

Quantum Efficiency Seminar und Colloquium

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Supramolecular Photophysics and Photochemistry of van der Waals Complexes of Molecular Oxygen X-O2

Optical transitions in molecular oxygen are strictly forbidden by spin and/or orbital symmetry within spectral range from IR to very important UV region. The enhancement of photoabsorption in molecular oxygen O2 induced by intermolecular interaction is a well-known phenomenon. The enhancement factors can be of many orders of magnitude depending on interaction partner X and this dictates the interest to the nature of this enhancement and to the "enhanced" photochemistry of oxygen in molecular environment which are the subject matter of presented work. The van der Waals (vdW) complex of molecular oxygen X-O2 is an ideal model for the study of these phenomena. To assign the nature of the electronic states involved, to identify generated reactive species and mechanism of their formation the photo processes in van der Waals complexes X-O2 excited within and out of Herzberg continuum have been investigated. The techniques of velocity map imaging of the photofragments, the REMPI-TOF-MS and spectroscopy of "collisional" complexes as well as ab initio calculations have been applied. The study of energy distribution and angular anisotropy of the recoil directions for the photofragments arising in the photodissociation of X-O2 complexes was found to be the very efficient way for identification of the elementary processes governing the principal steps in photophysics and photochemistry of vdW complexes. The recent results obtained in collaboration of Novosibirsk and Nijmegen groups reveal "dramatic" change in the mechanism of photodissociation of oxygen in vdW complex X-O2 as compared with the free O2 molecule and clearly indicate supramolecular nature of the photoabsorption and photodissociation of oxygen in the molecular environment. Implementation of the new approach for measurements of binding energy in weakly bound molecular complexes is also considered.

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