AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

---

1 of 1

DOE/ER/13150--75

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

Richard R. Cavanagh and David S. King
National Institute of Standards and Technology
Gaithersburg, Md 20899 USA

(DOE I.A. Number DE-AI05-84ER13150)

Progress Report (9/91)

Our study of the dynamics of photodesorption of NO from Si(111) 7x7 under conditions of low NO coverage has been completed. The role of surface electronic states in mediating the desorption dynamics is supported by both wavelength dependent studies and by coadsorption experiments. By comparison with results from inverse photoemission and scanning tunneling microscopy studies, it has been possible to establish that two different surface sites are involved in the desorption process. Optical excitation creates a hole in the rest atom localized S_2 surface state, and subsequently charge transfer occurs between this site and an adatom site where the NO species is bound. From the observed population of internal states, it was deduced that the adsorbed NO was best described as an $NO^{\cdot-}$, and that upon charge transfer to the S_2 hole, there is rapid release of a neutral NO. Additional support for this mechanism was found in the independence of the desorption dynamics on either doping of the substrate or presence of excited substrate carriers. The precise dynamics that transpire between photon absorption and NO release remain at issue, since there are several potential energy surfaces that could be involved. However, strong analogies exist between the internal state populations observed in the NO/Si(111) system and those observed in the photolysis of aliphatic nitroso compounds. A manuscript has been submitted to the Journal of Chemical Physics reporting these findings.¹ A preliminary manuscript addressing the significantly different wavelength dependence and product energy distributions observed at saturation NO coverage has been published,² and more

MASTER
ds

complete account is being written.

Having carefully documented photodesorption processes involving hot carriers in the substrate {NO/Pt(111)} and optically excited surface states {NO/Si(111) 7x7}, we recognized that some of the earlier concepts relating angle-of-incidence effects in optically driven surface chemistry to the actual excitation mechanism were somewhat naive. We have now given greater thought to conditions where the dielectric properties of the interface can complicate the otherwise clean distinction between adsorbate and substrate localized phenomena, and have attempted to clarify the role of local electric fields and substrate absorption effects. These results have been accepted for publication in Chemical Physics Letters.³ As a consequence of the clearer picture of the factors which restrict adsorbate localized optical processes, we have turned our attention to the photodecomposition of adsorbed Mo(CO)₆, where optical excitation of the adsorbate has been reported. We plan to use laser-induced fluorescence and single reflection FTIR to contrast the photolysis of this hexacarbonyl adsorbed on metal and semiconductor surfaces. Our studies to date have been on Si(111).

To establish dose conditions in our laboratory that correspond to coverages used by other groups, and to identify the molecular nature of any surface-bound photofragments that might be generated, we have applied FTIR spectroscopy to this system. 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 in a single external reflection configuration. 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. An eight wavenumber splitting can be resolved in the transverse mode, indicating that the octahedral symmetry of the Mo(CO)₆ has been lifted through interactions with the Si. These spectral features show a strong dependence on annealing temperature, but remarkably little dependence on coverage. Based on TPD and 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. As the Mo(CO)₆ layer increases in thickness, it has been possible to

observe a transition in the spectrum indicative of a change between amorphous and crystalline Mo(CO)_6 .

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 of a number of new absorption features in the CO stretch spectral region. These features grow at different rates during the irradiation process, and have different adsorption enthalpies than the molecular parent. They have tentatively been assigned to modes of two different classes of Mo(CO)_x fragments. The growth of features near 2098, 1986 and 1908 cm^{-1} are in good agreement with a Mo(CO)_5 fragment, based on comparison with solution and matrix isolation studies. The identity of the other fragments(s) remains ambiguous. These FTIR observations are being prepared for publication.⁴

The vacuum ultraviolet (VUV) generation facilities that were developed last year⁵ for state-resolved detection of CO have now been adapted to the UHV chamber used in the desorption studies. We have successfully modified the UHV system to accommodate VUV radiation and to accept new photodetection hardware. Initial measurements have been made characterizing the photolysis yield of CO from Mo(CO)_6 on Si(111). The data to date for Mo(CO)_6 coverages between 1 to 2.5 monolayers reveals that there is very little coverage dependence in the energy content of the photoejected CO fragment. The rotational-state resolved velocity distributions are characterized by two components. The slower of the two components has a velocity representative of the surface temperature of 100 K, while the fast component is close to 500 K. The rotational state population distributions for the fast and slow components can be characterized by temperatures comparable to their respective kinetic energies. In terms of both the kinetic and rotational energy distributions, the energy content is significantly less than that observed in gas phase photolysis experiments, where the gas phase rotational temperatures were almost 1000 K, while the kinetic energy was roughly 1500 K. Further experiments are in progress to better quantify the energy distribution in these fragments, including characterization of the

degree of vibrational excitation.

1. L.J. Richter, S.A. Buntin, D.S. King and R.R. Cavanagh, "State-Resolved Studies of the Laser-Induced Desorption of NO from Si(111) 7x7: Low Coverage Results." Submitted 8/14/91 to J. Chem. Phys.
2. L.J. Richter, S.A. Buntin, D.S. King, and R.R. Cavanagh, "Laser-Induced Desorption of NO from Si(111): Effects of Coverage on NO Vibrational Populations," J. Electron Spectroscopy & Related Phenomena 54/55, 181-190 (1990).
3. L.J. Richter, S.A. Buntin, D.S. King, and R.R. Cavanagh, "Constraints on the Use of Polarization and Angle-of-Incidence to Characterize Surface Photoreactions," Chem. Physics Letters (in press).
4. L.J. Richter, S.A. Buntin, and R.R. Cavanagh, "External-Reflection FTIR studies of the thermal- and photo-chemistry of Mo(CO)₆ on Si(111) 7x7," in preparation.
5. S.A. Buntin, R.R. Cavanagh, L.J. Richter, and D.S. King, "Photodissociation Dynamics of Mo(CO)₆ at 266 nm and 355 nm: CO Photofragment Kinetic Energy and Internal State Distributions," J. Chem. Phys. **91**, 6429 (1991)

*reprints + preprints
removed
ds*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DATE

FILMED

8/12/94

END