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The main thrust of our program was directed towards the study collision-induced dissociation (CID) of hyperthermal molecules on insulators (MgO), semiconductors (GaAs) and metals (Ag). Supersonic beams of nitroso compounds entered the UHV chamber with kinetic energies variable between 0.5 and 7 eV. NO products were detected state-selectively using two-frequency laser ionization. CID yields were measured as a function of surface temperature and incident kinetic energy, and complete energy deposition in the NO product was determined in each case. CID yields rise sharply with incident kinetic energy, with non-vanishing values even slightly below dissociation threshold at high surface temperature. The yield depends on the stiffness of the surface. The NO distributions are similar to those obtained in the gas-phase unimolecular decomposition of these molecules and indicate a broad distribution of internal energies. In the newest phase of this program, the photodissociation of CINO adsorbed on a rough MgO surface is studied at 365 nm. The NO state distributions differ greatly from those obtained in gas-phase photodissociation and suggest that CINO aggregates as islands on the surface and the NO and Cl undergo multiple collisions before desorption.

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***GAS-SURFACE INTERACTIONS NEAR
DISSOCIATION THRESHOLD***

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I. SUMMARY

The main thrust of our program was directed towards the study collision-induced dissociation (CID) of hyperthermal molecules on insulators (MgO), semiconductors (GaAs) and metals (Ag). Supersonic beams of cold, seeded aliphatic nitroso compounds were skimmed and collimated and entered the differentially pumped UHV chamber with kinetic energies variable between 0.5 and 7 eV. NO products were detected state-selectively using two-frequency laser ionization. CID yields were measured as a function of surface temperature and incident kinetic energy, and complete energy deposition in the NO product was determined in each case. The scattering of the molecules from the surface is direct inelastic in all cases. CID yields rise sharply with incident kinetic energy, with non-vanishing values even slightly below dissociation threshold of the molecule at sufficiently high surface temperature. The yield depends greatly on the stiffness of the surface. The NO distributions are similar to those obtained in the gas-phase unimolecular decomposition of the same molecules and indicate a broad distribution of internal energies acquired in the collision with the surface. In the newest phase of this program, the photodissociation of ClNO adsorbed on a rough MgO surface was studied at 365 nm. The NO product state distributions differed greatly from those obtained in gas-phase photodissociation and suggest that ClNO aggregates as islands on the surface and the NO and Cl products undergo multiple collisions before desorption.

II. PROGRESS DURING NOV. 1988 - NOV. 1991

II.1 MOLECULE-SURFACE COLLISION INDUCED DISSOCIATION

During the previous funding period (11/88 - 10/91), we made original contributions toward a fundamental understanding of CID on insulating single-crystal surfaces [*e.g.*, MgO(100)], while also obtaining preliminary results for CID on semiconductors and metals. In addition, major modifications have been introduced in order to be able to cool the surface and dose it with well-controlled amounts of adsorbates. Results on the photodissociation of ClNO on rough MgO(100) surface have been obtained, and experiments on well-characterized, clean surfaces are now in progress.

Our first step was to establish that MgO(100) behaves like an insulator in collisional processes. This was done by looking for vibrational excitation in NO following direct inelastic scattering of a pulsed supersonic beam of NO seeded in H₂ or He ($T \sim 5$ K, $E_{\text{incident}} \leq 0.57$ eV). The most relevant result was the *absence* of vibrational excitation in

NO, in sharp contrast with scattering from conducting Ag(111) crystals, where substantial NO vibrational excitation had been observed, and interpreted as occurring via an *electronic* mechanism involving the formation and neutralization of transient NO⁻ ions. Such electronic interactions presumably are smaller for insulating surfaces than for metals, although we caution that differences in NO vibrational excitation may also reflect different corrugations and/or methods of surface preparation.

Our next step was to develop sensitive diagnostics for surface characterization and cleanliness. We found He diffraction, which routinely provided reliable diffraction patterns, to be a cost-effective and sensitive diagnostic for structural changes at the top-most surface layer. In addition, we developed Xe scattering as a diagnostic. It yields an essentially background-free scattering peak that is indicative of an atomically clean surface, as seen by a physically large and heavy collider, much like the molecules used in the CID experiments. The width of the angular distribution yields valuable information about the effective surface corrugation and topography as a function of E_{incident} .

These techniques, which are sensitive to surface corrugation, have now been complemented by Auger spectroscopy, which probes the atomic composition of the surface, and by temperature programmed desorption (TPD) which is used extensively in our experiments with physisorbed molecules. With the former, it was possible to obtain good Auger signals even for Mg(100), despite the fact the MgO(100) is an insulator. This is in agreement with the results of other investigators.

Accurate control of E_{incident} using seeded, supersonic beams, as well as the sensitive and state-specific 2-frequency, 2-photon NO ionization detection method developed for the NO scattering experiments, have proven reliable and efficient in the CID experiments as well. They enabled us to obtain complementary information regarding both dissociation yields and NO fragment E,V,R distributions.

In studying CID of molecules initially in their ground electronic state, the best candidates are molecules that can be accelerated to high collision energies and have low dissociation energies. Thus, a series of fluorinated nitroso molecules was chosen for the first experiments. H → F substitution increases the mass without affecting (significantly) the electronic structure, while the C-NO bond dissociation energy of nitroso compounds is very low (~ 1.7 eV) and does not differ significantly for various aliphatic nitroso molecules. Since MgO(100) is a stable, corrugated and well-studied surface, which is inert

towards NO, and binds it only very weakly (ΔH_{ads} is estimated to be 0.1-0.2 eV), it was used for the most extensive series of experiments.

So far, the following molecules have been studied: CF_3NO , $\text{C}_6\text{F}_5\text{NO}$, n- and i- $\text{C}_3\text{F}_7\text{NO}$, and $\text{C}(\text{NO}_2)_4$. $\text{Mg}(100)$, $\text{GaAs}(100)$ and $\text{Ag}(111)$ were used to study the effects on CID of insulating, semiconducting, and metallic surfaces, respectively. In all experiments, supersonic beams of cold, seeded RNO molecules were skimmed and collimated, and entered the differentially pumped UHV chamber with $\sim 0.3^\circ$ angular resolution and rotational temperatures of a few K. E_{incident} values up to 7 eV were used in favorable cases (E_{incident} depends on the mass of the molecule and the dilution ratio). For each E_{incident} , NO fragment densities were measured state-selectively using 2-frequency, 2-photon ionization, and summed over internal states and scattering angles. Full density/flux transformations could not be carried out due to insufficient information about scattered product velocities, and a detailed discussion of the relationship between the measured yields and the dissociation probabilities is given in the publications. In brief, the product yields are similar to the reaction probabilities when E_{incident} is much larger than D_0 , but may differ near threshold. Absolute yields were derived by scaling to scattered NO reference beams of known flux.

To date, we have observed, or attempted to observe, the following collision-induced processes (with the molecules listed in parentheses): (1) simple bond-fission unimolecular reaction (CF_3NO , $\text{C}_6\text{F}_5\text{NO}$, n-,i- $\text{C}_3\text{F}_7\text{NO}$); (2) ionization ($\text{C}_6\text{F}_5\text{NO}$); and (3) isomerization followed by unimolecular reaction [$\text{C}(\text{NO}_2)_4 \rightarrow \text{C}(\text{NO}_2)_3\text{ONO}^\dagger \rightarrow \text{C}(\text{NO}_2)_3\text{O} + \text{NO}$]. With the latter, NO signals were observed, but sticking of $\text{C}(\text{NO}_2)_4$ to the UHV chamber walls made interpretation difficult, and contributions from NO generated on the $\text{MgO}(100)$ surface could not be deconvoluted with confidence.

The most comprehensive set of data concerns item (1) above - CID of RNO molecules on $\text{Mg}(100)$, $\text{GaAs}(100)$ and $\text{Ag}(111)$ surfaces. The aspects studied were:

- (i) CID yield as a function of E_{incident} and T_S .
- (ii) NO E,V,R distributions as a function of E_{incident} and T_S .
- (iii) Dependence of CID yields and NO product state distributions on the choice of surface.

These results have been summarized in several publications, and enabled us to propose the first model for CID on surfaces. Some of the observations concerning simple bond-fission CID are listed below:

- a) The scattering of n- and i-C₃F₇NO from MgO(100), GaAs(100) and Ag(111) appears to be direct inelastic with no evidence of sticking or trapping-desorption.
- b) CID is verified unambiguously for C₃F₇NO and C₆F₅NO by detecting NO state-selectively using 2-photon, 2-frequency ionization.
- c) CID yields rise sharply with E_{incident} , with values of $\sim 5\%$ at 6 eV ($D_0 \cong 1.7$ eV), and non-vanishing values even slightly below D_0 when T_S is sufficiently high (see Fig. 1).
- d) The yields depend sensitively on T_S for both MgO(100) and GaAs(100). The fractional enhancement of the yield with increasing T_S is particularly strong for E_{incident} near D_0 .
- e) The absolute CID yields are molecule-dependent and increase in the order $\text{CF}_3\text{NO} < \text{C}_6\text{F}_5\text{NO} < \text{C}_3\text{F}_7\text{NO}$ for a given E_{incident} . However, the two structural isomers, n- and i-C₃F₇NO exhibit identical CID yields.
- f) The absolute CID yields of C₃F₇NO appear to scale with the surface Debye temperature, and increase in the order $\text{Ag}(111) < \text{GaAs}(100) < \text{MgO}(100)$. For example, Ag(111) yields are a factor of four smaller than the Mg(100) yields.
- g) The NO E,V,R distributions are temperature-like, reminiscent of statistical unimolecular decomposition, and depend only weakly on E_{incident} , T_S and the nature of the surface.

Most of the experimental observations can be reconciled with a preliminary model that involves direct inelastic scattering of the hyperthermal molecules, accompanied by collisional excitation during impact, which is then followed by statistical unimolecular reaction in the gas-phase. Collisional excitation produces a broad distribution of E_{internal} in the scattered molecule and for the E_{incident} values of the present experiments, molecules with $E_{\text{internal}} > D_0$ are at the tail of the distribution. The average energy gained upon collision depends on the nature of the molecule, the coupling to the surface, and the stiffness of the surface. Some of the molecules (*i.e.*, with $E_{\text{internal}} > D_0$), subsequently dissociate giving rise to NO E,V,R distributions that can be fit by statistical theories. Since for all E_{incident} values the majority of the *dissociating* molecules have internal energies close

to D_0 , (*i.e.*, at the tail of the internal energy distribution), the NO distributions depend only weakly on E_{incident} . On the other hand, since the *number* of molecules with $E_{\text{internal}} > D_0$ increases sharply with E_{incident} (*i.e.*, the distribution broadens and shifts to higher energies), the dissociation yield increases rapidly. Within this framework, the influence of surface temperature may be to broaden the distribution of relative collision energies, in analogy with the energy spread caused by thermal motion in gas-phase reactions. Surface vibrations and their couplings to the incident molecule may thus play an important role, and the coupling may also depend on E_{incident} .

It appears, therefore, that most of the molecule- and surface-specific effects are in the activation step, an impulsive collision where the molecule digs into the surface, inducing efficient $T \rightarrow V$ couplings, whereas subsequent dissociation is statistical. The amount of energy transferred per collision depends on the nature of the molecule and the stiffness of the surface, with stiff surfaces and flexible molecules that have low frequency modes resulting in the highest dissociation yields.

Perhaps most important, the surface CID technique is general and can lead to significant dissociation probabilities at modest values of E_{incident} , especially when T_S is high. Thus, it can serve as a useful way of energizing molecules in environments where high relative kinetic energies are common. Although the present results can be rationalized by a surface-impact activation step followed by a statistical dissociation mechanism, there presently exists no proven model, nor are theoretical calculations available. Several open questions still remain and further experiments, as well as theoretical support are needed. Some of the open questions are:

- What is the role of *electronic* excitation? Can we see collision-induced emission from electronically excited states? Do molecules dissociate from electronic states such as T_1 in RNO? Does impact-induced distortion of the nuclear frame enhance electronic excitation?
- What is the reason for the strong dependence of the CID yield on T_S ? It cannot be due to accommodation, but is it a dynamical effect that relates to surface phonon motion adding to the relative kinetic energy?
- What is the role of ions? In order to explain our results, we do not need to invoke mechanisms involving transient ions and their neutralization, as was done in other work,

but are ions important in certain cases? We hope to be able to answer some of these questions during the next funding period.

II.2 PHOTODISSOCIATION OF CINO ADSORBED ON MgO(100)

The use of UV lasers to induce photochemistry at the gas-surface interface is of both technological importance and scientific interest. Its applications include catalysis and photochemical deposition and etching for use in the microelectronics industry. The challenge is to understand the many different types of photoinduced processes on surfaces and how the presence of the surface perturbs the photodissociation dynamics of the adsorbate. Insulator surfaces typically transmit ultraviolet and visible light, thereby making substrate-induced processes less probable than on metal surfaces. This makes them better substrates for studying processes driven by adsorbate excitation.

CINO was chosen for a variety of reasons. The gas-phase photochemistry has been studied in great detail and exhibits many characteristic features. The dissociation proceeds on a repulsive surface, and thus should occur before energy is transferred to the surface. The NO product can be very sensitively detected with resonance-enhanced multiphoton ionization. This provides an unambiguous identification of NO photoproducts. In addition, rotational and vibrational state distributions can provide valuable dynamical information lacking in TOF studies.

CINO has a fairly low bond dissociation energy ($D_0 = 13,000 \text{ cm}^{-1}$) and absorbs light in the visible and ultraviolet, a region easily accessible with tunable dye lasers. At 365 nm, excitation is via a parallel transition $S_3(2^1A') \leftarrow S_0(1^1A')$ yielding rotationally hot NO ($J''_{\text{peak}} = 46.5, v''=0$). Both NO spin-orbit states are nearly equally populated and there is a large propensity to form NO $\Pi(A'')$, the Λ -doublet component perpendicular to the plane of NO rotation. These signature features make it very easy to determine if the presence of the inert crystal perturbs the photodissociation dynamics of CINO.

The main modification to the UHV chamber necessary for these experiments was the introduction of LN₂ cooling, in addition to the ability to heat the surface. The crystal was dosed with CINO using a pulsed molecular beam. The coverage on the surface was varied by either changing the opening of the nozzle by controlling the voltage on the

piezoelectric crystal, or by varying the dosing time, Δt . TPD experiments were also incorporated in order to characterize the adsorption of ClNO on the surface.

The surface was cooled with an open loop liquid nitrogen flow system. Liquid nitrogen flowed from a dewar outside the apparatus through an insulated feedthrough into the UHV chamber. Inside, flexible stainless steel bellows connected to a small liquid nitrogen reservoir. A sapphire plate joined the molybdenum surface holder to the reservoir. The sapphire acted as a thermal switch permitting cooling down to 85 K as well as high temperature annealing. Auger electron spectra (AES) of the MgO crystal could be taken at room temperature with a primary energy of 3 kV, but not at liquid nitrogen temperature due to charging of the crystal.

The photolysis laser was a XeCl excimer pumped dye laser system operating at 365 nm. In order to obtain a uniform beam profile, the beam was expanded using a telescope and only the center portion was used. The laser beam diameter could be varied from 1 to 5 mm. For TOF measurements the laser beam diameter was ~ 5 mm. Resonance-enhanced multiphoton ionization (REMPI) was used to measure the rotational state distribution of NO molecules leaving the surface after photolysis, as described before. In order to quantitatively determine the ClNO dosage in this experiment, a method which is typically used for ionization gauge calibration was used. It makes use of the fact that the flux of molecules from a pressure stabilized reservoir through a known conductance into an evacuated chamber is fully computable.

ClNO was adsorbed molecularly on the 85 K rough MgO(100) surface. Contrary to what has been seen with many other systems, no parent desorption is seen. Only one channel, photodissociation of ClNO, was seen. Time-of-flight distributions of the Cl and NO photofragments were very broad and slow compared to gas-phase photodissociation distributions. NO rotational distributions were cold and could be fit with a Boltzmann temperature of ~ 140 K, very different from the 'hot' nonstatistical gas-phase distributions. These results, in addition to the temperature programmed desorption (TPD) data, suggest that ClNO aggregates as islands on the surface. The islands may originate from defect sites. Photolysis products produced within the islands probably undergo multiple collisions, quenching their nascent distributions before their release.

III. PUBLICATIONS

1. *Molecule-Surface Dissociative Scattering of n-C₃F₇NO from MgO(100) at Hypethermal Energies: Nascent NO(X²Π)*, E. Kolodney, D. Baugh, P.S. Powers, H. Reisler and C. Wittig, *J. Chem. Phys.* **90**, 3883 (1989).
2. *Molecule-Surface Collision-Induced Excitation and Dissociation: n,i-C₃F₇NO, C₆F₅NO, 2-Methyl, 5-Vinyl Tetrazole and C(NO₂)₄ with MgO(100) Surfaces at E_{incident} ≤ 7.5 eV*, E. Kolodney, P.S. Powers, L. Iwata, H. Reisler, C. Wittig, I.B. Mishra, and C. Capellos, *Proceedings of the 9th Int. Symposium on Detonation, Portland, Oregon* (1990).
3. *Molecule-surface collision-induced dissociation of neutral polyatomics: Product state resolution, mechanisms and extensions at E_{incident} < 7.5 eV* C. Wittig, E. Kolodney, P.S. Powers, L. Iwata, H. Reisler, I.B. Mishra, and C. Capellos, *JANNAF Proceedings* (1990).
4. *NO(X²Π) product state distributions in molecule-surface collision-induced dissociation: Direct inelastic scattering of n,i-C₃F₇NO from MgO(100) at E_{incident} ≤ 7.5 eV*, E. Kolodney, P.S. Powers, L. Iwata-Hodgon, H. Reisler, and C. Wittig, *J. Chem. Phys.* **94**, 2330 (1991).
5. *Effect of surface temperature on the collision-induced dissociation of i-C₃F₇NO scattered from MgO(100), GaAs(100) and Ag(111)*, P.S. Powers, E. Kolodney, L. Hodgson, G. Ziegler, H. Reisler, and C. Wittig, *J. Phys. Chem.*, **95**, 8387 (1991).
6. *Photodissociation of ClNO on MgO(100)* L. Hodgson, G. Ziegler, H. Reisler, and C. Wittig, manuscript in preparation.

IV. TALKS AND PRESENTATIONS AT MEETINGS

1. C. Wittig, "Molecule-Surface Collision-Induced Dissociation," Reilly Lectureship, University of Notre Dame, Fall 1988
2. E. Kolodney, "Molecule-Surface Dissociative Scattering of n-C₃F₇NO from MgO(100)," ACS Meeting, Los Angeles, September 1988.
3. P.S. Powers, "Molecule-Surface Dissociative Scattering from MgO(100)," Gordon Research Conference on Surface Dynamics, August 1989.
4. C. Wittig, "Molecule-Surface Collision-Induced Excitation and Dissociation: n,i-C₃F₇NO, C₆F₅NO, 2-Methyl, 5-Vinyl Tetrazole and C(NO₂)₄ with MgO(100) Surfaces at E_{incident} ≤ 7.5 eV," 9th Int. Symposium on Detonation, August 1989.

5. C. Wittig, "Collision-Induced Dissociation on Surfaces", AFOSR Contractors Meeting, Captiva Island, Fl., Oct. 1989.
6. C. Wittig, E. Kolodney, P.S. Powers, L. Iwata, H. Reisler, I.B. Mishra, and C. Capellos, "Molecule-Surface Collision-Induced Dissociation of Neutral Polyatomic: Product State Resolution, Mechanisms and Extensions at $E_{\text{incident}} \leq 7.5 \text{ eV}$ ", JANNAF Meeting, Oct. 1989, Pasadena, CA.
7. C. Wittig, "Molecule-Surface Collision Induced Dissociation", UC Santa Barbara, Nov., 1990.
8. H. Reisler, "Molecule-Surface Collision Induced Dissociation", Northwestern University, May 1991.
9. H. Reisler, "Molecule-Surface Collision Induced Dissociation", University of Illinois, Chicago, May 1991.
10. E. Kolodney, P.S. Powers, L. Hodgson, G. Ziegler, H. Reisler and C. Wittig, *Collision-induced dissociation on surfaces*, Symposium on Chemistry at Surfaces, UC Irvine, Oct. 21-24, 1990.

V. RESEARCH PERSONNEL

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