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Theoretical treatment of excited electronic states of adsorbates on metals: electron attachment to CO_2 adsorbed on Pt(111)*[1] JERRY WHITTEN, LAURA SREMANIAK, North Carolina State University — Photochemistry involving adsorbates on metals often proceeds by photoexcitation of the metal followed by transient attachment of photoemitted electrons to the adsorbate. First principles theoretical methods suitable for describing electronic states embedded in a near continuum of metal to metal excitations are described and an application to electron attachment to CO_2 adsorbed on Pt(111) is reported. Wavefunctions are constructed by *ab initio* configuration interaction methods which allow a rigorous resolution of states and differentiation between competing pathways of molecular desorption and dissociation. An embedding theory is used to achieve high accuracy in the adsorbate-surface region. The overall process can be understood as formation of an electron attached state at an energy lower than the work function of the metal, localization of the metal hole and attraction of the charged adsorbate to the metal. Optimum geometries are calculated and pathways between these geometries determine whether molecules will desorb, dissociate by bond rupture directly in the excited electronic state, or dissociate after return to the ground state potential energy surface via vibrational processes. The influence of a coadsorbed potassium electron donor atom on the energy required to form the electron attachment state is also reported.

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