PROGRESS PERFORMANCE REPORT

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Surface Oriented Molecules

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II. SUMMARY OF OVERALL PROGRESS

The period 8/01/91-7/31/92 is the first year of a new project titled "Photochemical Dynamics of Surface Oriented Molecules", initiated with DOE Support. The main objective of this project is to understand the dynamics of elementary chemical reactions by studying photochemical dynamics of surface-oriented molecules. In addition, the mechanisms of photon-surface interactions need to be elucidated. The strategy is to carry out experiments to measure the translational energy distribution, as a function of the angle from the surface normal, of the photoproducts by time-of-flight (TOF) technique by varying the photon wavelength, intensity, polarization, and pulse duration. By choosing adsorbates with different bonding configuration, the effects of adsorbate orientation on surface photochemical dynamics can be studied.

A number of accomplishments were achieved during this first year. One of the main goals we set out at the beginning was to make TOF measurements for the system of O_2 coadsorbed with CO on Pt(111). The TOF mass spectrometry using the pulse counting technique has been assembled and successfully put into commission. This detection system was put into an existing vacuum chamber in order to make the initial measurements as soon as possible. In addition, this vacuum system was interfaced to the femtosecond laser system, allowing a direct comparison of the desorption dynamics with the nanosecond laser system. The system of O_2 coadsorbed with CO on Pt(111) was chosen for two reasons. First, very interesting photochemistry is exhibited by this system, including the desorption and dissociation of O_2 and photoproduction of CO_2 . Second, extensive studies have been made in our laboratory on the adsorption properties by a combination of surface probes and the photochemistry using continuous wave (cw) arc lamp for O_2 coadsorbed with CO on Pt(111) at 75-85 K.

In our previous studies with cw irradiation, the system of O_2 coadsorbed with CO on Pt(111) was shown to be a useful model system to investigate bimolecular surface

photochemistry and its implications for our basic understanding of elementary chemical reactions. This is the most clear example to-date of this important class of reactions. In order to extract as much information as possible from this system, it is necessary to investigate how the energy from the initial photon absorption is distributed. An important channel involved in the photochemistry is the translational energy of the photoproducts. Measurement of this energy channel is the focus of the DOE project.

We have assembled the mass spectrometer and the associated TOF instrumentation in order to measure the translational energy distribution of the photodesorbed products. The mass spectrometer is mounted on a translational stage in order to measure directly the absolute kinetic energy of the products. Data acquisition is interfaced to an IBM PC/AT. Data is then transferred to the CONVEX/SUN/IBM RS 6000 Workstation network in the laboratory and analyzed. A significant part of the past 9 months was invested in the writing of the software to accomplish the task of computer controlled data taking and data analysis. In addition, the electronics was optimized in order to minimize the background noise. The mass spectrometer is running in the pulse counting mode to allow maximum signal-to-noise ratio and to detect small signals. Other laboratory activities were mainly in the set-up of the lasers and the optics for the TOF photochemical experiments.

Initial experiments have been performed to study the photodesorption of O_2 and the photoproduction of CO_2 from coadsorbed O_2 and CO on Pt(111) at 75 - 85 K using the 620 nm and 310 nm pulsed light of about 150 fs duration from the femtosecond laser system and the 355 nm pulsed light of about 5 ns duration from the nanosecond laser system. Very interesting differences are observed for these two excitation sources of light with approximately a factor of 30,000 difference in the time duration of the pulses, or the time scale of the photoexcitation. In our studies with the cw arc lamp, no measurable photochemistry is observed with 620 nm irradiation while a linear dependence of the photodesorption and photodissociation yields is obtained with 310 nm irradiation. In contrast, with the femtosecond excitation, a large O_2 desorption signal is recorded both at 620 nm

and 310 nm irradiation with super linear dependence on the intensity. The O_2 desorption yield versus the laser intensity at 620 nm is $N \propto I^{4.6}$ while at 310 nm it is $N \propto I^{2.5}$. In addition to photodesorption, photodissociation of O_2 also occurs and is confirmed through the observation of adsorbed O and the production of CO_2 when O_2 is coadsorbed with CO. The production of CO_2 occurs both with 620 nm and 310 nm irradiation.

The TOF spectra of the desorbing O_2 and CO_2 can be fit to Boltzmann distribution. The average kinetic energy of desorbed O_2 molecules at saturation coverage with 310 nm irradiation is about 380 K. As the coverage is depleted, the average kinetic energy decreases to 300 K. The higher translational temperature of the molecules compared with that of the sample is consistent with a nonthermal process. The cross section and quantum efficiency at saturation coverage for 620 nm irradiation are approximately 10^{-17} cm^2 and 10^{-2} , respectively. As the coverage is depleted, the cross section and the quantum efficiency decrease by an order of magnitude. For 310 nm irradiation, the cross section and the quantum efficiency at saturation coverage are approximately 10^{-16} cm^2 and 10^{-1} , respectively. As the coverage decreases, the cross section and the quantum efficiency also decrease by an order of magnitude. Compared with measurements performed with cw arc lamp, the cross section obtained with femtosecond laser irradiation is almost three orders of magnitude higher.

The kinetic energy of the CO_2 molecules is similar to that of the O_2 molecules, except that as the coverage is depleted, the average kinetic energy of the CO_2 molecules increases. The CO_2 molecules are leaving the surface with average kinetic energy of approximately 0.05 eV. In contrast, with nanosecond pulse laser irradiation, the average kinetic energy is about an order of magnitude higher, approximately 0.5 eV, however, the cross section is approximately three orders of magnitude lower and is similar to that with cw arc lamp irradiation. The characteristic features of femtosecond laser desorption can be accounted for by the mechanism of multiple electronic transitions.

II. SUMMARY OF WORK TO BE PERFORMED DURING THE SUCCEEDING FUNDING PERIOD

The experiments performed to-date suggest additional investigation into the interesting and information-rich system of O_2 coadsorbed with CO on Pt(111) at 75 - 85 K. The contrast between nanosecond and femtosecond pulse laser irradiation needs further study. More detailed dependence of the translational energy as a function of the wavelength is required in order to obtain a deeper understanding of the photochemical dynamics. Modeling of these results is highly desirable. Extension of these studies to other systems is planned, especially the system of O_2 coadsorbed with CO on Ag(110) where the surface is anisotropic and CO thermally desorbs at a significantly lower temperature than on the Pt(111) surface.

It is also important to measure the dependence of the translational energy on the desorption angle of the photoproducts. During the succeeding funding period, we will design and construct the optical and mechanical system in order to vary the detection angle while keeping the angle of incidence of the light constant. A special UHV chamber will be made in order to house this optical/mechanical system. The range of wavelength tunability of the laser systems will be extended, allowing a more comprehensive study of the photochemical dynamics.

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