

Photoinduced Electron Transfer at Nanostructured Surfaces: Effect of Varying Light Wavelength, Temperature, Non-adiabatic Electronic Couplings and Oscillator Strengths

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The electronic dynamics at surfaces of nanostructured semiconductors, induced by absorption of visible light, is described by means of the reduced density matrix equations of motion to include dissipative phenomena due to coupling of electrons at the surface with medium electronic and vibrational excitations. [1] Instantaneous dissipation is constructed from rates of electronic excitation, and delayed dissipation is obtained from time-correlation functions of atomic vibrations of the medium. [2] A model for Ag adsorbed at a Si(111) surface, based on ab initio electronic calculations, is studied in detail to obtain populations and coherences of electronic states over time, induced by absorption of both short and long light pulses. [3] These are calculated as functions of varying light wavelength, light pulse length, and temperature. The model also inspects the effects of changing non-adiabatic (vibrational momentum) coupling between electronic states, and of varying the strength of transition dipoles in the photoexcitation. Results of calculations show that within an indirect excitation model, increasing the oscillator strengths of the intermediate or final state leads to an increase of electronic charge separation. Furthermore, when we increase the coupling between electronic states the populations of the higher vibronic states in those electronic states remain high throughout the excitation and then as a result decay into the ground state. Also light with a 620 nm wavelength produces the largest charge separation. Finally it was found that while increasing the temperature produced greater charge separation in the short term, the charge separation was decreased in the long term. Unexpected results can be attributed to increase of the short term populations of the higher energy vibronic states and thereby allowing electronic coupling to dominate the final charge separation.

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