Abstract Submitted
for the MAR11 Meeting of
The American Physical Society

Near- and Far-Field Effects on Excited States at Organic Semiconductor and Metal Interfaces OLIVER MONTI, MARY STEELE, NAHID ILYAS, LEAH KELLY, University of Arizona — We present an investigation of the evolution of excited states at the interface of the dipolar organic semiconductor vanadyl naphthalocyanine on highly oriented pyrolytic graphite. Using two-photon photoemission we observe several excited states at sub-monolayer to few-monolayer coverages. Excited states of this organic semiconductor are progressively stabilized with coverage, an effect that is somewhat mirrored in the image state manifold as well. These findings can be understood in the context of a simple electrostatic model that considers how molecular levels and vacuum level are influenced differentially by the the strong electrostatic fields present at the interface with dipolar molecules: While the vacuum level rises continuously with coverage, the molecular states are significantly depolarized as a function of electric fields in the near-field regime. This indicates that the interfacial excited state electronic structure is strongly sensitive to long-range intermolecular interactions mediated by the surface, with direct implications for energy level alignment and charge transfer dynamics at the interface. Interfacial electrostatic fields may therefore be used to manipulate in a concrete fashion interfacial charge transfer processes such as photoinduced interfacial electron transfer.

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Date submitted: 28 Nov 2010 Electronic form version 1.4