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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. Following collision, it had enough internal <i>plus</i> 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 ClNO was examined on MgO 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 at high rotational levels, whereas adsorbed ClNO always yielded cold NO. The results suggested that ClNO aggregated on the surface in a way that affects photon-induced processes. The gas-phase photodissociation dynamics of FNO and methyl nitrite were examined as candidates for comparisons with surface photolysis.				
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(Grant No. F49620-92-J-0230)

FINAL TECHNICAL AND EVALUATION REPORT

5/1/ 1992 - 4/30/1995

PARENT AFOSR AWARD: Grant No. F49620-92-J-0168

**GAS-SURFACE INTERACTIONS NEAR
DISSOCIATION THRESHOLD**

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Final Technical Report:

The amount of funding under the AASERT program for the period 05/01/92 - 04/30/95 is \$94,091 (\$31,364 per year) and two (2) graduate students, James Singleton and James Brandon, were supported under this award for the period.

The graduate students (partial support) were involved in work on two projects: (i) the photodissociation dynamics of XNO molecules (X=Cl,F) on surfaces, and (ii) the collision induced dissociation of NO₂ on MgO single crystal surfaces.

The 365 nm pulsed laser photolysis of nitrosyl chloride adsorbed on a rough and smooth MgO(100) surfaces at 90 K has been studied. Mass spectrometric detection was used to record TOF product distributions by monitoring Cl⁺ and NO⁺ ions as a function of flight time. These ions can derive from parent ClNO, which fragments completely in the mass spectrometer, as well as from Cl and NO photofragments. The TOF distributions are considerably slower than for the corresponding gas phase photodissociation process. NO was also detected state selectively by using resonance enhanced multiphoton ionization (REMPI) and a product channel is seen corresponding to direct photolysis of the adsorbate. State-selective detection of the NO photofragment shows that rotations are quenched markedly yielding a Boltzmann distribution at T ~ 100-140 K, even at low coverages, which is close to the surface temperature. At a similar wavelength, gas-phase photodissociation of ClNO produces highly rotationally excited NO with a distinctive non statistical distribution. Our studies suggest that, contrary to the gas-phase photolysis results, Cl and NO are not ejected rapidly following photolysis of surface-bound species on a repulsive potential energy surface. We postulate that ClNO grows on the surface in islands with MgO defects serving as nucleation centers. Photofragment rotational and translational energy is quenched efficiently due to strong attractive interactions that equilibrate NO to the surface temperature. Desorption of intact ClNO may also take place, but following (i.e., not during) the

photolysis pulse. Such desorbed species can contribute to the TOF spectra, but not the REMPI spectra. Results on "smooth" vs. the "rougher" surfaces do not show qualitative differences. Work in collaborations with Prof. Bruce Koel, using FTIR spectroscopy concerned the determination of the structure of surface-bound ClNO using FTIR spectroscopy. It showed that ClNO probably lies rather flat on the surface, without a specific orientation. In general terms, it corroborates the mechanism proposed by us.

Other molecules whose photodissociation was looked at carefully was FNO and methyl nitrite. These molecules are very good candidates for surface studies, and in fact, in Prof. Koel's group FTIR studies of methyl nitrite on surface are now in progress. In the FNO experiments reflection-type structures in the rotational distributions of NO were studied. Exciting quasi bound states with zero quanta of bending vibration in the FNO(S₁) state yields Gaussian-type rotational distributions, while excitation of states with one bending quantum leads to bimodal distributions. In the latter case, the ratio of the two intensity maxima depends on the number of NO stretching quanta in the S₁ state. The experimental rotational state distributions can be explained as the result of a dynamical mappings of the stationary wave functions on the transition line onto the fragment rotational quantum number axis. Preliminary observations of the adiabatic and nonadiabatic state-specific NO spin-orbit and Λ -doublet population ratios were also made. For all excitation energies both the vibrationally adiabatic and nonadiabatic channels exhibited the same spin-orbit preference, $\text{NO}(^2\Pi_{3/2}) = \text{NO}(^2\Pi_{1/2})$ and the Λ -doublet component perpendicular to the NO plane of rotation, $\Pi(A'')$ is preferentially populated.

In the S₁ ← S₀ state-specific photofragment yield spectra (PHOFRY) of jet-cooled FNO strongly asymmetric features were observed and interpreted as Fano profiles, arising from interference between direct and indirect dissociation following excitation to a region near the top of a barrier on the S₁ potential energy surface. NO

final state selected spectra were fitted to a Fano line shape equation. The profiles obtained when monitoring NO in $v = 1$ and $v = 2$ in the region $S_1(200) \leftarrow S_0(000)$ transition are different due to different phase-shifts associated with the vibrationally adiabatic ($v = 2$) and nonadiabatic ($v = 1$) dissociation channels. This leads to coherent control of the NO [$v = 1, J / v = 2, J$] ratios which can vary by a factor of ~ 40 when the dissociation wavelength is changed within the (200) resonance.

In addition, the state-specific photofragment yield spectra of methyl nitrite in the $S_1 \leftarrow S_0$ absorption system at wavelengths $\lambda = 344\text{-}400$ nm were investigated, by monitoring selected rotational levels in NO $v = 0, 1$ and 2. The spectra exhibit bands which are assigned to both the syn- and anti-rotamers with origins at 380 nm and 388 nm, respectively. The energy separation of the band origins suggests that the order of stability for the two rotamers is reversed in the excited state, with the anti-rotamer more stable by ~ 290 cm^{-1} . The appearance thresholds and relative intensities of the monitored NO rovibrational levels support the previously proposed mechanism where nonadiabatic vibrational predissociation is preferred.

Our earlier studies of molecule-surface CID were extended to the case of NO_2 , which has been implicated as the emitting species in shuttle glow phenomena. The glow is believed to derive from the recombination of NO and atomic oxygen, yielding internally excited NO_2 . Because the NO_2 zeroth order $2B_2$ excited state is strongly coupled to the $2A_1$ ground state, levels formed in recombination reactions emit throughout the visible. In our experiments, the reverse process was examined. Namely, NO_2 entrained in a molecular beam was directed at a crystal surface and was photoexcited 2 cm (10 ms) before reaching the surface. The incident molecules had enough internal *plus* translational energy to undergo CID, which was observed for a range of NO_2 internal excitations. Unexcited NO_2 yielded no signal. Additionally, NO was detected with state and angular resolution and it was shown

that products were scattered preferentially in the specular direction, ruling out a long residence time on the surface. It is most likely that NO_2 decomposes rapidly following impact with the surface, in accord with $k(E)$ measurements that indicate subpicosecond lifetimes for excess energies $> 500 \text{ cm}^{-1}$. This was the first demonstration of such an effect and supports the thesis that NO_2 is responsible for the shuttle glow.

Two students worked on this project. James Brandon obtained his Ph.D. in 1995 with a thesis entitled, "State-Specific Photodissociation of Small Polyatomic Molecules: Nitrosyl Fluoride and Methyl Nitrite". James Singleton has decided to leave with an M.Sc. degree and his thesis entitled, "Gas-Surface Collision Induced Dissociation of Highly Excited NO_2 " is now in preparation. James Brandon and James Singleton are United States citizens. Verification was made through presentation of their birth certificates stating their birthdates and birthplaces, as well as their social security numbers.

List of people involved in the project

Prof. Curt Wittig, Prof. Hanna Reisler, Dr. Günter Ziegler, Dr. Hans Ferkel, Dr. Peter Blass, Lori Hodgson.

List of Publications by the students:

Experimental probes of dissociative states: Fano profiles in the state-specific photodissociation of FNO, J.T. Brandon, S.A. Reid, D.C. Robie and H. Reisler, J. Chem. Phys., 97, 5246 (1992).

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