**LABORATORY DIRECTED RESEARCH AND DEVELOPMENT**

**PROPOSAL TITLE: ULTRAFAST SURFACE CHEMICAL TRANSFORMATION AT THE X-RAY LASER LCLS**

<table>
<thead>
<tr>
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<th>FRANK ABILD-PEDERSEN</th>
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<td><strong>Date:</strong></td>
<td>April 25&lt;sup&gt;th&lt;/sup&gt; 2014</td>
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<td><strong>Department/Division/ Directorate:</strong></td>
<td>SUNCAT, Photon Science</td>
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<tr>
<td><strong>Other Scientists:</strong></td>
<td>Staff Scientist Hirohito Ogasawara, SSRL SLAC National Accelerator Laboratory, MS 69, Menlo Park, CA 94025</td>
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<tr>
<td><strong>Proposal Term</strong></td>
<td>From: 10/2014</td>
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<tr>
<td></td>
<td>Through: 09/2016</td>
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<td></td>
<td>If continuation, indicate year (2&lt;sup&gt;nd&lt;/sup&gt;/3&lt;sup&gt;rd&lt;/sup&gt;):</td>
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</tbody>
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<table>
<thead>
<tr>
<th><strong>Business Manager:</strong></th>
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Abstract

The present proposal seeks to develop a methodology for understanding energy transfer processes of molecules/atoms on surfaces towards control of chemical reactivity. We will study oxidation and reduction of CO on a relevant metal surface using ultrafast soft x-ray spectroscopy at LCLS and ab initio calculations.

Summary of Proposal

Description of Project

Most conversion processes are performed via chemical reaction on a catalyst surface. The transition kinetics is greatly influenced by the dynamic motion of the molecules and the energy exchange process when the reaction is taking place. The present proposal aims at developing a methodology that can identify important signatures in energy transfer processes during a reaction, which in turn could provide ways to control chemical reactivity and selectivity. We will utilize ultrafast soft x-ray spectroscopy at LCLS to probe evolving transient species on a metal surface to identify the energy exchange processes: phonon-mediated and/or electron-mediated. We will also develop theoretical methods to simulate the reaction dynamics of transient species using the Born-Oppenheimer approximation with and without electronic friction. This research is well aligned with the DOE BES mission to understand, model, and control chemical reactivity and energy transfer processes in the gas phase, in solution, at interfaces, and on surfaces for energy-related applications, employing lessons from inorganic and biological systems.

Expected Results

The aim is to expand our understanding of surface chemical processes on the ultrafast timescale through a combined experimental/theoretical effort. We expect to develop new tools and methodologies based on our studies. The proposal has the potential to become a new program at SLAC that couples soft x-ray spectroscopy at LCLS and ab initio simulations to understand energy transfer processes in surface reactions.
Proposal Narrative

Purpose/Goals
The goal is to gain fundamental understanding of the energy exchange mechanism occurring between the surface of a solid and adsorbed reactants and reaction intermediates during a catalytic reaction on an ultrafast time scale using soft x-ray spectroscopy at LCLS combined with \textit{ab initio} calculations. Through this study, we will obtain insight into the energy transfer channels, which controls the dynamics of chemical reactions on catalyst surfaces.

Approach/Methods
Using ultrafast pump-probe soft x-ray spectroscopy at LCLS, we will probe the evolution and decay rate of transient species during a surface mediated chemical reaction. Aided by theoretical simulation, we will gain deeper insights into how the energy exchange occurs between the photon and electron systems in the catalyst and the nuclear motion of adsorbed reactant (Figure 1). Reactions to be considered include both oxidation and reduction of CO. Especially hydrogenation of CO is chosen to enhance the understanding of key elementary steps in fuel catalysis, such as methanol synthesis, methanation and Fisher-Tropsch synthesis.

Figure 1. Uniting experimental and theoretical efforts to understand and control reaction dynamics on the ultrafast time scale.

In heterogeneous catalysis a solid catalyst typically reacts with a molecule or reactant from either liquid or gas phase. The transfer of thermal energy through the surface of the catalyst to the reactant initiates the nuclear motion along the reaction coordinate. The way thermal energy is carried in the system is either through phonon-phonon coupling or via electron-phonon coupling. When the reactant is adsorbed on the surface, both the electron and phonon systems of the catalyst will couple independently to the nuclear motion of the adsorbed reactant through friction on different time scales.
For a reaction to occur, the metal/reactant system has to overcome the barrier along the reaction coordinate between two states. When the Boltzmann distributed phonon system couples, the energy of the phonons in the high-energy tail of the distribution will activate the nuclear motion of the reactant and if that energy is large enough the system will overcome the reaction barrier. In addition, on metal surfaces, a sudden temperature rise can also excite the electronic system. In this case, the reaction can be activated when high-energy electrons in the thermal Fermi–Dirac distribution are transferred to unoccupied states in the adsorbed reactant. Since, the frictional coupling constants along the reaction pathway govern the overall kinetics of converting the reactants into products, understanding the detail in this energy exchange is extremely important. The phonon- and electron–mediated energy exchange processes are essentially different and can at a given temperature provide different reaction dynamics. Unfortunately, these processes are not distinguishable under steady state conditions, where electrons and phonons are in equilibrium due to the electron-phonon frictional coupling.

In recent years, we have made a major effort to develop a scheme to probe transient species on a metal surface using LCLS. The first surface chemistry measurement at an x-ray laser with the goal to measure the simplest chemical reaction on a surface, namely CO desorption from the Ru(0001) surface were performed. It was demonstrated that our scheme successfully probed the emergence of a short-living precursor prior to the desorption process [1-4].

Dr. H. Ogasawara, played a key role in the success of these studies at LCLS and the present proposal in large part builds on this strong expertise in ultrafast soft x-ray spectroscopy and surface chemistry.

In this proposal, we will apply optical laser pumping and soft x-ray methods to probe chemical reactions between adsorbed CO and O on Ru. This system will be our benchmark towards studying the CO hydrogenation step.

Irradiating a solid catalyst by an ultrashort laser pulse, (<100 fs), leads to a rapid rise of the temperature of the electronic system. The electronic and phonon systems are out-of-equilibrium until the energy in the electronic system is dissipated to the phonon system via the frictional coupling. The coupling occurs within a time span of a few picoseconds (Figure 1). Using soft x-ray spectroscopy, we will identify chemical processes occurring through the electron-mediated channel by probing transient species that form in this time span. We will scan the delay of the soft x-ray probe pulse with respect to the optical laser excitation as well as the soft x-ray excitation energy. Chemical processes through the phonon-mediated channel will be probed by identifying transient species that evolve beyond this time span. We will also utilize the soft x-ray probe pulse as a post-ionization source for the mass spectrometer to
analyze products desorbed from the surface. By measuring the delay dependence of post ionization mass analysis, we obtain information about the time scale of product formation.

Theoretical calculations will be used to gain insight into the surface dynamics during the first picoseconds after the laser excitation. Initially, we will be focusing on dynamical effects that occur after the optical laser induced excitations have equilibrated between the electronic and phonon degrees of freedom in the surface region. That is, we are going to assume that the effect of the probe laser is to suddenly increase the temperature of the system. We will study the surface chemical effects of such a perturbation in two ways. First, we will perform \textit{ab-initio} molecular dynamics simulations [5] of the first picosecond of the system after a sudden increase in temperature. We will identify reaction paths and possible intermediates that have lifetimes in a range, which makes them observable experimentally (in the ps timeframe). Secondly, we will map out the free energy landscape and the changes in the electronic densities along the reaction pathways (as determined e.g. from the molecular dynamics calculations). Folding these with the thermal distribution of states and comparing to experimental spectra will provide an average temperature of the equilibrated system.

In addition, we will study the dynamics beyond the Born-Oppenheimer approximation. This is particularly important within the first couple of picoseconds after pumping the system with the optical laser. During this initial period, the hot electrons generated from the optical excitation can scatter into surface species and induce reaction channels that are not accessible from thermally induced excitations. To describe such excitations we will use the \textit{Ab Initio} Molecular Dynamics method with electronic friction [6]. This approach is well known, but the lead PI and his colleagues have recently implemented it within the framework of the Atomic Simulation Environment (ASE) and Quantum ESPRESSO. At each MD step, a friction force and a thermal fluctuation force will be calculated on-the-fly and added to the force obtained from the potential energy surface. This allows us to unambiguously identify the role of the hot electrons on the reaction dynamics and this understanding will aid in the design of novel catalytic processes with enhanced selectivity and efficiency.

**Specific Location of Work**

The theoretical work will be performed at SUNCAT, SLAC and all calculations will run on the SUNCAT cluster located at SLAC in B50. Experiments will be conducted at the LCLS at SLAC.
Anticipated Outcomes/Results

We expect to develop this LDRD into a strong experimental/theoretical collaboration. We aim to understand how the energy exchange occurs between the photon and electron systems in the catalyst and the nuclear motion of surface reactants. The results obtained under this proposal will have a high impact on the field of surface science and a successful demonstration of the scientific potential of LCLS in this area coupled with theory will establish a basis for further grant applications to DOE BES (chemical science).
VITA (Lead Scientist)

Frank Abild-Pedersen

Contact Information

SUNCAT Center for Interface Science and Catalysis, Photon Science Division, SLAC National Accelerator Laboratory, MS 31, Menlo Park, CA 94025
Email: abild@slac.stanford.edu

Education

Copenhagen University  B.S.  1998  Physics
Copenhagen University  M.S.  2001  Physics
Technical University of Denmark Ph.D.  2005  Physics

Appointments

2005-2006  Post Doctoral Research Fellow, Technical University of Denmark
2006-2007  Project Manager, Technical University of Denmark
2007-2009  CTO (part time), Computational Materials Design ApS, Denmark
2007-2010  Staff Scientist (part time), Technical University of Denmark
2010-      Staff Scientist, SLAC

Research

In my research group which at present consists of 2 postdoctoral associates and 3 graduate students we are mainly interested in understanding the interplay between the complex electronic structure at the catalysts surface and how that affects the chemistry that can take place. We have developed ways of reducing the complexity of the reaction network at the surface such that information about the chemistry can be obtained without an overwhelming computational effort and we are constantly developing new methods and models to describe important surface aspects.
Literature Cited


Budget Explanation

The budget period spans two years, 10/01/2014 through 09/30/2016. The budget assumes 3.5% escalation labor costs in year 2, and 2.5% per year non-labor escalation.

A. Senior Personnel:

Frank Abild-Pedersen: Principal Investigator and staff scientist of SLAC National Accelerator Laboratory, is an expert in electronic structure theory calculations. As the PI, Abild-Pedersen will ensure that research goals are met in a timely manner, with scientific integrity, and completed within budgeted amounts. The PI will ensure that project activities and expenditures are in compliance with Stanford University and Department of Energy. Dr. Abild-Pedersen will devote 1% (0.12 months) of his effort to this project. Co-PI Hirohito Ogasawara who is an expert in ultrafast soft x-ray spectroscopy will be supported at 1% (0.12 months) salary per year.

B. Other Personnel:

It also includes salary for one half post doctoral scholar for performing experiments on soft x-ray spectroscopy and one half post doctoral scholar to do theoretical calculations at SUNCAT/SLAC.

Fringe Benefits:

Fringe benefit rates are negotiated between Stanford and the Office of Naval Research (ONR), which is the cognizant federal agency overseeing Stanford.

Fringe benefit rates for FY 13
Regular Benefits-eligible Employees 30.8%
Post-Doctoral Research Affiliates 28.3%

C. Travel: Domestic travel covers travel to meetings such as the American Chemical Society meeting, American Institute of Chemical Engineers, and the American Physical Society meeting.

D. Trainee Support costs: None

E. Other Direct Costs:

Experiment M&S is estimated to be $30,534 over the two year period.
For purchasing sample holder, quadrupole mass analyzer, chemicals and gases.

Theory M&S is estimated to be $6,000 over the two year period. The M&S is for purchasing notebook computers, tablet computers and miscellaneous computer supplies for the postdoctoral scholar to perform the tasks outlined in the proposal.

F. **Total direct costs:**

<table>
<thead>
<tr>
<th>Year</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year One</td>
<td>$97,130</td>
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<tr>
<td>Year Two</td>
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<td><strong>Total</strong></td>
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G. **Indirect costs:**

Current SLAC indirect rates for activities funded are indicated below:

<table>
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<th>Category</th>
<th>Rate</th>
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<tr>
<td>Labor and travel</td>
<td>53%</td>
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<tr>
<td>Procurements</td>
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There is a 9% Program Support rate applied to labor.

Summary of indirect costs:

<table>
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<th>Amount</th>
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<tr>
<td>Year One</td>
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<tr>
<td>Year Two</td>
<td>$54,263</td>
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<td><strong>Total</strong></td>
<td><strong>$107,134</strong></td>
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H. **Total Direct and Indirect Costs:**

<table>
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<th>Amount</th>
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<tbody>
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<td>Year 1</td>
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<tr>
<td>Year 2</td>
<td>$150,000</td>
</tr>
<tr>
<td><strong>Total Costs</strong></td>
<td><strong>$300,000</strong></td>
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Approvals

Signing indicates you have reviewed the contents of this proposal, and support its submission to the LDRD process. Signatures are required.

X
Associate Director, Chemical Science Division

X
Director, Chemical Science Division

X
Associate Lab Director, Photon Science Directorate