LBL-16830
Preprint c.2

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

FEB 21 1984

LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular Research Division

Submitted to the Journal of Chemical Physics

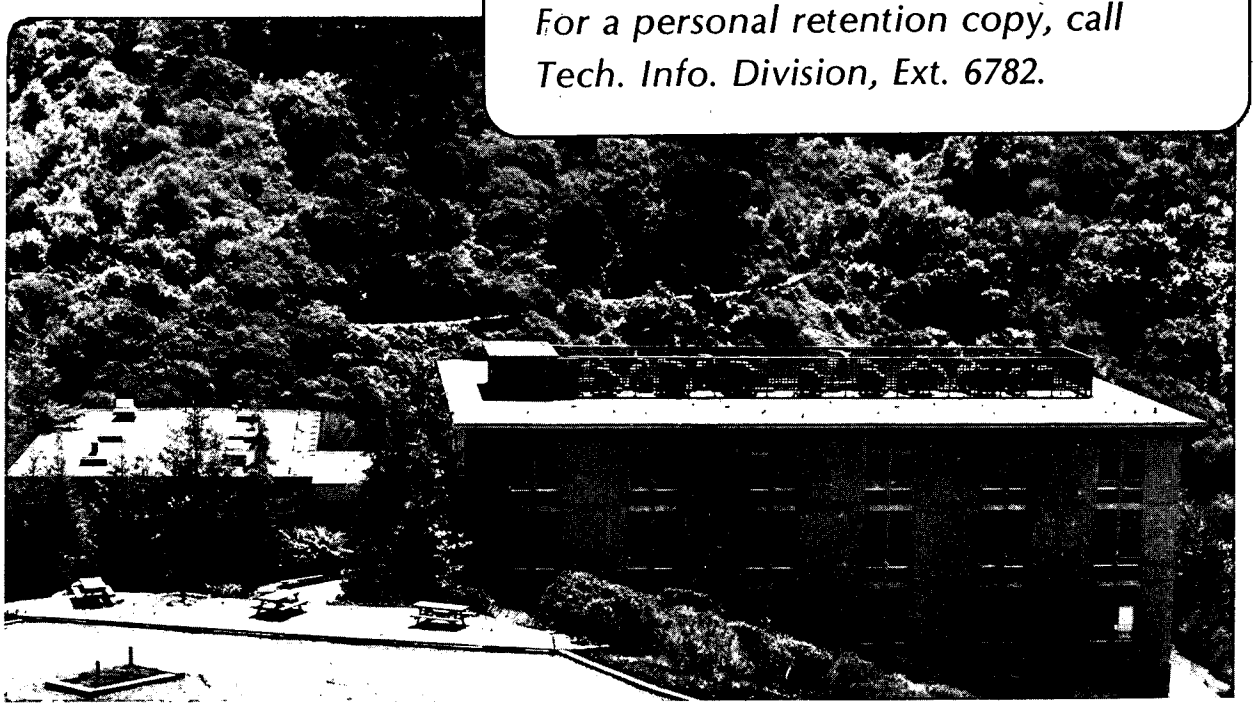
VIBRATIONAL EXCITATION AND DEEXCITATION RATES OF MOLECULES ADSORBED ON METAL SURFACES

M. Asscher, G.A. Somorjai, and Y. Zeiri

October 1983

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.



LBL-16830 c.2

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Vibrational Excitation And Deexcitation Rates of Molecules Adsorbed on Metal Surfaces

Micha Asscher* and Gabor A. Somorjai

Materials and Molecular Research Division

Laurence Berkeley Laboratory and Department of Chemistry

University of California Berkeley, California 94720

and Yehuda Zeiri*

Arthur Amos Noyes Laboratory of Chemical Physics

California Institute of Technology

Pasadena, California 91125

(Received)

Abstract

The rates for vibrational excitation and deexcitation of adsorbed molecules on metal surfaces are studied. The desorption of the adsorbed molecules is shown to compete with the excitation process resulting "vibrationally cold" desorbing molecules. Simple rate equations together with the available experimental data are used to estimate the rates for vibrational excitation and deexcitation of NO molecules on Pt (111) surfaces as a function of the crystal temperature. The application of this approach for other systems is discussed.

*Chaim Weizmann Postdoctoral Fellow

I. INTRODUCTION

The interaction between gas phase molecules and solid surfaces are of fundamental importance for the understanding of catalytic and other chemical processes occuring on solid surfaces. In recent years the dynamical aspects of such interactions were studied both experimentally [1] and theoreticaly [2] for many molecule-solid surface systems. Molecular beam-surface scattering experiments were used to study the translational energy distribution of the scattered molecules [1], as well as, their internal energy distribution between the rotational [3] and vibrational [4] modes as a function of surface temperature. Energy transfer between vibrationally excited molecules and metal surfaces was studied during a collision with the surface [5]. The decay rate of vibrationally excited molecules adsorbed on a metal surfaces was studied theoretically [6] and experimentally [7] by Persson *et al.* who employed an electrodynamic model in which electron-hole pairs are formed by energy transfer from the vibrationally excited molecule to the surface. This model was used to interpret measurements of the linewidth of excited C-H and C-D bonds in methoxide adsorbed on the Cu (100) surface using IR reflectance-absorbance spectroscopy. They concluded that for this system a deexcitation rate of $3\times10^{12}\ sec^{-1}$ describes the experimental data [7]. A different study by Zhdanov *et al.* [8] presents a review of the possible mechanisms for vibrational deexcitation on metal surfaces. In this work it is shown that if multiphonon interactions dominate, then the deexcitation rates are expected to be very slow (less than $10^{7}\ sec^{-1}$). Such interactions usually incorporate a few phonons to dissipate the vibrational energy of the adsorbed molecule. When the vibrational energy is assumed to be channeled to the excitation of plasmon states in the metal, deexcitation rates

as high as 10^9-10^{11} sec^{-1} are predicted [9]. Similar conclusions were presented by Brus [10], who applied classical electrodynamic theory to study the same problem. In all these studies it is predicted that the relaxation rate via electronic states in the metal should be temperature independent [9].

Most common experiments conducted to date, examine the vibrational relaxation rate due to collisions with solid surfaces by measuring the average probability to transfer the vibrational energy [8]. Direct measurement of the IR emission decay time of an excited CO_2 molecule due to collisions with different solid walls, as a function of the wall temperature, were reported recently [11]. In all these studies the relaxation of the vibrational energy is adressed, none however discusses the related process of vibrational excitation.

In this work we will examine the magnitude of vibrational exitation and deexcitation rates of molecules adsorbed on metal surface, using a simple kinetic model. The competing processes that control the flux of vibrationally excited molecules which desorb from the surface are the vibrational excitation and deexcitation on the surface as well as the desorption rate of the adsorbed ground state molecules. The kinetic model together with experimental results available for the NO/Pt (111) system [4a], are used to estimate the vibrational excitation and deexcitation rates of NO adsorbed on the metal. The significance of these rates for the understanding of the mechanism of such energy transfer processes in this system is discussed.

II. KINETIC MODEL

Consider two types of adsorbed molecules on a metal surface; molecules in their ground vibrational state, N_a^0, and the same molecule in its first vibrationally excited state, N_a^1. For simplicity, we shall not consider in the following, adparticles which are vibrationally excited to states higher than v=1, although such molecules were detected experimentally [4d]. In the kinetic model that will be described, we shall consider an experiment in which a supersonic beam of molecules in their ground vibrational state and at translational energy much smaller than the vibrational spacing, are impinging on the metal surface. The flux of molecules that adsorb on the surface is given by

$$f(T) = f_0 S(T) , \tag{1}$$

where T is the surface temperature and $S(T)$ is the sticking probability (which is estimated in Ref. [4a]). The adsorbed molecules may react on the surface to yield vibrationally excited species in addition to their probability to desorb to the gas phase where they are detected. The concentration (on the surface) of the ground and vibrationally excited adsorbates will be given by

$$\frac{dN_a^0(t;T)}{dt} = f(T) - k_{ex}(T)N_a^0(t;T) + k_{dex}(T)N_a^1(t;T) - k_d^0(T)N_a^0(t;T) \tag{2a}$$

and

$$\frac{dN_a^1(t;T)}{dt} = k_{ex}(T)N_a^0(t;T) - k_{dex}(T)N_a^1(t;T) - k_d^1(T)N_a^1(t;T) . \tag{2b}$$

In Eqs. (2) k_d^0 and k_d^1 represent the desorption rate of the ground and the vibrationally excited molecules respectively, while, k_{ex} and k_{dex} represent the vibrational excitation and deexcitation rates respectively. We have assumed, in writing Eqs. (2), first order kinetics for the excitation and

deexcitation processes.

It is easy to solve Eqs. (2), using the Laplace transform method, to obtain the time dependent concentration of the ground state and excited adsorbed molecules (for a given surface temperature)

$$N_a^0(t;T) = f(T)\left[\frac{a_1}{b_1} + \frac{a_2}{b_2} - \left[\frac{a_1}{b_1}\exp(-b_1 t) + \frac{a_2}{b_2}\exp(-b_2 t)\right]\right] \quad (3a)$$

and

$$N_a^1(t;T) = k_{ex} f(T)\,[\,\frac{1}{K_1}(\frac{a_1}{b_1} + \frac{a_2}{b_2}) - \frac{a_1}{b_1(b_1+K_1)} - \frac{a_2}{b_2(b_2+K_1)} \quad (3b)$$

$$+ \frac{a_1}{b_1(b_1+K_1)}\exp(-(b_1+K_1)t) + \frac{a_2}{b_2(b_2+K_1)}\exp(-(b_2+K_1)t)$$

$$- \frac{1}{K_1}(\frac{a_1}{b_1} + \frac{a_2}{b_2})\exp(-K_1 t)\,]$$

where

$$K_1 = k_d^1 + k_{ex} \qquad K_2 = k_d^0 + k_{ex}$$

$$K_3 = K_1 + K_2 \qquad K_4 = K_1 K_2 - k_{ex} k_{dex}$$

$$b_1 = 2K_4\left[K_3 + (K_3^2 - 4K_4)^{1/2}\right]^{-1}$$

$$b_2 = \tfrac{1}{2}\left[K_3 + (K_3^2 - 4K_4)^{1/2}\right]$$

$$a_1 = \frac{b_1 - K_1}{b_1 - b_2} \qquad a_2 = \frac{K_1 - b_2}{b_1 - b_2}$$

In the solution of Eq. (3) we have assumed that the initial concentration ($T = 0$) of the molecules on the surface is zero, e.g. $N_a^0(0;T) = N_a^1(0;T) = 0$. Once the concentrations N_a^0 and N_a^1 are known, the flux of the desorbing molecules, which are the experimentally detected quantities, may be obtained

$$N_g^0(t;T) = k_d^0 N_a^0 \tag{4a}$$
$$N_g^1(t;T) = k_d^1 N_a^1 \tag{4b}$$

In many experimental set ups, steady state concentrations of the adsorbates are maintained. In such cases, Eqs. (3) may be rewritten in a simpler form,

$$N_a^0(T) = \frac{f(T)[k_{dex}(T) + k_d^1(T)]}{k_{dex}(T)k_d^0(T) + k_d^1(T)[k_{ex}(T) + k_d^0(T)]} \tag{5a}$$

$$N_a^1(T) = \frac{k_{ex}(T)N_a^0(T)}{k_{dex}(T) + k_d^1(T)} \tag{5b}$$

In order to use Eq. (4) to calculate the flux of ground and vibrationally excited state molecules desorbing from the surface, few comments are necessary. There are four rate constants that determine the kinetics on the surface: k_{ex} , k_{dex} , k_d^0 and k_d^1. The desorption rate of ground state molecules can be measured using thermal desorption spectroscopy or modulated molecular beam experiments. In the following we shall assume that due to the relatively weak coupling between the molecule-surface bond and the internal vibrational modes of the adsorbate (large difference between the stretch frequencies), the desorption rates of the ground and vibrationally excited molecules are equal, e.g. $k_d^0 = k_d^1 = k_d$. Even though k_d is not always known very accurately and contraversial values exist even for the best studied system, yet the range of this rate constant is known for many systems. The complete unknown quantities are therefore k_{ex} and k_{dex}. As mentioned in the introduction, the deexcitation process became recently a subject for both theoretical and experimental studies, in which an order of magnitude estimate of k_{dex} and its variation with the surface temperature is possible. For systems in which metalic surfaces were used the internal vibrational energy of the

adsorbed molecule exceeds the Debye frequency of the substrate phonons significantly. Thus, the interaction between vibrationally excited states of the adsorbate and the substrate is thought to be via plasmon states [8,9,10] or local electron-hole pair formation [6]. In such cases it is expected that k_{dex} will exhibit a weak temperature dependence [9]. Indeed, it was recently shown experimentalty [11a] that the deexcitation rate of the (001) band of CO_2 when colliding with Ag surface, was invariant in the relatively narrow range of temperatures, 298 to 475 K.

The experimental results of Asscher *et al.* [3f,4a] indicate that nearly equilibrium conditions between the concentrations of the ground state and excited ad-molecules is maintained on the surface for a wide range of temperatures. This suggests that the ratio between the excitation and deexcitation rates may be approximated by,

$$\frac{k_{ex}}{k_{dex}} = \exp[-E_v/kT], \tag{6}$$

where E_v is the vibrational energy spacing of the adsorbed molecule and k is Boltzmann constant. At low surface coverages ($\vartheta < 0.1$) neither k_{ex} nor k_{dex} are expected to depend on the coverage [7,11]. Hence, one may assume that Eq. (6) is valid also at high temperatures where the ratio between the fluxes N_g^1 and N_g^0 deviate from the Boltzmann distribution.

III. RESULTS and DISCUSSION

In this section we shall first discuss some general aspects of the kinetic model described above and point out some features which are common to many molecule-metal surface systems. Following this general discussion we shall describe the application of the kinetic model to the NO/Pt (111) system, for which experimental data is available, and obtain values for k_{dex} and k_{ex}.

To examine the extent of vibrational excitation of molecules on metal surfaces, as a function of some of the microscopic parameters involved in this process, we have performed model calculations in which the dependence of N_g^1 on the magnitude of k_{dex} and D_e were studied. It was assumed in these calculations that the molecular beam pulse has a rectanguler step type shape, thus, during the pulse steady state conditions are maintained (Eq. (5b)). In order to evaluate the flux of the desorbing vibrationally excited molecules via Eq. (5b) one needs to know the magnitude of $k_{dex}(T)$ and $k_d(T)$ [$k_{ex}(T)$ is related to $k_{dex}(T)$ via Eq. (6)]. The functional form of a first order desorption rate is usually assumed to be,

$$k_d(T) = A(T)\exp(-\frac{D_e}{kT}) \tag{7}$$

where $A(T)$ is a preexponential factor and D_e the adsorbate-surface binding energy. Following Ref. 12, $A(T)$ may be related to the microscopic parameters of the system and has a form $A(T) = C/T$. To evaluate the constant C one has to know the stretching (Ω_0) and bending (frustrated rotation, Ω_r) frequencies associated with the molecule-surface bond [12]. In the following model calculations we have used $C = 1\times10^{18}$.

Recently it was shown experimentally [11a] that the deexcitation rate k_{dex}, is temperature independent for the CO_2/Ag system. In addition several model calculations [6-10] predicted that k_{dex} should be temperature independent if the vibrational energy is channeled into the electronic degrees of freedom of the metal. Moreover, the calculations by Persson *et al.* [6,7] predicted k_{dex} values of the order of $10^{12}sec^{-1}$ which agreed well with available experimental results. These calculations suggested that the quenching of vibrational energy is due to the excitation of

a local electron-hole pair in the metal. Hence, in the following we shall assume that k_{dex} is temperature independent.

The variation of N_g^1 as a function of T, k_{dex} and D_e is shown in Fig. 1. Note that a change in D_e results in a marked change of k_d and hence of the residence time of the molecule at the surface. Fig. 1a shows the calculated values of $N_g^1(T)$ for a given deexcitation rate ($k_{dex} = 1\times10^{12} sec^{-1}$) and a number of different D_e values. Similarly, in Fig. 1b we have plotted $N_g^1(T)$ for a fixed binding energy ($D_e = 25 Kcal/mole$) and a few k_{dex} values. It is evident from these results that there is a competition between the desorption and excitation processes. An increase of the desorption rate (decrease in the value of D_e, Fig. 1a) causes a substential decrease in the formation of N_g^1 due to the short residence time of the adsorbate on the surface. A decrease of k_{dex} (and hence of k_{ex}) also reduces the formation of vibrationally excited molecules. A support to the primary conclusion which emerges from these results, namely that the extent of vibrational excitation of molecules on metal surfaces is rather limited in cases of weakly bounded molecules (physisorption) is provided indirectly by two experiments. Asscher *et al.* [4a] reported that by modifying a Pt (111) surface with a graphitic overlayer, in which the interaction between the NO and the modified surface decreases dramatically (D_e is about $2 kcal/mole$), no evidence for vibrationally excited NO was found. When the NO molecules were scattered from a clean Pt (111) at the same temperature, more than 2% of the adsorbed molecules were vibrationally excited. For a different system, e.g. NO/Ag (111), it was found that only a negligible amount of vibrationally excited NO molecules were formed, even at incident kinetic energies that exceeded the vibrational spacing of the NO molecules [16]. Again, the reason for the absence of vibrational excitation

in this system is due to the weak adsorbate-surface interaction (about 5 $kcal/mole$).

In the remaining of this section we shall examine in more detail the NO/Pt (111) system for which extensive vibrational excitation of the scattered NO molecules were reported [4a,4b]. The desorption rate, k_d, for this system was estimated using the expresions of Ref. 12. The streching, Ω_0, and the frustrated rotational, Ω_r, frequencies were taken to be $450cm^{-1}$ and $306cm^{-1}$ respectively, following Ref. 13. These frequencies yield a preexponential factor of $A(T) = 1.147\times10^{18}/T sec^{-1}$. The most reliable value of D_e for this system is due to a recent study by Serri *et al.* [15] who estimated the NO-Pt (111) binding energy to be $25 Kcal/mole$. This value correspons to the desorption of NO from a perfect Pt (111) terrace. The justification for using this value to interpret the results of Ref. 4a, is due to the high temperatures (e.g. fast desorption rates) at which these experiments were performed. Under these conditions the molecules on the surface desorb from terraces rather than from steps or defects as was argued to occur at lower temperatures [15]. In Ref. 3f and 14 the values of the ratio $R(T)$, between the flux of N_g^1 and N_g^0, as well as the independently measured values of $N_g^1(T)$ are given respectively. We have used Eqs. (3) and (5) together with Eq. (6) to perform a numerical fit of the experimental data (the use of Eqs. (3) and (5) in this fit was in order to check the validity of the steady state assumption).

The resulting curves together with the experimental data are shown in Fig. 2. The values of the best fit of $N_g^1(T)$ (Fig. 2a) and of $R(T)$ (Fig. 2b) are $5\times10^{12} sec^{-1}$ and $5\times10^{11} sec^{-1}$ respectively. Despite the one order of magnitude discrepancy between these two rates, they both are in a good agreement with results obtained in other experimental studies. For

example, for the CO/Cu (100) system an estimate of $k_{dex} = 7.7\times10^{11} sec^{-1}$ was reported [11b] while for CO/Pt (111) the deexcitation was found to be $5\times10^{11} sec^{-1}$ [11c] as derived from IR linewidth measurements. Since it is experimentally less complicated to measure $N_g^1(T)$, thus having a smaller experimental uncertainty we belive that the higher value is more accurate. The magnitude of k_{dex} we have astimated for the NO/Pt (111) system implies that the vibrational damping mechanism is dominated by an electron-hole pair excitation [7]. These rate values suggest that multiphonon processes have a negligible contribution to the excitation/ deexcitation mechanism since for such a process at least 10 bulk Pt phonons are required and one would expect in this case much lower rates [8] (of the order of $10^6 sec^{-1}$). Recently, Haller and coworkers [4d] reported a high vibrational temperature of NO molecules scattered from an ill defined polycrystaline Pt foil at 1430 K. This value is higher than what is expected from a similar experiment on a Pt (111) single crystal face. However, this result [4d] is consistent with the above analysis if one conciders the higher D_e values associated with such a high step concentration surfaces [15]. The higher D_e values result in a longer residence time, thus, enabling more efficient vibrational excitation.

IV. CONCLUSION

A kinetic analysis is presented in which the vibrational excitation and deexcitation of molecules on metal surfaces is discussed. It was shown that the desorption process compete effectively with the excitation process resulting in vibrational temperatures that are colder than the surface temperature. For the NO/Pt (111) system vibrational deexcitation and excitation rates were calculated. These rates were too high to associate the excitation and the deexcitation processes with phonon-

adsorbate interaction. The good agreement between results of this work and previous estimates of k_{dex} for other systems, indicate that these processes are related to energy transfer between the adsorbate and the electronic states of the surface. Based on previous theoretical and experimental work we have assumed that the deexcitation rate is practically temperature independent. Consequently any temperature dependence of processes in which vibrationally excited molecules are formed is due to k_{ex}. The analysis of the NO/Pt (111) system indicates a Boltzmann type variation of $k_{ex}(T)$ with the crystal temperature. It is suggested that this temperature dependence of the excitation rate holds even at high T values where the experimental data deviate from the Boltzmann distribution. This deviation is therefore associated only with the competition between the desorption and excitation processes.

Finally, we have shown that molecular beam-surface scattering experiments that provide data about the evolution of vibrationally excited molecules, followed by an analysis similar to the one presented here, can provide an importent tool to obtain information about the interaction between surfaces and the vibrational degrees of freedom of adsorbed molecules.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract DE-AC03-76SF00098.

REFERENCES

[1] M.Y. Cardillo, Ann. Rev. Phys. Chem. 32 (1981) 331.

[2] J.C. Tully, Ann. Rev. Phys. Chem. 31 (1980) 319.

[3] (a) F. Frankel, J. Hager, W. Krieger, H. Walther, C.T. Campbell, G. Ertl, H. Knipers and K. Segner, Phys. Rev. Lett. 46 (1981) 152; (b) G.M. McCleland, G.D. Kubiak, H.G. Rennagel and R.N. Zare, Phys. Rev. Lett. 46 (1981) 831; (c) A.W. Kleyn, A.C. Luntz and D.J. Auerbach, Phys. Rev. Lett. 47 (1981) 1169; (d) R.R. Cavanagh and D.S. King, Phys. Rev. Lett. 47 (1981) 1829; (e) J.W. Halpern, E.J. Northrup, G.L. Ogram, J.C. Polanyi and A. Williamson, Chem. Phys. Lett. 85 (1982) 127; (f) M. Asscher, W.L. Guthrie, T.-H. Lin and G.A. Somorjai, Phys. Rev. Lett. 49 (1982) 76.

[4] (a) M. Asscher, W.L. Guthrie, T.-H. Lin and G.A. Somorgai, J. Chem. Phys. 78 (1983) 6992; (b) D.A. Mantell, S.B. Ryali, G.L. Haller and J.B. Fenn, J. Chem. Phys. 78 (1983) 4250; (c) J.B. Cross and J.B. Lurie, to be published; (d) D.A. Mantell, Y.-F. Maa, S.B. Ryali, G.L. Haller and J.B. Fenn, J. Chem. Phys. 78 (1983) 6338.

[5] (a) A.O. Bawagan, L.H. Beard, R.B. Gerber and D.J. Kouri, Chem. Phys. Lett. 84 (1981)339; (b) H. Zacharias, M.M.T. Loy and P.A. Roland, Phys. Rev. Lett. 49 (1982) 1790.

[6] B.N.J. Persson, J. Phys. C 11 (1978) 4251.

[7] (a) B.N.J. Persson and R. Ryberg, Phys. Rev. Lett. 48 (1982) 549; (b) Ph. Avouris and B.N.J. Persson, J. Phys. Chem. submitted for publication.

[8] V.P. Zhdanov and K.I. Zamarev, Catal. Rev. Sci. Eng. 24 (1982) 373.

[9] M.A. Kozhushner, V.G. Kustarev and B.R. Shub, Surf. Sci. 81 (1979) 261.

[10] L.E. Brus, J. Chem. Phys. 73 (1980) 940.

[11] (a) J.Misewick, C.N. Plum, G. Blyholder, P.L. Houston and R.P. Marrel, J. Chem. Phys. 78 (1983) 4245; (b) R. Ryberg, Surf. Sci. 114 (1982) 627; (c) R.A. Fhigeishi and D.A. King, Surf. Sci. 58 (1976) 379.

[12] (a) A. Redondo, Y. Zeiri and W.A. Goddard III, Phys. Rev. Lett. 49 (1982) 1847; (b) Y. Zeiri, A. Redondo and W.A. Goddard III, Surf. Sci. in press; (c) A. Redondo, Y. Zeiri, J.J. low and W.A. Goddard III, J. Chem. Phys. in press.

[13] H. Ibach and S. Lewald, Surf. Sci. 76 (1978) 1.

[14] M. Asscher, W.L. Guthrie, T.-H. Lin and G.A. Somorjai, unpublished results.

[15] J.A. Serri, M.J. Cardillo and G.E. Becker, J. Chem. Phys. 77 (1982) 2175.

[16] D. Auerbach, private communication.

FIGURE CAPTIONS

1 (a) Variation of N_g^1 as a function of surface temperature and adsorbate-surface binding energy. The deexcitation rate used in these calculations was $1\times10^{12} sec^{-1}$. (b) Variation of N_g^1 as a function of surface temperature and deexcitation rate. The adsorbate-surface binding energy used in the calculations was $25 kcal/mole$.

2 (a) Numerical fit of the experimental $R(T)$ points. Solid line-calculated values (using Eqs. (3) and (5)), deshed line-experimental data and doted line-Boltzman distribution. We have used in these calculations $D_e = 25 Kcal/mole$ and $k_{dex} = 5\times10^{11} sec^{-1}$. (b) Numerical fit of the experimental $N_g^1(T)$ points. Solid line-calculated values (using Eqs. (3) and (5)), deshed line-experimental data and doted line-Boltzman distribution. We have used in these calculations $D_e = 25 Kcal/mole$ and $k_{dex} = 5\times10^{12} sec^{-1}$. t 1 line-Boltzman distribution. We have used in these calculations $D_e = 25 Kcal/mole$ and $k_{dex} = 5\times10^{12} sec^{-1}$.

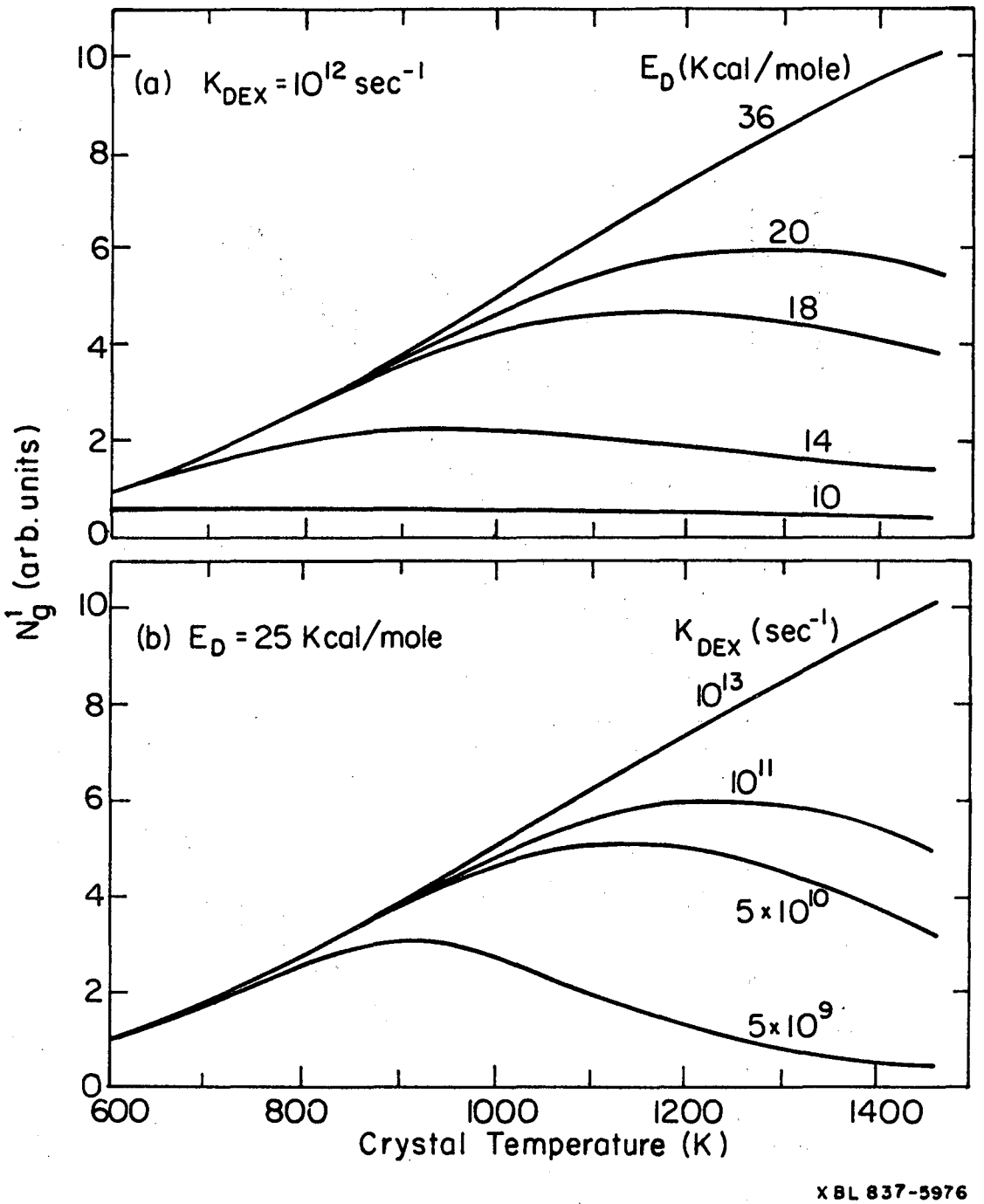

(a) $K_{DEX} = 10^{12}$ sec^{-1}
E_D (Kcal/mole)
36
20
18
14
10
(b) E_D = 25 Kcal/mole
K_{DEX} (sec^{-1})
10^{13}
10^{11}
5×10^{10}
5×10^{9}
N_g^1 (arb. units)
0
2
4
6
8
10
600
800
1000
1200
1400
Crystal Temperature (K)
XBL 837-5976

Fig. 1

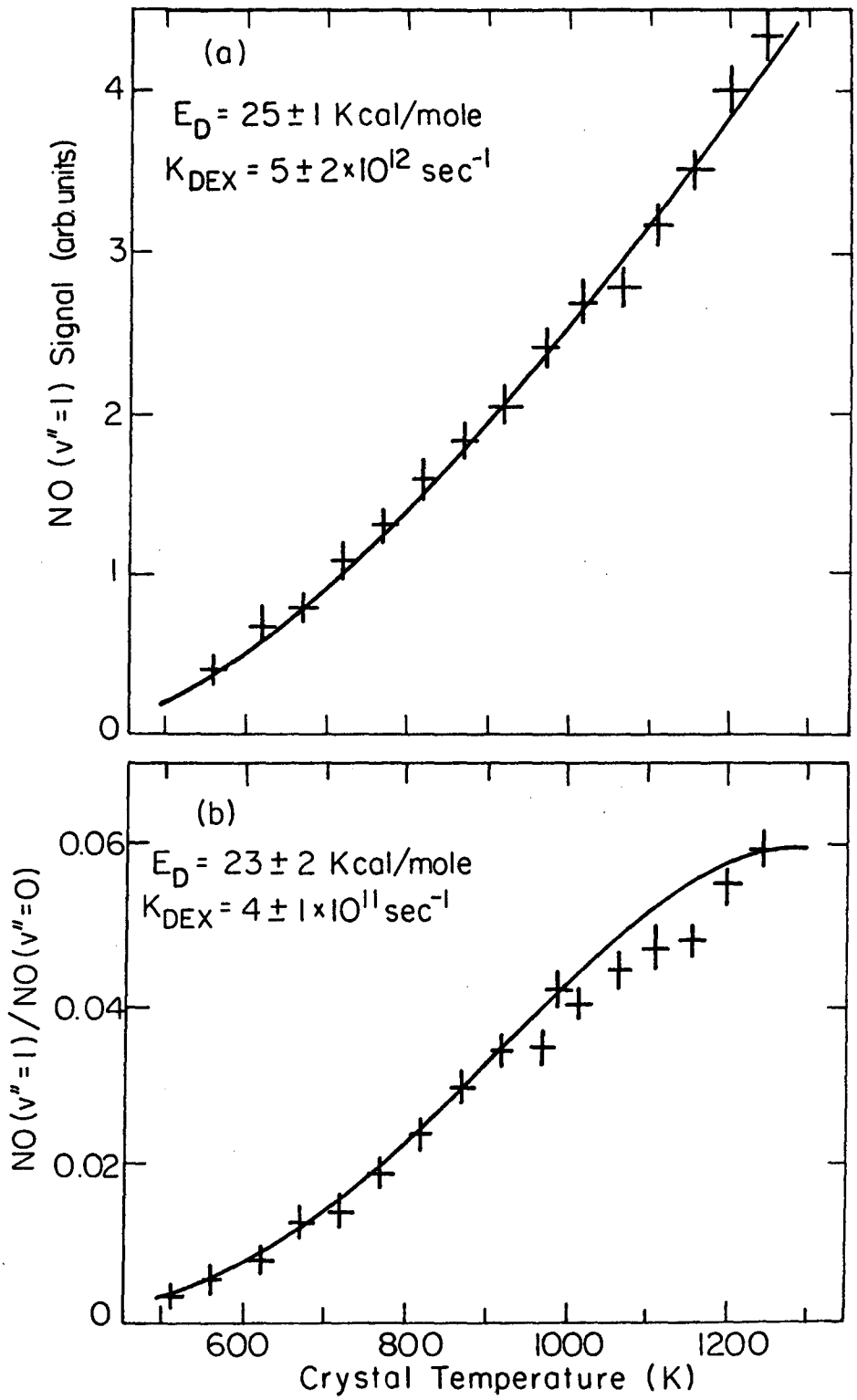

(a)
E_D = 25 ± 1 Kcal/mole
K_{DEX} = 5 ± 2×10^{12} sec^{-1}
NO (v"=1) Signal (arb. units)
0
1
2
3
4
(b)
E_D = 23 ± 2 Kcal/mole
K_{DEX} = 4 ± 1×10^{11} sec^{-1}
NO (v"=1)/NO (v"=0)
0
0.02
0.04
0.06
600
800
1000
1200
Crystal Temperature (K)
XBL 837-5977

Fig. 2

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720