

## Electron-Stimulated Desorption of Neutral NO from Ni: State-Specific Resonance-Ionization Detection

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(Received 5 February 1985)

Laser resonance-ionization spectroscopy of nitric oxide (NO) molecules desorbed by electron impact from a polycrystalline nickel surface is discussed. This is the first time that ground-state rotational and vibrational populations have been probed for neutrals in electron-stimulated desorption. The results support previous studies that indicate that shallow valence-level excitations dominate the neutral desorption mechanism.

PACS numbers: 79.20.Hx, 33.10.Jz, 34.80.Gs, 68.45.Da

Electron-stimulated desorption (ESD) of atoms and molecules from surfaces is recognized as a bond-breaking process that is initiated by electronic transitions in the adsorbate-substrate complex.<sup>1</sup> Most of the work in this area has been concerned with ion desorption, but it is of great importance to the current overall understanding of the mechanisms that the processes of neutral desorption be examined. Previous efforts to detect the ESD of neutrals have relied on methods such as electron-ionization mass spectrometry,<sup>2,3</sup> time-of-flight detection of metastables,<sup>4</sup> optical radiation from electronically excited neutrals,<sup>5,6</sup> and laser-induced fluorescence.<sup>7</sup> In this paper, a tunable uv laser is used in a two-step resonance-ionization process to detect desorbed NO in specific rotational states of the  $v=0$  and  $v=1$  levels of the ground state. The results indicate that the molecules have high, nonthermal internal energies that do not obey Boltzmann statistics. This is an important result in that the energetics of the desorption process is reflected in the internal states of the molecule after it has left the surface. Furthermore, the population of specific rotational and vibrational levels can be monitored as a function of excitation energy in order to reveal thresholds and desorption channels. For the present system of NO adsorbed on Ni, the NO desorption thresholds for both the  $v=0$  and  $v=1$  rotational levels are below 9 eV, and there is no evidence for reneutralization above the thresholds.

There are two basic mechanisms that have been used to explain stimulated ion and neutral desorption. In the Menzel-Gomer-Redhead model,<sup>1</sup> the bond-breaking process is initiated by the promotion of valence electrons to a manifold of excited states, whereby neutral desorption can proceed from antibonding and nonbonding states or from the reneutralization of ions that fail to leave the surface. Threshold measurements<sup>2</sup> indicate that neutral desorption is predominantly initiated by shallow valence-level transitions. In the Knotek-Feibelman mechanism,<sup>1</sup> which was formulated specifically for maximal-valency oxides, Auger decay processes initiated by core-level excitations result in the departure of at least two elec-

trons in the adsorbate-substrate complex. A highly charged state is thus created, which decreases the probability of reneutralization<sup>8</sup> and can cause dissociation of the adsorbate.<sup>9-14</sup> The stimulated desorption of  $\text{NO}^+$ ,  $\text{CO}^+$ , and  $\text{O}^+$  from NO- and CO-covered transition-metal surfaces has received considerable attention recently<sup>9-14</sup> because of the appearance of multielectron excitations induced by core-level transitions. These excitations can arise either from Auger decay or by direct excitation *via* shakeup. Thus, one immediate interest in the NO/Ni system is to see if there are signs of the highly energetic core-level excitations in the rotational and vibrational populations of NO desorbed by electrons having energies greater than the  $\text{N}(1s)$  and  $\text{O}(1s)$  thresholds.

The experimental arrangement of the present study is similar to that used by Winograd, Baxter, and Kimock<sup>15</sup> for the detection of sputtered indium neutrals. The sample is a polished 99.99% pure polycrystalline Ni surface mounted in an UHV chamber which has a base pressure of  $2 \times 10^{-10}$  Torr. The Ni surface was initially cleaned by ion bombardment and thereafter by repeated resistive heating to 1300 K. Only trace amounts of ESD  $\text{H}^+$  and  $\text{F}^+$  ions and no  $\text{O}^+$  ions were observed from the bare Ni surface. Immediately after the resistive heating, the sample was cooled to 80 K before it was exposed to a saturation coverage [6 L, where 1 L (langmuir) =  $10^{-6}$  Torr sec] of NO from a dosing tube.

The tunable uv laser beam is generated by mixing of the second harmonic of a pulsed Rhodamine-590 dye laser with the 1064-nm fundamental of a Nd:YAlG (Nd-doped yttrium aluminum garnet) laser, which results in a bandwidth of  $2 \text{ cm}^{-1}$ . The 220–230-nm laser beam enters and exits the UHV chamber with minimal scattering through  $\text{MgF}_2$  windows and propagates parallel to the surface of the sample at a distance of 0.5 cm. The beam was focused by a cylindrical lens which produces a sheetlike ionization region approximately  $1 \text{ cm}^2$  in area and nearly 0.01 cm thick. The area of the electron beam on the sample surface is  $0.20 \text{ cm}^2$ ; thus, most of the desorbed neutrals pass through the laser-ionization region. The intensity of

the laser in the ionization region was generally 30 MW/cm<sup>2</sup>. All ion signals were collected with a quadrupole mass spectrometer.

The primary electron beam is pulsed on for 1–5  $\mu$ sec at a current density of  $3 \times 10^{15}$  electrons/sec-cm<sup>2</sup> and at a repetition rate determined by that of the YAlG laser (10 Hz). The delay time between the electron pulse and the 5-nsec ionizing laser pulse is adjusted to produce the maximum density of neutrals in the laser beam. In the present experiment, this density was close to  $10^8$  NO molecules/cm<sup>3</sup> for 300-eV electrons if we assume that the laser-ionization region is filled with desorbed neutrals. A 3- $\mu$ sec optimum delay indicates an average kinetic energy of  $0.1 \pm 0.05$  eV. This measurement is consistent with the recent values obtained by Feulner *et al.*,<sup>3</sup> using electron-impact neutral detection. The density of neutrals in the laser beam is estimated by the bleeding of NO into the chamber at a pressure that reproduces the ESD signal intensity. Given a velocity of  $10^5$  cm/sec, and a peak density of  $10^8$  molecules/cm<sup>3</sup>, the instantaneous flux,  $\Phi_n$ , of neutrals from the surface is  $10^{13}$  molecules/cm<sup>2</sup>-sec. For a surface coverage,  $\sigma$ , of  $10^{15}$  molecules/cm<sup>2</sup>, and a primary electron flux,  $\Phi_e$ , of  $3 \times 10^{15}$  electrons/sec-cm<sup>2</sup>, the cross section,  $Q$ , for the desorption of neutral NO by 300-eV electrons is estimated by the relation  $Q = \Phi_n / \sigma \Phi_e$  to be  $3 \times 10^{-18}$  cm<sup>2</sup>. This value, which ignores possible contributions from secondary electrons, is consistent with the neutral desorption cross sections previously estimated for covalent adsorbates.<sup>16,17</sup>

Rotational spectra for the transition<sup>18</sup>  $A^2\Sigma(v=0) \leftarrow X^2\Pi_{1/2}(v=0)$  are shown in Fig. 1 for NO molecules desorbed by 300- and 600-eV electrons. Similar spectra for the  $A^2\Sigma(v=1) \leftarrow X^2\Pi_{1/2}(v=1)$  transition were also obtained. The rotational and vibrational constants used to calibrate the spectra were obtained from Herzberg.<sup>18</sup> Although the data are currently limited by the laser bandwidth to a resolution of 2 cm<sup>-1</sup>, the separations of the  $R_{21}$  and  $R_{11} + Q_{21}$  transitions are adequate from  $J = \frac{15}{2}$  to  $J = \frac{33}{2}$  to permit the analysis of the rotational distributions in the  $v=0$  and  $v=1$  levels of the electronic ground state. The signals from the  $v=2$  and higher vibrational levels are too weak at the present time for adequate analysis. Also, no effort at this time was made to look for NO molecules that were desorbed in metastable electronic states. Before each spectrum was obtained, the surface was cleaned and redosed as discussed above. Each datum point of the 500-point spectra was averaged over at least fifty acceptable laser pulses before the dye laser was advanced to the next wavelength; if the laser energy did not fall within a window of  $\pm 50\%$  of the average, the signal from that pulse was discarded. The reproducible intensities of the rotational transitions were later normalized by a

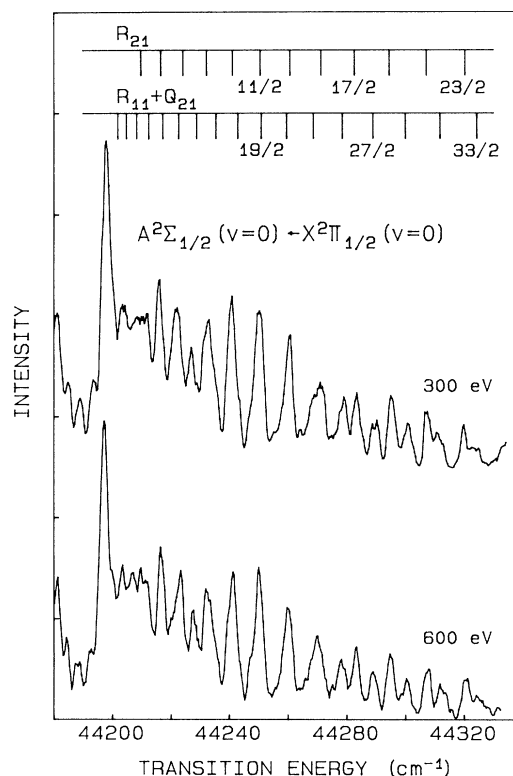


FIG. 1. Rotationally resolved spectra ( $v=0$ ) of NO molecules desorbed by 300-eV (top curve) and 600-eV (bottom curve) electrons from a polycrystalline Ni surface cooled to 80 K. The spectra are generated by resonance absorption of a 266-nm photon in this region, followed by the absorption of another 226-nm photon for photoionization.

300-K gas-phase NO calibration spectrum obtained at the same laser intensity in order to eliminate saturation effects. The results are plotted in Fig. 2.

It is clear from these initial results that the NO molecules are desorbed from the 80-K surface with high rotational energies that exceed 400 K and, thus, do not obey Boltzmann statistics. This also can be seen by the large and reproducible deviations from the Boltzmann line in Fig. 2. Furthermore, the 700-K vibrational "temperature," which is determined from the ratio of the summed rotational line intensities for the  $v=0$  and  $v=1$  transitions, is much larger than the 400-K rotational "temperatures." As discussed earlier, the translational energy is even higher at 1200 K (0.1 eV). Thus it appears that most of the nonthermal neutral molecular energy is translational, followed by vibration and rotation. A recently discussed dynamical model<sup>3</sup> for neutral desorption emphasizes the role of the repulsive region of the ground-state interaction potential between the adsorbed molecule and the surface in producing the high kinetic energies. The present results lend further support to this model, although

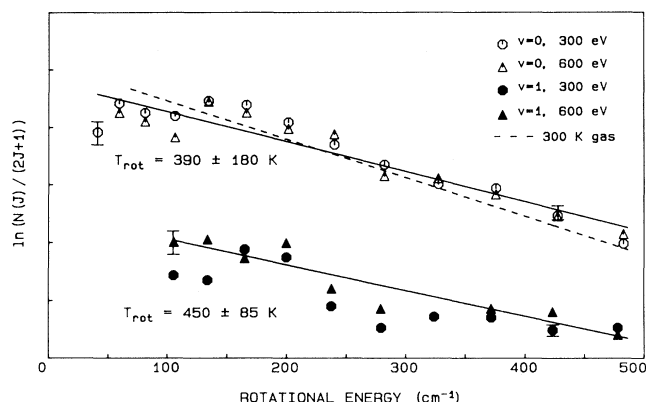


FIG. 2. Rotational distributions for the  $v=0$  and  $v=1$  states of NO desorbed by electron excitation energies of 300 and 600 eV. A plot of  $\ln[N(J)/(2J+1)]$  vs  $BJ(J+1)$  should be a straight line if Boltzmann statistics are applicable. For comparison, the Boltzmann distribution for a thermalized NO gas sample at 300 K is shown (dashed line).

much more work needs to be done in terms of correlation of the internal and translational energies with the substrate potential-energy surface. In a similar vein, Cavanagh and King<sup>19</sup> have attributed anomalous rotational distributions in thermally desorbed NO to molecule-surface potential-energy interactions.

Spectra taken at 300 and 600 eV reveal that the rotational and vibrational distributions are unchanged within experimental error when the primary electron energy is raised from below to above the N(1s) and O(1s) core-level thresholds of 402 and 532 eV, respectively. One would expect the highly energetic core-level process to leave the molecule in a very excited internal energy state. A possible reason why no core-level effects are seen here is that the final state prior to desorption is independent of the initial excitation mechanism.<sup>20</sup> However, when the state-specific neutral NO yield as a function of electron energy is analyzed, as in Fig. 3, there is no observation of any yield enhancements at the core-level thresholds, which would be due to reneutralization processes. Thus, both the spectra and the yield curves confirm previous studies<sup>2</sup> that there is a negligible core-level excitation cross section which leads to neutral NO desorption.

The current-normalized yield curves shown in Fig. 3 are obtained by a computer-controlled scan of the electron energy from 9 to 1000 eV. The focus of the gun is also controlled by the computer in order to ensure a constant spot size on the surface. Each of the 500 data points in the scans is processed in the same manner as discussed above for the rotational spectra, and the surface is cleaned and redosed before each energy scan. In order to record an appreciable NO<sup>+</sup> or O<sup>+</sup> signal, the data acquisition gate had to be increased by a factor

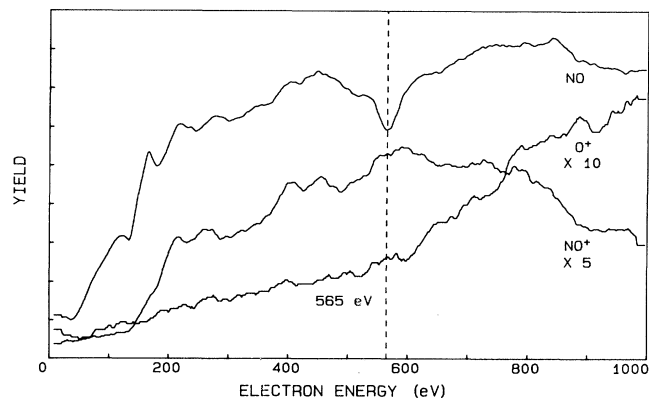


FIG. 3. Yield of neutral NO (measured at the  $v=0$   $P_{21} + Q_{11}$  bandhead), NO<sup>+</sup>, and O<sup>+</sup> as a function of primary electron energy. The relative yields shown here are scaled from the raw data for visual purposes. The actual ratio of neutral-to-ion yield is nearly  $10^5$ . The dashed line at 565 eV indicates the electron energy at which the onset of molecular dissociation is believed to occur (see text).

of 10, the delay following the electron pulse was eliminated, and twice as many electron pulses were averaged for each datum point. When these differences are taken into account, along with the fact that the laser pulse is only 5 nsec long, the ratio of the desorbed neutral flux to the desorbed ion flux is about  $1.5 \times 10^4$  for electron energies of 400–800 eV. In addition, the neutral signal at the  $P_{21}$  bandhead ( $J = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$ ) is only a portion of the total neutral yield. When the other rotational states and vibrationally excited molecules are counted, the neutral yield is almost  $10^5$  times that of the ion yield.

A significant neutral NO signal was observed at the lowest attainable electron energy of 9 eV, and energy which is still high enough for Menzel-Gomer-Redhead valence ionization. Ultraviolet photoelectron peaks have been observed for NO on Ni(111) at 8.8- and 2-eV binding energies (relative to the 6-eV Fermi level).<sup>21</sup> The latter peak is attributed to the interaction of the NO  $2\pi$  level and the Ni  $d$  band, which is expected to affect desorption thresholds. Thus, it is not possible at this time to tell if there is a direct neutral desorption channel or if reneutralization following shallow valence-level ionization is dominant. The most peculiar feature in the neutral yield curves is the recurring dip at 565 eV. The O<sup>+</sup> yield shows a small but reproducible enhancement at the same energy. The dip appears for neutrals in both the  $P_{21} + Q_{11}$  bandhead ( $J = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$ ) at  $44196 \text{ cm}^{-1}$ , the  $P_{11}$  bandhead ( $J = \frac{15}{2}, \frac{17}{2}, \frac{19}{2}, \frac{21}{2}$ ) at  $44175 \text{ cm}^{-1}$ , and the  $v=1$   $P_{21} + Q_{11}$  bandhead at  $44662 \text{ cm}^{-1}$ . Thus there is no evidence that a redistribution of internal energy may be the cause. At this time it is believed that the dip is the result of molecular dissociation initiated by the

ionization of the  $O(1s)$  and, possibly,  $N(1s)$  core levels. The shift in this feature to energies above the 531-eV  $O(1s)$  threshold has also been reported by Jaeger *et al.*,<sup>12,13</sup> who attribute the 35-eV delay in the  $O^+$  yield enhancement to a valence ionization coupled to the  $O(1s)$  core-level ionization (shakeup).

It seems reasonable that molecular dissociation will proceed at the expense of neutral molecular desorption, but the recovery of the molecular yield at higher energies is more difficult to understand. The answer to this question may lie in the very low threshold ( $< 9$  eV) for neutral desorption. It is possible that the signal recovery is due to an ever-increasing yield of low-energy secondary electrons.<sup>22</sup> Clearly, more experiments need to be performed to unravel this mystery. One important set of experiments that is underway involves the laser-ionization detection of neutral N and O desorbed at these electron energies. These experiments will help to determine the extent of molecular dissociation and also provide an insight into atomic reneutralization following the creation of localized multihole states.

In conclusion, this work represents the first time that specific rotational and vibrational states of ESD neutrals in the ground state have been examined. These data, along with the 0.1-eV kinetic energy measured by time-of-flight, indicate a repulsive final state reached by electronic excitation. Both the internal energies and the state-specific yields as a function of electron energy indicate that the mechanism for NO desorption in this system involves valence-level excitations with very little, if any, contribution from core-level excitations.

The author wishes to acknowledge fruitful discussions with M. L. Knotek and T. A. Green, and the able technical assistance of R. W. Willey. This work performed at Sandia National Laboratories was supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP0078.

<sup>1</sup>An excellent review is *Desorption Induced by Electronic*

*Transitions, DIET I*, edited by N. H. Tolk, M. M. Traum, J. C. Tully, and T. E. Madey (Springer-Verlag, New York, 1983).

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