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Energy Redistribution in Diatomic Molecules on Surfaces

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1. ABSTRACT

Translational and internal degrees of freedom of a scattered beam of NO molecules from a Pt(111) single crystal surface were measured as a function of scattering angle and crystal temperature in the range 450-1250K. None of the three degrees of freedom were found to fully accommodate to the crystal temperature, the translational degree being the most accommodated and the rotational degree of freedom the least. A precursor state model is suggested to account for the incomplete accommodation of translational and vibrational degrees of freedom as a function of crystal temperature and incident beam energy. The vibrational accommodation is further discussed in terms of a competition between desorption and vibrational excitation processes, thus providing valuable information on the interaction between vibrationally excited molecules and surfaces. Energy transfer into rotational degrees of freedom is qualitatively discussed.

2. INTRODUCTION

Energy transfer processes at gas-solid interfaces are of great importance for the understanding of the dynamics of interactions between gas phase atoms or molecules and solid surfaces. For atomic scattering studies, the momentum changes as measured by angular and translational energy distributions of the scattered particles provide most of the necessary information to describe the collision process(1). For molecules, however, changes in the internal energy states (rotation and vibration) can also occur in addition to changes in the translational energy of the incident species. Determination of the internal state distributions of molecules scattered from surfaces received an increased attention in recent years. They were monitored by employing laser induced fluorescence or two photon ionization techniques that provide information on stronlgy as well as weakly interacting gas molecule-surface systems(2-10). In most of these studies the rotational distribution of the scattered molecules were measured, and were found to be at or close to a Boltzmann distribution with rotational temperatures lower than that of the crystal temperature. When higher incident energies were used in the NO/Ag(111) system deviation from the Boltzmann distribution occurs at the high rotational states, due to a rotational rainbow effect(4). Vibrational excitations as a result of the interaction of molecules with surfaces were observed only in a few strongly interacting molecular-surface systems(7,11,12). In these cases only partial accommodation of the molecules with the surface was reported(7). The only system for which complete energy transfer and accommodation information exists, e.g. for translation rotation and vibration, is the scattering of NO molecules from the Pt(111) single crystal surface(2,7,8).

In this paper we shall present the experimental data obtained for the redistribution of the translational, rotational and vibrational states of supersonic NO molecules upon scattering from a Pt(111) surface. We found that the accommodation on the surface is best, but not complete, for translation, then for vibration and the poorest for the rotational degrees of freedom. A precursor state model will be presented with an approximate one dimensional potential for the NO/Pt(111) system, which accounts well for the translational and vibrational data. A more detailed analysis of the vibrational excitation process of NO, while it is in the chemisorption state, will be discussed and be shown to provide a unique insight into the interaction between vibrationally excited molecules and metal surfaces. Finally the poor rotational accommodation will be rationalized in terms of models that were recently suggested for rotational excitation of molecules on surfaces.

3. EXPERIMENTAL

The experiments to be described involve a supersonic molecular NO beam scattered off a Pt(111) single crystal surface under UHV conditions. Different detectors were employed for monitoring the translational energy and the internal energy distribution of the scattered molecules. For the translational energy distributions measurements, a time of flight detector, equipped with a two stages differentially pumped quadrupole mass spectrometer, rotatable around the crystal for angular resolution was utilized. The details of this apparatus and the time of flight results were given previously(13,14). Briefly, a supersonic NO beam is generated by expanding through a 75μm nozzle with stagnation pressure of 200 torr. The beam scattered from a Pt(111) disc located at the center of a UHV chamber at a base pressure of low 10^{-10} range. A pseudorandom slit chopper is mounted on the detector, thus chopping the scattered beam instead of the incident beam. This way the time of flight measurements of the scattered molecules are not affected by the unknown surface residence time. The incident beams' mean kinetic energy was 265K, 615K and 1390K, by antiseeding with xe, pure NO and seeding with He respectively. The crystal temperature range was 475-1200K. The measurements were done at two scattering angles, e.g. 7° from the normal to the surface and at specular angle which is 51° from the normal(14).

Internal states e.g. vibrational and rotational states distributions determination of the scattered NO molecules required an optical detector(15). The time of flight detector was removed, therefore, and a set of quartz deflecting prisms and a focusing lens allowed a tunable UV laser beam at 225 and 236 nm ranges to be focused 2.5 cm above the crystal, intersecting the NO molecules at the scattering plane. At the focus of the laser, a two photon ionization process occurs via a bound electronic excited state of the NO molecules ($A^2\Sigma^+(v'=0)$. An electron multiplier was attached to the detector, at a fixed distance from the laser focus, and by applying bias voltages of 2000-3500V, the NO^+ ions were collected. Tuning the laser around 225 nm, the rotational states distribution of the ground vibrational state of NO was measured, while at 236 nm the rotational states distribution of molecules that were two photon ionized from the first vibrationally excited state could be detected. Thus relative ion currents at these two wavelengths provided vibrational and rotational state distributions. Details of the relevant spectroscopy of NO and the laser system are described elsewhere(15). Both the supersonic beam source and the Pt(111) sample were identical in the time of flight and the internal state distribution experiments.

The sample cleaning and surface composition determination were carried out with typical UHV techniques e.g. Ar^+ ion sputtering followed by oxygen treatment and annealing and Auger electron spectroscopy (AES) respectively. If scattering experiments were longer than 20 minutes at crystal temperature above 900K, oxygen coverages were built up to 0.1 of a monolayer were detected by AES, presumably due to slow NO decomposition at surface defects. To prevent further oxygen accumulation, experiments aimed at the determination of rotational spectra were interrupted to regulate the clean surface.

4. RESULTS AND DISCUSSION

The interaction between NO molecules and the Pt(111) single crystal surface is the first and yet the only molecule-surface interaction example for which a complete characterization of energy transfer and excitation of the three degrees of freedom of the scattered molecule, e.g. translation, rotation and vibration were obtained experimentally (7,14,15). The purpose of this paper is, therefore, to summarize the experimental results and to present new models which will account for the observed energy accommodation. As described in previous studies of the angular and velocity distributions of the NO/Pt(111) system, scattering occur by at least two different mechanisms, usually referred to as direct inelastic and trapping desorption processes(8,14,16). No attempt was made, however, to use this data for better understanding of the interaction potential between the NO molecules and the Pt(111) surface. In the first section the experimental results will be presented, in the second section we shall present a model, based on the assumption of a precursor state prior to chemisorption, which combines the data from both translational and internal (vibrational in this case) energy accommodation studies . In the third section a kinetic model for the vibrational excitation process at the chemisorption state will be outlined and be shown to provide an important insight into the interaction between vibrationally excited molecules and metal surfaces. Finally the poorly accommodated rotational degree of freedom will be discussed in view of recent interpretations of such observations that appeared in the literature.

4.1 Experimental Results

The experimental data for translational and vibrational energy exchange of NO molecules in a supersonic beam, upon scattering from a Pt(111) crystal surface are briefly outlined in this section. Time of flight distribution measurements were taken at three incident beam energies $\langle E\rangle/2K=265K$, 615K and 1390K and were scattered from crystal at temperature range of 475-1200K. In Fig. 1 a typical time of flight distributions are presented for an incident beam of 615K with the detection at 7° from the surface normal and at the specular angle. Note that the fit to a Boltzmann distribution (solid line in Fig. 1) is better near the surface normal than at the specular angle. The accumulation of scattered molecules' average kinetic energy (temperature) as a function of crystal temperature for three different incident kinetic energies are shown in Fig. 2. The detector is at 7° from the normal to the surface. Note that even at large scattering angle where contribution from direct inelastic scattering is negligible, there is some memory of the incident beam energy. The full line is the calculated scattered molecules' temperature which will be discussed in the next section. Similar results were obtained at the same incident beam energies with the detector at the specular angle of 51° from the normal to the surface. These results are summarized elsewhere(14) and discussed within the framework of the precursor model (next section) elsewhere(19). A typical angular distributions of the scattered NO molecules are shown in Fig. 3. Note the increased flux at the specular angle by increasing the crystal temperature. Similar effect is seen at a given crystal temperature by increasing the incident beams energy(14).

The vibrational temperature of scattered NO molecules as a function of crystal temperature is presented in Fig. 4. Such a presentation assumes a Boltzmann vibrational distribution and is derived from the measurements of the ratio of scattered NO(v"=0) molecules (7,15). Note

Fig. 1: Time of flight distributions for a) T_B=615K, T_S=475K detector at 7° from the surface normal b) T_B=615K, T_S=475K, specular detection. The solid curves are the Maxwellian distributions at the corresponding surface temperature.

that here there is no complete vibrational accommodation even at the lowest crystal temperature. The incident beam's vibrational energy was not measured but is estimated to be 200K. The results on the rotational excitation will be presented and discussed in sec. 4.4.

4.2 A Precursor State Model for Vibrational and Translational Energy Accommodation.

Fig. 5 describes the main features of the proposed precursor state. The shallow physisorption state has a well of E_∞ kcal/mole while a barrier of E_S kcal/mole separates the precursor and the deep chemisorption well. We assume that the incident molecules are trapped in the precursor state with a unity probability. It is further assumed that the molecules are equilibrated with the surface in their vertical momentum component only while the momentum component parallel to the surface is conserved. The distinction between the vertical and horizontal components is based on the "hard cube" model which is believed to be applicable for physisorbed states such as our precursor state where the lateral motion of the molecules is practially free. Since the diffusion parallel to the surface should not affect the probability of chemisorption, one can assign the crystal temperature, T_S to the molecules. Then the probability, P, for chemisorption is given by:

Fig. 2 Translational temperature of scattered NO molecules from Pt(111) surface. Solid circles denote the experimental measurements at 7° from the normal to the surface, the full line is the calculated tempertures (sec. 4.2 eq 3) and the dashed line represents a complete accommodation.

$$P = \frac{k_1}{k_1 + k_2} = \frac{1}{1 + \frac{k_2}{k_1}} \qquad (1)$$

where k_1 and k_2 are the rate constants for chemisorption and desorption from the precursor state, respectively. If first order processes are assumed, described by an Arrhenius rate constant, eq. 1 becomes:

$$P = [1 + \exp(-\Delta E/kT_s)]^{-1} \qquad (2)$$

where $\Delta E = E_\infty - E_s$. Note that the preexponential factors for these processes are assumed to be identical. Being a shallow well, the residence time of the molecule in the precursor state should be very short, thus vibrational accommodation is not expected. Moreover the coupling between translational and vibrational degrees of freedom is predicted to be weak(18). Once chemisorbed, however, both momentum components as well as the vibrational degree of freedom are accommodated to the surface temperature.

If we denote O_{in} as the incident beam angle with respect to the surface normal, T_{in}^t as the incident beam translational temperature, defined as $\langle E_k \rangle/2K$, where $\langle E \rangle$ is the average incident kinetic energy, and T_f^t is the final translational temperature, then the expression for the final translational temperature is given by:

$$T_f^t = P \cdot T_s + (1-P)\{T_s \cdot \cos^2\theta_{in} + T_{in}^t \cdot \sin^2\theta_{in}\} \qquad (3)$$

Fig. 3: Angular distributions for $T_B = 1390K$
a)$T_s = 475K$; b)$T_s = 725K$; c)$T_s = 1195K$.

The first term in the right hand side of eq. 3 denotes a complete accommodation from the chemisorbed state, while the second term partial accommodation due to the precursor state. The final vibrational temperature is calculated similarly. If the molecules desorb from the precursor state they will retain their initial vibrational temperature, which was not measured in this study but may be estimated at a maximum of T_{in}^{v}=200K(15). The molecules that desorb from the chemisorbed state were completely accommodated with the surface. The resulting final vibrational temperature is:

$$T_f^v = P \cdot T_s + (1-P) \cdot T_{in}^v \qquad (4)$$

Note that in this model, only one adjustable paramter e.g. ΔE, is used for evaluating both the vibrational and the translational temperatures of the scattered molecule.

The vibrational accommodation coefficient γ_v is usually defined as:

$$\gamma_v = \frac{T_f^v - T_{in}^v}{T_s - T_{in}^v} \qquad (5)$$

By using eq. 2 and 4, eq. 5 becomes:

$$\gamma_v = P = [1 + \exp(- \Delta E/kT_s]^{-1}) \qquad (6)$$

Fig. 4: Vibrational temperature as a function of crystal temperature. Crosses are experimental data (derived from the measurements of the ratio of NO(v"=1)/NO(v"=0) of scattered molecules). The dashed-dotted line are the calculated values (see section 4.2, eq. 4) and the full line represents a complete accommodation.

Thus the vibrational accommodation coefficient can be interpreted as the probability of being chemisorbed from the precursor state. The translational accommodation coefficient is similarly transformed to:

$$\gamma_t = P \cdot \sin^2\theta_{in} + \cos^2\theta_{in} \qquad (7)$$

We found that with $\Delta E = 2.5 \pm 0.2$ kcal/mole the agreement with the the experimental data for NO scattering from the Pt(111) crystal surfaces is excellent.

In Fig. 4 a fit of eq. 4 to the measured final vibrational temperature as a function of crystal temperature is shown. The dash-dotted line is the calculated T_f^v from the precursor model, while the crosses are the experimental vibrational temperatures, measured as the intensity ratio of scattered NO(v"=1) to NO(v"=0)(15).

In Fig. 2, the calculated final translational temperatures (dashed lines) are shown together with the experimentally measured points (filled dots) at 7° from the normal to the surface and at three different incident translational temperatures(14). The agreement is again remarkably good.

Fig. 5: A one dimensional potential describing the interaction between a diatomic molecule and a metal surface.

It should be noted that in this model we assumed a unity sticking coefficient into the precursor state. This is not accurate since, as mentioned earlier, there is a noticeable contribution to the scattering process from molecules which undergo direct inelastic scattering. This fraction enhances the flux of molecules scattered into the specular direction (see Fig. 3). The contribution of these molecules near the normal to the surface, however, is minimal, since the angular distribution of direct inelastically scattered molecules is centered near the specular angle(8,14,16) therefore is assumed to be negligible. In this case, the non unity sticking probability into the precursor state should not affect the measurements of either the translational or the vibrational temperatures which are presented in Figs. 2 and 4 since those were measured at the normal to the surface.

When measured at the specular angle(14), however, one has to consider this portion of the molecules and to take their contribution to the scattered translational temperature into account. A more detailed analysis of this kind is presented elsewhere(19).

The precursor model described here is not new, it has been utilized before to describe the adsorption process. It was suggested by Lennard Jones(20) in the early days of adsorption studies on metal surfaces, that the interaction potential should have two minima, a shallow one due to a physisorption state and a deeper one, closer to the metal which represents the chemisorption state. Later two different precursor mechanisms were suggested by Kisliuk(21) and Ehrlich(22). Kisliuk's mechanism attributes the shallow minima to molecules physisorbed on top of already occupied chemisorption sites prior to chemisorption. this mechanism was recently invoked to explain the chemisorption kinetics of NO on Pt(111) surfaces at high coverages(8,23). This model, however, cannot be aplied to the current study where most of the measurements were carried out at crystal temperatures where the NO coverage is very small(14,15). The precursor mechanism suggested by Ehrlich (22), describes the two adsorption wells situation with different rates for removal of molecules from the precursor state either to the chemisorption well or to the gas phae. The model presented here, therefore, is very similar to the one suggested by Ehrlich. Similar precursor state was recently suggested also as a possible explanation for the small sticking probability of N_2 molecules on Fe(110)(24). In this case, the activation energy for chemisorption from the precursor state exceeds the initial kinetic energy of the incident N_2 molecules, making this system a case of activated adsorption. Note that in the present model ΔE is positive, therefore there is no energy barrier higher than the initial kinetic energy, thus high sticking probability is possible, as reported for the NO/Pt(111) system(8,16,23). Note also that the experimental data available from refs. 14 and 15 are not sufficient to obtain information about the well depth of the precursor (E_∞) or the barrier for chemisorption (E_s).

4.3 Vibrational Excitation and Deexcitation of the Chemisorbed Molecules

The precursor model presented in the previous section does not consider the source for the vibrational excitation of the NO molecules on the Pt(111) surface nevertheless the prediction of the extent of vibrational excitation is very good (see Fig. 4). If one extends this model to higher crystal temperatures than what was employed in the experiments, however, one obtains the following expression for the vibrational temperature (see eq. 4) of the scattered molecules:

$$T_f^v \underset{(T_s \to \infty)}{=} 1/2(T_{in}^v + T_s) \tag{8}$$

This expression is obtained since $p \to 1/2$ at $T_s \to \infty$. In fact, for the NO/Pt(111) system with $\Delta E = 2.5$kcal/mole, already at $T_s > 1200$, T_f^v can be obtained from eq. 8. The question is whether this is a physically sound prediction.

The residence time of NO molecules on the Pt(111) terrace, using the kinetic parameters suggested by Serri et al(16) ($\nu = 10^{16}\,\mathrm{sec}^{-1}$; $E_d = 25$ kcal/mole) is calculated to be $3.7 \cdot 10^{-12}$ sec at 1200K and drops to $5.5 \cdot 10^{-14}$ sec at 1400K. Unless an unreasonably high vibrational excitation mechanism is assumed for the adsorbed NO molecules, one must consider the possibility that desorption of ground state molecules may compete with the vibrational excitation. In the following, we shall examine this question by developing a simple kinetic model, that takes into account the various kinetic processes which take place during the residence time of a chemisorbed molecule on the surface. The results of this model and the informtion that may be obtained from it as to the interaction between vibrationally excited molecules and surfaces, will be discussed and compared to the previous model.

Consider a population of adsorbed molecules on a metal surface established during a molecular beam-surface scattering experiment as in (15). The flux of molecules into the surface is $F(T_s) = F_o \cdot S(T_s)$ where $S(T_s)$ is the sticking coefficient. The molecules which stick to the surface may be vibrationally excited by their interaction with the metal or desorb as ground state molecules. The rate equations describing the concentration of ground (N_a^o) and vibrationally excited (N_a^1) molecules on the surface are given by:

$$\frac{d\ N_a^o(T_s)}{dt} = F(T_s) - k_{ex}(T_s) \cdot N_a^o(T_s) + k_{dex} \cdot N_a^1(T_s) - k_d^o(T_s) \cdot N_a^o(T_s) \tag{9a}$$

$$\frac{d\ N_a^1(T_s)}{dt} = k_{ex}(T_s) \cdot N_a{}^o(T_s) - k_{dex} \cdot N_a^1(T_s) - k_d^1(T_s) - k_d^1(T_s) \cdot N_a^1(T_s) \tag{9b}$$

In eqs. 9, $k_d^o(T_s)$ and $k_d^1(T_s)$ are the desorption rate constants of the ground and vibrationally excited molecules respectively, while k_{ex} and k_{dex} are the vibrational excitation and deexcitation rates respectively. In the experiment of ref. 15 the desorbing flux of $NO_g^{(1)}$ was compared with that of $NO_g^{(o)}$. Once the concentrations on the surface are known, these values can be obtained as follows:

$$N_g^o = N_a^o \cdot k_d^o(T_s) \tag{10a}$$

$$N_g^1 = N_a^1 \cdot k_d^1(T_s) \tag{10b}$$

Applying steady state conditions on eqs. 9, (which is typical to the experiment in ref. 15), one gets the concentraiton of N_a^o and $N_a{}^1$ at steady state:

$$N_a^o(T_s) = \frac{F(T_s)[k_{dex}(T_s) + k_d^1(T_s)]}{K_{dex}(T_s)\cdot k_d^o(T_s)+k_d^1(T_s)[k_{ex}(T_s)+k_d^o(T_s)]} \quad (11a)$$

$$N_a^1(T_s) = \frac{k_{ex}(T_s)\cdot N_a^o(T_s)}{k_{dex}(T_s) + k_d^1(T_s)} \quad (11b)$$

Four rate constants determine the concentrations on the surface: k_d^o, k_d^1, k_{ex} and k_{dex}. The value of k_d^o can be determined from thermal desorption or modulated molecular beam experiments. These experiments measure the total flux of ground and vibrationally excited molecules, but at the temperature range at which these techniques apply, the fraction of excited molecules is less than 2% and is therefore negligible. We assume that due to a weak coupling between the molecule-surface bond and the internal stretch of the adsorbed molecule, which originates from a large difference in these frequencies, the desorption rates for ground and vibrationally excited molecules are identical - $k_d^o=k_d^1=k_d$. We also assume that k_d may be described as a first order process. For the case of NO/Pt(111), k_d was carefully measured (16). The values of k_{dex} and k_{ex} however are unknown, and so are their possible crystal temperature dependencies. Recent theoretical(25-28) as well as experimental(29) studies on the nature of the deexcitation process, predicted very weak if any crystal temperature dependence, as long as an electronic excitation/deexitation mechanism in the metal is involved in quenching the vibrational energy of the adsorbed molecules. If equilibrium between the adsorbed molecules and the surface exists the ratio k_{ex}/k_{dex} may be approximated by:

$$\frac{k_{ex}}{k_{dex}} = \exp[-Ev/kT_s] \quad (12)$$

where E_v is the vibrational energy spacing of the adsorbed molecule and k is the Boltzmann constant. We assume that at higher crystal temperatures, where the concentrations of N_a^o and N_a^1 may deviate from the Boltzmann expression, the ratio between the rate constants is still given by eq. 12. With the above model, we attempt to fit the data for the NO/Pt(111) system(15). It should be mentioned that due to the large temperature range of the experiment, the preexponential factor used was not the fixed number given by Serri et al(16) sec^{-1}, but rather a crystal temperature dependent parameter suggested by Redondo et al(30). These authors developed a theory where this preexponential factor is related to microscopic parameters of the system such as the bending and stretching frequencies of the molecule-surface bond(30). For the NO/Pt(111) system the resulting preexponential is $v=1.15{\cdot}10^{18}/T_s sec^{-1}$, which is somewhat smaller than the value suggested by Serri et al(16). In Fig. 6 the resulting fit is shown. These are calculated for three values of the vibrational deexcitation rate constant $k_{dex}=1x10^{13}$, $5x10^{11}$ and $5x10^{10} sec^{-1}$ as indicated in Fig. 6. Two facts emerge from this fit: a. This model does not predict the observed vibrational temperature. b. The high temperature trend is very different from the precursor model, and predicts an increased deviation of the vibrational temperature $T_f^v(T_s)$, from the crystal temperature. In this model $T_f^v(T_s)$ has a maximum which corresponds to the value of k_{dex} and thus also of k_{ex} (see eq. 12). $T_f^v(T_s)$ shifts to higher values at higher T_s as k_{dex} increases. One may improve the quality of the fit by using the assumption that $k_d^1 = 0.67k_d^0$ which was suggested (however not well understood) in ref. 15. If such an assumption is made the predicion of the kinetic model will look as in Fig. 7. Here the ratio NO(1)/NO(0) is calculated and compared with the experimental values. While such an approach provides a rather accurate prediction of the unknown rate constants $k_{dex} = 4\times10^{11}$ $\sec^{-1}$, it is still unclear whether the assumption made for the values of k_d^1 and k_d^0 is justified.

For the NO/Pt(111), however, one may combine the two models presented here and evaluate a quite accurate lower limit for the rate constant k_{dex}, without the need to assume different desorption rates for the ground and vibrationally excited molecules. It is suggested that instead of assuming a full accommodation for those molecules which reside in the chemisorption well (eq. 4), the vibratinal temperature predicted by this kinetic model should be used. For the NO/Pt(111) case(15), the highest crystal temperature was 1245K. It is clear from Fig. 6, that in order to obtain a more accurate fit and therefore better values for k_{dex}, experimental values at higher crystal temperatures of 1600 to 1800K are necessary. One can, however, argue using the existing data, that the fit shown in Fig. 4 could not be as accurate

Fig. 6: Vibrational temperature of Scattered NO molecules from a Pt(111) surface for three values of the deexcitation rate constant k_{dex}= — — 1×10^{13}, ---5×10^{11} and ....5×10^{10} $\sec^{-1}$. The crosses are some of the experimental vibrational temperature values. The light solid line is the precursor model prediction at high temperatures. The heavy solid line presents a complete vibrational accommodation.

unless $k_{dex}>1x10^{12}sec^{-1}$.

In conclusion, it appears that for the NO/Pt(111) system the best way to explain the data given in ref. 15, is to assume a precursor state adsorption mechanism. The vibrational excitation occurs only inside the chemisorption well, where at high crystal temperatures, the competition between the desorption of ground state molecules and the vibrational excitation process should be considered. It is believed that the present model could be best utilized for somewhat less strongly interacting systems than the NO/Pt(111). In such systems deviations from either full accommodation or from the precursor model predictions should be observed at lower crystal temperatures, therefore easier to measure experimentally. In such cases one may obtain better values for the deexcitation and excitation rates. Finally, the lower limit for $k_{dex}(10^{12}sec^{-1})$ obtained from the model described here, is well within the range predicted by recent theories (25-28) to reflect an interaction between vibrationally excited molecules and electronic states in the metal. This supports the assumption we made in the model as to the temperature independence of k_{dex}. The value of at least $10^{12}sec^{-1}$ for k_{dex} seem to agree with the electron-hole pair excitation as the most probable mechanism for vibrational deexcitation in the NO/Pt(111) system, since this mechanism predicts values in this order of magnitude (25,31). Multiphonon excitation can be ruled out for this system, since rates that are 5 orders of magnitude slower were predicted for this mechanism(26).

Fig. 7: The ratio NO(1)/NO(0) as a function of crystal temperature. The solid line represents the calculated values using the kinetic model with $K_{dex}=4\cdot10^{11}sec^{-1}$ and $E_d=25kcal/mole$, while the crosses are from the experiment (15).

4.4 Rotational Energy Accommodation of the Scattered NO Molecules.

The rotational temperature of NO scattered from Pt(111) surface was measured in this study and found to be lower than the crystal temperature. In Fig. 8, the rotational temperature is shown as a function of crystal temperature. The details of the experiment are given elsewhere(15). Very similar results were recently reported for the same system by Segner et al(8). It is evident that the accommodation is rather poor, and the rotational temperature seem to level off at around 450K, regardless of the crystal temperature. None of the models presented here treated the rotational excitation process. It is not clear whether a different rotational temperature is expected from molecules scattered from the precursor-physisorption state as compared with those which undergo the trapping desorption process. On the contrary, it seems that molecules which experience only weak interaction with the surface, have somewhat higher rotational temperature, even though their incident rotational temperature is very cold. This is shown by the measurements carried out by Segner et al.(8), who scattered NO from an oxygen covered Pt(111) surface and observed slightly higher rotational temperature as compared with the clean metal surface. Similar observation was made in the present study, where at specular angle (see Fig. 8) the contribution from direct inelastically scattered molecules increase the overall rotational temperature(15). Similar results were obtained also for the weak interaction between NO

Fig. 8: Rotational temperature of scattered NO molecules from a Pt(111) surface.

and Ag(111)(4). In such a case the precursor model is not expected to account correctly for the processes that are behind the rotational excitation mechanism. If exit channel effects are important in the dynamics of desorption(5) and direct inelastic scattering of NO molecules, then possibly there is only little difference in the outcome rotational distribution of the scattered molecules by the two mechanisms. At high incident translational energies, however, an efficient surface mediated translational to rotational energy transfer must be considered for weakly interacting gas-surface systems(4). It is believed, therefore, that more detailed dynamical treatments, such as those by Gadzuk et al(32), Zamier et al(33) and Tanaka et al(34) are necessary to understand and predict the crystal temperature dependence of the observed rotational temperature.

5. CONCLUSION

The energy transfer and accommodation data involving the translational and vibrational energy distributions of NO molecules scattered from a Pt(111) surface were analyzed in terms of a precursor model. With a single parameter, e.g. the difference in activation energy (ΔE) for desorption (E_∞) and chemisortpion (E_s) from the precursor state, we could account quite accurately for the data taken at different scattering angles, crystal temperatures and various incident kinetic energies. The vibrational excitation data was further treated by a kinetic model from which a lower limit for the deexcitation rate constant of vibrationally excited NO molecules on the Pt(111) surface of $1x10^{12} sec^{-1}$ was estimated. Using this model, a crystal temperature dependence for the excitation process, possibly via an electron hole pair annihilation mechanism is suggested. The rotational excitation in this NO/Pt(111) system is poorly accommodated to the surface. Further study of the detailed dynamical effects during the desorption process is necessary in order to understand this process.

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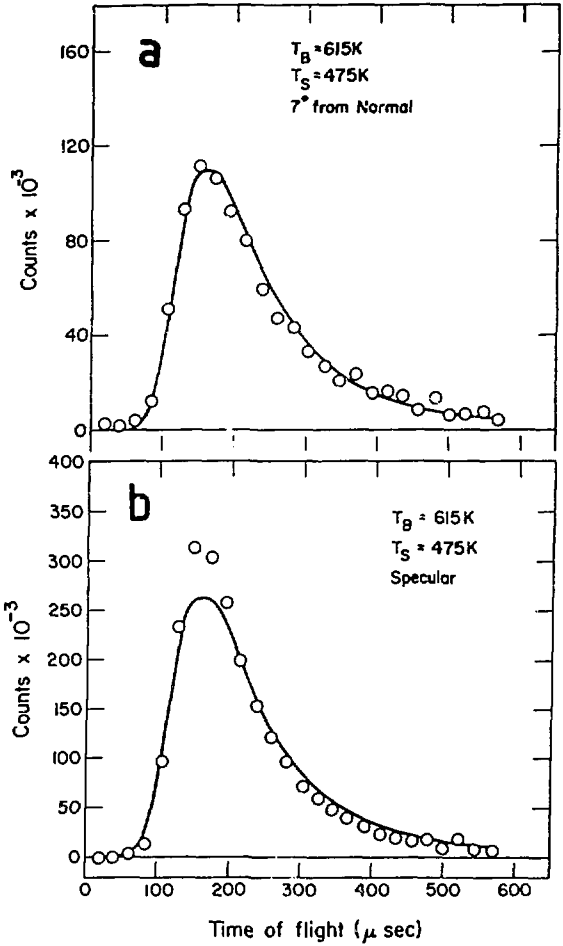

Fig. 1 XBL 818-11064A

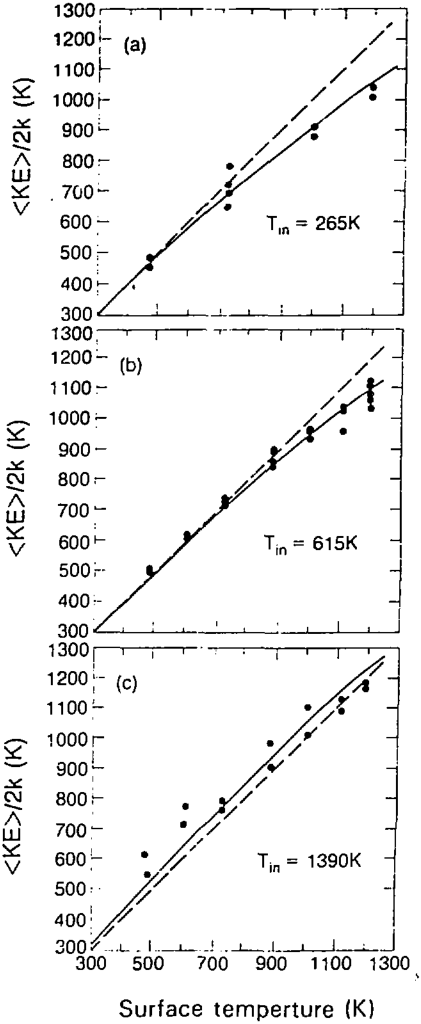

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Fig. 2

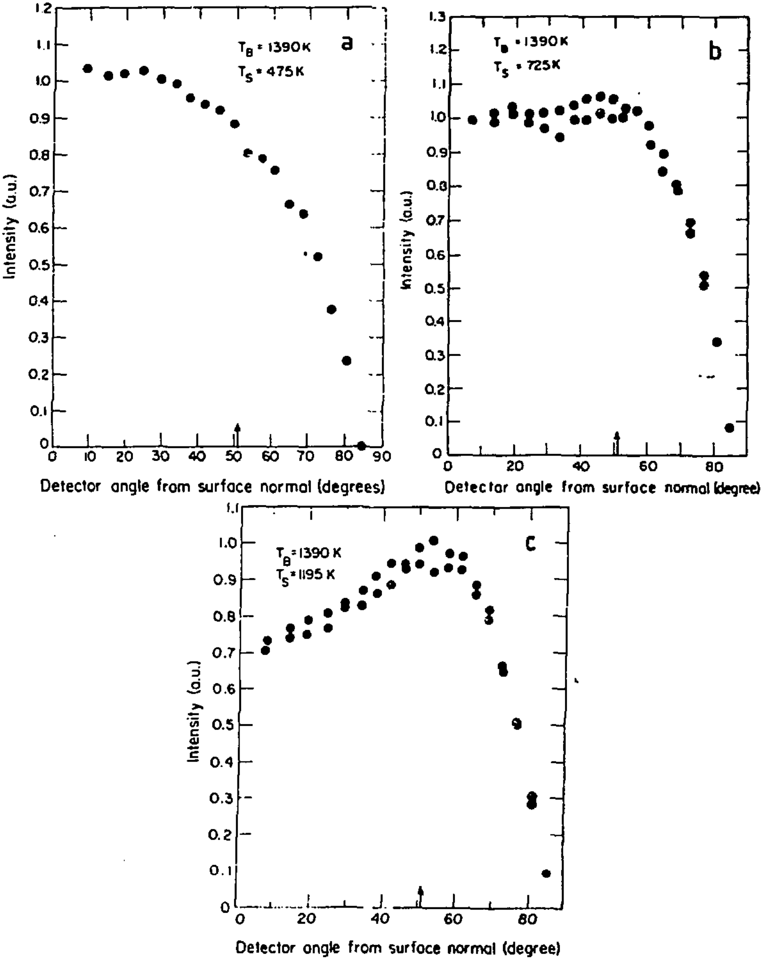

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Fig. 3

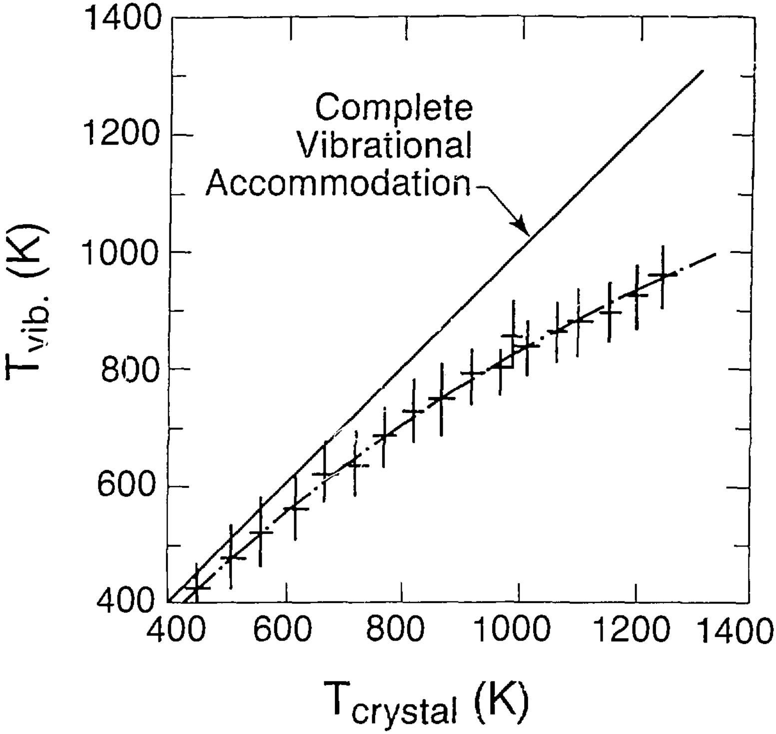

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Fig. 4

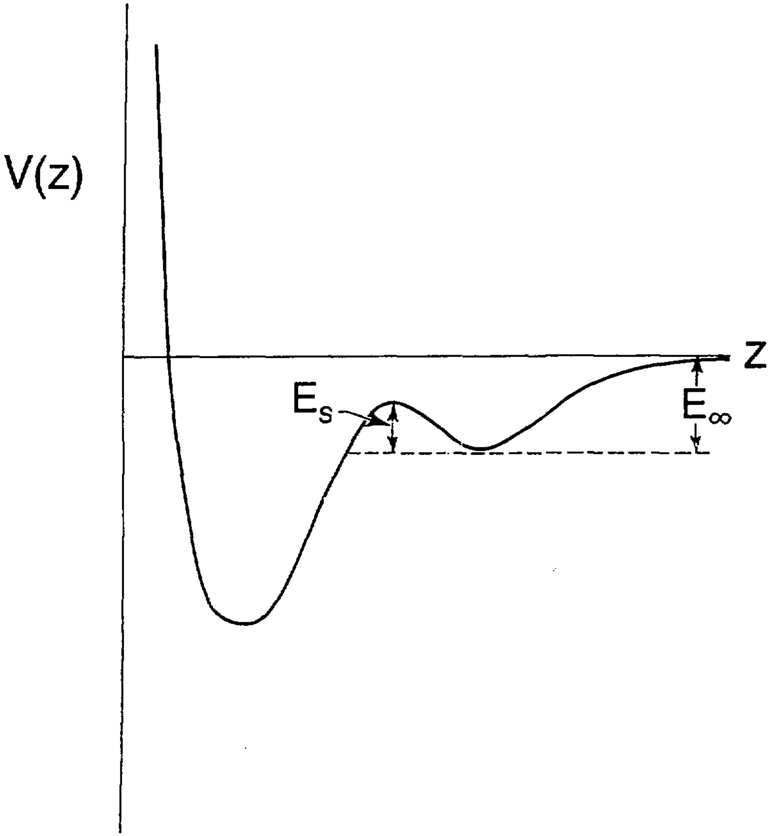

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Fig. 5

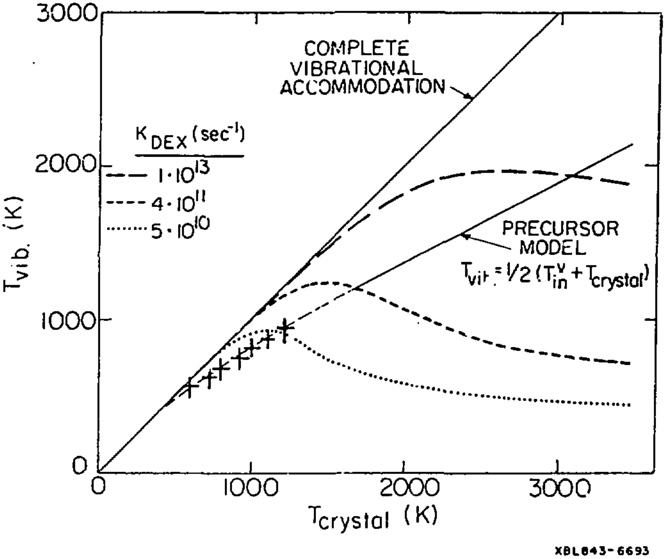
3000
2000
1000
0
Tvib. (K)
0
1000
2000
3000
Tcrystal (K)
COMPLETE VIBRATIONAL ACCOMMODATION
K DEX (sec⁻¹)
1·10¹³
4·10¹¹
5·10¹⁰
PRECURSOR MODEL
Tvib = 1/2 (Tᵛin + Tcrystal)
XBL843-6693

Fig. 6

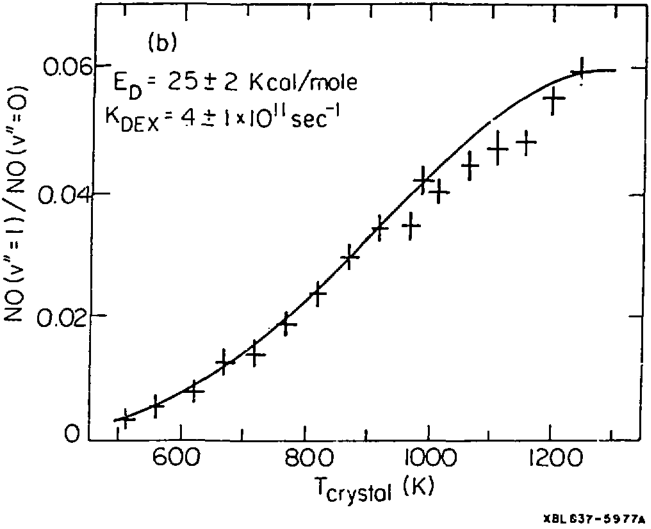
(b)
E_D = 25 ± 2 Kcal/mole
K_{DEX} = 4 ± 1 x 10^{11} sec^{-1}
NO(v″=1)/NO(v″=0)
0.06
0.04
0.02
0
600
800
1000
1200
$T_{crystal}$ (K)
XBL 837-5977A

Fig. 7

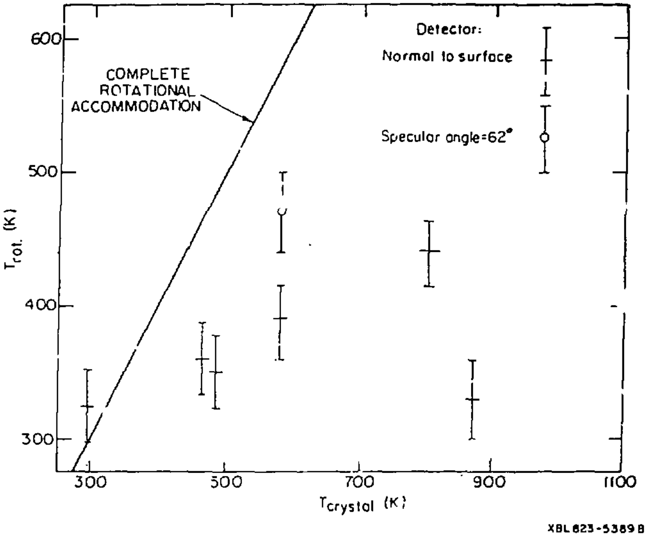
600
500
400
300
$T_{rot.}$ (K)
COMPLETE ROTATIONAL ACCOMMODATION
Detector:
Normal to surface
Specular angle=62°
300
500
700
900
1100
$T_{crystal}$ (K)
XBL 823-5389 B

Fig. 8