**Optically Driven Surface Reactions:
Laser Probes of Surface Dynamics**

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APR 17 1998
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(DOE I.A. Number DE-AI02-93ER14330)

Final Report
March 11, 1997

Overview

Our efforts in the past three and a half years have been directed towards providing the ground work for applying REMPI detection to the dynamics of surface oxidation and desorption reactions. Our initial efforts addressed the oxidation of carbon films that had been prepared on metal supports. The photolysis of adsorbed N_2O was chosen as the initial oxygen atom source. However, a number of alternative O atom precursors were also evaluated. Results from Auger electron spectroscopy (AES), temperature programmed desorption (TPD), and state-resolved studies of the photochemistry of N_2O , NO_2 , or O_2 coadsorbed with carbon on Pt(111) have been obtained. In the last eighteen months, we have focused on a stringent test of current theories of femtosecond laser-induced desorption of CO/Cu(100). The results indicate that an electronic friction model is sufficient to account for essentially all of the results in this system, indicating that a predictive tool for femtosecond laser-induced surface chemistry may be in hand.

OXIDATION OF CARBON SURFACE LAYERS:

Experimental

Three different techniques were used to generate carbon films on the Pt(111) crystal. In method #1, the Pt(111) crystal at 100 K was exposed to a saturation dose of ethylene followed by annealing the surface to 800 K (for 5 min.) or 1100 K (for 2 min.) to dehydrogenate the adsorbed layer. This results in the formation of carbidic and graphitic carbon islands, respectively.¹ In attempts to deposit at least a full monolayer of carbon on the surface, method #2 consisted of heating the Pt(111) crystal to different temperatures (500 and 1100 K) in ethylene flowing from the capillary array doser. Finally, using method #3, thicker films of carbon were created by exposing the Pt(111) crystal to 10^{-5} - 10^{-4} Torr backfills of C_2H_4 and using an ion gun to sputter deposit carbon onto the crystal.² In each case the amount of carbon deposited on the surface was monitored with AES. From the ratio of the AES peaks of C at 272 eV to that of Pt at 237 eV (I_C/I_{Pt}) the carbon coverage for samples prepared by method #1 was estimated³ to be 0.15 monolayer. Method #2 resulted in carbon coverages ranging from 0.65 to > 1.0 ML, while the higher coverages for method #3 were not quantified.

In one set of experiments, a carbon overlayer was irradiated with the filtered output of a xenon arc lamp, and I_C/I_{Pt} was recorded as a function of sample treatment. Alternatively, the sample could be irradiated with either the 213 or 266 nm output of a Nd^{+3} :YAG laser. The desorption laser

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pulse energy resulted in a calculated peak surface temperature jump of 30 K. The generation of photodesorbed CO was monitored via resonance-enhanced (2+1) multiphoton ionization (REMPI).

RESULTS - Thermal Oxidation

Previous studies of N_2O adsorption on Pt(111) identified two distinct thermal desorption peaks, one at 97-102 K attributed to the first monolayer, and a second at 75-87 K from multilayers of N_2O .⁴ The integrated intensities of both the thermal desorption features seen in this laboratory as a function of N_2O dose times show a small break in the N_2O uptake suggesting the completion of the first monolayer. Using the same dosing conditions as for the carbon-free substrate, the thermal desorption of N_2O from a carbon-covered platinum surface revealed shifts in the desorption features plus a 35% decrease in the integrated intensity. This suggests that N_2O has a lower sticking probability on the carbon-covered surface at 95 K.

The adsorption of NO_2 on both Pt(111)⁵ and graphite⁶ surfaces has been previously studied at low temperatures (≈ 100 K). Our measurements of the thermal desorption for NO_2 on clean Pt(111) were quite similar to previous studies.⁵ A low coverage desorption peak is evident at 320 K and a high coverage, multilayer feature appears with a temperature onset of ≈ 120 K for both $m/e = 30$ (NO^+) and $m/e = 46$ (NO_2^+). The peak shapes for these two masses are different for the 320 K feature possibly indicating the presence of NO on the sample. There are subtle differences for the thermal desorption of NO_2 from carbon-covered Pt(111). In this case, the low coverage feature at 320 K only appears at $m/e = 30$ and a peak at 100 K appears at high coverages. The lack of signal at $m/e = 46$ suggests the presence of NO and/or the complete thermal decomposition of NO_2 for the carbon-covered surface.

The O_2 studies were performed with submonolayer coverages of carbon (method #1) on the Pt sample since the reported desorption temperature of O_2 from graphite⁷ is much lower than the capabilities of our sample mount. Below 150 K, oxygen is known to adsorb on Pt(111) producing a molecular chemisorbed species with a 0.44 ML saturation coverage.⁸ TPD following O_2 exposure on the clean surface matches the results previously reported: O_2 dissociation competes with desorption at ≈ 150 K and O atom recombinative desorption occurs around ≈ 750 K.⁸ For the carbon treated surface, there is a 70% decrease in the integrated area of the low temperature feature and no evidence for the high temperature desorption corresponding to a 0.15 ML O_2 coverage for the carbon treated surface.

RESULTS - Photoinduced Oxidation

As an initial test, the irradiation of O_2 on Pt(111) with the arc lamp was used as a diagnostic to ensure that photolytic changes could, in fact, be induced. The resultant O_2 desorption profile agrees with previous reports that 240 - 546 nm irradiation of $\text{O}_2/\text{Pt}(111)$ decreases the O_2 desorption signal at 150 K while increasing the recombinative O_2 desorption at 750 K.⁹ Irradiation also caused both peaks to broaden and shift to lower temperatures. AES results were analyzed for a carbon-covered Pt surface prepared by method #1 and #2 for adsorbed O_2 and NO_2 . Although a significant reduction of the $I_{\text{C}}/I_{\text{Pt}}$ was noted for the $\text{NO}_2/\text{C}/\text{Pt}(111)$ system prepared using method #1 after thermal annealing, *no photo-enhanced* depletion of the carbon layer beyond that seen thermally was observed within the uncertainty of these measurements.

REMPI of CO was used to monitor the photodesorption of CO from three C/Pt(111) preparations using a variety of adsorbates including: N_2O , NO_2 , O_2 , CO and NO. Attempts to detect CO desorbing in anticipated internal states ($v=0$ or 1, $0 \leq J < 20$, and with reasonable translational

energies) were unsuccessful. It is interesting to note, however, for the $\text{NO}_2/\text{C}/\text{Pt}(111)$ system, that using either 266 or 213 nm irradiation of the sample, a signal at $m/e=30$ was observed with an ion intensity that was relatively insensitive to the probe-laser wavelength. This was attributed to non-resonant ionization of the photodesorbed species, presumably NO_2 or NO to give NO^+ . There may be two different desorption features in the $m/e = 30$ time-of-flight distribution for $\text{NO}_2/\text{C}/\text{Pt}(111)$ with the carbon layer formed by method #1. The fast feature has a flux-weighted mean kinetic energy of $\langle KE \rangle / 2k_B = 1700 \pm 500$ K. The slow signal is obtained independent of the presence of the desorption laser, therefore it is unlikely that the slow signal originates from a photodesorption process. Since the $m/e=30$ ions are generated through non-resonant ionization, the internal energy distributions could not be characterized.

DISCUSSION

From the uncertainties in the AES results a detectable change in the carbon layer requires approximately a 20% change in the AES I_C/I_{Pt} signal. This corresponds to an ≈ 0.01 ML change in the carbon coverage. For the $\text{O}_2/\text{C}/\text{Pt}(111)$ sample, an upper limit for the reaction probability can be estimated by assuming that the entire 0.15 ML of O_2 dissociates upon irradiation with the arc lamp. The O atom reaction probability to remove a carbon atom from the graphitic islands is less than 3×10^{-2} . Making similar assumptions for a 1 ML coverage of NO_2 on $\text{C}/\text{Pt}(111)$ indicates that the photoinitiated reaction probability is less than 10^{-2} .

The REMPI studies monitored desorbed CO as an alternative to probing changes in the carbon layer. Although REMPI is a state-specific detection technique, it is limited by the fact that only the CO $v=0$ or 1 states can be detected by the B-state (2+1) scheme. With 1×10^{-7} Torr CO in the chamber, calibration of the detector demonstrated that the apparatus has a CO detection sensitivity of about 1×10^{-9} Torr or 3×10^7 molecules/cm³. Assuming that the cross section for oxygen atom production is 3×10^{-19} cm²,⁹ our experimental conditions should generate $\approx 2 \times 10^8$ O atoms at the surface. If every O atom leads to CO ejection with a $\cos \Theta$ distribution, the corresponding product density in the ionization region would be 2×10^8 molecules/cm³.

The absence of photolytic oxidation of these carbon surfaces is intriguing. Based on other work in the literature, one would anticipate that photo-induced channels should be detectable. One factor that may have limited the ability to stimulate this reaction optically is the number of C-C and C-Pt bonds that need to be broken. The optically driven surface reactions that lead to the formation of new bonds in the desorbing species typically have been restricted to adlayers where the two components are well mixed and do not form stable islands. The segregation of the carbon from the oxygen precursors appears to impede the anticipated reactivity. To establish more stringent yield limits, a state integrating probe is essential, as the state-selective nature of the REMPI approach argues against its application to systems where the desorbed species populate a large number of different quantum states.

FEMTOSECOND LASER-INDUCED DESORPTION OF CO/Cu(100)

Photo-induced desorption from metal surfaces has received considerable attention over the past ten years.¹⁰ For most of the systems that have been studied, the processes have been found to be linear in photon exposure, both for direct photoexcitation of the adsorbate and for hot-carrier driven processes. Several other laboratories have extended the earlier NIST work in this area, leading to recent reports of a new class of photostimulated desorption that occurs when using

femtosecond lasers to excite the surface.¹¹ In these systems, a highly nonlinear dependence on incident laser intensity is characteristically observed.

A significant opportunity to glean new insights into this novel desorption processes presented itself recently. A novel molecular orbital-based scheme emerged that could directly address electron/adsorbate coupling strengths. The theoretical efforts of Tully and Head-Gordon^{12,13} have modeled the coupling between adsorbed CO and a copper surface, a system where the time-resolved response has been extensively characterized by the NIST group.¹⁴ The theoretical approach has had impressive success replicating and/or predicting those experimentally observed coupling strengths with the surface for each of the different adsorbate degrees-of-freedom. In fact, these calculations agree to within a factor of two with all of the experimental results for mode-specific coupling strengths in the modeled system. The impressive predictive capacity of this model for static coupling suggests that its predictions for the femtosecond desorption processes should be taken quite seriously. If the theoretical approach resulted in coupling strengths that describe equilibrium energy transfer AND energy transfer far away from equilibrium, then the utility of the theory will be extremely broad. As the NIST group was in a position to conduct a laboratory determination of the energy disposal that had been predicted by this theory, we proposed a redirection of our DOE project in an effort to provide this bench-mark data.

Experimental

In addition to the surface diagnostics and REMPI lasers utilized in the carbon oxidation studies, a recently acquired Ti:Sapphire laser system was used to generate femtosecond laser pulses of approximately 150 fs duration at 400 and 800 nm to induce desorption of CO from a Cu(100) surface. The spatial profile of the desorption pulse was routinely monitored by a CCD camera located in a conjugate position to the Cu crystal. Due to the nonlinear dependence of the yield on absorbed laser fluence, it was found to be essential to normalize all signals base on a pixel-by-pixel analysis of the laser beam as viewed by the CCD camera.

Results

We have successfully examined the dependence of desorption yield on pulse duration, pulse energy, pulse wavelength, and surface temperature. We find a remarkably strong dependence of the desorption yield on pulse fluence, with the yield increasing as the fluence to the eighth power. This observation is in reasonable agreement with prior femtosecond desorption experiments. State-resolved measurement of the vibrational, rotational, and translation energy distributions are now complete¹⁵, and are summarized in Table I. Examination of the table reveals that the fluence dependence, yield, and pulse-pulse correlation signals are in reasonable agreement with theoretical predictions by Head-Gordon, et al. The experimental results also support the energy disposal predicted by Head-Gordon et al, finding translations and vibrations to be of comparable total energy, with the energy in rotations significantly reduced. The quantitative agreement between the Head-Gordon theory and experiment is improved if the energy in each CO degree-of-freedom is reduced by 23% to account for the higher fluence used in the theory compared to that used in the experiment. The agreement is excellent, indicating that the results from the theoretical model are characteristic of the physical events, suggesting that trajectory studies using these theoretically determined coupling strengths are likely to provide a meaningful picture of the desorption dynamics.

Table I

	Head-Gordon et al (60 J/m ²)	Experiment (43-46 J/m ²)	Empirical Model (46 J/m ²)
Yield (F^n) ML/shot	n=5.6 2.5×10^{-3}	n=8±1 $\sim 10^{-4}$	n=8.4 3×10^{-4}
$\langle E \rangle_{rot}$	0.034±0.004 eV 395 K	0.019±0.002 eV 225 K	440 K
$\langle E \rangle_{trans}$	0.068±0.006 eV 525 K	0.028±0.002 eV 215 K	440 K
$\langle E \rangle_{vib}$	0.068±0.007 eV 1940 K	0.029±0.006 eV 1330 K	1300 K
Two-pulse correlation width	2-3 ps	3 ps	3 ps

The desorption process that was modeled by Tully and Head-Gordon is based on an electronic friction picture of energy transfer, where energy initially absorbed by the electronic system of the substrate is subsequently coupled into the adsorbate degrees-of-freedom. An alternative picture of femtosecond laser-induced desorption exists that invokes multiple electronic transitions which occur when the arrival rate of photons at the surface is greater than the energy relaxation rate of adsorbates. In this model, the adsorbate accumulates energy due to multiple electronic excitations that lead to desorption. These DIMET models do not make predictions of the energy partitioning, but they do provide an intuitive picture for the desorption dynamics. In the absence of a prediction of the energy partitioning that would be implied by a DIMET process, we have attempted to test the validity of the Head-Gordon calculations. We have constructed an empirical model for the frictional coupling events that lie at the heart of the Head-Gordon theory. Starting from the set of coupled diffusion equations that describe the transient electronic and lattice temperature of the copper, energy is then coupled into the various degrees-of-freedom associated with the CO/Cu layer. Specifically, we take experimentally determined coupling strengths (either from time-resolved measurements or from linewidth measurements), and establish the mode specific coupling strength between adsorbed CO and the electronic and lattice degree-of-freedom. For instance, the coupling strength of the CO stretch to the electrons and phonons have been determined in time-resolved measurements, while linewidth studies place limits to the electron and phonon coupling to the Cu-CO mode. The final column in Table I indicates the average energy predicted for each CO degree-of-freedom using this empirical model. Note, that there is good agreement with the predictions of Head-Gordon, both in terms of partitioning and absolute energy.

It is significant that all of the data are so well accounted for by either modeling effort. This suggests that the friction model captures most of the energy transfer that is observed, and that predictions based on a friction model of laser-induced desorption can be expected to be reasonably accurate. Given the uncertainties associated with the experimental determinations and with the trajectory studies, it is clear that a more definitive test of where the model begins to

break down will require substantial experimental and theoretical effort. Aside from a factor of two in the rotational energy and a persistent background signal in the wings of the correlation trace, the current models do extremely well.

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Publications and talks as a result of funding for this project are listed below.

Publications:

1. Richter, L.J., Buntin, S.A., King, D.S., and Cavanagh, R.R., "State-Resolved Studies of the Laser-Induced Desorption of NO from Si(111): The Importance of Localized Excitations," Desorption Induced by Electronic Transitions V, edited by A.Burns, D. Jennison, and E. Stechel, (Springer-Verlag, 1993) pg. 227-232.
2. Cavanagh, R.R., King, D.S., Stephenson, J.C., and Heinz T.F., "Dynamics of Nonthermal Reactions: Femtosecond Surface Chemistry" - Feature Article in J. Phys. Chem. **97**, 786-798 (1993).
3. Buntin, S.A., Cavanagh, R.R., and Richter, L.J., "Photodecomposition Dynamics of Mo(CO)₆/Si(111) 7x7: CO Internal State and Translational Energy Distributions." J. Chem. Phys. **98**, 7651-7654 (1993).
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7. L.M Struck, L.J. Richter, S.A. Buntin, R.R. Cavanagh, and J.C. Stephenson, Phys. Rev. Lett. **77**, 4567 (1996).

Talks and Posters:

"Photodissociation Dynamics of Mo(CO)₆/Si(111): Localized Adsorbate Excitation," Chemistry Department Seminar, Notre Dame University, Notre Dame, IN. Jan 1993.

"Photodissociation Dynamics of Mo(CO)₆/Si(111): Localized Adsorbate Excitation," Chemistry Department Seminar, Mount Holyoke College, South Hadley, MA. Feb 1993.

"External Reflection FTIR Spectroscopy Investigation of the Thermal and Photochemistry of Mo(CO)₆ Adsorbed on Si(111) 7x7 at 100 K," 39th American Vacuum Society National Symposium, Chicago, IL., Nov. 13, 1993.

"Optically Driven Surface Reactions: Laser Probes of Surface Dynamics," Department of Energy/Basic Energy Sciences Heterogeneous Catalysis and Surface Chemistry Research Conference, Oconomowoc, WI, May 1994.

"Photodecomposition Dynamics of Mo(CO)₆/Si(111) 7x7," Adriatico Research Conference on Lasers in Surface Science, Trieste, Italy, August 1994.

"State-Resolved Studies of Surface Photoreactions," Physics Department Seminar, University of Pennsylvania, Philadelphia, PA., November 8, 1994.

"Time- and State-Resolved Measurements of CO/Cu(100): When Qualitative Pictures are not Good Enough" Physical Chemistry Seminar, Department of Chemistry, MIT, Cambridge, MA, March 1996.

"Femtosecond Desorption of CO from Cu(100): State-resolved test of ultrafast desorption models" ACS National Meeting, New Orleans LA, March 1996.

"Femtosecond laser-induced desorption of CO from Cu(100): Comparison of theory and experiment" Poster at the DOE contractors meeting in Montgomery, Texas. May 21-24 1996.

"Femtosecond Laser-induced Desorption of CO from Cu(100): Comparison of Theory and Experiment" AVS National Symposium, Philadelphia, PA, October 1996.