Correlation and Electronic Level Alignment at Metal-Molecule Interfaces: Benzene on Graphite

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The electronic structure of a model metal-molecule interface, benzene (C_6H_6) on graphite (0001), is computed within the GW approximation. The benzene HOMO-LUMO gap is predicted to be 7.2 eV in this environment, a large reduction relative to its calculated gas-phase value of 10.5 eV, and slightly smaller than its computed solid-phase gap of 7.5 eV. This decrease is attributed to dynamical correlations between the molecule and graphite substrate. In particular, the screened exchange contribution to the self-energy is responsible for the gap narrowing predicted here. Implications for the electronic properties of organic and molecular nanostructured systems in contact with metallic surfaces are discussed. This work was supported by DOE under Contract No. DE-AC03-76SF00098, by the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award Number CHE-0117752 and by the New York State Office of Science, Technology, and Academic Research (NYSTAR). Computational resources have been provided by NERSC.