

Letter of intent for experiments at LCLS for new exciting science (B)

Ultrafast Soft X-ray Studies of Surface Chemical Reactions and Hydrogen Bond Dynamics in Aqueous Systems

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The ultimate goal in chemistry is to understand on a fundamental level how bonds are broken and reformed during chemical reactions. In many cases we can draw simple pictures of how electrons flow with respect to electron pair redistributions or electrostatic interactions along a reaction path. For many systems bonding can often be understood in terms of molecular orbitals and reactivity in dynamical rearrangements of different molecular states. Such knowledge provides the basis for the understanding of chemical trends and predicting chemical reactivity for many chemical compounds. Since the excitation and probe steps with conventional optical lasers involve valence electrons that are delocalized over many atomic centers it is difficult to study complex systems. It would be an important development if we can probe how molecular orbitals are transformed during a chemical reaction in an atom-specific way around the center where the interesting chemistry takes place. This can be achieved using core level excitations and decay spectroscopy [1]. Nearly all chemical systems of importance contain C, N and O atoms. In order to access the C1s, N1s and O1s levels for ultrafast spectroscopy we need to use soft x-rays in the energy region between 280-550 eV. This would open new prospects to study time-resolved changes in the electronic structure of complex systems, such as surface reactions, catalysis, hydrogen-bonded systems, aqueous solutions, polymers and biological molecules.

I propose to initiate an exploratory activity to perform experiments at LCLS for ultrafast soft x-rays with a 200 femtosecond time resolution. It would be a desire if LCLS could lower the energy to reach the O K edge at 530 eV and a dream to go all the way to the C K edge at 280 eV. The results from exploratory experiments could form the basis for future development of LCLS into the soft x-ray regime with a second undulator. It will allow potential users to develop a scientific case using ultrafast soft x-rays in several different scientific areas. In the present letter I propose to develop experiments using soft x-rays in two important areas, surface reactivity in catalysis and dynamics in aqueous chemistry.

X-ray spectroscopy

X-ray Emission Spectroscopy (XES) has the unique ability to provide *an atom-specific probe of the electronic structure* [2,3]. Fig. 1 illustrates the XES process for an adsorbed N₂ molecule on a nickel surface [4]. The atomic sensitivity arises from the creation of a core hole during the absorption process and that this core hole can only be filled by

valence electrons in the proximity of the excited atom. Furthermore, the chemical shift in the N 1s core level allows for selective probing of the two inequivalent nitrogen atoms [1,4]. The final state of the x-ray emission process is a valence hole state similar to the final state in valence band photoemission but here the valence electronic structure is projected onto a specific atom. Another essential aspect of the spectroscopy is that the polarization of the incident radiation and the direction of the emitted radiation allow directional sensitivity to the bonding, providing a direct measure of the molecular orbital symmetry.

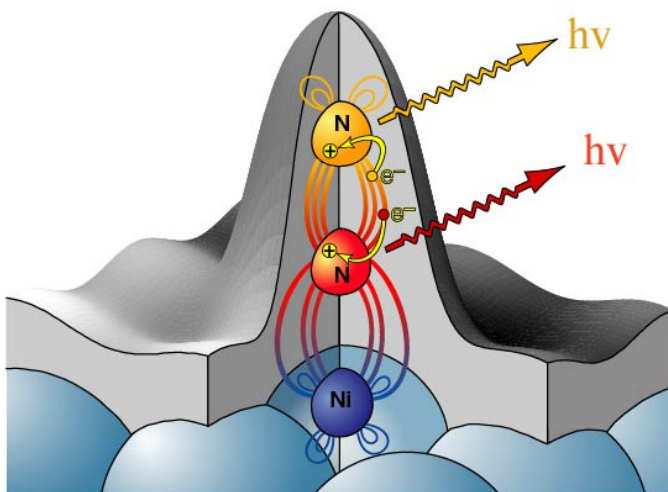


Figure 1. Schematic picture illustrating the local probe character in XES for N₂ adsorbed on a Ni surface. From the total charge density (gray envelope) valence electrons with p-angular momentum (contour lines) decay into the N 1s core hole.

The adsorption of glycine on Cu(110) illustrates what can be learned from a XES study of a more complex system. The molecule is an amino acid with both a carboxylic and amino functional group; the molecular skeleton is intact upon adsorption except for the removal of the acidic hydrogen. The molecule is oriented perpendicular to the Cu rows on the two-fold symmetric surface allowing for projection of the 2p_x, 2p_y and 2p_z valence orbitals [5]. The carbon atoms in the COO and CH₂ groups have different chemical shifts allowing for a selective separation of these atoms in the excitation process. Fig. 2 shows XE spectra measured on 4 different atomic sites projected in three directions [6]. The picture that emerges is an experimental version of the LCAO (Linear Combination of Atomic Orbitals) approach to molecular orbital theory. We can study how molecular orbitals of a specific symmetry are distributed over different atomic sites in a complicated molecular adsorption complex. Combined with theoretical calculations, details in the surface chemical bonding can be obtained from such studies. We can investigate separately how the different functional groups are affected by the bonding to the surface or hydrogen bonding to neighboring molecules.

There are many different samples that can be studied using XES, solids, surfaces, gases and liquids. The method is well suited to study gases and liquids and their solid interfaces since it is an x-ray-in/x-ray-out technique that does not require vacuum. We can make windows of different materials strong enough to withstand atmospheric pressure and thin enough to allow sufficient transmission of soft x-ray photons. This opens up the potential to study chemical reactions at surfaces under atmospheric pressures and in liquids [7,8]. We can also use XES as a means to obtain fluorescence-detected x-ray absorption spectra

(XAS) [7]. Furthermore, many spectroscopic techniques such as photoelectron spectroscopy are based on electron detection that will have severe limitations for ultrafast studies where the large peak intensity will build up space charge on the surface. In XES all involved particles are photons and the spectra will not be distorted due to the development of space charge.

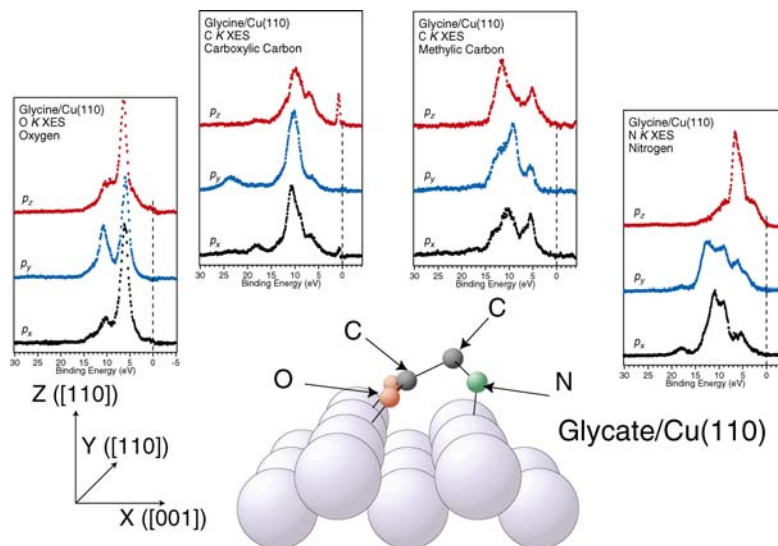


Figure. 2 $2p_x$, $2p_y$ and $2p_z$ symmetry resolved x-ray emission spectra for glycine adsorbed on Cu(110). Inserted is a structural model of the backbone of the adsorption complex. The spectra are measured at the O atom, the C atom in the (COO) group, the C atom in the (CH₂) group and at the N

Surface reactions and catalysis

The microscopic understanding of heterogeneous catalysis requires a detailed understanding of the dynamics of elementary processes at surfaces, such as charge and energy transfer between molecular adsorbates and catalytic substrates and the appearance of different reaction intermediates [9]. There is an enormous fast growing activity using theoretical studies to model catalytic reactions using total energy based density functional theory calculations (DFT) [10,11]. Several theoretical estimations of activation barriers for the rate-limiting steps seem to be in good agreement with kinetic measurements of the total reaction rate. However, there are experimental indications that there are important energy dissipation channels that provide evidence for strong nonadiabatic coupling in adsorption and dissociation processes [12,13]. It was suggested that the nonadiabatic damping of vibrational motion close to the activation barrier was due to creation of electron-hole pairs in the substrate. It will be extremely important to experimentally resolve the elementary steps during a surface reaction and thereby reach a mechanistic understanding on a microscopic level that can be compared with theory. We propose to use ultrafast pump (optical lasers) and probe (FEL-XES) experiments in order to identify short lived reaction intermediates, inaccessible to static XES. From knowledge of the details of the electronic structure we can derive how the electrons have flowed between

the substrate and reactants and related this to changes in the nuclear coordinates. A detailed knowledge of the time dependent evolution of reactants, products and intermediates will allow for the construction of detailed kinetic models and estimations of the various activation barriers in complex catalytic reactions.

The oxidation of CO on Ru(001) has been a model system for simple catalytic reactions [14] and is the most efficient catalyst among the Platinum metals for CO conversion under high pressure conditions. Under ultra high vacuum (UHV) conditions heating the surface with CO and O coadsorbed does not lead to CO₂ formation. However, the CO oxidation reaction can be initiated with strong optical femtosecond laser pulses [15]. Thus, a new reaction pathway is opened which is not accessible via thermal excitation at low pressures. It was concluded that the activation of the Ru-O bond is the rate determining step in the oxidation process. The time scale of the coupling of the adsorbate degrees of freedom to hot substrate electrons is of the order of 500 fs. Simultaneous movement of O and CO towards each other will lead to reaction. With a femtosecond laser we will initiate the oxidation of CO, which we will be probed with ultrafast x-rays from the FEL. With these femtosecond soft x-rays we will be able to selectively probe CO or O and follow how each of these species evolve using atom specific XES. To study this process with the FEL/XES technique we can selectively excite CO or O and use the soft x-ray pulse as a probe and follow how each of these species progress using atom-specific spectroscopy. Furthermore, there is a chemical shift for CO in different adsorption sites that can be utilized to investigate site-dependent reactivity [1]. The electronic structure is significantly different for different substrate coordinations [16]. Using angle-resolved measurements we can follow changes in both σ and π orbitals. The goal would be to identify and characterize short-lived intermediates where the CO and O atoms are in close proximity to each other.

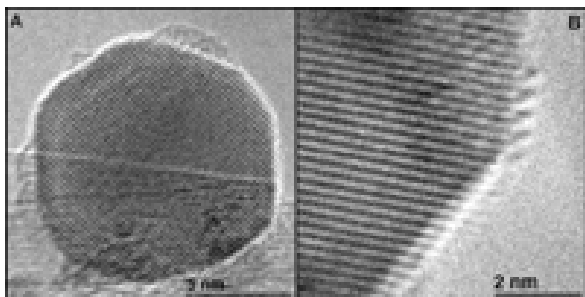


Figure 3 In situ transmission electron microscope images of Ba-promoted Ru catalyst recorded under reaction conditions.

The concept of "active sites" is fundamental in heterogeneous catalysis. There is clear evidence that many catalytic surfaces are not uniformly active, but the activity occurs only at specific sites where a special arrangement of surface atoms or special chemical composition exists. It was recognized more than 30 years ago that certain reaction rates are sensitive to the particle size distribution in supported metal catalysts [16,17]. Variation of particle size gives rise to changes in the surface structures where the relative concentrations of atoms in steps, kinks and terrace sites are altered. Different additives and support interaction often cause certain particle shapes to be stabilized which can affect the concentration of active sites. As an example, it has recently been shown that barium promoted Ru exhibits unprecedented activity and stability in the catalytic

ammonia synthesis [19]. Figure 3 shows a transmission electron microscopy image of a Ru catalyst under reaction conditions [20]. The Ba promoter can be seen to be located at the edge of the crystal creating unique active step sites where it is assumed that the reaction proceeds. These findings are along the line of results of measurements of the dissociative sticking probability of N_2 on Ru(0001) steps which find that these constitute the active site for the dissociation of dinitrogen [21]. There are 9 orders of magnitude difference in dissociative sticking probability between step sites and terrace sites. Furthermore, it has recently been shown that not only N_2 but also CO, NO and O_2 have a much higher probability for dissociation at step sites [22-24].

We propose to follow the dissociation process of N_2 that has been initiated by a laser pulse through electron heating on a stepped Ru surface. Figure 4 shows a large number of possible intermediates based on DFT calculations together with simulated XES spectra. The angular resolved spectral changes between the species are relatively large and can be further enhanced by imposing polarization control of the incoming ultrashort x-ray pulses. Depending on the orientation of the incident E-vector and specific photon energy, different resonances in the XAS-mediated excitation process will enhance the contrast of certain species over others. We can in that sense follow different species as they evolve over time. We can expect that for some of the species, when the core level shift is large enough between the different N atoms, we can perform atom resolved measurements. From the projected spectra in the 3 different directions the changes are rather large due to σ - π rehybridization when both N atoms start to interact with the surface. We can anticipate to probe the upright, lying-down and dissociated species with XES. It will be interesting to see if the perpendicular N_2 adsorbed at the step edge will have a different electronic structure compared with N_2 at the flat terrace surface sites. It is interesting to note the rather large difference in spectra of the atomic adsorbate for the in plane p-orbitals pointing towards or parallel to the step. We can expect that the two atoms above and below the step will have different electronic structures. The latter could be important in order to understand the following hydrogenation step involving adsorbed nitrogen atoms.

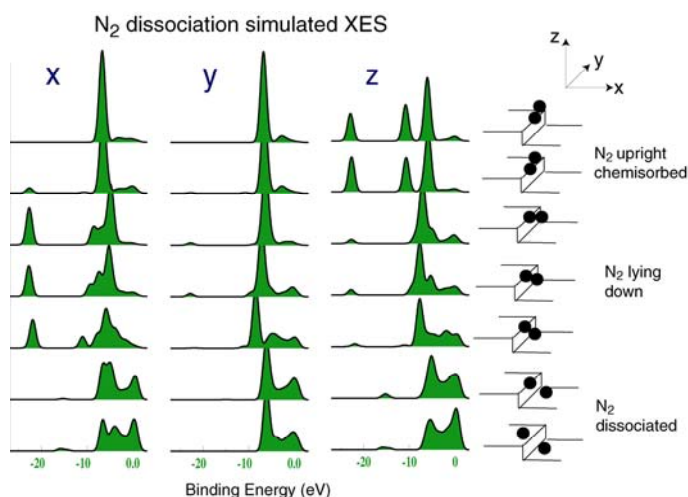


Figure 4 Simulated XES spectra for both nitrogen atoms in the dissociation of N_2 at steps. The spectra have been projected in the 3 high-symmetry directions.

Hydrogen bonding in aqueous systems

Water is the key compound for our existence on this planet and it is involved in nearly all biological, geological and chemical processes. Knowledge about the hydrogen-bonded (H-bond) network structure in water is essential for understanding its unusual chemical and physical properties. Recently the structure of first hydration shell of a water molecule in bulk liquid water was studied by probing its electronic structure using x-ray Absorption Spectroscopy (XAS) and x-ray Raman Scattering (XRS) [25]. From carefully designed experimental models as well as theoretical spectra simulations it could be concluded that the local surrounding of a water molecule in the liquid resembles that in the topmost layer of ice, i.e., it is characterized by a substantial number of broken H-bonds. The results deviate strongly from water models derived from molecular dynamics simulations which overestimate the amount of tetrahedral coordination in water [26,27].

The structure that is formed in the liquid phase is due to the dynamical motion of water molecules causing the H-bonds to break and reform on a fast time scale. Time-resolved pump-probe photoecho [28] and transient hole burning [29-32] experiments using infrared (IR) lasers indicate that there are 3 different distinct time scales of H-bond motion, <100 fs, 700-950 fs and 5-15 ps. Currently it is not fully understood what these timescales correspond to in terms of H-bonding. New experimental techniques will be extremely important to obtain additional information. We propose to use IR laser pump and FEL probe experiments on liquid water using ultrafast pulsed soft x-rays. The XAS spectrum of liquid water has a well defined pre-edge peak that does not exist in bulk ice and is related to broken H-bonds. We can follow the intensity of this spectral feature for different delay times between an IR laser and the FEL pulse using fluorescence detection in the x-ray spectrometer. By allowing different orientations of the IR laser pulse E-vector and x-ray pulse E-vector with respect to each other it will be possible to angle-resolve H-bond dynamics. We could distinguish if the breaking of the H-bonds after an O-H stretch vibration involves bending around the H-bond. Using similar techniques we can also detect OH groups in alcohols and NH groups in amino acids and peptides dissolved in water.

An understanding of electron-driven processes in aqueous systems and the subsequent radical chemistry of these processes is of great importance for a number of diverse fields such as waste remediation and environmental clean up, radiation processing, nuclear reactions and medical diagnosis and therapy. The initial stage of relaxation after x-ray absorption generates a primary photoelectron that relaxes, in part, by creating a cascade of secondary electrons. These secondary electrons become solvated by other water molecules [33] or induce dissociation of water molecules to OH species or other radicals. We propose to use an optical laser to promote solvated electrons in water and follow the time evolution of solvated electrons using FEL excited O K edge XES measurements. The solvated electrons should provide an additional spectral feature well above the valence band of water. We can also expect to detect OH species and other radicals through their unique spectral signatures. This experiment could become unique with an optical delay line where the FEL can act both as a pump and probe allowing for full synchronization.

Experimental Considerations

We propose to perform pump probe experiments using IR and optical lasers for initiating a transformation and FEL excited XES for probing the local electronic structure. The LCLS could be used to generate the core hole state prior to the X-ray decay process. A grazing incidence x-ray spectrometer will be used to detect the C, N and O K emission spectra. The lifetime of the core hole is less than 3-5 fs and the XES process can be regarded to be instantaneous for the dynamic range of interest. The energy resolution, $E/\Delta E$, required is of the order of 100-1000 depending on the experiment. In order to generate a well-defined core hole state without additional initial state satellites a resolution of 2-5 eV is satisfying. On the other hand, if a separation of chemically shifted core levels of the same elements is required a resolution around 0.5-1 eV is necessary. The experiments would be carried out by measuring spectra with different delay times between pump and probe pulses as performed today using ultra fast IR and optical lasers. We propose to use similar schemes to measure the time difference afterwards between pump and probe pulses that is currently being used at the SPPC. The experiments can be performed without monochromator since the XES process only requires intermediate band pass for the FEL pulse. This would provide an extremely high peak flux. The experience from the initial experiments will provide an estimate if peak power can be handled without to severe beam damage of the sample. The beam damage can be partly handled by continuous movement of the sample which has been successfully used in previous studies.

Estimated costs for experimental endstation 650k

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