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The Solvated Electron in Acetonitrile STEPHANIE DOAN, ARTHUR BRAGG, BENJAMIN SCHWARTZ, Dept. Chem. & Biochem., UCLA — The nature of solvated electrons in liquid acetonitrile is of great interest as it appears that excess electrons in this solvent are stabilized in two forms, a dipole-bound (DB) electron (i.e. a typical solvated electron) and a valence-bound electron (VB) electron (e.g. a solvated CH3CN dimer anion). Previous work has suggested that these two species are in equilibrium and can interconvert. We performed 3-pulse transient hole-burning experiments aimed at better understanding the nature of the VB and DB electrons. We found that photoexcitation of VB electrons produces an increased population of DB electrons, but that exciting DB electrons does not produce VB electrons. This suggests a significant asymmetry in the solvent motions that accompany photoexcitation of the electron: it is easier for a DB electron to relax back into the solvent location from which it came than for the local solvation structure to change enough to create a VB electron, whereas excitation of a VB electron disrupts the local solvent structure to the point where the excited electron can relax into the bulk solvent rather than back to the molecules on which it initially resided.

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