

# Influence of Wet Electron States on the Water-Oxygen Surface Chemistry of TiO<sub>2</sub>

## Frontiers in Chemical Physics and Analysis Seminar Series

### Presented by...



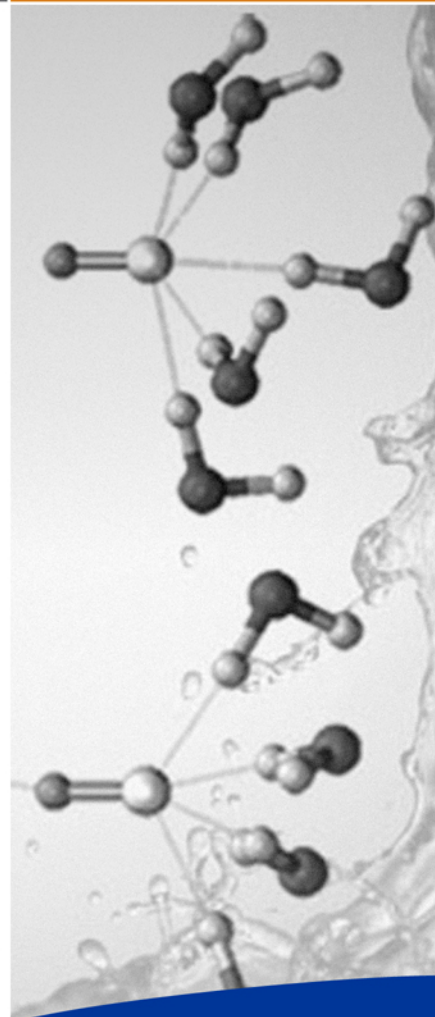
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Oxygen vacancies on metal oxide surfaces have long been thought to play a key role in the surface chemistry. For the (110) surface of TiO<sub>2</sub>, this view was recently challenged by work which suggested that a quasiparticle bandgap state involved in the reactivity arises from near-surface Ti interstitials. Here I describe some recent experiments that tested this idea. We find that vacancies provide the dominant contribution to the band gap state. As for the reaction with molecules, such processes have been directly visualised in the case of the model photocatalyst surface TiO<sub>2</sub>(110) in reactions with water and dioxygen. These vacancies have been assumed to be neutral in calculations of the surface properties. However, by comparing experimental and simulated scanning tunneling microscopy images and spectra, we show that oxygen vacancies act as trapping centres and are negatively charged. We demonstrate that charging the defect significantly affects the reactivity by following the reaction of dioxygen with surface hydroxyl formed by water dissociation at the vacancies. Calculations with charged hydroxyl favour a condensation reaction forming water and surface oxygen adatoms, in line with experimental observations. This contrasts with simulations using neutral hydroxyl where hydrogen peroxide is found to be the most stable product. An interesting question remains as to the relevance of these results to the liquid water – TiO<sub>2</sub> interface. Surface X-ray diffraction measurements after dipping the (110) surface in water reveal that the surface is hydroxylated in the first layer of the interface, with ordering of water in the second layer. This is in contrast to the results of recent calculations of the perfect surface, which suggest no dissociation at the liquid/TiO<sub>2</sub>(110) interface.

### More info?

See <http://www.pnl.gov/cmsd/seminars/>



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