Vortrag

“Photochemical Processes on TiO₂ Semiconductor Surfaces and in Astronomical Ices in Deep Space”

des Preisträgers 2013

Professor John T. Yates, Jr.
Department of Chemistry
University of Virginia, Charlottesville, VA, USA

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Freie Universität Berlin
Konrad-Zuse-Zentrum
Hörsaal
Takustr. 7
14195 Berlin-Dahlem
The electronic excitation of semiconductors is of broad importance in photovoltaic cells and in solar-driven surface chemistries of the future such as CO$_2$ reduction and water splitting. We have monitored electron-hole (e-h) pair production and recombination rates in TiO$_2$ by measuring the kinetics of a simple photon-driven surface process. Surface studies on single crystal TiO$_2$(110) have discriminated second-order bulk e-h recombination processes from first-order surface recombination processes. The effects of band bending on electron transfer at the surface have also been monitored, showing that controlled band bending can be used to discriminate hole- and electron-mediated surface photochemical reactions as well as to control their rates. We also report the long-range influence of adsorbed surface hydroxyl groups causing the spreading over the TiO$_2$(110) surface of electrons related to surface oxygen-vacancy defects.

In the second part of the talk I will discuss astrochemically-important photochemical processes in CO$_2$(ice) which are induced by Lyman-$\alpha$ (10.2 eV) radiation. We observe a large $^{12}$C/$^{13}$C isotope effect in CO$_2$(ice) photodissociation which may be explained using the Menzel-Gomer-Redhead mechanism, familiar to surface scientists. Here electronically-excited CO$_2$, undergoing C-O bond breaking, is electronically quenched in its ice matrix leading to the isotope effect. In addition, we see that vibrationally-hot CO$_2$ molecules in CO$_2$(ice) experience a vibrational quenching resonance with neighbor CO$_2$ (ice) molecules. The resonance quenching can be detuned by isotopic substitution leading to enhanced CO$_2$ photodesorption rates from vibrationally-hot CO$_2$ molecules. Over cosmic time scales, such effects accumulating in ice films condensed on interstellar dust particles may influence the isotopic ratios observed in the interstellar medium or in planetary systems.