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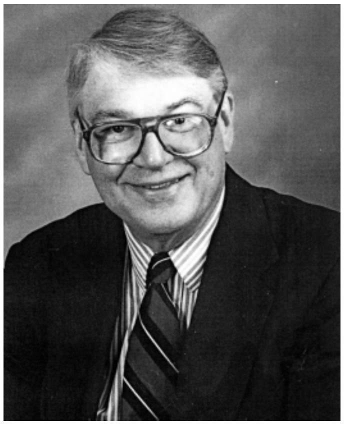
Introduction: Photochemistry and Photophysics on Surfaces



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Hrvoje Petek received his undergraduate and graduate education in chemistry at MIT and the University of California at Berkeley. He joined the Department of Physics and Astronomy at the University of Pittsburgh in 2000 after spending 15 years at the Institute for Molecular Science and Hitachi Advanced Research Laboratory in Japan. Currently he holds the positions of the Professor of Physics and Chemistry and the co-Director of Petersen Institute for NanoScience and Engineering. His current interests include the ultrafast electron and nuclear dynamics in solids and at solid surfaces. He is also the Editor-in-Chief of *Progress in Surface Science*.

The interaction of light with free electrons in metals has been a source of fascination for more than 5000 years, ever since ancient Egyptians brought metallic mirrors into everyday use. It has been only 101 years since Einstein explained how light quanta couple with electrons in the photoelectric effect based on experiments by Lenard (1900). Following the work by Richardson and Compton (1912), Millikan first employed the photoelectric effect in 1916 for the first accurate measurement of a surface property, the work function. Since then, the study of the interaction of photons with surfaces has been one of the major driving forces in condensed matter and surface physics, resulting in the widespread development of photoelectron spectroscopy as a tool for studying the electronic structure of solids, adsorbed species on solid surfaces, liquids, as well as gases. The application of photoelectron spectroscopy to adsorbed atoms and molecules has been fundamental to the understanding of their bonding to surfaces, using both the core as well as valence level excitation, and proceeding today to high energy-resolution measurements of chemical shifts and resonance bandwidths.

The excitation of surfaces and surface species by photons, leading to nuclear motion (chemistry), is an outgrowth of the investigation of the effect of electronic excitation of adsorbed species by electron bombardment, the so-called DIET (desorption induced by electronic excitation) processes, for which the first understanding was established by Menzel and Gomer and separately by Redhead in the early 1960s. Later, Zewail and co-workers developed the tools of femtochemistry, which made it possible to probe and control the outcome of chemical reactions in the gas phase on the fundamental time scale of a molecular vibration. Application of the ideas and techniques of femtochemistry to DIET and related processes on solid surfaces has been dauntingly difficult because of the extremely fast electronic relaxation of adsorbed molecules on solids. Nevertheless, advances in surface femtochemistry are emerging from experiments that exploit the femtosecond time resolution of lasers, the extreme sensitivity of photoemission, and the atomic spatial resolution of STM.

As the title of this thematic issue indicates, the excitation of surfaces by photons is an active endeavor of both the chemistry and the physics communities, and this collection of reviews is an attempt to bring together the latest developments in both communities. There are many key unsolved surface-photochemical/photophysical problems today. These problems include the full understanding of fast time-resolution photoelectron spectroscopy measurements

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that witness the production and decay of electronic excitations at surfaces in the femtosecond time regime. The electronic excitation processes create the nonadiabatic interaction between the electronic and nuclear degrees of freedom that leads to both the electronic relaxation and the excitation of nuclear motion. Imaginative and detailed studies of nuclear motion within adsorbed species, induced by electronic or vibrational excitation, provide an incisive connection to surface chemical processes. Studies of such processes transcend thermally excited chemistry at surfaces. For example, surface processes induced by charge transfer to single molecules at the scanning tunneling microscope (STM) junction are now investigated with atomic resolution on surfaces, overcoming the uncertainties inherent in studies of the photodynamics of randomly oriented gas-phase target molecules. Since the photoexcitation of adsorbed molecules (via charge transfer from the solid) is a dominant surface excitation process in many cases, studies of the excitation of single molecules with the STM form an important part of our surface science toolbox devoted to surface photochemistry.

The photoinduced charge transfer excitation of molecules is directly related to issues of interfacial and molecular conduction in molecular electronics and to charge transfer processes in organic semiconductors. The electronic excitation of molecules (by light or by tunneling electrons) provides the means to actuate single molecule machines and devices that can now be assembled a single atom or a single molecule at a time. The capture of sunlight by semiconductors for the generation of electricity is strongly influenced by the electronic state alignment between the adsorbate and substrate, and molecule−surface coupling. The use of semiconductor TiO_2 for photooxidation of pollutants and for photoinduced antimicrobial applications, and the potential application of TiO_2 to the solar-driven splitting of water offer new technological vistas by which we hope to resolve environmental problems of ever increasing concern.

The papers in this thematic issue are arranged starting with those dealing primarily with theoretical physical issues, and then moving to those dealing primarily with experimental physical issues involved in photoexcitation at surfaces. These papers are followed by reviews of the more chemical aspects of surface photoexcitation, addressed primarily from the experimental point of view.

Saalfrank deals with the quantum-dynamical approach for describing the process of bond breaking in adsorbed molecules upon electronic excitation. Processes are divided into electronically adiabatic, weakly nonadiabatic, and strongly nonadiabatic regimes. Issues of direct desorption of adsorbed molecules, desorption from insulator surfaces where weak coupling occurs (leading to gas-phase-like processes), and attempts to control surface photoreactivity by nanostructured substrates are treated. Many examples are given of chemical systems undergoing photoexcitation and subsequent nuclear evolution.

Chulkov, Borisov, Gauyacq, Sánchez-Portal, Silkin, Zhukov, and Echenique begin with a beautiful description of the various types of electronic states that can exist at the surface of a metal. Topics dealing with the calculation of the electron self-energy, the propagation of wave packets, the interaction between electrons and phonons, and the calculation of surface response functions to evaluate the energy and width of surface plasmons are well treated. Theoretical lifetimes are compared to experimental lifetimes for excited electrons at surfaces. Rich research areas for the future are described, including the development of theoretical methods for studying heavy metal and semimetal surfaces, the effect of spin−orbit splitting, which is expected to strongly influence electron and hole dynamics, and the behavior of quantum-well states confined to a surface.

Frischkorn and Wolf introduce femtochemistry at metal surfaces, presenting the basic concepts of energy transfer to metal surfaces and substrate−adsorbate coupling. They then proceed to a description of experimental methods and how experimental observations may be related to reaction dynamics in adsorbed molecules. So far, the systems studied may be successfully described with a one-dimensional frictional model with a single degree of freedom, and they pose the question of when the frictional approach is likely to break down as a result of strong coupling to the surface. They conclude with a challenge—namely how to control surface reactions through coherent control of vibrational wave packet motion.

Matsumoto and Watanabe’s review is concerned with similar issues to those described by Frischkorn and Wolf, namely the coherent vibrations induced by femtosecond laser excitation of surface species. They concentrate on time-resolved nonlinear spectroscopies and supply an introduction to how electronic excitation can lead to coherence in molecular vibrations and in phonon modes in a solid. A comprehensive discussion of CO chemisorbed on metals is presented, with emphasis on the intermolecular and molecule−surface interactions.

Güdde, Berthold, and Höfer’s review is concerned with the dynamics of electron transfer processes at the metal/insulator interface, where insulator here refers primarily to layers of adsorbed inert gases with atomically defined thickness. Here, image potential states may exist predominantly on the outside of an overlayer if the electron affinity of the overlayer is negative; for a positive electron affinity, the image potential state will reside predominantly inside the overlayer, opening the possibility of the production of quantum well states. The review offers an introduction to 2-photon photoemission spectroscopy (2PPES).

Lindstrom and Zhu are also concerned with photoinduced electron transfer to molecules adsorbed on metals, aiming in their review to promote a closer interaction between the well-developed theories of electron transfer and molecular conduction, and experimental studies of metal surfaces. Their key question is, “What determines the rate of photoinduced charge transfer?” The theories employed are often borrowed from molecular and solid-state physics concepts, where they have been developed to treat near-equilibrium phenomena. A major question addressed concerns the factors governing direct vs indirect excitation of adsorbed molecules, and the geometrical and electronic criteria for the system’s selection of the excitation process.

Watanabe, Menzel, Nilius, and Freund address the use of quantum confinement in nanoparticulate metals for tuning the coupling of the substrate with adsorbed molecules in photoexcitation. This relatively unexplored area of research offers the potential for tailor-making photosystems to do desired photochemistry. Topics such as the “antenna effect” of nanoparticle metals bound to molecules, as well as the confinement of hot electrons in nanoparticles, are explored. An emphasis is placed on nanoparticles (2−20 nm diameter) produced and deposited on supports under atomically clean conditions, providing a baseline for many studies of similar particles made chemically under less stringent conditions.

At this point, the thematic issue turns to more chemically oriented studies of surface photochemistry. McNab and Polanyi discuss the concept of patterned reactions on surfaces, where an adsorbed molecule, upon becoming excited by the STM tip, dissociates in a manner where the capture of the product species forms a “footprint” of the original adsorbed molecule. The question of energy and momentum loss by the energetic molecular fragments is central to realizing patterning of reactions on surfaces. Such writing connects powerfully to concepts in gas-phase kinetics and dynamics which have intrigued chemists for almost 100 years. In addition, a massive and useful review of the literature for many molecule/surface systems is given.

Mayne, Dujardin, Comtet, and Riedel discuss the electronic control of single molecule dynamics. They provide an historical review of the use of STM techniques to excite single molecules, treating bond breaking, desorption, and bond making with the surface, as well as electron (hole) attachment, electron−hole pair attachment, and competing processes in the STM-induced excitation of single molecules. This is followed by a discussion of the Si−H surface bond dynamics upon excitation by the STM and the behavior of a single adsorbed CO molecule on Cu(111). The effect of electric fields on adsorbates is also discussed.

Osgood develops a picture of the UV photoreaction dynamics of molecules on semiconductor and oxide surfaces. Here, laser excitation is used to produce large concentrations of fragments and transient surface species. The role of the molecular orientation of the parent molecule in controlling the photodynamics is emphasized, much as in the Polanyi review. Alkyl halides and thiols adsorbed on GaAs(110) are particularly emphasized, and the quenching of direct and indirect excitation processes by the surface is discussed. Semiconductor surface passivation by the fragments of CH_3Br photodissociation is discussed.

Zhao, Li, Onda, Feng, and Petek address the behavior of solvated electrons in molecular overlayers on metal oxide surfaces. Protic solvent overlayers are used to decouple energetic electrons from substrates in order to enhance their effectiveness in inducing surface femtochemistry. The nature of electrons solvated in surface overlayers is compared and contrasted to the more extensively studied solvated electrons in bulk solvents and solvent clusters. The review focuses on H_2O and CH_3OH on the $TiO_2(110)$ surface as electron hosts, and discusses how the crystalline structure of the surface defines the chemisorption structure of molecular overlayers and ultimately the properties of electrons photoinjected into these overlayers. Studies of the solvation of electrons by these ordered molecules using time-resolved 2PPES and density functional theory form the core of the paper.

Thompson and Yates review the photochemistry of TiO_2 surfaces, especially those investigations which employ a high degree of control of the surface conditions. The kinetics of the hole-induced photodesorption of O_2, chemisorbed on O-vacancy defects in the $TiO_2(110)$ surface, is emphasized as a model system for understanding more complex photooxidation processes. This system provides a basis for observing the 1/2 order light-flux dependence of the O_2 photodesorption kinetics caused by the dynamic equilibrium established between electrons and holes in TiO_2 during irradiation. A method to measure the hole trap concentration in the TiO_2 single crystal is presented. In addition, surface science studies of the origin of the photoinduced hydrophilicity of TiO_2 surfaces are presented.

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