to the solvating H_2O along the chain and another hydrogen that bonds to Cl^- . The solvating water molecule acts as a proton donor to two chloride ions. The computed average O \cdots O distances along the chain are 2.46, 2.67, and 2.69 Å, respectively, corresponding to the short bond and the two normal hydrogen bonds at the two ends of $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$; the corresponding values derived from X-ray diffraction are 2.43, 2.65 and 2.75 Å, respectively.

Similar to the dihydrate case, the solvating environment of the protonated dimer is asymmetric; the O \cdots O and O \cdots Cl $^-$ distances at the two ends of the protonated dimer are 2.65 and 3.01 Å and 2.75 and 3.05 Å, respectively. This asymmetry appears underestimated in the present model; as noted above, the calculated difference between the short and the long O \cdots O distance is 0.02 rather than 0.10 Å. The calculated mean difference between the two O \cdots H $^+$ distances in the protonated dimer unit is only 0.03 Å. As explained below, the asymmetry resulting from dynamic fluctuations of the environment is much larger than this mean difference.

The spectrum of the trihydrate is displayed in Figures 1, 8, and 9. As seen in Figure 1, the general shape of the trihydrate spectrum appears to be related to that of the dihydrate. Bond trajectories exemplifying the corresponding vibrational dynamics are shown in Figure 10.

The trihydrate vibration dynamics is more fluxional than that of the dihydrate, the apparent reason being the presence of the H-bonded water chains. Recall that in the case of the dihydrate, the proton displayed much of the time preference for one side of the protonated dimer unit, with occasional bouts of more egalitarian proton sharing between the two water molecules. In the case of the trihydrate, the proton forms temporary “hydronium” units with the water molecules on either side of the protonated water dimer. This proton dynamics is demonstrated in Figure 10B. The proton oscillates for a fraction of a picosecond near one of the O atoms (at a distance of ~ 1.1 Å), and then, a quick transition to the vicinity of the other O atom

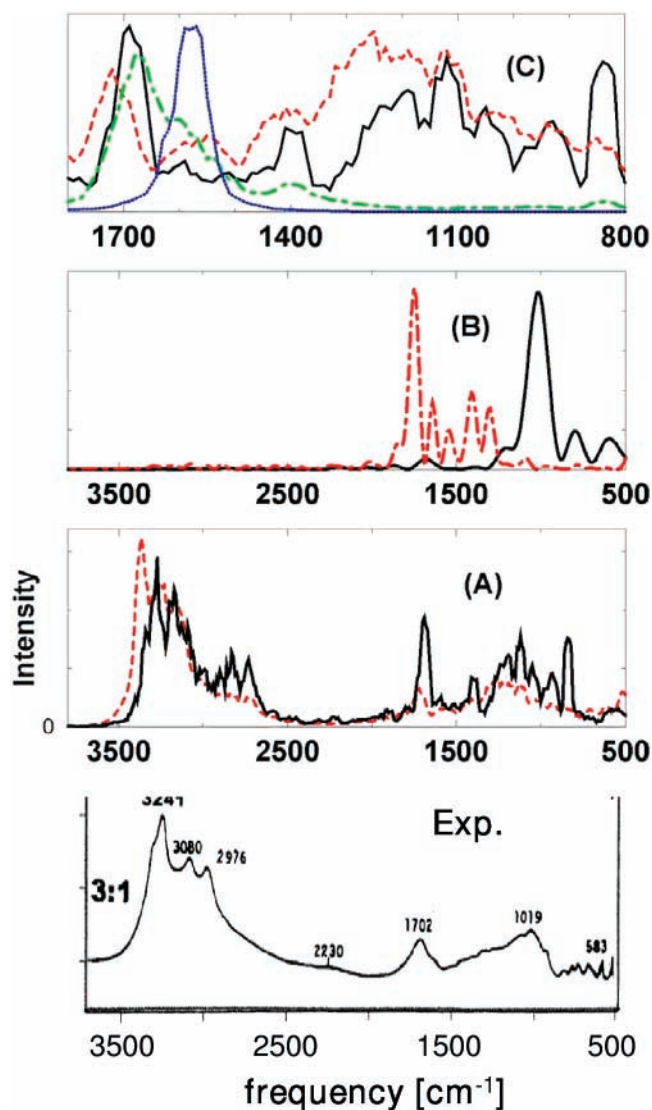


Figure 8. Bottom panel: Experimental spectrum of the crystal HCL trihydrate, same as Figure 1. (A) The black solid curve represents the spectrum of the trihydrate, calculated from the Fourier transform of the system dipole, for a 3 ps trajectory at a mean temperature of 117 K. The red dotted curve represents the OH density of frequencies, calculated as an average Fourier transform of all OH bonds. For the center O \cdots H $^+$ distance of the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ units, that distance which is shorter at equilibrium was used. (B) Fourier transforms of sections of the trajectory of the shorter of the two O \cdots H $^+$ distances for one of the protonated dimer units; the respective sections are marked by arrows in Figure 10B. Solid and dot-dashed spectra correspond to trajectory sections at 1100–1400 and 1600–2000 fs, respectively. (C) Analysis of contributions to the dipole spectrum in the 800–1800 cm^{-1} range. The black solid curve represents the dipole spectrum; the red dotted curve corresponds to the average Fourier transform of all OH bonds; the green and blue curves represent the average Fourier transform of the HOH bending in the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ units and in solvating water, respectively.

occurs. Due to the asymmetry of the average solvating environment, there is some preference for one of the sides, but both are visited. As in the case of the dihydrate, the proton responds to the temporary solvation environment of the protonated water dimer, as determined by the phase of the local lattice motion. Similarly to the dihydrate, it is found that the temporary “equilibrium distance” of the proton fast oscillations correlates strongly with the vibrations of the asymmetric solvation coordinate $r_{\text{asy}} = (r_{\text{O}\cdots\text{Cl}(1)} + r_{\text{O}\cdots\text{O}(1)}) - (r_{\text{O}\cdots\text{Cl}(2)} + r_{\text{O}\cdots\text{O}(2)})$, where the indices 1 and 2 refer to the near-neighbor distances for the two ends of the protonated dimer unit; see panels A and

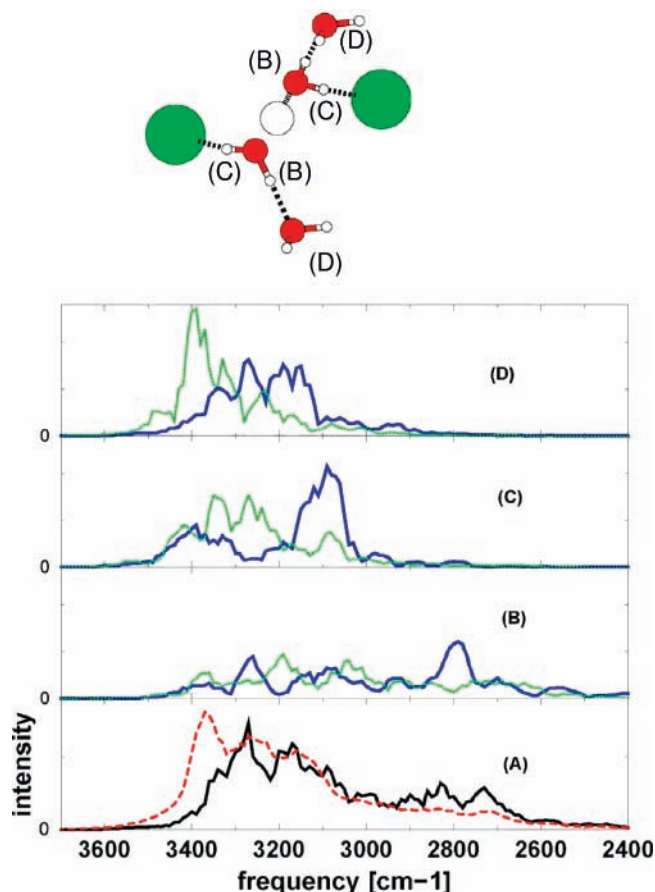


Figure 9. Bottom: The black solid curve is the spectrum of crystal trihydrate, calculated from the Fourier transform of the system dipole, in the OH stretch region. The red dotted curve corresponds to the average Fourier transform of all of the OH bonds. (B–D) Fourier transforms of bond trajectories for different types of OH bonds. (B) OH bonds at the edge of $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$, for bonds which are H-bonded to water along the chain. (C) OH bonds at the edge of $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$, for bonds which are H-bonded to halide ions. (D) OH bonds of solvating H_2O . The dotted green and the solid blue curves refer to the more weakly and more strongly H-bonded OH, respectively. The inset at the top displays a section of the trihydrate crystal structure. Cl, O, and H correspond to large green, medium red, and small white circles, respectively. The large white circle denotes the proton at the center of the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit. The location of the OH bonds (B–D) is marked in the inset.

B of Figure 10. The frequency of proton oscillation in the “ $\text{H}_3\text{O}^+\cdots\text{H}_2\text{O}$ ” configuration, that is, at the extrema of r_{asy} , is relatively high, $\sim 1700\text{ cm}^{-1}$; see Figure 8B. A peak around this frequency is seen both in the density of the $\text{O}\cdots\text{H}$ frequencies and in the IR spectrum (dashed and solid curves, respectively, in Figure 8A). Occasionally, the solvating environment of the protonated dimer becomes approximately symmetric for several hundred femtoseconds, as in the section of the trajectory at $\sim 1200\text{ fs}$ in Figure 10A,B; during this section, the amplitude of the r_{asy} oscillation is especially small. During that time, proton sharing takes place, and the dimer accesses a Zundel-like configuration. The proton frequency drops to $\sim 1000\text{ cm}^{-1}$ (Figure 8B, black curve), with a concurrent significant increase in the proton infrared absorption intensity, resulting in an intense broad IR band in the $800\text{--}1400\text{ cm}^{-1}$ range (Figure 8A). The Zundel band has an experimental counterpart peaking at 1019 cm^{-1} and decreasing gradually toward high frequency (Figure 8, bottom panel).

One may raise a question of which percentage of protonated dimer dynamics represents a “true Zundel” configuration, that

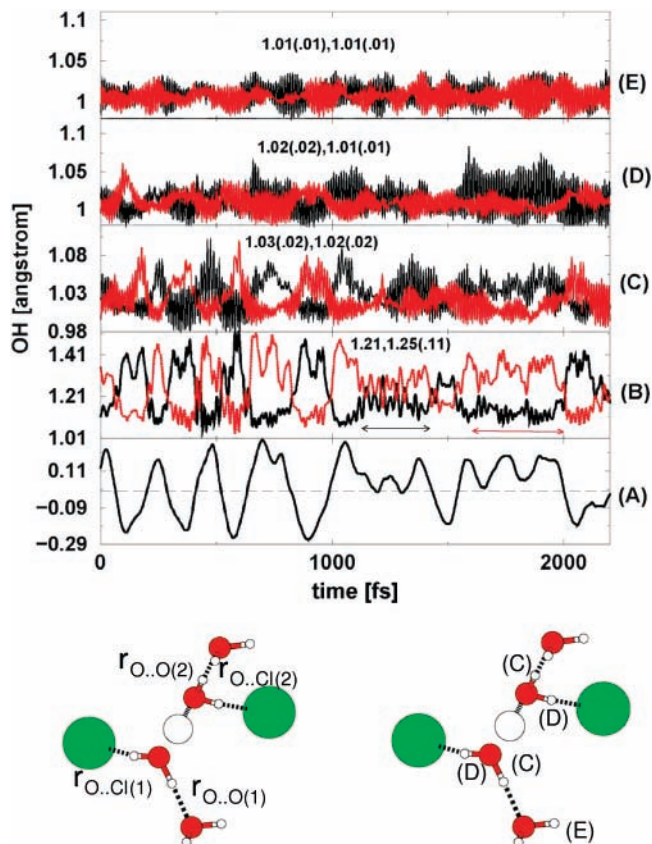


Figure 10. The two insets at the bottom display a section of the trihydrate crystal structure. Cl, O, and H are marked green, red, and white, respectively. The large white circle denotes the proton at the center of the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit. (A) The trajectory of the asymmetric solvation coordinate of one of the protonated dimer units in the trihydrate; $r_{\text{asy}} = (r_{\text{O}\cdots\text{Cl}(1)} + r_{\text{O}\cdots\text{O}(1)}) - (r_{\text{O}\cdots\text{Cl}(2)} + r_{\text{O}\cdots\text{O}(2)})$, where the indices 1 and 2 refer to the near-neighbor distances for the two ends of the protonated dimer unit; see left inset at the bottom. (B) time dependence of the two $\text{O}\cdots\text{H}^+$ distances in the same dimer. (C) OH bond lengths at the edge of the dimer unit for bonds which are H-bonded to water along the chain. (D) OH bond lengths at the edge of the dimer unit for bonds which are H-bonded to halide ions. (E) OH bond lengths of one of the neighboring solvating water molecules. The black and the red curves in C–E pertain to the more strongly and more weakly H-bonded OH, respectively. The numbers denote average bond lengths, with a standard deviation. For comparison, the mean OH bond length for the edges of the dihydrate protonated dimer units was 1.01 \AA . The location of the OH bonds (C–E) is marked in the right inset at the bottom.

is, more or less egalitarian proton sharing. For that purpose, contour plots are displayed similar to those shown for the dihydrate (Figure 11). Of present interest are the bottom contours, which are averaged over 30 fs consecutive stretches of a trajectory, on the order of the proton oscillation period. The bottom-left plot includes a maximum around the zero value of the asymmetric solvation coordinate and a large average $\text{O}\cdots\text{H}^+$ distance ($\sim 1.21\text{ \AA}$). This maximum can be reasonably assigned to “true Zundel”, while the extension of the contour plot toward higher r_{asy} /lower $r(\text{O}\cdots\text{H}^+)$ values can be viewed as excursions toward hydronium. A similar maximum is observed in the bottom-right contour plot pertaining to $r_{\text{O}\cdots\text{O}}/r(\text{O}\cdots\text{H}^+)$. Accordingly, “true Zundel” is defined to correspond to $r(\text{O}\cdots\text{H}^+) \geq 1.175\text{ \AA}$, that is, the range in the vicinity of the contour plot maxima. Figure 6 shows the distribution of the average $r(\text{O}\cdots\text{H}^+)$ values for the trihydrate (open circles); the arrow marks the 1.175 \AA cutoff. With this definition, “true Zundel” corresponds to $\sim 30\%$ of the trihydrate trajectory.

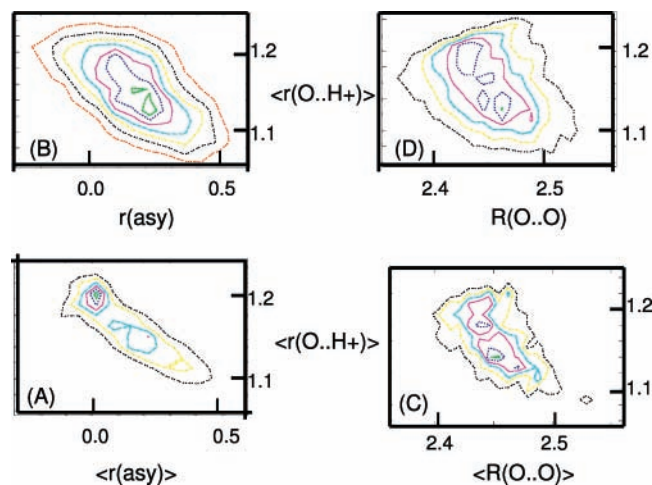


Figure 11. As in Figure 7, for the trihydrate; $r_{\text{asy}} = (r_{\text{O}\cdots\text{Cl}(1)} + r_{\text{O}\cdots\text{O}(1)}) - (r_{\text{O}\cdots\text{Cl}(2)} + r_{\text{O}\cdots\text{O}(2)})$, where the indices 1 and 2 refer to the neighbor distances for the two ends of the protonated dimer unit; see left inset of Figure 10. Contour range, spacing: (A) 0.01–0.06, 0.01; (B) 0.003–0.021, 0.003; (C) 0.004–0.024, 0.004; (D) 0.002–0.012, 0.002.

Another notable dynamic effect is the correlation between the proton motion and the OH-bond vibrations along the chain. This effect can be seen as an incipient “proton wire”. The correlation is apparent from panel C of Figure 10, which shows bond trajectories for the two OH bonds along the chain at the two sides of the protonated dimer unit. Whenever the proton moves to the vicinity of one of the O atoms (see panel B), the neighboring OH, which is bonded to the same O atom, is extended to ~ 1.06 Å. The effect is not unexpected because the transition occurs from a “water-like” to an “hydronium-like” environment near the pertinent O atom and hydronium has longer OH bonds than water. Interestingly, the OH bonds which are hydrogen-bonded to the oxygen along the chain are much more responsive to proton fluctuations than the donor OH bonds of the same O atoms, which are H-bonded to the chloride ions (Figure 10D). Because of the coupling to the proton motion, the spectrum of the OH bonds along the water chains is relatively broad, extending from 2500 to 3400 cm^{-1} (Figure 9). Clearly, these OH bonds dominate the low-frequency wing of the OH stretch band, seen both in the calculated IR spectrum and in the experiment (Figures 8 and 9).

The measured OH stretch band displays several sub-peaks in the 2970–3300 cm^{-1} range and a low-frequency wing extending down to 2350 cm^{-1} (Figure 8, bottom). The calculation yielded a structured band in a somewhat higher frequency range (3050–3350 cm^{-1}) and a low-frequency wing extending down to 2550 cm^{-1} , which however includes a distinct bump (Figure 8A). The substructure of the OH stretch band is due to the presence of six inequivalent OH bonds, whose frequency spectra are moreover broadened by coupling to the lattice motions (Figure 9). As in the case of the monohydrate,³⁴ the IR spectrum differs significantly from the OH density of frequencies (dotted curve, Figure 9A). It is seen that the high-frequency end of the density of frequencies, which is due to solvating water molecules donating H bonds to the anions, carries limited IR intensity.

The proton band complex below 1800 cm^{-1} (Figure 8) includes (both in experiment and in calculation) a peak at 1700 cm^{-1} , a dip around 1500–1600 cm^{-1} , and a broad band extending beyond 1000 cm^{-1} . The computed proton feature is overstructured with respect to experiment, most likely from finite dimensionality of the model and a limited duration of the

trajectory and, also possibly, neglect of nuclear quantum effects. The interplay between asymmetric proton stretch and water bending appears to be more complex than that in the case of the dihydrate, where the bending signature was the antiresonance “dip” in the proton spectrum at 1600 cm^{-1} . In the case of the trihydrate, the densities of the bending frequencies peak at 1580 and 1670 cm^{-1} for the solvating water and the protonated dimer units, respectively (Figure 8C). The higher protonated dimer bending frequency with respect to the dihydrate may be due to coupling to the solvating water bending or to different solvating environments. As seen in Figure 8C, the peak of the trihydrate dipole spectrum at 1690 cm^{-1} appears at the region of overlap between peaks in the densities of frequencies of asymmetric proton stretch and of protonated dimer bending. Thus, the modes which contribute to this IR feature appear to include both proton stretch and protonated dimer bending components, and the “dip” in the spectrum in the 1500–1600 cm^{-1} range appears to be an antiresonance with the solvating water bending.

The trihydrate was studied in the past by von Roseninge, Tuckerman, and Klein et al.³⁷ using CPMD and CP-PIMD. The latter scheme includes nuclear quantum mechanical effects, which were not included in the present study and which are expected to be nonnegligible in the proton-rich hydrate systems. It was, in fact, shown in ref 37 that substantial broadening of the proton spatial distribution takes place due to the quantum mechanical effects. A contour plot is presented in that study of the $r_{\text{OO}}, [r_{\text{p}\cdots\text{O}(1)} - r_{\text{p}\cdots\text{O}(2)}]$ distribution, which in classical treatment is unimodal at the most probable r_{OO} distance but becomes bimodal at larger distances; it is shown that quantum effects wipe out the latter bimodality. The corresponding contour plot for the present simulation resembles their classical result. On the other hand, the main dynamical effect described in the present study does not seem to depend heavily on the use of classical dynamics. The proton motion is shown above to be coupled predominantly to the solvation coordinate r_{asy} , and proton oscillations take place around a temporary minimum determined by the current r_{asy} location. The frequency spectrum of r_{asy} peaks in the 100–200 cm^{-1} range; therefore, this motion is not that far from the classical limit. Nevertheless, the classical condition that $k_{\text{B}}T \geq \hbar\omega$ is not satisfied, except for the lowest-frequency oscillations of the system. However, this is true for most of the current computational research of molecular systems employing classical molecular dynamics.

The spectroscopy of the HCl trihydrate was investigated in the past in refs 40 and 41 using harmonic normal-mode analysis in conjunction with DFT. The OH stretch band complex was reproduced, but without the low-frequency tail. The computed spectrum included also a peak at 1600 cm^{-1} , assigned to water bending, and a clump of peaks at ~ 1100 cm^{-1} , assigned to bending and torsional vibrations of the ion, coupled to other modes of water and lattice. Thus, the assignment is quite different than the one proposed above based on ab initio molecular dynamics.

VII. HCL Hexahydrate

The hexahydrate structure is depicted in Figure 12. The structure was generated using coordinates derived from X-ray experiment²⁶ as input and subjecting them to BLYP/DZVP minimization. Some of the OH bond lengths derived from X-ray data do not make sense since bond lengths in the range of 0.77–0.98 Å were proposed. (X-ray data are however not expected to be very sensitive to the location of the H atoms). QUICK-STEP minimization resulted in more physically reasonable OH bond lengths in the range of 0.99–1.06 Å; the larger values

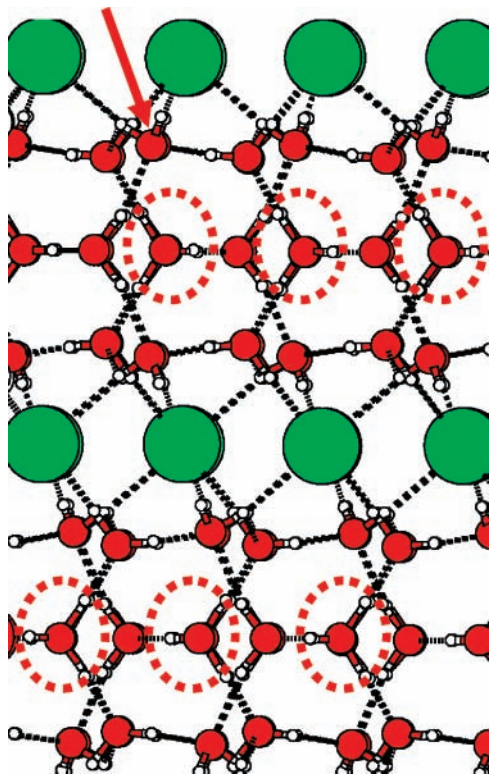


Figure 12. Structure of the crystal hexahydrate, generated by the BLYP/DZVP-level minimization which employed the published X-ray structure as input.²⁶ Hydronium ions are encircled by dashed lines. Large spheres denote chloride ions; note that the depth coordinate (“into the page”) alternates along the displayed rows of Cl^- . The arrow marks a water molecule which forms the unusual bifurcated proton-donor H bond to the near-neighbor Cl^- and to another H_2O , both to the left of it, as described in the text.

correspond to the constituent hydronium ions. The minimized location of the heavy atoms is within 0.02–0.12 Å from the location in the unit cell derived from X-ray data. In accord with ref 26, the minimized structure is fully ionized, with hydronium ions solvated by a 3D network of water molecules. This is unlike the case of the monohydrate, in which the hydronium is solvated directly by the chloride ions. The difference in the solvation environment results in the longest hydronium OH bond length distribution peaking at ~ 1.08 Å, as compared to 1.05 Å in the case of the monohydrate (Figure 6). Also, unlike H_3O^+ in the monohydrate, the water-solvated hydronium ion undergoes occasional excursions toward the Zundel structure, with the longest OH reaching lengths as large as 1.15 Å. Figure 13 shows contour plots of instantaneous values of $r(\text{O}\cdots\text{H}^+)$ against the asymmetric solvation coordinate r_{asy} (left) and against $r_{\text{O}\cdots\text{O}}$ (right). The plots are analogous to the top plots of Figures 7 and 11 for the di- and trihydrate. In Figure 13, the $\text{O}\cdots\text{H}^+$ “distance” was defined as the instantaneous longest OH distance of the H_3O^+ unit in the hexahydrate. The solvation coordinate is defined analogously to the di- and trihydrate as $r_{\text{asy}} = (r_{\text{O}\cdots\text{O}(1)} + r_{\text{O}\cdots\text{O}(2)}) - (r_{\text{O}\cdots\text{O}(3)} + r_{\text{O}\cdots\text{O}(4)})$ (see inset to Figure 3; replace chlorine ions by O atoms of the solvating water molecules). The $r(\text{O}\cdots\text{H}^+)$ distance range typical of the hexahydrate is significantly shorter than those of the di- and trihydrate; nevertheless, both contour plots in Figure 13 display some incipient anticorrelation between $\text{O}\cdots\text{H}^+$ and either r_{asy} or the $\text{O}\cdots\text{O}$ distance; this anticorrelation becomes much more pronounced for the di- and trihydrate (Figures 7 and 11); it is more pronounced for r_{asy} than for $r_{\text{O}\cdots\text{O}}$. The distributions maximize at values near the minimum-energy configuration.

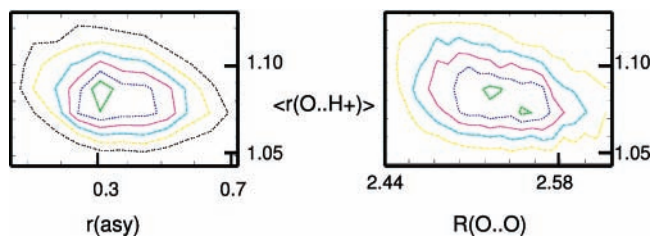


Figure 13. As in the top two panels of Figures 7 and 11, for the hexahydrate. The $\text{O}\cdots\text{H}^+$ distance is defined as the instantaneous longest OH distance of the H_3O^+ unit in the hexahydrate. The solvation coordinate is defined analogously to the dihydrate as $r_{\text{asy}} = (r_{\text{O}\cdots\text{O}(1)} + r_{\text{O}\cdots\text{O}(2)}) - (r_{\text{O}\cdots\text{O}(3)} + r_{\text{O}\cdots\text{O}(4)})$ (as in inset to Figure 3, with the water molecule bonded to the instantaneously longest OH of H_3O^+ ; replace chlorine ions in the inset by O atoms of the solvating water molecules). Contour range, spacing: left panel 0.01–0.035, 0.005; right 0.0043–0.0163, 0.003.

The solvating water molecules in the hexahydrate form donor bonds to each other and to chloride ions; the former H bonds tend to be stronger, as indicated by the slightly larger average OH bond length (by 0.008 Å at the minimum). One finds within the minimized hexahydrate structure an unusual bifurcated H bond, in which a H atom of one of the water molecules is nearly equidistant to a chloride ion and an O atom of another water molecule, at a distance of 2.4 Å. (Typically, a H atom of water in solution or in a solid phase forms a single shorter proton-donor bond to either another water molecule or to a negative ion.) A water molecule forming a bifurcated bond is marked by an arrow in Figure 12.

The computed hexahydrate spectrum is dominated by the water OH stretch band above 3000 cm^{-1} and by a broad hydronium OH stretch feature extending down to $\sim 2000\text{ cm}^{-1}$, to the red from the water OH stretch band (Figure 14A). This assignment is based on comparison with the respective contributions to the OH density of frequencies, shown in Figure 14B. The water OH stretch feature is dominated by OH bonds which are H-bonded to H_2O rather than to chloride since the former OH corresponds to stronger H bonds and correspondingly larger dipole derivatives (compare Figure 14A and C). The computed water OH stretch feature has an experimental counterpart in a similar frequency range, although the band substructure (which is due to inequivalent OH bonds in the crystal) is not reproduced accurately by the calculation. In the region to the red of the water band, one sees in the experimental spectrum a fairly intense continuum absorption ending with a “bump” at 1890 cm^{-1} . On the basis of comparison to the calculation, we assign this continuum absorption to the fluxional hydronium stretch oscillation, although the computation overestimates the relative intensity of the hydronium absorption with respect to the water band. In fact, in the case of the hexahydrate, the general shape of the measured spectrum is matched better by the OH density of states than by the dipole spectrum (compare the two curves in Figure 14A to experiment). This result may be an artifact of the asymmetry of the simulation box used ($12.6604 \times 6.4528 \times 17.8979$ Å), which was dictated by the asymmetry of the crystal unit cell ($6.3302 \times 6.4528 \times 17.8979$ Å); a larger box was beyond our computational means. The short y-dimension of the simulation box is expected to introduce artifact phase coincidences into the classical trajectory, which may result in the overestimated hydronium feature intensity. Similar assignment of the $1860\text{--}3000\text{ cm}^{-1}$ continuum to the hydronium stretch was made in refs 39 and 41, where the hexahydrate spectra were analyzed in the framework of the harmonic approximation. Within the latter, the hydronium stretch feature

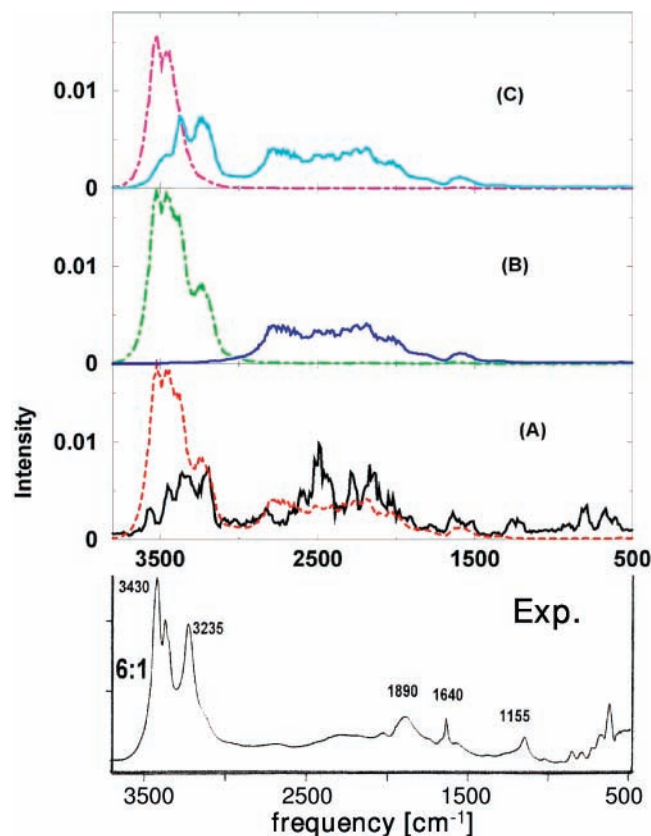


Figure 14. Bottom: experimental spectrum of the crystal hexahydrate, as in Figure 1. (A) The black solid curve corresponds to the spectrum of the hexahydrate, calculated from the Fourier transform of the system dipole, for a 3 ps trajectory at a mean temperature of 102 K. The red dotted curve represents the average Fourier transform of all OH bonds. (B) Average Fourier transform of all OH bonds of H_2O (green, dot-dashed) and of H_3O^+ (blue, solid). (C) Average Fourier transform of all OH bonds which are H-bonded to chloride (magenta, dot-dashed) and of OH bonds which are H-bonded to water (cyan, solid). The first category of OH belongs to water, while the second belongs to water and hydronium.

corresponded to a narrow clump of intense peaks in the 2119–2213 cm^{-1} range.

VIII. HCL Aqueous Solution

A. Structure and Spectroscopy of Acid Solutions: Some Past Results. There is considerable published literature on the subject; for reviews, see, for example, refs 13 and 14. The present summary is not designed to provide exhaustive coverage; rather, a brief overview is presented of select results and ideas focusing on two aspects, (a) interpretation of the IR spectra and (b) the debate on the relative contributions of the two protonated water forms, Eigen and Zundel, to the acid solutions.

The acid contributes to the spectrum a continuous IR absorption extending over several thousand cm^{-1} , from the water stretch band to the water-libration band (Figure 15). Borgis and Vuillemier⁵³ employed a multistate EVB model for the analysis of this continuum. The absorption in the 1000–1800 cm^{-1} range was assigned to a combination of bends and the $\text{O}\cdots\text{H}^+$ asymmetric stretch of the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ “complex”. The absorption of the Eigen form was proposed to peak at 2650 cm^{-1} , while the intermediate frequency range was assigned to a bridging region between the two forms, which involves a “special” $\text{O}\cdots\text{H}^+$ bond.

Kim et al.⁵⁴ also employed multistate EVB to analyze the spectra; there, the assignment was carried out with the help of

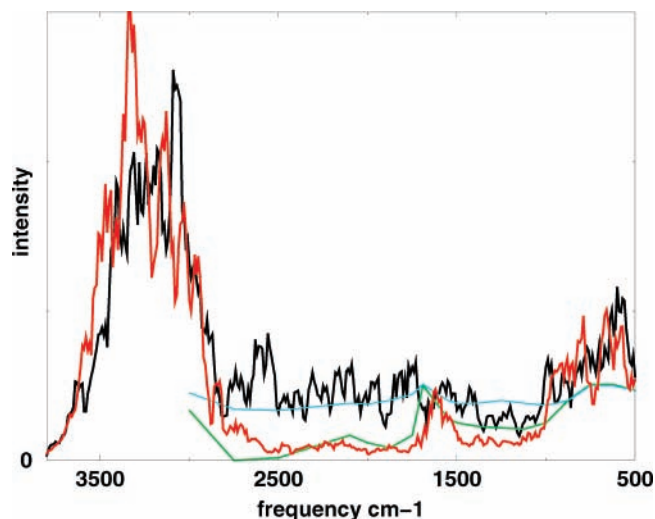


Figure 15. Red: calculated dipole spectrum of neat water, from a 7 ps trajectory of 64 water molecules at a mean temperature of 307 K. Black: dipole spectrum of a solution of 4 HCl in 60 H_2O , equivalent to a 3.5 M concentration, from a 2.5 ps simulation at an average temperature of 303 K. Green: digitized experimental absorption spectrum of water at 301 K. Cyan: the average of the measured spectra of 2.43 and 4.85 M solutions of HCl in water; from Figure 5 of ref 4.

instantaneous normal-mode analysis. The 1580–1640 and 1680–1880 cm^{-1} spectral regions were assigned to the Eigen and Zundel ion bending, respectively. The 2700–2950 cm^{-1} range was proposed to originate from an OH stretch of symmetrically hydrated hydronium. Additional absorption above 3000 cm^{-1} was assigned to water molecules in the first and the second solvation shells of the respective ions.

Smiechowski and Stangret⁵⁵ studied spectra of HDO isotopically diluted in an aqueous acid solution. The analysis was carried out with the help of ab initio calculations on protonated water clusters with two to eight water molecules. They identified “an asymmetric variant of the regular Zundel cation” as a dominant hydrated proton species in solution.

The percentage of the “Zundel-like” and “Eigen-like” configurations in liquid has been a subject of some debate. Tuckerman et al.³⁷ suggested a 40:60% ratio, based on inspection of CPMD trajectories. Multistate EVB calculations by Voth et al.¹⁴ indicated “a solvation structure composed of a roughly 65:35 mixture of the Eigen and Zundel”, although it was emphasized that the Eigen and Zundel cations are merely “limiting concepts”. In contrast, Asthagiri et al.⁵⁶ argued that the Zundel complex is the dominant species. The argument of ref 56 was based on quasichemical theory of solutions and on ab initio MD simulations. The argument is essentially that the observed $\text{O}\cdots\text{H}^+$ distances are too long and the corresponding $\text{O}\cdots\text{O}$ distances too short for the Eigen ion; still, the authors note that a “symmetrical ideal Zundel cation is not observed”.

Another recent ab initio MD study of HCl solutions by Heuft and Meijer⁵⁷ employed structural analysis based on the concept of embedded cluster species; H_7O_3^+ was suggested as the dominant local structural element ($\sim 50\%$), with the Zundel and the Eigen structures corresponding to ~ 30 and $\sim 15\%$, respectively.

Botti et al. analyzed neutron diffraction data on a HCl solution using Monte Carlo techniques and allowing bare H^+ hydronium or Zundel ions into the simulation box. The results could be interpreted alternatively either in terms of the formation of a high percentage of asymmetric Zundel complexes or in terms of the formation of distorted H_3O^+ and highlighted “the

difficulty of making a clear distinction between Eigen and Zundel complexes due to the continuous random network of hydrogen bonds formed between water and hydrated protons.”

Finally, Cavalleri et al.⁵⁹ tried to assess the percentage of the two protonated water forms using combined X-ray absorption spectroscopy and computational study of HCl aqueous solutions. It was concluded that in the 1–4 M concentration range, there is a transition from mostly “distorted Zundel-type species” to a predominance of the Eigen form.

From the above discussion, one gets a sense that semantics is involved. That is, the suggested contributions of the two types of structures depend crucially on the criterion used to differentiate between them. One may then ask whether an objective criterion exists at all. This topic is further discussed in the following section.

B. Solution: Results and Discussion. In this part, simulations were carried out for systems with N dissolved HCl molecules, $N = 1, 2,$ and $4,$ and $64-N$ water molecules, at an average temperature of 301–307 K. The results are presented below. An effort is made to transfer what we learned from hydrates to the liquid. Moreover, an attempt is made to address the question of whether protonated water in the liquid phase favors the hydronium or the Zundel form; a variety of opinions found in the literature was sampled above.

Some general considerations are first presented. In order to obtain true Zundel or Eigen, the solvating environment must acquire symmetry. In the case of Eigen, three equally strong proton-donor H bonds of the cation to water are needed. In case of the Zundel ion, the two ends of the ion must be solvated to a similar extent. Symmetry is not present typically in the liquid state and (as shown above) is commonly distorted even in the crystals by the librations of the solvating environment. Even in the case of the trihydrate for which the calculated equilibrium configuration is close to Zundel, the proton oscillates most of the time in the vicinity of either of the O atoms, in a short-lived local minimum dictated by the configuration of the solvating environment (see Figure 9). Simulations suggest that the hydrated proton in solution displays a continuum of states bracketed by these two configurations. In our view, there is no obvious criterion to separate this distribution to “hydronium-like” and “Zundel-like” components. To obtain clear separation, a bimodal distribution of some sort would be needed; otherwise, the division is arbitrary. We tried and did not succeed to locate any clearly bimodal distributions for the hydrated proton in solution.

Consider, for example, a distribution of $O\cdots H^+$ distances for the liquid acid solution, which is compared to that for the hydrates in Figure 6. In the case of the di- and trihydrate, the shorter of the two distances between O and the central proton of the $H_2O\cdots H^+\cdots OH_2$ unit was used to generate the distribution. In the case of the monohydrate and the hexahydrate, the distribution pertains to the longest OH distance of the H_3O^+ ion. In the case of the aqueous solution with a single (ionized) HCl, each H nucleus was assigned to its near-neighbor O atom. The “ H_3O^+ ” unit was identified by the O atom which serves as a near-neighbor to three H. The distribution shown in Figure 6 pertains to the longest of the corresponding three OH distances.

It is seen that the latter distribution for the proton in the aqueous solution peaks at 1.1 Å, only slightly above the peak of the hexahydrate at ~ 1.08 Å. Recall that the equilibrium structure of the hexahydrate corresponds to²⁶ $(H_9O_4^+)(H_2O)_2(Cl^-)$ and, thus, includes Eigen units. (Hexahydrate is used for the comparison with solution rather than the monohydrate since, in the hexahydrate, the hydronium is solvated by water, as in

solution, while in the monohydrate, solvation is solely due to the chloride anions.) Thus, the peak of the $O\cdots H^+$ distance distribution for the acid solution can be assigned to the “hydronium” or the “Eigen” ion. However the distribution includes a long tail extending up to ~ 1.2 Å, over the entire range of the trihydrate (whose calculated equilibrium structure $(H_5O_2^+)(H_2O)(Cl^-)$ includes a nearly perfect Zundel unit). Moreover, the $O\cdots H^+$ distance distributions for the hexahydrate and the trihydrate overlap since H_3O^+ in the hexahydrate undergoes occasional excursions toward the Zundel structure, while the $H_2O\cdots H^+\cdots OH_2$ unit in the trihydrate undergoes frequent distortions toward hydronium (see discussion in sections VI and VII). One might still try to separate “hydronium-like” and “Zundel-like” configurations in the liquid using some kind of cutoff value, for example, $r_{\text{cutoff}} = 1.116$ Å, corresponding to the point where the trihydrate and the hexahydrate distributions intersect. However, inspection of Figure 10B indicates that this $r(O\cdots H^+)$ value is within the range of proton oscillations during sections of the trihydrate trajectory, in which the proton clearly favors one of the ends of the $H_2O\cdots H^+\cdots OH_2$ unit (i.e., “hydronium-like” MD sections). Moreover, contour plots such as the bottom-left panel in Figure 11 suggest that the trihydrate protons spend only $\sim 30\%$ of their time in “true” Zundel-like configurations; see discussion in section VI.

Another possible way to address the division of proton configuration space in solution is to consider hydronium and Zundel “basins of attraction”, which include the entire ranges of motion covered by the protonated water in hexa- and trihydrate, respectively. This point of view may have some merit since the distance distribution for the solution in Figure 6 can be roughly reproduced as a linear combination of 35% of that for the hexahydrate and 65% of that for the trihydrate. Moreover, this analysis is qualitatively applicable to the spectrum. As discussed above, the protonated water spectrum of the hexahydrate extends roughly from ~ 1800 to 3000 cm^{-1} . On the other hand, the di- and trihydrate proton band complex extending from 900 to 1750 cm^{-1} represents absorption by the proton in the fluctuating “Zundel-like” basin of attraction. Both spectral ranges—for the “fluctuating hydronium” in the hexahydrate and for the “fluctuating Zundel ion” in the trihydrate—cover most of the regime of the acid solution continuum absorption. As seen in Figure 15 and also in Figure 5 of ref 4 (which show IR spectra in the HCl concentration range of 1.21–10.95 M), the integrated intensity of the hydronium-like contribution to the spectrum (to the blue from 1800 cm^{-1}) is somewhat larger than that of the “Zundel-like” contribution, which is in contrast to the estimates based on the $r(O\cdots H^+)$ distance distributions noted above. Therefore, it is our point of view that quantitative division into two distinct types of protonated water states in solution is not very meaningful.

An additional way to look at the $O\cdots H^+$ bond length distribution is to consider a rescaled asymmetry variable $\delta = [(0.5r(O\cdots O) - r(O\cdots H^+)]/r(O\cdots O)$ (Figure 16), in which the symmetric Zundel configuration corresponds to $\delta = 0$. In this presentation, the distribution for the solution covers a similar range as that for the trihydrate, with some excess at the high end corresponding to “semi-hydronium” configurations. The high tails of the two distributions extending toward the “hydronium” overlap with each other. The hexahydrate distribution peaks at this tail. In this presentation, the distribution for the solution cannot be represented, even qualitatively, as a linear combination of hexahydrate-like and trihydrate-like contributions.

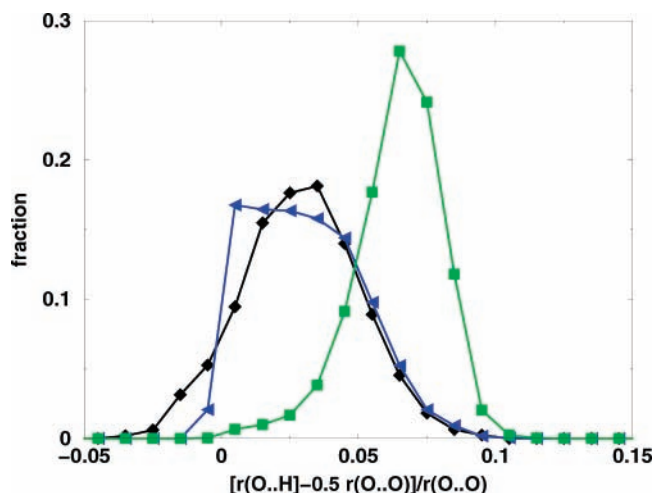


Figure 16. Distribution of the negative of the instantaneous rescaled asymmetry variable $\delta = [(0.5r(\text{O}\cdots\text{O}) - r(\text{O}\cdots\text{H}^+))/r(\text{O}\cdots\text{O})]$ from a 7 ps simulation of a solution of 1 HCl in 63 water molecules at an average temperature of 301 K. Definition of distances: The triangle represents the distance between O and the central proton of the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit in the trihydrate. The shorter of the two distances was used. The square and diamond correspond to the longest OH distance of the H_3O^+ unit in the hexahydrate and the aqueous solution, respectively. In water, the proton was assigned to the instantaneously near-neighbor H_2O molecule; see text for further explanation.

In further search of some kind of bimodality, which would yield a clear criterion for separation into two distinct proton forms in solution, we attempted also two-dimensional plots of protonated water properties. An example is shown in Figure 17. To generate contour plots (A–D), instantaneous H_3O^+ units in the dihydrate, trihydrate, hexahydrate and water were identified by (a) finding the nearest-neighbor O for each hydrogen and (b) locating O atoms which have three H atoms assigned to them. The horizontal axis of the contour plots corresponds to the largest OH bond length in the instantaneous H_3O^+ units, while the vertical axis corresponds to the average of the two shorter ones. Interestingly, two distinct (but not very well separated) maxima were found for the trihydrate (panel B), peaking at 1.175 and 1.02 Å (“Zundel-like” configuration) and at 1.14 and 1.02 Å (“semi-hydronium” configuration). For the dihydrate (panel A), a single maximum was observed at 1.14 and 1.02 Å at the “semi-hydronium” configuration. For the hexahydrate, a peak appeared at 1.07 and 1.06 Å, consistent with the hydronium form of protonated water in the equilibrium configuration; the extent of proton delocalization is much more modest than that in the case of the di- and trihydrate. For the HCl solution (panel D), the maximum appeared close to that of the hexahydrate, corresponding to the hydronium configuration (1.10 and 1.05 Å); however, a long tail of the distribution was observed, including the range covered by the di- and trihydrate. Still, within the numerical noise, there is no clear evidence for a secondary maximum at a “Zundel-like” configuration for the solution. Only a trace of evidence for a secondary feature in the Zundel region (near $r_{\text{asy}} = 0$) is observed in panel E, which shows a contour plot of the asymmetric solvation coordinate versus the longest OH distance of the instantaneous H_3O^+ unit for the solution. The correlation between the longest $r(\text{O}\cdots\text{H})$ distance and the asymmetric solvation coordinate appears to persist in the liquid phase, similarly to the hydrates (Figures 7 and 11). No clear separation into two states could be likewise inferred from the contour plot of the longest $r(\text{OH})$ distance versus the corresponding $r(\text{O}\cdots\text{O})$ (not shown).

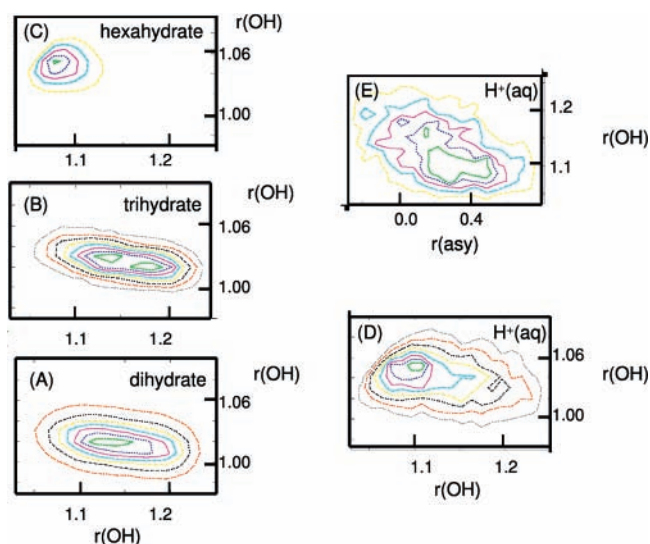


Figure 17. (A–D) Contour plots for OH distances in “ H_3O^+ ” for the dihydrate, the trihydrate, the hexahydrate, and a solution of a single HCl dissolved in 63 water molecules. All distances are in angstroms. In each system, the proton was assigned to the instantaneously near-neighbor water. The horizontal axis corresponds to the longest OH distance in the resulting “ H_3O^+ ” unit; the vertical axis corresponds to the average of the two shorter OH distances. (E) Contour plot of the instantaneous values of the longest OH distance in “ H_3O^+ ” against the asymmetric solvation coordinate r_{asy} for the same HCl solution. The solvation coordinate is defined analogously to the hydrates as $r_{\text{asy}} = (r_{\text{O}\cdots\text{O}(1)} + r_{\text{O}\cdots\text{O}(2)}) - (r_{\text{O}\cdots\text{O}(3)} + r_{\text{O}\cdots\text{O}(4)})$ (see inset to Figure 3; replace chlorine ions by O atoms of the solvating water molecules). Contour range, spacing: (A) 0.0025–0.0265, 0.004; (B) 0.0025–0.0305, 0.004; (C) 0.01–0.07, 0.015; (D) 0.0025–0.02, 0.0025; (E) 0.002–0.01, 0.002.

IX. Summary

The study presented ab initio MD studies of vibrational dynamics and spectra of HCl hydrates and of the aqueous HCl solution. Dipole derivatives with respect to the OH and $\text{O}\cdots\text{H}^+$ stretch modes (which dominate the spectra of our interest) were also investigated in the pertinent systems.

First, the question was addressed why hydrogen bonding dramatically increases the OH stretch intensity and why the $\text{O}\cdots\text{H}^+$ stretch band of the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit in the gas phase and in the condensed phases is unusually intense. The effect of H bonding on the OH stretch dipole derivatives was analyzed with the help of the Wannier centers. For the purpose of the calculation of the system dipole, the Wannier centers represent the “average locations” of the system electron pairs and thus are a convenient means for qualitative analysis.^{44,49} In the water monomer, the dipole derivative with respect to OH stretch is reduced significantly with respect to the value obtained from bare proton displacement by concurrent electron cloud displacement; that is, the electron cloud follows the displaced proton and thus cancels much of the change in the system dipole. For the H-bonded OH of the water dimer, the dipole derivative increases dramatically with respect to the monomer due to reduced electron following; that is, the electron pair localized at the OH bond is repulsed by the acceptor lone pair and therefore does not follow the proton displacement as effectively as in the isolated molecule. Moreover, the acceptor electron cloud is displaced toward the proton due to Coulombic attraction, enhancing the net dipole change. The effect is amplified in extended H-bonded systems in which the ability of the donor electronic cloud to follow the proton is further reduced by additional hydrogen bonding.

In the case of the Zundel ion $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$, the dipole derivative with respect to central proton displacement is larger than the value which would be obtained solely from H^+ displacement. As the proton is shifted toward one of the water molecules and away from another, the displacement of electron clouds on both water molecules occurs in the opposite direction (due to the respective strengthening and weakening of the two $\text{O}\cdots\text{H}^+$ bonds), amplifying the dipole by a factor of ~ 2 . An even larger dipole derivative with respect to proton displacement was obtained for the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit in the dihydrate and in the acid solution since the electronic cloud displacements, which are coupled to the proton displacement, now extend to the surrounding solvation shell.

BLYP/DZVP calculations of the HCl hydrate spectra did a reasonably good job of reproducing the main measured spectral features and, in particular, the broad bands which are due to the proton motion (see Figure 1 and Figures 4, 8, 9, and 14). In the dihydrate, the entire band complex from 1000 to 1800 cm^{-1} is assigned to the asymmetric stretch of the central proton in the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit. The large width is due to coupling between the proton motion and the asymmetric solvation coordinate of the protonated dimer by the halide ions ($r_{\text{asy}} = (r_{\text{O}\cdots\text{Cl}(1)} + r_{\text{O}\cdots\text{Cl}(2)}) - (r_{\text{O}\cdots\text{Cl}(3)} + r_{\text{O}\cdots\text{Cl}(4)})$). Lattice vibration associated with r_{asy} occurs on a time scale which is an order of magnitude longer than the $\text{O}\cdots\text{H}^+$ vibration period. In the course of the lattice vibrations, the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit probes solvation environments ranging from symmetric to significantly asymmetric ones. In an approximately symmetric solvation environment, the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ unit samples proton-sharing configurations approaching “ideal Zundel” and absorbs radiation at the low-frequency end of the proton band. In the asymmetric solvation environment, the proton favors the better-solvated H_2O , and a “semi-hydronium” unit is obtained, absorbing radiation at the high-frequency end of the band. The “dip” in the spectrum at $\sim 1600 \text{ cm}^{-1}$ corresponds to antiresonance with respect to water bending. A similar interpretation is given to the trihydrate spectra.

The hydronium of the hexahydrate displays a broad absorption band from ~ 1800 to 3000 cm^{-1} ; again, the large width is attributable to fluctuations of the crystal solvation environment, which result in occasional excursions of the hydronium toward the Zundel structure. The assignment of the hexahydrate proton band is in accord with the past calculations of Martin-Llorente et al. employing normal-mode analysis,⁴¹ which however yielded a narrow clump of peaks instead of a broad band.

The broad proton feature of the hexahydrate (which can be viewed as due to the fluctuating hydronium in the Eigen complex) and the broad proton feature of the trihydrate (which can be assigned to the fluctuating Zundel ion) cover most of the range of the intense continuum IR absorption contributed by acid to the spectrum of the aqueous solution. This result is consistent with the physical picture of the hydrated proton continuously interconverting between a range of solvation states bracketed by Eigen and Zundel forms.^{7,13,14} One should emphasize however again that the protonated water dimer in the trihydrate spends much of its trajectory time in a “semi-hydronium” configuration reflecting the temporary (asymmetric) solvation states while the hydronium in the hexahydrate undergoes distortions toward Zundel structures.

An effort was then made to contribute to the ongoing debate^{13,14,55–57,59} on the relative contribution of the “hydronium-like” and “Zundel-like” configurations in the liquid acid solutions. On the basis of the ab initio simulations of the HCl solution and their comparison to the hydrate results, we

concluded that there is no unique objective criterion for separating the configurations into the two groups. This is because distributions of configurational properties related to the hydrated proton appear to be continuous and unimodal, covering the range bracketed by the two limiting forms. The ideal Zundel and Eigen forms themselves are not commonly accessed in the liquid phase because of the asymmetry of the solvating environment.

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