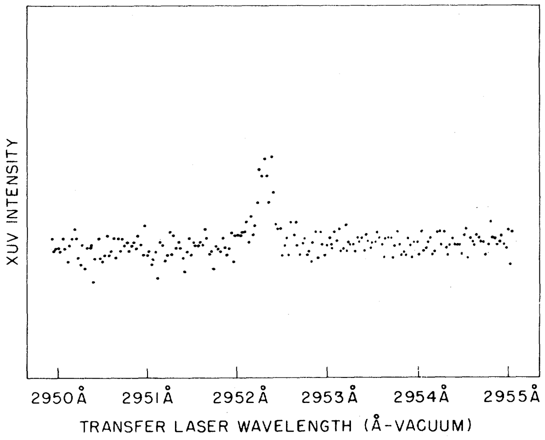

FIG. 4. XUV intensity vs laser wavelength for $1s2s2p\,^4P_{5/2}\rightarrow 1s2p^2\,^2P_{3/2}$ transfer in neutral ^{6}Li.

total scanning time of about 2 h, corresponding to 150 scans of the 2950–2955-Å wavelength region, was required to obtain the data shown. The measured separation between the levels is $33\,872\pm 2$ cm^{-1}. On the basis of the longer metastability of the 5/2 component of the $1s2s2p\,^4P$ level, and the ratio of calculated oscillator strengths of the fine structure components,[7] it is likely that the largest component of our signal occurs on $^4P_{5/2}$-$^2P_{3/2}$. Our measured separation is about 5 cm^{-1} greater than that recently calculated by Jáuregui and Bunge[3] for ^{7}Li. The discrepancy probably is due to the uncertainty of experimental beam-foil results used in the calculation, and to the isotope shift between ^{6}Li and ^{7}Li.

In summary, we have described a new technique for connecting metastable and radiating manifolds which lie in the XUV spectral region. The method complements the high-resolution anti-Stokes absorption technique described by Rothenberg *et al.*[9]; both provide unprecedented resolution in the XUV. This work also bears on recent proposals for XUV lasers.[6,11,12]

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Rotational- and Spin-State Distributions: NO Thermally Desorbed from Ru(001)

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Rotational-state distributions have been measured for the first time in molecules thermally desorbed from a metal single crystal. Laser-excited fluorescence has been used to monitor, under ultrahigh-vacuum conditions, the desorption of NO from Ru(001). The population distribution for those states with less than 400 cm^{-1} of rotational energy (including spin) can be represented by a single Boltzmann factor, $T_{\rm rot} = 235\pm 35$ K, significantly lower than the surface temperature at the desorption maximum, $T_S = 455\pm 20$ K.

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One of the severe obstacles in theoretically modeling the dynamics of reactive processes occurring at a gas-surface interface is the absence, until very recently, of experimental data on the details of the partitioning of energy within the incoming or exiting gas-phase species.[1] Such state-to-state studies of bimolecular gas-phase processes have resulted in a detailed understanding of potential-energy hypersurfaces and of molecular dynamics.[2] It is now becoming practical to apply sensitive internal-state–specific diagnostics (e.g., laser-excited fluorescence) to the study of chemical reactions and molecular energy transfer on well-characterized metal single-crystal surfaces.

To date, two types of gas-surface experiments have been examined: heterogeneous reaction and inelastic molecular scattering. Under the classification of heterogeneous reaction, most systems studied exhibit a significant barrier to the reverse reaction (adsorption). This barrier provides the exiting molecular species with excess energy which can appear as vibrational,[3] translational,[4,5] or rotational[6] excitation. In the inelastic-scattering experiments a high degree of energy accommodation (i.e., nearly full equilibration with the surface) has been associated with trapping/desorption, while lower degrees of accommodation have been thought to indicate direct impact-type interactions.[7] Laser-excited fluorescence (LEF) measurements of the rotational distribution of NO molecules scattered from NO- or graphite-covered Pt(111) (Ref. 8) and clean, single-crystal Ag(111) (Refs. 9–11) have shown that the rotational-state populations can be described by Boltzmann-like distributions. The degree of accommodation is strongly dependent on the *nature* of the surface.

In this paper we report the first measurements of a nascent internal energy distribution obtained from thermal desorption experiments from a single-crystal metal surface under ultrahigh-vacuum (UHV) conditions. The experiment consisted of measuring the density, via LEF, of the resulting gas-phase NO species in various rotational levels (J'') of the ground $\tilde{X}\,^2\Pi_{1/2,3/2}$ electronic state. Since molecular NO evolution only occurs during the 5–10-sec period that the temperature increases from 435 to 475 K, only one level can be probed during each temperature-programmed desorption (TPD). This system was chosen for study for two significant reasons. First, Ru(001) is highly reactive to NO, and therefore this system will provide a useful complement to the nonreactive NO/Ag(111) system.[9-11] Second, the surface properties of this system have been studied extensively. The vibrational modes of the adsorbed NO,[12] the thermal desorption spectrum,[13,14] and the coverage dependence of binding-site occupation[13] have been well established.

The sample chamber used in this work is a stainless steel UHV ($P \leqslant 4\times10^{-10}$ Torr)[15] apparatus equipped with an ion pump, titanium sublimators, effusive molecular beam doser, and quadrupole mass spectrometer. The Ru(001) crystal was mounted on a rotatable manipulator and could be cooled to 180 K with nitrogen or heated to 1670 K by conduction from resistively heated tantalum support leads. The Ru crystal was cleaned by repeated heating in O_2 in front of the doser at 1390 K followed by flash annealing to 1660 K to remove residual oxides. This cleaning procedure has been shown to yield clean surfaces reproducibly.[12] The quadrupole mass spectrometer was used to establish the NO exposure at the doser required to saturate the 0.5-cm^2 crystal at 273 K. All TPD reported herein were obtained following saturation coverage of the freshly cleaned and cooled Ru crystal and for a heating rate of 12 K sec^{-1}.

The thermally desorbing NO was probed by a laser beam of 40 μJ, 0.1-cm^{-1} spectral bandwidth (full width at half maximum), and 10-ns pulse duration, tunable about the origin of the $\tilde{A}\,^2\Sigma^+$-$\tilde{X}\,^2\Pi_{1/2,3/2}$ transition at 44 140.78 cm^{-1} (in NO, the spin components of the ground state are split by 123.2 cm^{-1} by spin-orbit coupling).[16] After traversing the UHV system, the probe laser passed thru a NO gas-phase reference cell into an absolute-energy meter. The UV beam was well collimated over the 1-m path length with a beam area of 0.06 cm^2. In the UHV system the laser beam passed parallel to the surface plane with its center 0.5 cm from the crystal surface. The LEF signals resulting in the UHV system and reference cell were detected in comparable fashion, with use of 1P28-B type photomultiplier tubes (PMT). The reference cell gas was a 46-ppm mixture of NO in dry nitrogen,[17] flowing through the cell at a total pressure of 50 mTorr. Typically the reference cell LEF intensity was attenuated 10^3-fold by UV neutral density filters to make the reference signal comparable to the thermal desorption LEF. The output of the two PMT's were fed into a matched pair of gated integrators, digitized, ratioed, and accumulated in a multichannel averager.

Figure 1 (top trace) shows typical data obtained for a single TPD while probing a single rotational state. The maximum in the laser-detected thermal desorption spectrum occurs at 455 K and corresponds to a peak NO($J''=6\frac{1}{2}$) density of 2×10^6 cm^{-3}. For comparison, a thermal desorption spectrum at $m/e=30$ monitored by the mass spectrometer is presented. Desorption experiments

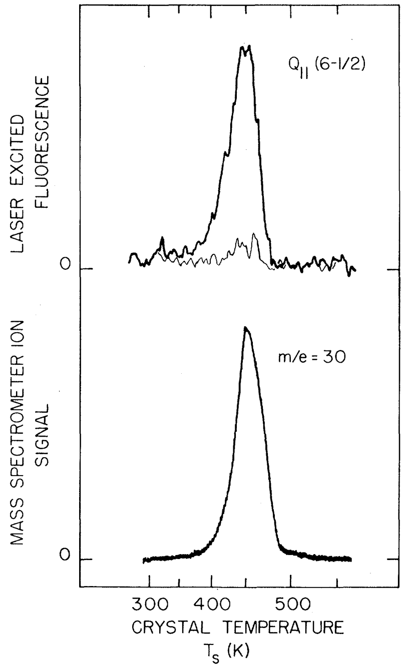

FIG. 1. Laser-excited fluorescence and mass-spectrometer–detected thermal desorption spectra. Each trace is the result of a single temperature-programmed desorption. The baseline LEF trace is the observed signal when the crystal is rotated to be 3 cm below the laser beam.

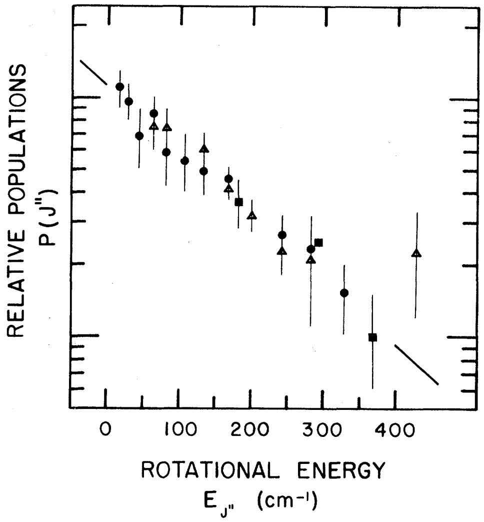

FIG. 2. Rotational- and spin-state population distribution for NO thermal desorption from Ru(001) at 455± 20 K. A single Boltzmann temperature, $T_{\rm rot} = 235 \pm 35$ K, describes the total angular momentum distribution. The various symbols represent population densities, as defined by Eq. (2) in the text, for excitation on the $R_{11}(J'')$ (circles), $Q_{11}(J'')$ (triangles), and $Q_{22}(J'')$ (squares) branch transitions.

conducted with the crystal rotated to be 3 cm below the laser beam indicated that contributions from NO which had undergone wall collisions were insignificant in the gettered system (baseline LEF trace). Each TPD resulted in a single measurement of the NO density in one particular spin-rotation state. As the Ru crystal was being cycled through the annealing/dosing procedure[12] the laser wavelength was tuned to probe a new, randomly selected J''. The LEF signal observed while exciting a specific $J' \leftarrow J''$ transition is dependent on the population density ${}^{\rm TPD}N_{J''}(t)$ at the time of the laser probe, a line strength (e.g., Hönl-London factor) for that transition, the laser energy and overlap of the laser frequency and bandwidth with the Doppler-broadened rovibronic line profile, and detection efficiency factor. To minimize potential errors arising from random fluctuations in laser energy, frequency, and bandwidth, the reference cell LEF was always recorded simultaneously during TPD. The recovered, ratioed signal $I_{J''}(t)$, observed at time t during the TPD, is simply

$$I_{J''}(t) = [{}^{\rm TPD}N_{J''}(t)/{}^{\rm ref}N_{J''}]C_{\rm rel}^{-1}, \qquad (1)$$

where $C_{\rm rel}$ is the relative detection efficiency for the two optical systems. Since the reference cell is at thermal equilibrium, ${}^{\rm ref}N_{J''}$ is proportional to $(2J''+1)\exp(-E_{J''}/k\,{}^{\rm ref}T)$, where $E_{J''}$ is the rotational level energy and ${}^{\rm ref}T = 293$ K. In Fig. 2 we have plotted the relative probability, $P(J'')$, of a thermally desorbed NO molecule having total rotational energy (including spin) of $E_{J''}$. The quantity $P(J'')$ is defined by

$$\begin{aligned} P(J'') &\equiv {}^{\rm TPD}N_{J''}({\rm max})/(2J''+1) \\ &= I_{J''}({\rm max})\exp(-E_{J''}/k\,{}^{\rm ref}T) \\ &= C_{\rm rel}^{-1}\exp(-E_{J''}/k\,{}^{\rm TPD}T). \end{aligned} \qquad (2)$$

The rotational-state populations in the lower-lying ${}^2\Pi_{1/2}$ spin component were obtained by monitoring of $Q_{11}(J'')$ and $R_{11}(J'')$ branch transitions; in the ${}^2\Pi_{3/2}$ component, the $Q_{22}(J'')$ branch was measured. Each datum point in Fig. 2 represents the average of some 10–15 individual TPD measurements, each with an individual signal-to-noise ratio of 10, and incorporates data taken during runs on several days. To the extent that the rotational-state population distribution of the thermally desorbing NO can be characterized by a Boltzmann distribution one would expect a linear plot of $\ln P(J'')$ against $E_{J''}$, defining a rotational temperature T_{rot}. The data, plotted in this fashion in Fig. 2, give a linear regression correlation coefficient of -0.98 for all points $E_{J''} \leq 400\ \mathrm{cm}^{-1}$ indicating the thermally desorbed NO to be accurately described by a Boltzmann rotational temperature. A least-squares analysis gives $T_{rot} = 235 \pm 35$ K (95% confidence level).

The important result of this work is that the distribution of *total* rotational energy (including electronic spin) of those NO species desorbing from singly coordinated sites on Ru(001) at 455 ± 20 K is well represented by a *single Boltzmann temperature* $T_{rot} = 235 \pm 35$ K *significantly lower than the surface temperature.*

Although the construct of an adsorbed yet highly mobile, freely rotating activated complex has proven useful in modeling certain surface reactions (including desorption[18]), if the desorbing NO were to pass through such a precursor state, a rotational temperature in the nascent gas-phase NO equal to the surface temperature should result. This is not observed experimentally. Our measurements indicate an integrated NO flux of only 2%–6% of a monolayer during TPD from an initially clean crystal. The dissociated species could provide a barrier to free migration of the remaining atop-bound molecular NO. We believe, therefore, that the gas-phase NO is derived directly from a well-characterized chemisorption state. The *small* degree of rotational energy in the NO fragment apparently results from dynamical effects occurring along the exit channel of the molecular-surface potential-energy hypersurface. Most simply, this result is consistent with a weakly noncentral repulsive force and a negligible barrier (i.e., 1–2 kcal mole^{-1}) to the reverse adsorption process. In addition, we find the observed equilibrium between electronic spin (S) and the resultant of orbital and nuclear rotational angular momenta (K) striking. This equilibrium indicates that the nuclear rotational angular momentum and electronic spin both develop in the same region of the potential-energy surface.

These experiments, as compared to static surface spectroscopies, provide the first measurements which directly probe the chemisorption-bond making/breaking region of the adsorbate/substrate potential-energy hypersurface.[8-11] Careful analysis of the internal-state distributions of molecules interacting with well-characterized surfaces involving either negligible exit-channel barriers [as in the NO/Ru(001) system] or more strongly repulsive interaction potentials will stimulate theoretical efforts aimed at understanding molecule-surface dynamics.

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