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Electronic Excitation in Aqueous Anions

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Anions when hydrated in water exhibit new features in their electronic absorption spectrum. In the completely hydrated medium of bulk water, charge transfer bands are fully developed and valence transitions exhibited in vacuum can also lead to production of solvated electrons. Using broadband femtosecond transient absorption spectroscopy, we have recorded two-photon absorption spectra that characterize the spectrum of electronic states of aqueous organic and inorganic anions and explored the electronic relaxation dynamics occurring after excitation of valence and charge-transfer-to-solvent states. The detachment dynamics typically are strongly dependent on the excitation energy. The overall solvated electron yields can be understood in terms of competing non-adiabatic, solvation and vibrational relaxation pathways in the excited state. Understanding these electronic states and pathways provides several critical tests for solution electronic structure theories.