

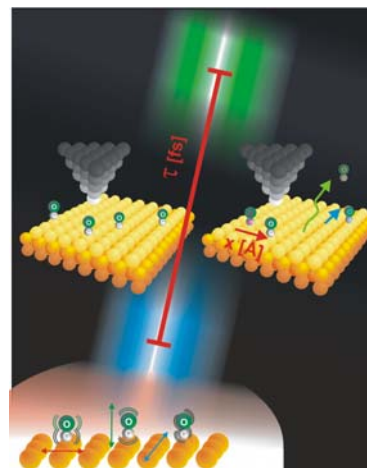
REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 10/07/11		2. REPORT TYPE Final		3. DATES COVERED (From - To) 08/01/2008-09/30/2011		
4. TITLE AND SUBTITLE Surface Reactions following Ultra fast Substrate Excitation: A Path towards Atomic Scale Resolution of High-temperature Reactions at Metal Surfaces				5a. CONTRACT NUMBER FA9550-08-1-0401		
				5b. GRANT NUMBER		
				5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Ludwig Bartels				5d. PROJECT NUMBER		
				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of California, Riverside, CA 92521				8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 875 N. Randolph St. Arlington, VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR		
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-OSR-VA-TR-2012-0876		
12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution A						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT This project aims at elucidating the dynamics of small molecules at metal surfaces at the atomic scale in a high-temperature environment. Scanning tunneling microscopy (STM) is used to image the location and chemical identity of molecular species at a copper surface. Because STM has an image acquisition time on the seconds to minutes scale, the sample generally needs to be cooled down to keep molecular adsorbates in place during imaging. A slight increase in temperature then allows the study of diffusion, but the adsorbates generally diffuse so fast that they cannot be studied anymore before other surface processes get into play. This leaves only molecular diffusion to be studied and it does not allow a realistic vista on what may occur at surfaces at elevated temperatures. To circumvent this obstacle, we use energetic femtosecond laser pulses to heat the top atomic layers of the substrate, thereby creating temperature transients with hundreds of Kelvin amplitude but only picoseconds duration. We also use pores in adsorbate films to confine reactants.						
15. SUBJECT TERMS Research in Surface Chemistry						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT uu	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Ludwig Bartels	
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (Include area code) 9518272041	

Towards the Investigation of Molecular Dynamics at a Metal Surface Following Femtosecond Energetic Irradiation

Award No: FA9550-08-1-0401

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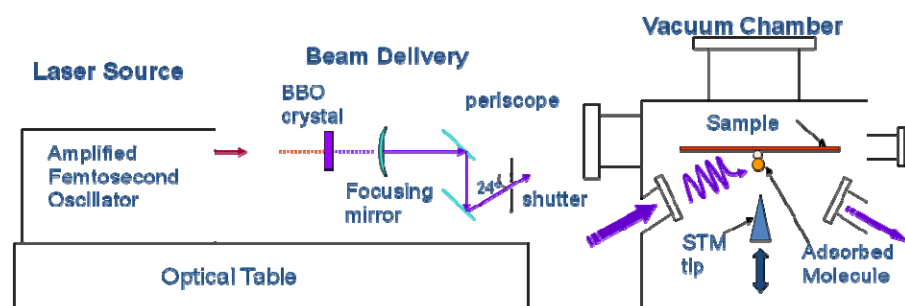
This project aimed at elucidating the dynamics of small molecules at metal surfaces at the atomic scale in a high-temperature environment. Scanning tunneling microscopy (STM) was used to image the location and chemical identity of molecular species at a copper surface. Because STM has an image acquisition time on the seconds to minutes scale, the sample generally needs to be cooled down to keep molecular adsorbates in place during imaging. A slight increase in temperature then allows the study of diffusion, but the adsorbates generally diffuse so fast that they cannot be studied anymore before other surface processes get into play. This leaves only molecular diffusion to be studied and it does not



Schematic representation of the anticipated experiments and temperature transient of substrate electrons, phonons and adsorbates following ultrafast substrate irradiation.

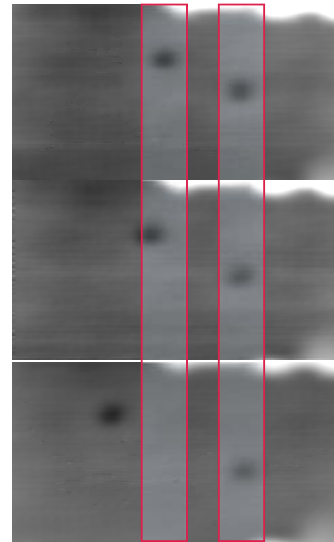
allow a realistic vista on what may occur at surfaces at elevated temperatures. To circumvent this obstacle, we use energetic femtosecond laser pulses to heat the top atomic layers of the substrate, thereby creating temperature transients with hundreds of Kelvin amplitude but only picoseconds duration [1]. Acquiring images of the same set of molecules before and after irradiation generates snapshots of surface dynamics only a few picoseconds in reaction time apart. Using corrals created from anthraquinone, we locally confine adsorbates

To this end a system combining a powerful femtosecond laser system and a low temperature scanning tunneling microscope has been assembled.

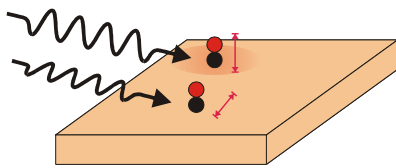


Experimental setup consisting of laser system on optical table (left) and ultra-high vacuum chamber contain scanning tunneling microscope (right)

Our measurements addressed the diffusion of carbon monoxide molecules on the Cu(111) surface. Working at 20K, i.e. well below the native diffusion threshold of 35K, we observe ample diffusion of adsorbed species following irradiation with 3.4mJ/cm^2 at 400nm and 100fs. To correlate the measurements with the energy redistribution in the surface, we currently acquire a dataset, in which we compare the threshold to obtain molecular motion between s and p polarization of the incident irradiation. Interaction of the metal surface with irradiation of different polarization planes is fundamentally different: while the field of an electromagnetic wave oscillating plane parallel to the surface can be compensated by rearrangement of the electrons in the surface plane leading to reflection, the same is not possible for a wave polarized perpendicular to the surface. Rather, such a wave is aligned with the molecular axis and can, potentially, couple more directly and athermally to the molecule.



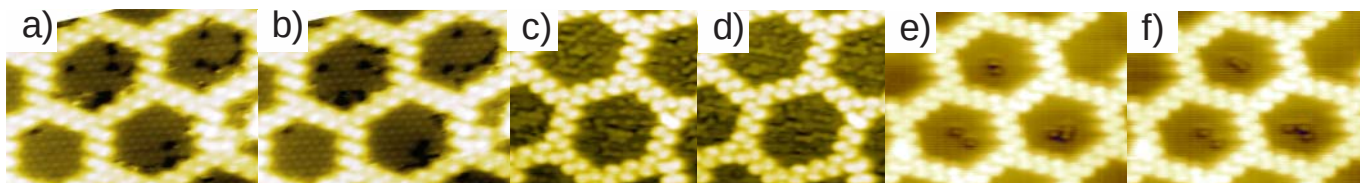
Diffusion of CO molecules on Cu(111) following irradiation with 100fs, 3.4mJ/cm^2 , 400nm pulses



Our measurements show that the amount of molecular excitation is not increased for p polarization, thus affirming that the molecular motion we induce in our experiments is indeed a thermal effect and validating that the methods is

suitable to provide us a vista on the high-temperature molecular dynamics at the focus of this proposal.

To facilitate tracking of the molecules addressed, we developed a technique that involves molecular corrals formed by anthraquinone adsorbates on Cu(111)[2]. The pores of this network are capable of confining CO molecules within a very small area, thus preventing that they run across extended terraces. This allows following tens of events for one molecule[3].



Different number (a,b: ~60; c,d: ~20; e,f: 2-3) of CO molecules confined in anthraquinone networks and their diffusion.

References:

1. Bartels, L., et al., *Real-space observation of molecular motion induced by femtosecond laser pulses*. Science, 2004. **305**(5684): p. 648-651.
2. Pawin, G., et al., *A homomolecular porous network at a Cu(111) surface*. Science, 2006. **313**(5789): p. 961-962.
3. Cheng, Z., et al., *The Power of Confinement: Adsorbate Dynamics on Nanometer-Scale Exposed Facets*. NANO LETTERS, 2010. **10**: p. 1022018