

Light-induced molecular processes on ice

Water is omnipresent in processes relevant from both technological and fundamental point of view. Knowledge concerning the interfacial water structure at metal surfaces is crucial for the understanding of many important surface phenomena involving water in e.g. electrochemistry, corrosion processes and the photo-catalytic decomposition of water as a renewable energy source. In addition, understanding of electron-mediated processes in water and aqueous systems is of interest for elucidating processes of importance for biology, environmental sciences and astrochemistry, as well as for applications in radiation processing, medical diagnosis and therapy.

On the other hand, water ice particles in the Earth's polar stratospheric clouds (PSCs) play a critical role in processes leading to ozone destruction. The activation of halogen "reservoir compounds" into reactive halogen gases, otherwise very slow, occurs more rapidly when these are adsorbed on the surface of PSC particles. Under the influence of solar UV radiation, these reactive halogen gases subsequently generate halogen radicals active in ozone depletion cycles.

The presentation deals with two main issues: first, the interaction of water with a platinum surface, under very well-defined conditions (at liquid nitrogen temperature in a very low-pressure environment (Ultra-High Vacuum (UHV): pressure 2×10^{-11} mbar)), along with the dynamics of the laser-induced desorption of water from amorphous solid water, and second, the photochemistry of small, naturally occurring, organic molecules such as bromoform (CHBr_3) molecules on ice surfaces. The interaction of water with a platinum surface having a controlled distribution of the superficial defects - strict monitored under the UHV conditions under which the processes are studied - may represent a model for electrochemistry, where water-metal interactions are crucial in determining the system's reactivity. In addition, laser-induced desorption of water from amorphous solid water films supported on a single-crystal platinum substrate has been studied. Electron injected from the metal substrate into the water layer at the metal-water interface, result in water desorption from the water-vacuum interface. A surprisingly large mean free path of an electron-excited water molecule (~ 1 nm, corresponding to several water molecules) has been determined.

The fundamental steps of the photochemical reaction of bromoform on ice surfaces induced by UV light are elucidated as well in this thesis. This reaction constitutes an

important step in the ozone depletion cycle, which greatly affects our atmosphere. Photodissociation studies reveal a rich UV-induced photochemistry of bromoform on ice: various direct fragmentation pathways, as well as formation of new, ice-mediated C—C and C—O bond containing chemical species. Given the previously reported detection of bromoform in the stratosphere, these observations may have significant implications for current models describing stratospheric ozone depletion.