Optically Driven Surface Reactions: Evidence for the Role of Hot Electrons

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(Received 2 May 1988)

Evidence is presented for the role of excited conduction electrons in the laser-induced desorption of NO from Pt(111). State-specific detection of the desorbed NO establishes that the rotational distributions are non-Boltzmann, that the spin-orbit population is inverted, and that both the translational and vibrational distributions are uncorrelated with the laser-induced surface-temperature jump. The role of optically excited substrate electrons in driving the desorption process is evidenced by a dramatic dependence of the vibrational and translation energy distributions on the desorption-laser wavelength.

PACS numbers: 82.20.Rp, 68.45.Da, 82.20.Kh, 82.65.Pa

A range of recent experiments have sought to utilize lasers to drive chemical and physical processes at surfaces.[1-5] Many of the ensuing reactions can be understood phenomenologically in terms of thermal pictures in which the laser simply creates a transient, elevated thermal phonon bath. While exploitation of the spatial and temporal attributes of lasers to induce controlled chemistry and physics is of great interest, the ability to understand responses to nonthermal and molecule-specific transients driven by the incident photon field offers a tremendous opportunity for advancing our knowledge of surface processes. In this Letter we report the results of final-state–resolved experiments that implicate *nonthermal* mechanisms in the laser-induced molecular desorption of NO from single-crystal Pt(111). The experiments described herein differ from earlier studies of laser-induced–desorption (LID) dynamics[1-5] in two important regards: (1) the photon energies used were well below both the substrate work function and the gas-phase electronic transitions associated with the adsorbate species; (2) the wavelength dependence of the desorption process was examined. We observe a remarkable dependence on the desorption-laser wavelength of the translational and vibrational energy distributions, providing a novel window onto the role of hot electrons in molecular excitation processes at metal interfaces.

The ultrahigh-vacuum chamber and specimen used in this work, along with the details of surface preparation and characterization, have been described previously.[6] The sample was a 7-mm-diam by 1-mm-thick Pt(111) crystal which had either been saturated with NO at 120 or 220 K. Results from a variety of laboratories indicate that the latter sample preparation procedure produces a 2×2 low-energy electron diffraction (LEED) pattern (corresponding to a coverage of $\frac{1}{4}$ monolayer[7]) with the NO adsorbates binding primarily in atop sites with the N-end down.[8,9] Temperature-programmed desorption gives a major desorption feature at 350 K characterized by the first-order kinetic parameters $\nu = 10^{16}\ \mathrm{s}^{-1}$ and $E_a = 25$ kcal/mol (1.08 eV).[10] Saturation exposures at 120 K result in ≈50% greater coverage of NO compared to saturation exposures at 220 K. There is little corresponding change reported in the LEED[7] or electron-energy-loss spectroscopy[8] (EELS) results and the nature of the binding site of the additional NO is uncertain. The excess adsorbate desorbs around 195 K.

The desorption-laser pulse was derived from a *Q*-switched yttrium-aluminum-garnet (YAlG) laser. The laser output was multimode with an output temporal profile at 1064 nm between Gaussian and "top hat" with a 15-ns FWHM. Second- and third-harmonic generation gave pulses of 11 and 9 ns FWHM, respectively, again with a nearly top-hat temporal profile. The spatial beam profile was shaped by a series of apertures. Typically the beam cross section at the Pt(111) crystal position, monitored with a beam sampler and linear diode array (0.25-μm element spacing), was intermediate between Gaussian and top hat in character, with a beam diameter of 1.0 mm FWHM (all wavelengths). Pulse energies were adjusted by use of a half-wave retardation plate and thin-film polarizer. With use of the laser-heating formulation discussed by Ready,[11] pulse energies of the fundamental and the harmonics were adjusted to produce equivalent 100-K temperature jumps (e.g., 380-μJ pulses at 355 nm; 560 μJ at 532 nm; 960 μJ at 1064 nm). Under these irradiation conditions about 10^{-5} of the local adsorbate coverage was desorbed on each shot, resulting in a decrease in LID signal of about 10% over 1.2×10^4 shots. The sample was regularly redosed to minimize effects due to changes in coverage.

The desorbed molecules were probed with a tunable, frequency-doubled dye laser around 225 nm by laser-induced fluorescence (LIF). Kinetic-energy distributions for a specific internal state (vibrational v; spin-orbit Ω, rotational J, and lambda doublet Λ; total internal energy E_{int}) were extracted from optically detected time-of-flight (TOF) spectra obtained by the variation of the time delay between the firing of the desorption- and probe-laser pulses. Internal-state distributions were obtained by our scanning the probe-laser wavelength through the NO absorption spectrum at fixed time delays. The output of the probe laser had a bandwidth of 0.07 cm^{-1}, a pulse length of 7 ns FWHM, a beam diameter of 1.0 mm, and an energy of 30 μJ. The relative timing jitter between desorption and probe lasers was ±10 ns. Control experiments were performed to confirm that the LIF intensities recorded as functions of (Ω, J, Λ) for a room-temperature reference cell were linear with laser energy and gave an equilibrium internal-state distribution.

Typical TOF spectra following laser excitation at 532 nm are shown in Fig. 1. These were acquired at a flight distance, Δz, of 3.81 mm while probing desorbed $\mathrm{NO}[v=0; F_1, J=6.5, \Pi(A'); E_{\mathrm{int}}=80.3\ \mathrm{cm}^{-1}]$. The TOF spectra were analyzed by nonlinear least-squares fits with the general form $I(v)=v^4\exp[-(a+bv+cv^2)]$, which reduces to that of a Maxwell-Boltzmann number-density distribution for $b=0$.[2,12] TOF spectra for surfaces saturated at 120 K [see Fig. 1(a)] were best fitted by the sum of two velocity distributions, similar to reports for visible LID from NO/Pt(foil)[2,12] and ultraviolet LID from NO/Ni(100)-oxide.[5] The TOF spectra for surfaces saturated at 220 K [see Fig. 1(b)] were well represented by a single, nearly Maxwell-Boltzmann velocity distribution. In this communication we concentrate on results for the 220-K saturated surface where the nature of the adsorbed NO is more fully characterized. The flux-weighted average kinetic energy $\langle E_k \rangle/2k$ for the 220-K saturated surface was ≈1200 K, substantially in excess of the calculated[11,12] $T_s(\mathrm{max})=320$ K. TOF spectra were recorded for values of Δz ranging from 3.17 to 10.16 mm and gave equivalent kinetic-energy distributions. Measurements were made for several $F_1(^2\Pi_{1/2})$ and $F_2(^2\Pi_{3/2})$ rotational levels in $v=0$ of total internal energy up to 738 cm^{-1}, and for $v=1$ up to 2330 cm^{-1}. $\mathrm{NO}(v=0; F_2)$ species were observed to have slightly higher average kinetic energies ($\langle E_k \rangle$) than $\mathrm{NO}(v=0; F_1)$ species of either the same J or E_{int}, and the $\mathrm{NO}(v=0; F_2)$ $\langle E_k \rangle$ increased slightly (≈10%) with J over the range $125 \leq E_{\mathrm{int}} \leq 738\ \mathrm{cm}^{-1}$. The $\langle E_k \rangle$ for $\mathrm{NO}(v=1; F_2)$ between $2038 \leq E_{\mathrm{int}} \leq 2330\ \mathrm{cm}^{-1}$ was identical to that for $\mathrm{NO}(v=0; F_2)$, $125 \leq E_{\mathrm{int}} \leq 738\ \mathrm{cm}^{-1}$.

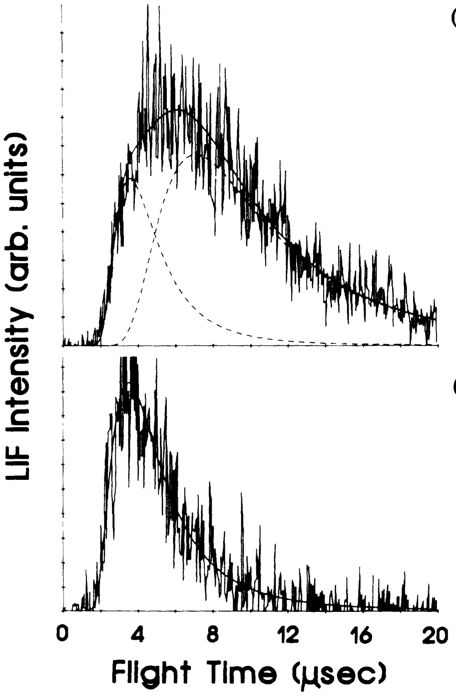

FIG. 1. LIF signal as a function of uv-probe delay acquired at a flight distance Δz of 3.81 mm for desorbed $\mathrm{NO}[v=0; F_1, J=6.5, \Pi(A'); E_{\mathrm{int}}=80.3\ \mathrm{cm}^{-1}]$. NO saturated surface: (a) $T_s=120$ K, (b) $T_s=220$ K.

The measured kinetic energies for several F_2 rotational levels, ranging in E_{int} from 125 cm^{-1} ($J=1.5$) to 738 cm^{-1} ($J=18.5$), are given in Fig. 2 for 355-, 532-, and 1064-nm excitation. The kinetic energies are quantitatively different for excitation at the YAlG fundamental compared to the harmonics. While 355- and 532-nm excitation gave $\langle E_k \rangle/2k$ centered about 1210±60 K, for 1064-nm excitation the $\langle E_k \rangle/2k$ is centered about 840±80 K. That is, regardless of internal energy, excitation at 1064 nm resulted in desorbed NO which is approximately 30% less translationally energetic than that observed with either 355- or 532-nm excitation. The desorption yields per photon absorbed for 532- and 355-nm excitation were comparable, approximately 5×10^{-8}. Excitation at 1064 nm resulted in a fourfold lower yield.

The density of $\mathrm{NO}(v=1)$ showed a marked wavelength dependence. Excitation at 355 nm resulted in a ratio of $v=1$ to $v=0$ signals which was identical (±30%) to that observed with 532-nm excitation, corresponding to a relative $v=1$ population of approximately

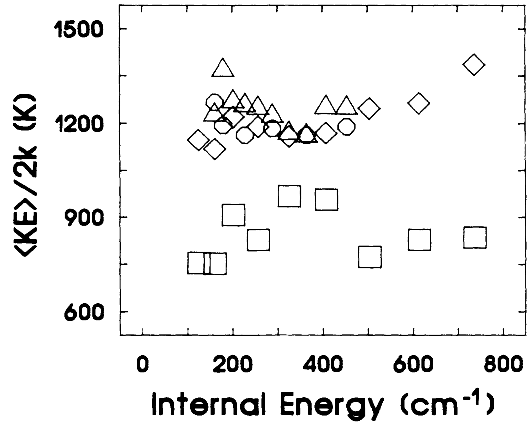

FIG. 2. Kinetic energy as a function of internal energy for O_{12} and P_{22} transitions at three excitation wavelengths: (□) 1064 nm, O_{12}, $\langle E_k \rangle/2k=840\pm80$ K; (◇) 532 nm, O_{12}, $\langle E_k \rangle/2k=1210\pm80$ K; (○) 532 nm, P_{22}, $\langle E_k \rangle/2k=1190\pm40$ K; (△) 355 nm, P_{22}, $\langle E_k \rangle/2k=1240\pm60$ K.

4% for either excitation wavelength. Efforts using the YAlG fundamental to induce desorption were unsuccessful in generating detectable levels of NO($v=1$). With correction for the reduced yield of NO in $v=0$ observed with use of 1064-nm compared to 532-nm excitation, the ($v=1$)/($v=0$) population ratio with 1064-nm excitation must be $<0.4\%$. This suggests that the $v=1$ channel is effectively closed with use of 1064-nm excitation.

LIF excitation spectra recorded for both spin-orbit states for excitation with the fundamental and harmonics at a time delay of 3.5 μs (corresponding to desorbed molecules with speeds of 10^5 cm/s) appear in a separate publication.[13] Interestingly, a spin-orbit-state population inversion was observed, with the population in the higher-energy F_2 ($\Delta E_{\text{s.o.}}=124$ cm^{-1}) state 4 times larger than in F_1. The J-state population distribution was non-Boltzmann, appearing to be independent of rotational energy for levels $E_{\text{int}} \leq 350$ cm^{-1}, and then rapidly decreasing for higher E_{int}. The rotational- and spin-orbit-state distributions were insensitive to desorption-laser wavelength.

The observed desorption-laser wavelength dependence of the internal- and kinetic-energy distributions allows a critical examination of the mechanisms coupling the incident photon energy to the subsequent desorption dynamics. In the present experiment, the low-energy photons are absorbed by the near-surface metal ($\alpha \approx 10^6$ cm^{-1}), creating low-energy electron-hole pairs. The optically excited electrons relax to some thermal electron distribution T_e on a subpicosecond time scale.[14] These hot electrons subsequently relax via electron-phonon scattering, producing a hot phonon distribution on the time scale of tens of picoseconds. It is this thermal phonon distribution that is credited for the laser-induced temperature jump discussed in the literature.[11,12] If this thermal phonon distribution were responsible for providing the energy necessary to desorb the NO in these experiments, one might expect rotational and translational accommodation as for NO thermally desorbed from Pt(111),[6] or the rotational and translational "cooling" seen for trapping desorption of NO from Pt(111) at higher T_s.[15] The results of the current work clearly do not show either of these effects.

The non-Boltzmann rotational population distributions are reminiscent of those obtained in gas-phase, electronic-excited-state photochemistry.[16] However, results from gas-phase experiments have also established that thermally driven reactions can produce non-Boltzmann product distributions because of the presence of steric and/or energy barriers along the reaction coordinate.[17-19] On surfaces, a variety of desorption processes, such as associative desorption, may occur and have been predicted to produce desorbed species with excess translational and internal energy.[20] However, for LID driven by interactions with the substrate phonons, exit-channel effects should be *independent* of the wavelength of the driving laser. Although exit-channel effects might be responsible for forming the observed rotational and spin-orbit population distributions, the observed dependence of mean kinetic energy and vibrational excitation on desorption-laser wavelength indicates that the desorbed NO retains some "memory" of the incident photon energy. Thus, it is the observed wavelength dependence which provides clear evidence for a desorption mechanism which is not solely driven by the lattice bath.

The precise nature of the excited states in the NO/Pt(111) system which give rise to this nonthermal process remains in question. We propose that optically generated electrons drive the desorption process. The optically generated electrons scattering at the adsorbate-covered surface interact with the adsorbed NO through the unoccupied $2\pi^*$ levels. These levels are located in a broad band centered approximately 1.5 eV above the Fermi level, as measured by inverse photoemission.[21,22] All of the desorption wavelengths used in this experiment are capable of generating nascent electrons which could couple to these states. Since the activation energy for desorption is approximately 1.08 eV, it is possible for a single-photon process to desorb the NO at any of the three wavelengths. From a simple characterization of the desorption energetics, two facts are apparent: (1) Essentially the total energy is required to desorb the nonthermal NO when exciting at 1064 nm [$E_{\text{photon}}(1.17\text{ eV}) - E_a \approx (E_{\text{int}}+E_k)_{\text{NO}}$]. (2) The $v=1$ desorption channel is closed for one-photon processes at the YAlG fundamental [$E_{\text{photon}}(1.17\text{ eV}) - E_a \ll (E_{\text{vib}}=0.23\text{ eV})_{\text{NO}(v=1)}$]. The lower kinetic energy and the failure to observe NO($v=1$) with 1064-nm excitation, and the observed linear dependence of yield on laser fluence, support a mechanism involving a single "hot" electron. An analogous model in which photogenerated charge carriers induce desorption has recently been proposed for NO on Si.[23,24]

This mechanism both accounts for the wavelength dependences in the desorption yields and dynamics, and addresses the source of the observed vibrational, rotational, and spin-orbit population distributions. Electron scattering through the adsorbate $2\pi^*$ state is analogous to the "harpooning" process observed in the gas phase, and could produce a transitory negative-ion resonance. This negative-ion state might be an intermediate state in the desorption process.[25] The anticipated differences in NO_a^- vs NO_a equilibrium geometries and vibrational frequencies should produce vibrationally excited desorbing species with vibrational-level population distributions determined by Franck-Condon factors. Although the specific rotational population distributions might arise from either dynamic or kinematic effects, the spin-orbit propensity most probably reflects electron symmetry considerations and nonadiabatic coupling.[26]

The wavelength dependences measured in these experiments demonstrate the capability of optically generated transients to drive chemical processes at surfaces through substrate-mediated channels. The role of nonthermal electrons and the subsequent implications for negative-ion resonances are strongly suggested by the observed kinetic-energy and vibrational-level distributions. The ability to both qualitatively and quantitatively account for the complex internal- and kinetic-energy distributions observed in such laser-induced desorption experiments is important for the development of a correct theoretical understanding of the relaxation of adsorbate-metal systems. The correct application of existing theories to the optical perturbation of an adsorbed layer is not trivial, and requires a detailed knowledge of the bound states and structure of the system. However, manipulation of nonthermal reactions in optically, *e*-beam, or ion-bombardment driven processes holds great promise for controlling chemical reactions at surfaces.

This work was partially supported by the U.S. Department of Energy, Office of Basic Energy Sciences (D.E.-AI05-84ER13150). We thank J. W. Gadzuk for many stimulating discussions. Two of us (S.A.B. and L.J.R.) are National Research Council–National Bureau of Standards Postdoctoral Research Associates.

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