

Low translational energy mechanisms in the dissociative chemisorption of methane on iridium and platinum surfaces

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Abstract

Recent molecular beam studies of methane dissociative chemisorption on Ir(110), Ir(111) and Pt(110) surfaces show evidence of a low translational energy pathway to dissociation that had not been seen previously for methane dissociation on any transition metal surface. Earlier molecular beam studies on a variety of transition metal surfaces indicated only a direct dissociative mechanism for methane dissociation, which is active only at high translational energies. Recent studies on Ir and Pt show that at low translational energies the dissociative chemisorption probability decreases as the translational energy increases in contrast to the behavior at higher translational energies, where the direct mechanism is known to be dominant and the chemisorption probability increases with increasing translational energy. The exact mechanism of this low energy pathway is under debate and has been described as either a trapping-mediated mechanism or a steering-assisted direct mechanism. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Natural gas, which is composed primarily of methane, is a cheap and renewable feedstock for the production of a wide range of commodity chemicals. Typically, the initial step in the production of these chemicals is the reaction of natural gas with steam over a supported metal catalyst to form synthesis gas, a mixture of hydrogen and carbon monoxide. Additionally, methane can be catalytically converted to higher hydrocarbons by oxidative coupling or to methanol by partial oxidation. The rate-limiting step in these processes is often the dissociation of the methane C–H bond on the catalyst surface. Therefore,

a fundamental understanding of the kinetics and dynamics of methane dissociation on metal surfaces is important to the optimization of the steam reforming process as well as for the development of new processes. Consequently, there have been a number of studies that have tried to elucidate the mechanism(s) for the dissociative chemisorption of small alkanes [1–45] through the use of ultra-high vacuum molecular beam techniques [46–48]. These techniques allow for the measurement of dissociative chemisorption probabilities on clean, well-characterized, single-crystal transition metal surfaces as a function of the incident translational energy, incident angle, and internal energy of the molecule as well as surface temperature.

These studies indicate that in cases where dissociative chemisorption is facile, there are two contrasting mechanisms available for the dissociation of ethane and higher alkanes on metals: a direct dissociative

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mechanism operative at high translational energies and a low translational energy pathway that has been identified as trapping-mediated [1–8,49]. The direct mechanism involves dissociation of the molecule on impact with the surface, provided that the molecule has sufficient translational and vibrational energy to overcome activation barriers to dissociation. Therefore, the chemisorption probability should increase as the incident translational energy of the impinging molecule is increased. In the case of trapping-mediated chemisorption, the opposite trend is expected. Here, the impinging molecule first impacts the surface, transferring some of its translational energy to the surface, and becomes physically adsorbed, or trapped, on the surface. As the incident translational energy of the molecule is increased, more of this energy must be dissipated in order to allow physical adsorption. Once the molecule is trapped, it thermally accommodates to the surface and undergoes a kinetic competition between desorption to the gas phase and dissociative chemisorption to the surface. The rate at which a molecule chemisorbs or desorbs from the physically adsorbed state is determined by the temperature of the surface. In systems, where the activation barrier to desorption is greater than the barrier to chemisorption, an increase in surface temperature will decrease the chemisorption probability.

Conversely, for systems where the barrier to chemisorption is greater than the barrier to desorption from the physically adsorbed state, the magnitude of the chemisorption probability should be much smaller, and the value should increase as the increase in surface temperature. Until recently, there has been no evidence to support the viability of trapping-mediated chemisorption in such a system. In fact, it has been suggested that increasing the surface temperature may actually inhibit trapping-mediated chemisorption in systems where the physical adsorption well is shallow and the barrier to chemisorption is large [50]. As the surface temperature is raised (supplying the physisorbed species with sufficient energy to surmount the barrier to chemisorption) the lifetime of the physically adsorbed species on the surface decreases. At very high surface temperatures, the lifetime of the molecule on the surface may be comparable with the time scale of molecular motion, and a distinct physically adsorbed state may not be accessed.

Methane has a shallow physical adsorption well and a high barrier to chemisorption on transition metal surfaces. Thus, it has been speculated that low translational energy pathways to chemisorption on these surfaces might not exist [38] and that significant chemisorption probabilities could only be obtained at high translational energies through the direct dissociation channel. However, very recent molecular beam studies have demonstrated the existence of a low translational energy pathway to dissociation on the Ir(1 1 0) [36,42], Ir(1 1 1) [43] and Pt(1 1 0) [44,45] surfaces. The exact mechanism of this low energy pathway is under debate and has been described as either a trapping-mediated mechanism or a steering-assisted direct mechanism. Understanding this low energy pathway could significantly impact our understanding of the physics of the dissociative chemisorption of methane and its relation to studies of methane dissociation using thermally equilibrated ('bulb') gases.

2. Previous studies of methane dissociation: evidence for a high translational energy pathway to dissociation

Over the past two decades, a number of molecular beam experiments have been conducted to determine the mechanism(s) of methane dissociation on transition metals. Early molecular beam experiments of methane interacting with W(1 1 0) [9], Ni(1 1 1) [10–12], Ni(1 0 0) [13,14], Pt(1 1 1) [15–18], Pt(1 1 0) [19], Pd(1 1 0) [20], Ir(1 1 0) [3,21–24] and Ru(0 0 1) [41] (Fig. 1) have shown that the chemisorption probability increases with increasing translational energy, indicating the dominance of a direct dissociation mechanism. None of these studies gave evidence for a low energy pathway to chemisorption and most researchers believed that the dissociation of methane on any metal surface, at any translational energy, was dominated by the direct dissociation mechanism. However, only two of these investigations (CH₄/W(1 1 0) and CH₄/Ru(0 0 1)) [9,41] probed translational energies <0.20 eV, where trapping or steering is most efficient. The studies of methane dissociation on W(1 1 0) and Ru(0 0 1) showed a monotonic increase in the chemisorption probability with increasing translational energy over the entire range

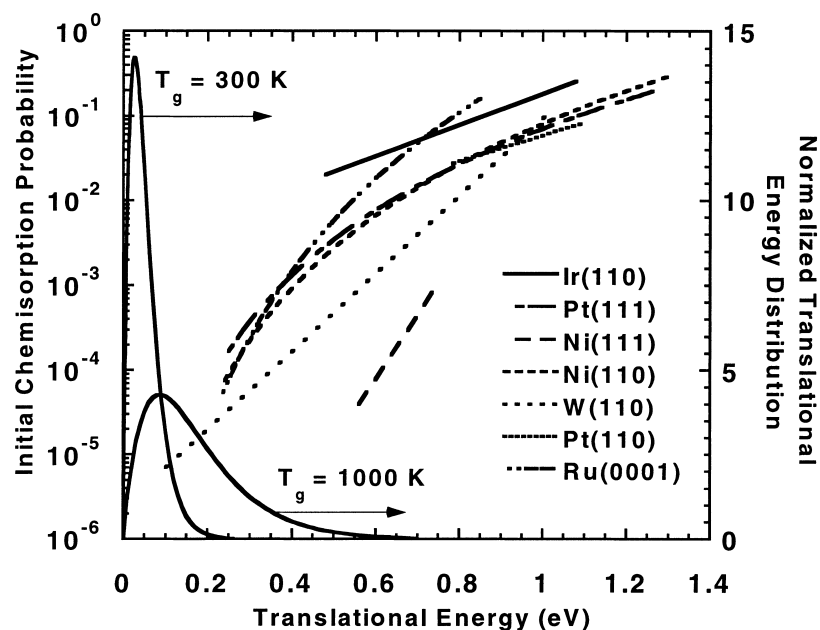


Fig. 1. Initial dissociative chemisorption probability of methane on various transition metal surfaces as a function of normal kinetic energy overlaid with Maxwell–Boltzmann translational energy distributions at gas temperatures of 300 and 1000 K.

of translational energies, ruling out any significant trapping-mediated component to the chemisorption probability and indicating that the direct mechanism is probably the dominant pathway for dissociation on these surfaces, at least at the substrate temperatures studied.

3. Recent discoveries of a low translational energy pathway to dissociation

Recently, investigators have revisited these systems in order to determine how the chemisorption of methane depends on translational energy in the low energy (<0.2 eV) regime. A study of methane dissociation on Ir(1 1 0) [36,42] at low translational energies by Seets et al. was the first to show the evidence of a low translational energy pathway to methane dissociation (Figs. 2 and 3). The data indicated that at translational energies below about 0.2 eV, the chemisorption probability *decreases* and then begins to increase as the translational energy is increased above about 0.2 eV. This behavior, in the low energy regime, was interpreted as a trapping-mediated mechanism for the

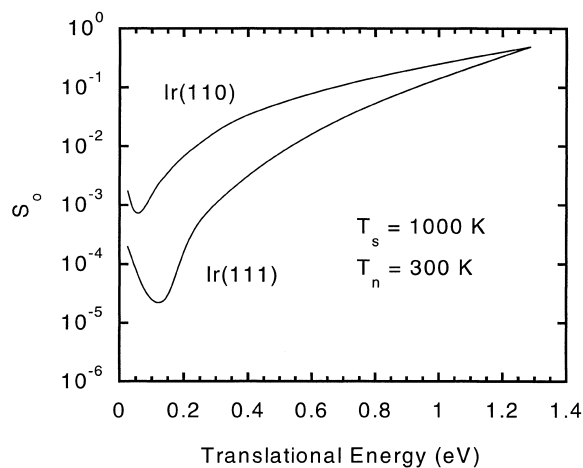


Fig. 2. Schematic representation of the initial dissociative chemisorption probability of methane on Ir(110) and Ir(111) [36] vs. translational energy. The data for the $\text{CH}_4/\text{Ir}(111)$ system scales with normal translational energy over the entire translational energy range, whereas the data for the $\text{CH}_4/\text{Ir}(110)$ system scales with normal translational energy at high energies and with the total translational energy at low energies. The minimum in the chemisorption probability depicted in the Ir(110) curve is most evident for measurements at 60° incidence.

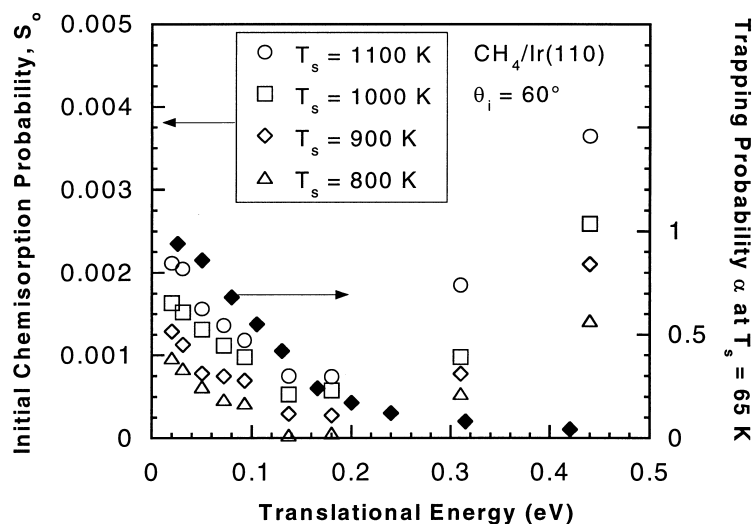


Fig. 3. Plot of the dependence of the translational energy on the dissociative chemisorption probability of CH_4 on Ir(110) [36] at several different surface temperatures (left ordinate) and the trapping probability at $T_s = 65$ K (right ordinate) at $\theta_i = 60^\circ$.

following reasons. First, the chemisorption probability in this energy regime decreases with increasing translational energy. Second, the functional form of the decrease in chemisorption probability with translational energy is self-similar (within experimental uncertainties) to the functional form of the decrease in trapping-probability with translational energy, which was experimentally measured at a surface temperature of 65 K (Fig. 3). In other words, the chemisorption probability (S_0) has the same dependence on translational energy (E_i) and incident angle (θ_i) as that of the trapping probability (α), which is consistent with a simple model of trapping-mediated chemisorption (Eq. (1)).

$$S_0 = \alpha(E_i, \theta_i) \frac{k_c(T_s)}{k_c(T_s) + k_d(T_s)} \quad (1)$$

Note that the trapping probability is assumed to be independent of surface temperature in this simple model. Also, the angular dependence in the low energy regime was shown to be different than the angular dependence of the chemisorption probability at high translational energies, indicating the presence of two distinct mechanisms. At low translational energies, the trapping probability, as well as the chemisorption probability, is a function of the total translational energy of the incident molecule, i.e. is independent of

incident angle. This dependence has been observed for trapping of molecules on corrugated surfaces [49,51] like that of Ir(110). Early studies of the trapping dynamics of methane and rare gases on flat surfaces [52–54] (such as Pt(111)) indicated that momentum exchange with the surface is much more efficient in the direction normal to the surface than in the direction parallel to the surface. In these cases, a plot of α versus $E_i \cos^2 \theta$ produces a smooth curve and this behavior has been termed “normal energy scaling”. However, parallel momentum can be redirected into the normal direction on more corrugated surfaces (such as Ir(110)). In cases where all of the parallel momentum must be dissipated, trapping is said to observe “total energy scaling” and a plot of α versus E_i produces a smooth curve at all incident angles. At high translational energies, the chemisorption probability scales with the translational energy associated with the component of the momentum directed normal to the surface. This is consistent with the previous studies of methane dissociation at high translational energies [3,9–24] and with theoretical models [55,56] of the direct dissociation pathway. This “normal energy scaling” of the direct mechanism is believed to be due to the fact that only the normal momentum can be used to overcome the barrier to dissociation since the reaction coordinate lies along the normal

direction. Third, the chemisorption probability at low translational energies is described well by a simple model of trapping mediated chemisorption and yields values of activation barriers and pre-exponentials for chemisorption and desorption that are consistent with density functional calculations [57].

An analogous study was conducted by Seets et al. on the flat, close-packed Ir(1 1 1) [43] surface (Fig. 2). The results of this study were similar to that of the Ir(1 1 0) surface; however, the chemisorption probability on the (1 1 1) surface was typically an order of magnitude less than that on the (1 1 0) surface, except at very high translational energies, where the direct dissociation mechanism is clearly dominant and surface structure is believed to be less important. The chemisorption probability was shown to depend on the normal component of the translational energy over the entire energy range studied. Although the trapping probability could not be experimentally measured for this system, normal energy scaling of the trapping probability would be consistent with the early studies of rare gas trapping on flat, close-packed surfaces as mentioned above.

Arguments against the assignment of a trapping-mediated mechanism in the low translational energy regime typically stem from a question of the ability of methane to thermally accommodate to the surface at these high surface temperatures due to the short lifetime on the surface. In the studies on Ir(1 1 0) and Ir(1 1 1), the data was taken at surface temperatures between 800 and 1100 K. At these high temperatures, and with a physisorption well depth of only about 0.2 eV, the lifetime of methane on the surface is on the order of picoseconds, and is of the same order of magnitude as the time scale for trapping to occur. To help resolve some of these issues, Sitz has performed classical molecular dynamics simulations [58] of methane trapping on Ir at elevated temperatures. In these computations, methane is treated as a simple monatomic species. These studies indicate that methane does become thermally accommodated to the surface even at surface temperatures as high as 1465 K. Methane 'atoms' that are classified as trapped in the simulations are shown to desorb in a cosine angular distribution with an average energy that increases as the surface temperature increases but that does not depend on the residence time of the methane. Simulations of ethane trapping on Pt(1 1 1) [59] performed by Stinnet et al.

also suggest that surface temperature may have only a small effect on trapping. Their simulations indicate that over the surface temperature range of 95–700 K, the trapping probability drops by not more than a factor of 2.

It would be useful to measure the time-of-flight of methane scattered from an Ir surface held at high temperature as a function of angle. It is expected that directly scattered molecules will reflect from the surface close to the specular angle. Molecules that have trapped should desorb from the surface in a near cosine distribution with velocities characterized by a Boltzmann distribution at the surface temperature. The presence of a bimodal time-of-flight distribution would indicate the presence of trapping since trapped molecules will reside on the surface for some finite time whereas directly scattered molecules will not. However, these measurements are experimentally very difficult. Although bimodal distributions have been seen for *rare gases* scattered from metal surfaces, bimodal distributions have never been measured for scattering of *molecules*. This is due to the large number of modes into which energy can be transferred during collision with the surface, which results in a single broad time-of-flight distribution. Therefore, interpretation of such data will be difficult and possibly ambiguous.

There is also a possibility that the CH₄/Ir system is unique, and that this low translational energy pathway is not universal to all metals. It is known that Ir is the most active [32,60,61] of the transition metals toward alkane dissociation under ultra-high vacuum conditions. Perhaps, the barrier to chemisorption is too high on other metal surfaces for this low energy pathway to be significant.

Methane dissociation on Pt(1 1 0) [44,45] was also recently shown to exhibit a low translational energy pathway (Fig. 4). The data presented by Walker and King show a decreasing chemisorption probability with increasing translational energy up to about 0.15 eV. Above 0.15 eV, the chemisorption probability increases with translational energy. Walker and King propose that in the low translational energy range a steering-assisted direct mechanism is responsible for the decrease in chemisorption probability instead of a trapping-mediated mechanism. Experimental measurements [62–66] of the dissociative chemisorption probability of H₂ on metals also show a decrease

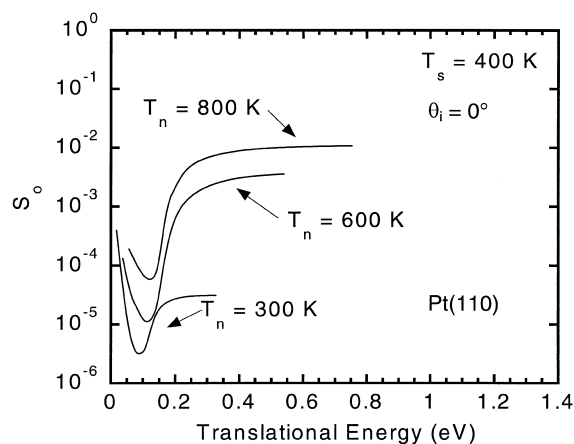


Fig. 4. Schematic representation of the initial dissociative chemisorption probability of methane on Pt(110) [44,45] vs. translational energy. Data are shown for nozzle temperatures of 300, 600 and 800 K at normal incidence.

in the chemisorption probability with increasing translational energy in the low energy regime. The existence of a trapping-mediated mechanism for the chemisorption of H_2 on metals is questionable due to the weak physisorption potential and poor mass match between H_2 and metals, leading to small trapping probabilities. Recent theoretical studies [67,68] indicate that at low translational energies the potential energy surface can steer H_2 into a favorable orientation before impact with the surface, thereby reducing the barrier to direct dissociation. At higher translational energies, the molecules have less time to be steered by the potential energy surface resulting in the observed decrease in chemisorption probabilities. This mechanism was recently used to explain the observed decrease in chemisorption with increasing translational energy at low energies for H_2 on Pt(100) [69].

The data of Walker and King also show a strong nozzle temperature dependence of the chemisorption probability in the low translational energy range. By increasing the temperature of the nozzle used to make the supersonic molecular beam, the vibrational energy distribution of the molecules is shifted to higher energies. It is well known that increased vibrational energy of the incident molecules can promote direct dissociative chemisorption [9,10,13,16,31]. It has been

speculated that vibrational excitation of molecules that physically adsorb, or trap, to a metal surface will be quenched very quickly through the creation of electron hole pairs. Although the vibrational lifetime of excited methane physisorbed on metals has not been measured, the vibrational lifetime of CO chemisorbed on metals has been extensively studied [70–73]. The lifetime of excited vibrations of CO on metals is very short (~ 2 ps); however, there are some important differences between CO and CH_4 to consider when trying to estimate the lifetime of an excited vibration in methane on metals. CO will molecularly chemisorb to metals, whereas methane will only physically adsorb. Therefore, CO has a stronger interaction with the metal than physically adsorbed methane. Also, CO has a permanent dipole moment, whereas CH_4 does not. These two facts indicate that the lifetime of an excited vibration in methane physically adsorbed to a metal may be >2 ps. Persson and Persson have performed calculations [74] of the lifetime of excited CO on Cu. These calculations indicate that if you consider CO as a *physisorbed* molecule, then the lifetime of an excited vibration on Cu could be on the order of 100 ps, whereas the experimentally measured lifetime for molecularly *chemisorbed* CO on Cu(100) is 3.5 ps.

The notion of steering is currently being called into question by experiments conducted by Hayden and coworkers. In this study, a Pt(533) surface (stepped (111) surface) was employed in the investigation of low translational energy pathways to hydrogen dissociation [75]. On the clean, stepped surface, a decrease in dissociative chemisorption was observed up to translational energies of ~ 0.10 eV. Such behavior on other metal surfaces has previously been interpreted in terms of a trapping-mediated pathway, although a steering mechanism has also been suggested, since the trapping probability of hydrogen on metals is low at translational energies above about 0.03 eV. However, Hayden and coworkers have found that, if the steps of the Pt(533) surface were decorated with either CO or O, halting step-edge adsorption, then the component of adsorption that could be assigned to a steering mechanism was eliminated, and only classic trapping-mediated (ending at 0.03 eV) and direct dissociation were observed (just like on the clean Pt(111) surface) [76]. This seems inconsistent with the idea of a steering mechanism,

which is believed to be a low energy direct process, and suggests that the apparent steering mechanism is likely not steering at all, but rather chemistry mediated by the step-edge (defect) from a quasi-trapped species.

4. Implications of low translational energy mechanisms to catalysis

A gas which is in thermal equilibrium has a Maxwell–Boltzmann distribution of translational energies defined by the temperature of the gas. When considering the relevance of a low translational energy mechanism to catalysis, it is important to note that a significant fraction of molecules in a Maxwell–Boltzmann gas have translational energies below 0.2 eV, in an energy range where this mechanism is important. Indeed, at a gas temperature of 300 K, almost all the molecules have translational energies below 0.2 eV (Fig. 1). However, until recently, it has been assumed that the direct mechanism is the dominant mechanism for chemisorption at all translational energies. Under this assumption, several groups [13,25] have tried to calculate the average chemisorption probability for a thermalized gas at low pressures by convoluting molecular beam data with the Maxwell–Boltzmann distribution at the appropriate temperature. Chemisorption probabilities at low translational energies were assumed by extrapolating the high translational energy data to low energies. These calculations typically resulted in an average chemisorption probability two or more times less than the experimentally determined value. However, in the case of CH₄/Ir, Seets et al. were able to calculate an average chemisorption probability within 20% of the experimental values [42,43]. Seets et al. state two factors that were critical to the success of their calculations: (1) the inclusion of the low energy pathway and (2) using molecular beam data taken with a nozzle temperature equal to that of the gas temperature used to make the thermalized gas measurements. The second factor was necessary to ensure that molecules in the molecular beam and in the thermalized gas have the same vibrational energy distribution. This result indicates that a low translational energy pathway may exist for many of these previously studied systems.

5. Conclusions

The existence of a low energy pathway to methane dissociation on transition metal surfaces has recently been shown. Although the exact mechanism is unclear, it is apparent that this pathway can play a significant role in the dissociative chemisorption of methane under real process conditions. In order to clarify the mechanism responsible for this low energy pathway, more experimental data and theoretical input is needed.

Although there are data that indicate this low translational energy mechanism may play a role on very reactive surfaces, there is still no evidence for this mechanism on other surfaces. These observations may be due to the surface temperature necessary to allow this low energy mechanism to become active. In the studies by Seets et al. on Ir(1 1 0) and Ir(1 1 1), measurements of the chemisorption probability were taken at relatively high surface temperatures (between 800 and 1100 K). As mentioned before, Ir is also the most reactive of the transition metals studied for methane activation under ultra-high vacuum conditions. However, on other surfaces such as Ni(1 1 1), the dissociation of methane has a much higher activation barrier. This means that the surface temperature may need to be quite high (possibly physically impossible) in order to observe this low translational energy pathway. Experimental measurements of the chemisorption probability at these high surface temperatures may be impossible due to the diffusion of carbon into the bulk of Ni.

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