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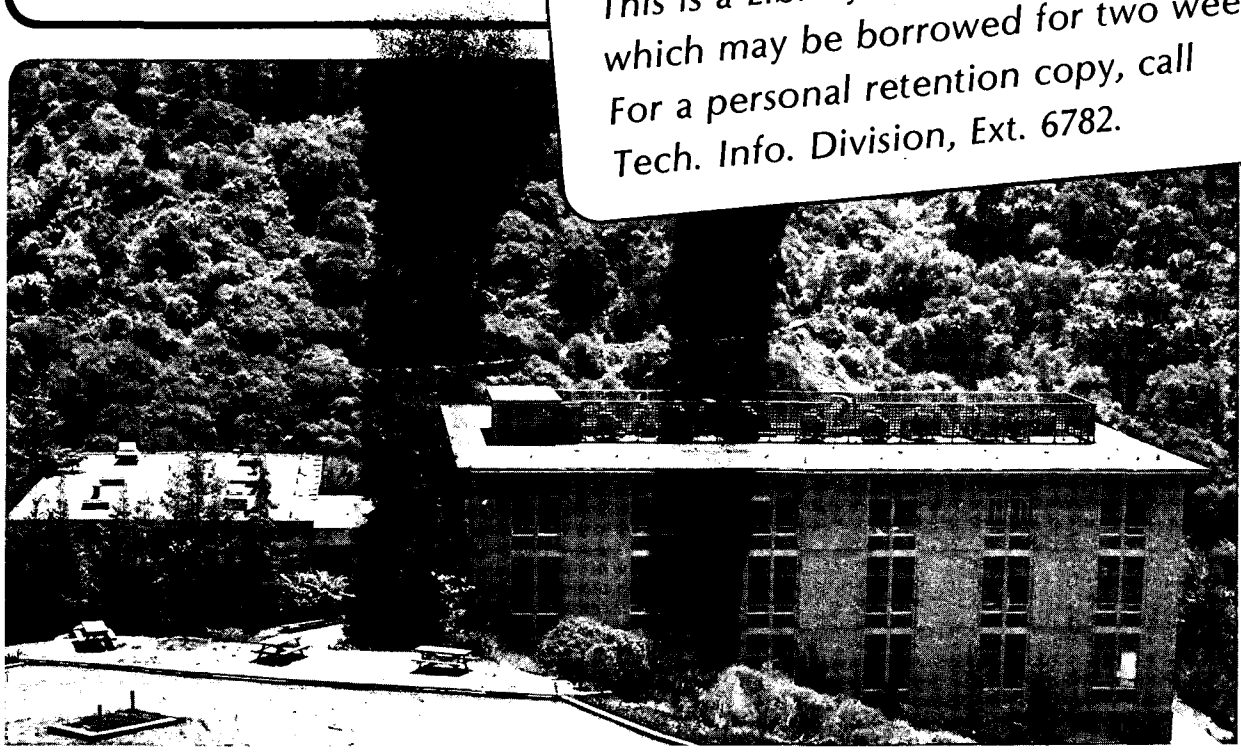

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ABSTRACT

A model is formulated and applied to the recently measured vibrational and translational accommodation of NO scattered from a Pt(111) crystal surface. The model assumes that the initial adsorption of NO occurs via a precursor state. Experimentally observed memory of the incident energy by the scattered molecules is a result of competition between chemisorption and desorption from the precursor state.

I. INTRODUCTION

One of the most extensively studied systems of inelastic molecule-surface scattering is the scattering of nitric oxide molecules from a platinum single crystal surface. It is well known that NO strongly interacts with the platinum surface[1-3]. In their molecular beam studies Lin and Somorjai[1] report high sticking probabilities and first order desorption kinetics from both the (111) and a stepped (557) platinum crystal surfaces. Similar qualitative data were obtained by Campbell, Ertl and Segner[2] as well as Serri, Cardillo and Becker[3]. The results of all these measurements were integrated into a single model by Serri, Tully and Cardillo[4], whose main result is a 25 kcal/mole activation energy for desorption from terraces and 34 kcal/mole for desorption from steps.

Angular and velocity distributions of NO scattered from Pt(111) have been measured by Gurthrie et al[5]. One of the surprising results of this study was that seemingly the scattered NO did not have a total loss of memory of its incident velocity. Both the angular distributions and the final kinetic energy depended on the translational temperature of the incident beam. In view of the long surface residence time of the adsorbed NO molecules (Ca 10 μsec at 500K on the (111) terraces), this result is unexpected - any statistical theory would, at these residence times predict total accommodation.

At the same time, the rotational and vibrational accommodation of NO scattered from Pt(111) crystal surfaces were also measured by Asscher et al[6], using two photon ionization of the scattered NO molecules. Here too, the measured accommodation was incomplete.

The purpose of this paper is to suggest a model which provides a possible explanation for the lack of accommodation in this system. The main assumption of the model is that scattering of NO from platinum occurs in two stages. First, the molecule is physisorbed in a precursor state, then it is either chemisorbed or desorbed. The lack of total accommodation is a reflection of the competition between these two processes.

The model treats both vibrational and translational accommodation the same way and has only one adjustable parameter - the difference in activation energy for desorption and chemisorption from the precursor state. The model is presented in Section II. It is applied to the scattering of NO from the Pt(111) surface in Section III. Note that we are not addressing the question of rotational accommodation, which has been discussed in recent publications[6,7,8]. The major assumptions of the present model are discussed in Section IV.

II. THE MODEL

The basic features of the model are outlined in Fig. 1. We assume that initial adsorption and scattering occur through a precursor state which is separated from the deep well of the chemisorbed state via a barrier whose height is E_S. The precursor state has a well depth E_∞ relative to the gas phase. If an incident molecule reaches the precursor state and is fully equilibrated with the surface whose temperature is T_S, then the probability p of being chemisorbed may be evaluated using standard statistical theory's expression[9]:

$$p = [1 + \exp(-\Delta E/kT_S)]^{-1} \qquad \Delta E \equiv E_\infty - E_S \qquad (1)$$

In the model, however, we assume that only the perpendicular component of the translation energy of the incident NO molecule is fully equilibrated with the surface. As estimated by Serri et al[4], the activation energy for diffusion parallel to the surface in the chemisorption well is 5 kcal/mole, therefore such diffusion in a physisorption state should have a much smaller barrier. Thus as long as the incident molecule is in the physisorbed precursor state we will assume that the component of the incident translational energy parallel to the surface is conserved. Since motion parallel to the surface cannot cause desorption it does not affect the chemisorption probability. The statistical expression, Eq. (1), is thus justified since we are assuming that the perpendicular momentum component equilibrates with the surface. If, the molecule is chemisorbed, then we assume that the parallel momentum component is also fully thermalized.

If we denote θ_{in} as the incident beam angle (relative to the normal to the surface), T_{in}^{T} as the incident translational temperature defined as $\langle E\rangle/2k$, where $\langle E\rangle$ is the average incident kinetic energy[5] and T_f^T as the final translational temperature, then the statements in the previous paragraph is summarized by the expression:

$$T_f^T = p \cdot T_s + (1-p)[T_s \cos^2 \theta_{in} + T_{in}^T \sin^2 \theta_{in}] \qquad (2)$$

The first term on the right hand side denotes total accommodation in the chemisorbed state, the second term a partial accommodation in the precursor state.

Vibrational accommodation is treated similarly. Here we assume, that within the residence time of the molecule in the physisorbed state there is

only very weak coupling between the NO vibrational mode and the translational mode. Thus if the molecule is desorbed from the precursor state it retains its initial vibrational temperature - T_{in}^{V}. If it becomes chemisorbed then it will be totally accommodated. Thus, if T_f^V is the final vibrational temperature, the model implies that:

$$T_f^V = p \cdot T_s + (1-p)\, T_{in}^V \qquad (3)$$

Except for a few additional refinements, Eqs. 1-3 summarize the model. Note that we have only one free parameter - ΔE - the difference in activation energies for chemisorption and desorption from the precurser state, all other variables are determined by the experimental conditions.

An interesting consequence of the model is a simple physical interpretation for the vibrational accommodation coefficient γ_V which is defined as:

$$\gamma_V = \frac{T_f^V - T_{in}^V}{T_s - T_{in}^V} \qquad (4)$$

It is easy to see that in terms of the model:

$$\gamma_V = p = [1 + \exp(-\Delta E/kT_s)]^{-1} \qquad (5)$$

Thus the vibrational accommodation coefficient may be interpreted as the probability of being chemisorbed on the surface. Similarly the translational accommodation coefficient γ_T, is given by the model as

$$\gamma_T = p \sin^2\theta_{in} + \cos^2\theta_{in} \qquad (6)$$

Thus far we have assumed that any collision of the molecule with the surface will at least lead to physisorption in the precursor state. This is

of course not the general case, in principle one must allow for direct inelastic collisions. In fact, the angular distributions for NO scattered from Pt(111)[2,5] present a clear contribution from direct inelastic collisions at the specular angle. However, at zero or 90 degrees to the surface normal one may assume that this contribution is minor and therefore negligible. At the specular angle, one may estimate the fraction of the direct inelastic process denoted as $1-P_s$, by comparing the measured angular distribution with a statistical cos θ distribution. Thus at the specular angle the final translational temperature is estimated as:

$$T_f^T = (1-P_s)T_{in}^T + P_s[p \cdot T_s + (1-p)(T_s \cos^2 \theta_{in} + T_{in}^T \sin^2 \theta_{in})] \quad (7)$$

$$T_f^V = (1-P_s)T_{in}^V + P_s[p \cdot T_s + (1-p)T_{in}^V] \quad (8)$$

In all applications described in the next section, P_s will not be a parameter, it will be evaluated from the experimental angular distributions.

III. APPLICATION TO NO-Pt(111) SCATTERING

We first apply the model to the vibrational accommodation measured by Asscher et al[6]. To determine the parameter ΔE, we fit Eq. (3) to the results provided in Fig. 9 of Ref. 6. Although the incident vibrational temperature was not experimentally measured in Ref. 6, we estimate it as 200K. Changing this estimate by 50% does not change the final result for ΔE by more than 10%. We find that ΔE = 2.5 kcal/mole, and the quality of the fit is shown in Fig. 2. Note that the vibrational temperatures measured by Asscher et al[6] are for NO scattered to the surface normal and therefore we may avoid correcting for the probability (P_s) as expressed in Eq. (8).

Given the value of the ΔE we may apply the model to the translational energy measurements of Guthrie, et al[5]. In Fig. 3 we compare the model with their results measured at 7° from the normal (The incident angle is 51°). Here again we are far away from the specular angle so that we may safely assume that direct inelastic contributions are negligible, i.e. we use Eq. (2). Note the quantitative agreement of the model with the experimental measurements at all three incident kinetic energies. We stress that the only parameter used in Fig. 3 is the value of ΔE derived from the fit of the vibrational accommodation plot shown in Fig. 2.

Guthrie et al[5] also measured the translational temperature at the specular angle. Here, one must take into account the direct inelastic process. Fortunately though, these authors also measured product angular distributions for different incident energies and surface temperature. Specifically, for both T_{in}^{T} = 615K and T_{in}^{T} = 1390K they measured angular distributions at T_s = 475K, 725K and 1195K. For T_{in}^{T} = 265K they measured at T_s = 725K and 1195K. Using their results, we may evaluate (as outlined in the previous section) the direct inelastic contribution at the specular angle. Furthermore, for a given incident kinetic energy one can approximately fit the experimental[5] surface temperature dependence of P_s to a linear form:

$$P_s = \alpha(T_{in}) - \beta(T_{in}) \cdot T_s \qquad (9)$$

the fitted values of α,β are provided in Table 1. Given P_s one can use the model - Eq. (7), and compare with the measured translational temperatures at the specular angle. This is shown in Fig. 4 for specular scattering at the three incident kinetic energies. Although the fit is not quite as good as

for normal scattering (Fig. 3) the qualitative trends are well accounted for. One must take into account that there is a large (~20%) uncertainty in our determination of P_s.

IV. DISCUSSION

A statistical model has been formulated and applied to the vibrational and translational accommodation of NO observed upon its scattering from Pt(111) crystal surface. The good agreement of the model with the available experimental data confirms our expectation that a chemisorbed system will behave statistically - products desorbed from a chemisorbed state have no memory of their incident energy. All deviations from total accommodation are the result of either desorption from a physisorbed state or direct inelastic scattering processes. However, some of the assumptions of the model might seem restrictive, and therefore should be discussed in more detail. A key element of the model is the assumption that the NO molecules approaching the surface occupy a percursor state, prior to chemisorption. This is not a new idea in the description of chemisorption processes. In fact, in the early days of chemisorption studies on metal surfaces, it was already suggested by Lennard-Jones[10] that the potential which describes the interaction between a molecule and a metal surface should have two minima: a shallow physisorption state, whose well depth is typically less than 7 kcal/mole, and a much deeper chemisorption state. Note that the present model is not sensitive to the precise well depths of either the precursor or the chemisorbed state. The nature of the precursor state and its origin are discussed by Kisliuk[11] and Ehrlich[12]. Kisliuk describes the precursor as a layer of molecules weakly held on top of already filled surface sites[11]. This model was used to explain the sharp decrease in the sticking probability of NO on Pt(111), at coverages approaching one monolayer[2]. Most of the experimental

data used for the model presented here, however, are collected at crystal temperatures in which the NO coverage is very small, where the Kisliuk model is not expected to be important. The topography of the one dimensional potential energy surface assumed in the present model is very similar to that proposed by Ehrlich[12]. He postulates a double minimum potential in order to calculate the sticking probability of N_2 molecules on tungsten surfaces, as a function of coverage and crystal temperature. However, no experimental information on energy transfer and accommodation is available for the system studied by Ehrlich to support or disprove his model. Nevertheless, recent studies of N_2 scattering from tungsten single crystals imply the existence of a barrier to chemisorption[13]. The dissociative adsorption of N_2 on iron single crystals was also treated theoretically by means of a precursor state with kinetic arguments similar to those presented here[14]. In both the N_2/W and the N_2/Fe systems, the value of $\Delta E = E_\infty - E_S$, as defined in Fig. 7, is negative, namely the adsorption process has an activation energy. This activation barrier is at least partially responsible for the small sticking probability in these systems[13,14]. Note that in the NO/Pt(111) case ΔE is positive, thus allowing for a much higher sticking probability, as is also observed experimentally[1-3].

In deriving our model we have utilized (Eq. 2) one of the assumptions of the "hard cube" model[15]: The tangential momentum component is conserved while the vertical component is fully accommodated. Note though, that even if the vertical momentum component is not fully accommodated, the calculated translational temperature would shift only slightly from the fit shown in Figs. 3 and 4 and would still be within the experimental error.

In order to treat the specular scattering the same way we approached

scattering into the surface normal, we used the empirical parameter P_s which is inferred from the experimental results of Guthrie et al[5]. P_s is related to the extent of occupation of the precursor state by the incident NO molecules.

One might well ask how the NO molecule is scattered off the surface without reaching the precursor state. We note that one has to consider the possibility that scattering, especially at high incident kinetic energy and crystal temperature[5], may originate from partial oxygen coverage of the Pt(111) surface as noted previously by several authors[2,3,7]. A substantial decrease in the interaction between NO and Pt(111) occurs in the presence of oxygen coverage. In fact, Segner et al[7] have reported enhanced specular scattering of NO from a preoxidized Pt(111) surface. In any case, we should stress that P_s is based purely on the assumption that the angular distribution of molecules scattered from the precursor state is statistical (e.g. cos θ). It may well be, that at increased incident and surface temperatures, scattering from the precursor state tends to be more specular. This would serve to increase P_s (smaller direct inelastic contribution) and would only <u>improve</u> the agreement between the model prediction and the experiment. Increased P_s would imply less memory and thus, less deviation from total accommodation. This is the trend needed to obtain better agreement, in Fig. 4.

In this paper we have treated only translational and vibrational accommodations. Of course, rotational state distributions have also been measured for NO scattered from Pt(111)[6,7]. The overall result is that rotational accommodation is quite poor. Our model does not account for rotational accommodation, moreover it is not readily evident whether there

should be any difference between the rotational distributions of NO scattered from the precursor state or the chemisorbed state. If exit channel effects are important, then possibly there is little difference between the two channels. Moreover, exit channel interactions tend to be nonstatistical in nature so that our model is not easily applicable. We believe that more detailed dynamical studies [8b,16] are needed to explain the observed poor rotational accommodation. One possible method for attacking this problem is via an information theoretic synthesis of dynamic constraints within a statistical framework, as was shown by Zamir et al[16]. Levine et al[17] have also successfully applied such an approach for translational energy accommodation of physisorbed systems.

V. CONCLUSION

A precursor state model is used to analyze translational and vibrational energy accommodation data for NO molecules scattered from Pt(111). Translational and vibrational energy distributions at different scattering angles, surface temperatures and at various incident kinetic energies, could all be fitted with a single parameter ΔE. This parameter is the difference in activation energies for desorption (E_∞) and for chemisorption (E_s) from the precursor state. Its value was determined to be 2.5 kcal/mole. The positive value of ΔE ensures a nonactivated adsorption process in agreement with experimental observation. The model is of general applicability since it is relatively insensitive to the precise binding energies of either the physisorbed or the chemisorbed state.

VI. ACKNOWLEDGEMENTS

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TABLE 1. Parameters for Sticking Probabilities

T_{in}(°K)	α	β(°K^{-1})
265	0.825	1.1×10^{-4}
615	0.80	2.25×10^{-4}
1390	1.00	4.9×10^{-4}

VII. FIGURE CAPTIONS

1. Schematic diagram of the precursor state model for accommodation. Here z denotes the (normal) distance of the molecule from the surface, V(z) is its potential energy.

2. Vibrational temperature of scattered NO molecules (T_{vib}) as a function of the Pt(111) crystal temperature. The dash-dotted line is the model prediction of the scattered vibrational temperature if ΔE = 2.5 kcal/mole. The crosses denote the experimental results [6].

3. Translational accommodation in NO-Pt(111) collisions. Solid circles denote experimental measurements[5] with the detector at 7° from the normal to the surface. Solid line is the result of our model calculations, based on Eq. 2. Dashed line represents total accomodation.

4. Translational accommodation in NO-Pt(111) collisions. Open circles denote experimental measurements[5] at the specular angle (51° from normal to the surface). Solid line is the result of model calculations based on Eq. 7 and P_s values given in Table 1. Total accommodation yields the dashed line.

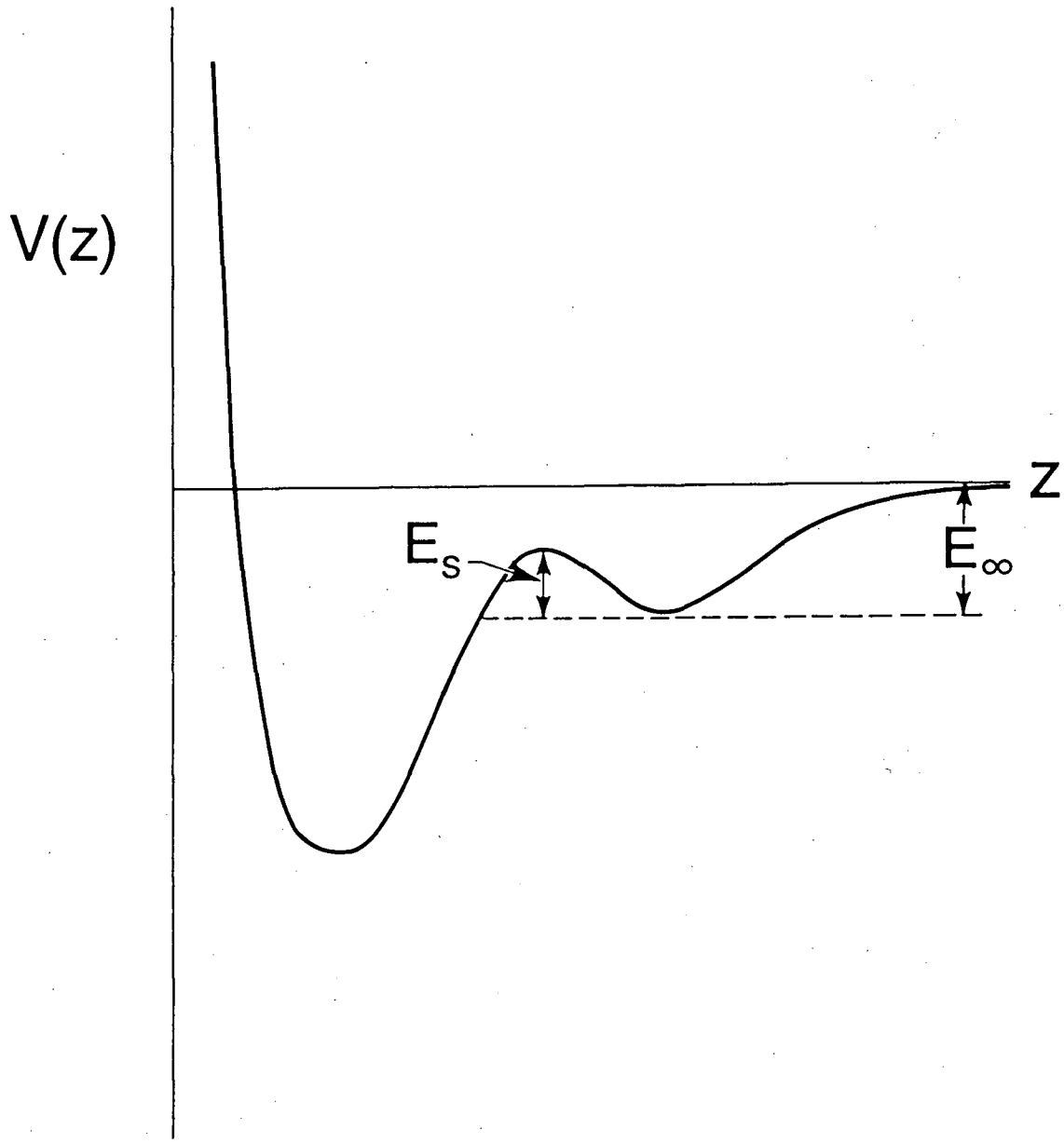

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Fig. 1

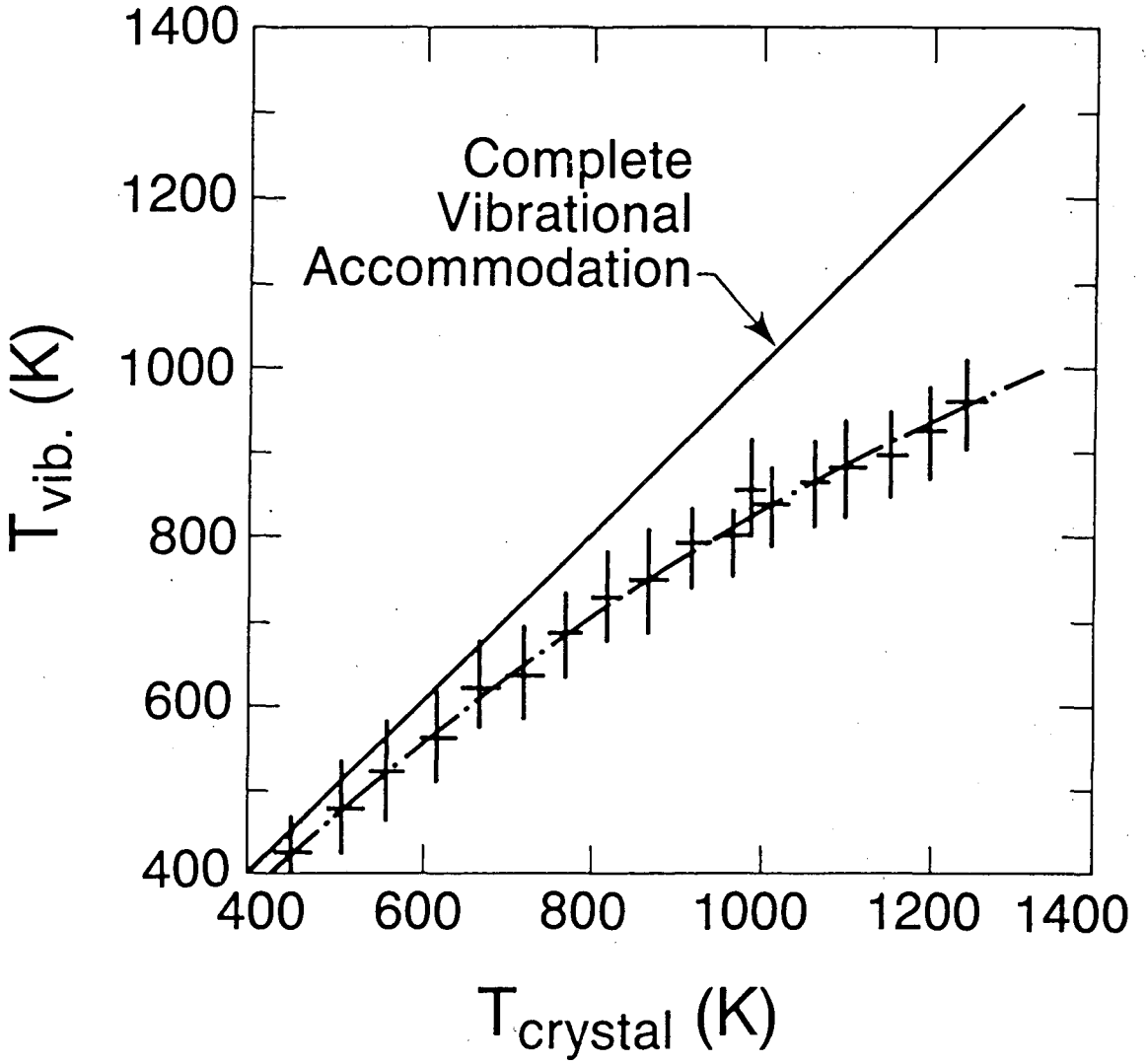

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Fig. 2

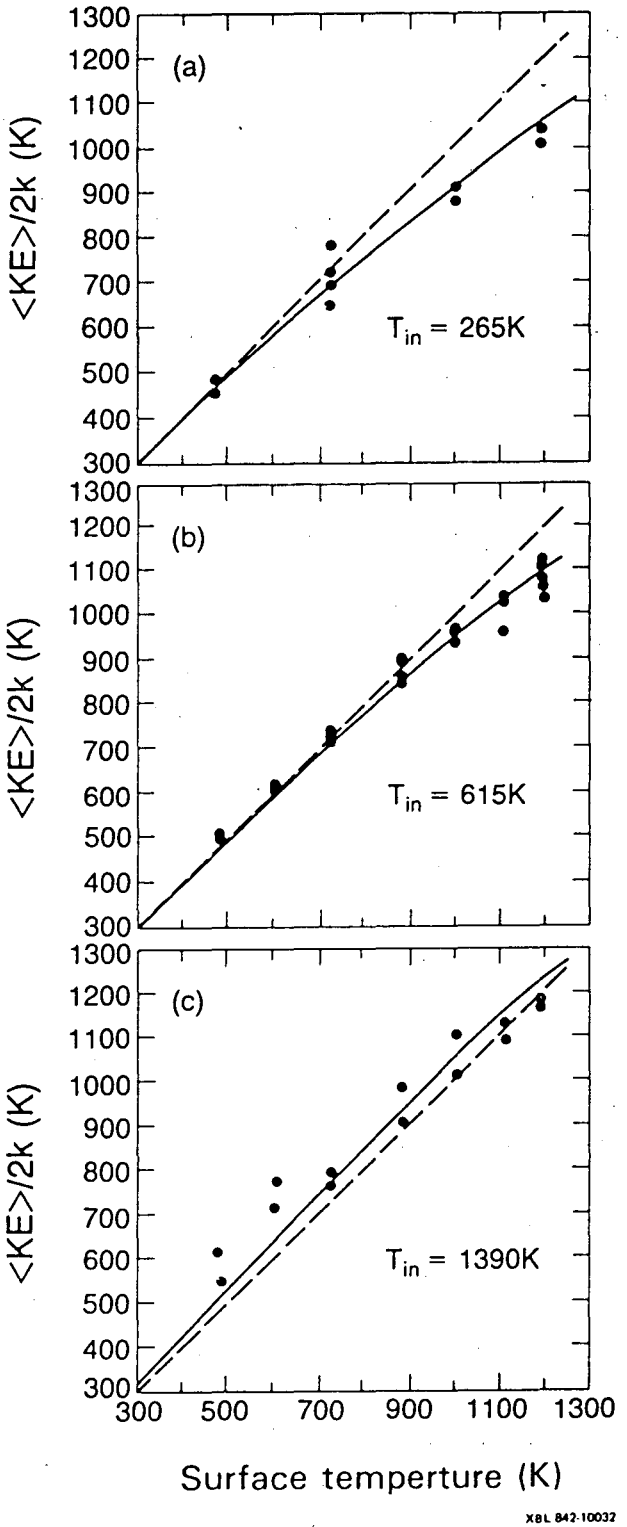
(a)
(b)
(c)
T_{in} = 265K
T_{in} = 615K
T_{in} = 1390K
<KE>/2k (K)
Surface temperture (K)
300
400
500
600
700
800
900
1000
1100
1200
1300
XBL 842-10032

Fig. 3

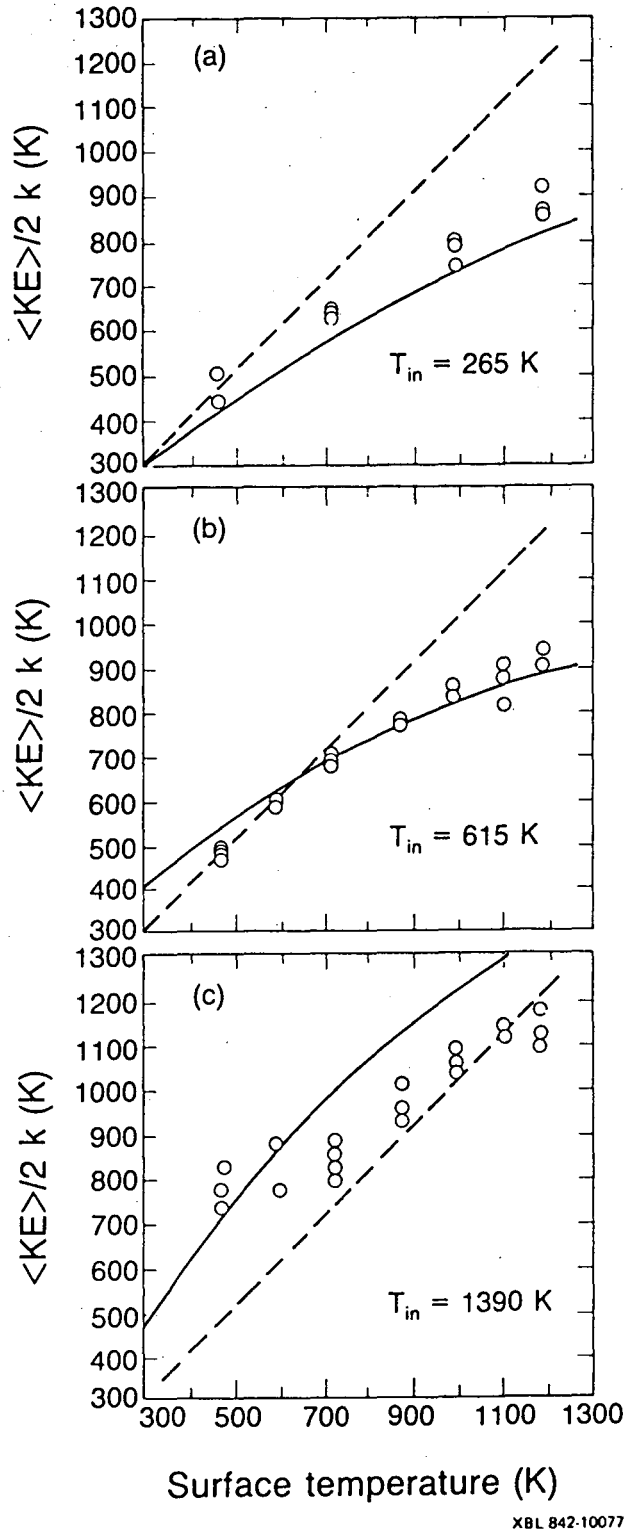
(a)
(b)
(c)
<KE>/2 k (K)
T_{in} = 265 K
T_{in} = 615 K
T_{in} = 1390 K
300
400
500
600
700
800
900
1000
1100
1200
1300
Surface temperature (K)
XBL 842-10077

Fig.4

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