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Theoretical/Computational Probes of Homogeneous and Interfacial Electron Transfer: Electronic Structure and Energetics¹

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Theoretical and computational techniques are used to elucidate the physical and chemical factors that control the kinetics of homogeneous and interfacial electron-transfer (ET) reactions. These latter include systems for which standard rate constants ($k^0(l)$) have been measured electrochemically for ET between substrate Au electrodes and redox couples attached to the electrode surfaces by variable lengths (l) of oligomethylene (OM), oligophenylenevinylene (OPV) and oligophenyleneethynylene (OPE) bridges. These oligomers, spanning a range of \sim 1-4 nm, are components of mixed self-assembled monolayers (SAMs), coupled to the substrate via S atom linkers. The mechanistic analysis of the kinetic behavior, including polaron-based activation and electronic tunneling, is supported by calculations of electronic structure and molecular and medium energetics. Band structure calculations for neat phenylthiolate SAMs on Au and Cu substrates were used to probe the properties of the interface, including surface dipole layer and work function, the electronic nature of the 'thiolate' linker atoms, and the competition between direct and substrate-mediated coupling.

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