Role of Rotational Motion in the Dissociative Adsorption and Associative Desorption Dynamics of $D_2/Cu(111)$

Wilson Agerico Diño,[1] Hideaki Kasai,[2] and Ayao Okiji[1]
[1]Department of Applied Physics, Osaka University, Suita, Osaka 565, Japan
[2]Department of Material and Life Science, Osaka University, Suita, Osaka 565, Japan

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We point out the importance of the incidence energy of D_2 to account for the nonmonotonic behavior of the adsorption probability of $D_2/Cu(111)$ as a function of its initial rotational state. We then show that a very prominent initial cooling, a mild heating, and then a final cooling of the rotational temperature with respect to the surface temperature, for increasing rotational energies, should be observed for the desorption of D_2 from Cu(111). We finally show that the desorption results could be consistently connected with the adsorption probability data. [S0031-9007(96)02157-6]

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One of the most exciting challenges of present-day surface science is, undoubtedly, the task of developing a detailed microscopic picture of dynamical processes occurring on solid surfaces. To this purpose, many systems have been subjects of considerable interest and studies, one of which is the hydrogen on Cu system [1], particularly on the nature of the dissociative adsorption process, and the reverse process of association and desorption. From these studies, we now know that dissociation for this system is hindered by a considerable energy barrier. This means that a certain amount of energy must be fed to the translational degree of freedom of the hydrogen molecule before dissociative adsorption on a Cu surface could occur (cf. [1] and references found therein). It has also been found that the dissociative adsorption probability of hydrogen approximately obeys normal-energy scaling [2], suggesting that only the component of the molecule's momentum perpendicular to the surface is effective in promoting dissociation. Studies have also shown that vibrational excitation of the impinging hydrogen molecule always promotes dissociation on the low index surface of Cu. And for a fixed initial state of the impinging hydrogen molecule, increasing the surface temperature slightly promotes dissociation for incidence energies a little lower than the effective energy barrier, and slightly hinders dissociation for incidence energies a little higher than the effective energy barrier, without changing the energetic location of the inflection point of the corresponding adsorption curves [3–6]. Furthermore, we also know that the dissociation of hydrogen on Cu is an orientation-dependent process, i.e., parallel-oriented hydrogen molecules, with respect to the Cu surface, dissociate more easily compared to perpendicularly oriented ones [7]. However, it is only now that we are beginning to understand how rotational energy or the molecular rotational degree of freedom actually influences hydrogen dissociation.

Recently, time-of-flight (TOF) distributions for hydrogen molecules associatively desorbing from Cu(111) could be determined rotationally state resolved [8–10]. The distributions show a nonmonotonic behavior with respect to the detected rotational state. Molecules with intermediate rotational states (e.g., $j = 4, 5, 6$) reach the detector faster than those that do not rotate at all ($j = 0$) or those in higher rotational states ($j \geq 10$). By invoking detailed balance, the dissociation behavior of hydrogen on Cu can be derived from these distributions [8–12]. The nonmonotonic behavior of the TOF peaks can be related to a nonmonotonic sticking (dissociation) coefficient [13]. At low initial rotational states j, rotation inhibits sticking. While at high j, rotation promotes sticking.

When an impinging hydrogen molecule approaches a Cu surface, it encounters an orientation-dependent potential energy (hyper-) surface (PES) [7,14–17]. In order for the molecule to dissociate and be adsorbed on the Cu surface, it must be able to find the *path of least resistance* (path of least potential), and have enough energy to reach the surface. This process depends on what the initial rotational and vibrational states of the impinging hydrogen molecule are, what its incidence energy is, and how long it stays under the influence of the anisotropic PES [15]. In the case of rotation, there are two opposing factors working for and against the dissociation process, *viz.*, *steering* (dynamical reorientation) and *R-T* (rotational-translational) *energy transfer* (cf. [15] for a detailed explanation of these two terms). The first, steering, which originates from the orientational dependence of the dissociative adsorption process, pertains to a dynamical reorientation of the impinging molecule towards a more favorable orientation (a predominantly parallel orientation). Steering dominates when the impinging molecule does not have sufficient rotational energy to assist in its adsorption. The second, *R-T* energy transfer, which originates from the strong coupling between the rotational and translational degrees of freedom, pertains to the effective transfer of rotational energy to translational energy. *R-T* energy transfer dominates when the impinging hydrogen molecule has sufficient rotational energy to assist

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in its adsorption. The combined effect of these two factors is an initial decrease and then, eventually, an increase in the sticking probability as the initial rotational state of the impinging molecule is increased for a fixed incidence energy (cf., e.g., curve corresponding to 0.6 eV in Fig. 1). However, up to now, the influence of the incidence energy has been neglected in accounting for the nonmonotonic behavior of the sticking probability of hydrogen molecules (on Cu surfaces) with respect to its rotational state. We will show here, for the first time, just how important the incidence energy is in accounting for this interesting behavior. We will also show that by using the same simple model adopted for adsorption, we can independently derive desorption data that qualitatively agree with experimental results [9,18]. Furthermore, we will show that these independently derived adsorption and desorption data can be consistently related to each other.

To show the significance of the incidence energy E_t in determining which of the two factors (steering or *R-T* energy transfer) dominates for fixed initial rotational state j of the impinging molecule, we considered the reaction of a D_2 molecule impinging a *flat* Cu(111) at *normal incidence.* We did quantum mechanical calculations of the sticking probability by solving the time-independent Schrödinger equation for a D_2 molecule moving under the influence of an orientation-dependent PES corresponding to the D_2/Cu(111) system using the coupled-channel method [11,12] and the concept of a local reflection matrix [19]. The dynamical variables we have considered are the center-of-mass distance of the molecule from the surface, Z, and the polar and azimuthal angular orientation of the molecule with respect to the surface, θ and φ, respectively. The D_2 molecule is restricted to its vibrational ground state ($\nu = 0$) throughout the adsorption (desorption) process. Our orientationally anisotropic model potential is based on *qualitative features* of available PES plots for $H_2(D_2)$/Cu-surface systems [15–17]. The energy barrier for a perpendicular-oriented D_2 molecule was set at $V_{\max} = V_{\perp} \approx 0.9$ eV, and gradually decreases to a value $V_{\min} = V_{\parallel} \approx 0.5$ eV for parallel-oriented molecules. The final sticking probability data result from a sum over *all* the contributions from *all* possible types of rotation (helicopter-type—with the rotational axis of the molecule prependicular to the surface, cartwheel-type—the rotational axis of the molecule parallel to the surface, or a rotation intermediate between the two former ones). Readers are referred to Ref. [15] for more details regarding the calculation method, and the actual form of the model potential adopted. We can see in Fig. 1 that the location of the minimum for each sticking probability curve shifts as the incidence energy is varied. This is because when the incidence energy is comparable to or lower than the minimum energy barrier, $V_{\min}$, steering will not be sufficient to aid in dissociation. Thus, *R-T* energy transfer will be dominant, and we see only an increase in the sticking probability as the initial rotational state is increased for low incidence energies (cf., e.g., curves corresponding to 0.55 and 0.6 eV in Fig. 1). As the incidence energy is gradually increased, the efficacy of steering also increases, and we see corresponding minima appearing (cf. curves corresponding to 0.575 ~ 0.625 eV in Fig. 1) that shift towards higher initial rotational states. As the incidence energy is increased to a value that becomes comparable with the energy barrier maximum $V_{\max}$, the efficacy of *R-T* energy transfer increases, and we see a corresponding shift in the curve minimum towards lower initial rotational states (cf. curves corresponding to 0.80 and 0.6 eV in Fig. 1).

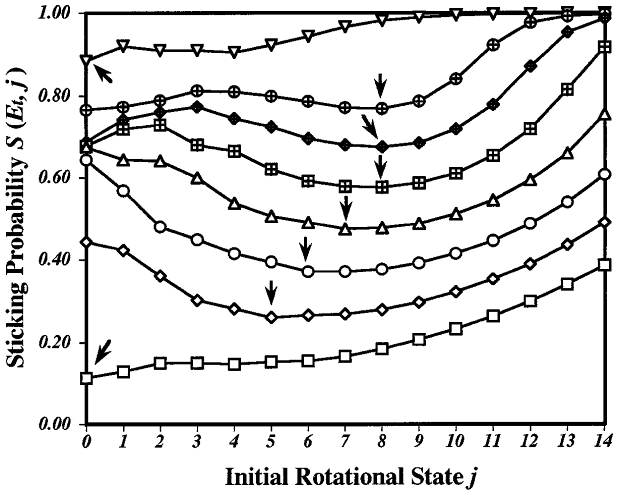

FIG. 1. Numerical results for the j-dependent sticking probability curves for D_2 in the vibrational ground state and fixed incidence energies, E_t. Arrows point to the corresponding minima for each curve. [□ : $E_t = 0.55$ eV, ◇ : $E_t = 0.575$ eV, ○ : $E_t = 0.60$ eV, △ : $E_t = 0.625$ eV, ■ : $E_t = 0.65$ eV, ◆ : $E_t = 0.675$ eV, ⊕ : $E_t = 0.70$ eV, and ▽ : $E_t = 0.80$ eV.]

When the adsorption probability of molecules colliding with a surface is independent of the distribution of molecular internal states, orientations, and velocities, equilibrium statistical mechanics predicts that the molecular quantum state distributions in desorption will be determined solely by the surface temperature T_S. However, this is often not the case, as we have here for the hydrogen on Cu system. Thus it would also be interesting to study how the desorption probability will behave, as such studies could elucidate the nature of those special forces and configurations experienced by the desorption flux when we relate them to the adsorption probabilities. By invoking the principle of microscopic reversibility [11,12], we calculated for the desorption probability, independent of the adsorption probability result, using the same simple model mentioned above (cf., [11,12,19] for a detailed description of the method). We then took a Boltzmann average of the raw, numerical desorption probability results over the initial energy distribution on the surface at surface temperature T_S. We show in Fig. 2 a Boltzmann plot of the resulting

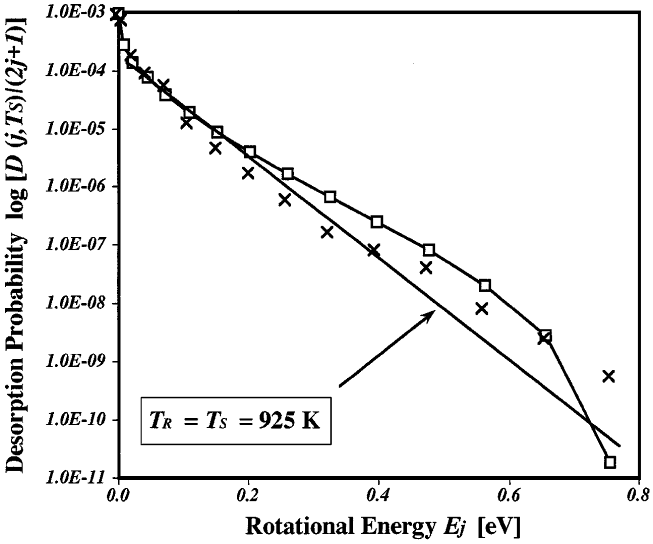

FIG. 2. Boltzmann plot of desorption probability *vs* rotational energy E_j of the state j. The line $T_R = T_S = 925$ K is plotted for reference. Points marked × correspond to experimental data [9].

desorption probability of D_2 molecules as a function of the rotational energy. A Boltzmann distribution would appear as a straight line (cf. Fig. 2). However, we see that the calculated desorption probability result shown in Fig. 2 is not represented by a single temperature, and the mean rotational energy is less than T_S [12]. These qualitative features are also observed experimentally [8–10,18].

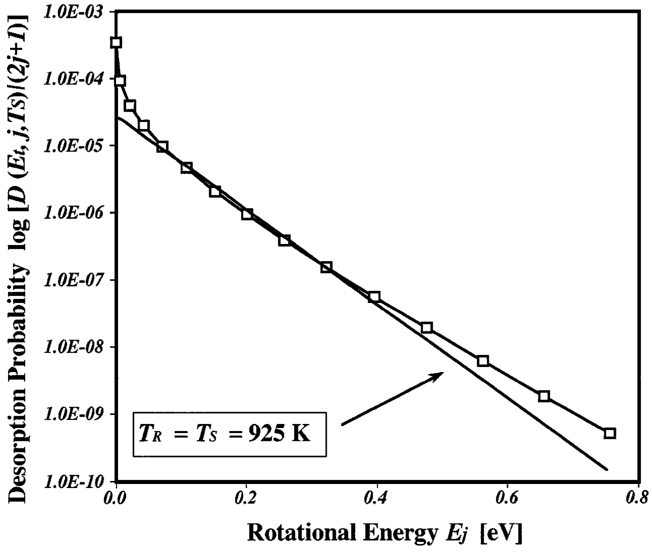

FIG. 3. Boltzmann plot of the desorption probability vs rotational energy E_j of the state j ($\nu = 0$), for fixed translational energy $E_t = 0.60$ eV. The line $T_R = T_S = 925$ K is plotted for reference.

In order to relate the desorption results in Fig. 2 to the adsorption probability results in Fig. 1, we show, in Fig. 3, a Boltzmann plot of our numerical results for the desorption probability of D_2 molecules as a function of the rotational energy for a fixed incidence energy. Recall from the principle of microscopic reversibility, and the conservation of energy [11,12], that the dynamic behavior of the adsorption probability will be reflected in the distribution of molecular quantum states in desorption in the following manner:

$$D(E_t, j) \propto S(E_t, j) \exp\left(-\frac{E_t + E_j}{k_B T_S}\right), \qquad (1)$$

where E_t is the translational energy of the molecule, and j is its rotational state with a corresponding rotational energy E_j. The initial decrease in the sticking probability curve corresponding to an incidence energy of $E_t = 0.6$ eV in Fig. 1 is reflected as a decrease in the rotational temperature in desorption (Fig. 3). The final increase in the sticking probability curve is reflected as an increase in the rotational temperature relative to the former decrease. You will notice that the increase in rotational temperature is not as dramatic as that expected from the corresponding sticking probability curve in Fig. 1. This is because the Boltzmann factor in Eq. (1) decreases much more rapidly compared to the increase in the sticking probability. If we then sum over all the incidence energies, we get the Boltzmann plot shown in Fig. 2, where the initial decrease in the rotational temperature with respect to the surface temperature for low rotational energies, $E_j \leq 0.05$ eV, is due to an initial mean decrease in the sticking probability for low initial rotational states, and the mild increase in the rotational temperature for higher rotational energies, $0.05 \leq E_j \leq 0.5$ eV, is due to a mean increase in the sticking probability for higher initial rotational states (cf. Figs. 1 and 2). The final decrease again of the rotational temperature can be understood by considering the result shown in Fig. 3 and the relation between the sticking probability and the desorption probability [Eq. (1)]. As the rotational energy E_j appearing in the Boltzmann factor increases, the only relevant contributions will come from the sticking probabilities corresponding to those incidence energies $E_t \ll V_{\min}$. In this energy region, the sticking probabilities are not much different from 0, even for $j = 14$. As a result, we will observe this final decrease in the rotational temperature for the desorption probability of hydrogen molecules in their vibrational ground state ($\nu = 0$).

In summary, we want to stress the following points. First, the nonmonotonic dependence of the sticking probability on the initial rotational state (j) of a hydrogen molecule impinging on a Cu surface can be explained by considering two effects, *viz.*, *steering* (dynamical reorientation) and *R-T* (rotational-translational) energy transfer. For fixed incidence energies, steering is dominant for low j and is responsible for the initial decrease in the sticking probability as a function of j. *R-T* energy transfer is dominant for high j and is responsible for the final increase in the sticking probability as a function of j.

Second, the effect of steering and *R*-*T* energy transfer is incidence energy (E_t) dependent. As a result, the minimum of the sticking probability curve as a function of j shifts from low j to high j depending on the value of E_t relative to the minimum energy barrier, and shifts from high j to low j depending on the value of E_t relative to the maximum energy barrier. Third, we have verified the validity of the relation given in Eq. (1) [11,12] by comparing direct numerical calculations for the desorption probability and predictions of its behavior from the sticking probability by using Eq. (1), and its utility in explaining experimental results [8–10,18]. Finally, it would be interesting to check experimentally whether the minima of the sticking probability curves shift with respect to j when the translational energy is varied by comparing desorption distribution data for different j when the translational energy is fixed.

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