

# New mechanism shaping the distribution of particles desorbed from a surface

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Even a weak interaction of molecules with phonons as they move under the influence of surface forces can strongly affect the distribution of desorbed molecules. For the first time, a noncontradictory explanation is found for experimental data on the associative desorption of hydrogen from the surface of the metal. The explanation is based on a kinetic theory which incorporates a relaxation of an ensemble of desorbed particles involving phonons.

Research on the dynamics of the adsorption and desorption of chemisorbed particles has recently attracted increased interest.<sup>1-3</sup> It had been shown some time ago<sup>4</sup> (Fig. 1a) that the average energy ( $\epsilon$ ) of  $D_2$  molecules desorbed from the Ni (111) surface at small emission angles ( $\vartheta$ ) is higher than the corresponding equilibrium value (twice the surface temperature,  $2T$ ). At large angles  $\vartheta$  the energy is observed to fall off, and  $\epsilon$  becomes smaller than  $2T$  (this is a “cooling” of the desorbed molecules). Qualitatively the same results were recently found<sup>5</sup> in the desorption of hydrogen from a different face, Ni (100). This dependence of the energy of the desorbed molecules on the emission angle contradicts the prevailing opinion<sup>3,6-9</sup> that dissociative chemisorption is a process involving an activation energy. It is not difficult to verify that if an activation barrier did exist, then it would lead to a relatively high energy of molecules desorbed nearly along the normal (there would be a “heating” of molecules,  $\epsilon > 2T$ ) and also to a monotonic increase in  $\epsilon$  with increasing emission angle<sup>6,7</sup> (see the dashed curve in Fig. 1a).

In the present letter we show that the distribution of desorbed molecules observed in Refs. 4 and 5 can be explained on the basis of a coexistence of, and a competition between, two physical factors. The first is the activation barrier which we just mentioned (which would lead to a heating of molecules desorbed at small values of  $\vartheta$ ), and the second (a new factor) is the relaxation of molecules in a process involving phonons over the time it takes the molecules to traverse the region of the interaction with the surface. One might expect at first glance that this relaxation would be negligible, since the interaction of hydrogen molecules with phonons is known<sup>10</sup> to be extremely weak. However, that assertion is true only on the average. For molecules which are moving at sufficiently small angles with respect to the surface and which spend a long time in the interaction region, the relaxation involving phonons can be arbitrarily strong. The analysis below leads to a result which would be unexpected from the standpoint of kinetic theory: The effect of the interaction with the phonons on the energy  $\epsilon$  of the

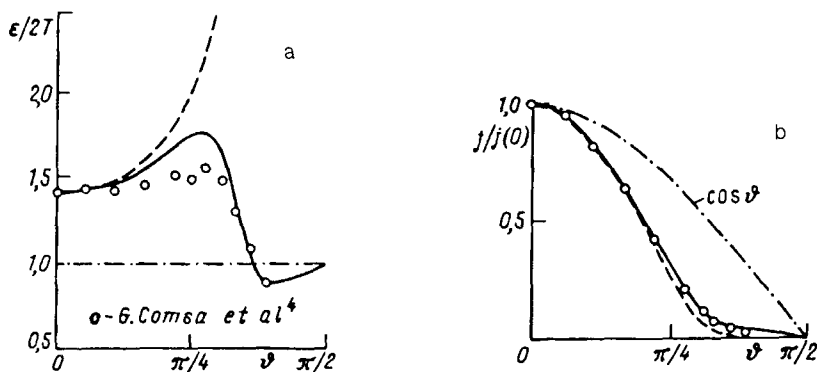


FIG. 1.

desorbing molecules is effectively strong even at intermediate emission angles  $\vartheta$ . The decrease in  $\epsilon$  at intermediate values of  $\vartheta$  observed experimentally then becomes understandable immediately, since the relaxation tends to move  $\epsilon$  toward its equilibrium value of  $2T$ , and the energy of the "superheated" molecules should effectively fall off. The cooling of molecules ( $\epsilon < 2T$ ) observed at large angles is also a natural result, as we will see below. It is of the same nature<sup>11</sup> at the microscopic level as the familiar cooling during the desorption of physically adsorbed particles.<sup>12</sup>

Regardless of the nature of the chemisorption (dissociative or activated, both in the case under consideration here and in any other case), in determining the distribution function of the desorbed molecules we must allow for the circumstance that after the particles leave their chemisorbed state they continue to interact with the lattice of the solid until they escape from the effective range of the surface forces and therefore undergo a relaxation involving phonons. To describe the state of the ensemble of particles which undergo a relaxation involving phonons, we use the semiclassical kinetic theory which we worked out previously<sup>11,13</sup> for the case of physisorption of particles on a surface. We note that under experimental conditions the desorption of the molecules from the surface occurs into vacuum, and for our purposes it is sufficient to consider only the distribution function ( $\rho^+$ ) of the molecules moving away from the surface. The kinetic equation for the distribution function  $\rho^+$ , averaged along the coordinate ( $z$ ) running normal to the surface in the interaction region, as in Refs. 13 and 11, is

$$\frac{d\rho^+}{dt} = \frac{\rho_0^+ - \rho^+}{\tau} - \theta(E_z + E_d) \frac{\rho^+}{t_{fl}} + \theta(E_z - E_a) \frac{\chi}{t_{fl}}. \quad (1)$$

Here  $E_z$  is the total energy (kinetic plus potential) of the motion of the molecules in the direction normal to the surface,  $E_a$  is the height of the activation barrier for chemisorption,  $E_d$  is the activation energy for desorption from a physisorption state,  $\tau$  is the time scale of the relaxation of the ensemble of particles involving phonons,  $t_{fl}$  is the time of flight of the molecules across the region of the interaction with the surface, and  $\rho_0^+$  is the (locally) equilibrium distribution function, which is proportional to the density of particles moving away from the surface. The function  $\theta(x)$  has

the value 0 at  $x < 0$  and the value 1 at  $x \geq 0$ . The "collision integral" representing molecule-phonon collisions in Eq. (1) is written in the relaxation-time approximation (the simplest approximation). As we have shown previously,<sup>11,13</sup> that approximation is quite sufficient for describing the dynamics of physical adsorption and desorption. For simplicity, here and below we ignore possible fine effects stemming from vibrational<sup>2</sup> and rotational<sup>14,15</sup> degrees of freedom of the molecules and also fine effects stemming from variations in the interaction with the surface along the tangential direction. The distribution function  $\rho^+$  in (1) thus depends on  $E_z$  alone. A new (and important) point, which distinguishes Eq. (1) from the equations derived in Refs. 11 and 13, is the incorporation of a "source" of molecules which are formed by the association of chemisorbed atoms on the surface [the third term on the right side of Eq. (1)]. The distribution function of such molecules,  $\chi$ , is assumed below to have its equilibrium value  $\chi_0$ ; this assumption has essentially always been used previously.<sup>6-8</sup>

Solving Eq. (1) in the steady state, we find the following expression for the distribution function of the desorbed molecules outside the range of the surface forces,  $f^+ = \theta(E_z)\rho^+$ :

$$f^+(v, \vartheta) = A_1(v, \vartheta) + A_2(v, \vartheta), \quad (2)$$

$$A_1(v, \vartheta) = [1 - \alpha(v, \vartheta)]\theta(v_z - v_a)\chi_0(v), \quad (3)$$

$$A_2(v, \vartheta) = \alpha(v, \vartheta)\chi_0(v) \left( \int_0^\infty \alpha(v_z)\exp(-mv_z^2/2T)v_z dv_z \right)^{-1} \\ \times \left[ \int_{v_a}^\infty \alpha(v_z)\exp(-mv_z^2/2T)v_s dv_z \right]. \quad (4)$$

Here  $v_a = (2E_a/m)^{1/2}$ . The quantity  $\alpha(v, \vartheta)$  in Eqs. (2)–(4), which constitutes the probability for the relaxation of particles involving phonons,<sup>11</sup> is given by

$$\alpha(v, \vartheta) = \frac{1}{1 + (\tau/t_{\text{fl}})} = \frac{1}{1 + \beta(v/\bar{v})\cos\vartheta}. \quad (5)$$

In writing the second equation in (5) we assume the following for simplicity:  $\tau = \text{const}$  and  $t_{\text{fl}} = L/v_z$ , where  $v_z = v\cos\vartheta$  is the normal component of the velocity of the particles,  $\vartheta$  is the emission angle,  $L$  is the size of the region of the interaction with the phonons, and  $\bar{v} = (2T/m)^{1/2}$ . The relaxation parameter  $\beta$  is determined by the ratio of the characteristic relaxation time and the characteristic time required to traverse the interaction region:  $\beta = \tau\bar{v}/L$ . The function  $\chi_0$  is given by

$$\chi_0 = (m^2 j_s / 2\pi T^2) \exp[-(mv^2/2T) + (E_a/T)],$$

where  $j_s$  is the number of gas particles which form per unit time per unit surface area as a result of the association of chemisorbed atoms.

Using the distribution function  $f^+$ , we can easily calculate the basic characteristics of the desorbed molecules, in particular, the particle flux density  $j$  and the energy density  $j_e$ , as functions of the emission angle  $\vartheta$ :

$$j(\vartheta) = 2\pi \int_0^\infty v \cos \vartheta f^+(\vartheta) v^2 dv, \quad j_e(\vartheta) = 2\pi \int_0^\infty v \cos \vartheta (mv^2/2) f^+(\vartheta) v^2 dv. \quad (6)$$

We can also calculate the average energy of the desorbed particles,  $\epsilon(\vartheta) = j_e(\vartheta)/j(\vartheta)$ .

In the absence of a relaxation of the particles among phonons [i.e., in the limit  $\beta \rightarrow \infty$  or  $\alpha = 0$  in Eqs. (2)–(5)], the  $\vartheta$  dependence of  $j$  and  $\epsilon$  found from Eqs. (2)–(6) reduces to that found previously<sup>6,7</sup> (see the dashed curves in Fig. 1). The sharp decrease in the flux density  $j$  and the unbounded increase in the average energy  $\epsilon$  (this increase contradicts experimental data!) with increasing emission angle  $\vartheta$  predicted here stem from the existence of an activation barrier and are easily understood. Since the energy of the molecules leaving the chemisorbed state satisfies  $E_z > E_a$ , while the total energy is  $E = E_z / \cos^2 \vartheta$ , the particles must have a larger energy in order to be emitted at larger angles  $\vartheta$ ; the probability for the emission of such particles falls off exponentially for statistical reasons. From the mathematical standpoint, the reason is a cutoff of the integration over velocity in Eqs. (6) due to the unit step function in (3) corresponding to the activation barrier.

A calculation of  $j(\vartheta)$  and  $\epsilon(\vartheta)$  from Eqs. (2)–(6) for the case with a relaxation involving phonons leads to results (the solid curves in Fig. 1) which give a satisfactory description of the experimental data<sup>4</sup> on both  $j(\vartheta)$  and  $\epsilon(\vartheta)$ . The value of the relaxation parameter turns out to be  $\beta = 85$ , and the height of the activation barrier is  $E_a = 1660$  K. These values of  $\beta$  and  $E_a$  agree qualitatively with values found previously from independent experimental data in one of our studies<sup>11</sup> and in Ref. 16, respectively.

As expected, the relaxation leads to a broadening of the peak-shaped  $j(\vartheta)$  distribution (i.e., to a tendency toward an equilibrium cosine law) at large values of the angle  $\vartheta$ , at which the interaction with the phonons becomes more important, according to (5). Although the agreement with experiment does worsen a bit in this case (Fig. 1), there is no significant qualitative change in the  $j(\vartheta)$  curve. [It was apparently for this reason that previous measurements of  $j(\vartheta)$  by several investigators, for a variety of systems, have yielded no contradiction with the classical model.<sup>5</sup>]

On the other hand, relaxation leads to a qualitative change in the  $\vartheta$  dependence of the average energy  $\epsilon$  (Fig. 1a). To see the physical reasons for this change, we rewrite the expression for  $\epsilon$  as  $\epsilon = (j_e^{(1)} + j_e^{(2)}) / (j^{(1)} + j^{(2)})$ . Here the superscripts 1 and 2 specify quantities which are determined by the parts  $A_1$  and  $A_2$  of distribution function (2). Since we have  $A_1 \propto (1 - \alpha)$  and  $A_2 \propto \alpha$ , these quantities can be interpreted as the fluxes which correspond to particles that pass through the interaction region without and with relaxation involving phonons. Since we have  $\beta \gg 1$ , at small emission angles  $\vartheta$  we have  $\alpha \ll 1$  and  $A_1 \gg A_2$  in (2)–(5); we thus have  $\epsilon \approx j_e^{(1)} / j^{(1)}$ . The  $\epsilon(\vartheta)$  dependence is then determined primarily by only the activation barrier; the condition  $\epsilon > 2T$  holds, and  $\epsilon$  increases with increasing  $\vartheta$ . In the other limiting cases,  $\vartheta \rightarrow \pi/2$ , we have  $\alpha \approx 1$  and  $A_1 \ll A_2$  in (2)–(5), so we find  $\epsilon \approx j_e^{(2)} / j^{(2)}$ . This result is the same as the expression derived for  $\epsilon$  in Ref. 11 for the desorption of physisorbed particles under conditions of a pronounced relaxation involving phonons. A calcula-

tion of  $\epsilon$  from this formula leads to the experimentally observed cooling of the desorbed particles ( $\epsilon < 2T$ ; Fig. 1a). The physical reason for this effect is<sup>11</sup> the dependence of the flight time  $t_{fl}$  on the velocity of the molecules. As  $\vartheta$  increases, we should thus see a transition from a heating of the molecules to a cooling, which would explain the observed decrease in  $\epsilon$  with increasing  $\vartheta$ .

An important point is that the maximum on the plot of  $\epsilon(\vartheta)$  and the decrease in  $\epsilon$  due to relaxation involving phonons are seen even at intermediate emission angles  $\vartheta \sim \pi/4$ , not in the limit  $\vartheta \rightarrow \pi/2$ , as might be expected in the case of a weak relaxation involving phonons ( $\beta \gg 1$ ). This result, which is not at all obvious, looks completely natural within the framework of the theory derived here. The fluxes  $j^{(1)}$  and  $j_e^{(1)}$  fall off with increasing  $\vartheta$  not so much because of the  $\alpha(\vartheta)$  dependence mentioned above as because of the small probability for the emission of particles from a chemisorption state at a large angle  $\vartheta$ . As can be shown without difficulty by working from Eqs. (2)–(6), in which we set  $\alpha = \text{const}$  for simplicity, we have  $j^{(1)}$ ,  $j_e^{(1)} \propto \exp(-E_a/T \cos^2 \vartheta)$ . In the experiments of Ref. 4 the temperature was  $T = 1143$  K, and the condition  $T \sim E_a$  held, so the maximum on the plot of  $\epsilon(\vartheta)$  should indeed have been observed at intermediate angles.

In summary, the incorporation of a relaxation of the desorbed molecules in a process involving phonons leads to a natural resolution of contradictions which were observed some time ago<sup>4</sup> and recently confirmed.<sup>5</sup> These contradictions had previously been explained away either by introducing<sup>7,8</sup> some additional nonactivation adsorption centers at the surface (that assumption is at odds with direct experimental data on thermal desorption<sup>9</sup>) or by invoking<sup>3,5</sup> the operation of some hypothetical adsorption-desorption mechanism.

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