

Can Energetic Terahertz Pulses Initiate Surface Catalytic Reactions on the Picosecond Time Scale?

Bruce D. Patterson^{*a}, Jacinto Sa^a, Anastasija Ichsanow^{ab}, Christoph P. Hauri^a, Carlo Vicario^a, Clemens Ruchert^a, Izabela Czekaja^a, Regula Gehrig^a, Hans C. Sigg^a, Jeroen A. van Bokhoven^{ab}, Bill Pedrini^a, and Rafael Abela^a

Abstract: In preparation for picosecond pump-probe experiments at the SwissFEL X-ray laser facility, the feasibility of collectively initiating surface chemical reactions using energetic pulses of terahertz radiation is being tested.

Keywords: Surface catalysis · SwissFEL · X-ray free electron Laser (XFEL)

Introduction

The importance of surface catalysis for modern society is immense and growing, as is evident from the demand for catalytic systems with improved efficiency, selectivity and environmental compatibility. Characteristic spatial and temporal scales in surface catalysis are dictated by the length of a chemical bond (0.1 nm) and by a typical molecular vibration period (0.01 ps). These match well the photon wavelength and pulse duration of X-ray Free Electron Lasers (XFELs), a prime example of which, the SwissFEL,^[1] is planned to go into operation at the Paul Scherrer Institute, in Würenlingen/Villigen, Switzerland, in 2017.

Pump-probe experiments at XFELs will, with the use of energy-dispersive detectors, allow single-shot measurements of near-edge X-ray absorption spectra, which will yield time-resolved information on the electronic and geometrical structure of short-lived intermediate states during a catalytic reaction.^[2] The trigger pulse for such studies should be non-ionizing, of sub-picosecond duration and capable of manipulating the local chemical environ-

ment. A candidate for such a trigger is an energetic single or few-cycle electromagnetic pulse in the terahertz (THz) frequency region. The inclusion of a synchronized source of THz pump pulses is envisaged for the SwissFEL project. In preparation for these developments, we are undertaking a demonstration, on model systems, of the effectiveness of THz pulses to initiate surface catalytic reactions.

THz and IR Initiation of Chemistry

Various mechanisms have been discussed for the initiation of surface chemistry using THz and IR pulses. Ogasawara *et al.*^[3] have suggested that such initiation can proceed *via* a) local heating, b) resonant excitation of molecular motions or c) collective displacement of polar species. Redlich *et al.*^[4] have demonstrated the IR-induced desorption of adsorbed N₂O from NaCl (100) when an energetic pulse is resonant with an IR-active mode of the molecule. Using multiple-photon IR absorption, Hamilton *et al.*^[5] have triggered a reconfiguration of N₂O adsorbed on a Rh cluster. Experimental and theoretical studies of bio-enzymes by Masgrau *et al.*^[6] indicate that proton-tunneling reactions are promoted by short-range protein motions in the THz frequency range. Finally, avoided-level crossings induced by the Stark effect in a time-dependent electric field have been predicted by Murgida *et al.*^[7] to control the LiNC ↔ LiCN isomerization reaction in the gas phase.

THz-induced Dissociative Adsorption

We consider as a model system for catalytic initiation by a THz pulse the

dissociative adsorption of a simple molecule on a reactive surface, such as CO on a transition metal. At room temperature, CO is known^[8] to adsorb associatively, as a molecule, on the surface of transition metals to the right of Co, Ru and Re in rows 4, 5 and 6 of the periodic table, respectively, and to undergo dissociative adsorption on metals to the left. The adsorbed molecule is generally situated perpendicular to the surface, with its C-atom bound atop a single metal atom.^[9] Two characteristic vibrations of the adsorbed molecule^[10] are the CO stretch and the hindered-translation bend modes, at frequencies of approximately 2000 and 80 cm⁻¹, respectively. The first corresponds to an IR wavelength of 5 μm and the second to a frequency of 2.5 THz.

The adsorbed CO has a dipole moment; on the Ni (111) surface, work function measurements^[11] yield a value of 0.28 Debye, corresponding to 0.052 elementary charges separated by the 1.13 Å CO bond distance. Hence, for a metal surface just to the right of the associative/dissociative-adsorption boundary, *e.g.* Rh, an oscillatory electric field applied parallel to the surface and which is resonant with the hindered-translation mode may excite angular excursions and C–O bond stretching, leading to adsorptive dissociation (Fig. 1). (Note: local screening of the THz field by the metal surface may be avoided by using an ultrathin metallic layer on an insulating substrate.) Semi-empirical calculations for CO adsorbed on Rh (111) predict^[12] that the transition state along the absorptive-dissociation reaction pathway is reached at a 70° tilt and a 60% stretch. One may expect the dipole-THz field interaction, when resonant with the hindered-translation mode, to drive a lowering of the dissociation barrier along a direction parallel to the THz polarization.

*Correspondence: Prof. B. D. Patterson^a

Tel.: +41 56 310 4524

E-mail: bruce.patterson@psi.ch

^aPaul Scherrer Institut

CH-5232 Villigen

^bInstitute for Chemical and Bioengineering

ETH Zürich

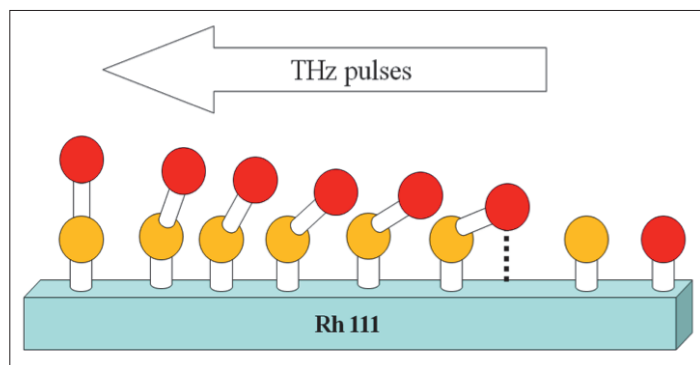


Fig. 1. A schematic representation of THz-induced dissociative absorption of CO (yellow = C, red = O) on a Rh surface.

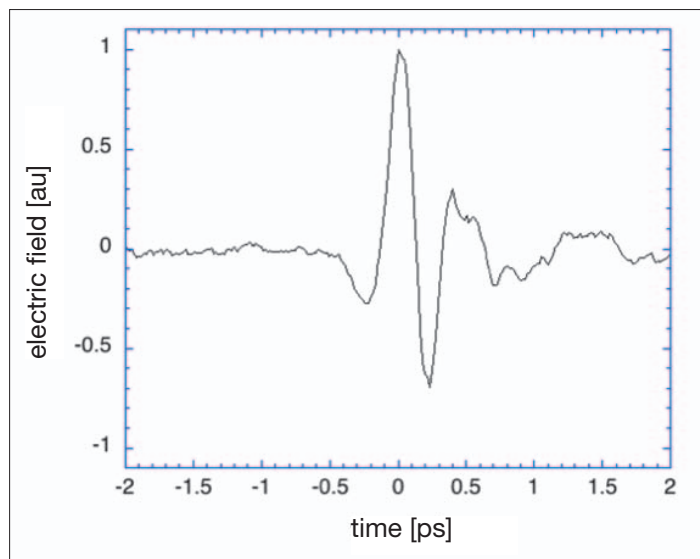


Fig. 2. An electro-optic sampling trace of the THz signal from the PSI optical rectification setup.

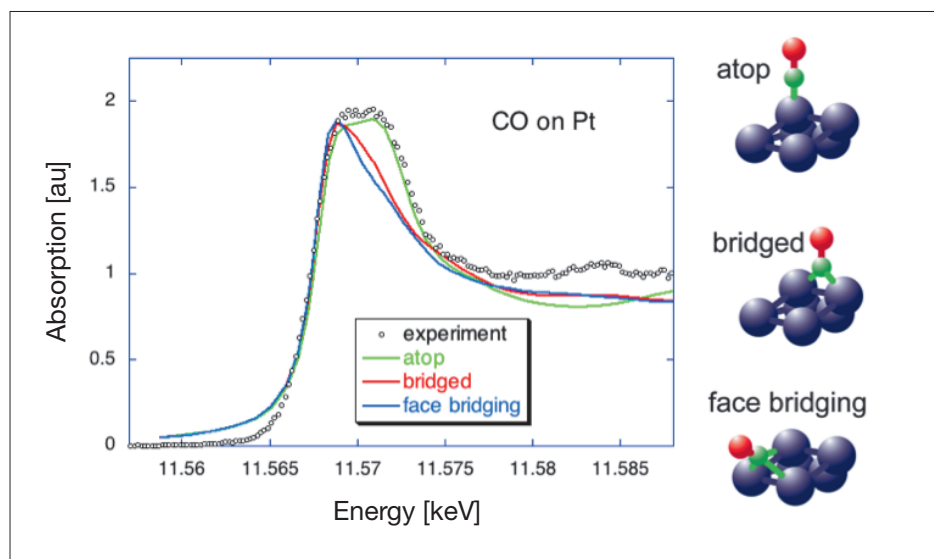


Fig. 3. A (static) near-edge X-ray absorption spectrum taken at the Pt edge at a synchrotron.^[18] From the good match with theory, it is clear that the adsorbed CO is situated in the *atop* position.

The influence on adsorptive dissociation of a *static* electric field applied *perpendicular* to the surface has been investigated experimentally and theoretically for the case of NO on Pt (111). Hückel calculations^[13] yield a reversed dipole moment on atop-bound NO, *i.e.* with the O end *positively* charged. And with a field of 4 V/nm, electron redistribution among the molecular orbitals causes a dramatic

reduction in the dissociation barrier. This is in accordance with the E-field induced dissociation observed^[14] using pulsed field desorption mass spectrometry.

In preparation for an experiment at the XFEL, we plan to observe the effect of resonant excitation of the 2.5 THz hindered-translation mode by monitoring the frequency of the 5 μm CO stretch mode in a time-resolved THz-pump/IR-probe

measurement. Our preliminary DFT calculations, with non-optimized atomic positions, of adsorbed CO on a (111) Rh₁₀ cluster indicate a 5% softening of the CO stretch frequency upon rotation of the molecular axis by 90° with respect to the surface normal.

Laser-based THz Generation

Our source of energetic THz pulses is the laser-based optical rectification setup at the PSI-SwissFEL test injector. Incident pump pulses (0.7 mJ, 80 fs) at 1.3 μm wavelength are produced by an optical parametric amplifier, and optical rectification to THz frequencies is performed in the organic crystal DAST.^[15] After focusing, the setup is presently capable of producing few cycle THz pulses (Fig. 2) with a peak electric field in excess of 0.3 MV/cm (0.03 V/nm). Significantly stronger fields are anticipated with the use of an organic crystal with improved conversion efficiency.^[16] We are also pursuing the possibility of employing microfabricated antenna structures to dramatically increase the field strength; a 100-fold field enhancement at 1 THz has been observed within a 70 nm wide slit in a 60 nm thick gold film.^[17]

THz Pump/X-ray Probe

When the SwissFEL becomes operational, THz-pump/XFEL-probe experiments will be performed, in which a surface catalytic reaction will be initiated with a THz pulse and the subsequent time-dependent intermediate states will be probed with synchronized XFEL measurements of near-edge X-ray absorption spectroscopy^[2,18] (Fig. 3). The use of wavelength-dispersive X-ray detectors^[19] will allow the measurement of the entire near-edge absorption spectrum in a single SwissFEL shot, lasting only 20 fs. When operating in the so-called *overchirped broadband* mode,^[1] the SwissFEL will have a relative bandwidth of 1.5%, corresponding to ± 90 eV at the 11.57 keV L₃-edge of platinum.

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