Surface Temperature Dependence of the Inelastic Scattering of Hydrogen Molecules from Metal Surfaces

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The surface temperature dependence of activated inelastic scattering and dissociation of D_2 from the Cu(111) surface has been computed using quantum wave-packet methods. It is found, in agreement with experimental data, that the surface temperature dependence generally has an Arrhenius form with an activation energy dependent on molecular translational energy and on the initial and final internal molecular states. The translational energy dependence of the activation energy is linear up to the threshold energy, with an abrupt change thereafter. On the basis of the wave-packet calculations, a model has been developed to explain these findings and highlight their general nature.

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The scattering and dissociative chemisorption of molecules on metal surfaces have been intensively studied in recent years [1,2]. Developments in experimental techniques, notably molecular beam methods, have accompanied great improvements in theoretical work, in the computation of the energetics [3] and in molecular dynamics methods. This is particularly true for hydrogen adsorption on metals [4], which provides the best studied paradigms of gas-surface reaction dynamics, for which the results of fully quantum computation of S-matrix elements have been directly compared to experimental cross sections [5–8]. The greater the level of detail provided by experiment, the more we can say about the energetics and topography of the potential energy surface (PES) governing the reaction dynamics. Recent experiments [9,10] using stimulated Raman pumping of the initial molecular state have approached the state-to-state scattering limit needed for quantitative comparison with theory.

Yet a key ingredient is missing from theory, namely the influence of the surface vibrational (phonon) and electronic (electron-hole pair) excitations on the dynamics. While the influence of electron-hole pairs is still unclear [11], low-dimensional models for phonons show that the molecule loses energy as the surface recoils on impact. For direct dissociation (where there is no trapping of molecules before reaction) the thermal motion of the surface atoms causes a Doppler downshift of the dissociation barrier, and enhanced dissociation at low energy [12,13]. For hydrogen on transition metals, substrate recoil is small because of the mismatch between the molecular and surface atom masses, but energy from vibrationally excited surface atoms can be transferred to the molecule. Experimentally, this should result in temperature-dependent scattering and dissociation cross sections. Surprisingly, recent experiments have shown [14,15] that this surface temperature dependence for the H_2/Cu system is very well described by an Arrhenius law. This might lead one to propose trapping and thermal activation from a state in equilibrium with the substrate, yet H_2/Cu is the archetypal activated

direct scattering/dissociation system—there is no trapping of molecules to allow the establishment of thermal equilibrium with the surface. Similar results have been observed for H_2 scattering from Pd surfaces [16,17], which show more complicated, steering-dominated reaction [18,19]. In this paper, we address the role of substrate phonons in the direct reactive scattering of hydrogen molecules from metals. Explicit computation of cross sections using quantum wave-packet methods yields exactly the Arrhenius behavior observed in experiment. On the basis of this, we develop a simple model that can be used to rationalize the Arrhenius behavior and the molecular translational energy dependence of the observed "activation energy."

The quantum calculations describe dissociation at a single surface site, 4 molecular degrees of freedom were treated: molecular center of mass to surface distance, z, molecular bond length, r, and its orientation (θ, ϕ). A model form with parameters appropriate for $H_2/Cu(111)$ was used for the PES [20]. Substrate motion was treated as a single Einstein oscillator having the mass of one Cu atom and a vibrational frequency, ω_s, equal to the surface Debye frequency [14 meV for Cu(111)]. Following Hand and Harris [12], the motion of this oscillator couples to molecular motion via a rigid shift of the z coordinate, i.e., $V(z, r, \theta, \phi, y) = V(z - y, r, \theta, \phi)$, where y is the oscillator coordinate. The five-dimensional wave function was expanded in the eigenfunctions of the surface harmonic oscillator, and represented on a finite-element grid in the molecular coordinates. The time-dependent Schrödinger equation was solved with the split-operator method [21], using a Chebychev expansion [22] of the nondiagonal potential operator. The kinetic energy operator was computed with an extended symmetry adapted discrete variable representation method [20]. The initial wave function was a product of the appropriate molecular state wave function and a surface harmonic oscillator eigenfunction. The phonon expansion included nine channels centered on the initial phonon state; this was sufficient for convergence. Thermal averaging of the cross

sections was obtained by summation of the results for 15 initial phonon states, Boltzmann weighted according to ω_s and surface temperature. The use of a single oscillator is an approximation for which there is no firm foundation despite its extensive use [23]. Therefore, we limit the present study to a moderate range of surface temperatures, $200 < T_s < 900$ K, the same range covered in experiment [14,15].

In Fig. 1 we present probabilities obtained from the wave-packet calculations for rotational excitation of D_2 scattered from Cu(111) as a function of the reciprocal of T_s. Two rotational transitions are shown: ($v = 0$, $J = 0 \rightarrow 4$) and ($v = 0, J = 0 \rightarrow 6$), with threshold energies, E_T, for scattering from a rigid surface of 75 meV and 157 meV, respectively. The upper panel
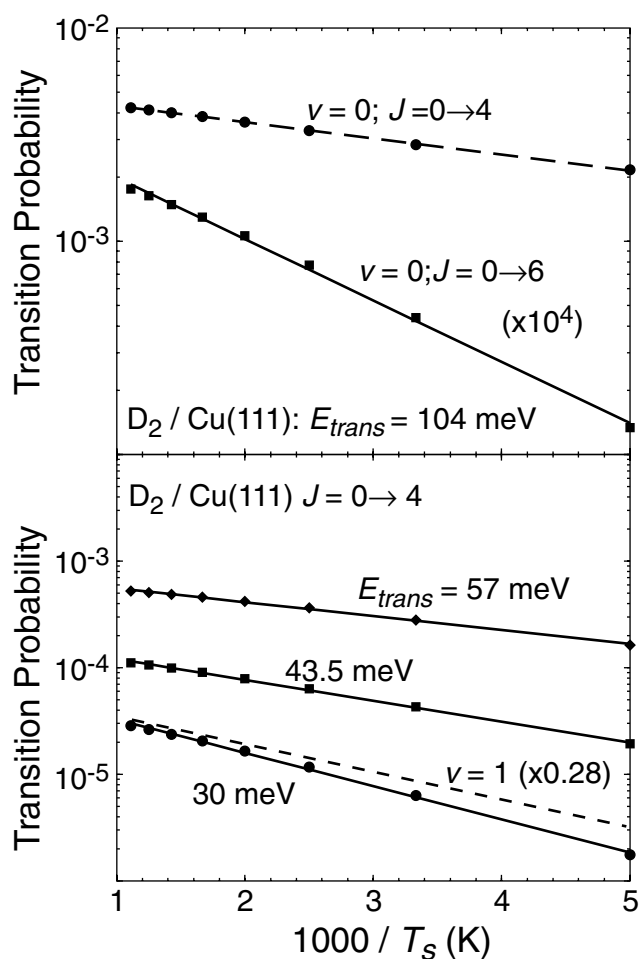

FIG. 1. Transition probabilities, S, versus inverse surface temperature for the rotationally inelastic scattering of D_2 from Cu(111). The results of the wave-packet calculation (symbols) are well reproduced by fits using an Arrhenius form (lines). Top panel: S versus $1/T_s$ for rotationally inelastic channels $0 \rightarrow 4$ (circles) and $0 \rightarrow 6$ (squares) in the vibrational ground state, $v = 0$, for $E_{trans} = 104$ meV. Bottom panel: S versus $1/T_s$ for the $0 \rightarrow 4$ rotational excitation for several E_{trans}. Solid lines indicate results for $v = 0$, while the dashed line is for $v = 1$ at $E_{trans} = 30$ meV, for which the apparent activation energy is 51 meV compared to 62 meV for $v = 0$.

shows the transition probabilities at a translational energy, E_{trans}, of 104 meV, while the lower panel shows the results for ($J = 0 \rightarrow 4$) transitions, for varying E_{trans}. Clearly, over the temperature range shown, the results are described well by the Arrhenius form, $S(E_{trans}, T_s) \sim \exp[-E_a(E_{trans})/kT_s]$, shown as the solid lines, where $S(E_{trans}, T_s)$ is the transition probability, E_a the energy-dependent *apparent* activation energy, and k the Boltzmann constant. We find this common form for all scattering and dissociation cross sections in this system. Arrhenius dependences were also observed experimentally for rotationally inelastic cross sections of H_2 scattering from Cu(100) [15], and for the dissociative adsorption probability on Cu(111) [14]. This suggests that a common mechanism gives rise to the surface temperature dependence of these quite different activated processes.

We stress that these are *direct processes,* with no trapping of molecules, and no thermal equilibrium between molecules and surface. Surface temperature appears through the kinetic energy distribution of the surface atoms. In the simplest approximation, the kinetic energy gives a Doppler shift increasing/decreasing E_{trans} as the molecule and surface atoms move together/apart. In the quantum computations the wave packets represent ensembles of scattering molecules sampling all surface atom positions and motions for a particular surface oscillator eigenstate. The effect of scattering from a thermal distribution of oscillator states is obtained by a Boltzmann-weighted average of the cross sections over the initial oscillator states. This is similar in principle to a simple treatment of the Debye-Waller factor in diffraction.

The Arrhenius behavior applies over a wide range of E_{trans}, but E_a depends on the quantum transition considered; there is a marked difference between ($J = 0 \rightarrow 4$) and ($J = 0 \rightarrow 6$) transitions, and even a difference in the ($J = 0 \rightarrow 4$) transition for molecules in the $v = 0$ or $v = 1$ states. A difference between apparent activation energies for the same rotational transition in two different vibrational states has been observed experimentally [15] for the ($J = 1 \rightarrow 3$) transition of H_2 scattered from Cu(100). It was found to be 29 meV compared to 11 meV found here for a transition of comparable internal energy change. E_a also depends strongly on E_{trans}. As shown in Fig. 2, E_a decreases linearly up to E_T, where there is a marked change: the variation is weaker, and a linear fit is poor. A linear E_{trans} dependence of E_a below E_T has been observed experimentally in dissociation of H_2 and D_2 on Cu(111) [14], but a deviation from linearity above E_T has yet to be verified. For all cross sections computed, we found the same general E_{trans} dependence of E_a. The slope of the linear fit is determined by the particular cross section; the slopes are clearly different for the ($J = 0 \rightarrow 4$) and ($J = 0 \rightarrow 6$) transitions shown. The slope is determined by what fraction of thermal energy feeds from molecular translation (in the center-of-mass frame) into internal motion, as highlighted in the model below.

All of the trends in surface temperature dependences for activated inelastic scattering and dissociation can be reproduced using a simple form for the E_{trans}-dependent cross section,

$$f_n(E_{\text{trans}}) = \begin{cases} 0 & E_{\text{trans}} < E_T^n, \\ a_1(E_{\text{trans}} - E_T^n) + a_2(E_{\text{trans}} - E_T^n)^2 + \cdots & E_{\text{trans}} \geq E_T^n, \end{cases} \quad (1)$$

where n labels the surface oscillator state. In the lowest order model, the effect of surface motion is a linear decrease in threshold energy with increasing n, $E_T^n = E_T^0 - n\Delta E$, while the shape of the cross section is independent of n. ΔE is the amount of energy the surface motion contributes to assist the molecule in undergoing a specific transition and is a parameter of the model. Surface temperature is introduced as in the wave-packet calculations by thermally averaging the cross sections,

$$S(E_{\text{trans}}, T_s) = \frac{1}{N} \sum_n f_n(E_{\text{trans}}) \exp(-n\omega_s/kT_s), \quad (2)$$

with normalization $N = \sum_n \exp(-n\omega_s/kT_s)$, where ω_s is in atomic units. The inset of Fig. 3 shows the T_s dependence of $S(E_{\text{trans}}, T_s)$ in the range $200 < T_s < 900$ K, retaining only the linear term in Eq. (1) with $a_1 = 0.1$ and $\Delta E = \omega_s$. Clearly this is well represented by the Arrhenius form, although deviations are more marked over a larger T_s range [24]. The appearance of the curves is fairly insensitive to the details of $f_n(E_{\text{trans}})$. We can change a_1 or use a higher order polynomial without altering the general behavior, an Arrhenius dependence is always followed over a finite temperature range. The value of E_a does, however, depend on the polynomial order: $E_a \approx 40$ meV at E_T^0 for a linear f_n, but rises to ~ 100 meV for a third order polynomial. E_a also depends on the maximum phonon state contributing to the summation in Eq. (2), as discussed below.

The main part of Fig. 3 shows the translational energy dependence of E_a, relative to E_T^0, for ΔE of $\omega_s/2$ and ω_s. The change of the slope at threshold is more clearly evident than in Fig. 2. This is due to the difference in the thresholds used; E_T^0 differs slightly from the rigid surface threshold, E_T, used in Fig. 2 because of recoil of the oscillator. Also, in the full quantum results, the shape of $f_n(E_{\text{trans}})$ does depend on n, and the shift of the threshold energy is not linear (or even always monotonic) in n. ΔE should be thought of as an effective downshift taking account of these changes in an average fashion. However, comparing Fig. 3 with Fig. 2, we can see that all the main trends are reproduced; the linear dependence below E_T^0, the sudden change at E_T^0, and the slower decrease at higher energies.

For $E_{trans} < E_T^0$, we can see that varying ΔE alters the gradient, E_a', of $E_a(E_{\text{trans}})$, with smaller ΔE giving larger gradients. This can be simply explained from Eq. (2). When $E_{\text{trans}} < E_T^0$, there is a minimum $n' \neq 0$ satisfying $E_T^{n'} < E_{\text{trans}}$, and we can rewrite Eq. (2) as

$$S(E_{\text{trans}}, T_s) = \frac{1}{N} \sum_{n=n'} f_n(E_{\text{trans}}) \exp(-n\omega_s/kT_s)$$

$$= \frac{e^{-n'\omega_s/kT_s}}{N} \sum_{n=0} f_{n+n'}(E_{\text{trans}})$$

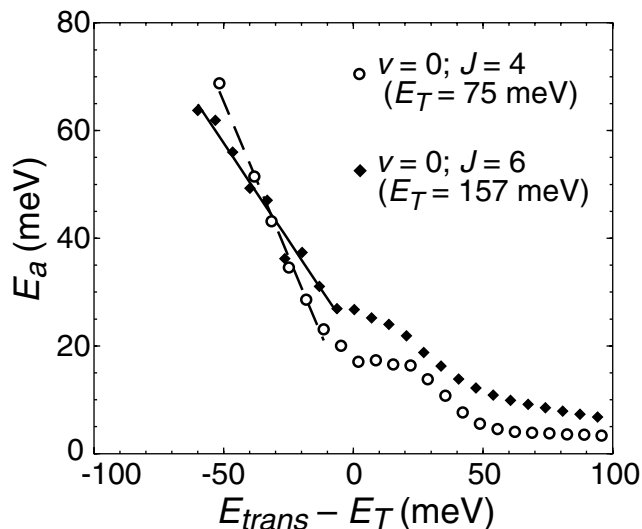$$\times \exp(-n\omega_s/kT_s). \quad (3)$$

FIG. 2.   Apparent activation energies, obtained from Arrhenius fits to the surface temperature-dependent transition probabilities shown in Fig. 1. The error in the fit is no greater than 2%. Results are shown as a function of energy relative to the threshold for excitation on a rigid surface for the rotational excitations ($J = 0 \rightarrow J = 4$) and ($J = 0 \rightarrow 6$) for $v = 0$.
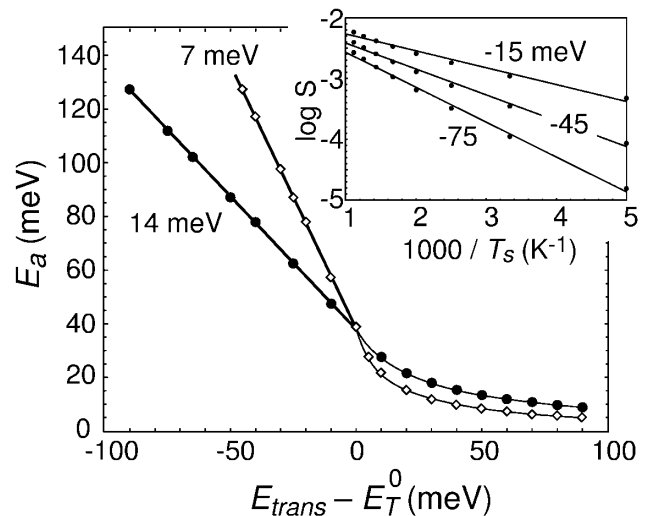

FIG. 3.   Apparent activation energy versus translational energy relative to threshold for excitation on a 0 K surface, E_T^0, obtained with Eq. (2). Results are shown for ΔE of 7 meV (diamonds) and 14 meV (circles) for a surface phonon frequency of 14 meV. The inset shows the surface temperature dependence of S at three different E_{trans} relative to threshold (symbols) and the Arrhenius fits (lines). One hundred phonon channels were included in the Boltzmann average. The Arrhenius fits apply well, with errors ranging from 2% at the lowest energy to 5.5% at threshold.

The smaller is E_{trans}, the larger is n' and hence also E_a, deriving mainly from the prefactor $\exp(-n'\omega_s/kT_s)$, is larger. For a given E_{trans}, n' is also greater for smaller ΔE, giving a larger E_a'. If E_a' was determined exactly by Eq. (3) we could write $E_a' = -\omega_s/\Delta E$, with an upper limit of -1 because $\Delta E < \omega_s$. In reality, the threshold does not continue to shift down in energy with increasing n, there is saturation at some high $n = n_{\text{max}}$, truncating the summation and making $E_a' > -1$, only approaching -1 as $n_{\text{max}} \to \infty$. This occurs for the $(v = 0, J = 0 \to 6)$ transition in Fig. 2 for which $E_a' = -0.72$. We can also see from Fig. 2 that E_a' depends on the transition considered, for $(v = 0, J = 0 \to 4)$ it has decreased to -1.15. In the model, this reflects a smaller ΔE for this transition; in the full quantum results there is a combination of different threshold shifts and changes in the form of f_n with increasing n. E_a can thus be seen to depend very sensitively on the precise dynamics coupling the substrate motion with the internal molecular motion [25].

The success of the analytical model strongly suggests that the Arrhenius dependence observed in experiment and in results from the present wave-packet calculations for the cross sections for hydrogen scattering from Cu surfaces is mainly due to the Boltzmann distribution of substrate phonon states. An Arrhenius dependence should thus be a general characteristic of the influence of surface thermal motion on direct molecular processes on surfaces, manifesting itself most remarkably at subthreshold E_{trans}, where E_a rises sharply as E_{trans} decreases. This has been confirmed by applying the wave-packet model to dissociative adsorption and activated, vibrationally inelastic scattering [25]. All results show a critical behavior of E_a at threshold: a linear dependence on E_{trans} below threshold decays into a weaker dependence above, in good agreement with the predictions of the analytical model. Further analysis shows [25] that this distinctive behavior does not occur in the semiclassical surface mass model [26], where the energy exchange between molecule and surface is treated as a continuous quantity. The Arrhenius law still applies, but with neither the linear dependence of E_a below nor the abrupt change at E_T. The present model is fully quantum-mechanical taking account of the discrete levels of the phonon spectrum. The difference between this and the surface mass model suggests that the critical threshold behavior is a manifestation of the quantum nature of the molecule-surface energy exchange. The predictions of the linear dependence below threshold and the sudden change at threshold are subject to future experimental test.

In conclusion, we have developed a high-dimensional, quantum wave-packet model for diatomic molecules interacting with finite-temperature metal surfaces, and applied it to investigate the effects of surface thermal motion on rotational excitation of D_2 molecules scattered from Cu(111). We have found a common Arrhenius law for the transition probabilities with apparent activation energies increasing linearly with decreasing translational energy below threshold, but having a slower nonlinear variation above threshold. These findings agree very well with the trends observed in experiment. A simple model in which the effect of phonons is a rigid downshift of the excitation threshold reproduces all of the trends, in particular the linear variation of the activation energy below threshold, the slope of which depends largely on the fraction of phonon energy involved in assisting the transition.

[1] *Dynamics of Gas-Surface Interactions,* edited by C. T. Rettner and M. N. R. Ashfold (Royal Society of Chemistry, London, 1991).
[2] G. R. Darling and S. Holloway, Rep. Prog. Phys. **58**, 1595 (1995).
[3] M. J. Gillan, Contemp. Phys. **38**, 115 (1997).
[4] H. A. Michelsen, C. T. Rettner, and D. J. Auerbach, in *Surface Reactions,* edited by R. J. Madix (Springer, Berlin, 1993), p. 123.
[5] A. Groß, Surf. Sci. **363**, 1 (1996).
[6] G. J. Kroes, Prog. Surf. Sci. **60**, 1 (1999).
[7] W. A. Diño, H. Kasai, and A. Okiji, Prog. Surf. Sci. **63**, 63 (2000).
[8] E. Watts *et al.,* J. Chem. Phys. **114**, 495 (2000).
[9] M. Gostein, H. Parhikhteh, and G. O. Sitz, Phys. Rev. Lett. **75**, 342 (1995).
[10] A. Hodgson, P. Samson, A. Wight, and C. Cottrell, Phys. Rev. Lett. **78**, 963 (1997).
[11] J. R. Trail, M. C. Graham, D. M. Bird, M. Persson, and S. Holloway (to be published).
[12] M. Hand and J. Harris, J. Chem. Phys. **92**, 7610 (1990).
[13] M. Dohle and P. Saalfrank, Surf. Sci. **373**, 95 (1997).
[14] M. J. Murphy and A. Hodgson, J. Chem. Phys. **108**, 4199 (1998).
[15] E. Watts and G. O. Sitz, J. Chem. Phys. **114**, 4171 (2001).
[16] M. Gostein, E. Watts, and G. O. Sitz, Phys. Rev. Lett. **79**, 2891 (1997).
[17] E. Watts and G. O. Sitz, J. Chem. Phys. **111**, 9791 (1999).
[18] A. Groß, S. Wilke, and M. Scheffler, Phys. Rev. Lett. **75**, 2718 (1995).
[19] G. R. Darling, M. Kay, and S. Holloway, Surf. Sci. **400**, 314 (1998).
[20] G. R. Darling, Z. S. Wang, and S. Holloway, Phys. Chem. Chem. Phys. **2**, 911 (2000).
[21] M. D. Feit, J. A. Fleck, Jr., and A. Steiger, J. Comput. Phys. **47**, 412 (1982).
[22] H. Tal-Ezer and R. Kosloff, J. Chem. Phys. **81**, 3967 (1984).
[23] R. M. Logan and J. C. Keck, J. Chem. Phys. **49**, 860 (1968).
[24] G. A. Gates, G. R. Darling, and S. Holloway, J. Chem. Phys. **101**, 6281 (1984).
[25] Z. S. Wang, G. R. Darling, and S. Holloway (to be published).
[26] A. C. Luntz and J. Harris, Surf. Sci. **258**, 397 (1991).