O 98: Metal and Semiconductor Substrates: Adsorption and Reactions of Small Molecules

Time: Friday 10:30–12:30 Location: H8

O 98.1 Fri 10:30 H8

Bonding properties of a CO molecule with metallic adatoms — •Fabian Stilp, Marco Weiss, Maximilian Krüger, and Franz J. Giessibl — Department of Physics, University of Regensburg

CO terminated AFM tips are often used to investigate molecules on surfaces as they are a powerful tool to make the internal structure of such molecules visible. Their chemical inertness results in high resolution of the single atoms and bonds in such molecule via Pauli repulsion. However, it was shown by Huber et al. [1] that CO terminated tips can form weak bonds to some species of adatoms on a Cu (111) sample such as Fe and Cu as evident by an attractive center within a repulsive ring in constant height AFM measurement. In contrast, Si adatoms only interact via van der Waals attraction and Pauli repulsion.

Can one predict the strength of the bond between the CO molecule and an arbitrary atom just from its electron configuration? To set the rules for this prediction we expand our collection of AFM measurements on various adatoms by adding Ni and Ag.

Ni has a partially filled d-shell and thus forms a chemical bond of similar strength as Fe. Surprisingly, Ag with its similar electron configuration as Cu, immediately goes to Pauli repulsion while Cu first forms a weak bond.

[1] Huber et al., Science 366, 235-238 (2019).

O 98.2 Fri 10:45 H8

Adsorption sites of merocyanines on the Ag(100) surface determined by NIXSW — •Anna Juliana Kny[1], Anja Haags[2], Sergey Subach[2], and Moritz Sokolowski[1] — [1]Clausius Institut für Physikalische und Theoretische Chemie, Universität Bonn, Germany — [2]Forschungszentrum Jülich, Germany

The growth of thin organic layers is strongly influenced by the interactions between the molecule and the substrate surface. We report about the adsorption sites of a series of merocyanine (MC) molecules on the Ag(100) surface. MCs are prochiral donor-acceptor molecules which are in focus for applications due to high transition dipole moments. [1] Remarkably, SPA-LEED data reveal commensurate structures for all of our investigated MCs, although the size of the unit cells depends on the length of the alkyl side chains.[2] In order to answer the question of what is behind the commensurate growth of these complex molecules, we performed an XPS and an NIXSW investigation. We find a strong binding of the two sulfur heteroatoms, located in the thiophene and the thiazole rings, to the Ag surface. This can be seen in charge transfer and an adsorption of the S-atoms close to on-top sites. This is found for all investigated structures. Furthermore, compatible with the symmetry of the unit cell, the results reveal that the four molecules per unit cell sit on two different adsorption sites.

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[1] JACS 137 (2015) 13524. [2] Nanoscale 15 (2023) 10319.

O 98.3 Fri 11:00 H8

Electron-Induced Dehydrogenation of Acetylene and Ethylene on Si(100) — Rafik Addou, Damian Allis, Ryan Groome, Si Yue Guo, Aru Hill, Hadiya Ma, Cameron Mackie, •Oliver MacLean, Marc Savoie, Marco Taucer, Alexander Therien, Finley van Barr, and Ryan Yamachika — CBN Nanotechnologies Inc.

Low-Temperature Scanning Tunneling Microscopy (STM) is a powerful tool for manipulating individual atoms and molecules on surfaces. The Si(100) surface is a technologically relevant substrate; however, its high reactivity and structural complexity has led to limited examples of molecular manipulation. Here, we demonstrate the electron-induced dehydrogenation of two simple hydrocarbons on Si(100) at 4 K. Excitation by tunneling electrons at or above +3.2 V led to rotation, migration, or desorption of acetylene, consistent with previous observations on ethylene. At similar biases, dehydrogenation to C2 was also observed, which bound in on-dimer, inter-dimer, and inter-row configurations, as supported by STM simulations. At +4.2 V and above, excitation induced rotation of C2 between configurations, but conversion back to the starting adsorbates was never observed. Tunneling-electron excitation of ethylene yielded the same C2 products. Dehydrogenation of acetylene by field emission was also observed, with an effect ranging from a single to thousands of molecules, depending on the parameters chosen. This exploration of electron-induced dehydrogenation and rotation points to new possibilities in molecular manipulation on semiconductors.

O 98.4 Fri 11:15 H8

Selectivity on and off: adsorption of allyl ethers on Si(001) — •Sophie Göbel[1], Timo Glaser[1], Alexa Adamkiewicz[2], Jannick Peters[1], Julian Heep[1], Ulrich Höfer[2], and Michael Dürr[1] — [1]Institut für Angewandte Physik and Zentrum für Materialforschung, Justus-Liebig-Universität Giessen, Germany — [2]Fachbereich Physik, Philipps-Universität Marburg, Germany

Adsorption of organic molecules with more than one functional group on solid surfaces is of importance in the field of molecular electronics as they can be the starting point for multilayer systems [1]. To obtain well-organized monolayers of such bifunctional molecules, the understanding of their adsorption behavior, in particular in terms of their selectivity, is mandatory.

For allyl methyl ether (AME) and allyl ethyl ether (AEE), which combine an ether group with a C=C double bond, we show by means of XPS and STM that the adsorption of these molecules on Si(001) proceeds selectively via ether cleavage up to room temperature. The results are surprising as both functional groups involved show in general high reactivity on Si(001) and the ether group is less reactive when the isolated functional groups are compared. In contrast to AME and AEE, no such selectivity was observed for methoxy butene, where both functional groups are separated by an additional CH_2 unit. The results are discussed in terms of the interplay of electronic and geometric structure and its influence on the adsorption process.

[1] T. Glaser, et al., Chem. Mater. 36, 561 (2024).

O 98.5 Fri 11:30 H8

The Effect of Doping in Inelastic H Atom Scattering from Silicon — •Malte Opfermann, Sophia Tödter, Kerstin Krüger, and Oliver Bünermann — Institut für physikalische Chemie, Georg-August-Universität Göttingen, 37077 Göttingen, Germany

Recent inelastic H atom scattering experiments from the semiconducting Ge(111)c(2x8) have shown a bimodal energy loss distribution. One of the components was narrow with a small energy loss. The other component has shown a broad and large energy loss with an onset equal to the surface band gap.[1] While the low energy loss channel is explained by an adiabatic molecular dynamics simulation, the high energy loss component is not described theoretically yet.

To gain a better understanding of the underlying mechanism, we extended our studies to the Si(100)2x1 surface which is semiconducting as well. Despite its electronic structure being similar to the Ge(111)c(2x8) surface, it shows a different H atom energy-loss distribution. The first component is much broader and the second component does not show a clear onset at the surface band gap, both indicators of electronic effects. To further investigate, we carried out scattering experiments from samples with various doping levels.

[1] Krüger et al., Nat. Chem., DOI:10.1038/s,41557-022-01085-x (2022)

O 98.6 Fri 11:45 H8

Adsorption and bowl inversion of sumenene adsorbed on Au(111): a density functional theory — •Ikutaro Hamada[1], Ranmaru Kuno[1], Kota Iwata[2], Yoshiaki Sugimoto[2], and Hidehiro Sakurai[3] — [1]Department of Precision Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan — [2]Department of Advanced Materials Science, The University of Tokyo, Kashiwa, Chiba 277-8561, Japan — [3]Division of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Sumanene, a bowl-shaped π-conjugated compound, has been shown to form an ordered overlayer on noble metal surfaces. It has also been shown to exhibit conformation change, namely, bowl inversion, depending on its environment [1,2]. Experimentally, we have found that on Au(111), sumanene forms an ordered overlayer that differs from the previously reported structure for Au(111), but resembles the one observed on Ag(111). Moreover, we have demonstrated that bowl inversion can be induced using an atomic force microscopy tip. In this work, we employ van der Waals density functional to investigate the geometric and electronic structure of sumanene on Au(111). We also investigate the detailed mechanism of the bowl inversion of sumanene within the overlayer on the surface.

[1] R. Jaafar et al., J. Am. Chem. Soc. 136, 13666 (2014). [2] S. Fujii et al., J. Am. Chem. Soc. 138, 12142 (2016).

O 98.7 Fri 12:00 H8

Enhancing the electronic-coupling and conductivity of monolayer film of ferrocenyl molecules by Pd and Cu doping

— •Sunny M P Gautam, Himani Malik, Vikash Meghwal, Sruthi Manoharan, Vinithra Gurunarayanan, Ramesh Ramapanicker, and Thiruvancheril G Gopakumar — Department of Chemistry, Indian Institute of Technology Kanpur, India

Enhancing the conductivity and tuning the electronic structure of molecular films is crucial for their application in electronics. In this study, we explore the impact of metal doping (Pd and Cu) on the electronic structure and conductivity of two custom-designed ferrocenyl molecules, 3-ferrocenyl propanoic acid (FcC3) and 5-ferrocenyl pentadienoic acid (FcC5), on a graphite surface. Although the microscopic arrangement of the molecules within the film remains largely unchanged after doping, the incorporation of Pd and Cu at the 4-coordinated carboxyl dimer site of FcC3/FcC5 leads to a significant increase in conductivity. Electronic structure calculations of the FcC3/FcC5 dimers with metal show a substantial reduction in the HOMO-LUMO gap compared to their hydrogen-bonded counterparts, indicating stronger intermolecular electronic coupling through the Pd and Cu atoms, which lowers the barrier for electron/hole transport.

O 98.8 Fri 12:15 H8

Ge(CH2I)4 on Si(100) - Matching the Molecule to the Surface

— •Brandon Blue, Rafik Addou, Damian G. Allis, Eduardo Barrera-Ramirez, Jeremy Barton, Adam Bottomley, Nina Cullum, Michael Drew, Tyler Enright, Alan Godfrey, Ryan Groome, Aru Hill, Taleana Huff, Robert J. Kirby, Samuel Lilak, Cameron J. Mackie, Oliver MacLean, Terry McCallum, Mathieu Morin, Matthew Moses, Jonathan Myall, Ryan Plumadore, Adam Powell, Henry Rodriguez, Marc Savoie, Benjamin Scheffel, Marco Taucer, Denis Alexander Therien, Dusan Vobornik, and Janice Wong — CBN Nanotechnologies Inc.

We present an on-surface, multi-technique analysis of a synthetic, custom molecule for Si(100): tetrakis(iodomethyl)germane - Ge(CH2I)4, or TIMe-Ge. TIMe-Ge consists of four iodomethyl (CH2I) legs bound to a Ge atom core in a tetrahedral geometry. TIMe-Ge was selected based on its expected reactivity and surface behavior with Si(100)-2x1 as part of a set of design criteria which we'll present and discuss. The suitability of TIMe-Ge with respect to these criteria were supported by simulations and literature precedent. TIMe-Ge was found to covalently bond with Si(100)-2x1 in a limited number of configurations via C-I dissociative addition by STM, DFT, and XPS. The fourth CH2I is oriented away from the surface and towards the SPM for interaction, including controlled generation of C-centered radicals via bias pulses and UV photochemistry. We anticipate that TIMe-Ge and its congeners will aid in the development of molecular nanotechnologies and the study of requisite intermediates.