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A statistical interpretation of the rotational temperature of NO desorbed from Ru(001)

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The area of gas-surface interactions has received much attention in the recent past. In particular, the processes of chemisorption and desorption have been of acute interest because of the apparent implications in heterogeneous catalysis. Recently, Cavanagh and King have studied the rotational distributions of NO being thermally desorbed from Ru(001). The rotational distribution of the desorbed NO was probed with laser excited fluorescence at short distances from the crystal face and at very low pressures \( p < 10^{-10} \) Torr, so that the measured rotational distribution was presumably not perturbed by any gas phase intermolecular interactions. The authors noted that when the Ru(001) crystal was heated to 455 \( \pm 20 \) K, the NO was desorbed from the surface and in fact, the gas phase rotational distribution of the desorbed NO was found to be thermal with a characteristic rotational temperature of \( T_R = 235 \pm 35 \) K. Because of the significant differences in temperatures, it was proposed that the NO molecule was significantly perturbed upon desorption resulting in the overall lowering of rotational temperature. However these data are also consistent with a two-dimensional rotator absorbed species model.

To model the two-dimensional rotator, one may consider the adsorbed NO as being tilted at some angle \( \theta \) to the surface normal (see Fig. 1). The molecule will rotate about the adsorption site through an angle \( \phi \), and two interdependent angular momenta will result; one from the two-dimensional rotation of the NO molecule about its center of mass in molecule based coordinates and another momentum from the rotation of the NO about the adsorption site. The Hamiltonian for the center of mass molecular rotation is

\[
H = -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2},
\]

where \( I = \mu \cos^2 \theta \rho \), \( \mu \) being the reduced mass and \( \rho \) being the internuclear distance of the NO molecule. The solution to the wave equation is

\[
\psi_R = \left( \frac{1}{2\pi} \right)^{1/2} \exp \{ \pm i m \phi \},
\]

with energies

\[
E_R = \frac{m^2 \rho^2}{2I} = m^2 k \theta_R,
\]

where \( k \) is the Boltzmann constant. The energy levels

![FIG. 1. An illustration of the NO molecule prior to desorption. The angle \( \theta \) is that between the internuclear NO axis and the normal of the surface and \( \phi \) is the angle of rotation of the molecule about the adsorption site. Rotations of the adsorbed NO molecule give rise to angular momentum about the adsorption site axis (AS) and angular momentum about the center of mass (CM) axis in the molecule based coordinate system.](image-url)
of this two-dimensional rotator have a characteristic quantum number $m$, and each level has degeneracy of two corresponding to clockwise or counterclockwise rotation.

Of the most significance to these studies are the heat capacities of the rotating molecule both adsorbed and in the gas phase. The high temperature $T \gg \theta_p$ heat capacity for the gas phase species is the familiar relationship $C_v^m = R$. The heat capacity for the adsorbed species can be obtained from the rotational partition function. The high temperature rotational partition function obtained by integration of Eq. (3) is $Q(R) = (2\pi T/\theta_p)^{R/2}$, and the heat capacity from this result is $C_v^R = R/2$, as one would expect based on equipartition of energy arguments.

For a weak desorption potential both the adsorbed and the desorbed species will have an internal rotational energy of $RT_{\text{surface}}/2$, i.e., no energy is gained or lost during desorption. In this case the apparent rotational temperature of the desorbed species will be $T_{\text{surface}}/2$, since the rotational energy increases by a factor of 2 on going from the adsorbed state to the desorbed state. This statistical interpretation is consistent with the data of Cavanagh and King in which the rotational temperature of the desorbed species was approximately 1/2 of that of the surface. When analyzed with the above considerations, the desorption data suggests the possibility of a two-dimensional rotator that is being released from the surface through a negligible barrier. This species may be a weakly constrained mobile precursor to desorption.

Another point to be considered from this model is that of the translational momentum of the desorbed NO. In addition to the angular momentum about the center of mass of the NO molecule, there also exists a momentum due to the rotation of the center of mass of the NO molecule about the adsorption site. This momentum eigenfunction must satisfy the same wave equation and since angular momentum must be conserved, it results in the same statistical energy as the molecular based coordinate system. However, this rotational momentum must be lost when the species is desorbed, resulting in linear momentum parallel to the crystal plane. This rotational energy is $E_R = \frac{1}{2} k T_{\text{surface}}$ which must equal $\theta_p/2 M$. Thus, one would predict an excess momentum in the parallel plane of $\theta_p = k T_{\text{surface}}$.

It should be pointed out that these statistical considerations do not depend on the particular orientation of the adsorbed NO molecule. Since the rotational energy constant $\theta_p$ does not enter into the heat capacity calculation, the rotational temperature of the desorbed species is only a function of the desorption temperature. The exact distribution of adsorbed species cannot be implied from that of the desorbed species without a more exact knowledge of the desorption potential energy surface. However, the recent desorption data interpreted in the simple statistical manner given here is consistent with the findings of Thomas and Weinberg.

In the later study it was found that "linear" molecular NO was stable up to 500 K, at which point NO was rapidly desorbed from the Ru(001) surface. Finally, if the adsorbed species is very weakly bound to the surface one would expect that three-dimensional rotation might occur. In this case, the desorbed species rotational distribution would be characterized by a rotational temperature equal to that of the surface, desorption would occur at a lower temperature, and the momentum would be isotropic.

5. D. S. King and R. R. Cavanagh have recently measured the parallel velocity of NO thermally desorbed from Ru(001) at 455 ± 20 K [J. Chem. Phys. 76, 5634 (1982)]. The distribution was found to be thermal with $T = 235 ± 45$ K. This measurement is in good agreement with the statistical interpretation given here since the one degree of rotational freedom will result in two degrees of translational freedom. If energy is to be conserved, the translational temperature parallel to the surface must be one-half of that of the surface.