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Surface Electronic Structure of Semiconductors Probed by H Atom Scattering

Inelastic scattering plays a pivotal role in unraveling the intricacies of chemical dynamics, offering valuable insights into the fundamental processes governing the interactions of atoms, molecules and surfaces. Inelastic scattering experiments enable the investigation of energy transfer and redistribution, excitation, and reactive pathways at the atomic level. Through the accurate analysis of the scattered particles, one can probe the energy loss of the scattered atoms or molecules, study energy transfer mechanisms, and gain a deeper understanding of the underlying forces driving chemical reactions. The gained insights pave the way for advancements in fields such as catalysis, astrochemistry and materials science. Inelastic scattering experiments are also important as benchmark for the advancement of theoretical models in chemical dynamics, for example to test the validity of the Born-Oppenheimer approximation. Atoms provide an exclusively surface sensitive tool to study the properties of surfaces. One exemplary application of inelastic scattering of atoms from surfaces is helium atom scattering (HAS) [1]. HAS provides valuable information about the surface structure, phonon modes, and surface dynamics of materials. However, helium atoms are chemically inert and tell us little about surface chemistry. In contrast, hydrogen atoms, being chemically reactive, can participate in chemical reactions with surface species.

H atoms, a unique probe

When an H atom comes close to a surface, it wants to share its electron with the surface to form a chemical bond. By forming such a transient bond with the surface, the surface structure is strongly perturbed, which can result in very efficient energy transfer of the translational energy carried by the H atom into the nuclear and/or electronic degrees of freedom of the surface. Therefore, H atoms can interact both with the phonon modes and with the electronic excitations of the surface. The H atom energy loss spectra observed are defined by the electronic structure of the surface. Figure 1 A compares the energy loss distribution of H atoms scattered from an insulating Xe surface and a metallic Au(111) surface [2]. The distributions are very different: while in case of Xe we see a very narrow energy loss

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distribution that peaks at low energy losses, Au(111) produces a broad distribution that peaks at much higher energy losses. This discrepancy is due to the different electronic structures of the surfaces: For insulating surfaces, no electronic excitations are energetically accessible due to the large band gap and only lattice vibrations can be excited. For metallic surfaces, the partially filled conduction band provides low-energy intraband excitations and electron-hole pairs can be excited in addition to phonons. MD simulations that were performed for both surfaces and compared to the experimental results support this interpretation [2, 3]. While for Xe the simulation agrees almost perfectly with the experiment (blue line in Fig. 1 C), the MD simulation fails to describe the Au(111) experiment (blue line in Fig. 1 B). Only when accounting for electronic excitations, good agreement is achieved (Fig. 1 B red line). These results clearly show that insulating and metallic surfaces can be distinguished based on their H atom energy loss spectrum.
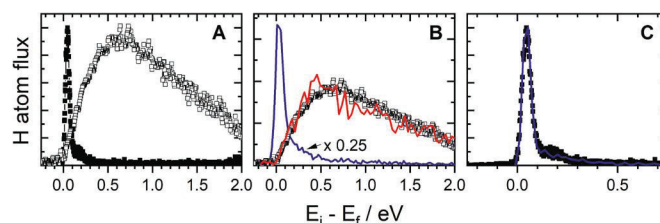

Fig. 1: Comparing the energy loss of H atoms scattered from a metal and an insulator surface.

Panel A compares the energy loss of H atoms scattered from a Xe (filled black squares) and a Au(111) (open black squares) surface. The experimental conditions are: E_i = 2.72 eV, $\vartheta_i = \vartheta_f$ = 45°, $T_{S,Au}$ = 300 K, $T_{S,Xe}$ = 45 K. Panel B shows the experimental results for Au(111) (open black squares) in comparison to MD simulations (solid blue line) and MD simulations with electronic friction (solid red line). Panel C shows the experimental results for Xe (filled black squares) in comparison to MD simulations (solid blue line) [2, 3].

What about semiconducting surfaces?

Just as insulators, semiconductors are band gap materials, but have significantly smaller band gaps. This makes excitations of electrons over the band gap energetically possible in our scattering experiments. To answer the question of whether such excitations occur and how likely they are, we have extended our studies to the surfaces of semiconductors [4]. As sample we choose the Ge(111) surface that reconstructs into the c(2x8) structure at room temperature. Ge(111)c(2x8) provides an

ideal model system in this context because it is a well-studied reconstruction that is easily prepared in an UHV environment and can still be handled in theoretical simulations. The surface reconstruction creates a surface state in the bulk band gap that leads to a surface band gap of about half an electron volt, making the surface semiconducting. We measured the energy loss of H atoms scattered from the Ge(111)c(2x8) for various H atom incidence kinetic energies above and below the surface band gap (Fig. 2 A-C). If the incidence energy is below the band gap (Fig. 2 A) only one component is observed in the energy loss distribution. For incidence energies above the surface band gap, a second component emerges and we observe a bimodal energy loss distribution (Fig. 2 B+C). Thereby, the first component exhibits low energy loss and the second channel is characterized by a large energy loss with an onset close to the surface band gap. Adiabatic molecular dynamics simulations by Hua Guo and coworkers can reproduce the first component, but the second component is absent in their simulations [4]. Based on these observations, we attribute the first channel to an adiabatic process leading to phonon excitation and the second channel to a non-adiabatic process leading to excitation of an electron over the surface band gap. Thereby, the second channel is related to an interband excitation, a transition between two electronic surface states. Fig. 2 D and E show energy resolved angular distributions of H atoms scattered from Ge(111)c(2x8) for two incidence energies. A broad angular distribution is obtained for the adiabatic channel, reflecting the strong corrugation of the surface due to reconstruction. The non-adiabatic channel exhibits a narrower angular distribution for an incidence energy of 0.99 eV (Fig. 2 D). This indicates that a specific surface site must be hit in a certain way to allow electronic excitation. For twice the incidence energy, the angular distribution of the second channel becomes broader (Fig. 2 E), pointing to a strongly reduced site selectivity. In conclusion, a semiconducting surface also shows a characteristic energy loss spectrum that can easily be differentiated from insulating and metallic surfaces.
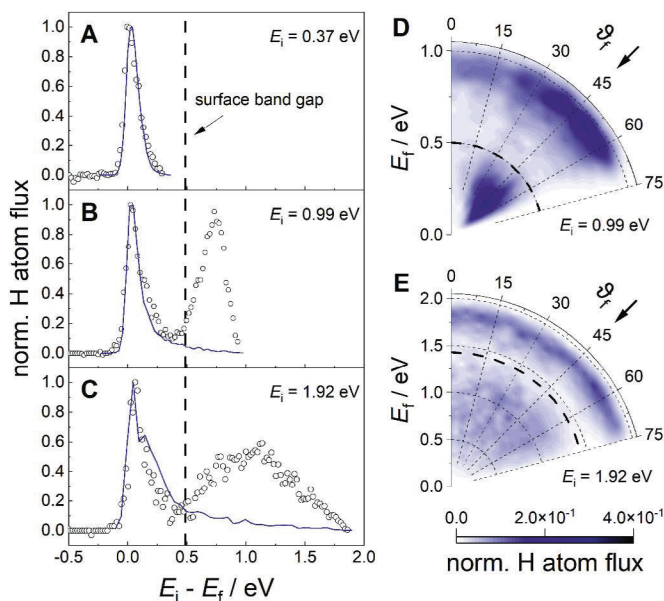

Fig. 2: Energy loss of H atoms scattered from the Ge(111)c(2x8) surface.

Panel A-C show the experimentally obtained energy loss distributions (black, open circles) of H atoms with three different incidence energies scattered from Ge(111)c(2x8) for specular scattering with an incidence angle of 45°. Results of MD simulations are shown as blue lines. Panel D-E show the energy resolved angular distributions for H atoms scattered from Ge(111)c(2x8) with two different incidence energies. The black arrow marks specular scattering. In all panels, the black dashed line marks the energy loss equal to the surface band gap. [4].

Understanding the mechanism

A common experimental approach to elucidate reaction, scattering and energy transfer mechanisms of atom- or molecule-surface interactions is the study of the isotope effect, mostly using H/D substitution. Systems showing energy transfer to phonons or EHPs respond differently to H/D substitution, so that the isotope effect can give evidence for the underlying mechanism. We performed the same experiments as shown above for deuterium and observed very similar energy loss distributions. The adiabatic channel shows the expected isotope effect confirming our assignment. Surprisingly, the second channel shows no isotope effect. Based on these findings we argue that the ability to excite an electron over the band gap depends on the surface site the H atom hits. In another set of experiments, we were able to follow the temperature-induced metallization of the Ge(111)c(2x8) surface in the H atom energy loss spectrum. Due to thermal occupation of the conduction band, intraband excitations characteristic for a metallic surface also become available on a semiconducting surface at sufficiently high temperatures. While the discussed bimodal energy loss distribution is observed for low temperatures, the H atom energy loss spectrum is very similar to a metal surface for surface temperatures of about 950 K.

In summary, inelastic H atom scattering is sensitive to the electronic structure of surfaces. Insulating, metallic and semiconducting surfaces show characteristic H atom energy loss distributions and we believe that this method has great potential to provide detailed insights into the electronic properties of surfaces. To learn about the underlying energy transfer mechanism observed for the Ge(111)c(2x8) surface we studied the isotope effect as well as the surface temperature dependence. A detailed understanding of the energy loss of H atoms on semiconducting surfaces is still pending, and the system poses a challenge to theoretical models of surface dynamics. Further experiments on different semiconductor surfaces as well as theoretical developments are on the way to elucidate further the very efficient excitation of electrons over the surface band gap observed for semiconducting surfaces.

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Oliver Bünermann received his PhD in Physics from the University of Bielefeld in 2006. During his postdoctoral stays at the University of Freiburg and University of California, Berkeley he became attracted by the field of physical chemistry and moved from electronic spectroscopy of molecules in the gas phase to atoms interacting with surfaces and became group leader at the Institute of Physical Chemistry of the University of Göttingen in 2010. In 2021 he received his habilitation in Physical Chemistry. In Göttingen, he developed a new experiment to study inelastic scattering of H atoms from surfaces. His research interest is in understanding elementary processes of surface reactions on the atomic scale.

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