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# The Electron Attachment Energy of the Aqueous Hydroxyl Radical Predicted from the Detachment Energy of the Aqueous Hydroxide Anion

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The maximum in the photoelectron spectrum (PES) of the aqueous hydroxide anion is separated by only 0.7 eV from the PES edge for liquid water at 9.9 eV.[1] In comparison the 10.8 eV difference between the gas-phase ionization potentials (IP) of $OH^-$ and $H_2O$ is more than an order of magnitude larger. If solvation has such a large effect on the vertical detachment energy (VDE) of $OH^-$(aq), what will be the effect on the vertical attachment energy (VAE) of the oxidation product, the aqueous hydroxyl radical $OH^•$(aq)? Using experimental data from the literature and input from molecular dynamics simulation, we estimate the VAE of $OH^•$ (aq) to be 2.2 eV. This is not very different from an electron affinity of 1.8 eV of $OH^•$ in vacuum, leaving a 7.0 eV gap between the VDE of $OH^-$(aq) and VAE of $OH^•$(aq). The simulation also shows that the reorganization of the aqueous solvent responsible for this large gap is nonlinear.

The experimental estimates of the vertical ionization energies quoted above are from a recent investigation by Winter et al.[1] The energy resolved PES data of ref 1 provide considerably more detail than the older Photoemission Threshold (PET) energy measurements by Delahay.[2] With new and more accurate PES results in hand, we can now repeat the comparison to the adiabatic ionization potential (AIP), previously carried out using the PET data.[2,3] The key step in this comparison is putting PES and thermochemical energies on the same absolute (vacuum) scale (see Figure 1). One way to achieve this is starting from the values for absolute solvation free energies ($\Delta G_{\text{sol}}$) of ions produced by the cluster ion method developed by Coe and co-workers.[3,4] The number given for $OH^-$(aq) in ref 4 is $\Delta G_{\text{sol}}(OH^-) = -4.46$ eV. Combined with the vacuum ionization potential (IP = 1.83 eV) and the solvation energy of the neutral radical ($\Delta G_{\text{sol}}(OH^•) = -0.2$ eV),[5] the free energy of oxidation of $OH^-$(aq) becomes AIP $= -\Delta G_{\text{sol}}(OH^-) + \text{IP} + \Delta G_{\text{sol}}(OH^•) = 6.1$ eV. The difference VDE − AIP = 3.1 eV is the free energy gained by resolvation of the nonequilibrium $OH^•$ created by vertical oxidation of $OH^-$(aq).

A more direct route to absolute oxidation free energies is converting electrode potentials to a vacuum scale using the absolute value of the Standard Hydrogen Electrode (SHE).[6] The recommended value[7] for the $OH^•$(aq)/$OH^-$(aq) couple is $E° = 1.9$ V (ref 5 gives $E'$ $OH^•$(aq)/$OH^-$(aq) = 1.77 V at pH = 7). Adding 4.44 V, the absolute SHE potential according to ref 6, we find an AIP of 6.3 eV leading to a relaxation energy of 2.9 eV. Note that the electrochemical AIP is a reversible work function which includes a contribution from the water surface potential.[6] PES data also contain a surface contribution. Electrochemical AIPs are therefore preferred for estimation of relaxation energies, and we have based our considerations on the 2.9 eV value.

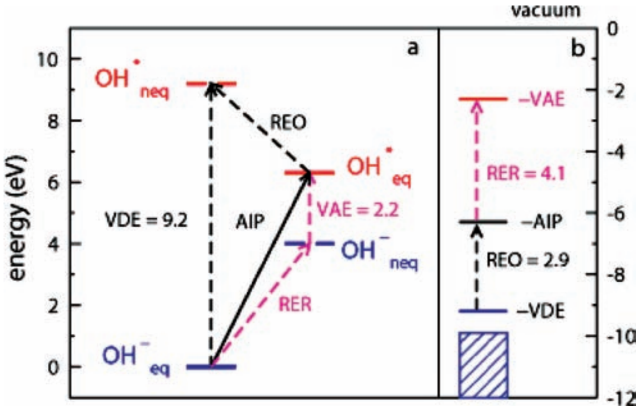

***Figure 1.*** Level schemes comparing the energy for vertical detachment (VDE) of an electron from $OH^-$(aq) to the adiabatic ionization potential (AIP) and the energy for vertical electron attachment (VAE) to $OH^•$(aq). REO and RER are the reorganization free energies of oxidized respectively reduced species. (a) Free energies referred to $OH^-$(aq). Arrows in black indicate energies taken from PES[1] and electrochemical experiments[7] (see text). Magenta arrows are predictions based on these experimental data and calculation. (b) Corresponding electronic energy levels referred to vacuum. The hatched blue area represents the top edge of the density of states of liquid water as determined by PES.[1,2]

To relate attachment, detachment, and adiabatic energies, allowing for a possible nonlinear response to ionization, we use a generalization of Marcus theory[8] for half-reactions $R \rightarrow O + e^-$. The equations we need are VDE = AIP + REO and VAE = AIP − RER (see Figure 1; the AIP can also be viewed as an adiabatic attachment energy[3]). In the linear response approximation the reorganization energies in the reduced (RER) and oxidized (REO) state are equal. If relaxation on the reduced and oxidized potential energy surface is asymmetric, RER and REO are different. The reorganization following vertical ionization of $OH^-$ takes place in the oxidized state, and hence the 2.9 eV relaxation energy deduced above must be identified with REO.

For the computational investigation of the $OH^•$(aq)/$OH^-$(aq) reaction we used the Density Functional Theory (DFT) based molecular dynamics (DFTMD) method building on previous studies of redox half-reactions.[9] $OH^-$(aq) has already been the subject of extensive DFTMD simulations (for a review see ref 10). Application of DFTMD to $OH^•$(aq), in contrast, has been impeded by serious technical difficulties related to the open shell nature of $OH^•$. The problem is that the DFT approximation employed in DFTMD tends to delocalize unpaired electrons. For the aqueous $OH^•$ radical this leads to the formation of a false hemibond with a $H_2O$ molecule.[11,12] The root of the problem, the self-interaction error in DFT, has recently received a lot of attention, and substantial progress toward resolving this issue has been made.[13] Constrained by the high computational expense of DFTMD we have suppressed the formation of hemibonds by an empirical self-interaction correction (SIC) applied to the unpaired

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electron only.[12] The same BLYP based SIC scheme is used here but in reparametrized form (see Supporting Information).

In accordance with earlier work,[11,12] we find that OH$^\bullet$ is essentially hydrophilic. Judging from the degree of structure exhibited by the radial distribution functions (Figure 2), hydrogen bonds can even be of similar strength to that for OH$^-$. However, while OH$^-$ is a stronger hydrogen bond acceptor than donor, it is the other way around for OH$^\bullet$ (see also the schematic representation of the TOC graphics). Evidently, neutralization of OH$^-$ rearranges hydrogen bonding rather than eliminates it. The central quantity in the calculation of redox energies is the instantaneous energy gap $\Delta E$ between an oxidized (O) and reduced (R) state.[8,9] Averaging $\Delta E$ over an equilibrium MD trajectory of the reduced system gives the VDE. Similarly, averaging over a trajectory of the oxidized system gives the VAE. The AIP is computed by thermodyamic integration of $\Delta E$, summing over a series of linear superpositions of the R and O potential energy surfaces transforming R into O.[8,9] The results we obtained are VDE = 4.1 eV, VAE = 0.9 eV, and AIP = 3.1 eV (the duration of a typical trajectory was 10 ps). Substituting in the generalized Marcus relations, we find REO = VDE − AIP = 1.0 eV and RER = AIP − VAE = 2.2 eV with a statistical uncertainty of 0.1 eV.

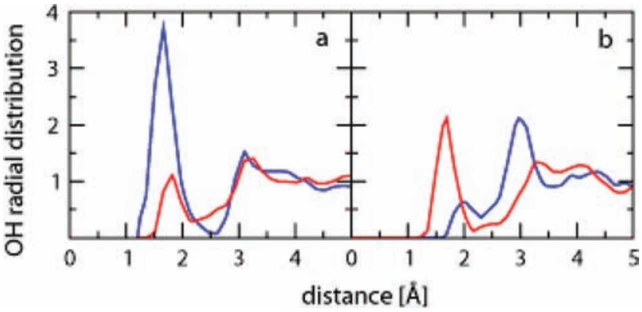

***Figure 2.*** Radial distribution function of the OH$^-$(aq) anion (in blue) and OH$^\bullet$(aq) radical (in red) compared. (a) Correlation between the H atoms of the $H_2O$ molecules of the solvent and the O atom of the solute. (b) Correlation between H atom of the solute and O atoms of the solvent $H_2O$. The DFTMD model system consists of 31 $H_2O$ molecules and one solute (OH$^-$ or OH$^\bullet$) in a cubic MD cell of length $L = 9.86$ Å. Periodic boundary conditions (PBC) are applied.

An asymmetry of DRE = RER − REO = 1.2 eV in relaxation energies is significant. The rearrangement of hydrogen bonding (Figure 2) responsible for this nonlinearity is short-range and therefore relatively insensitive to finite system size errors. The small size of our MD model system has however a large effect on absolute energies as is evident from the poor agreement of the computed AIP and REO with experiment. An important source of error is the net ionic charge created by our half-reaction scheme.[9,14] Under PBC this charge is neutralized by a homogeneous distribution of countercharge. For the system size used in our calculation ($L \approx 10$ Å) the direct electrostatic interaction between solute ion, its periodic images, and neutralizing background charge is in the eV's. However, screening by the polar solvent reduces the net effect on oxidation free energy. The finite size error on AIP can be estimated using a periodic generalization of the Born cavity model.[14] With a Born radius fitted to the experimental solvation energy of OH$^-$(aq), the continuum expression of ref 14 gives a correction of only 80 meV. The finite size error for reorganization energy, in contrast, is large and, for one-electron oxidation, can be approximated[14] by $\Delta\mathrm{RE} = -p\xi_{\mathrm{EW}}/2L$. With a Pekar factor $p \approx 0.6$ for water, $\xi_{\mathrm{EW}} = -2.84$, and $L = 10$ Å, this amounts to having to add $\Delta$RE = 1.2 eV to the computed reorganization energies.

DFTMD oxidation energy calculations are subject to a second error, namely, a shift in the reference of the electrostatic potential under PBC.[15] This offset, called the Poisson potential shift (PPS), is for sufficiently large systems independent of cell size and, at low concentration, determined by the solvent only. The PPS can therefore be estimated by matching the solvation free energy $\Delta G_{\mathrm{sol}}$ of a reference ion with the (absolute) experimental value. We choose the proton for this purpose exploiting a recently developed DFTMD proton insertion scheme for the computation of p$K_a$'s.[16] The difference of the $\Delta G_{\mathrm{sol}}(\mathrm{H}^+) = -15.5$ eV we calculated[16] relative to the cluster ion value (−11.53 eV)[4] gives the desired PPS after a correction for zero-point energy (0.3 eV). Addition of the resulting 3.7 eV offset to the bare PBC number raises the AIP from 3.1 to 6.8 eV. The VDE, being equal to AIP + REO, needs a further correction for size effects. Using the continuum approximation $\Delta$RE = 1.2 eV, we find VDE = 9.0 eV. Application of these two corrections brings the DFTMD estimates of AIP and VDE within 0.5 eV of the experiment values (Figure 1).

A similar correction procedure adjusts the VAE to 0.9 + 3.7 − 1.2 = 3.4 eV (because VAE = AIP − RER, we now must subtract $\Delta$RE). Due to the limitations of our DFT approximation the uncertainty in this prediction is considerable. The error can reduced by combining experiment and computation. We can add the asymmetry DRE, as computed by DFTMD, to the experimental REO to obtain an estimate of RER. This yields RER = 1.2 + 2.9 = 4.1 eV. Then subtracting from the experimental AIP = 6.3 eV, we find VAE = 2.2 eV. We estimate the uncertainty in this result to be no larger than 0.5 eV. This places the (inverse) PES level of OH$^\bullet$(aq) at −2.2 eV below vacuum (see Figure 1b) or ~1.5 eV below the conduction band of liquid water.[3] While this is surprisingly high considering OH$^\bullet$ is an aggressive oxidant, this observation can be rationalized in the framework of the Marcus theory of electron transfer. A large reorganization energy is required to make a highly exoergonic reaction fast (barrierless). Furthermore, the critical energies are taken from experiment. The only input from calculation is a relative relaxation energy. We believe, therefore, that the argument for a VAE of OH$^\bullet$(aq) of ~2 eV is compelling.

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**Supporting Information Available:** Parametrization and validation of the empirical BLYP based SIC functional. This material is available free of charge via the Internet at http://pubs.acs.org.

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