Examining the hydrated electron's excited state lifetime through temperature-dependent femtosecond transient absorption

The hydrated electron has been extensively characterized since its observation in the 1960s. Despite efforts to broadly describe solvated electrons in various media, and particularly in water, there remain outstanding questions about their fundamental behavior including basic features such as their structure. There exist several competing theoretical models for the structure of the hydrated electron: at one extreme the hydrated electron is depicted as residing in a cavity created by excluding water molecules, at the other extreme the electron has been predicted to encompass water molecules with locally increased density—with its wave function residing largely in the interstitial spaces between molecules. Despite these drastic changes in predicted geometry, many of the calculated observables are similar enough to be experimentally indistinguishable. One important predicted difference between the two models is temperature dependence of the excited-state lifetime. Recent simulations in our group show the non-cavity model changes structure as a function of temperature, leading to a prediction that the lifetime is highly temperature dependent. Cavity models, on the other hand, are quite rigid, leading to little dependence of the predicted lifetime with temperature. Furthermore, previous femtosecond transient absorption (fsTA) measurements at room temperature have been unable to conclusively assign a lifetime matching the ~100 fs value measured via time-resolved photoelectron spectroscopy (TRPES) at room temperature. To differentiate the theoretical models, understand the effects of temperature on dynamics, and rectify previous problems with fsTA measurements, we present a set of temperature dependent fsTA experiments with a 65 fs cross-correlation time over the range of 0 to 45 C in liquid water. The measured dynamics consist of ~130 fs and ~1 ps timescales, with both processes exhibiting a factor of 2 change over our studied temperature range. Using this observed temperature dependence in a global fitting procedure across data from all available temperatures, we have broken the fitting-parameter correlation which has previously prevented conclusive assignment of the hydrated electron's excited-state lifetime measured by fsTA—which for the first time is in excellent agreement with measurements by TRPES. Finally, we present evidence of the hydrated electron's stimulated emission which decays in less than 150 fs. The strong temperature dependence and stimulated emission dynamics are unambiguous indications of non-cavity behavior

Presented by:

Erik Farr
Professor Ben Schwartz’s Group
Department of Chemistry & Biochemistry
University of California, Los Angeles

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