GERHARD ERTL LECTURE

2013

Vortrag

"Photochemical Processes on TiO_2 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

Dienstag
10. Dezember 2013
15:00 Uhr c.t.

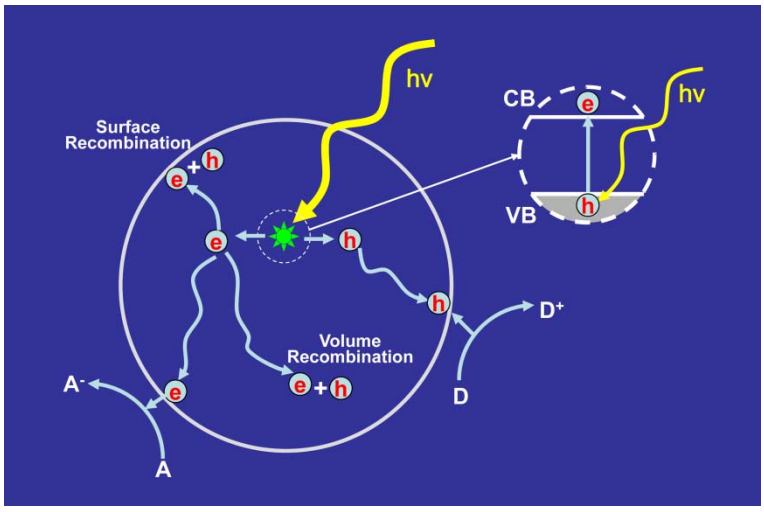
Freie Universität Berlin
Konrad-Zuse-Zentrum
Hörsaal
Takustr. 7
14195 Berlin-Dahlem

Photochemical Processes on TiO_2 Semiconductor Surfaces and in Astronomical Ices in Deep Space

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

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-α (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 photodesoption 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.



Photochemical Processes on TiO_2 Semiconductor Surfaces and in Astronomical Ices in Deep Space