

Desorption by Electronically Stimulated Adsorbate Rotation

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Time-of-flight laser resonance ionization is used to measure state-selective translational energies of neutral NO, CO, and metastable CO($a^3\Pi$) desorbed from Pt(111) upon electron impact. A novel and dominant NO channel has a threshold of ~ 6 eV and a peak translational energy of 0.05 eV. Lifetime calculations reveal a long-lived simple excitation ($5\sigma^{-1}$). Dynamical calculations reproduce translational and rotational energy distributions and suggest that the excitation frees the hindered rotation of NO.

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Electronic excitations can stimulate the desorption of atoms and molecules from surfaces. A detailed understanding has been elusive because a number of factors involving electronic structure, dynamics, and experiment are involved¹: the electronic and geometric structure of the surface, the lifetime and localization probabilities of excitations, the dynamics of atom motion on the relevant potential energy surfaces, the importance of various energy loss processes, and the yields and translational- and internal-energy distributions of the products. We combine here state-selective experiments on neutral NO and CO desorption from Pt(111) with theoretical analyses of electronic structure and dynamics. A relatively detailed model for a new mechanism of stimulated neutral desorption emerges.

We find evidence for a very low-energy desorption channel which dominates neutral NO production but not CO. The threshold for this channel correlates with a single-particle excitation which our lifetime calculations show to be a 5σ hole. Such an excitation in CO increases the number of 2π electrons through screening by the metal, which suggests that excited CO resembles the ground state of NO in bonding character (terminally bound and strongly rotationally hindered). By the same reasoning, excited NO would resemble O₂ and thus be a weakly bound, relatively unhindered rotor (O₂ is bound side-on by only ~ 0.3 eV). Dynamical calculations indicate that if the hindered-rotor to free-rotor transition is not considered, excitation decay retraps NO with high probability; however, its inclusion allows excited NO to access weakly binding regions of the ground-state potential energy surface, greatly enhancing the escape probability. Hence, the model that emerges is a two-step (Raman-type) process: The initial hindered-rotor ground state makes a transition to a long-lived and relatively free-rotor excited state,² followed by a second transition to a continuum level of the ground-state potential. Dynamical calculations based on this model closely reproduce the observed NO ($\nu=0$) translational and rotational energy distributions.

The experimental arrangement for the laser resonance-ionization detection of electron-stimulated desorp-

tion (ESD) neutrals is improved compared to that reported earlier³: The ion detector is now a 1.0-in.-diam dual microchannel-plate array. A tunable uv laser beam propagates parallel to the surface at a distance of 0.5 ± 0.02 cm. The translational energy is measured by variation of the time delay between the 250-nsec electron beam pulse and the 4-nsec laser pulse. The time delay, electron beam energy, and focus are under computer control.³ To obtain threshold measurements, the electron beam energy is scanned at a fixed delay time, with the electron pulse width lengthened to 800 nsec to increase the "window" of translational energies (e.g., $E_{\text{trans}} = 0.045\text{--}0.055$ eV).

The base pressure in the vacuum chamber is 8×10^{-11} Torr. The surface of the Pt(111) crystal was initially cleaned by heating to 1300 K in oxygen, followed by Ar⁺-ion bombardment. Before each run, it is again heated to 1300 K and rapidly cooled to 80 K for gas dosing. Auger-electron spectroscopy is used to determine the adsorbate coverage and monitor surface cleanliness. Unless otherwise stated, experiments were conducted at 80 K and saturation coverage.

NO is photoionized in a (1+1)-photon scheme with the laser tuned to the state-selective $A^2\Sigma^+(\nu') \leftarrow X^2\Pi_{1/2}(\nu)$ transition.³ To probe vibrational populations, the $(\nu',\nu) = (0,0)$ and (1,1) transitions provide a good signal-to-noise ratio, whereas the best signals for $\nu=2,3$ are found at (0,2) and (1,3).⁴ We found that the most sensitive (2+2)-photon scheme for CO ground-state detection incorporates the $A^1\Pi(\nu'=1) \leftarrow X^1\Sigma^+(\nu=0)$ transition.⁵ The $a^3\Pi$ is the most likely CO metastable to be observed⁶ in time-of-flight experiments, since its lifetime⁴ is 9 msec. We have confirmed this using a 1+1 ionization scheme involving the resonant step $b^3\Sigma^+(\nu'=1) \leftarrow a^3\Pi(\nu=2)$.

The ESD translational-energy distributions of neutral NO [Fig. 1(a)] show a peak at ~ 0.05 eV for $\nu=0$ and 1, dramatically lower than previous results from chemisorbed species on metals.⁷ However, $\nu=2$ and 3 exhibit a second peak at ~ 0.35 eV, clearly indicating the existence of two channels. The higher-energy channel yields vibrationally excited NO almost exclusively. The

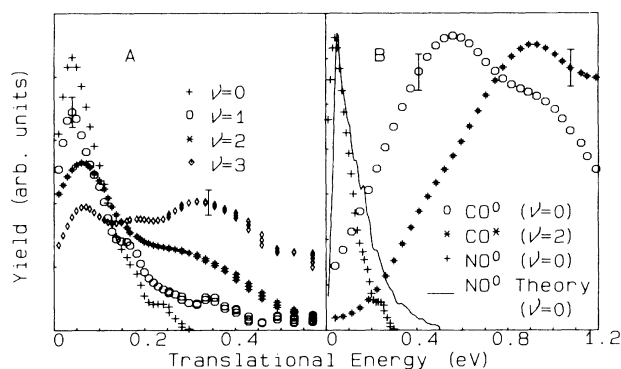


FIG. 1. (a) Translational-energy distributions for NO/Pt(111). The electron energy was 315 eV. For clarity, the vibrational populations are *not* relative (see text). The overall error in translational energy is less than 20%. (b) Translational-energy distributions for CO/Pt(111). Also shown is the comparison between the calculated and experimental $\nu=0$ NO^0 translational distribution.

$\nu=0$ and 1 distributions are independent of coverage, adsorption temperature up to 300 K, and excitation energy from 10 to 700 eV (precluding intermolecular interactions, specific site geometries, or physisorbed species as the origin of the low-energy channel). The vibrational populations for the window $E_{\text{trans}} = 0.045\text{--}0.055$ eV are 1.00, 0.58, 0.26, 0.43 for $\nu=0, 1, 2,$ and 3, respectively, obtained by summing of each rotational spectrum normalized by Franck-Condon factors.⁴ The rotational distributions in the range from 100 to 1800 cm^{-1} were approximately Boltzmann varying from 500 to 640 K. In contrast, the CO data [Fig. 1(b)] have no low translational energy peaks [ground-state CO ($\nu=0$) at ~ 0.5 eV and $a^3\Pi$ metastable CO ($\nu=2$) at ~ 1.0 eV], consistent with previous non-state-selectable observations.⁷

The thresholds for low- E_{trans} NO are shown in Fig. 2(a) and for high- E_{trans} NO and CO in Fig. 2(b). Since our thresholds are higher than those of observations on CO/Ru(0001) and CO/W,⁸ which had no E_{trans} selectivity, it is still possible that a low-probability low-energy CO channel exists.

The low-energy NO channel is a true stimulated process since the 6-eV threshold is well above the thermodynamic minimum and the product species are vibrationally hot. We model it as follows: We neglect the dissipation of vibrational energy through either substrate phonon or particle-hole creation as the characteristic times are slow.⁹ We also neglect trace impurities and defect sites, since the large desorption yields³ and the inverse coverage dependence in the specific yield¹⁰ suggest that majority-site contributions dominate.

The low energy threshold correlates with a single-electron excitation. The uv photoelectron spectrum¹¹

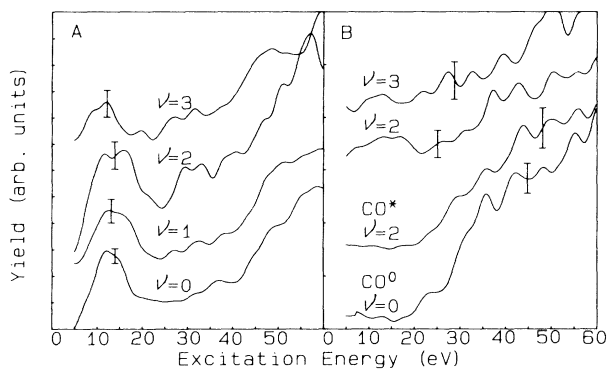


FIG. 2. (a) Threshold region for "slow" NO ($E_{\text{trans}} = 0.045\text{--}0.055$ eV). (b) Threshold region for "fast" NO ($E_{\text{trans}} = 0.3\text{--}0.5$ eV), ground-state CO ($E_{\text{trans}} = 0.28\text{--}0.46$ eV), and $a^3\Pi$ CO* ($E_{\text{trans}} = 0.91\text{--}2.5$ eV). The excitation energy is relative to the Fermi level of the substrate.

(UPS) for NO/Pt(100) has peaks (with respect to E_F) at 2.7 eV and 9.6 eV from the $2\pi_b$ (bonding) and the (near-degenerate) $5\sigma, 1\pi$ levels, respectively. For CO/Pt(111), the $5\sigma, 1\pi$ levels are at ~ 9 eV¹² with a total experimental width of ~ 4 eV. Thus the ~ 6 -eV threshold correlates with the 5σ level, the 1π being ruled out by lifetime arguments given below.

The final states available for the exciting and promoted electrons have a resonance from the $2\pi_a$ (antibonding) orbital. Although the $2\pi_a$ has not been observed for NO/Pt(111), inverse photoemission¹³ on CO/Pt(110) places it ~ 3 eV above E_F with ~ 3 eV total width. If we assume a similar resonance for NO/Pt, an enhancement in the 5σ excitation cross section would be expected at ~ 12 eV with total width of ~ 6 eV [as seen in Fig. 2(a)]. Similar density-of-states effects have been observed for OH* desorption from TiO_2 .¹⁴ The width of the $2\pi_a$ resonance suggests rapid ($< 10^{-15}$ sec) relaxation to the adiabatic excited state and thus permits us to focus on a screened 5σ hole.

The lifetimes of simple excitations in chemisorbed molecules have not previously been determined. We performed self-consistent *ab initio* calculations on several model NO-metal clusters. Since the 5σ and 1π orbitals are not involved in NO-metal bonding¹⁵ nor degenerate with substrate valence levels, the results are independent of the cluster used and holes in these orbitals decay most rapidly via a valence Auger process: A 2π electron fills the hole and another 2π electron is ejected into the continuum (2π orbital occupancy is increased by about one electron because of the efficient screening of the hole by the metal¹⁶). All other channels, such as those involving the metal orbitals directly or optical processes, are slower.

Although multicenter continuum functions are difficult to compute, an upper bound on the lifetime width

(Γ) may be found with use of a single-atom approximation. For the 5σ hole, we find a maximum Γ of 0.06 eV, with a most probable value of ~ 0.01 eV (obtained by separately summing contributions from each site). The 1π hole, whose Γ is tenths of volts, is too short lived to contribute substantially to the large observed desorption yield. This result is easily understood: No angular momentum needs to be transferred in order to fill a 1π hole with a 2π electron. However, one or two units of angular momentum must be exchanged in order to fill a 5σ hole (having atomic s and p_z character) by a 2π electron (of p_x or p_y character). Since the rate scales as $1/(2l+1)^2$, where l is the angular momentum transferred, more than an order of magnitude difference is found for the lifetime of 5σ vs 1π holes.

The excited-state potential energy surface corresponding to a screened 5σ hole is unknown. However, we can infer its character by an examination of the general trends of CO, NO, and O₂ binding to the metal. We propose that adsorbed CO, excited with a 5σ hole which has increased the 2π orbital occupancy through screening, bonds somewhat like ground-state NO. Similarly, excited NO may be expected to bond somewhat like ground-state O₂. This argument leads to our central concept: Excited- 5σ CO, mimicking ground-state NO,¹⁵ is strongly bound terminally and rotationally hindered as is the ground state of CO. Thus it does not desorb with high probability since substantial nuclear motion does not occur in the excited state because of the similarity of the two potential energy surfaces. However, excited- 5σ NO, mimicking O₂, is weakly bound by ~ 0.3 eV and prefers to lie down,¹⁷ in strong contrast to the above case.

Quantum dynamical calculations, which test this model against the observed translational- and rotational-energy distributions of the low-energy NO desorption channel, are made possible because only two modes are

strongly coupled, namely translation normal (z) to the surface or the Pt-NO stretch (306 cm^{-1})⁹ and hindered rotation (465 cm^{-1}).⁹ This is also a key finding of Tully and co-workers.⁹ The remaining four modes (if we neglect surface atom motion) are the two low-frequency hindered translations parallel to the surface (60 cm^{-1}),⁹ taken as frozen, the high-frequency NO vibration ($1516\text{--}1718\text{ cm}^{-1}$),⁹ taken as adiabatically separated, and the projection of the rotation onto the z axis, taken as conserved (uncorrugated surface). Thus for each projection (M) and NO vibration (ν) the molecule moves on a two-dimensional potential energy surface, dependent on the normal distance (z) of the center-of-mass (c.m.) from the surface and the angle θ that the NO bond makes with the surface normal. We take the ground state¹⁸ to be bound at all angles while strongly hindered in rotation by the narrow and deep well which corresponds to the N atom down ($\theta=0$), whereas we expect excited NO (with a 5σ hole) to be weakly bound with a slight preference to lie down ($\theta=\pi/2$). Thus we model the excited molecule as a free rotor in a weak Morse potential.

We compute the quantum time evolution of the ground-state wave packet ($|g(0)\rangle$) excited at $t=0$ from the ground level of the unexcited, vibrationless electronic potential energy surface to the excited electronic surface with ν' quanta of NO vibration weighted by the Franck-Condon (FC) overlap factor $|\langle\nu'|0\rangle|^2$. Then we integrate over excitation energies. The wave packet $|g(0)\rangle$ is initially highly localized about both $\theta=0$ and $z_e(0)$, the equilibrium distance of the c.m. from the surface with the N atom pointing down. The wave packet evolves under the influence of the excited-state Hamiltonian $H_2(M\nu')$ for various times weighted by the excited-state lifetime. Subsequently, it deexcites to the ground electronic surface with ν quanta, weighted again by the FC factor $|\langle\nu'|\nu\rangle|^2$. Hence, $P(Ej;M\nu)$ (the probability of desorbing into state $|Ej;M\nu\rangle$) is given by

$$P(Ej;M\nu) = \sum_{\nu'} |\langle\nu'|\nu\rangle|^2 |\langle\nu'|0\rangle|^2 \int_0^\infty dt e^{-\Gamma t} |\langle E_j; M\nu | g(t; M\nu') \rangle|^2, \\ |g(t; M\nu')\rangle = e^{-iH_2(M\nu')t} |g(0; M0)\rangle,$$

where $|Ej;M\nu\rangle$ is a scattering state of the unexcited Hamiltonian $H_1(M\nu)$ with total energy $E > 0$ and (asymptotically as $z \rightarrow \infty$) j rotational quanta.

Because of the flatness of the (free rotor) excited surface and the shifted equilibrium position (+0.8 bohr) of the weakly bound excited state, the wave packet spreads in angle and moves away from the metal surface. Those molecules deexciting near $\theta=0$ find themselves re-trapped by the strong binding potential, whereas NO molecules deexciting after reaching angles much greater than zero find themselves in a weakly bound potential and thus have a large probability of escaping.

The calculated NO ($\nu=0$) kinetic-energy distribution

with $\Gamma=0.01$ eV (the distribution is insensitive over $\Gamma \approx 0$ to 0.05 eV) is shown in Fig. 1(b). The calculated rotational distribution (obtained by integrating over all kinetic energies for each j) is non-Boltzmann, but is within experimental error in the range from 100 to 1200 cm^{-1} . Between 1200 and 1800 cm^{-1} of rotational energy, calculated populations are slightly above experimental values, possibly because the latter were obtained with a window of $E_{\text{trans}}=0.045\text{--}0.055$ eV. The qualitative agreement between theory and experiment is particularly significant because there was no optimization of the potential energy parameters. We therefore suggest that a

long-lived simple excitation which frees the adsorbate hindered rotation produces the dominant desorption mechanism for NO/Pt(111).

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