

On the Enthalpy of Formation of Hydroxyl Radical and Gas-Phase Bond Dissociation Energies of Water and Hydroxyl

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Carefully executed experimental photoionization mass-spectrometric measurements, an exhaustive analysis of spectroscopic data, and very high-level ab initio calculations converged toward a new value for the bond dissociation energy of water and, accordingly, a new bond dissociation energy and enthalpy of formation of hydroxyl radical. This is the powerful message conveyed by the front page illustration of the March 21, 2002 issue of the *Journal of Physical Chemistry A*. The accompanying caption points to a paper that resulted from a multi-institutional effort led by ANL, which produced a significant correction to the bond dissociation energy in water by demonstrating convergence in the three arenas mentioned above.

The bond energy of water is of fundamental importance in chemistry and affects many chemical processes, ranging from environmental and industrial to biological. The knowledge of its correct value is critical in developing predictive computer models of complex systems. The change in the bond dissociation energy of water profoundly affects a substantial number of other thermochemical quantities.

The paper (Branko Ruscic, Albert F. Wagner, Lawrence B. Harding, Robert L. Asher, David Feller, David A. Dixon, Kirk A. Peterson, Yang Song, Ximei Qian, Cheuk-Yiu Ng, Jianbo Liu, Wenwu Chen, and David W. Schwenke, *J. Phys. Chem. A* 106 (2002) 2727-2747) addresses in great detail (necessary to give a definitive answer) the relevant experimental and theoretical aspects leading to the new value. Several new experiments presented in the paper (mass-selected photoionization measurements, pulsed-field-ionization photoelectron spectroscopy measurements, and photoelectron-photoion coincidence measurements), which utilize the power of the positive ion cycle to derive the O-H bond energy, produce a consensus value of the bond dissociation energy of water $D_0(\text{H-OH}) = 41128 \pm 24 \text{ cm}^{-1} = 117.59 \pm 0.07 \text{ kcal/mol}$, corresponding to $\Delta H_{F0}(\text{OH}) = 8.85 \pm 0.07 \text{ kcal/mol}$, and hence $D_0(\text{OH}) = 35593 \pm 24 \text{ cm}^{-1} = 101.76 \pm 0.07 \text{ kcal/mol}$. In contrast, the previously accepted values of the two successive bond dissociation energies of water differ by 0.5 kcal/mol. The paper provides an analysis of the methods used previously to obtain the bond energy, demonstrating explicitly why they have led to incorrect values. The new experimental values are completely supported by the most sophisticated theoretical calculations ever performed on H_2O and OH : CCSD(T)/aug-cc-pVnZ, n=Q, 5, 6, and 7, extrapolated to the CBS limit and including corrections for core-valence effects, scalar relativistic effects, incomplete correlation recovery, and diagonal Born-Oppenheimer corrections.

The new bond dissociation energy of water affects directly or indirectly a large number of other thermochemical quantities. The paper illustrates the impact by providing a discussion of several reaction enthalpies, deprotonation enthalpies, and proton affinities, from which it is already clear that the changes introduced by the new bond energy are significant. However, these immediately understood consequences present just the tip of the iceberg, and the full magnitude of the impact has yet to be determined.

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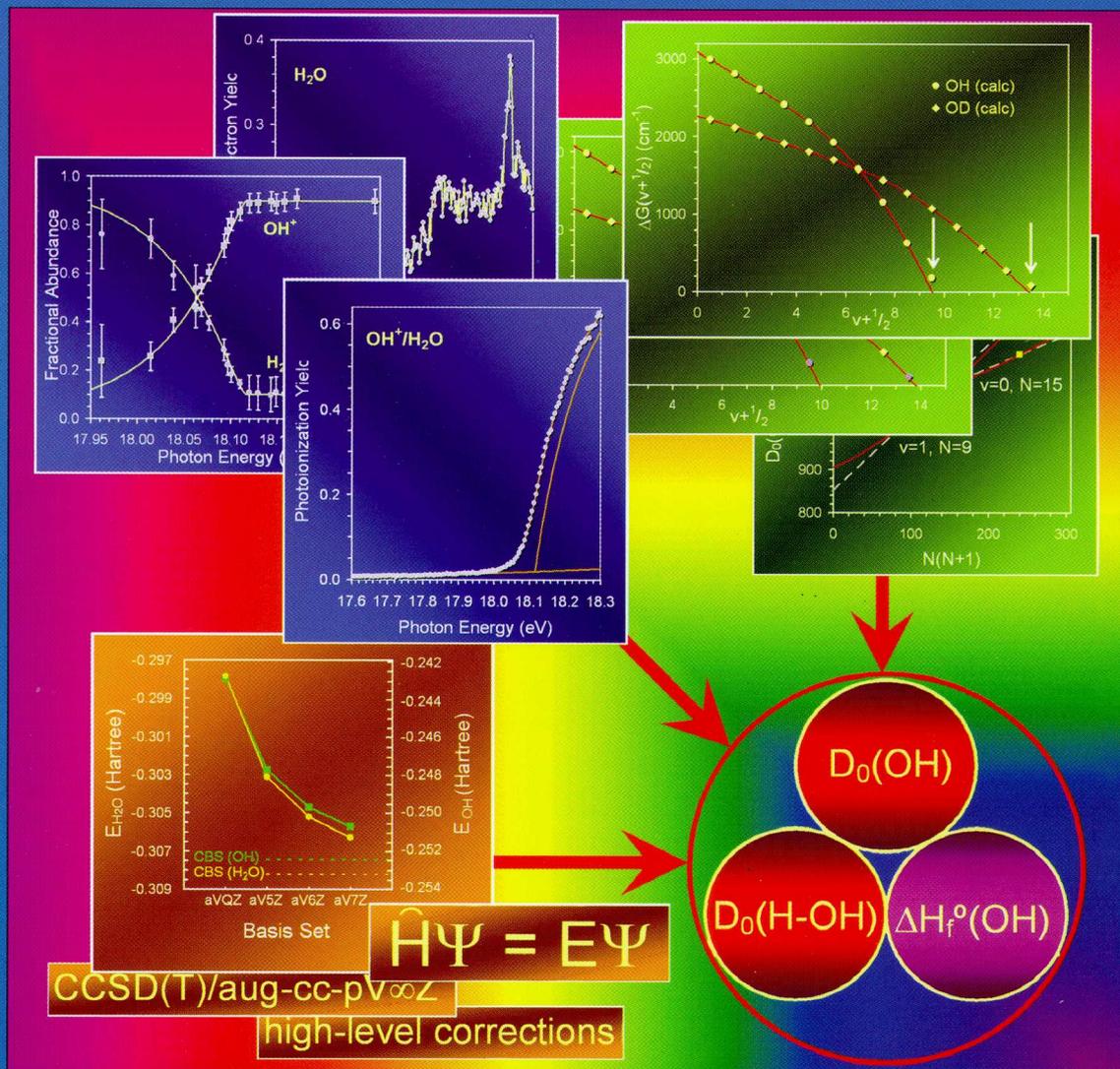
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Careful Experiments, Spectroscopic Arguments, and High-Level Theory Converge to New Thermochemistry for Water (see page 2727)

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