ULTRAFAST COHERENT CONTROL AND CHARACTERIZATION OF SURFACE REACTIONS USING FELS

Hirohito Ogasawara, Dennis Nordlund, Anders Nilsson

Stanford Synchrotron Radiation Laboratory, P.O Box 20450, Stanford, CA 94309, USA

Abstract

The microscopic understanding of reactions at surfaces requires an in-depth knowledge of the dynamics of elementary processes on an ultrafast timescale. This can be accomplished using an ultrafast excitation to initiate a chemical reaction and then probe the progression of the reaction with an ultrashort x-ray pulse from the FEL. There is a great potential to use atom-specific spectroscopy involving core levels to probe the chemical nature, structure and bonding of species on surfaces. The ultrashort electron pulse obtained in the linear accelerator to feed the X-ray FEL can also be used for generation of coherent synchrotron radiation in the low energy THz regime to be used as a pump. This radiation has an energy close to the thermal excitations of low-energy vibrational modes of molecules on surfaces and phonons in substrates. The coherent THz radiation will be an electric field pulse with a certain direction that can collectively manipulate atoms or molecules on surfaces. In this respect a chemical reaction can be initiated by collective atomic motion along a specific reaction coordinate. If the coherent THz radiation is generated from the same source as the X-ray FEL radiation, full-time synchronization for pump-probe experiments will be possible. The combination of THz and X-ray spectroscopy could be a unique opportunity for FEL facilities to conduct ultrafast chemistry studies at surfaces.

REACTIONS AT SURFACES

Most of the important chemical reactions in nature and technology take place at surfaces and interfaces. There are a vast number of economically important processes which rely on these reactions, such as catalysis in chemical and energy production, the fabrication of computer chips, weathering and corrosion, the behavior of biomaterials and the fate of contaminants in the environment. One important example is the Haber-Bosch process that synthesizes ammonia from nitrogen and hydrogen on an iron or ruthenium catalyst.

$$N_2 + H_2 \rightarrow NH_3$$
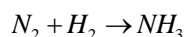
This process has been suggested to be the most important invention during the 20th century that has had the largest impact on mankind since it provides the basis for fertilizers and has revolutionized the agriculture industry. There is an underlying proposed reaction mechanism involving the dissociative chemisorption of dinitrogen followed by hydrogenation of atomic nitrogen in several steps on the catalyst surface.

$$\overset{Fe}{N_2 + H_2 \rightarrow N(ad) + H(ad) \rightarrow \rightarrow NH_3(ad) \rightarrow NH_3}$$
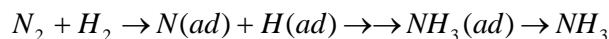
The verification of different reactive intermediates is important to understand the catalytic reaction mechanism. Since the reaction intermediates are present only for a short period of time and at extremely low concentrations, they are undetectable under steady-state conditions. In consequence, it has been extremely challenging to visualize the underlying reaction mechanism and dynamics of catalytic processes at surfaces.

At the surface of a catalyst, breaking/formation of chemical bonds takes place on a femtosecond time scale. Thus, in order to observe the dynamics of bond breaking/formation at surfaces, it is necessary to follow the reactions using ultrafast methods. Femtosecond visible laser pulses have been used to initiate a surface reaction with optical excitations at t=0 and the time evolution has subsequently been followed through products released into the gas phase [1-3]. The ultrafast visible laser pulse produces short lived and highly excited (hot) electrons and holes at the surface. The reaction can be driven either directly by these hot carriers or indirectly by the heat generated through phonon coupling of hot charged particles. The hot carrier mediated reactions are relevant in the area of photocatalysis. However, most of the catalytic processes of interest in many applications are driven by thermal excitations and not by optical
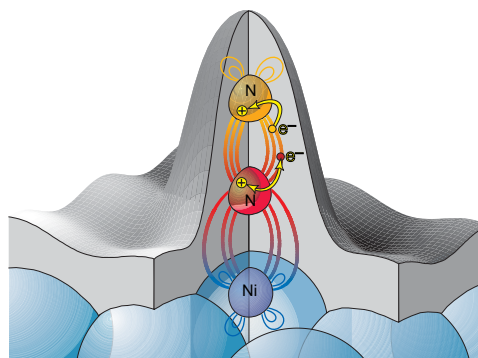

Figure 1: The local probing character of core level spectroscopies applied to N_2 adsorbed on Ni. The grey area represents the charge density outside the metal surface with a cut into the molecular adsorbate. A valence molecular orbital extended over all atomic centers and the two core orbitals on the nitrogen atoms are displayed. Electronic transitions between the core and valence electrons are indicated with arrows.
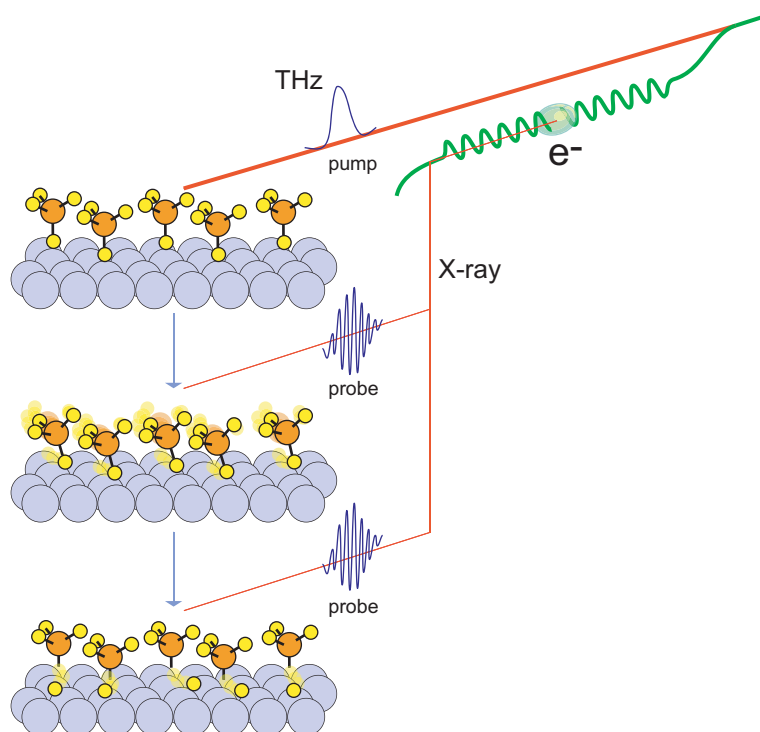
Figure 2: Schematic sketch for the THz pump and X-ray probe experiment. The molecular motion at surfaces to initiate the reaction is optically triggered by the ultrashort coherent THz radiation. Time evolution of the reaction is probed using an ultrashort X-ray pulse.

excitations. At the moment, there exists no direct way to thermally induce a catalytic reaction on an ultrafast timescale

With optical laser spectroscopy it is extremely difficult to probe species on surfaces since there is no direct separation of adsorbate signal from the substrate signal. Core level spectroscopies provide the direct way to evaluate chemical, electronic and geometric properties centered around one atomic site [4,5]. This is important in particular when investigating complex systems with many different atomic sites. Figure 1 shows a N_2 molecule adsorbed on a Ni surface in a perpendicular geometry. The grey zone represents the charge density of the valence electrons extending outside the metal surface and we have made a cut around the adsorbate to see more deeply into the molecule. Inside we can see one particular molecular orbital overlapping both the nitrogen and Ni atoms and the core electrons that are localized to one atom. The core-levels can be used to probe the valence electrons in two different ways. First, the binding energy of the core-level as determined through ionization is affected by the valence electrons. Since the two nitrogen atoms are in-equivalent, inner and outer atoms, the core-levels are shifted relative to each other. Secondly, we can have transitions between core and valence levels providing a direct probe of the valence electronic structure. Since the core electrons are localized to one atom we can in an atom-specific way study the valence electrons. We thus have a tool to look into the nature of the surface chemical bond by disentangling the contributions from the different atoms. Furthermore, the valence electrons are sensitive to the local geometry and we can expect that the core-levels will be chemically shifted depending on chemical nature, adsorption sites, distance to the surface and molecular orientations.

Here we propose a "dream experiment" to observe thermally induced catalytic reactions at surfaces in the ultrafast time domain in an atom-specific way. Using x-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Spectroscopy (XAS) and X-ray emission spectroscopy (XES) with an X-ray FEL, it is possible to probe the short lived reaction intermediate in an atom-specific manner. We can optically initiate and probe by x-rays thermally driven reactions at surfaces using coherent THz radiation from FEL. If the THz radiation is generated from the same source as the FEL radiation [6], full time synchronization for pump-probe experiments is possible as visualized in Fig. 2.

THZ EXCITATION AT SURFACES

What are thermal excitations at surfaces? Fig. 3 shows excitations at surfaces in the low energy regime. The black body radiation has a peak maximum in the THz regime at ambient temperature. In this regime there are excitations of phonons (Fig. 3a, substrate lattice vibration), frustrated vibrational motion of molecular adsorbates (Fig. 3b and 3c) and translational and rotational motion of molecular adsorbates in the physisorption or chemisorption potential well. These vibrations are excited thermally at ambient temperatures
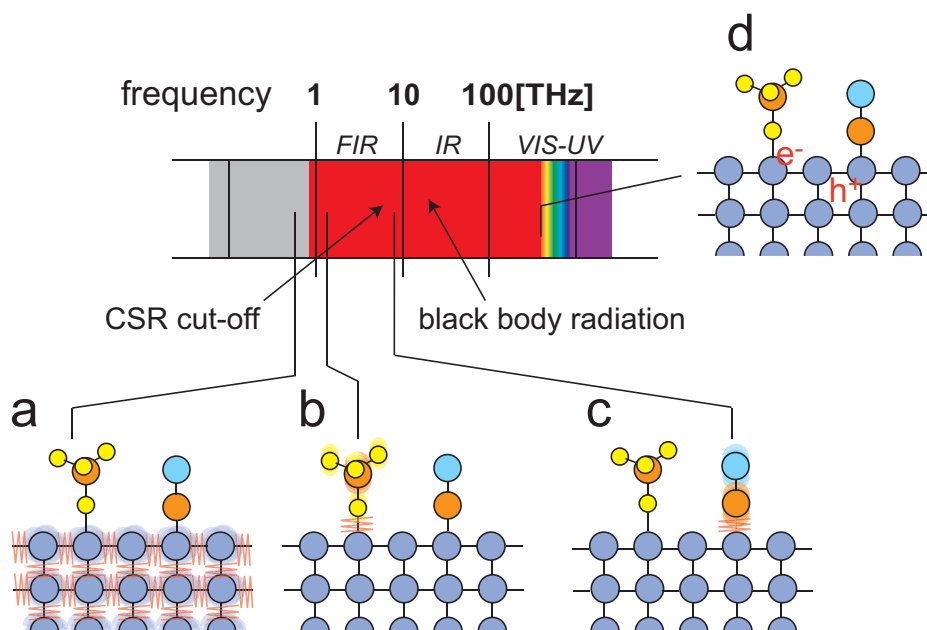
Figure 3: Excitation at surfaces. a) lattice vibration of the substrate (photon), b) frustrated vibrational motion of the physisorbed (weakly adsorbed) species, c) frustrated vibrational motion of the chemisorbed (strongly adsorbed) species, d) Visible ultrafast laser pulses predominantly produce electron-hole pairs in the substrate. The arrows indicate the maximum frequency of black body radiation at room temperature and typical coherent synchrotron radiation cut-off.

and play an important role in surface chemical reactions. When chemical bonds break/form during the reaction, the excitation of these vibrations is necessary to mediate the nuclear motion along the reaction coordinate.

The temperature-jump method is the most direct way to initiate thermally driven reactions at surfaces. It is important to increase the temperature on an ultrashort time scale comparable to the time of bond breaking/formation at surfaces. Using electron-hole pair excitation with ultrafast optical lasers, the rate of heating becomes very fast, sufficient enough to provide temperature jumps of a few 100 K in a few picoseconds (a typical fluence of a few mJ/cm2 [1,2]). With this approach it has been demonstrated that surface chemical reactions can be induced. The key process in the laser-induced temperature jump is the creation of hot electrons and holes that are not in thermal equilibrium with the lattice. These hot electrons and holes subsequently decay through excitations of phonons in the substrate and low frequency vibrational excitations on the adsorbates, increasing the temperature of the system. However, unwanted non-thermal reactions can be initiated prior to the decay of the hot charged carriers.

As an important alternative, intense ultra short coherent THz radiation generated by the electron beam in a FEL can be a suitable source for a temperature-jump. Assuming an electron pulse width of 100 fs, broadband radiation will be obtained with a high frequency cut-off at 10 THz. The radiation has a frequency close to black body radiation at room temperature (or a few 100 K above). Using this radiation, we can directly excite low-energy vibrational modes below 10 THz resulting in a temperature jump. There are no other excitations that generate any large amount of charged hot carriers. Since the atoms and molecules in gas phase do not have these excitations, optical access to the thermally induced phenomena is constrained to the surface.

COLLECTIVE CONTROL OF MOLECULES

One of the important developments in the last decade is direct control and manipulation of atoms and molecules. In studies of free molecules, the strong photon field generated in optical lasers has become a powerful tool to control atomic and molecular motions. In condensed matter studies, manipulation of individual molecules on solid surfaces is demonstrated by means of scanning tunneling microscopes (STM) [7]. These manipulations are achieved by orienting atoms or molecules through the application of a strong electric field ($1\text{-}3 \times 10^9$ V/m typically), see Fig. 4a.

The coherent and broadband character of THz radiation from FEL also generates a strong electric field. A quasi half cycle pulse character of the radiation corresponds to a strong ultrashort half-cycle unipolar pulse, followed by a weak extended tail of opposite polarity where the total integrated phase is zero. During the peak of the ultrashort half cycle pulse the atoms and molecules experience a mean field similar to the static field applied in scanning probe microscopies.
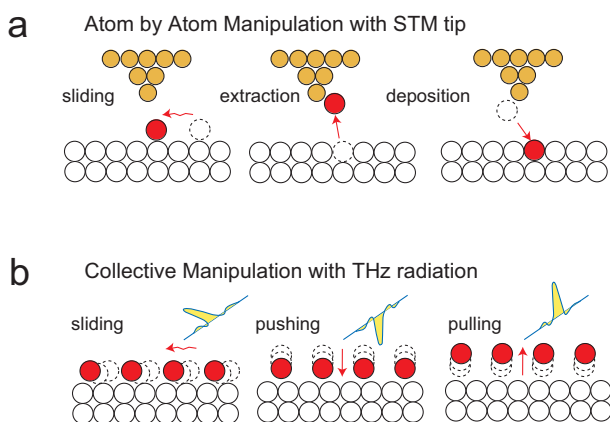
Figure 4: a) Atom by atom manipulation with a STM tip [8]. b) Collective manipulation with strong photon field with half cycle electric field pulse in different directions to the surface.

Can such a strong photon field influence the electronic structure of a molecule in order to manipulate its motion? Let us take a free hydrogen atom as an example. The electron is bound to the nuclei by a 5×10^{11} V/m electric force. This can be related to an energy density of 7×10^{12} W for a THz pulse focused in a 100μm x 100μm spot on the sample. By applying a photon field that has a comparable force to the internal molecular electric field, it is possible to deform the potential energy surface to align the molecule on the surface. Similar phenomena have been demonstrated by using ultra fast lasers in the optical regime [8]. Assuming that we generate the THz radiation from a 100 fs short electron bunch providing coherent radiation in the energy range of 10 to 300 cm^{-1}, an average radiation power of 2.3 mJ/cm^{-1}/pulse is required to match the electron binding force in the hydrogen atom.

When the duration of the photon pulse becomes shorter than the half period of a molecular vibrational period, it will be possible to excite vibrational motion impulsively (often denoted coherent phonon). The excitation of coherent phonons at surfaces was recently demonstrated using visible lasers [9]. The frequency of the excited motion will be the same as obtained through thermal excitation with a difference in terms of coherence. In the case of coherent excitations, all the molecules on the surface oscillate in phase (i.e. coherently), whereas for thermally excited vibrations the molecules oscillate randomly. A 100 fs THz pulse generated by the electron beam in a FEL can coherently excite lattice and molecular vibration frequencies of up to 330 cm^{-1}. From another point of view, the average bond length will change with time during a collective excitation, but does not during a thermal (random) excitation. In Fig 4b, we show how we can manipulate atoms at the surface using the THz pulse. At the surface, adsorbed molecules are aligned and positioned. We can align the direction of the electric pulse to impact the surface such that the direction of coherent motion to be initiated can be controlled. On the impact of the THz pulse, a collective change in the bond length along a desired direction can be initiated. Activation of nuclear motion along the reaction coordinate is essential to initiate the breaking/formation of chemical bonds. The change in the bond length on the impact of the THz pulse can initiate the chemical reaction collectively. The time evolution of the reaction can subsequently be probed with X-ray spectroscopies (Fig.2).

CONCLUSIONS AND OUTLOOK

It has been a "dream experiment" to visualize thermally initiated catalytic processes at surfaces in an atom-specific way. The x-ray FEL will allow us to trigger the thermal process at surfaces and follow the change in the electronic structure at each reaction step.

The breaking/formation of chemical bonds at catalyst surfaces can be depicted in a time domain using x-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Spectroscopy (XAS) and X-ray emission spectroscopy (XES) using the FEL x-ray radiation. The intense THz radiation from the same accelerator can optically access and stimulate the thermal motion of atoms and molecules at surfaces. Nuclear motion along the reaction coordinate is essential for breaking/formation of chemical bonds. Using a short THz pulse comparable to the vibrational period, a coherent nuclear motion along a desired coordinate can be initiated. It is possible to drag the nuclei along the reaction coordinate by time control of the nuclear coordinate and the average bond length. If the THz radiation is generated from the same source as the X-ray FEL radiation, full time-synchronization for pump-probe experiments will be possible. The combination of THz and X-ray spectroscopy offers a unique possibility for FEL facilities to study ultrafast chemistry at surfaces.

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