PHOTOELECTRON SPECTROSCOPY OF SOLVATED ELECTRONS IN LIQUID MICROJETS

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The solvated electron is a bare electron in solution. Lacking any internal degrees of freedom, it can be thought of as the simplest possible quantum mechanical solute, thus this relative simplicity makes the solvated electron an excellent model system for studying chemistry in solution. Furthermore, the solvated electron has proven to be an important transient in radiation chemistry and biology where it acts as an extremely reactive reductant. Research in the Neumark group over the past 10 years has contributed much to the understanding of the solvated electron via the study of anionic solvent clusters, the gas-phase analogues of the bulk solvated electron. By extrapolation to the limit of infinite cluster size, these results have been used to infer the binding energies and internal conversion lifetimes of the solvated electron in various bulk solvent systems; however, some controversy exists over this extrapolation method. Liquid microjets allow us to test these extrapolations by direct investigation of the bulk solvated electron in the liquid phase.

First measurements of the vertical binding energy (VBE) of the solvated electron in water were performed in 2010 and are in remarkable agreement with the predictions from anionic water clusters. Investigations into the binding energies of the solvated electron in methanol, ethanol, and tetrahydrofuran are presented, which yield some surprising results. Like in water, results in tetrahydrofuran are consistent with the VBE extrapolated from the cluster data; however, in methanol the result is significantly different from the predicted value. Moving on from the vertical binding energy experiments, we are beginning a study of the dynamics of the electron in aqueous solution. There are three known timescales for the relaxation of the solvated electron following excitation to its single, bound excited state; however, the transient absorption experiments used to measure these timescales originally are unable to conclusively determine a relaxation mechanism. We propose to repeat these measurements using time resolved photoelectron spectroscopy. These measurements are currently in progress and preliminary results are presented.