Dynamics of the Dissociative Adsorption of Methane on Pt{110}(1×2)

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An exhaustive molecular beam study of methane dissociation on Pt{110}(1×2) provides a new data base for modeling this process. Major new features include a sharp rise in dissociative sticking probability, s_0, with increasing translational energy, E_t, corresponding to a barrier of 238 meV, a dramatic increase in s_0 at higher E_t with increasing vibrational energy, and a significant rise in s_0 as E_t is lowered below $\sim$100 meV. It is concluded that the low energy process is a distinctive steering-assisted direct adsorption pathway. [S0031-9007(99)09442-9]

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The dissociative interaction between methane and a metal surface has been extensively studied as an example of *activated* adsorption. Early work [1,2] indicated an activation energy in the range of 310 to 420 meV. A consensus appears to be emerging from a series of molecular beam studies that this is a direct activated process [3–19]. In particular, Rettner *et al.* [9] on W{110} and Luntz and Bethune [11] on Pt{111}, working at translational energies above 100 meV, and Lee *et al.* [7] on Ni{111}, working over the narrower range 550 to 750 meV, showed that the dissociative initial (zero coverage) sticking probability s_0 increases logarithmically with translational energy. Rettner *et al.* [9] and Lee *et al.* [7] also reported a strong increase in s_0 with increasing incident vibrational energy, for which there is now a general consensus [3,6–10].

Recently Seets *et al.* [20–22] studied the dissociative adsorption of CH_4 on Ir{110} and Ir{111}. At incident energies above 100 meV they again report a significant increase in s_0 with increasing energy, but at lower energies they reported a small upturn in s_0. Following the early work on the dissociative adsorption of N_2 on W{100} [23], this was assigned to a thermalized precursor mediated process. In this interpretation, the barrier to dissociation from the precursor state is larger than the barrier to desorption. In the present work, we observe a large, 100-fold increase in s_0 as the incident translational energy is lowered from 100 to 25 meV and we discuss the mechanistic implications.

A range of models have been developed to describe the high translational energy activated dissociation process. Brass and Ehrlich [10], noting the strong influence of both *gas and surface temperature* on the process, proposed a complex mechanism involving three channels. Lee *et al.* [7] proposed that dissociation involved activation of the angular deformation mode of the CH_4 molecule, enabling a C-metal bond to be formed; here the translational energy is coupled to this deformation mode on impact. Luntz and co-workers [16,24] developed an alternative model, involving a concerted, direct dissociation of the incident molecule breaking a single C-H bond on impact. Here it is the C-H stretching mode which plays a critical role. Finally, Ukraintsev and Harrison [25] adapted statistical unimolecular rate theory to develop a model in which direct dissociation is treated as occurring through energy randomizing collisions between incident molecules and local clusters of surface metal atoms.

The experiments were conducted using a supersonic molecular beam apparatus which has been described previously [26]. The sample was a clean single-crystal surface oriented to within 1° of the {110} plane and mechanically polished. Initially the Pt{110} surface was cleaned using prolonged Ar sputtering, annealing and oxygen treatments. Afterwards, the surface was cleaned by heating to 1240 K, oxygen treatment, and annealing at 950 K.

The sticking probability is defined as the ratio of the number of dissociatively adsorbed CH_4 molecules to the total number of molecules incident on the surface from the flux and time. In agreement with Solymosi [27], no other moieties from the breakup of methane were detected apart from C_a. The amount of C_a was determined by heating to 650 K to desorb H_2 and any CO adsorbed during the experiment, followed by titration with an O_2 beam to CO and CO_2. We estimate that the uncertainty in the sticking probability is $\pm 7\%$.

The translational energy of the molecular beam, generated with 1 to 2 bars behind the nozzle, was determined using time-of-flight techniques, and the flux was measured using a stagnation tube. To increase or decrease the translational energy without altering the internal energy, methane was seeded in He, Ar, or Kr. The translational energy and the internal energy of CH_4 could be changed by heating or cooling the nozzle. The highest nozzle temperature used was 850 K; we have evidence for methane cracking at the Mo nozzle above 900 K. All data here are reported for normal incidence.

In presenting the CH_4 dissociative sticking probability data we have taken great care to separate the contributions from the translational and vibrational energy components of the incident molecule. The object has been to collect a comprehensive body of data so that the detailed contribution of these two energy modes can be analyzed over a wide range of translational energies. We estimate that the maximum rotational energy in these experiments is $\sim$80 K

($J_{\max} \approx 3$); under these conditions, vibrational excitation is dominant, and we therefore ignore the former.

The variation of s_0 with incident translational energy E_t in the range 25 to 690 meV, at a surface temperature of 400 K, is shown in Fig. 1. Each of the six curves corresponds to a constant nozzle temperature T_n and, hence, vibrational energy E_v in the range 300 to 800 K. The results display a range of important novel features which we highlight here. (i) At the lowest nozzle temperature (300 K), s_0 is relatively high at low E_t (4×10^{-4} at 25 meV) and falls sharply with increasing E_t to a minimum value of 3×10^{-6} at $E_t = 100$ meV. (ii) In this range of low E_t, the sticking probability rises sharply with increasing vibrational energy; at $E_t = 75$ meV the rise is from 4.5×10^{-6} at $T_n = 300$ K to 1.4×10^{-4} at $T_n = 800$ K. (iii) In the energy range of E_t between 100 and 190 meV, s_0 rises sharply; the half-width of the linear derivative, $\partial s_0 / \partial E_t$, is $\sim$20 meV, which is close to the estimated energy spread of the incident beam, $\sim$15 meV, at these energies. There is therefore a sharp threshold indicative of a single, well-defined activation barrier for the dissociation process. As with the minimum in s_0 as a function of E_t, the turning point or threshold energy E_t^0 *increases* with increasing T_n. (iv) For incident translational energies above 170 to 240 meV, depending on T_n, $\ln s_0$ approaches an asymptotic value which is strongly dependent on vibrational energy, rising from $\sim 3 \times 10^{-5}$ at $T_n = 300$ K to $\sim 9 \times 10^{-3}$ at $T_n = 800$ K.

There are significant differences between the present results and a wide range of data obtained on other transition metal surfaces. Since, with the exception of the recent work of Seets *et al.* [20–22] on Ir{110} and Ir{100}, previous studies were restricted to the higher range of translational energies ($\geq$100 meV), important differences lie in this range. In particular, the present work demonstrates an unusually sharp rise in s_0 with E_t at $\sim$180 meV, followed by a plateau for a given vibrational energy. All previous studies show a logarithmic increase in s_0 with incident "translational" energy. However, the logarithmic s_0 dependence collated, for example, by Schoofs *et al.* (see Fig. 6 in Ref. [12]) is the variation with *total* energy, i.e., translational plus vibrational energies, and includes data with nozzle temperature variations between 300 and 1000 K; only the data for Pt{111} was at constant nozzle temperature and, here, the nozzle temperature used, 993 K, is questionably high. The failure to previously observe a sharp threshold in s_0 with translational energy may derive from (a) a failure to separate vibrational and translational contributions, and (b) the range of translational energies used being too high to observe the true threshold. On Pt{110}(1×2), Luntz and Winters [16] determined s_0 in a "bulb," i.e., a nonbeam, experiment, at a nominal gas temperature of 300 K. Their s_0 values range from 4×10^{-7} at $T_s = 300$ K to 2×10^{-4} at $T_s = 1000$ K, which match well with our low E_t data.

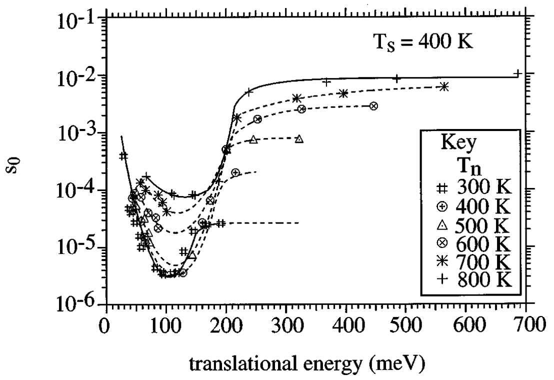

FIG. 1. Dependence of s_0 on incident translational energy for methane dissociative adsorption at $T_s = 400$ K; normal incidence and nozzle temperatures $300 \leq T_n \leq 800$ K.

Each of the new results must be accounted for in a model for methane dissociation, but it is useful first to briefly summarize our studies of the influence of surface temperature, T_s, and isotopic substitution on the processes involved. We take the latter first. At surface temperatures between 400 and 1000 K, s_0 was measured for both CH_4 and CD_4 at $E_t = 95$ meV and $T_n = 300$ K. At this value of E_t, s_0 increases from 3.4×10^{-6} at $T_s = 400$ K to 4.2×10^{-5} at $T_s = 1000$ K, and over the whole range $s_0^{\mathrm{CH_4}} / s_0^{\mathrm{CD_4}} \approx 2$, in agreement with Luntz and Winters [16]. However, the isotopic sticking probability was found to be sensitive to vibrational energy: At a fixed $E_t = 188$ meV, at $T_n = 300$ K, the ratio is 1.11, compared to 1.78 at $T_n = 800$ K. This result is consistent with the observed sensitivity of s_0 to vibrational excitation in the incident molecule; the population of the first excited states increases more for CH_4 than for CD_4 over this range of T_n.

Now we consider the influence of crystal temperature T_s. The results in Fig. 1 indicate two adsorption regimes: the first corresponds to translational energies below $\sim$100 meV, where s_0 decreases with increasing E_t, and the second to energies above 100 meV, where s_0 increases with increasing E_t. Each regime is considered separately.

The influence of T_s on s_0 for the high translational energy regime is shown on a linear plot of s_0 vs E_t in Fig. 2 for T_s between 400 and 1000 K, obtained at constant nozzle temperature, $T_n = 800$ K. Since the energy spread of the incident molecular beam approximates to the width of the transition from low s_0 to relatively high s_0, the threshold energy E_t^0 for the onset of the high translational energy process is estimated from the point of inflection of these s_0 vs E_t linear plots. This threshold energy shifts to lower values with increasing surface temperature. We note that *above* E_t^0, s_0 increases approximately linear with E_t. The dependence of E_t^0 on T_s is also nearly linear:

$$\begin{aligned} E_t^0 &= (238 - 8 \times 10^{-2} T_s)\ \mathrm{meV} \\ &= (22.9 - 0.9 R T_s)\ \mathrm{kJ/mol}. \end{aligned} \tag{1}$$

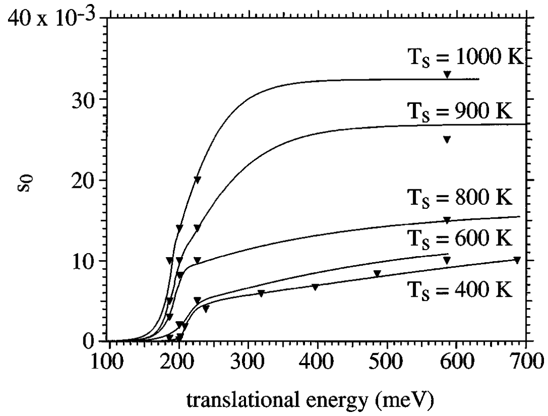

FIG. 2. Variation of s_0 with E_t at surface temperatures between 400 and 1000 K; normal incidence $T_n = 800$ K.

It is important to note that the measured threshold energy decreases linearly with thermal energy RT_s of the solid surface. Energy is provided for the dissociation process by *both* the incoming molecule *and* the surface, i.e., by both reactants. The incident CH_4 translational energy is strongly coupled to, or randomized with, the phonon modes of the impacted region of the solid. Hence the true activation energy for the dissociative adsorption process is the limiting value of the threshold energy E_t^0 at $T_s = 0$ K which, from Eq. (1), is $E_a = 238$ meV.

The influence of surface temperature was also studied in the low translational energy regime at $E_t = 38$ meV, and again significant enhancement in s_0 with increasing T_s was found: at $E_t = 38$ meV and $T_n = 300$ K, $s_0 = 4 \times 10^{-5}$ at $T_s = 400$ K and rises to 4×10^{-4} at $T_s = 500$ K.

The role of vibrational motion in CH_4 is more complex since, as mentioned in (iii) above, E_t^0 *increases* with increasing T_n which is contrary to the anticipated trend. Thus at $T_n = 400$ K, from Eq. (1), we derive a barrier height of $\sim$160 meV, compared with 238 meV at $T_n = 800$ K. Vibrational excitation *inhibits* dissociation for E_t close to the threshold, despite the enormous increase at energies above threshold. We have considered the possibility that this inhibitive effect could be attributed to an increase in rotational energy of the incident molecule, but dismissed this due to the low rotational temperatures achieved in our beam, $\leq 0.1 T_n$ [28]. It is more likely that different vibrational modes of CH_4 are involved in the enhancement of the process above threshold and in the increase in the threshold energy. We show below that the stretching modes produce the enhancement and hence conclude here that the barrier height for the direct activated process is probably increased when the *deformation* modes are excited. This result is inconsistent with both the quantum tunneling [24] and the unimolecular rate theory [25] models. In particular, in the latter model, randomization of the vibrational energy should lead to a decrease in E_t^0 with increasing E_v, in line with the observed decrease with increasing T_s.

To evaluate which internal vibrational modes of CH_4 are involved in enhancing s_0 at low and high translational energies, we have used a simple two-state model analysis. Thus

$$s_0 = f_{\nu=0} s_0^{\nu=0} + f_{\nu=1} s_0^{\nu=1},$$

where f is the fraction of incident molecules in the given vibrational state and s_0^{ν} is the appropriate sticking probability. Plots of $\ln(s_0 - s_0^{\nu=0})$ vs $1/T_n$ at $E_t = 60$ meV are linear with $s_0^{\nu=0} = 9 \times 10^{-6}$ (close to the experimental value at $T_n = 300$ K), $g s_0^{\nu=1} \approx 6 \times 10^{-3}$ (where g is the degeneracy of the mode involved), and a mode frequency $\omega = 1400 \pm 200$ cm^{-1}. This value of ω spans the lowest frequency modes of CH_4, the ν_4 symmetric deformation mode at 1306 cm^{-1}, and the ν_2 antisymmetric deformation at 1526 cm^{-1}. From this analysis, at $E_t = 60$ meV, $s_0^{\nu=1}$ is 2.5×10^{-3}, about 300 times larger than $s_0^{\nu=0}$. We note that both $s_0^{\nu=0}$ and $s_0^{\nu=1}$ decrease as E_t is increased up to $\sim$85 meV.

In the high energy regime the vibrational analysis yields a linear plot with $g s_0^{\nu=1} \approx 1$ and $\omega = 2800 \pm 400$ cm^{-1}. This frequency is close to the C-H stretching frequencies, $\nu_1 = 2914$ cm^{-1} and $\nu_3 = 3020$ cm^{-1}. In this regime, it would appear that the treatment of methane as a quasidiatomic molecule [24], R-H, may be justified. Provided that the combined methane translational and surface phonon energies are sufficient to surmount the barrier E_a, dissociative adsorption is strongly assisted by excitation of one C-H bond in the molecule; according to this analysis, the sticking probability approaches unity in the $\nu = 1$ vibrationally excited state, a (2×10^3)-fold increase over the ground state.

Now we turn to the question of direct adsorption and precursor state trapping. There are two possible models for the low E_t data, where s_0 falls sharply with increasing E_t. This is the behavior anticipated for trapping into a weakly held precursor state, followed by dissociation [23], and this is the model favored by Seets *et al.* [20–22] for CH_4 on Ir{111} and Ir{110}. However, in recent experimental studies of D_2 on Pt{100} [29] and theoretical studies of H_2 adsorption [30,31], the increase in s_0 at low E_t has been attributed to dynamic steering in a direct dissociation process, the steering at low energies being required by the topology of the potential energy surface. Since the lifetimes of excited vibrational states of adsorbates on metal surfaces ($\sim$1 to 50 ps) [32] are similar to the lifetime of trapped CH_4 at T_s from 400 to 800 K ($\sim$10 to 1 ps) [33], the current observation that vibrational excitation of incident CH_4 has a favorable effect on s_0 (Fig. 1) is equivocal. Accommodation of the incident translational energy, with incomplete accommodation of the vibrational energy, could assist the activated transition from precursor to dissociated states. Increased vibrational excitation in the incident molecule and phonon excitation in the surface both increase the rate of dissociation, provided that the translational energy in the incident molecule is sufficiently low for translational trapping to occur, as found. However, we note that a *different* vibrational mode is involved in this low E_t process. This implies a different potential energy pathway for the reaction, which is not the activated pathway observed at high E_t. This indicates that at low E_t the incident methane molecule, for a given set of impact parameters, can be steered into a very low activation barrier dissociation process which cannot be accesses as E_t is increased.

This work demonstrates again that surface temperature also plays a strong role in enhancing direct dissociative adsorption processes [16–18,24,29]. Here both the direct activated process with a barrier height of 160 to 238 meV, depending on CH_4 vibrational energy, and the steering process are assisted by surface temperature. In the former case the threshold barrier for adsorption at a given CH_4 translational energy decreases with increasing thermal energy of the surface, given by Eq. (1), and is readily understood. However, the activation energy for the process observed at low E_t is apparently close to zero, since there is no sign of the s_0 vs E_t plot (Fig. 1) reaching a limiting low value as $E_t \rightarrow 0$ meV—the plot appears to be extrapolating towards $s_0 = 1$. Here the surface temperature plays a similar role to that of excitation of the deformation mode in the incoming molecule: Phonon excitation of the surface can lead to a higher reactivity of surface metal atoms, as in the model of Pasteur *et al.* [29].

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