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Electron Binding Energies of Hydrated H_3O^+ and OH^-: Photoelectron Spectroscopy of Aqueous Acid and Base Solutions Combined with Electronic Structure Calculations

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The ability of water molecules to spontaneously dissociate into hydronium and hydroxide ions is probably the most important chemical property of liquid water, which is behind all pH-related phenomena. Despite an immense interest in the ionic product of water and spectacular progress in experimental and computational description of its structure and dynamics, many open questions remain.[1] Recently, a lot of effort has been devoted to elucidating the proton transfer mechanism in hydrated H_3O^+ and OH^-.[2,3] The goal of the present work is complementary to these studies. By means of EUV photoelectron spectroscopy of aqueous acid and base solutions, supported by ab initio and molecular dynamics calculations, we characterize the electron binding energies of H_3O^+ and OH^-. Although a photoionization threshold for aqueous OH from a total electron yield measurement has been published previously,[4] this is the first time photoemission data are reported on the aqueous phase electronic structure of these ubiquitous ions and interpreted computationally.

Photoemission (PE) experiments were performed at BESSY, using a 10 μm liquid jet; the experimental setup has been described in detail elsewhere.[5] All spectra presented here were obtained for 100 eV photon energy, corresponding to 5−10 Å electron inelastic mean free path;[6] hence both bulk and surface emissions contribute to the spectra. Figure 1 shows the PE spectrum of pure liquid water and that of 3 m (i.e., 10 wt %) aqueous HCl solution. The reduced water signal in the acid spectrum is due to lower water concentration. Hydrated $Cl^-(3p)$ gives rise to the lowest energy feature at 9.6 eV. A clearly discernible emission from the hydrated proton is the small peak at 20 eV. In addition, the absence of water signal decrease for the $3a_1$ orbital, near 14 eV, suggests additional unresolved H_3O^+ emission at this energy. These effects increase proportionally to the H_3O^+ concentration (inset to Figure 1). Note also the apparent peak narrowing near the high-energy side of the $3a_1$ feature, indicated by arrows, which results from the reduced vapor pressure at higher concentration. For the $1b_2$ contribution, this effect is masked by strong 20 eV H_3O^+ emission, increasing for higher concentration.

Figure 2 compares the 3 m aq HCl PE spectrum with those of aq HNO_3, aq NaCl, and aq NaOH, all at similar concentrations. In each case, the specific anion emission gives rise to the lowest energy shoulder. As expected, the nitric acid spectrum also exhibits a pronounced peak at 20 eV; the broadening and shift of this feature, and also the extra intensity at 16 eV, presumably result from contributions from the more complex NO_3^- spectrum. Our assignment of the 20 eV peak to H_3O^+ is further supported by the absence of this feature in NaCl and NaOH aqueous solutions. Both of these spectra are nearly identical with the corresponding water spectrum, except for the water intensity decrease and the emerging Cl^- or OH^- features. The OH^- peak appears at 9.2 eV, with 1.15 eV fwhm. The chloride peak position observed in HCl is identical to that in alkali chloride solutions (at 9.6 eV).[6]

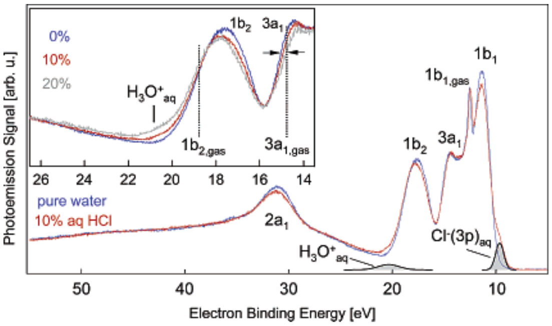

Figure 1. PE spectra of 10 wt % (3 m) aq HCl and of pure liquid water, measured at 100 eV photon energy (intensities are normalized to photon flux). Water orbital features and the major H_3O^+ and Cl^- contributions are indicated. Inset: enlargement of the H_3O^+ region; data for 20 wt % (6.8m) aq HCl are also included. Lines locate the gas-phase water positions.

In our previous study of aqueous salt solutions, we have explored various computational approaches to evaluating electron binding energies of solvated ions.[7] We have shown that for anions a viable computational strategy consists of running first a classical molecular dynamics (MD) simulation of a single anion in a periodic box of water molecules. The vertical ionization potential (IP) is then evaluated ab initio at the MP2/aug-cc-pVTZ level as a difference between the anionic and neutral energies sampling the series of water configuration from the MD trajectory, with water molecules represented by fractional charges (or possibly with the first solvation shell waters treated quantum mechanically). We used the same approach here for OH^-, with computational details presented in the Supporting Information.

The resulting distribution of IPs (from detachment from either of the two $2p\pi$ orbitals OH^-), peaking at 9.7 eV, is depicted in gray in Figure 2d. The local asymmetry of the solvent splits the degeneracy of the $2p\pi$ by 0.2 eV, but the inhomogeneity in solvent sites provides most of the peak broadening (0.9 eV). The next IP is at 13.5 eV and corresponds to removal of the $2p\sigma$ electron. Unfortunately, this peak is hidden in the experiment under the strong water structure. For 10 representative geometries, we also included the first solvation shell around OH^- quantum mechanically. This

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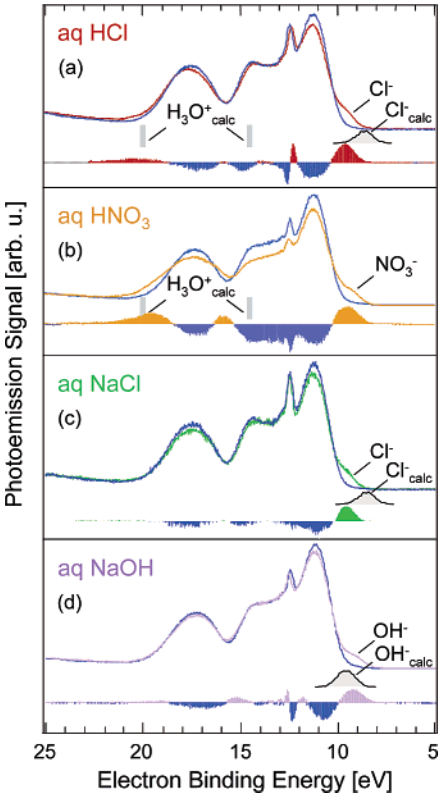

Figure 2. Photoemission spectra of aqueous solutions of (a) 3 m HCl, (b) 4 m HNO_3, (c) 3 m NaCl, and (d) 2 m NaOH. For comparison, the pure water PE spectra and the differential spectra are also shown. Solute emission contributions can be identified as the positive contributions in the difference spectra. Gray shaded features indicate the calculated ionization energies of (a,b) H_3O^+, and PE bands for (a,c) Cl^-,[5] and (d) OH^-. The calculated widths for the anionic bands are drawn to scale.

results in a 0.1−0.2 e charge transfer from OH^- to neighboring waters, but has a minor effect on the IP (average blue shift of less than 0.2 eV).

For positively charged ions, the above approach, however, overestimates the IPs due to the neglect of solvent electronic polarization, which is particularly important for stabilizing the nascent dication. Actually, much better results were obtained for alkali cations using a polarizable continuum model (PCM) for the solvent, despite the implicit relaxation of the solvent nuclear polarization.[7] Therefore, we have evaluated the electron binding of the aqueous cation by embedding H_3O^+ (implicitly assuming the prevalence of Eigen-like structures for the hydrated proton[8]) using a PCM for the solvent. Calculations were performed at the MP2/aug-cc-pVTZ (and TD-B3LYP/aug-cc-pVTZ for the higher states of the nascent dication); for details, see Supporting Information. The lowest IP lies at 14.5 eV (Figure 2) and reflects ionization from the highest ($3a_1$) p-orbital of H_3O^+. The next IP at 19.8 eV corresponds to ionization from the degenerate set of the remaining two valence (1e) p-orbitals, while the following IP of 32.3 eV correlates with the removal of a valence ($2a_1$) s-electron. For comparison, we also tested the Zundel $H_5O_2^+$ structure of the hydrated proton; a strong shift (by more than 2 eV) to lower IP is observed compared to the Eigen core.

The present calculations are complementary to the Car−Parrinello MD simulations of hydrated hydronium and hydroxide ions.[9] Those simulations account for the electronic structure of the whole system, thus opening a window for the description of important phenomena of proton delocalization and hopping in water. However, within that approach, it is very difficult to calculate IPs as energy differences between electronic states before and after electron removal, particularly for cases where the final state is an excited state of the whole system. The IPs must then be estimated from the local density of states, based on the one-electron Kohn−Sham orbitals. However, the application of the Koopman's theorem in density functional theory is not well justified and leads to sizable errors. For example, the computed positions of the H_3O^+, OH^-, and water peaks[9,10] are all shifted by 3−5 eV to lower IPs compared to the present experiments. Within our approach, where electronic structure calculations of the relevant states of the solute account for the solvent approximately either as fractional charges (aq OH^-) or within a polarizable continuum model (aq H_3O^+), we avoid issues of charge transfer relaxation in the final states and can, therefore, focus on the vertical IP without resort to Koopman's theorem. As a result, we are obtaining IPs closer to experiment, although it is clear that we still neglect important aspects of the solute−solvent interactions and have to invoke different approaches for the anion and cation.

Several of the solute lines are obscured by water features in the experiment. However, spectral signatures of the lowest IP of OH^- at 9.2 eV and of the second lowest IP of H_3O^+ at 20 eV are clearly resolved and are both in a very good agreement with the present calculations. The present peak position and width for OH^- is also consistent with a previously determined threshold energy of 8.45 eV.[4] The observed IP of hydronium is in better agreement with calculations which assume an Eigen rather than a Zundel core.

Note that our calculations are pertinent to the bulk, while the experiment samples both bulk and surface regions. Our recent simulations indicate that in base solutions OH^- is weakly repelled from the surface, while in acid solutions H_3O^+ shows a weak propensity for the surface.[11] Given the experimental probing depth, we suggest that the signal, therefore, originates predominantly from completely or almost completely solvated ions. Moreover, earlier work suggests that ionic IPs in the interfacial layer may be similar to those in the aqueous bulk.[12]

The results presented here fill a gap in our knowledge on the electronic properties of hydrated H_3O^+ and OH^-. The existing thermodynamic, spectroscopic, and computational data on the ionic product of water are complemented by first reliable values for the ionization potentials. We also believe that these results will provide a useful calibration point for developing quantitative ab initio molecular dynamics models for ions in water.

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Supporting Information Available: Computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Geissler, P. L.; Delago, C.; Chandler, D.; Hutter, J.; Parrinello, M. *Science* **2001**, *291*, 2121.
(2) Agmon, N. *J. Phys. Chem. A* **2005**, *109*, 13 and references therein.
(3) Chen, B.; Ivanov, I.; Park, J.-M.; Parrinello, M.; Klein, M. L. *J. Phys. Chem. B* **2002**, *106*, 12006 and references therein.
(4) vonBurg, K.; Delahay, P. *Chem. Phys. Lett.* **1981**, *78*, 287.
(5) Winter, B.; Weber, R.; Widdra, W.; Dittmar, M.; Faubel, M.; Hertel, I. V. *J. Phys. Chem. A* **2004**, *108*, 2625.
(6) Faubel, M. Photoelectron Spectroscopy at Liquid Surfaces. In *Photoionization and Photodetachment*, Part I.; Ng, C.-Y., Ed.; World Scientific: Singapore, 2000; p 634.
(7) Winter, B.; Weber, R.; Hertel, I. V.; Faubel, M.; Jungwirth, P.; Brown, E. C.; Bradforth, S. E. *J. Am. Chem. Soc.* **2005**, *127*, 7203.
(8) Schmitt, U. W.; Voth, G. A. *J. Chem. Phys.* **1999**, *111*, 9361.
(9) Tuckerman, M.; Laasonen, K.; Sprik, M.; Parrinello, M. *J. Chem. Phys.* **1995**, *103*, 150.
(10) Hunt, P.; Sprik, M.; Vuilleumier, R. *Chem. Phys. Lett.* **2003**, *376*, 68.
(11) Mucha, M.; Frigato, T.; Levering, L.; Allen, H. C.; Tobias, D. J.; Dang, L. X.; Jungwirth, P. *J. Phys. Chem. B* **2005**, *109*, 7617.
(12) Bradforth, S. E.; Jungwirth, P. *J. Phys. Chem. A* **2002**, *106*, 1286.

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