

UHV-IR-spectroscopy on metal oxide surfaces

Maria Buchholz¹, Mingchun Xu¹, Yuemin Wang², Alexei Nefedov¹, Christof Wöll¹

*Institute of Functional Interfaces, Karlsruhe Institute of Technology,
76344 Eggenstein-Leopoldshafen, Germany
(corresponding author: M. Buchholz, e-mail: maria.buchholz@kit.edu)*

¹ *Chair of Industrial Chemistry, Ruhr University Bochum, 44801 Bochum, Germany*

The role of metal oxides is central in many technological areas such as gas sensing, catalysis and thin film growth. In particular, zinc and titanium oxides are very important for photocatalysis and photooxidation^[1]. Moreover, in the Graetzel-cell, organic molecules bound to TiO₂ substrates via carboxylate bonds effectively convert photons into electric energy. Owing to the fact that many Dye Sensitized Solar Cells (DSSCs) consist of dyes grafted to the oxide support via carboxylate groups, determination and control of the adsorption of carboxylic acids on oxide substrates is fundamental for understanding the energy transfer from the molecule to the substrate.

In last decades numerous IR investigations of metal oxide powders, including the different modifications of TiO₂, have been reported, however an unambiguous assignment of the features in the complex IR spectra recorded for molecules bound to the oxide powders is quite complicate. Otherwise, it could be possible on the basis of data recorded for well-defined reference systems, e.g. surfaces of single crystals, but, unfortunately, studies on oxide single crystals are extremely scarce due to the fact that the sensitivity of reflection IR-spectroscopy for molecular adsorbates is two orders of magnitude lower for oxides than for metal single crystals. Only recently it became possible to overcome these technical problems by employing a novel, advanced spectrometer.^[2]

Here, we demonstrate the performance of this highly sensitive IRRAS-setup by presenting high-quality IR-spectra obtained for different molecules, namely small acids and alcohols. For the present experiments, monolayers of terephthalic acid (TPA) and benzoic acid (BA), as well as methanol and ethanol were deposited under UHV conditions on a rutile TiO₂(110) surface at room temperature. Subsequently the sample was transferred in the main chamber for a characterization in a highly sensitive UHV IRRAS system. The deposition and measurement of the alcohols on the surface were done directly in the analysis chamber. While for BA the expected bidentate carboxylate bonding is observed, for TPA molecule the presence of two carboxylic acid groups leads to interesting complications. The IR-spectra allow, in particular, to answer on the question which could not be answered by the results from x-ray absorption spectroscopy and the scanning probe techniques^[3], whether the carboxylic acid group is still protonated for the TPA species on the surface. Since we can detect the carbonyl stretching vibration and the carboxylic acid stretching vibration we conclude that the TPA molecules adsorb on the TiO₂(110) surface in the protonated state.

M. Buchholz gratefully acknowledges the financial support from the Helmholtz Research School “Energy-Related Catalysis”.

- [1] M. C. Xu, Y. K. Gao, E. M. Moreno, M. Kunst, M. Muhler, Y. M. Wang, H. Idriss, C. Wöll, *Phys. Rev. Lett.* **2011**, *106*, 138302.
- [2] Y. Wang, A. Glenz, M. Muhler, C. Wöll, *Rev. Sci. Instrum.* **2009**, *80*, 113108-113106.
- [3] P. Rahe, M. Nimmrich, A. Nefedov, M. Naboka, C. Wöll, A. Kühnle, *Journal of Physical Chemistry C* **2009**, *113*, 17471-17478.