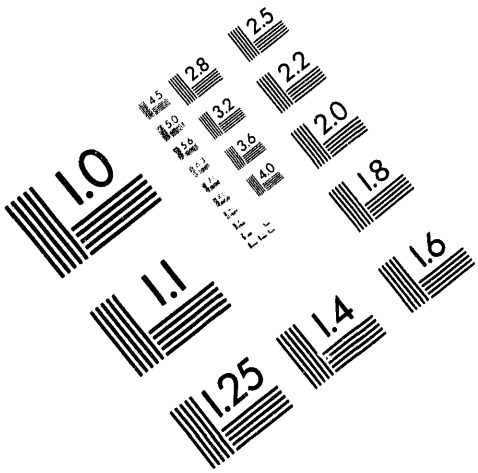

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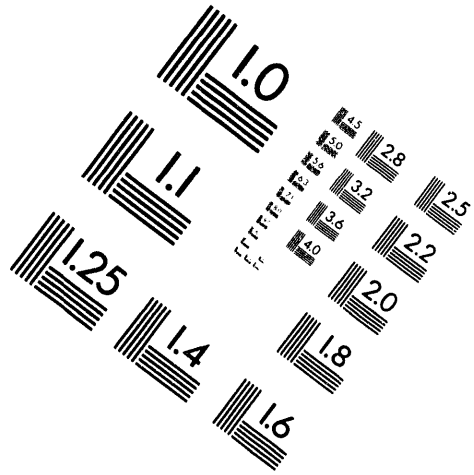

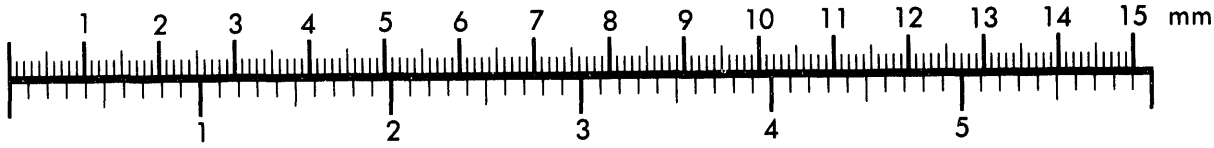

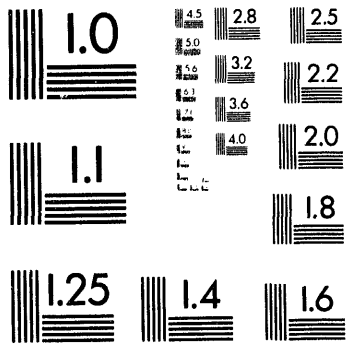

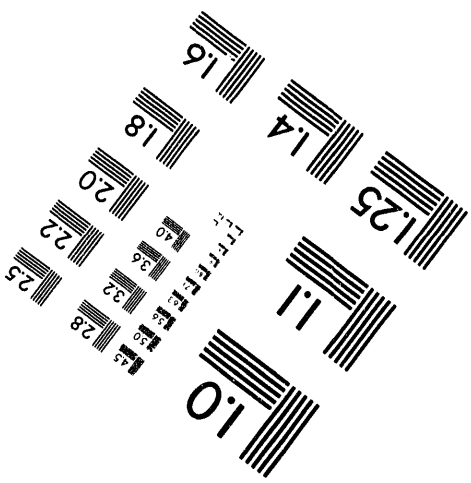

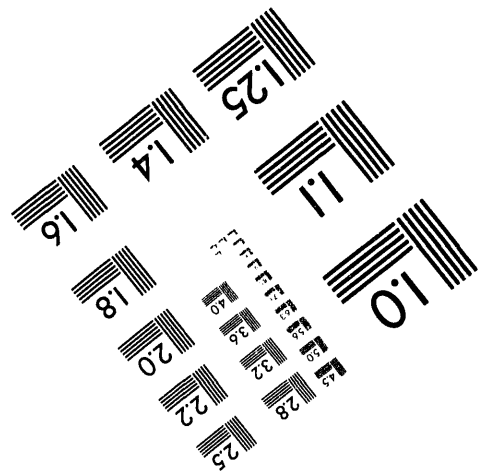

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Project Summary
11/93

Final Report- DE-AI05-84ER13150

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Optically Driven Surface Reactions: Laser Probes of Surface Dynamics

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Research Scope and Objectives

Optical stimulation of surface reactions has attracted considerable attention, both as a test bed for probing fundamental chemical events and as an avenue for novel low temperature surface modification. The impact areas for the associated optically driven reactions range from materials synthesis and modification to environmental remediation. To optimally exploit lasers in these surface processes it is essential to understand reaction and energy transfer pathways of adsorbates on surfaces.[1] This project is directed at establishing the dominant energy transfer mechanisms in these reactions.

Description of Research Effort

We have focused our efforts on deposition systems where the relevant adsorbates are typically organometallic molecules. Ideally, the laser radiation will strip away the ligands, which desorb into the gas phase, leaving behind a patterned layer of metal atoms. In reality there are a number of competing pathways, such as energy transfer and ligand interactions, which interfere with this ideal picture. To serve as a model system in the characterization of laser-induced deposition, the photodecomposition dynamics of $Mo(CO)_6$/Si(111) 7x7 have been probed by applying surface sensitive diagnostics to follow the photomodified surface and state-selective detection techniques to establish the energy content of the evolved CO photoproduct.

Progress to Date:

a) FTIR Characterization of Novel Adlayer Structure

Conventional FTIR techniques have been used to establish dose conditions and to identify the molecular nature of surface-bound species generated in the photodissociation of $Mo(CO)_6$/Si(111). Contrary to most studies probing adsorbates on semiconductor substrates, which use infrared spectroscopy in a multiple total internal reflection configuration, we have made our measurements utilized a single external reflection. By using an angle-of-incidence near Brewster's angle, it is possible to observe both the longitudinal and the transverse optical modes of the adlayer. For the strong CO stretch mode, this leads to a 100 cm^{-1} separation of the two features. An eight wavenumber splitting can be resolved in the transverse mode, indicating that for adsorption directly on the 7x7 surface $Mo(CO)_6$ forms a distinct 2D lattice, which is in registry with the underlying substrate. Furthermore, given the strong dipole-dipole coupling observed in the FTIR data, it appears that even at low coverage, the $Mo(CO)_6$ forms islands on the Si(111) surface rather than binding to uniformly dispersed sites.

Following irradiation of low coverage samples with 266 nm laser pulses, the disappearance of the molecular $Mo(CO)_6$ features is readily monitored using FTIR. This is accompanied by the growth

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of a number of new absorption features in the CO stretch spectral region. These features grow in at different rates during the irradiation process, and they have been attributed to two different types of $Mo(CO)_x$ fragments. Symmetry arguments and consideration of tabulated IR frequencies for unsaturated metal carbonyl fragments has allowed the assignment of one of these species as being $Mo(CO)_5$ bound to the Si substrate. The precise nature of the second species was not determined. These FTIR observations have been accepted for publication.[2]

b) Gas Phase Photodissociation Dynamics of $Mo(CO)_6$

Previous studies have indicated that the photochemistry of $Mo(CO)_6$ on Si(111) 7x7 proceeds *via* an adsorbate-localized mechanism. As a result, characterization of the energy disposal in the photodecomposition of the isolated gas phase $Mo(CO)_6$ should provide a benchmark for the photochemistry in the adsorption system. As these results were previously unavailable, we conducted state-resolved studies of the 266 and 355 nm photolysis of $Mo(CO)_6$, using single-photon vacuum ultraviolet laser-induced fluorescence (LIF) as a state-specific probe of the CO photofragments. It is noted that for $Mo(CO)_6$ three (two) CO ligands can energetically cleave for 266 nm (355 nm) single-photon absorption. The gas phase experimental results are summarized as follows.[3] For 266 nm photolysis, rotational state distributions for CO in v=0 and v=1 are represented well by Boltzmann distributions with comparable rotational temperatures, T_r, of 950±60 K and 935±80 K, respectively. The rotational-state-integrated v=1/v=0 population ratio, N(v=1/v=0), is 0.19±0.03. For 355 nm photolysis, again both the CO v=0 and v=1 rotational state distributions are Boltzmann with $T_r(v=0)=750\pm60$ K and $T_r(v=1)=1150\pm250$ K. Here N(v=1/v=0)=0.09±0.02 and no CO(v=2) was detected. Doppler profiles are Gaussian in shape, and give similar translational temperatures (independent of photolysis wavelength and internal state) characterized by an average value of 1350±250 K.

The experimental results are not at all consistent with a dissociation mechanism involving the impulsive ejection of one or two CO groups. Additionally, calculated internal state distributions performed within the framework of a sequential and purely statistical decomposition of the $Mo(CO)_6$, are not entirely consistent with the results. The results seem to indicate that the dissociation is predominantly statistical in nature, but that additional perturbations exists in the energy disposal.

c) (2+1) Photoionization of CO from $Mo(CO)_6$/Si(111):

A time-of-flight mass spectrometer detector has been assembled and installed in our UHV system to improve our detection limit for desorbed CO beyond that afforded by our earlier LIF diagnostics. This system has now been used to measure quantum state population distributions for CO which were probed *via* a (2+1) resonance-enhanced multiphoton ionization (REMPI) scheme through the $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ electronic transition. The REMPI detector has been used to complete our earlier study[4] of the photolysis of $Mo(CO)_6$/Si(111). As a result of this capability, we discovered a previously unrecognized channel in the photoresponse of this system. Specifically, a photoinduced reaction channel was identified that most likely involves CO bound to ion beam etching-induced defect sites on the Si(111) surface.[5] We have used this REMPI technique to establish that the CO ejected as a result of this mechanism has a kinetic energy that approaches 3000 K. The internal energy of the CO is characterized by high vibrational excitation [(v=1/v=0) = 0.4 or about 3300 K], and a rotational temperature of only 200 K. Of particular interest for photoinduced catalysis was the high yield observed for these sites (photodesorption cross section of about 10^{-16} cm^2), indicating a very efficient

coupling of photon energy to the desorption coordinate.

Under $Mo(CO)_6$ dosing conditions where the defect sites did not contribute to the photodesorbed CO signal, two velocity components were evident in the time-of-flight distributions; a fast component with a kinetic energy of 900 K and a slow component with a kinetic energy of 150 K (see Fig. 1). These two features confirmed the general interpretation derived earlier in this laboratory. That is, the two channels can be viewed as due to a directly ejected CO (the fast channel) and a CO that undergoes extensive interactions with the surface (the slow channel). With the REMPI detector, it has additionally been possible to assess the role of vibrational populations. These new data are consistent with a fast channel with a high degree of vibrational excitation that is taken as the nascent population, and a slow channel in which the degree of vibrational excitation reflects the surface residence time of the CO product. The slow component displays a contribution from CO(v=1) which increases with increasing surface temperature. This observation can be rationalized most simply by associating the degree of vibrational excitation with the residence time on the surface of the CO photolysis product. The shorter the residence time, the greater the degree of vibrational excitation.

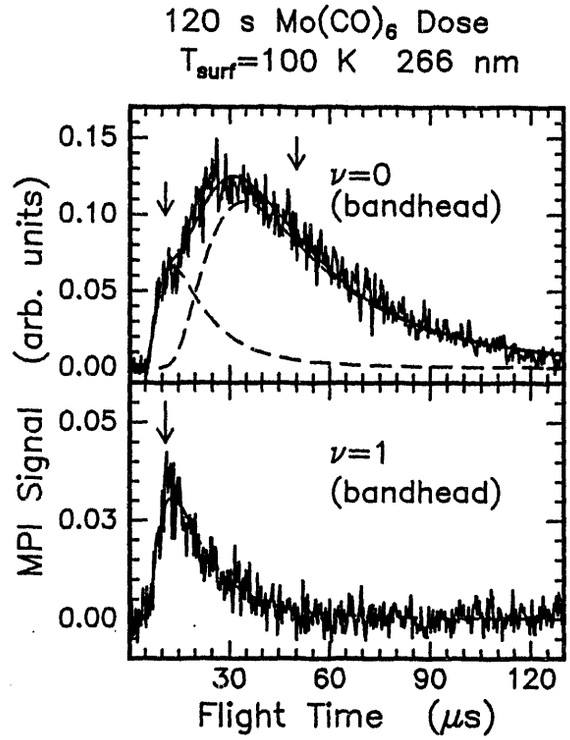

Figure 1

Time of Flight distributions for CO photolysis products from $Mo(CO)_6$/Si(111). The fast component (v=0 and 1) corresponds to 900 K and the slow component (v=0) corresponds to 150 K.

The ability to pursue the coverage dependence of this photoprocess into the submonolayer regime has provided enlightening results.[6] The data for both the fast and the slow channels show a distinct, step-like increase of about a factor of three in cross section in going from the submonolayer to the multilayer regime, with an absence of any marked change in photofragment energy partitioning. Our parallel FTIR studies have indicated that $Mo(CO)_6$ adsorption for all coverages show extensive dipole-dipole coupling. Taken together, these data implicate 2-D island formation in the submonolayer regime. The observed change in photodesorption cross section at the completion of a monolayer suggests that excited state quenching is more pronounced for $Mo(CO)_6$ that is in contact with the Si surface. It is also noted that the cross sections for all coverage regimes are markedly lower (about a factor of 30) than in the gas phase suggesting that near-neighbor $Mo(CO)_6$ interactions are of primary importance with regard to excited state energy quenching.

Future Research

Our efforts in the next year will lay the essential ground work for probing the dynamics of surface oxidation reactions. Carbon films will be generated either by thermal decomposition of ethylene

adsorbed at low temperatures or by ion beam deposition techniques. N_2O will serve as the photolytic O atom precursor. These measurements will include IR, Auger, and TPD characterization of the low temperature adsorption and thermally induced reactions of N_2O on these carbon surfaces. Based on extensive experience with FTIR in this group, we feel that this technique can provide the essential molecular level characterization of the initial surface layer. We will initially rely on arc lamps as the photolysis source and exploit our proven surface sensitive techniques to characterize the optically induced changes in the surface layer. In addition, we will use mass spectroscopy to monitor the composition of the desorbed species.

Subsequent REMPI experiments, probing the energy disposal in the CO photo-oxidation product, will utilize 200 nm photolysis pulses, as they are known to be resonant with N_2O localized excitations that lead to the generation of N_2 and $O(^1D)$ fragments. In future efforts, photolysis wavelengths will be extended to the red to determine if carriers can induce surface reactions that are comparable to those that result when direct photoactivation of the adsorbate is possible. Comparison of the efficacy of the different wavelengths should help to reveal the photolysis mechanism, and examination of the energy content of the photofragments will address of the role of the incident O atom energy in the subsequent reaction dynamics.

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