

Direct and Indirect Electron Transfer at Semiconductor Surfaces: A Numerical Treatment of $\text{Ag}_3\text{Si}(111):\text{H}$

Andrew S. Leathers, Dmitri S. Kilin, and David A. Micha
Quantum Theory Project, University of Florida
Gainesville, Florida 32611, USA

Electron transfer between a metal cluster and a semiconductor surface induced by a pulse of light can occur via two pathways: direct excitation, where the pulse excites the system directly to the final (electron transferred) state, and indirect excitation, where the pulse excites the system to an intermediate state, which then relaxes to the final state. Quantum state populations are affected by energy dissipation, which occurs on two different time scales - a fast dissipation due to electronic energy relaxation, and a slow (delayed) dissipation arises from vibrational energy relaxation. A theoretical and computational treatment of these phenomena has been done in terms of a reduced density matrix satisfying a generalized Liouville-von Neumann equation.[1] Instantaneous dissipation is described by a Lindblad term containing electronic transition rates, while the delayed dissipation is given by a time integral with a memory supermatrix term derived from the time-correlation of atomic displacements in the medium.[2] Photoinduced excitations are computed using Franck-Condon overlap factors, while interactions between the intermediate state and the final state are treated within a Landau-Zerner approximation. We present the example of $\text{Ag}_3\text{Si}(111):\text{H}$, using electronic parameters from density functional theory [3].

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2. A. S. Leathers and D. A. Micha, *J. Phys. Chem.* **110**, 749 (2006)
3. D. S. Kilin and D. A. Micha, work submitted to *Phys. Rev. Lett.* and in progress (2007)

Work partly supported by the NSF of the USA.