

O 68: Surface dynamics: Reactions, elementary processes and phase transitions I

Time: Wednesday 15:00–16:30

Location: MA 043

O 68.1 Wed 15:00 MA 043

2-Dimensional Vibrational Sum Frequency Generation Spectroscopy of Organic Monolayers — ●ANNA K SCHIFFER, MIKE HEMSWORTH, and GARY W LEACH — Simon Fraser University, Chemistry Department, Laboratory for Advanced Spectroscopy and Imaging at 4D Labs, Burnaby, BC, Canada

Vibrational sum frequency generation (SFG) spectroscopy is a non destructive interface-specific non linear optical spectroscopy that delivers information about the structure and composition of interface environments. SFG spectroscopy leverages the non centrosymmetric environment of the interface to mix two incident electric fields and provide a coherent scattered field at the sum of incident frequencies. If one of the fields is resonant with the vibrational modes of interface molecules, the sum frequency signal will provide information about the local interface structure. The extension to a 2-dimensional (2D-SFG) spectroscopy provides direct information about the interactions between molecules and their dynamics at the interface by employing pulse sequences. Here, we describe the construction of a collinear 2D-SFG spectrometer and its application to the vibrational spectroscopy of highly ordered organic monolayers at the CaF₂/Air interface. A three pulse IR sequence is generated by using a dual output optical parametric amplifier (OPA) pumped by an amplified Ti:sapphire laser system and a pair of birefringent wedges. The wedges create a highly phase stable pair of IR pulses with controllable time delays. The signals are subsequently processed to provide 2D-SFG spectra and provide information about the dynamics of the sample in the CH spectral region.

O 68.2 Wed 15:15 MA 043

Analyzing and Tuning the Energetic Landscape of H₂Pc Tautomerization — ●LUCAS KLEIN¹, JENS KÜGEL¹, MARKUS LEISEGANG¹, and MATTHIAS BODE^{1,2} — ¹Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Wilhelm Conrad Röntgen Center of Complex Material Systems (RCCM), Universität Würzburg, Am Hubland, 97074 Würzburg

Many chemical and biological reactions are associated with the quantum tunneling of hydrogen atoms through a potential barrier in the reaction path [1]. Whereas quantum tunneling is often identified by temperature-dependent measurements or a large kinetic isotope effect, we demonstrate a new method working at a fixed temperature. As a model system we used the tautomerization—the switching of hydrogen protons between different adsorption sites—of phthalocyanine (H₂Pc) molecules adsorbed on a Ag(111) surface which are probed by scanning tunneling microscopy. We will show, that the tautomerization of this molecule is exclusively triggered by the excitation of the N–H stretching mode. Interestingly, a step-like increase of the tautomerization rate is observed at a bias voltage that corresponds to the second harmonic of this vibrational mode, which we attribute to a crossover from quantum tunneling through the tautomerization barrier to an excitation over the barrier. This explanation is further supported by modifying the energetic landscape of the tautomerization of pristine H₂Pc by single silver atom manipulation and/or deprotonation.

[1] M. Koch *et al.*, J. Am. Chem. Soc. **139**, 12681–12687 (2017)

O 68.3 Wed 15:30 MA 043

Free energy landscape of graphene surface reactions from *ab initio* simulations — ●MATEUSZ WLAZLO and JACEK MAJEWSKI — Faculty of Physics, University of Warsaw, Poland

We study methane (CH₄) and carbon dioxide (CO₂) decomposition and adsorption processes on monolayer graphene. These classes of reactions are important in chemical vapor deposition (CVD) growth of graphene or in CH₄-CO₂ exchange reactions, for example. The occurrence of this exchange is advantageous in the removal and storage of atmospheric CO₂.

The studies are based on *ab initio* molecular dynamics methods implemented in the framework of planewave density functional theory. Free energy profiles featuring energy barriers for different steps of the reaction are computed using the so-called *Blue Moon ensemble* method. The barriers are much lower than experimental bond dissociation energies for gaseous species, strongly indicating that graphene surface acts as a catalyst of decomposition reactions. However, the

barriers are still much higher than on nickel surface. This suggests that monolayer formation should be favored over multilayer graphene, which reinforces the position of nickel as a suitable substrate for large-scale, high-quality CVD graphene growth.

Calculations show different preferred mechanisms of CH₄ and CO₂ adsorption, depending on surface morphology. On ideal graphene, dissociative adsorption is preferred whereas on defect sites, such as the Stone-Wales defect, direct chemisorption of CO₂ occurs with higher likelihood.

O 68.4 Wed 15:45 MA 043

Femtosecond laser-induced associative desorption of molecular hydrogen from graphite — ●LORENZO MADDII FABIANI, ROBERT FRIGGE, JOHN THROWER, and HELMUT ZACHARIAS — Physikalisches Institut, Westfälische-Wilhelms-Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Deutschland

The formation of molecular hydrogen via radiation-induced associative desorption from dust particles may play an important role in photon dominated regions of the interstellar medium. In this study we investigate the desorption of molecular hydrogen and deuterium from HOPG following surface excitation with fs-laser pulses at $\lambda = 400$ nm. Desorbed neutral species are analyzed by internal state selective two-photon ionization (1+1) REMPI in the XUV region.

The desorbing hydrogen molecules show strongly non-equilibrium state populations. The vibrational ground state is less populated than the first excited one, while measurements for higher vibrational states are on-going. State specific kinetic energy measurements result in a value for $v'' = 1$, $E_{kin} = 100$ meV, significantly lower than for $v'' = 0$, $E_{kin} = 170$ meV. The rotational populations present a non-thermal distribution that can be fitted by two rotational temperatures for low and high J'' . The average rotational energy is determined to $E_{rot} = 390$ cm⁻¹ for $v'' = 0$ and 480 cm⁻¹ for $v'' = 1$. A nonlinear fluence dependence of the desorption yield allows two-pulse correlation measurements, which give an insight into the relevant desorption mechanisms. The FWHM of ca. 450 fs suggests an electron induced desorption mechanism.

O 68.5 Wed 16:00 MA 043

Water formation reaction physically confined below silica thin films: real time observation using LEEM and PEEM — ●MAURICIO PRIETO¹, HAGEN KLEMM¹, FENG XIONG², DANIEL GOTTLOB¹, DIETRICH MENZEL¹, THOMAS SCHMIDT¹, and HANS-JOACHIM FREUND¹ — ¹Department of Chemical Physics, Fritz Haber Institute of the Max Planck Society, Berlin - Germany — ²Department of Chemical Physics, University of Science and Technology of China, Hefei - P. R. China.

Thin oxide films are interesting models for the studying fundamental properties of real catalysts [1]. Among the more studied oxides, silica has caught the attention due to its relevance in the field of heterogeneous catalysis as a support or active component [2]. In addition, silica thin films supported on Ru(0001) have shown the ability of intercalating molecules into the confined space existing between the crystal surface and the oxide film [3]. We will show results regarding the study of the hydrogen oxidation with the aberration corrected spectromicroscope SMART [4] at the synchrotron light source BESSY-II in Berlin, by means of local XPS, LEED and LEEM. For instance, the reaction occurs as a front characterized by a sudden change in intensity in LEEM. The apparent activation energy of the process could be evaluated and compared with data obtained for bare Ru(0001), thus addressing the effect of confinement on the chemical reaction.

[1] Libuda, *et al.*, Microchim. Acta 156, 9 (2006) [2] Ulrich, *et al.*, Phys. Rev. Lett. 102, 016102 (2009) [3] Emmez, *et al.*, J. Phys. Chem. C 118, 29034 (2014) [4] Schmidt, *et al.*, Ultram. 110 1358 (2010)

O 68.6 Wed 16:15 MA 043

Electron-mediated phonon-phonon coupling drives the vibrational relaxation of molecules at metal surfaces — ●DINO NOVKO¹, MAITE ALDUCIN^{2,4}, and JOSEBA IÑAKI JUARISTI^{2,3,4} — ¹Freie Universität, Institut für Chemie und Biochemie, Berlin — ²Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), San Sebastián, Spain — ³Departamento de Física de Materiales, Facultad de Químicas UPV/EHU, San Sebastián, Spain — ⁴Donostia International Physics Center (DIPC), San Sebastián, Spain

Growing experimental evidences highlight a key role of nonadiabatic coupling in adsorbate relaxation at metal surfaces. Even though many nonadiabatic theories have emerged to comprehend these experimental endeavours, our understanding of the microscopic mechanisms that underlie the dynamical processes at metal surfaces is still incomplete. For instance, the state-of-the-art theories are still unable to give precise quantitative estimations of the experimental vibrational relaxation rates. In this contribution we propose a new relaxation process, i.e., the so-called electron-mediated phonon-phonon coupling (EMPP), that is

able to elucidate the vibrational relaxation mechanism of the internal stretch mode of CO on Cu(100). In fact, we show that the EMPP process dominates over the commonly-used first-order nonadiabatic contribution. The results demonstrate a strong electron-mediated coupling between the internal stretch and low-energy CO modes, but also a significant role of the surface motion. Our nonadiabatic theory is also able to explain the temperature dependence of the internal stretch phonon linewidth, thus far considered a sign of the direct anharmonic coupling.