Computational Chemistry

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The Molecular Origin of the "Continuous" Infrared Absorption in Aqueous Solutions of Acids: A Computational Approach**

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The dissociation of weak acids in water is a process of fundamental importance in chemistry and biochemistry. The familiar reaction shown in [Eq. (1)] that describes the

$$HA_{(aq)} + H_2O \rightarrow A^-{}_{(aq)} + H_3O^+{}_{(aq)} \quad (1)$$

dissociation process of the weak acid HA has been the object of numerous experimental and theoretical investigations, which have focused on the chemical nature of the solvated reactants and products[1] and stable or transient intermediate structures.[2]

However, the deceptive simplicity of reaction (1) masks a wealth of microscopic behavior that remains largely unexplained. Important insights into the dissociation mechanism can be gleaned from infrared (IR) spectra of aqueous solutions of weak acids.[3] In particular, the IR spectra of these acids exhibit a broad absorption band extending from the lower range of the OH stretch band of water at $\tilde{\nu} = 3000\,\text{cm}^{-1}$ to the HOH bending peak at $\tilde{\nu} = 1500\,\text{cm}^{-1}$ and in some instances all the way down to the onset of the water libration band at $\tilde{\nu} = 1000\,\text{cm}^{-1}$. This "continuum of absorption" is reminiscent of that seen for solutions of strong acids, where its origin can be explained in terms of frequent proton-transfer events between H_3O^+ and H_2O units. In the case of weak acids, however, the early transmission spectroscopy investigations of Leuchs and Zundel[3] as well as the more recent attenuated total reflection measurements of Max and Chapados[4] strongly suggest that it is either the unionized hydrated acid $HA_{(aq)}$ or some relatively stable supramolecular

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ionic assembly of A^- with a protonated cluster of water molecules that is directly responsible for the observed continuous absorption.

Herein, we employ Car–Parrinello ab initio molecular dynamics[5] to investigate the ability of IR spectroscopy to differentiate between unionized molecules and the solvent-separated, solvent-shared, and contact ion pair supramolecular intermediates that appear in theoretical treatments of the dissociation of weak acids (see Figure 1).[6,7] The conclusion that emerges from the present investigation is that the concentration of the ion pairs is proportional to the intensity of the continuous IR absorption between $\tilde{\nu} = 1500$ and $1000\,\text{cm}^{-1}$. In contrast, we find that the intensity of the absorption between $\tilde{\nu} = 3000$ and $1800\,\text{cm}^{-1}$ depends essentially as much on the concentration of the ion pairs as on that of the unionized molecules. These results complement and enhance the utility of existing IR spectra decomposition approaches[4] and suggest new ways in which these experiments can be used to elucidate the nature of the chemical species that exist in weakly acidic media.

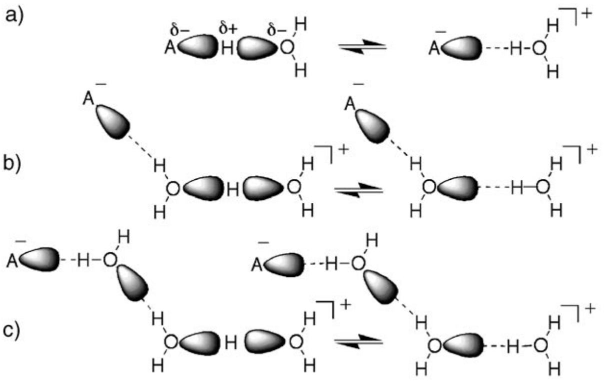

Figure 1. A schematic representation of some of the possible stable and transient intermediates in reaction 1: a) contact ion pairs, b) solvent-shared ion pairs, and c) solvent-separated ion pairs. If the oppositely charged ions are separated by more than 8 Å (roughly two intervening water molecules), they tend to diffuse away from each other[6] to form the products of dissociation shown in reaction (1). The structures on the left-hand side of the equilibria correspond to ideal "Zundel" structures, in which a proton can move freely between two electronegative atoms. The structures on the right-hand side correspond to ideal "Eigen" structures in which a distinct hydronium ion H_3O^+ is formed.

The theoretical investigation consists of simulating the absolute IR dielectric spectra of two systems containing 0.85 M aqueous solutions of either unionized or ionized (but not dissociated) forms of the weak acid HF. The nature of the chemical species in the two systems was predetermined by the choice of the starting configuration. The initial configuration for the first system was generated by replacing a molecule of H_2O by a molecule of HF from an equilibrated system that contained 65 water molecules. The initial configuration of the second system was prepared by first equilibrating an aqueous solution of dissociated HCl and then replacing Cl^- with F^-. The HF molecule maintained its identity throughout the equilibration and the production stages of the simulation in the first system. In contrast, a Zundel-like contact ion pair (see Figure 1 a) was formed during the equilibration period in the second system. This contact ion pair remained stable for most of the production run, except for a period of 1.5 ps in the middle of the trajectory when an Eigen-like contact ion pair and a Zundel-like solvent-shared ion pair were transiently formed.

The short 10 ps timescale accessed in our simulations and the limitations of the density functional theory (DFT) for investigating hydrogen-bonded systems precludes us from computing the concentration of the ion pairs with adequate confidence. Nevertheless, these limitations are most likely unimportant for calculations of the continua of absorption in IR spectra. Indeed, the timescale of the vibrations responsible for the continua of absorption is significantly shorter than our simulation timescale, while the performance of the exchange correlation functional employed is reasonably accurate in the prediction of vibrational frequencies for stable structures.[8]

With $\alpha(\tilde{\nu})$ denoting the Beer–Lambert absorptivity $(-1/l\ln(I/I_0))$ and $n(\tilde{\nu})$ representing the index of refraction, difference spectra $\Delta(\tilde{\nu})$ as a function of wavenumber $\tilde{\nu}$ between the absorption $[\alpha(\tilde{\nu})n(\tilde{\nu})]_c$ of an aqueous solution of HF of concentration "c" $(\text{mol}\,\text{L}^{-1})$ and the absorption $[\alpha(\tilde{\nu})n(\tilde{\nu})]_0$ of pure water were computed (see Equation (2)) using an approach recently developed by us.[10]

$$\Delta(\tilde{\nu}) = [\alpha(\tilde{\nu})n(\tilde{\nu})]_c - [\alpha(\tilde{\nu})n(\tilde{\nu})]_0 \qquad (2)$$

The new methodology allows both terms on the right-hand side of Equation (2) to be obtained from the simulation of the aqueous solution. Specifically, we employed on-the-fly Wannier orbital dynamics[11] to compute the trajectories of the dipole moments of those water molecules that were not hydrogen-bonded to HF or to its products of ionization. The "bulk" water spectrum was then computed from the cross-correlation of the solution dipole moment with the dipole moments of these selected water molecules by means of linear response theory. We have recently demonstrated[10] that this procedure dramatically improves the statistical accuracy of the reported difference spectra $\Delta(\tilde{\nu})$ thanks to substantial error cancellation in Equation (2).

After subtracting the contribution of the bulk water from the total absorption as illustrated in Equation (2), one is left with the continuous absorption generated by the presence of the various forms of HF. The difference spectra depicted in Figure 2 suggest that unionized species can be differentiated from ionized and dissociated acids because the presence of the former in an aqueous solution does not lead to significant absorption enhancements between $\tilde{\nu} = 1000$ and $1500\,\text{cm}^{-1}$. The present results suggest that an analytical investigation of the aqueous solutions of weak acids in terms of unionized, ion pairs, and dissociated species should be possible by quantitative IR spectroscopic methods. The key aspect of such an analysis is the decomposition of the absorption spectrum (after the contributions of bulk water and free hydronium ions have been removed) into a sum of two elementary spectra. One such spectrum should exhibit a continuous absorption pattern similar to that found in strong acids which is attributable to ion pairs. The remaining spectrum should

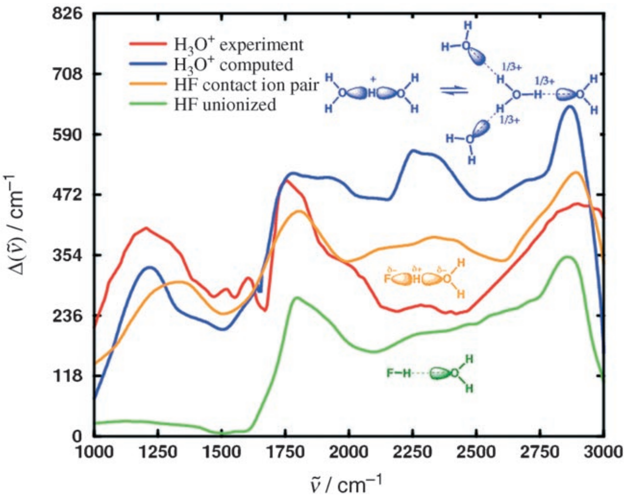

Figure 2. Comparison between difference spectra $\Delta(\tilde{\nu})$ as a function of wavenumber $\tilde{\nu}$ as defined in Equation (2) for different chemical species. Experimental results for a solution of HBr are taken from the study by Downing and Williams[9] and are scaled to a concentration $c = 0.85$ M. Although not directly comparable to the HF system studied here, Downing and Williams[9] provide values for $\alpha(\tilde{\nu})$ and $n(\tilde{\nu})$ separately so that direct comparison of the difference spectrum [see Eq. (2)] for H_3O^+ can be made. Note that theory[10] is able to describe quantitatively the "continuous absorption" in solutions of strong acids. Absorption in the region between $\tilde{\nu} = 1000$ and 1500 cm^{-1} is due to structural vibrations of Zundel-like symmetric structures. The absorption between $\tilde{\nu} = 1700$ and 3000 cm^{-1} is due to overextended FH and OH bonds as well as to transitions between Zundel and Eigen structures (see text).

exhibit a continuous absorption only between $\tilde{\nu} = 1800$ and 3000 cm^{-1} attributable to the unionized acid.

The present results are consistent with the recent interpretation of Asmis et al.[12] and Headrick et al.[13] regarding the assignment of spectra of liquid-phase acids. On the basis of the spectra of the bare protonated water dimer[12] and the Ar-tagged protonated multimers,[13] and of our computed difference spectra, we can confidently conclude that the broad absorption between $\tilde{\nu} = 1000$ and 1500 cm^{-1} in acid solutions can be attributed to the asymmetric stretch and the two bending modes of the $O \cdots H^+ \cdots O$ and of the $F^{\delta-} \cdots H^{\delta+} \cdots O^{\delta-}$ Zundel-like moieties. This band appears as three broad peaks in the gas-phase spectrum of the dimer[12] but is almost nonexistent in the difference spectrum of the unionized HF or in the argon matrix spectra of the trimer and tetramer, respectively.[13]

The broad band between $\tilde{\nu} = 1800$ and 3000 cm^{-1}, on the other hand, cannot be attributed to any structural vibration of an isolated Zundel-like ion because such vibrations do not appear in the spectra of the protonated water dimer in the gas phase[12] or in an argon matrix.[13] Several interpretations exist as to the molecular origin of this band in aqueous solutions of strong acids that emphasize the electronic changes associated with transitions between Zundel and Eigen structures.[14] Complementary to these interpretations, the present difference spectra of the unionized HF molecule suggest that one of the most important contributions to the intensity of the continuum of absorption between $\tilde{\nu} = 1800$ and 3000 cm^{-1} in solutions of weak acids is due to the anharmonic character of the HA bond stretch in the unionized acid and to the OH bond stretch modes in the water molecule whose oxygen atom acts as a Lewis donor to HA.

Interestingly, the computed spectra in Figure 2 suggest that the dissociation of the contact ion pair (spectrum in yellow) followed by formation of the bulk (solvated) hydronium ions (blue) is characterized by relatively minor changes in the continuum absorption in the $\tilde{\nu} = 1000$–1700 cm^{-1} region but involves more significant changes at larger wavenumbers. Similar patterns have been observed in recent IR experimental studies of the proton-pumping step in bacteriorhodopsin.[15] The possibility that contact ion pairs are involved as stable intermediates in the mechanism of the dissociation of weak aqueous acids cannot be readily dismissed in light of the present results and of previous experimental studies.[3,4] It is intriguing to consider the possibility that such molecular species play a role in the mechanism of proton-release pathways through intramolecular single-file water channels in bacteriorhodopsin and other biomolecules, a hypothesis that is supplementary to other theoretical investigations that have appeared recently.[16]

Our spectra can neither confirm nor affirm Giguère's interpretation of the IR spectra of concentrated HF solutions as containing a large fraction of contact ion pairs.[17] As can be seen from Figure 2, both the contact ion pair and the unionized acid shift the maximum of the HOH bending absorption from $\tilde{\nu} = 1730$ cm^{-1} in aqueous solutions of strong acids (blue curve) to approximately $\tilde{\nu} = 1800$ cm^{-1}. Therefore, we conclude that the question of the nature of the majority chemical species present in solutions of hydrofluoric acid should be resolved by carefully determining the difference spectra experimentally in the region of $\tilde{\nu} = 1000$ to 1500 cm^{-1}.

Experimental Section

Methods: Trajectories of the dipole moments were obtained using the Berry phase approach[18] and were utilized to compute the Beer–Lambert absorptivity $\alpha(\tilde{\nu})$ and refractive index $n(\tilde{\nu})$ spectra for wavenumbers $\tilde{\nu}$ varying between 40 and 4000 cm^{-1} by means of the time-correlation formalism of linear response theory[19] and the Kramers–Kronig relations.[19] The simulations were performed using Car–Parrinello molecular dynamics, density functional theory (DFT),[8] the B-LYP generalized gradient exchange-correlation functional,[20] plane-wave basis sets, and Troullier–Martin pseudopotentials.[21] The plane-wave basis set cut-off was taken to be 80 Ry, and a fictitious electron mass $\mu = 400$ a.u. in conjunction with an integration time-step of $\delta = 0.1$ fs were utilized. The Car–Parrinello molecular dynamics with localized orbitals was performed by employing multiple time-step integration algorithms in which the total dipole moment and the centers of the maximally localized Wannier orbitals were computed every 10 steps as described in reference [11]. The simulated systems consist of primitive cubic boxes containing 64 water molecules and one molecule of HF or HCl. All systems were equilibrated for a period of 10 ps using a Nosé–Hoover chain thermostat on each degree of freedom, after which the thermostats were removed and dynamical trajectories were collected for another 10 ps. The average temperature during the production runs was approximately 300 K in all simulations. All the calculations were carried out using the PINY MD package.[22]

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