

Investigating the solvated electron in transient solvent structures utilizing pump-repump-probe spectroscopy

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Time and frequency resolved investigations of the photoinduced electron detachment in liquids showed that the generation of solvated electrons proceeds via precursing intermediates [1], the nature of which still being subject to controverser discussion. In the course of the formation of the solvent shell the electron interacts with different structural configurations of the solvation shell manifesting in different spectral properties of the solvated electron. Former pump-probe spectroscopy of the solvated electron mainly concentrated on the equilibrated groundstate [2], leaving open questions regarding the early stages of solvation. In the present work we include the transient spectroscopy of precursing states in a detailed pump-repump-probe investigation of the solvated electron in methanol. Global analysis of the data with a kinetic model aims at a complete microscopic picture of the generation and relaxation dynamics. Using a 273 nm UV-pulse we generate electrons via two-photon-absorption in a freeflow jet of neat methanol. During the solvation process the electron is supposed to traverse the precursing states p' and s_{hot} before it arrives at the equilibrated groundstate s_{equil} . [3] To selectively excite each one of these states, we apply a secondary excitation pulse at 820 nm with 0.5, 5 and 60 ps delay after the UV generation pulse, corresponding to their maximum relative population density. The change in optical density of the sample is probed polarization resolved in a vast spectral range from 450 nm to 2.4 μ m with time resolution of 100 to 250 fs.

The self-consistent global analysis of the measured data based on a multilevel scheme yields time constants and spectral signatures for the observed transient states. The latter prove to be vitally important for the identification of the respective species. Our results for the generation experiment (without application of the repump pulse) nicely agree with earlier work by Scheidt et al., indicating the initial trapping of the detached electron within 100 fs in a preexisting trap in a p-like excited state p' as indicated by stimulated emission an spectral anisotropy features. We observe an early cooling process within 600 fs after which the p' state relaxes to a s-like s_{hot} state in a hot solvent environment within 3.5 fs. A final cooling process with a time constant of 8 ps leads to the equilibrated solvated electron in methanol, accompanied by a further blue-shift of the wellknown spectral absorption band.

Reexcitation of selected species verifies the relaxation scheme of the kinetic model, going upstairs on the relaxation ladder and observing corresponding intermediates thereof. Respective spectral signatures and relaxation times are observed with minor modifications depending on the energy deposited in the local environment (“temperature”). A clear correlation with the wellknown temperature dependence of H-bonds of the solvent molecules is found: With weakened H-bonds at higher “temperatures”, the energy transport from the electron to neighbouring solvent shells proceeds on a slower timescale, leading e.g. to longer excited state lifetimes and slower groundstate cooling. Convincing evidence is obtained that the precursor of the solvated electron (termed wet electron in the case of water) is a “hot” ground state electron.

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