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Two-photon photoemission spectroscopy study of phenol on Ag(111): "hot electrons" at organic-metal interface

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Photodissociation of many organic adsorbates on metal surfaces has been attributed to photoexcited "hot electrons". To address this issue, we have explored the interfacial electronic structure of phenol adsorbed on Ag(111) using time-resolved two-photon photoemission spectroscopy (2PPE). The photoinduced anion state of phenol was found at 3.1 eV above the Fermi level at one monolayer coverage, and the binding energy of this state remained constant at around $0.7 \sim 0.8$ eV for all coverages. Polarization dependence of the photoelectron signal revealed detailed mechanisms of each excitation step. Energy dispersion measurement showed the excess electron was localized on the molecule. The present study is the first 2PPE study that directly demonstrates the role of hotelectrons in photodissociation of adsorbates.