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13. ABSTRACT (Maximum 200 words)

Two aspects of molecular decomposition on MgO(100) surfaces were explored. Nitrogen dioxide entrained in a molecular beam was photoexcited and directed at a crystal surface. It had enough internal *plus* translational energy to undergo dissociation. The NO products, which were detected with state and angular resolution, were scattered preferentially in the specular direction and their internal energies were analyzed. The results showed that the collisional dissociation was rather efficient when the molecules possessed internal energies approaching dissociation energy. The photochemistry of CINO was examined on an insulator metal oxide and compared with the analogous gaseous phase photodissociation; a large, qualitative difference was observed. Defect-laden and relatively defect-free MgO(100) surfaces were used. Gas phase 355 nm photolysis yielded NO with a rotational distribution peaked sharply at N = 42, whereas adsorbed CINO always yielded NO with N < 10. The results suggested that CINO aggregated on the surface in a way that affects photon-induced processes.

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

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I. SUMMARY

The 365 nm photodissociation of nitrosyl chloride adsorbed on rough and smooth MgO(100) surfaces at 90 K has been studied with mass spectrometric product detection, as well as state-selective ionization detection of NO. Results of photofragment time-of-flight (TOF) spectra of Cl and NO, state-selective detection of the NO photofragment and temperature programmed desorption (TPD) can be rationalized by a mechanism in which ClNO grows on the surface in islands with MgO defects serving as nucleation centers. No significant differences are observed between the rough and smooth surfaces, although the number of defect sites, especially oxygen vacancies, on the latter is substantially reduced. An attempt was made to determine the geometry of the adsorbates on the surface using FTIR. The results did not show any particular order, reinforcing the conclusions of clustering and lack of orientation. Preliminary attempts to dissociate ClNO by impact of hyperthermal Xe atoms led to deposition of Xe on the surface without evidence of dissociation. Collision induced dissociation (CID) of highly excited NO₂ in the mixed $^2A_1/2B_2$ electronic system (NO₂^{*}) has been observed for the first time for well characterized MgO(100) surfaces with parent and product angular resolution at various internal and incident translational energies, and with product NO state-selected detection.

II. PROGRESS DURING 1 MARCH 92 - 31 MARCH 1995

II.1 PHOTODISSOCIATION OF ClNO ADSORBED ON MgO CRYSTALS

The photochemistry of adsorbed ClNO was examined on different MgO(100) crystals, *i.e.* rough versus relatively defect-free. In these studies, it was possible to demonstrate a large, qualitative difference in the photophysics and photochemistry of surface-bound versus gas phase moieties. Namely, the enormous dynamical bias that characterizes the gas phase system was eliminated in the corresponding surface-bound system.

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. Topics of interest include understanding 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 making substrate-mediated processes less probable than on metal surfaces. This makes them better substrates for studying processes driven by adsorbate excitation. In our studies of photodissociation of adsorbates on insulators, ClNO adsorbed at 90 K on both rough and

smooth MgO(100) surfaces was photolyzed at 365 nm. Reaction products were detected using a quadrupole mass spectrometer (QMS), and state distributions of NO fragments were determined using two-photon, two-frequency laser ionization. MgO is transparent to the 365 nm photolysis radiation, therefore substrate absorption and electron-induced processes seen on metal surfaces are unlikely. We assumed that since ClNO is weakly bound to the inert insulator surface, perturbation of its gas-phase potential energy surfaces should be slight. However, due to the weak bond to the surface, island formation is likely.

ClNO was chosen for several reasons. Its gas-phase photochemistry has been studied in great detail and exhibits several distinctive features. The dissociation takes place on repulsive surfaces, and thus should occur before energy can be transferred to the surface. The NO product can be very sensitively detected via resonance-enhanced multiphoton ionization (REMPI), thereby providing unambiguous identification of NO photoproducts. In addition, rotational and vibrational state distributions can provide valuable dynamical information lacking in TOF studies. ClNO 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. The 300 K absorption spectrum of ClNO consists of several broad absorption bands, which have recently been assigned by us. Its NO product state distributions, photofragment yield spectra, recoil anisotropy, rotational alignment, NO Λ -doublet populations, and the nature of the orbitals involved in the electronic transitions have been determined both experimentally and theoretically for excitation into several of its electronic states.

When ClNO is excited via the parallel transition, $S_3(2^1A') \leftarrow S_0(1^1A')$, at 365 nm, it yields rotationally 'hot' NO ($J''_{\text{peak}} = 42.5, v''=0$). 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 should facilitate the determination of perturbations by the inert crystal on the photodissociation dynamics of ClNO.

The experimental arrangement was largely similar to that used in previous work, and therefore only a brief description is given, emphasizing modifications introduced for the photodissociation experiments. The vacuum system consisted of three chambers - a source chamber containing the molecular beam, a buffer chamber and an ultrahigh vacuum (UHV) chamber. Recently the diffusion pumps have been replaced by turbomolecular pumps, resulting in a base pressure of 1×10^{-10} Torr. This low base pressure is especially important in experiments in which molecules are adsorbed on cold surfaces. The major

components are a rotatable sample manipulator equipped with liquid nitrogen cooling, two quadrupole mass spectrometers, an Auger electron spectrometer, a fast argon gun, a channeltron electron multiplier for ion detection via REMPI, a photolysis laser and a probe laser. The crystal was dosed with CINO using a pulsed molecular beam, and all experiments were performed at a backing pressure of 40-60 Torr neat CINO. 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 .

The MgO(100) crystal (Atomergic, 10 x 10 x 1 mm³) was cleaved in air. It was mounted on a molybdenum block which was resistively heated to 800 K for the experiments with the "rough" surface. In this case the surface can be characterized as clean but rough, exhibiting many steps, kinks and especially, oxygen vacancies. In order to "fill" the oxygen vacancies, the surface was annealed at 1000 K in 1×10^{-5} Torr of O₂ for several hours. The best results were obtained with a freshly cleaved surface, without prior Ar bombardment. Following this treatment, the diffraction patterns were greatly improved, and were typical of a "smooth" surface.

The surface was cooled with an open loop liquid nitrogen flow system. Inside, flexible stainless steel bellows connected to a small liquid nitrogen reservoir, and a sapphire plate joined the molybdenum surface holder to the reservoir. The sapphire acted as a thermal switch permitting cooling down to 90 K as well as high temperature annealing.

A quadrupole mass spectrometer oriented in line with the CINO molecular beam was used to determine the composition of the direct molecular beam. Another mass spectrometer, collimated with $\sim 5.5^\circ$ angular resolution, was used to detect products in the TPD and TOF experiments. The surface to ionizer distance was 8.4 cm.

In order to quantitatively determine the CINO dosage in this experiment, a method commonly 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. The determination of the sticking probability was achieved by dosing the surface with a CINO molecular beam, and comparing the background pressure in the UHV chamber when the surface was maintained well below and well above the CINO desorption temperature.

The TPD of CINO adsorbed on the smoother MgO(100) surface at 90 K was investigated under ultrahigh vacuum conditions. The crystal was treated in a way that

largely eliminated oxygen vacancies and yielded a relatively smooth surface. Angularly resolved TOF mass spectra were obtained. The TPD data indicated that ClNO desorbed at surface temperatures above 160 K for exposures (Θ) below 0.2 Langmuirs (L), while for higher values of Θ the main desorption peak was near 120 K. The higher temperature feature, which saturated at $\Theta \sim 0.3$ L was probably associated with binding to defect sites. Thermal desorption was believed to be molecular at all coverages.

Photolysis at 365 nm for $0.1 \leq \Theta \leq 5.0$ L yielded Cl and NO products having low average translational energies and broad translational energy distributions. State-selective resonance-enhanced multiphoton ionization (REMPI) spectra of NO photoproducts were recorded at $\Theta \geq 0.7$ L. The rotational distributions could be fit with a temperature of 110 ± 10 K, *i.e.* comparable to that of the substrate. These results differed dramatically from those obtained in the photodissociation of gas-phase ClNO, where the NO fragment had high translational and rotational energies. However, the results on smooth surfaces were similar to those obtained on rougher MgO(100) surfaces.

Our results indicate that the Cl and NO signals derive from direct photodissociation of ClNO adsorbed on MgO(100) both for a rough and the smooth surfaces. TPD studies have shown that ClNO adsorbs molecularly at 90 K and, therefore, the products cannot be due to laser-induced desorption of thermal decomposition products of ClNO on the surface. The most convincing evidence against gas-phase photodissociation came from the NO rotational distributions which were very different from those obtained in the gas-phase photolysis of ClNO at any wavelength. We also verified that the signal was not due to photodesorption of ClNO followed by photolysis, and that multiphoton absorption of the probe laser light by background ClNO is insignificant.

MgO(100) has many defect sites, predominantly oxygen vacancies. Our results suggest that some ClNO dissociatively adsorbs on the MgO surface with the chlorine occupying defect sites in the MgO crystal. These Cl atoms apparently are strongly bound to the surface; they cannot be removed at surface temperatures as high as 800 K, but can be removed with fast argon bombardment. Thus, it is possible that the nucleation center is a Cl atom attached to a defect. On the smooth surface, the oxygen vacancies defect sites are largely eliminated, but other point defects, as well as kinks and steps cannot be removed and may still serve as initial nucleation centers.

Our studies on both rough and smooth MgO(100) surfaces at 90 K reveal only one channel, photodissociation of ClNO. The TOF distributions of the Cl and NO

photofragments are very broad and slow compared to gas-phase photodissociation distributions. NO rotational distributions are cold and can be fit with a Boltzmann temperature of ~ 100 - 140 K, very different from the nonstatistical gas-phase distributions. These results, in conjunction with temperature programmed desorption (TPD) data, suggest that ClNO aggregates as islands on the surface, nucleating around the defect sites.

We postulate that defect sites serve as centers for 2- or 3-dimensional islands. Nucleation around the defect takes place, and since ClNO molecules are held more weakly to each other than to a defect site, the TPD peak shifts to lower energies with higher coverages, exhibiting pseudo-second-order desorption behavior. At higher coverages, the attraction between ClNO molecules dominates the adsorption. In this region zero order desorption, typical of multilayers, clusters and chains of adsorbates is seen.

It is surprising that the desorbates have average kinetic energies of ~ 10 meV since in the gas-phase photodissociation Cl and NO have 580 meV and 670 meV of translational energy, respectively. It appears that even at nominal submonolayer coverages photofragments can undergo multiple inelastic collisions with other molecules in the island and/or the surface before escaping, thereby losing their translational and rotational energies.

Since the nature and geometry of ClNO on the surface is yet unknown, it is difficult to determine the exact reaction dynamics. Therefore, in collaboration with Professor Bruce Koel of our department, the FTIR spectrum of ClNO on MgO(100) was investigated as a function of coverage. Good signals were obtained even for submonolayer coverages. The preliminary results suggested that ClNO adsorbed without preferred orientation, in accord with the interpretation that it aggregates in islands on the surface. Polarization experiments do not show a significant polarization dependence.

In another experiment we attempted to dissociate ClNO adsorbed on MgO(100) by impact of hyperthermal Xe atoms. No dissociation products have been detected, but Xe is deposited on the surface, and ClNO desorbes. This experiment was discontinued.

II.2 COLLISION INDUCED DISSOCIATION (CID) OF NO_2^* ON MgO

Combinations of translational and internal energies were employed for the first time to investigate the CID of molecules incident on a single crystal surface. NO_2 was chosen because of its almost continuous but structured absorption features and its long excited state lifetimes (*e.g.* ~ 50 μs), which are needed to achieve high concentrations of excited molecules striking the crystal surface. The surface used in the experiment was MgO(100),

an inert crystal that should minimize electron induced processes such as those seen on metal surfaces. Specifically, dissociation will be less likely due to electronic interactions with the crystal. The experiment was performed at various internal and incident translational energies, E_{inc} , with parent and product angular resolution and typical crystal temperatures of ~ 400 K. Besides the importance of this experiment to our understanding of activating chemical reactions, as well as intramolecular and crystal excitation, it is also relevant to the recombination of $O(^3P)$ with adsorbed NO.

When the probe laser was set to monitor a specific quantum state of NO and the excitation laser frequency was scanned, a CID yield spectrum was obtained. Comparing this spectrum to a similar one obtained in gas-phase collisions with an atomic beam of Ar revealed similar features for the NO_2^* CID on MgO(100) and in the gas phase. Both curves carry the fingerprint of the NO_2 absorption spectrum confirming the CID mechanism. For example, the peaks in both CID spectra were the same as those observed in fluorescence excitation spectra of expansion cooled NO_2 .

The NO rotational distributions obtained for two different NO_2^* internal energies and two different values of the angle of incidence were rather similar. The lower and upper spin-orbit states, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, respectively, had comparable populations, with a slightly higher population in the lower spin-orbit state. Overall, the rotational distributions were similar, and corresponded to 450 K Boltzmann distributions. Significant differences were only observed at high J'' .

The angular dependence of the NO state distribution on the scattering angle, θ_s , was investigated at $\theta_i = 40^\circ$. The yield was most intense near the specular angle, $\theta_s = \theta_i$. When monitoring NO at $\theta_s = 70^\circ$, the signal dropped, as with scattered NO, indicating that NO_2^* CID on MgO(100) occurred via direct inelastic scattering rather than trapping-desorption.

The NO rotational distributions were similar for the cases of NO_2^* CID and NO scattered inelastically from MgO(100), and the degree of spin-orbit excitation was also similar for these two experiments, *i.e.* the $[^2\Pi_{3/2}]/[^2\Pi_{1/2}]$ ratio is \sim unity. This is noteworthy, since gas phase NO_2 unimolecular decomposition is known to result in significantly colder spin-orbit ratios, which are thought to be established at large interfragment distances. However, if scattered NO_2 acquires enough internal energy to cause its unimolecular decomposition rate to be in the subpicosecond regime, it will fragment a few Å from the surface, and interaction of the NO product with the surface is inevitable. In this case, the decomposition step cannot be taken as separate from the molecule-surface

interaction. The θ_i dependence of the NO distributions suggests that the normal component of E_{inc} contributes more to dissociation than does the parallel component.

These experiments are continuing with an improved experimental arrangement that allows us to obtain better angular distributions and explore the role of attractive interactions between the surface and the O and NO dissociation products.

III. PUBLICATIONS

1. *The photodissociation of ClNO on rough MgO(100) surface*, G. Ziegler, H. Ferkel, L. Hodgson, H. Reisler, and C. Wittig, *Can. J. Chem.*, **72**, 737 (1994).
2. *365 nm photo-induced dynamics of ClNO on MgO(100)* H. Ferkel, L. Hodgson, J. Singleton, P. Blass, H. Reisler and C. Wittig, *J. Chem. Phys.*, **100**, 9228 (1994).
3. *Molecule-surface collision-induced dissociation of highly excited NO₂ on MgO(100)*, H. Ferkel, J. Singleton, C. Wittig and H. Reisler, *Chem. Phys. Lett.*, **221**, 447 (1994).
4. *FTIR spectroscopy of ClNO adsorbed on MgO(100)*, X. Chen, H. Ferkel, H. Reisler, C. Wittig and B.E. Koel, manuscript in preparation.

IV. PRESENTATIONS AT MEETINGS

1. L. Hodgson, G. Ziegler, H. Reisler and C. Wittig, *Photodissociation of ClNO adsorbed on MgO(100)*, ACS Meeting, San Francisco, April 1992.
2. H. Reisler, *Photodissociation Dynamics of Fast Evolving States*, ACS Meeting, Washington, D.C., August 1992.
3. H. Reisler, *Unimolecular and bimolecular reactions in crossed molecular beams and on surfaces*, Gordon Research Conference on Molecular Energy Transfer, June 1993.
4. H. Ferkel, J. Singleton, L. Hodgson, H. Reisler and C. Wittig, *The photochemistry of ClNO on MgO(100)*, Gordon Research Conference on the Dynamics of Surface Interactions, Aug. 1993.
5. H. Ferkel, J. Singleton, H. Reisler and C. Wittig, *The collision-induced dissociation of highly excited NO₂ on surfaces*, ACS Meeting, San Diego, March, 1994.

6. H. Reisler, *Unimolecular and bimolecular reactions in crossed molecular beams and on surfaces*, Inf. Conference on Photochemistry, Toronto, May 1994.

V. RESEARCH PERSONNEL

Lori Hodgson — graduate student, Ph.D. 1993, research described under II.1
James Singleton — graduate student, M.Sc. 1995, research described under II.2
Peter Blass — postdoctoral fellow
Hans Ferkel — postdoctoral fellow
Bruce Koel — senior collaborator, USC
Scott Powers — graduate student, Ph.D. 1992, research described under II.1
Günter Ziegler — postdoctoral fellow