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Benjamin J. Schwartz

Department of Chemistry and Biochemistry, University of California, Los Angeles

To be or not to be in a cavity: the hydrated electron dilemma

Solvated electrons are the simplest quantum mechanical solutes, consisting of excess electrons in common liquids. Because of their apparent simplicity, solvated electrons provide a unique opportunity for confrontation between experiments and quantum simulations. Yet, despite nearly five decades of interest in solvated electrons, there is still controversy over the nature of their molecular structure. Based on the results of simulations, the standard picture of solvated electrons (and of the hydrated electron in particular) has been that it occupies a cavity: the thought is that the excess electron expels the solvent, creating a small cavity in the fluid that supports a series of bound electronic states. We recently challenged this idea by suggesting a picture in which the hydrated electron is associated with a region of enhanced water density rather than a cavity (Science 329, 65 (2010)); our work has ignited a storm of controversy (see, e.g., Science 331, 1387 (2011)). This talk will work to better understand the structure of solvated electrons by making rigorous comparisons between experiment and the simulated cavity and non-cavity pictures of the hydrated electron. First, we examine the temperature and density dependence of the hydrated electron's absorption spectrum. We find that cavity models of the hydrated electron are unable to produce the experimental linear red-shift of the hydrated electron's absorption spectrum with increasing temperature at constant density, whereas our non-cavity model does produce the correct qualitative behavior. Second, we focus on connections between simulations and the experimental resonance Raman spectrum of the hydrated electron. We find that cavity models of the hydrated electron predict O--H stretching bands for the nearby water molecules that are narrower than that of bulk water, with most of the enhanced intensity on the blue side of the bulk water band, a result that is in poor qualitative agreement with experiment. In contrast, our non-cavity model predicts an O--H stretching band that is broader than that of bulk water and enhanced on the low-frequency side, in excellent qualitative agreement with experiment (Proc. Nat. Acad. Sci. USA 110, 2712 (2013)). Finally, we discuss the results of experiments and simulations addressing the question of whether or not hydrated electrons prefer to reside at the air/water interface.



Benjamin J. Schwartz received his Bachelor's degree in Physics and Chemistry from the University of Michigan in 1986, and his Ph.D. in Experimental Physical Chemistry from UC Berkeley in 1992 under the guidance of Charles Harris. After carrying out postdoctoral work in theoretical physical chemistry at the University of Texas, Austin (1993-5, with Peter Rossky) and in experimental semiconductor physics at UC Santa Barbara (1995-6, with Nobel Laureate Alan Heeger), he joined the faculty at UCLA in 1997. He was promoted to Associate Professor with tenure in 2002 and Full Professor in 2004. He has published over 150 papers in peer-reviewed journals and holds 2 U.S. patents with an additional patent pending. Prof. Schwartz has received Teacher-Scholar awards from both the Dreyfus Foundation and the

Research Corporation, and he is a Sloan Foundation Fellow. He has served as graduate advisor and is currently serving as vice-chair for the department of Chemistry and Biochemistry. Prof. Schwartz' teaching has been recognized by his receipt of both the department's Hanson-Dow award and UCLA's campus-wide Distinguished Teaching award. Finally, Prof. Schwartz has been serving as Senior Editor for the Journal of Physical Chemistry since 2005.