Thermally Assisted Tunneling: CH$_4$ Dissociation on Pt(111)

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The mechanism for the dissociation of CH$_4$ at metal surfaces has been and is still controversial. In large part, this is because many of the experimental data suggest a direct tunneling mechanism, which is not obviously compatible with an observed strong dependence on the surface temperature. We propose here that a new phenomenon, thermally assisted tunneling, caused by a coupling of the tunnel barrier to the lattice, resolves this controversy. Explicit calculations using a simplified model for this process agree qualitatively with a wide range of experimental data for CH$_4$ dissociation on Pt(111).

Steam reforming of natural gas to produce so-called syngas is the initial catalytic event in the conversion of natural gas to gasoline, a process of enormous technological and economic importance. Steam reforming is dominated by the relation CH$_4$ + H$_2$O → CO + 3H$_2$ on a supported metal catalyst, and proceeds through several steps. The rate-limiting step is believed to be the breaking of one of the C-H bonds of CH$_4$ by the metal. Accordingly, the initial dissociative chemisorption of CH$_4$ molecules on metal surfaces, so-called "C-H bond activation," has been the subject of great interest and intense investigation within the surface science community. Despite considerable effort extending over several decades, however, no consensus has been established as to the mechanism responsible for the dissociative chemisorption. Early experiments [1,2] showed a large isotope effect, which Winters interpreted in terms of vibrationally assisted tunneling via a molecular precursor [1]. Stewart and Ehrlich [2], however, claimed that a statistical model could explain the isotope effect equally well. Similarly, an exponential dependence of the initial dissociation probability S_0 on the incident translational energy ϵ_i of a CH$_4$ molecular beam has been interpreted as evidence for tunneling [3], but also in terms of CH$_4$ deformation upon surface impact ("splats") [4]. The debate as to whether tunneling is an important aspect of the dissociation has been quite heated [5,6]. A major difficulty has been reconciling data (isotope effect, dependence on ϵ_i) that point to tunneling with the observed exponential dependence of S_0 on surface temperature T_s. At low incident energies characteristic of the thermal regime, the T_s dependence could be rationalized in terms of tunneling via a thermally accommodated molecular precursor [1]. However, recent measurements of CH$_4$ and CD$_4$ dissociation on Pt(111) using molecular beams [7] showed a dramatic increase in S_0 with T_s under incidence conditions that preclude this interpretation. Further, the influence of T_s on S_0 depended strongly on ϵ_i. Luntz and Bethune [7] concluded that none of the models for CH$_4$

dissociation that have been proposed to date is consistent with all of the data for CH$_4$/Pt(111). In particular, the dependence on T_s found in the beam experiments suggested that some significant aspect of the picture was missing.

In this Letter we demonstrate that the missing ingredient is the phenomenon of *thermally assisted tunneling* caused by a coupling of the tunneling barrier to the lattice [8]. This coupling allows surface thermal motion to influence the tunneling probability dramatically. We present a theoretical model for CH$_4$ dissociation and show by explicit calculation that the dissociation behavior of the model with respect to surface temperature, incident energy, and isotopic variation is in excellent qualitative agreement with the data of Luntz and Bethune, and with new measurements reported here. This agreement strongly suggests that the mechanism for CH$_4$ dissociation on metals is via tunneling *on initial impact* with the surface.

Th mechanism we envisage is a concerted dissociation process that breaks a single C-H bond and chemisorbs a CH$_3$ radical and an H atom. While these species will in general undergo further reactions at high T_s, electron-energy-loss spectroscopy measurements for a Ni(111) substrate maintained at low T_s [4] have shown that initial dissociation is to a chemisorbed methyl radical and an H atom. It was shown also that this initial step dominates the dissociation dynamics at higher T_s. A reasonable reduced-dimensionality potential energy surface (PES) for low-energy reaction paths then results on treating the CH$_4$ as a dimer, R-H, with R representing CH$_3$. Two molecular coordinates, Z and D, are necessary and describe, respectively, the normal distance of the R-H center of mass from the surface and the R-H bond distance. The dependence of the energy on these coordinates is modeled via a PES, $V_s(Z,D)$, constructed from Morse potentials describing the R-H, R-M, and H-M bonds, where M stands for metal, and exponentials describing the CH$_4$-M repulsion in the entrance channel

and the R-H repulsion in the exit channel. $V_s(Z,D)$ exhibits a two-dimensional "stiff activation barrier" that links the region of large Z and small D where the CH_4 is chemically intact with the region of small Z and large D where the R-H bond is broken. The PES topology is similar to that used widely by a number of authors in connection with dissociation of diatomic molecules at surfaces (see [8] and references therein). The saddle point, of height 0.76 eV, was at $Z^* = 3.5$ a.u. above the surface and corresponded to a slightly extended R-H bond distance of $D^* = 2.4$ a.u. These features, as well as the dominance of the "dimer" interaction, are in good qualitative agreement with recent quantum chemical calculations of the transition state of CH_4 on Ni clusters [9]. The recoil and thermal motion of the surface are described via an Einstein oscillator which couples directly to the Z coordinate. More complex couplings could be invoked, as noted in Ref. [8], but the direct coupling of the CH_4 center of mass to the surface atom, which describes the normal recoil of this atom during the collision, dominates. The dominance of normal energy coupling is manifest experimentally in the general observation of strong phonon to normal kinetic energy transfer, but weak phonon coupling to molecular vibrations in direct molecule-surface collisions. The appropriate PES, now three dimensional, is then $V(Z,D,Y) = V_s(Z - Y, D) + \frac{1}{2}\kappa Y^2$, and describes an activation barrier that is no longer stiff but can recoil, or at elevated T_s oscillate, normal to the surface. The reduction of PES dimensionality to essential coordinates eliminates effects such as "steric hindering" (which inhibits some CH_4 from exploring low-energy paths on the true multidimensional PES). These effects will certainly influence dissociation behavior but are not likely to change the *nature* of the dependence on experimentally controllable parameters. A full discussion and justification of the reduced dimensionality PES will be given elsewhere [10].

The tunneling behavior of the potential given above was determined by propagating in time an initial wave packet comprising a Gaussian packet localized far from the surface and representing the translation of the CH_4 with incident energy ϵ_i, the vibrational ground state of the R-H bond, and a harmonic-oscillator eigenfunction. The packet was propagated on a mesh using the fast-Fourier-transform technique described elsewhere [8,11] with an energy resolution of order 10 meV. Tunnel probabilities $T_n(\epsilon_i)$, where n refers to the oscillator level used in the starting packet, were calculated by integrating the current flowing through an appropriately defined surface. The oscillator mass and frequency ω were taken to be the mass of a single Pt atom and the surface Debye frequency (20 meV), respectively. For energies in the subbarrier region, T_n was found to grow approximately exponentially with n and it was sufficient to perform explicit calculations for a few n values spanning the range of thermally occupied oscillator states and to determine the remainder

by extrapolation. The effect of finite surface temperature is then estimated from the T_n via $S_0(T_s, \epsilon_i) = \sum_n P_n(T_s) T_n(\epsilon_i)$, where the Boltzman factor

$$P_n(T_s) = \frac{\exp[-nw/k_B T_s]}{\sum_n \exp[-nw/k_B T_s]}$$

gives the probability that the oscillator is in state n in a thermal ensemble at T_s. The representation of the thermal motion via a single Einstein oscillator is reasonable because the collision energies and energy transfers are large compared with the phonon bandwidth.

Figure 1(a) shows the calculated behavior of $\ln[S_0(T_s,\epsilon_i)]$ vs $1/T_s$ for four values of ϵ_i. The saturation values for low T_s correspond to the tunnel probabilities with the oscillator in its ground state. In the far subbarrier region, S_0 increases with temperature by almost 2 orders of magnitude. At elevated temperature therefore, *thermally assisted tunneling* dominates the dissociation
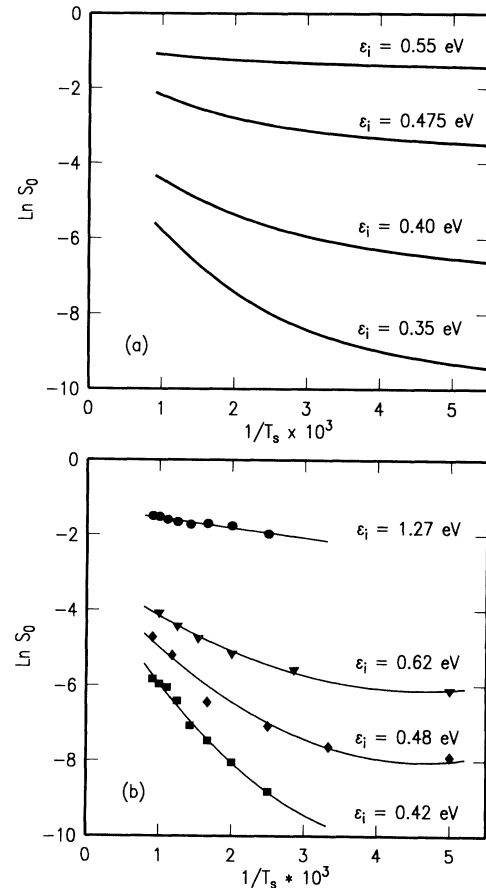

FIG. 1. (a) Calculated dependence of the dissociation probability of CH_4 as a function of inverse surface temperature for incident energies ϵ_i as noted. (b) Measured dependence of S_0 on inverse T_s for $CH_4/Pt(111)$ for incident energies ϵ_i as noted. The data at 0.42 and 1.27 eV are taken from Luntz and Bethune [7]; those at 0.48 and 0.62 eV are new (see text).

probability. The thermal enhancement can be viewed quantum mechanically in terms of phonon-gain processes "kicking" the tunneling particle "up the hill" or, in semi-classical language, as resulting from trajectories where the thermal velocities of the Pt atoms are directed outwards as the CH_4 reaches the tunnel barrier. This effectively "renormalizes" the barrier parameters [8]. The effect, though purely dynamical, can be simulated approximately within a stiff-barrier tunneling model via a temperature-induced modulation of the barrier parameters.

Experimental measurements for the T_s dependence of S_0 for CH_4 dissociation on Pt(111) are shown in Fig. 1(b). The results at $\epsilon_i = 0.42$ and 1.27 eV are from Luntz and Bethune [7], while those at 0.48 and 0.62 eV are new. These new measurements used essentially the same experimental techniques as Luntz and Bethune, but were performed on a different molecular-beam machine and with a different low-defect Pt(111) crystal. Despite these differences, the new measurements agreed absolutely with the earlier ones within 20%. As is apparent, the T_s and ϵ_i dependences of the experimental and theoretical probabilities are strikingly similar, though the energy scales are somewhat different. This may be a consequence of the reduction of the dimensionality in the theory [10]. The remarkable sensitivity of the subbarrier experimental curves to the incident energy *and* surface temperature is very strong evidence for the proposed mechanism of thermally assisted tunneling, and difficult to reconcile with any of the previously proposed ones. Since the general form of the PES governing CH_4 dissociation is not likely to be metal specific, we expect that the behavior we find for Pt(111) should be observed for other substrates. Other authors have reported a lack of sensitivity to T_s [4,12]. This, however, was based on limited experimental evidence at rather high ϵ_i, where the T_s effect is relatively weak. The important hallmark of thermally assisted tunneling is a strong coupling between the ϵ_i and T_s dependences deep in the subbarrier region.

In Fig. 2(a) we show the behavior of $S_0(T_s, \epsilon_i)$ vs ϵ_i calculated for CH_4 and CD_4 at $T_s = 800$ K and for $T_s = 0$ K. The isotope effect is quite pronounced, but is in fact considerably *reduced* at elevated temperatures. Although the $T_s = 0$ K CD_4 probability is much smaller than that of CH_4 at a given ϵ_i, the relative enhancement due to the surface temperature is greater for CD_4. This highlights the influence of thermally assisted processes on both the magnitude and the energy dependence of the isotope effect at low energies and elevated T_s. While the dominant behavior of S_0 with ϵ_i is clearly exponential, the logarithm plots are not straight lines but have a marked downward curvature due primarily to the tunnel barrier being bell shaped rather than parabolic. In Fig. 2(b) we show the experimental results of Luntz and Bethune for CH_4 and CD_4 at $T_s = 800$ K. Except for the energy scale, the magnitude and energy dependence of the isotope

effect is in excellent correspondence with that of the model PES and the downward curvature is clearly evident. Previous molecular-beam experiments using different substrates [3,4] showed a similar dependence of S_0 on ϵ_i but were interpreted in terms of a strictly linear logarithm plot. In general, the physical barrier will always depart from parabolic behavior at sufficiently low energy so a downward curvature is expected. The subbarrier energy at which this becomes pronounced, however, will depend on the barrier parameters and will differ from substrate to substrate.

Another important experimental observation that finds a natural explanation within our picture is the enhancement of S_0 with nozzle temperature at constant ϵ_i, which has been attributed to the presence in the beam of vibrationally excited CH_4, i.e., to *vibrationally assisted* dissociation [4,7,13]. This has been discussed exhaustively for the type of PES we consider here in connection with H_2 dissociation on Cu (see, for example, [14] and references therein). Excellent agreement of the observed effect for $CH_4/Pt(111)$ with theoretical predictions was obtained and will be reported elsewhere [10].
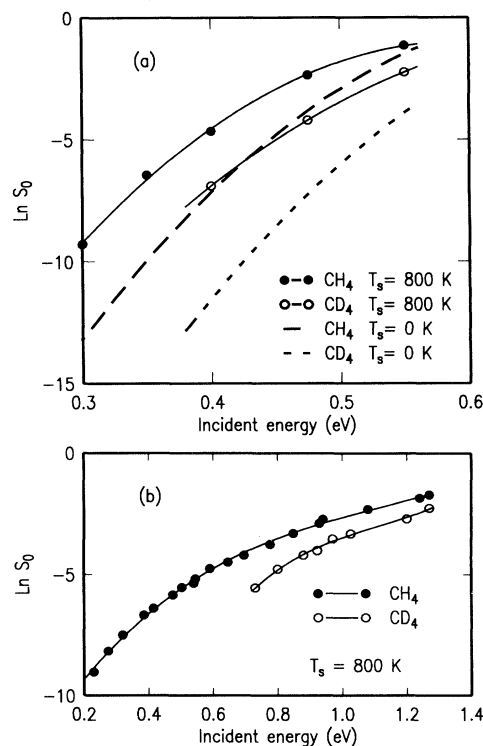
While the dynamical calculations pertain to relatively

FIG. 2. (a) Calculated dependence of the CH_4 (solid circles) and CD_4 (open circles) dissociation probability as a function of incident translational energy at $T_s = 800$ K. The dashed lines are fits through the $T_s = 0$ K calculations, with CH_4 uppermost. (b) The experimental dissociation probabilities of CH_4 and CD_4 from Luntz and Bethune [7] for comparison.

high incident energies, thermally assisted tunneling will occur also in the thermal regime, albeit with rates that are too low to allow numerical calculations to be carried out reliably. To obtain rough estimates, we use a simplified stiff-barrier model and simulate the temperature effect via a modulation of the tunneling length of a bell-shaped barrier. A plot of $\ln[S_0(T_s,\epsilon_i)]$ vs $1/k_B T_s$ for such a model at low incident energies is decidedly nonlinear, as observed in thermal experiments which sample a wide range of surface temperatures [1]. Over a limited range of temperatures, however, the plot looks reasonably linear even though the process underlying the temperature dependence has nothing whatsoever to do with thermal excitation over the top of a barrier. "Activation energies" deduced from the slope of such plots fall in the range covered by experimental values quoted typically in the literature. This suggests that thermally assisted tunneling may remain the dominant dissociation mechanism even under thermal conditions. A careful comparison of the model with thermal experiments will be given elsewhere [10].

In conclusion, we believe the above comparison between theory and experiment is rather convincing evidence that the dissociation of CH_4 on $Pt(111)$ under the conditions of the molecular-beam experiments proceeds via a direct impact tunneling process. We know of no other mechanism that can account for the dramatic dependences on translational energy, surface temperature, and isotope. We anticipate that this mechanism is quite general for CH_4 dissociation on metals. The key new element in our analysis is the demonstration that *thermally assisted tunneling* dominates over most of the accessible temperature and energy range. This effect results from the thermal motion of the substrate during the collision and influences the subbarrier tunneling probability in the same way as a temperature-induced reduction of the tunneling length. While the detailed comparison in this paper refers to molecular-beam experiments in UHV under nonthermal conditions, there is no compelling reason why this mechanism should not be the one that limits rates of reaction under thermal conditions, even at the high pressures and temperatures that are used in industrial reactions.

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