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**Energy Dependence of Ultrafast Electron Transfer at Interfaces.**

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Electron transfer at semiconductor interfaces is a critical process in surface catalysis, novel electronic applications and solar energy conversion. The fast kinetics (sub-100 fs) and the often inhomogeneous environment complicate identifying the parameters that dominate the reaction. We present ultrafast spectroscopic studies of electron transfer between molecular electron donors and metal oxide semiconductors with well-defined variations in excess energy and dipole moment. Three Zn(II) tetraphenylporphyrins (ZnTPP) with alternating dipole moment attached to TiO<sub>2</sub> colloidal films have been investigated. Surprisingly, electron injection dynamics does not show the expected dipole dependence. These results are substantiated by measurements employing a different molecular electron donor with two distinct excited states. Electron transfer times for both states were very similar and around 50 fs despite a 1 eV difference in excess energy. These results indicate that electron transfer at colloidal interfaces involves only a subset of the surface projected density of state (DOS) that is present in the metal oxide conduction band. This complicates predictions of electron transfer efficiency based on steady state DOS calculations.