Renormalization of Optical Excitations in Molecules near a Metal Surface

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The lowest electronic excitations of benzene and a set of donor-acceptor molecular complexes are calculated for the gas phase and on the Al(111) surface using the many-body Bethe-Salpeter equation. The energy of the charge-transfer excitations obtained for the gas phase complexes are found to be around 10% lower than the experimental values. When the molecules are placed outside the surface, the enhanced screening from the metal reduces the exciton binding energies by several eVs and the transition energies by up to 1 eV depending on the size of the transition-generated dipole. As a striking consequence we find that close to the metal surface the optical gap of benzene can exceed its quasiparticle gap. A classical image charge model for the screened Coulomb interaction can account for all these effects which, on the other hand, are completely missed by standard time-dependent density functional theory.
