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The role of steps in the dynamics of hydrogen dissociation on Pt(533)

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The dissociative adsorption of H_2 and D_2 on Pt(533) (Pt{4(111)×(100)}) has been investigated using temperature programmed desorption and supersonic molecular beams. Associative desorption of D_2 from (100) step sites is observed at lowest exposures in TPD (assigned β_3) at 375 K. Saturation of this peak at $\Theta_H = 0.14$ corresponds to the filling of half of the available four-fold sites at the (100) step edge. At higher coverages, additional desorption takes place from the (111) terraces in a broad peak below 300 K similar to that observed (assigned β_1 and β_2) for the Pt(111) surface. The incident kinetic energy (E_i), surface temperature (T_s), coverage (Θ_D), and incident angle (Φ) dependence of the dissociative sticking probability (S) was also measured. The initial dissociative sticking probability (S_0) first decreases with increasing kinetic energy over the range $0 < E_i(\text{meV}) < 150$ (low energy component), and subsequently increases (high energy component). Comparison with D_2 dissociation on Pt(111), where (S_0) increases linearly with E_i, leads to the conclusion that it is the step sites that are responsible for the low energy component to dissociation on Pt(533). The high energy component is a result of a direct dissociation channel on (111) terraces of the Pt(533) surface. The probability of dissociation through the direct channel on the (111) terraces is found to be independent of T_s. The probability of dissociation through the low energy component associated with the (100) steps, over most of the range of E_i where it contributes, is also shown to be independent of T_s. Only at the very lowest value (6.6 meV) of E_i investigated does S_0 exhibit a (negative) temperature dependence. A $(0.8\text{-}\Theta_D)^2$ dependence (where 0.8 is the measured saturation coverage) of S with Θ_D is observed at $E_i = 180$ meV where the direct channel dominates. However, the dependence of S on Θ_D exhibits characteristics similar to those expected for precursor mediated dissociation at $E_i = 16$ meV and $E_i = 6.6$ meV where the low energy channel dominates. The angular dependence $S_0(\Phi)$ scattering in a plane perpendicular to the step direction is asymmetric about the Pt(533) surface normal at both $E_i = 6.6$ meV and $E_i = 180$ meV. At 180 meV $S_0(\Phi)$ can be understood by considering direct dissociation at the (111) terrace and (100) step plane. At 6.6 meV, S_0 tends to scale with total energy. The observed characteristics of the low energy channel is discussed in the light of models [specifically the role steps and defects, precursors (accommodated and dynamical), and steering] suggested to account for the low energy component for H_2/D_2 dissociation and exchange on metal surfaces presenting low activation barriers. At lowest energies ($E_i = 6.6$ meV) dissociation through a conventional accommodated precursor takes place. In addition, more significant proportion of sticking in the range $0 < E_i(\text{meV}) < 150$ takes place through an indirect channel involving an unaccommodated precursor dissociating at step sites, and is unlikely to be accounted for through a steering mechanism. [S0021-9606(00)71416-4]

I. INTRODUCTION

The dynamics of hydrogen dissociation on metal surfaces has received considerable attention in the last decade. It is attractive experimentally since the process is generally direct, and control and measurement of energy partitioned in the molecule during dissociative adsorption or associative desorption measurements provides access to the potential energy surface (PES) in the region of the barrier. There are also an increasing number of *ab initio* calculations of hydrogen–metal potentials, and the short trajectory times of the direct dissociation or association process has lead to both classical and quantum dynamical simulations on such potentials with an increasing number of degrees of freedom. There is experimental evidence, however, that an additional channel to the dissociation of hydrogen on metal surfaces which exhibit relatively low activation barriers to dissociation may be important at low incident kinetic energies

Studies of dissociation dynamics using a Maxwellian source has identified two channels to dissociative adsorption on Ni and Pd surfaces.[1] Dissociation of H_2 on Ni(111) is activated and takes place through a direct channel over a distribution of barrier heights. Dissociation on Ni(110) exhibits an additional nonactivated route which dominates at low incident gas temperatures, and is suggested to be through a precursor. One of its characteristics is a fall in S_0 with gas temperature. A similar (less significant) contribution of this channel was observed on Ni(100). Hydrogen dissociation on Pd(100) also was suggested to exhibit a precursor channel with similar characteristics to that observed on Ni(110). Dissociation on Ni(997) (Ni{9(111)×(111)}) ex-

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hibits an additional nonactivated and precursor mediated channel[2] at low gas temperatures (T_{gas}) in addition to the direct channel associated with the (111) planes. The energy dependence and the angular variation of the initial sticking coefficient of H_2 on Pd(111) and Pd(110)-(1×2) indicated that adsorption of hydrogen on palladium occurs through a direct and a precursor path, with relatively little difference in the adsorption properties of the (111) and the (110) plane.[3] The existence of nonactivated adsorption channels on Pd(111) and Pd(110) accessible through mobile precursors, and the absence of such channels on Pt(111) and Ni(111), was rationalised in terms of the relative densities of occupied Shockley surface states.[3,4] The population of such surface states on Pt(111) was given as an explanation for the lower reactivity for H_2 dissociation on this surface, but the depletion of the density of such surface states at monatomic steps[4] we suggest provides potential sites for higher reactivity. There is, however, no experimental evidence for a stable chemisorbed molecular state on Pt, Pd, or Ni surfaces that could account for a precursor mediated channel to dissociation. Chemisorbed molecular states of hydrogen have also been observed on stepped Ni(510) and Pd(510) surfaces once the dissociation channel is blocked by a high coverage of adsorbed hydrogen atoms.[5]

A precursor mediated channel was also suggested to explain the S_0 component at low E_i which decays with increasing energy on various surfaces of W.[6] A direct channel was characterized at higher E_i. The same suggestion (i.e., direct and precursor channels to dissociation) was made in order to explain similar results found on W(100),[7] but since the indirect channel appeared to be less significant than the earlier measurements on the same surface[6] it was suggested that steps or defects may be responsible for the dissociation of an unaccommodated or resonantly trapped precursor:[7] The absence of a T_s dependence, the low physisorption well depth expected for hydrogen on tungsten, and the absence of a chemisorbed molecular state was considered sufficient evidence to question the accommodation of a conventional precursor state.[7] This channel (indirect dissociation at steps) was separated from the direct in measurements on W(100)-$c(2\times 2)$Cu[8,9] and W(100)-$c(2\times 2)$N surfaces[10] through an increase in the direct channel barrier in the surface unit cell. The indirect channel on this surface, despite having a coverage dependence consistent with a precursor type channel, exhibited practically no T_s dependence.[8,9] The results were cited as support for indirect dissociation through an unaccommodated precursor at step or defect sites.

Ab initio calculations[11] of the potential energy surface for H_2 dissociation on W(100) provided no evidence for a molecular precursor state. The PES showed evidence for a high corrugation in both the translational and rotational coordinates, and it was suggested that steering might be responsible for the decay in S_0 with E_i at low energies.[6,7] Classical and quantum mechanical calculations[12,13] of H_2 trajectories on the W(100) PES[11] confirmed that at low translational energies the dissociation is dominated by strong steering in both the rotational and translational (over the surface unit cell) coordinates in an essentially direct process. It has also been suggested that rotational steering (rather than precursor mediated dissociation) is responsible for the decay in S_0 with E_i observed for H_2 on Pd(100) (Ref. 1) on the basis of quantum mechanical trajectories carried out on an *ab initio* PES.[14–17] More recently classical and quantum mechanical simulations on a variety of model potentials have been carried out[18] in order to investigate the trends in the E_i dependence of S_0 with specific reference to the W and Pd systems. The results highlight, in addition to the effects of steering, the contribution to dissociative sticking of snarled trajectories which can result in precursor like behavior in the absence of dissipative processes: The steering assists the conversion of normal transitional to parallel transitional, or rotational, momentum. This process is enhanced significantly by the presence of a molecular well in the PES, and gives rise to the oscillations[14,18] in the quantum mechanical S_0 at low E_i. Although these have failed to be observed experimentally,[19,20] it is possible[18] that the coherence which is required for their existence may be quenched as a consequence of dissipation into electron–hole pairs or phonons. Trapping as a result of dissipation through electron–hole pair creation would not result in a strong T_s dependence.[21]

Evidence that steps or defects are important in the dissociation of hydrogen through a molecular precursor on platinum surfaces has been made on the basis of both dissociative sticking measurements on Pt(111) (Refs. 22–24) and the H_2/D_2 exchange reaction on Pt(111) and Pt(332).[25–29] Indeed it was the suggestion that a mobile precursor was responsible for the defect mediated channel on Pt(111) (Ref. 23) that resulted in the calculations made by Muller[30,31] which indicated that at $E_i < 200$ meV vibrational zero-point energy release to parallel translation motion could result in a long-lived mobile molecular precursor state at the surface when combined with an inelastic process. More recently, supersonic molecular beam measurements[32,33] of the dissociation of D_2 on Pt(111) revealed only a direct channel to dissociation over the entire range of E_i investigated. On Pt(110)-(1×2) a nonactivated channel associated with the valley or summit sites, in addition to the direct activated channel on the (111) microfacets, was suggested as responsible for the decay of S_0 with E_i at low gas temperatures.[34]

We have carried out a series of H_2 and D_2 sticking measurements using supersonic molecular beams on a Pt(533) surface. We have chosen this surface which exposes four atom wide terraces of (111) structure separated by (100) steps, in order to compare the results with similar measurements obtained on the Pt(111) surface measurements[32,33] in order to establish the role of the step sites in the overall dissociation dynamics, and establish the dynamical characteristics of such a channel if it exists.

II. EXPERIMENT

The apparatus and techniques used for this study have been described previously.[7,35,36] The platinum single crystal was aligned to within 0.5° of the (533) face and the structure confirmed by LEED. The surface was cleaned initially by cycles of ion bombardment and annealing at 1300 K. The surface temperature (T_s) was increased during this initial bombardment from 300 to 600 K over 10 cycles. Subsequent cleaning to remove carbon was achieved by exposure to oxy-

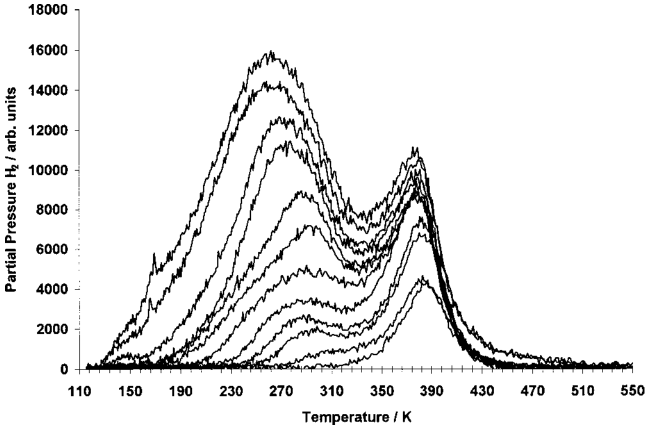

FIG. 1. Thermal desorption spectra of H_2 from the Pt(553) surface. The coverages are (a) $\Theta=0.09$; (b) $\Theta=0.11$; (c) $\Theta=0.17$; (d) $\Theta=0.19$; (e) $\Theta=0.26$; (f) $\Theta=0.32$ ML; (g) $\Theta=0.38$; (h) $\Theta=0.43$; (i) $\Theta=0.53$; (j) $\Theta=0.6$; (k) $\Theta=0.81$; (l) $\Theta=0.9$. H_2 has been dosed at $T_s=120$ K and the heating rate was 1 Ks^{-1}.

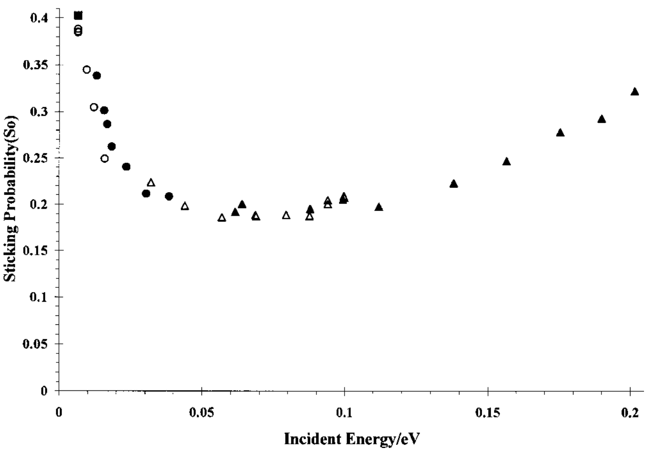

FIG. 2. The initial sticking probability (S_0) for H_2 (open markers) and D_2 (filled markers) on Pt(533) seeded in Ar (squares), Ne (circles), and He (triangles) as a function of hydrogen incident kinetic energy E_i. The beam was incident normal to the (533) plane ($\Phi=0°$) and $T_s=300$ K.

gen at $T_s<300$ K followed by heating to 1300 K to ensure desorption of oxygen, annealing of the surface, and dissolution of any residual silicon back into the bulk. Surface order and cleanliness was established by LEED and a comparison of the TPD of adsorbed oxygen with previous experimental measurements.[37] The molecular beam was generated at a nozzle pressure of 0.8–1.2 atmospheres, and constituted less than 2% H_2 or D_2 seeded in argon, neon, or helium. The kinetic energy was measured by time-of-flight (TOF). Sticking probabilities were measured by the reflection detection (King and Wells) technique.[38]

III. RESULTS AND DISCUSSION

A. Thermal desorption of hydrogen

Hydrogen was dosed using the molecular beam with the largest final aperture of diameter 4 mm resulting in a beam diameter at the sample of 10 mm. Subsequent thermal desorption was monitored by a quadrupole mass spectrometer measuring the resulting background pressure rise in the reaction chamber. Figure 1 shows a series of H_2 thermal desorption spectra from the Pt(533) surface after dosing the surface at $T_s=120$ K up to saturation coverage at an exposure of ca. 200 L. Absolute coverages have been estimated from the TPD results and a calculation of the pumping speed of the beam chamber for hydrogen. We have estimated the saturation coverage of H_2 on Pt(533) at 120 K to be 0.9 ± 0.05 ML, and at $T_s=150$ K (the surface temperature at which the S_0 coverage dependence is measured) is 0.8 ± 0.05. The latter value is similar to that found for the Pt(111) and Pt(997) surfaces.[22,39]

Low coverages of hydrogen produce a well-defined single desorption peak at 380 K. No such peak was observed in TPD at a heating rate of 10 Ks^{-1} for hydrogen on Pt(111),[39] or the platinum surface Pt(997) (Ref. 22) which has a lower step density of Pt(111) step sites. However, a high temperature shoulder was observed on an unannealed argon bombarded surface[22] (assigned as β_3) at the same temperature. The β_3 state was associated with hydrogen adsorbed at defects induced by the argon bombardment. We assign the peak at 380 K β_3 and associate it with recombinative desorption of atomic hydrogen adsorbed at the (100) steps of Pt(533). It saturates at a coverage of 0.14 ± 0.02 ML which corresponds to a filling of half of the fourfold sites at the (100) step edges with atomic hydrogen. It is likely that the hydrogen atoms occupy high coordination sites at the inside edge of the step on the basis of HREELS measurements which show a preference for three-fold hollow sites on the Pt(111) terrace.[40] TPD of higher coverages results in additional recombinative desorption of hydrogen below 360 K, the bulk of which is due to the atomic adsorption states at the terrace, but may also includes a contribution from the remaining step sites.

B. Kinetic energy dependence of dissociative adsorption

The dependence of the initial dissociative sticking probability S_0 of H_2 and D_2 on Pt(533) as a function of the incident kinetic energy (E_i) of the beam in the range 6.4–200 meV is shown in Fig. 2. The data has been obtained with the beam incident normal to the Pt(533) surface plane, at $T_s=300$ K. The most striking features of the curve are a decrease in S_0 with increasing E_i in the range $0<E_i\,(\mathrm{meV})<100$, and a steady increase in S_0 with increasing E_i for $E_i>110$ meV. Results for both D_2 (filled markers) and H_2 (open markers) were obtained in the region $0<E_i\,(\mathrm{meV})<100$ and indicate that there is no (or little) apparent isotope effect on dissociative sticking at these energies. Any mechanism requiring energy dissipation and accommodated molecular trapping should lead to some isotope effect in the trapping probability. There also appears to be no difference between sticking probabilities obtained at any E_i in this range for different nozzle temperatures with various seed gases shown in Fig. 2 for Ar (squares), Ne (circles), and He (triangles). It appears therefore that it is translational energy that is dominating the dissociative sticking probability at these energies.

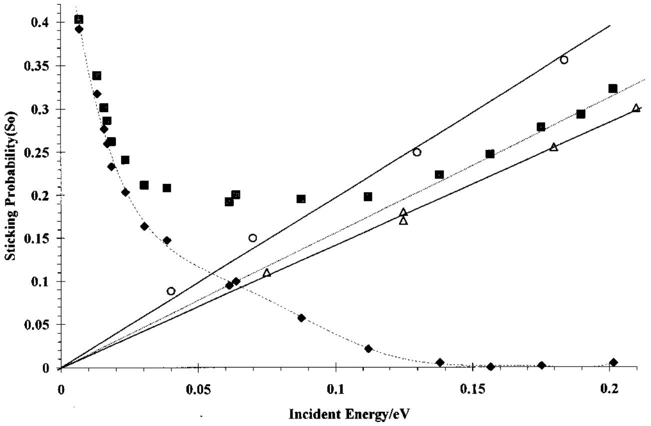

FIG. 3. The initial sticking probability (S_0) of D_2 on Pt(111) (open markers) taken from Ref. 32 (triangles) and Ref. 33 (circles) with the beam was incident normal to the (111) plane and $Ts = 300$ K. The data for S_0 on Pt(533) as a function of incident energy E_i is shown by the filled markers (summarized from Fig. 2) with the beam was incident normal to the (533) plane ($\Phi = 0°$) and $T_s = 300$ K. Linear fits for the direct contribution on the Pt(111) surfaces (Refs. 32, 33) are shown as solid lines, and our estimate for the direct contribution on the (111) terraces of Pt(533) is shown by the dashed line. Subtraction of this direct contribution from the original data provides an estimate (diamonds and dotted line) of the additional contribution at low E_i associated primarily with the Pt(533) step sites.

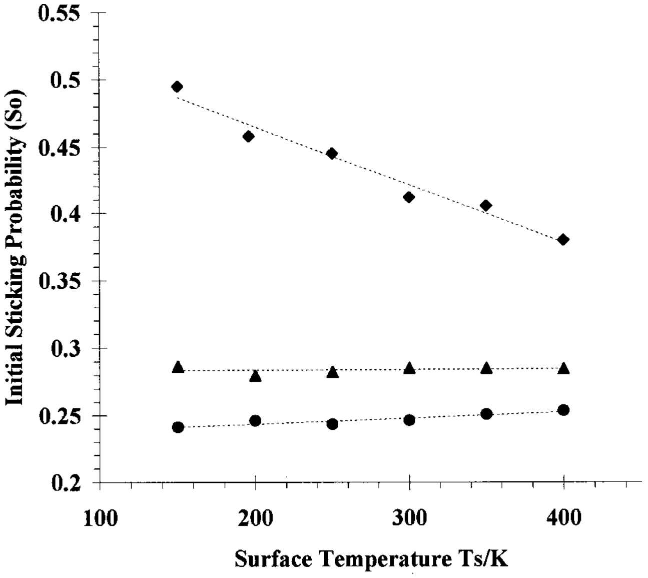

FIG. 4. Initial sticking probability (S_0) of D_2 on Pt(533) as a function of surface T_s at incident energies $E_i = 6.6$ meV (filled diamonds), $E_i = 18$ meV (filled circles), and $E_i = 180$ mev (filled triangles). The beam was incident normal to the (533) plane ($\Phi = 0°$).

Figure 3 summarizes the results from Fig. 2 obtained on Pt(533) (filled squares) and compares them with two independent sets of results (Ref. 32 open circles, Ref. 33 open triangles) obtained for the dependence of S_0 of D_2 on E_i for the Pt(111) surface. The results for Pt(111) have been obtained with the beam at normal incidence to the Pt(111) plane and $T_s = 300$ K. Dissociation on Pt(111) is characterized by a near linear increase (lines are included to guide the eye for the two sets of data) in S_0 with E_i over the measured energy range. The main difference between dissociation on the Pt(111) surface and the Pt(533) surface is the additional low energy channel in the energy range $0 < E_i\,(\text{meV}) < 100$ evident on Pt(533). We associate this additional contribution with the presence of the (100) steps on the Pt(533) surface. The increase at $E_i > 110$ meV on Pt(533) is ascribed to dissociation of D_2 on the four atom wide (111) terraces of Pt(533) through the same channel as evident on Pt(111). This channel is believed[32] to be the result of the direct dissociative chemisorption of the molecule. The increase in sticking with translational energy is due to the effective opening of a dynamical window (perhaps in the dimensions of the surface unit cell) giving access to barriers along nonoptimal reactive trajectories.

On the basis of the trends observed on the Pt(111) surfaces for this direct channel (Fig. 3), we have estimated the contribution of direct sticking on the (111) terraces of Pt(533) by a linear dependence (dotted line) based on the increasing sticking observed on Pt(533) at energies $E_i\,(\text{meV}) > 110$. Subtraction of this function from the measured sticking data provides an indication (filled diamonds) of the additional contribution to dissociative chemisorption which we associate with the (100) steps. A polynomial fit (dashed line) is included to guide the eye. The result is that this sticking component clearly decays with E_i in the energy range $0 < E_i(\text{meV}) < 150$. A similar low energy component to dissociative sticking of H_2 and D_2 with a similar T_{gas} dependence was associated with the steps on Ni(997), with a comparable (linearly increasing) direct contribution at higher T_{gas} from the (111) terraces.[2] Note also that the observed low energy component on Pt(533) exhibits the decay of S_0 with E_i in the same energy range as the low energy components on W(100),[6,7] W(100)-$c(2\times2)$Cu,[8,9] W(100)-$c(2\times2)$N,[10] Ni(110),[1] Pd(100),[1] Pd(110),[3] and Pt(110).[34]

The results presented here for Pt(533) are consistent with the increased sticking probability observed for a Maxwellian source of H_2 on Pt(997) over Pt(111).[22] It also provides direct evidence for an additional channel to dissociative adsorption through step sites which was invoked to explain the enhanced rate of H_2+D_2 exchange reaction at Pt(332) over that observed on Pt(111) surfaces investigated using a Maxwellian beam source.[28]

C. Surface temperature dependence of dissociative adsorption

The initial sticking probability (S_0) of deuterium was measured as a function of surface temperature in the range $150 < T_s(\text{K}) < 400$ at incident energies E_i of 6.6 meV (diamonds), 16 meV (circles), and 180 meV (triangles). The results are shown in Fig. 4 with linear fits shown for each set of data. At 180 meV, S_0 appears independent of surface temperature ($dS_0/dT_s = 6\times10^{-6}\,\text{K}^{-1}$) within experimental error. At this energy we expect (based on the arguments above in III B) the sticking to be dominated by the direct channel on the (111) terrace. This result is consistent with the weak temperature dependence ($dS_0/dT_s < 1\times10^{-4}\,\text{K}^{-1}$) observed on Pt(111) for the same channel[32] and what one may expect even with a recoil contribution[41] in view of the mass ratio between H_2 or D_2 and Pt. Only a very weak dependence of S_0 on T_s is observed at 16 meV, with $dS_0/dT_s = 5$

$\times 10^{-5}\,\mathrm{K}^{-1}$. What is significant about this latter result is that this corresponds to an energy E_i (Fig. 3) where ca 95% of the sticking is ascribed to a channel associated with the (100) step sites on Pt(533): This is the component that is characterized by a decrease in sticking probability with E_i (Figs. 2, 3). Only at a very low energy of 6.6 meV do we observe (Fig. 4) a clear T_s dependence of S_0, with $dS_0/dT = -4\times 10^{-4}\,\mathrm{K}^{-1}$.

One possibility is that this low energy channel is the same over the entire E_i range below 150 meV, and T_s is increasingly effective at the lowest energies. We suggest, however, that there are two separate components to dissociative adsorption which contribute to the channel in the energy range $0 < E_i(\mathrm{meV}) < 150$ (Fig. 3): One of these is temperature dependent and contributes only at very low E_i. The other is insensitive to surface temperature and contributes up to energies of ca. 150 meV. At E_i of the order of 6 meV, one may expect a significant probability of trapping in the physisorption well for H_2, even for the case where there is such poor matching of the substrate and adsorbate masses.[9] A temperature dependence in such a case would arise from either the change in trapping probability of the physisorbed state, or the partition of such a state between dissociation and desorption.

It is of interest to compare the temperature dependence of S_0 observed for H_2 or D_2 on other surfaces that exhibit similar E_i dependent dissociative sticking probabilities specifically in the low energy regime. H_2 dissociation on both Ni(997) and Ni(110) (Ref. 2) exhibit negative temperature dependence for a Maxwellian source at $T_{\mathrm{gas}} = 300\,\mathrm{K}$. No dependence in S_0 with T_s was detectable at energies ($E_i = 13\,\mathrm{meV}$) where the low energy channel was contributing on W(100).[7] At the same incident energy ($E_i = 13\,\mathrm{meV}$) on W(100)-$c(2\times 2)$Cu, where it was suggested that the indirect channel was responsible for all of the dissociative sticking, only a very small negative T_s dependence ($dS_0/dT_s = -3.2\times 10^{-4}\,\mathrm{K}^{-1}$) was observed.[8,9] Therefore in all cases and conditions where an indirect channel to dissociation has been suggested primarily on the basis of the E_i dependence, and where specific surface sites are implicated in the dissociation, either no, or a very small, negative temperature dependence has been reported.

In the case of a Pt(111) surface, under conditions it was suspected that the small proportion of defects ($< 10^{-3}$) were significantly contributing to S_0, a very small increase ($dS_0/dT_s = 6\times 10^{-5}\,\mathrm{K}^{-1}$) in S_0 with T_s was reported[23] for a Maxwellian source with $T_{\mathrm{gas}} = 291\,\mathrm{K}$. It was also suggested[23] that this increase was consistent with values for S_0 extracted (assuming a partition between desorption and dissociation of the H_2 at a defect site) from $H_2 + D_2$ reaction probabilities obtained at higher values of T_s.[28]

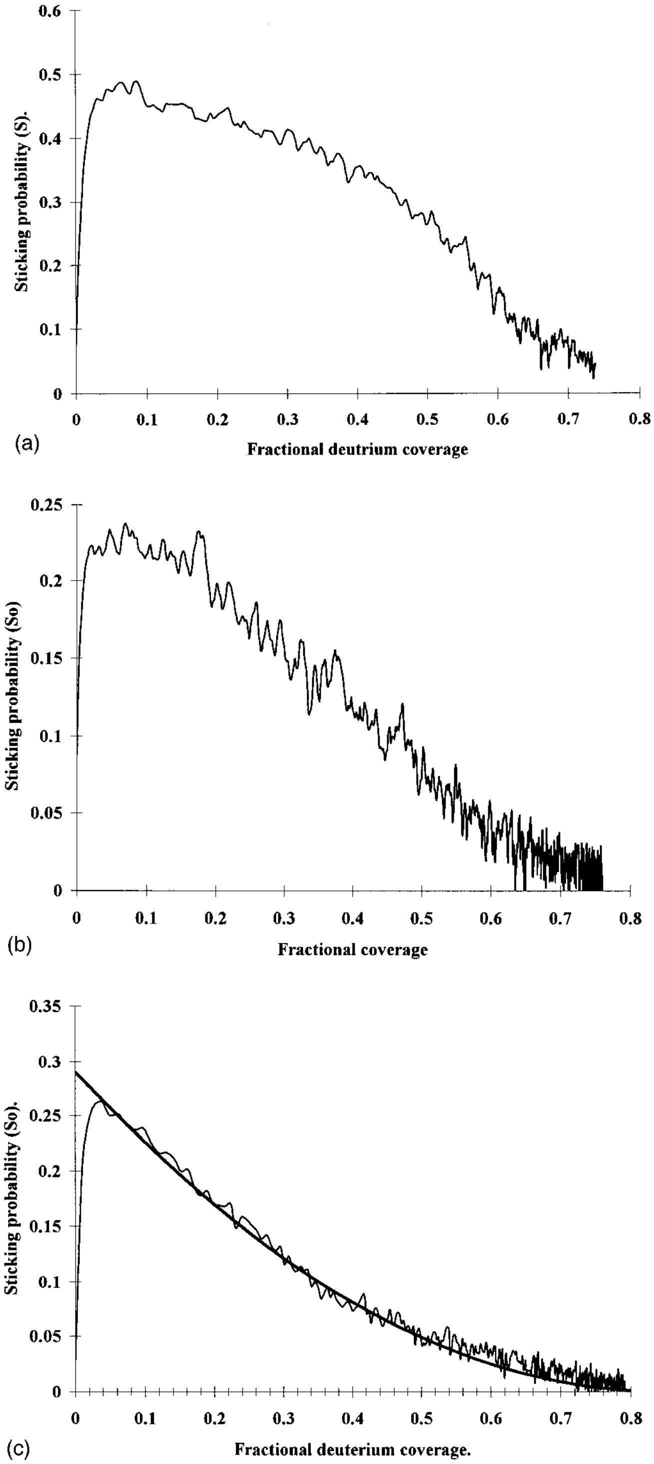

FIG. 5. Sticking probability (S) of D_2 on the Pt(533) surface as a function of coverage (Θ). The incident beam energy is (A) $E_i = 6.6\,\mathrm{meV}$; (B) $E_i = 18\,\mathrm{meV}$; and (C) $E_i = 180\,\mathrm{meV}$. The fit in (C) is $S = S_0(0.8\text{-}\Theta)^2$. The beam was incident normal to the (533) plane ($\Phi = 0°$) and $T_s = 150\,\mathrm{K}$.

D. The dependence of dissociative adsorption on coverage

The sticking probability $S(D_2)$ was measured as a function of deuterium coverage (Θ_D) at incident energies of 6.6, 18, and 180 meV and at $T_s = 150\,\mathrm{K}$ with the molecular beam at normal incidence to the Pt(533) surface. Saturation coverage at $T_s = 150\,\mathrm{K}$ has been measured from the TPD (Sec. III A) as 0.8 ± 0.05, and therefore this value has been taken as saturation in the reflection detection measurement at the same surface temperature. The results are shown in Fig. 5. At an energy of 180 meV where we suggest that sticking is dominated by direct dissociation at the Pt(111) terrace of Pt(533), there is a decrease in $S(D_2)$ with Θ_D [Fig. 5(c)] corresponding to second-order Langmurian behavior, i.e., where the dissociation probability is proportional to the square of the number of free surface sites. The fit shown together with the data in Fig. 5(c) corresponds to the function $S=S_0(0.8-\Theta_D)^2$. At low E_i, however, the coverage dependence of S_0 is far from the second order Langmurian dependence. It is also not linear, as found for coverage dependencies in the direct channel regime on W(100) (Ref. 7) and W(100)-$c(2\times 2)$Cu.[8,9] In fact it resembles that one may expect for a precursor route to dissociative adsorption, i.e., a less sensitive dependence of dissociative sticking on coverage during the initial adsorption. The latter is observed both at 6.6 meV [Fig. 5(a)] and at 18 meV [Fig. 5(b)]. Note that this behavior is observed in the same E_i region where S_0 decreases with increasing E_i (Fig. 3).

In the case of Ni(997) (Ref. 2) no coverage dependence reported. In the case of Ni(111), a monotonic decrease in S_0 with Θ_H is reported[42] consistent with the dominance of a direct channel on this surface.[2,42] In contrast a more complex dependence of S_0 with Θ_H was observed on Ni(110) and rationalized on the basis and precursor kinetics.[42] A similar trend in the coverage dependence of S_0 to that observed here in going from low E_i to high E_i was observed on W(110) (Ref. 7) and on W(100)-$c(2\times 2)$Cu.[8,9]

E. The dependence of dissociative adsorption on incident angle

The dependence of S_0 on the angle of incidence Φ was measured at $E_i=180$ meV and $E_i=6.6$ meV at $T_s=300$ K, and the results are shown in Fig. 6. The azimuth of the scattering plane was set within 15 degrees to be normal to the direction of the step edges, and positive angles are defined as scattering into the step edge as shown in the inset of Fig. 6. It is apparent immediately that for both energies, the angular dependencies are highly asymmetric. The step geometry therefore appears to influence S_0 at energies where one expects the direct channel to dominate (180 meV), and also under conditions (6.6 meV) where a low energy channel is dominating dissociation, but in quite a different fashion.

Under conditions where direct dissociation dominates the sticking process, one may expect to a first approximation that the overall process can be separated into two components. The first is associated with trajectories impinging on the (111) terrace, and the second is ascribed to trajectories impinging on the (100) step. In order to estimate the (111) component we have determined from the data obtained on Pt(111) (Ref. 32) that the angular dependence of S_0 at 180 meV depends on $\cos^3\Phi$. With the value of S_0 at normal incidence to Pt(111) (S_0^{111}) at 180 meV of 0.32, a function $S(\Phi)=(S_0^{111}/N)\cos^3(\Phi+\Phi^{111})$ has been fitted to the experimental data (Fig. 6) by placing the maximum of the (111) contribution at the expected angle of $-14.5°$ ($\Phi^{111}=14.5°$) and varying N. The best fit ($N=0.94$) is excellent at negative angles where the (100) step is shadowed i.e., for angles where the (111) plane will dominate sticking. We have neglected any shadowing of the (111) terrace by the (100) step at negative angles, but this will be $<12\%$ even at $\Phi=-60°$.

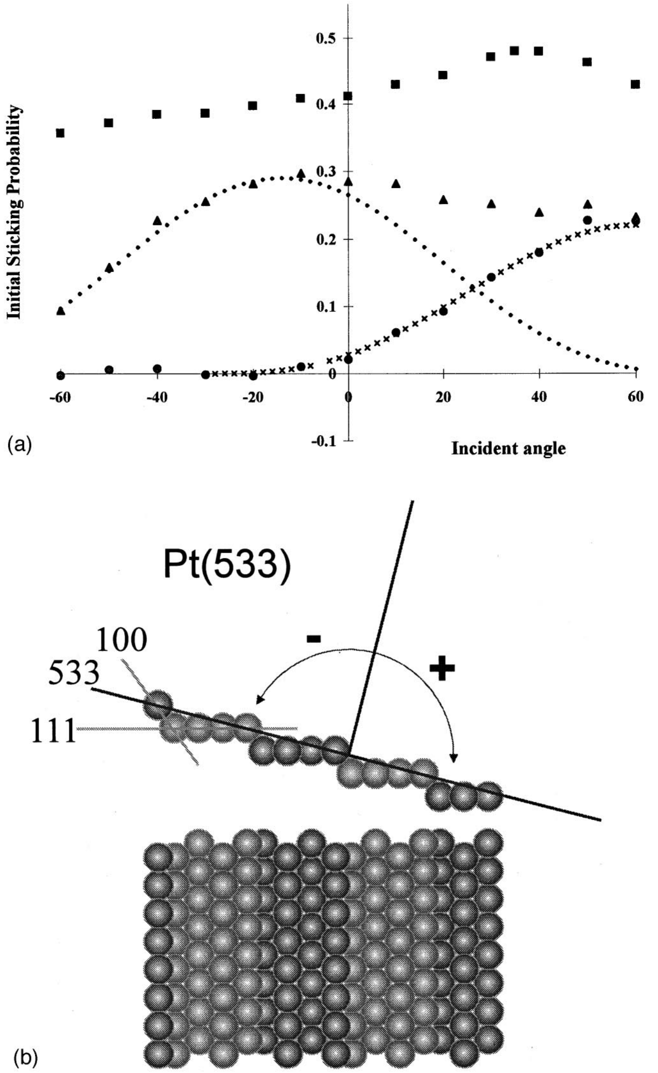

FIG. 6. The dependence of S_0 on the angle of incidence Φ:$E_i=180$ meV (triangles) and $E_i=6.6$ meV (squares). Measurements were made at $T_s=300$ K. The azimuth of the scattering plane was normal to the direction of the step edges, and positive angles are defined as scattering into the step edge as shown in the inset. The contribution to the direct channel ($E_i=180$ meV) associated with the (111) terraces has been estimated (small circles) using the function $S(\Phi)=(S_0^{111}/N)\cos^3(\Phi+\Phi^{111})$ (see text) and this subtracted from the experimental data at 180 meV yields $S(\Phi)$ which we associate with the step sites (circles). This is then fitted with the function $S(\Phi)=S_0^{100}\cos^3(\Phi+\Phi^{100})$ (small crosses).

Subtraction of the estimated (111) contribution from the measured $S_0(\Phi)$ for Pt(533) results in a second component [Fig. 6(•)] which we associate with the (100) step sites. It is evident therefore that the contribution that step sites have to the overall dissociation probability at normal incidence to the Pt(533) surface ($\Phi=0°$) is only about 17%. The maximum in the dependence for the step contribution corresponds to a large angle. We have fitted this (100) component to a function $S(\Phi)=S_0^{100}\cos^3(\Phi+\Phi^{100})$ and find a best fit at $\Phi^{100}=-61°$ and $S_0^{100}=0.22$. The angle $\Phi^{100}=-61°$ is significantly larger than that corresponding to the normal of the (100) plane ($\Phi=-40°$) and in fact corresponds more closely to the angle ($\Phi=-75°$) corresponding to trajectories parallel to the (111) terraces. It is likely therefore that the dissociation site with the lowest activation barrier associated with the step is not the four-fold site (i.e., in the step surface plane) but is atop or bridging the Pt atoms at the step edge.

It is impossible to analyze the $S_0(\Phi)$ data obtained at $E_i = 6.6\,\mathrm{meV}$ in a similar fashion, since we are much less sure about the nature of the low energy channels to dissociation on Pt(533). Qualitatively the $S(\Phi)$ dependence is quite flat, indicating a tendency for total energy scaling. This is clearly quite distinct from that observed in the direct channel regime. We also note that there is a tendency for an increased dissociation probability for trajectories into the step edge (positive angles), although we also note that for $\Phi > 40°$ this tendency is reversed.

It is interesting to compare the $S_0(\Phi)$ result obtained here on Pt(533) with the $S_0(\Phi)$ dependence observed for the HD exchange reaction on Pt(553).[26,27] The latter surface exhibits a slightly less dense array of (111) steps between (111) terraces. For the thermal beam source at 300 K one may expect the rate of reaction R_{HD} to be qualitatively similar to the $E_i = 6.6\,\mathrm{meV}$ data (Fig. 6) since $R_{\mathrm{HD}} \propto S_0$ in the steady state model.[26,27] We do observe an overall increase between $S_0(\Phi) = -60$ and 40 but of only ca. 35%. A similar but much larger increase (95%) is observed in R_{HD} over the same change in angle on Pt(533) (the same convention for Φ was used to define scattering into the step). We also note that the estimate we make of the absolute sticking probability for a thermal source based on the beam data for Pt(111) (Ref. 32) is about 0.07, and for Pt(533) is 0.21. The values obtained on the basis of R_{HD} were 0.07 for Pt(111) and $S_0 = 0.35$ for Pt(553).[26,27] The effect of steps on both the angular dependence and the absolute sticking probabilities for Pt(553) appear much greater than that observed for Pt(533), despite the greater step density of the latter. Therefore while there are some qualitative similarities between the two systems, we are unable to understand the qualitative differences at present.

F. The low energy channel to dissociation

On Pt(533) the E_i dependence indicates that there is a linearly increasing contribution dominating at higher energies associated with the Pt(111) terraces. This component has similar characteristics to those observed for the direct dissociation channel on Pt(111) (Fig. 3). Further, at $E_i = 180\,\mathrm{meV}$ where the channel dominates on both Pt(533) (Fig. 4) and Pt(111) (Ref. 32), S_0 exhibits only a weak dependence on T_s as one may expect for a direct channel. The coverage dependence $S(\mathrm{D}_2)$ is also characterized by classical second-order Langmurian adsorption behavior [Fig. 5(c)]. Finally the angular dependence $S_0(\Phi)$ at an energy associated with this direct dissociation regime can be understood in terms of two contributions with a $\cos^3\Phi$ dependence, i.e., that found on the Pt(111) surface for the direct channel under the same conditions. These two contributions correspond to direct dissociation at the (111) terrace and (100) step plane.

An additional contribution to the dissociative sticking on Pt(533) over Pt(111) which we associate with the presence of the steps is evident at low values of E_i. A similar difference is observed in S_0 as a function of T_{gas} for a Maxwellian source when comparing Ni(997) and Ni(111) surfaces,[2] i.e., a direct channel associated with the (111) terraces on which is superimposed a low energy contribution induced by the step. Subtraction of the estimate for the direct channel on Pt(533) provides us with an estimate of the contribution arising from the steps (Fig. 3). It is the characteristics of this component which we will consider specifically in the light of the suggestions made in the literature to explain the decay of S_0 for H_2 with E_i for metal surfaces with low activation barriers to dissociation.

The possible explanations for the additional step induced contribution are:

(i) An extension of the direct channel to low energies results in steering effects which can provide access to the lowest energy barriers in the PES.
(ii) The accommodation of a conventional molecular precursor at the (111) terraces which goes on to dissociate at a step site.
(iii) An indirect channel which provides a short-lived but highly mobile unaccommodated molecular precursor which goes on to dissociate at a step site.

The main characteristics of the additional step induced contribution are:

(a) S_0 decays with E_i over the range $0 < E_i(\mathrm{meV}) < 150\,\mathrm{meV}$. Note that this is the same range as similar low energy contributions on W(100),[6,7] W(100)-$c(2\times2)$Cu,[8,9] W(100)-$c(2\times2)$N,[10] Ni(110),[1] Pd(100),[1] Pd(110),[3] and Pt(110).[34]
(b) S_0 is effectively independent of T_s at $E_i = 16\,\mathrm{meV}$ ($dS_0/dT = 5\times10^{-5}\,\mathrm{K}^{-1}$), and shows a significant negative dependence at $E_i = 6.6\,\mathrm{meV}$ ($dS_0/dT = -4\times10^{-4}\,\mathrm{K}^{-1}$).
(c) S_0 depends in a more complex manner on Θ_{D} than the second-order Langmurian dependence one may expect, and indeed observes, at energies where the direct channel is clearly responsible for sticking.
(d) $S_0(\Phi)$ at 6.6 meV shows a sensitivity to the presence of the step sites through an asymmetry in the dependence. The fact that this dependence is very small indicates a tendency for S_0 to scale with total energy. This contrasts with the higher energy (direct) regime where S_0 depends strongly on the normal component of E_i.

The T_s dependence at $E_i = 6\,\mathrm{meV}$ ($dS_0/dT = -4\times10^{-4}\,\mathrm{K}^{-1}$) leads us to believe that at the very lowest energies, a conventional molecular physisorbed precursor is being trapped and accommodated. This molecule goes on to partition between dissociation and desorption at the Pt(533) surface. Calculations of the trapping probability using a hard cube model for such a badly mass-matched system predicts that trapping into a physisorption well of 30 meV can be expected at this low energy.[9] Because sticking data is not specifically available for Pt(111) surfaces at this low energy, it is not clear whether this channel requires steps for dissociation, or that it can take place on the (111) terrace.

The main contribution which contributes to S_0 in the range $0 < E_i(\mathrm{meV}) < 150\,\mathrm{meV}$ does not exhibit a significant temperature dependence. As pointed out previously,[7–9] this is an energy range over which trapping in a weak physisorbed precursor is improbable. At $E_i = 16\,\text{meV}$, $dS_0/dT = 5\times10^{-5}\,\text{K}^{-1}$ on Pt(533). What is significant about this result is that this is for an energy (Fig. 3) where ca. 95% of the sticking is ascribed to a channel associated with the (100) step sites on Pt(533). The absence of a significant T_s dependence on W(100) at $E_i = 13\,\text{meV}$,[7] and particularly on W(100)-$c(2\times2)$Cu at $E_i = 13\,\text{meV}$ where it was suggested that steps were responsible for 100% of the dissociation,[8,9] lead to the suggestion that an indirect channel to dissociation through an unaccommodated precursor was responsible for dissociation, and that steps or defects were the active sites. An additional similarity between the results presented here for the low energy channel on Pt(533) and those obtained for the same channel on W(100)-$c(2\times2)$Cu (Refs. 8, 9) concerns the angular dependence $S_0(\Phi)$. It was concluded that S_0 on W(100)-$c(2\times2)$Cu surface scaled not with the normal component of incident energy, but as $E_i \cos^{0.7}\Phi$. A similar tendency for S_0 to scale with total energy is observed for Pt(533).

The alternative was that steering (translational and rotational) in the W(100) unit cell resulted in the E_i dependence: This would also be consistent with the absence of a significant T_s dependence. The steering model as applied to H_2 dissociation on W(100) (Refs. 11–13) and Pd(100) (Refs. 15–17, 43), however, is not able to explain the low energy channel on Pt(533) since we have shown that it is directly related to the presence of the step sites. If a steering model was to explain the present results, the steering would have to be sufficiently strong in the translational coordinate to allow molecules to impinge primarily on the step sites, i.e., translational steering would be required over the distance associated with the (111) terrace width. Although we cannot rule out this possibility in the absence of trajectory calculations based on a realistic PES for Pt(533), on the basis of the limited translational steering predicted on W(100) and Pd(100), we consider it unlikely.

In cases of late barriers in the two-dimensional PES, the lowering of the vibrational zero-point energy resulting from a softening of the H–H bond through interaction of the molecule with the surface results in a dynamical well.[31,44] The possibilities of redistribution of energy provided an explanation for temperature independent trapping of H_2 on W(100) and provided an explanation for the Θ_H dependence of S_0.[7] It was the absence of the required barrier in the *ab initio* PES that resulted in the rejection of this mechanism, particularly since steering could provide an alternative mechanism. In the case of Pt(111), and (111) terraces on Pt(533), the E_i dependence of the direct scattering channel indicates that there are a majority of trajectories which experience a significant activation barrier (Fig. 3). Therefore at least in the case of Pt(533) the possibility of an indirect channel to dissociation at the (100) step of a resonantly trapped precursor on the (111) terrace provides a more clear cut possibility.

There are, however, other possible explanations for an indirect channel which exhibits precursor type behavior without the need for significant energy dissipation:[45] Steering enhanced trapping provides a mechanism for normal translational to parallel translational and rotational energy conversion, and this is strongly enhanced with the presence of even a weak molecular well before the barrier. In addition the introduction of steps provides a corrugation simply in the repulsive part of the PES which may result in normal to parallel energy conversion. The origin of the step induced indirect component on Pt(533) can only be better understood through dynamical simulations on realistic potential energy surfaces. These results nevertheless clearly indicate that steps can give rise to a dissociation channel with characteristics similar to those of the low energy channel observed on a number of surfaces exhibiting low activation barriers.

IV. CONCLUSIONS

Temperature programmed desorption measurements indicate that associative desorption of H_2 from (100) step sites on Pt(533) is observed from lowest exposures at 375 K and assigned the β_3 state. Saturation of this peak takes place at $\Theta_H = 0.14$ and corresponds to the filling of half of the available four fold sites at the (100) step edge. Additional associative desorption takes place at higher coverages in a broad peak below 300 K. This is associated with desorption from the (111) terraces being similar to that observed (and assigned β_1 and β_2) for desorption from the Pt(111) surface.

The initial dissociative sticking probability (S_0) of H_2 and D_2 first decreases over the range $0 < E_i(\text{meV}) < 150$ (low energy component), and subsequently increases (high energy component). Comparison with D_2 dissociation on Pt(111), where (S_0) increases linearly with E_i, leads to the conclusion that it is the step sites that are responsible for the low energy component to dissociation on Pt(533). The high energy component we associate with a direct dissociation channel on (111) terraces of the Pt(533) surface. The probability of dissociation through the direct channel on the (111) terraces of Pt(533), like Pt(111), is found to exhibit a very small T_s dependence ($S_0/dT_s = 6\times10^{-6}\,\text{K}^{-1}$). The angular dependence $S_0(\Phi)$ scattering in a plane perpendicular to the step direction is asymmetric about the Pt(533) surface normal at $E_i = 180\,\text{meV}$. At 180 meV $S_0(\Phi)$ can be successfully analyzed by fitting the $\cos^3\Phi$ dependence [the observed dependence on Pt(111) at 180 meV][32] for the direct component on a (111) terrace. The remaining $S_0(\Phi)$ component is peaked at a very grazing angle, and in a direction far from the normal to the (100) step plane. This may indicate that direct dissociation takes place preferentially at an atop or bridged site at the step.

We have estimated the contribution to sticking on the (111) terraces on Pt(533) to estimate the step induced low energy component of S_0. The probability of dissociation through the low energy channel associated with the (100) steps, over most of the range of E_i where it contributes, is also shown to be independent of T_s($S_0/dT_s = 5\times10^{-5}\,\text{K}^{-1}$). Only at the very lowest values of $E_i = 6\,\text{meV}$ does S_0 exhibit a more significant (negative) temperature dependence of $dS_0/dT = -4\times10^{-4}\,\text{K}^{-1}$. These results indicate that there are two contributions to sticking below 150 meV. At very low energy, where trapping into the physisorbed precursor is possible, a conventional precursor channel mediated dissociation on Pt(533). It is the partition between desorption and dissociation which is likely to be responsible for the T_s dependence of this channel at 6.6

meV. A second channel contributes over a much wider proportion of energies up to 150 meV, and is much less T_s dependent. The angular dependence $S_0(\Phi)$ at 6.6 meV is quite different than that found in the direct dissociation regime at 180 meV. It exhibits asymmetry, indicating the importance of the step in dissociation at these energies, but the angular dependence is very weak and suggests that at 6.6 meV S_0 tends to scale with total energy.

A second-order Langmurian dependence of S with Θ_D is observed at $E_i = 180\,\text{meV}$ where the direct channel dominates, but the dependence of S on Θ_{D} exhibits characteristics similar to those expected for precursor mediated dissociation at both $E_i = 16\,\text{meV}$ and $E_i = 6.6\,\text{meV}$ where the low energy channel dominates

The dynamical characteristics of the low energy channel induced by the steps on Pt(533) are similar to those for the same component observed on Ni(997) (Ref. 2) using a thermal beam source. They are also similar to a number of other surfaces exhibiting low activation barriers, particularly clean and adsorbate modified or alloyed W(100) (Refs. 7–9) where it was suggested that steps play an important role in the dissociation process at low energies. An explanation for the step induced channel on Pt(533) purely in terms of steering appears less compelling than a model involving an indirect channel and an unequilibrated molecular precursor.

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