

# **DYNAMIC PROCESSES**



# RESONANT CORE-LEVEL PROCESSES IN ADSORBATES: POLARIZATION AND ANGULAR DEPENDENCES

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Auger resonant Raman scattering has been shown to be a powerful tool to study dynamic processes at surfaces on a fs-timescale [1] as well as the electronic structure and electron correlation of bulk materials [2]. Especially in the latter case exploiting the angular and polarization dependence of Auger resonant Raman scattering and the interfering direct photoemission channel have been found to be very important [2]. In this contribution we present angular and polarization dependent results of Auger resonant Raman scattering for adsorbates on metal surfaces. As an example, the distinct angular dependence is shown for Ar/Cu(111) in Fig. 1, with strong variations for different final states. Consequences for the application of Auger resonant Raman scattering data to determine ultrafast electron relaxation processes will be discussed.

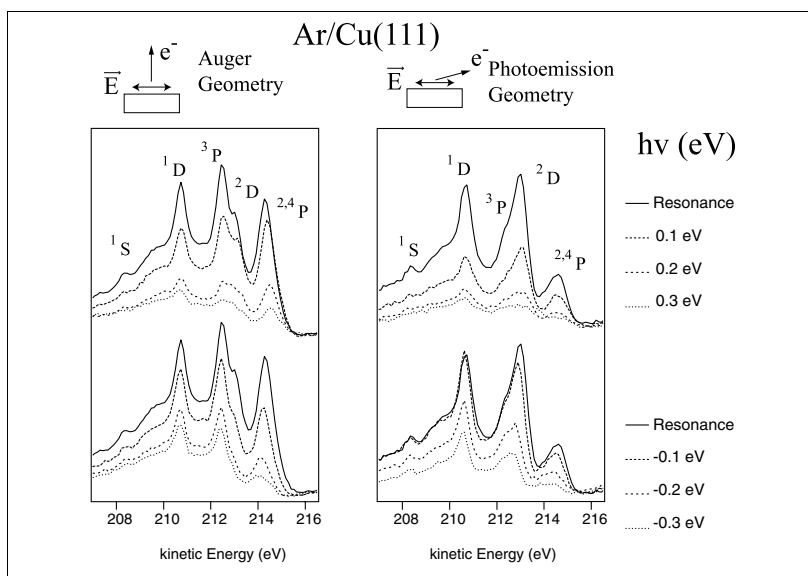


Figure 1: Angular dependence of Auger resonant Raman scattering on Ar/Cu(111). Strong angular variations are observed, i.e. for the <sup>3</sup>P and <sup>2</sup>D final states.

Furthermore, we investigated the coupling of core-hole states across different atomic centers. For these processes weak polarization dependence has been found. This research was supported by the Deutsche Forschungsgemeinschaft under contract SFB 338.

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# A COMBINED STUDY OF PHOTOEMISSION AND LASER FOR Si(111) SURFACE

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Recently, the research on the surface photovoltage (SPV) has been performed at super-ACO in France using the FEL light [1]. In the study, it was observed that the band bending is decreased when the synchronized FEL light and SR are irradiated for Si(111) 2x1 and GaAs-Ag surface. At UVSOR, SPV for GaAs surface was also observed using synchronized laser light and SR [2]. In these cases, SPV is caused to the direction decreasing the band bending between surface and bulk. The mechanism of SPV is explained by a model that the carrier induced by laser light irradiation transfers to the surface. However, it is not clear whether SPV is associated with the surface state. Moreover, it is not clear whether the same scenario is applied in the case of the metallic surface or in the case of the semiconducting surface. In order to investigate the relationship between SPV and the surface state, between SPV and the carrier concentration, we have performed the combined study of the photoemission and laser light irradiation.

Photoemission experiments were carried out at UVSOR (Okazaki) and at PF (Tsukuba). Typical energy resolution under Si 2p core-level photoemission measurements was  $\sim 100$  meV at  $h\nu = 130$  eV. The clean surface was obtained by annealing the sample at  $\sim 1200^\circ\text{C}$  irradiating the CW laser light (Nd YAG laser:  $h\nu = 1.165$  eV). The temperature of the sample was measured with an optical pyrometer.

It was observed that the Si 2p core-level photoemission spectra for the n-type (p-type) clean 7x7 Si(111) surface shift to higher (lower) binding energy side under the laser light irradiation. The shift direction for the n- and p-type surface was opposite. It is considered that the observed shift is caused by SPV. With increasing the carrier concentration, SPV is increased (decreased) for n-type (p-type) Si(111) surface. The shift is associated with the band bending because the band bending is increased with the carrier concentration. However, for the higher carrier concentration, the shift was not observed in our measurements. For the  $\sqrt{3}\times\sqrt{3}$  Si (111)-Bi surface, it is known that the surface state near the Fermi level disappears and the band gap is open. Under the laser light irradiation, the photoemission spectrum for the  $\sqrt{3}\times\sqrt{3}$  Si (111)-Bi surface shifts to higher binding energy side by  $\sim 0.2$  eV. The shift is identical to that for the clean 7x7 Si(111) surface. This means that SPV is not associated with the surface state in this system. The conclusion was also supported by the fact that the Si 2p surface-sensitive photoemission spectra with higher energy resolution shift without changing the spectral shape. In the conference, we discuss the laser induced effect and the temperature dependence for Si(111) surface.

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# Tracking molecular reactions and fragmentation by fast photoemission: SiC *via* thermally induced decomposition of fullerenes on Si(111)

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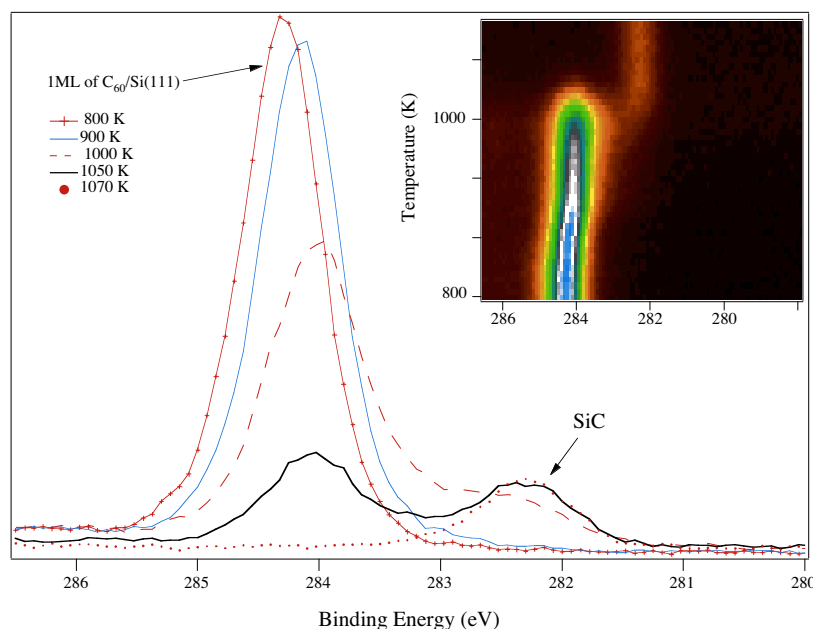
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## ABSTRACT

By exploiting the capabilities of the SuperESCA beamline (i.e. high photon flux and fast acquisition rate) at the ELETTRA Synchrotron in Trieste, we followed in real time the thermal reaction of fullerene molecules with the Si(111) surface by means of photoemission spectroscopy. The formation of SiC *via* fullerenes fragmentation on Si surfaces is used as a key example of the potentiality of fast photoemission, associated with a fine temperature control, in determining the nature of thermally induced chemical reactions. By monitoring every 10 sec the evolution of the C 1s core level photoemission spectrum, as a function of temperature and as a function of time at fixed temperature, we were able to show that there are two mechanisms, one kinetically limited and one activated at  $T \sim 1000$  K, responsible for the interaction and the fragmentation of C<sub>60</sub> on Si(111) and the consequent SiC formation. A model describing this reaction, in agreement with the experimental observation, has been proposed.



**Figure:** Some representative C 1s photoemission spectra as a function of temperature. A complete set of spectra, showing the evolution of the C 1s core level from 800 K up to 1100 K, is reported in the inset (intensity plot).

# INNER-SHELL EXCITATION AND FRAGMENT-ION DESORPTION PROCESSES DEPENDING ON POLARIZATION ANGLES

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It has been known that various kinds of fragment-ions desorb from solid surfaces when the solids are irradiated by VUV light or soft X-rays. This phenomenon is called Desorption Induced by Electronic Transition (DIET). In general, almost all bulk-derived ions are neutralized by electrons of bulk matters and can not desorb as ions. Thus, the desorption process of ions should be very sensitive to how the top-most surfaces are, namely, molecular orientation at the surface or the direction of bonds to be broken by electronic excitation. So far, however, this issue has not been fully investigated.

In this study we used linearly polarized synchrotron radiation (SR) as an excitation source, which allows us to selectively activate molecules with desired direction of the molecular axis according to the dipole selection rule in photoabsorption process. To measure the desorption yield spectra as a function of angles of impinging SR beam we have newly designed and constructed the time-of-flight mass-spectrometer (TOF-MS) that can rotate in the UHV chamber. H<sup>+</sup> and F<sup>+</sup> ions were detected as dominant ions from condensed fluorobenzene (C<sub>6</sub>H<sub>5</sub>F) around the C and F K-edges. The excitation-energy dependence of the fragment-mass patterns and desorption yields has been measured with various polarization angles. We have observed the following features: (i) the relative H<sup>+</sup> yields greatly increase at the C K-edge while enhanced F<sup>+</sup> yields are observed in the F K-edge, indicating that fragments are produced from the vicinity of (or the same as) primarily core-excited site; (ii) F<sup>+</sup> yields are enhanced in a lowest-energy resonance (F 1s→σ\*(C-F)) at the F K-edge when the incidence angles (θ) are small (as shown in Fig. 1), while H<sup>+</sup> yields increase in a π\* resonance at the C K-edge when θ are large. These findings mean that the fragment ions are preferentially produced from C-F or C-H bonds standing on the surface. The mechanism of the fragmentation and desorption processes will also be discussed on the basis of the translational energy distribution of desorbing particles.

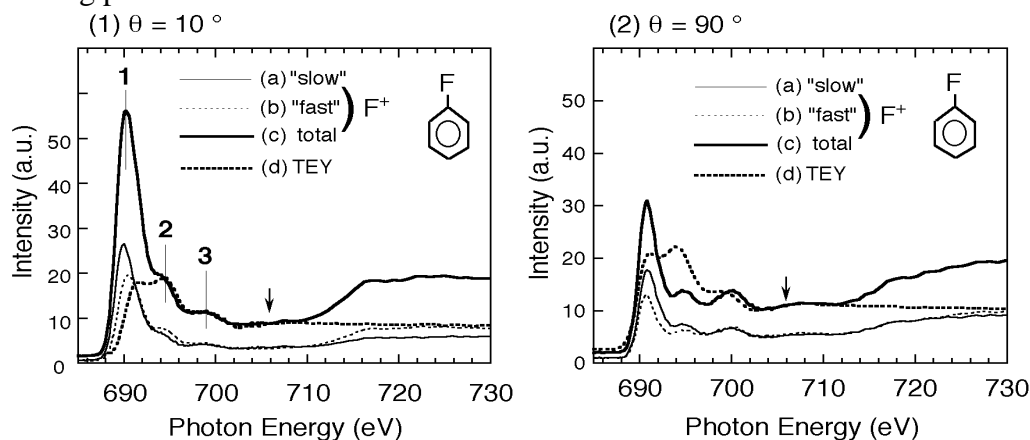


Fig. 1 (c) F<sup>+</sup> desorption yields and (d) photoabsorption spectra (TEY) at the F K-edge for the incidence angle of (1)10° and (2) 90°. Also shown are the (a) slow and (b) fast components of F<sup>+</sup> yields. The spectra were normalized at the position pointed by an arrow.

## High-pressure XPS: a new tool for environmental science and catalysis

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Most processes on surfaces in the environment, in the atmosphere, in biological systems or in catalytic reactors take place in gaseous environments. Photoelectron spectroscopy has been an extremely powerful tool in surface science for decades. Traditional electron spectroscopies are exquisitely sensitive to surface structure and composition but generally must operate in high vacuum due to the short mean free path of electrons in a gas phase (about 1 mm at 1 torr for 100 eV electrons).

To overcome these limitations, we have developed a new high-pressure electron spectrometer. Monochromatized soft x-ray photons from a synchrotron source pass through a thin silicon nitride window and strike the sample surface in a gas atmosphere with a pressure of up to 5 torr. Emitted photoelectrons are transmitted through a 1 mm diameter aperture approximately 1 mm above the sample surface. This aperture is the entrance to a differentially pumped electrostatic lens system (the unique feature of our instrument), which refocuses the electrons into the object plane of a standard electron energy analyzer situated downstream, in the high vacuum region.

We will present two examples for the application of this novel instrument to problems in environmental science and catalysis. Using a combination of electron-yield NEXAFS and XPS we have investigated the influence of hydrocarbon contamination on the premelting of the ice surface at temperatures close to the triple point. Our experiments show that hydrocarbon contaminants increase the degree of premelting. We have also investigated the catalytic reaction of methanol and oxygen over a copper catalyst. The correlation of XPS spectra of the copper surface and mass spectrometer data (that show the efficiency of the catalytic reaction) allow us to draw conclusions about the electronic state of the catalyst under different reaction conditions.

# DEVELOPMENT OF AN 'ENERGY DISPERSIVE SURFACE XAFS' IN THE SOFT X-RAY REGION

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A novel technique 'energy dispersive surface XAFS (x-ray absorption fine structure)' has been successfully developed by using a new soft x-ray beamline constructed at the bending magnet in the Photon Factory.

Soft x rays in the energy range of 100-1500 eV are available with three varied-line-spacing plane gratings. The schematic diagram for the measurements is illustrated in Figure 1. In the energy dispersive mode, horizontally dispersed x rays illuminate the sample, and Auger electrons emitted from each position of the sample surface are collected at once by a position sensitive electron analyzer (SCIENIA SES-2002). Accordingly, the Auger electron yield XAFS spectrum can be obtained with one shot.

Figure 2 shows an application of the new technique to the surface reaction of methanol on Ni(111). By using a 300- $\mu$ m grating, x rays dispersed in the energy range of  $\sim 20$  eV were obtained at once with  $\sim 10^{11}$  photons/s/eV around the O K edge. The energy dispersive XAFS was measured *in situ* during heating the substrate with the accumulation time of 10 s for each spectrum. At 210 K, two peaks deriving from the methoxy (CH<sub>3</sub>O) species were observed at  $\sim 534$  and  $\sim 544$  eV. The lower energy peak shifted to  $\sim 534.5$  eV and the higher energy one disappeared around 280 K. These changes can be attributed to the formation of carbon monoxide. No peaks were found above 420 K, indicating desorption of the adsorbate. Further performance and applications of the technique will be reported.

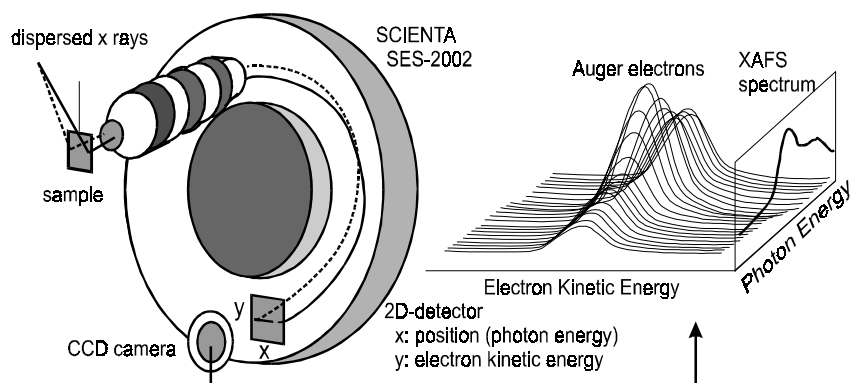


Figure 1: Schematic diagram for the energy dispersive surface XAFS. The horizontal position at the sample surface corresponds to the photon energy.

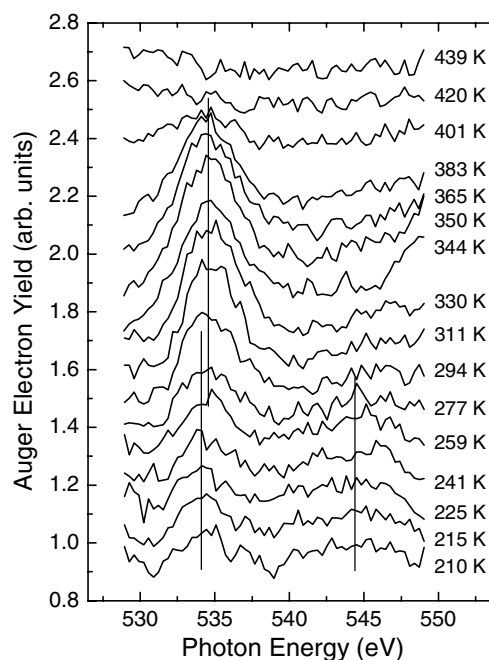


Figure 2: *In situ* O K-edge energy dispersive surface XAFS of methanol adsorbed on Ni(111) taken with increasing temperatures.



# AN ANALYSIS OF ELECTRON-HOLE RECOMBINATION IN SOLID KRYPTON USING TIME-RESOLVED SPECTROSCOPY

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Kr crystals exhibit simultaneously a strong broad-band self-trapped exciton (STE) luminescence as well as considerable narrow-band luminescence of free excitons (FE) in VUV region. For the first time, the FE luminescence decay curves are systematically investigated using photoexcitation in the energy region above band gap energy. Such measurements are possible due to the intense FE emission achieved in high-quality samples using Kr gas with highest available purity. The experiments are performed at the SUPERLUMI station of HASYLAB at DESY.

If the exciting photon energy is smaller than the band gap energy of solid Kr ( $E_g=11.59$  eV), a direct optical creation of excitons occurs. After their creation, excitons relax 'promptly' (in sub-ns region) to the lowest FE state and then emit the FE emission or become self-trapped. If photon energy exceeds the forbidden gap energy  $E_g$ , creating electron-hole pairs, then the FE decay curve exhibits along with the 'prompt' component also a 'slow' component with an additional maximum delayed some nanoseconds. It means that the 'slow' component is caused by FE creation through electron-hole recombination. More precisely, the 'slow' component is a convolution of the temporal evolution of electron-hole recombination into an excitonic state and the decay of the free excitons.

A detailed model for the dynamics of electron-hole recombination into the FE state has been developed. In this model, kinetic energy of the charge carriers is described using effective electron and hole temperature. The model includes (i) carrier thermalization via scattering on acoustic phonons and (ii) electron-hole recombination cross-section, both described by the deformation potential theory. Due to the very simple crystal structure, only acoustic phonons exist in rare gas solids. Hence, the phonon-assisted relaxation processes are much slower than in systems with optical phonons and take place in nanosecond scale.

Both thermalization rate and recombination cross-section depend strongly on values for the electron effective mass  $m_e$  and the deformation potential  $E_d$ . In earlier calculations for solid Xe [1], the values for  $m_e$  and  $E_d$  were based on theoretical considerations. But in the present work, these values are derived from the experimental value of the low-field electron mobility. This permits to reduce the number of fitting parameters of the model. The 'slow' component of FE decay curves can be reproduced with model calculations. Experimental and theoretical results will be compared in this report.

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## Picosecond Core-Level Dynamics in Laser-Perturbed Silicon

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Phase transitions driven by intense laser pulses are of fundamental interest (e.g. the nature of the solid-liquid phase transition) as well as applied interest (e.g. materials processing applications). We report, to our knowledge, the first direct measurement of core-level dynamics in a molten semiconductor. Experiments are performed at the Advanced Light Source (ALS, beamline 7.3.1.2) using ~400 eV synchrotron light and 800 nm (1KHz, ~200 fs) laser light. A hemispherical analyzer records x-ray photoelectron spectra (XPS) in the vicinity of the Si 2p photoemission peak as a function of x-ray/laser relative arrival time at a Si <111> sample. The ALS is operated in ‘cam-shaft’ mode whereby a single electron bucket is isolated from the remaining bunches in the storage ring; electronic gating is used to collect photoelectrons produced by ALS pulses temporally overlapped (or nearly overlapped) with laser pulses.

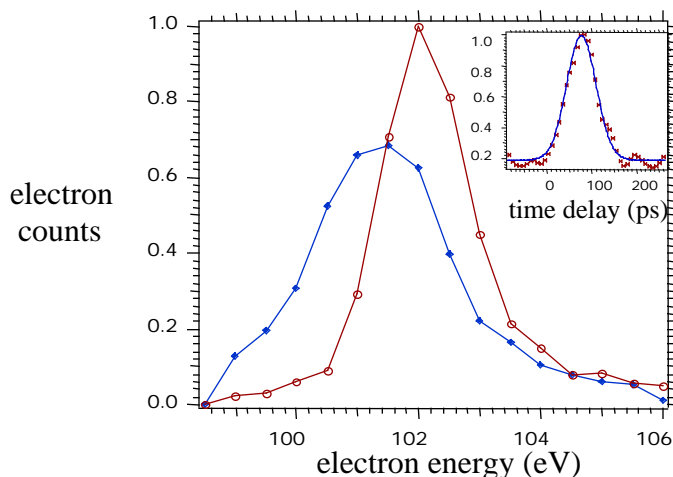


Figure 1. Silicon 2p photoelectron spectra obtained with (solid markers) and without (open markers) laser excitation. The inset shows electron counts near 100 eV as a function of x-ray/laser time delay.

Upon laser excitation (Fig. 1) the Si 2p peak shifts to lower binding energy by ~ 1 eV as a result of a laser driven solid-liquid phase transition. The peak shift recovers rapidly (<100 ps) due to rapid cooling. Previous x-ray measurements of liquid silicon focused on x-ray absorption and are dominated by modifications of the valence states. Photoelectron spectroscopy permits direct observation of the core-level dynamics; important to understanding the molten semiconductor.

## **A temperature programmed X-ray photoelectron spectroscopy study of the decomposition reactions of unsaturated hydrocarbons on Ni(100)**

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The surface chemistry of hydrocarbons on transition metals has received much attention reflecting the importance of such systems in elucidating the mechanisms of heterogeneous catalysis, e.g., alkyl fragments ( $\text{CH}_x$  where  $x = 0-3$ ) are proposed as key intermediates in the methanation of CO and  $\text{H}_2$ , Fischer-Tropsch synthesis, and other alkane conversion processes. In particular, the adsorption and reaction of small unsaturated hydrocarbons on the low index surfaces of Ni has been the focus of much research activity in an effort to develop an understanding of the selectivity for C-C and C-H bond cleavage/formation and hydrogen exchange. We present a temperature programmed X-ray photoelectron spectroscopy (TP-XPS) study of the adsorption and dissociation of acetylene, ethylene and propene on Ni(100) performed at BL I511 at MAX-lab. The use of third generation synchrotron sources makes it possible to measure high resolution photoemission spectra within a few seconds approaching the ideal of real-time analysis [1]. The evolution of the C 1s core level spectra at a resolution of 120 meV has been monitored in-situ as a function of sample temperature from 95 to 500 K. Analysis of the observed changes in photoemission lineshape and peak binding energy positions and correlation with TPD, HREELS and UPS data from the literature have allowed us to distinguish the surface intermediates formed during the decomposition reactions [2-5]. The resultant temperature-dependent intensity curves provide additional insight into dehydrogenation mechanisms involved in such systems.

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# **In-situ core-level photoelectron spectroscopy of adsorbates on surfaces involving a molecular beam – general setup and first experiments**

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Traditionally, spectroscopic surface science experiments dealing with adsorption and desorption are performed ex-situ, that is, after the adsorption or reaction process has taken place. The main reason for this is that the speed of these reactions is usually too fast for the measurements to follow in-situ. With the operation of third-generation synchrotron facilities this limitation could be overcome for photoemission experiments. In the past, a series of studies have been performed using what is called fast-XPS or temperature-programmed XPS (TP-XPS) (see, for example [1,2]). The next step forward is to include molecular beam techniques to control and vary the kinetic properties of the incident molecules, such as translational energy (e.g. for CO between 0.03 and 2.0 eV) or rotational motion, and to locally increase the pressure on the surface. In order to explore this idea we have designed and built a new apparatus, which combines high-resolution photoelectron spectroscopy with a three-stage supersonic molecular beam source. The transportable setup has been optimized for use at BESSY II, but also allows experiments and preparations in the laboratory using a monochromated x-ray source. In this contribution we want to introduce the general layout and its properties, and discuss some first experiments using synchrotron radiation.

For the beginning we have chosen the system CO/Pt(111) for which there exists a large number of publications, including some in-situ studies using a molecular beam [3]. CO is known to adsorb in two different adsorption sites (ontop and bridge), leading to core-level shifts not only in the C and O 1s levels, but also in the Pt 4f levels. During the CO uptake one can see that the on-top site is occupied first, with the bridge site occupation starting with some delay, in agreement with [3]. With the new setup we are able to measure core level spectra with good resolution (180 meV for C 1s, 120 meV for Pt 4f) with an acquisition time of 3 seconds per spectrum. That allows the observation of differences in site occupation between fast and slow adsorption experiments, depending on pressure and sample temperature. We also investigated the CO oxidation reaction on Pt(111) by predosing the surface with a c(2x2) oxygen layer. Again the influence of beam pressure and sample temperature on the reaction are investigated. Local pressures up to  $10^{-5}$  mbar are achieved on the sample surface, while maintaining UHV conditions in the analysis chamber. Using the tunability of the molecular beam energy we also studied activated adsorption processes, like methane on Pt(111). Interesting questions here are the adsorbed species as function of translational and rotational energy of the impinging molecules.

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## WATER ICE AND ITS INTERACTION WITH AMMONIA : A PSD-NEXAFS STUDY.

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The physics and chemistry of ice and the heterogeneous reactions occurring at its surface is of interest in a wide range of disciplines, as solid state physics, biology, environmental chemistry, etc. In most of these reactions, both surface adsorption and bulk diffusion play a key role. They are known to be strongly influenced by the temperature and the morphology of the ice's bulk and surface and by the nature of the interacting molecule [1], but are still not well understood.

We have studied the temperature dependence of the O K-edge X-ray absorption spectra of the bulk of ice (by use of conventional NEXAFS) and of the surface of ice (by use of Photo Stimulated Desorption-NEXAFS), starting from the amorphous microporous ice (38 K) to crystalline hexagonal ice  $I_h$  (160 K). From the variation of the  $\sigma^*(O-O)$  energy with the temperature in both the NEXAFS and PSD-NEXAFS signals, we have shown that :

- the surface of ice  $I_h$  owns a crystal structure, which differs from that of the bulk.
- the density of the ice surface is lower than in the bulk, and decreases as temperature increases.
- the bulk density (at a nanoscale) is constant in the whole temperature range, except between 38 K and 55 K where a steep densification of the bulk of ice is observed.

Other changes are also observed in the PSD-NEXAFS signal, related to the evolution of the surface OH dangling bond concentration and to the collapse of the micropores with temperature [2].

We have also studied at different temperatures the interaction of  $NH_3$  with ice - ammonia being a model of hydrophilic molecule -, in order to follow the adsorption modes, the bulk diffusion and the modifications induced at the ice surface by the interaction. We have shown that :

- $NH_3$  adsorbs at the dangling OH site in the monohydrate form  $NH_4OH$ .
- $NH_4OH$  quickly diffuses as it is in the bulk of ice, likely via a molecular transport mechanism [3]. Bulk diffusion is slowed when the temperature decreases, but does not change in nature.
- the ice surface reconstructs as the  $NH_4OH$  diffusion proceeds ; the number of dangling OH re-increases, so that the ice surface becomes again reactive for further reactions with  $NH_3$ .

Thus, we conclude that the strong reactivity of the ice surface towards  $NH_3$ , together with a molecular transport mechanism allowing a rapid dilution of the pollutant followed by the re-activation of the ice surface, make the water ice highly efficient for trapping and scavenging ammonia.

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## **The combination of a supersonic molecular beam with high-resolution core level photoemission at the SuperESCA beamline: real-time surface segregation study in a Pt-Rh alloy.**

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The process of surface segregation in a Pt<sub>50</sub>Rh<sub>50</sub>(100) single crystal alloy has been studied by combining a novel supersonic molecular beam with the real-time core level photoemission at the SuperESCA beamline of ELETTRA. The evolution of the surface and bulk components in the Pt4f<sub>7/2</sub> and Rh3d<sub>5/2</sub> core levels is followed with time-resolution down to 100ms/spectrum, while oxygen is dosed on the surface with a well defined temporal modulation. Detailed information about the relation between oxygen surface coverage (O1s signal), Rh-O bond configuration and variation of the vertical Pt population in a oxidizing and reducing ambient is obtained, shedding light on the structural and chemical properties of the Pt-Rh alloy. Time constant of the bulk-to-surface diffusion process and enthalpy of surface segregation have also been derived.

# Femtosecond electron dynamics of image potential states on bulk and thin film Ni surfaces

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Electrons in front of a metal surface can be trapped by their own image charge inside the metal. If there exists a band gap on the crystal side, which prevents the electrons from relaxing into the bulk, they form a series of Rydberg-like bound states localized in front of the crystal surface, with energies  $E_n \propto -1/n^2$  converging towards the vacuum level[1].

Lifetimes of image potential states (IPS) on noble metal surfaces are relatively well understood. But little is known about their behaviour on transition metal surfaces. We investigated lifetimes and binding energies of IPSs in front of Ni surfaces using time-resolved two-photon photoemission. With this technique, lifetimes of normally unoccupied electronic states can be measured with an accuracy of a fraction of the laser pulse duration. For the Ni(100) bulk surface we obtain a lifetime of  $13 \pm 3$  fs of the  $n=1$  IPS. This is much shorter than the lifetimes observed on Cu(100) and Ag(100)[2], as will be discussed below. For thin epitaxially grown Ni films on Cu(100) we obtain drastically reduced lifetimes as compared to bulk Ni.

We show that the lifetimes for noble as well as transition metal surfaces can be understood qualitatively by a simple model, which takes into account two parameters: First, the degree to which the wavefunctions extend into the crystal, determining the spatial overlap with bulk states. Second, the density of final bulk states into which the electrons can decay. The decay into these final states takes place by the creation of electron-hole pairs. One would expect from the model that this Auger decay is enhanced by partially unoccupied d-bands for transition metal surfaces, giving rise to a reduced lifetime for Ni, Pt and Pd as compared to noble metals[3,4,5].

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## Charge transfer on a few fs-timescale in model solar cells

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The monomer and the dimer of isonicotinic acid, cf. Figure 1, are active in the bonding of various dyes to the semiconducting substrate (nanoporous TiO<sub>2</sub>) in dye-sensitised solar cells [1]. We employed resonant photoemission (RPES) on multilayers and monolayers of these molecules on rutile TiO<sub>2</sub>(110) to characterise the extent of electron delocalisation upon N 1s excitation. The resulting CIS (Constant Initial State) curves for the bi-isonicotinic case in comparison to the X-ray Absorption Spectra (XAS) are shown in figures 2 and 3. Intensities in the CIS spectra indicate charge localisation on a timescale comparable to the core-hole lifetime (approx. 5 fs in case of an N 1s core-hole). One can derive charge transfer times on a few fs timescale by comparing the CIS to the XAS intensities.

In the multilayer case the degree of localisation is high for excitation to both  $\pi$ -resonances, while for the monolayer we find a strong dependence on the excited state. The lowermost resonance lies within the bandgap, which suppresses any charge transfer on the given timescale, while for the two higher  $\pi$ -resonances the transfer is faster than 2.5 fs.

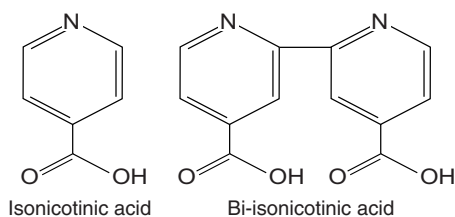


Figure 1: The isonicotinic acid monomer and dimer

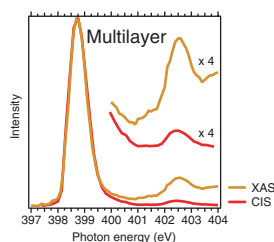


Figure 2: XAS and CIS for a multilayer of bi-isonicotinic acid

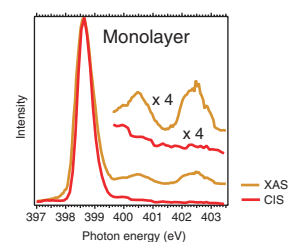


Figure 3: XAS and CIS for a monolayer of bi-isonicotinic acid/TiO<sub>2</sub>(110)

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# SYNCHROTRON-RADIATION PHOTOEMISSION AND INFRARED SPECTROSCOPY STUDY OF ADSORPTION AND DECOMPOSITION OF DICHLOROSILANE ON Si(100)(2X1)

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Dichlorosilane ( $\text{SiH}_2\text{Cl}_2$ ) is one of the most widely used molecular precursors for silicon epitaxial growth and silicon-germanium heteroepitaxy. Dichlorosilane is very competitive with silane for silicon chemical vapor deposition (CVD). The sticking probability of  $\text{SiH}_2\text{Cl}_2$  on silicon surfaces is greater than that of silane. Dichlorosilane can also produce higher quality silicon epitaxial layers at lower reaction temperatures than silane. Therefore, there has been much interest in dichlorosilane as a molecular precursor for atomic layer epitaxy (ALE).

We have used synchrotron-radiation photoemission (SR-PES) and infrared absorption spectroscopy (IRAS) to investigate in-situ the adsorption and thermal decomposition of  $\text{SiH}_2\text{Cl}_2$  on Si(100)(2x1). Si 2p core-level photoemission spectra and IRAS spectra in the Si-H stretching vibration region of the surface exposed to  $\text{SiH}_2\text{Cl}_2$  at room temperature have been measured to examine how  $\text{SiH}_2\text{Cl}_2$  dissociatively adsorbs on the surface. Si2p core-level photoemission spectra show that peaks due to monochloride (SiCl) and surface hydride species ( $\text{SiH}_x$ ) were monitored. IRAS spectra revealed that at initial stages of  $\text{SiH}_2\text{Cl}_2$  adsorption, the monohydride (Si-H) and the Cl-substituted hydride ( $-\text{SiHCl}$ ) species are present on the  $\text{SiH}_2\text{Cl}_2$ -adsorbed surface. With further exposure to  $\text{SiH}_2\text{Cl}_2$ , a peak due to Si dihydride species appeared. These findings indicate that at low  $\text{SiH}_2\text{Cl}_2$  exposure,  $\text{SiH}_2\text{Cl}_2$  dissociatively adsorbs onto the Si(100)(2x1) surface to generate Si monohydride, Si monochloride, and the Cl-substituted species  $-\text{SiHCl}$ . We suggest that  $-\text{SiHCl}$  sticks onto the bridge site between two adjacent dimers. With increase of  $\text{SiH}_2\text{Cl}_2$  exposure,  $\text{SiH}_2\text{Cl}_2$  adsorbs onto a single dimer to produce a Si chloride  $-\text{SiCl}$  and a Cl-substituted dihydride  $-\text{SiH}_2\text{Cl}$ .

The surface was annealed following saturation exposure to  $\text{SiH}_2\text{Cl}_2$  to examine how the surface species as mentioned above are decomposed. As the surface temperature was raised from room temperature to approximately 400 °C the dihydride absorption peak ( $-\text{SiH}_2\text{Cl}$ ) vanished completely, whereas the Si2p peak due to monochloride remained. This spectral change indicates that during thermal annealing  $-\text{SiH}_2\text{Cl}$  species is thermally decomposed to generate surface Si-H and Si-Cl bonds. We furthermore observed that with increasing the surface temperature, the absorption peak due to the monohydride shifts to higher wave numbers. Comparing infrared data with the density functional cluster calculation, we suggest that the peak shift is due to the formation of surface adatom dimer  $=\text{HSi-SiCl}=\text{}$ .

The present results show that comparison of SR-PES and IRAS data provides us with valuable information about the atomic bonding configuration of chemical species on semiconductor surfaces.

# DIRECT LIFETIME MEASUREMENTS OF $1snp$ STATES IN HELIUM

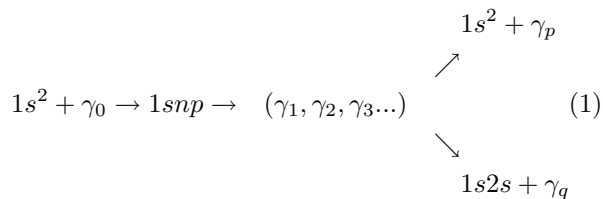
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The lifetimes of  $1snp^1P_1$  excited states in helium have been measured on beamline SA72 using a two-bunch mode operation of the SuperACO storage ring in Orsay, France. Every 120 ns the helium target was probed by short photon pulse, tuned to the excitation energy of  $1snp$  states. These states can decay only by a fluorescence cascade, ending either in helium ground state or in the singlet metastable state:



The metastable atoms and UV photons  $\gamma_p$  emitted from the target were detected by a large area MCP stack, having two properly biased grids in front to reject the entrance of charged particles<sup>1</sup>. The axis of MCP detector was aligned with polarization direction of the incoming light beam and placed with the surface perpendicularly to the gas inlet in order to intercept the metastable atoms (Fig. 1). Time coincidences were recorded between the START pulse signaling the arrival of the probing pulse and STOP pulse coming from the MCP detector. The coincidence spectra were recorded for  $1snp$  states up to  $n = 11$ . All the series display a sharp, exponentially decaying peak, pertaining to the prompt  $\gamma_p$  photons and flat background due to detection of metastables (Fig. 2).

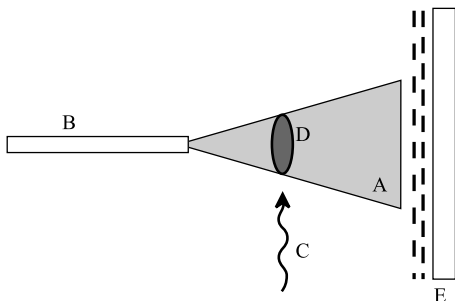


Figure 1. Experimental setup: He gas (A) enters through the needle (B) into the vacuum chamber. The photon beam (C) interacts with gas in the region D. The resulting photons and metastables are detected with MCP (E).

The time scale and to the lesser extent, the branching ratio of decay into the two available final states (1) depend on the quantum number  $n$  of the excited state. Indeed, the experimental decay time is seen to increase very fast with  $n$ , coming close to the time window of the experiment for  $n = 11$ . As our MCHF calculations show, the most probable are the direct transitions into the final states,  $p, q = 1$ , in agreement with previously tabulated data<sup>2</sup>. The branching ratio of the metastable to the ground state population is then approximately given by the ratio of direct transition rates, being about 0.1% for  $1s2p$  state and 3% for higher  $1snp$  states. At  $n = 8$  there is already about 2% of decays entering more complicated, the indirect path toward the final states,  $p, q > 1$ . To properly determine the branching ratio we have numerically solved the coupled system of differential equations, governing time dependent population of all the levels involved in the cascade. Using MCHF approach we have calculated *abinitio* the lifetimes of  $1snp$  states. The results of calculations are combined together and compared to parameters, extracted directly from the experimental spectra.

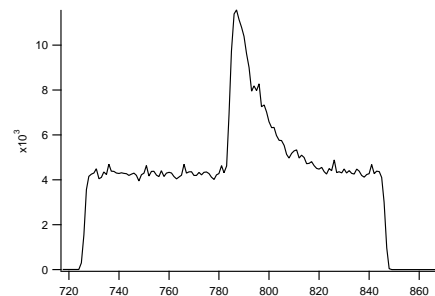


Figure 2. Coincidence spectrum of  $1s5p$  state.

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