New Mechanisms for Chemistry at Surfaces

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It is becoming increasingly apparent that chemistry at surfaces, whether it be heterogeneous catalysis, semiconductor etching, or chemical vapor deposition, is controlled by much more than the nature and structure of the surface. Recent experiments that principally make use of molecular beam techniques have revealed that the energy at which an incident molecule collides with a surface can be the key factor in determining its reactivity with or on the surface. In addition, the collision energy of an incident particle has proven essential to the finding of new mechanisms for reaction or desorption of molecules at surfaces, collision-induced activation and collision-induced desorption. These phenomena are often responsible for the different surface chemistry observed under conditions of high reactant pressure, such as those present during a heterogeneous catalytic reaction, and of low pressure of reactants ($<10^{-4}$ torr), such as those present in an ultrahigh vacuum surface science experiment. This knowledge of the microscopic origins of the effect of pressure on the chemistry at surfaces has allowed the development of a scheme to bypass the high-pressure requirement. Reactions that are normally observed only at high reactant pressures, and which are the ones most often of practical importance, can now be carried out in low-pressure, ultrahigh vacuum environments.

IN 1932, LENNARD-JONES DESCRIBED THE DISSOCIATION OR the dissociative chemisorption of a molecule on a surface with a diagram similar to that shown in Fig. 1 (*1*). It depicts the potential energy of interaction between a structureless, diatomic molecule as a function of its distance from a structureless, uniform surface. A long-range, attractive van der Waals interaction is observed to grow as the molecule approaches the surface but the attractive interaction gives way to a repulsive one as the distance between the two decreases. However, because some chemical interaction, such as the filling of the molecule's antibonding orbitals by the electrons at the surface or the dumping of its electrons into the empty surface bonding levels, turns on at shorter distances, the repulsion does not continue to increase. The interaction first becomes less repulsive and then turns strongly attractive, giving rise to a potential maximum. The inner, deeply attractive well is the dissociative state, and the potential maximum between the outer and inner well results in a barrier between the molecular adsorption or physisorption state and the dissociative chemisorption state. As Lennard-Jones noted, it follows straightforwardly that if the energy of the impinging molecule is lower than the potential energy at the top of the barrier, only molecular adsorption occurs, whereas higher incident energies can result in dissociative chemisorption. This kind of interaction potential where the maximum of the potential barrier lies above the zero of energy as defined for a molecular infinitely far from the surface is called activated dissociative chemisorption (*2*). What is important here to emphasize is that it is not the surface that is the primary source of energy effective in overcoming the barrier but the energy with which the molecule collides with the surface. For those molecules with the requisite energy, dissociation of the molecule and adsorption of its fragments occur directly upon impact.

Given that this mechanism was proposed almost 60 years ago, it can hardly be called a new idea. Yet, it is a mechanism for dissociative chemisorption that had largely been forgotten until recently. In its place was the notion that the surface as the all-important source of energy in a molecule-surface interaction. A molecule had to first adsorb molecularly so that it could soak up the energy from the solid necessary to activate its dissociation. These ideas persisted despite numerous observations of the absence of dissociation in thermodynamically favorable systems even at high surface temperature. Perhaps this state of affairs came about because a convenient method to vary the energy of the impinging molecule was lacking. The vast majority of surface studies had been and still are undertaken after adsorption of gas molecules from the ambient background where molecules strike the surface with thermally distributed energies. However, with the development of molecular beam techniques (*3, 4*), it became possible to investigate the effect of the incident energy. These techniques were first applied to the problem of dissociative chemisorption in the early 1970s (*5, 6*) but, despite these elegant experiments which clearly demonstrated the direct, activated dissociative chemisorption mechanism of Lennard-Jones, the importance of a molecule's incident energy was not widely appreciated or studied until the mid-1980s.

One purpose of this article is to illustrate how recent experiments have verified the interaction shown in Fig. 1 and how detailed dynamical information about this mechanism is obtained. However, as even more recent experiments have shown, the importance of the incident energy reaches far beyond the interactions described by Lennard-Jones. Investigations of the effect of incident energy have led to the discovery of new mechanisms for dissociative chemisorption, desorption, and absorption called collision-induced dissociation, desorption, and absorption. These new mechanisms, along with the newly appreciated mechanism of Lennard-Jones, have important implications for understanding the different surface chemistry observed under ultrahigh vacuum (UHV) conditions and under high-pressure conditions typical in heterogeneous catalysis (*7*). First the importance of incident energy and activated dissociative chemisorption will be shown.

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The Problem Created by the Lennard-Jones Potential Surface

Consider the steam reforming of methane, which is the reaction of CH_4 and H_2O to form CO and H_2. This commercial process for hydrogen production is carried out over a supported nickel (Ni) catalyst at about 30-atm pressure of reactants and at 1000 K (*8*). Because the extremely high pressures make it impossible to investigate the mechanistic details of this surface reaction in situ, it is desirable to be able to carry out this and other reactions at pressures below 10^{-4} torr where UHV surface science techniques can be used to probe the microscopic reaction events. However, attempts to carry out this reaction at 10^{-4} torr are unsuccessful, despite more favorable thermodynamics at this lower pressure. The absence of reactivity at the lower pressures has become known loosely as the pressure gap in the reactivity in heterogeneous catalysis (*9, 10*). An understanding of the origin of the pressure gap is crucial, because without it the lack of reactivity at the low pressures where UHV surface science techniques are operable certainly casts doubt on the relevance of UHV surface science to high-pressure processes such as catalysis, chemical vapor deposition, and etching reactions.

A closer examination of the steam reforming reaction reveals that the effect of pressure is manifested in at least the first step of this reaction, which is the dissociative chemisorption of CH_4. Dissociation of both reactants is necessary if the steam reforming reaction is to proceed. Methane is observed not to adsorb dissociatively when its pressure above the Ni surface is below 10^{-4} torr, whereas dissociation of CH_4 is readily observed at pressures above 1 torr (*11, 12*). A possible explanation for the effect of pressure lies in the Lennard-Jones interaction potential shown in Fig. 1. Because the barrier along the dissociative reaction coordinate can be overcome only by those molecules incident on the surface with energies higher than the energy of the barrier, the rate of reaction is limited by the flux of sufficiently energetic incident molecules. If the barrier is high compared to the energies of most of the molecules in a thermal sample, then only a very small fraction of molecules incident on the surface will have the requisite energies. In this case, the rate of dissociative chemisorption may be so slow that dissociative chemisorption may not be observable in the limited time during which the measurement is made. However, an increase in the pressure will increase the absolute number (but not the fraction) of molecules with energies sufficient to overcome the barrier, thereby increasing the rate and allowing the products of dissociative chemisorption to be readily observed.

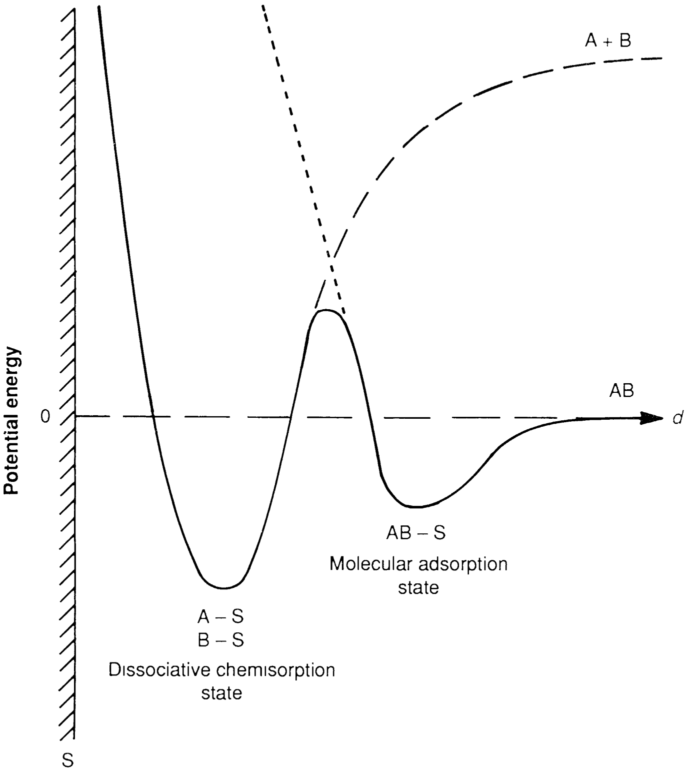


Fig. 1. Schematic diagram of the potential energy of interaction in one dimension between the center of mass of a molecule AB and a structureless surface as a function of the distance *d* between them. The outer well represents the molecular adsorption state and the deeper well represents the dissociative chemisorption state.

This then is the hypothesis for the lack of reactivity or dissociative chemisorption under low-pressure conditions. In order to test this hypothesis, it is necessary to verify the Lennard-Jones interaction potential shown in Fig. 1. This can be accomplished by experiments that probe the effect of a molecule's energy on its dissociative chemisorption. Barriers are especially accessible experimentally because they are extrema on the potential energy surface of interaction. Experiments that monitor first the threshold for and then the extent of dissociation as a function of the incident energy can determine the height of the barrier or the distribution of barrier heights, the nature and orientation of the barrier, and the occurrence of quantum-mechanical tunneling through the barrier.

Experimental Techniques

The experimental scheme combines molecular beam techniques with UHV surface electron spectroscopies (*13*). Molecular beam techniques allow the translational energy and the direction of the incoming adsorbate to be varied while electron spectroscopy detects results of the dissociative chemisorption event. Such an apparatus (*14, 15*) designed specifically for measurements of the adsorption probability as a function of the energy of the incident molecule is shown in Fig. 2. The molecular beam is formed by an adiabatic expansion of a high pressure (5 atm) of gas through a 25-μm orifice

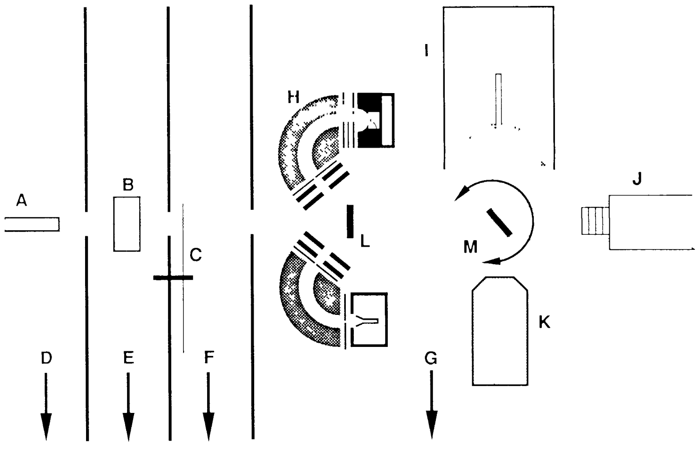


Fig. 2. Schematic diagram of a molecular beam–UHV apparatus: (A) nozzle molecular beam source; (B) electronic shutter; (C) rotating-disk chopper; (D) to source chamber 10-inch diffusion pump; (E) to first differential stage 6-inch diffusion pump; (F) to second differential stage 4-inch diffusion pump; (G) to main-chamber liquid N_2–trapped 10-inch diffusion pump; (H) HREEL spectrometer; (I) LEED; (J) quadrupole mass spectrometer; (K) cylindrical mirror analyzer (CMA) Auger spectrometer; and (L and M) possible positions for crystal mounted on a rotatable, liquid He–cooled sample manipulator.

into a vacuum. The resulting beam passes through a skimmer and through two circular apertures mounted in the walls of the differential pumping stages that collimate the beam to about 10^{-4} sr. The beam then enters the UHV chamber, which has a base pressure of 4×10^{-11} torr, and continues directly through the center of a high-resolution electron energy loss spectrometer, in front of a cylindrical mirror electron energy analyzer used for Auger electron spectroscopy (AES) and a low-energy electron diffraction (LEED) apparatus, and then directly into the line of sight of a quadrupole mass spectrometer. A Ni single crystal whose surface has a (111) orientation is placed in the beam's path either in position L or M in the diagram. The crystal is mounted on a liquid helium (He)–cooled manipulator (*16*) that enables rotation around an axis parallel to the crystal surface so that the angle of incidence of the beam on the crystal is variable. The temperature of the crystal is adjustable from 8 K to its melting point.

The type of molecular beam that is most useful in these experiments is known as a supersonic beam. In this kind of source, the pressure of the gas is so high that the mean free path is much smaller than the diameter of the orifice. The flow is hydrodynamic, where the molecules are literally dragged or pushed through the orifice by the very large number of collisions that occur as the gas makes its way through the orifice. The resulting beam is more focused than a beam resulting from effusive flow and more intense by about two orders of magnitude (*17*). The expansion of the gas is also adiabatic, which means that the enthalpy of the random atomic motion is converted to directed mass flow. The feature of an adiabatic expansion that is of importance here is the cooling of the gas or the narrowing of the velocity and energy distribution of the emerging molecules (*3, 4*). The ratio of the spread of energies (full width at half-maximum) to the total energy may be as small as 0.2% for He but is typically 10% for molecules. But not only do these experiments require the energy distribution of the incident molecules to be narrow, it is also necessary to vary and most often increase the average energy. For example, suppose one desires to accelerate CH_4. This can be accomplished with a seeding technique in conjunction with a supersonic expansion. About 1% of CH_4 is mixed with He prior to the expansion. During the expansion there are many collisions of the slow moving, heavy, minority CH_4 molecules with the rapidly moving He atoms. The collisions accelerate CH_4 to the He atom velocity and, because CH_4 is so massive compared to He, the resultant energy of the CH_4 is very large. A 1% mixture of CH_4 in He expanded from an orifice at 800 K will yield a translational energy for CH_4 of 17 kcal/mole. By adjusting the ratio of the heavy to the light gas and the source temperature, translational energies over a wide range can be achieved. The translational energy of the beam is measured by a time-of-flight technique in which a slotted disk chopper is mounted in the second differential pumping stage. An electronic shutter mounted in the first differential chamber controls the exposure time of the surface to the beam.

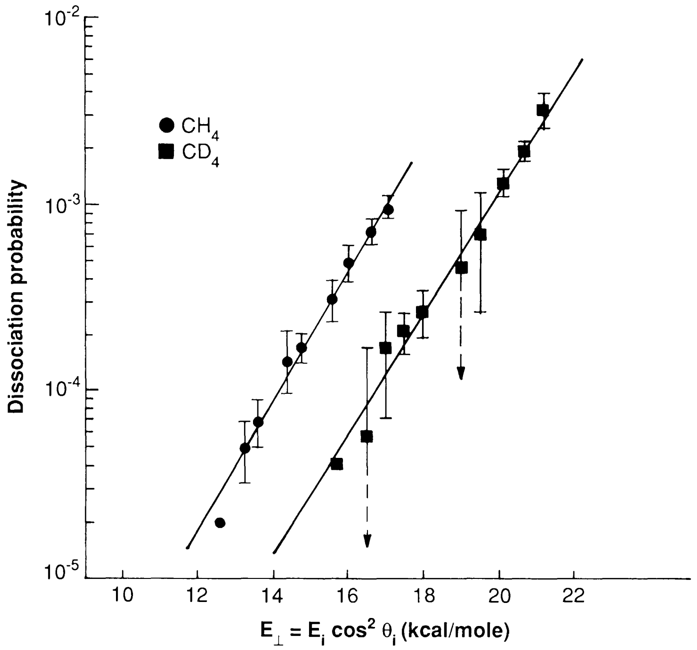


Fig. 3. The absolute dissociation probability of CH_4 and CD_4 as a function of the normal component of translational energy. The lines are linear least-squares fit to the data and the error bars are 95% confidence limits of a series of six to eight measurements for CH_4 and of a series of three measurements for CD_4.

Of course, the key measurement in these experiments is the probability of dissociative chemisorption. This probability is the ratio of the number of dissociatively chemisorbed molecules to the total number of molecules incident on the surface. The latter is evaluated from the absolute beam flux. The number of dissociatively chemisorbed molecules is determined from the surface concentration of carbon as measured by AES, which, however, is largely a tool for elemental analysis. It is often insufficient to identify chemically an adsorbed molecular species. Therefore, high-resolution electron energy loss spectroscopy (HREELS) is used, in which low-energy electrons probe the vibrational spectrum of adsorbed species. This spectroscopy allows the species that result from dissociative chemisorption to be differentiated from molecularly chemisorbed species. As is discussed below, novel species produced as a result of high incident energies can be readily identified.

Translational Activation of CH_4: Splats

The probability for dissociation of CH_4 on Ni(111) to produce an adsorbed CH_3 species and an adsorbed H atom has been measured as a function of the translational energy of the incident CH_4 molecule (*18*) (Fig. 3). Below an incident beam energy E_i of 12 kcal/mole, there is no dissociative chemisorption above the sensitivity limit for carbon detection. As the translational energy is increased to 17 kcal/mole, the dissociation probability, which is measured with the beam incident at the normal angle to the crystal, increases exponentially by two orders of magnitude. Dissociation probabilities measured at larger angles of incidence and plotted versus the translational energy in the normal direction, $E_i\cos^2\theta_i$, fall on the same straight line as in Fig. 3. This type of energy scaling, in which the dissociation probability correlates not with the total energy of the incident molecule but with the kinetic energy in the normal direction, has become known as normal energy scaling. The temperature of the surface is observed to have no effect on the dissociation probability. It is clear from these results that there is a barrier to the dissociative chemisorption of CH_4 and that only translational energy in the normal direction is effective in overcoming the barrier. Similar trends have been observed for the dissociative chemisorption of CH_4 on Ni surfaces of other orientations (*19*) and on other metals (*20–22*).

Why does the normal kinetic energy have such a large effect on dissociative chemisorption? An intriguing picture for the role of translational energy in overcoming the barrier is the distortion that it inflicts on the CH_4 molecule upon impact with the surface. Consider the basic requirement for C–H bond cleavage. A bond between a Ni surface atom and a H atom (~63 kcal/mole) and a bond between the Ni surface and the C atom (~40 kcal/mole) must be formed in order for sufficient energy to be released to break the

100–kcal/mole C–H bond. Methane appears as a spherical molecule to a flat surface, so that upon a low-energy collision most of the interaction with the surface occurs through the H atoms. Since the carbon atom cannot get sufficiently close to the surface to experience a strong attractive interaction, C–H bond cleavage does not occur. In a high-energy collision, the impact on the surface is so hard that the CH_4 "splatters" against the surface, bringing the carbon atom in close proximity to the Ni surface. Both a Ni–C bond and a Ni–H bond can then be formed, thereby breaking a C–H bond. Because the parallel velocity component of the CH_4 motion encounters no repulsive interaction, only the normal component of the translational energy is effective in bringing about the CH_4 deformation that leads to dissociation.

This model is strongly supported by the observation that vibrational excitation of the deformation modes of CH_4 is as effective as translational excitation in surmounting the barrier (*18*). The vibrational energy distribution of the expanded CH_4 is largely characterized by the temperature of the nozzle because the vibrational energy-level spacings are too wide for significant vibrational relaxation to occur during the beam expansion. Therefore, the amount of vibrational excitation can be varied by changing the nozzle temperature while adjusting the ratio of CH_4 to the carrier gas to maintain a constant translational energy. Measurements of the dissociation probability as a function of nozzle temperature for a fixed translational energy indicate that vibrational energy, most of it concentrated in the deformation modes, is at least as effective as translational energy (*23*). This observation is expected if the role of translational energy is the distortion of CH_4 upon impact with the repulsive wall of the surface. This distortion is essentially a conversion of translational energy into vibrational motion associated with the deformation vibrational modes in CH_4. Therefore, vibrational and translational energy in this energy range are interchangeable because they both ultimately lead to the same kind of motion of the nuclei moving along the reaction coordinate and over the barrier. These observations strongly suggest that the barrier to the dissociative chemisorption of CH_4 in this system and others is largely the energy required to deform CH_4. This model has also received support from some recent calculations of the CH_4-Ni potential energy surface (*24, 25*).

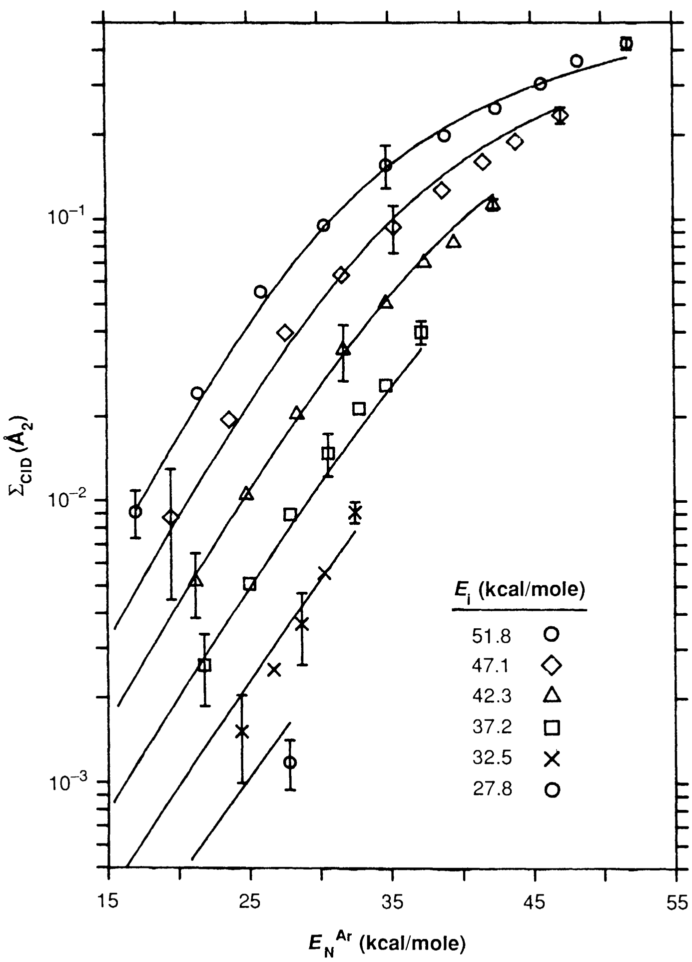


Fig. 4. Cross section for dissociation of CH_4 physisorbed on Ni(111) at 46 K induced by the impact of Ar atoms versus the kinetic energy of the Ar in the normal direction. Methane coverage is 0.3 monolayers. Each point at the same total energy (in kilocalories per mole) represents an incident angle from 0° to 55°: (○, top) 51.8; (◇) 47.1; (△) 42.3; (□) 37.2; (x) 32.5; and (○, bottom) 27.8. Error bars are 95% confidence limits based on a series of 4 to 12 measurements for each data point at normal incidence and 3 to 6 measurements for the data measured at higher angles of incidence. Some of the error bars have been omitted to maintain clarity; however, those presented are typical. The solid lines are the results of the model calculation discussed in the text.

Deformation of the molecule upon impact may only be part of the mechanism for dissociation. Also shown in Fig. 3 are the dissociation probabilities for CD_4 which are consistently an order of magnitude below those of CH_4. This large isotope effect may be suggestive of tunneling of the light hydrogen atom along the C–H coordinate once CH_4 is deformed. Thus, the following picture emerges. As CH_4 approaches the surface closer than the equilibrium distance for physisorbed CH_4, it encounters a repulsion due to the shielding of the carbon atom by the hydrogen atoms. This repulsion can be overcome by raising the incident normal translational or vibrational energy so as to push the hydrogen atoms away. At high energies where CH_4 is completely deformed, it proceeds along the classical reaction path over the barrier. However, it is not necessary to deform CH_4 to the fullest extent because at some energy, the attraction between the Ni surface and carbon begins to play a major role making the barrier sufficiently narrow to permit the light hydrogen atom to tunnel along the C–H coordinate and into the product region. This example illustrates how judicious variations of translational energy, internal energy and incident direction of the gas-phase molecule afforded by molecular beam techniques allow the major features of the potential energy surface that determine the dynamics and mechanism for dissociative chemisorption to be discerned.

An Origin of the Pressure Gap

It is clear from the above discussion that the CH_4-Ni surface interaction is well described by the activated dissociative chemisorption model of Lennard-Jones and that the barrier to dissociation is a viable explanation for the source of the unreactivity at low pressures. Corroboration of this proposal is obtained by comparing the rate constants for methane decomposition calculated from these low-pressure dissociation probability measurements with those measured under high pressure (1 torr CH_4) conditions (*26*). The thermal rate constant for CH_4 decomposition over a Ni(111) crystal is calculated by convoluting the probabilities for dissociative chemisorption $P(E)$ measured at low pressure (*18*) with a Maxwell-Boltzmann function $f(E, T)$ at some temperature as shown in Eq. 1.

$$k(T) = \int f(E,T)\ P(E)dE \qquad (1)$$

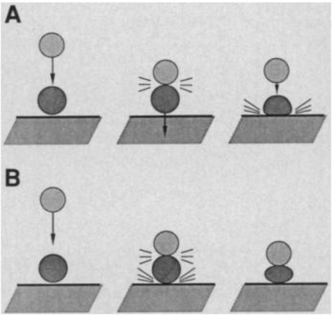
The rate constant $k(T)$ is the probability that a molecule with some energy E will react, integrated over all energies present in a thermal sample at temperature T. These calculated rate constants are then compared to those measured for CH_4 decomposition on a Ni(111) crystal under high-pressure conditions as a function of the temperature of the system (*26*). The temperature of the system refers to the temperature at which both the gas and the surface are held. Excellent agreement is found between the rate constants measured at high pressure and those calculated from the low-pressure dissociation probability measurements. There is a factor of 2 to 3 difference between the absolute magnitudes of the calculated and measured rate constants, but that factor is well within the experimental uncertainty.

This result clearly establishes the barrier to the dissociative chemisorption of CH_4 as an origin of the pressure gap in the reactivity. The presence of this barrier along the dissociative reaction coordinate provides a link between experiments carried out in UHV environments where the adsorbate pressures are $<10^{-4}$ torr and high-pressure processes such as heterogeneous catalysis, where the reactant pressures may be as high as hundreds of atmospheres. This implies that for reactions which have a reasonable rate only at high pressures because the dissociative chemisorption of one or both of the reactants is activated, the high-pressure requirement can now be bypassed by increasing the energy of the incident molecule. Establishment of this link means that high-pressure reactions can now be carried out at low pressure, where the entire arsenal of surface science techniques is available to study these practically important catalytic reactions. An example is presented below of how a reaction, which would only be observable at high pressure because of the activated dissociative chemisorption of the reactants, can now be effected at low pressure.

A New Mechanism for Dissociative Chemisorption: Chemistry with a Hammer

The fate of those CH_4 molecules whose energies are sufficiently high to surmount the barrier has been discussed, but now consider what happens to those molecules incident on the surface with energies too low for dissociation. Although many of these low-energy CH_4 molecules simply reflect from the surface, some of them transfer enough energy to the solid to be trapped on the surface by the outer molecular well shown in the Lennard-Jones interaction potential in Fig. 1. For this molecularly adsorbed species to chemisorb dissociatively, energy must be supplied to it. In principle, this energy could come from the solid if its temperature is sufficiently high. But, because phonon energies are so small compared to the energy necessary for dissociation, multiple quanta of energy would have to be transferred to the physisorbed molecule. If the activation barrier to dissociation is substantially larger than the binding energy, as it is in the case of CH_4, then the molecule will have desorbed long before the surface temperature was high enough to transfer sufficient energy to the molecule for dissociation. So, without an external energy source, these CH_4 molecules would remain undissociated for a very long time. But what if a gas-phase species were to collide with the physisorbed CH_4 molecule? For an incoming species with a sufficiently high velocity, a single collision could transfer enough energy to lead to dissociation. It certainly seems reasonable that because the barrier to CH_4 dissociative chemisorption is largely the energy required to deform CH_4, the impact of an inert gas species should be able to pound molecularly adsorbed CH_4 into the distorted shape of the transition state that leads to dissociation. Such a mechanism has indeed been demonstrated recently. Molecular beam techniques have been used to show that the collision of inert gas atoms with a CH_4-covered surface results in the dissociation of CH_4 (*27, 28*). This process represents a new kind of mechanism for dissociative chemisorption called collision-induced dissociation or activation.

Fig. 5. Schematic diagram of the possible mechanisms of kinetic energy transfer during collision of an incident inert gas atom with a physisorbed CH_4: (**A**) impulsive collision and (**B**) nonimpulsive collision.



The experiment is performed by measuring the dissociation rate as an argon (Ar) atom beam impinges on a layer of CH_4 physisorbed on a Ni(111) surface at 46 K. The dissociation rate is measured as a function of the energy of the incident Ar atoms. Since the dissociation rate is equal to the product of the collision-induced dissociation cross section times the Ar atom flux times the CH_4 coverage, the cross section is easily calculable. In Fig. 4 a plot is shown of the cross section for dissociation of the physisorbed CH_4 versus the normal component of the kinetic energy of the Ar for several total Ar kinetic energies. It is clear from this plot that the strict adherence to normal energy scaling, as was observed in the case of translational activation of CH_4 (*18*), is not observed in the case of in collision-induced activation.

To understand this complex energy dependence, it is necessary to consider the mechanism for collision-induced dissociation as consisting of two steps shown in Fig. 5A. In the first step, an impulsive, bimolecular collision of the incident Ar with the physisorbed CH_4 occurs at some impact parameter. This collision transfers a fraction of the Ar kinetic energy, as determined by the impact parameter, to CH_4. In the second step of this process, the CH_4 molecule is directed into the surface by its newly acquired energy, deforms upon impact and dissociates in a CH_4-surface collision identical to that in translationally activated dissociative chemisorption. The extent of dissociation is determined by the CH_4 energy in the normal direction. But because the impact parameter of the initial Ar-CH_4 collision varies widely, the resultant CH_4 energy in the normal direction varies widely for the same normal kinetic energy of the incident Ar beam. For example, a head-on collision at normal incidence transfers much more energy to CH_4 in the normal direction than a glancing collision. Therefore, because the energy transferred in the normal direction depends on the uncontrollable impact parameter, simple normal energy scaling in the Ar kinetic energy breaks down.

This model has been shown to be correct by comparing the experimentally determined cross section for collision-induced dissociation with that calculated from the probability for dissociative chemisorption integrated over the impact parameter (*28*). The dissociation probability at the normal energy acquired by CH_4 after its collision with the Ar atom is obtained from the translational activation results discussed above (*18*). The energy transferred to CH_4 in the normal direction is calculated from a hard sphere, impulsive collision model. The cross sections calculated from this procedure are plotted as a function of the normal component of the Ar energy as solid lines in Fig. 4. The agreement between the model predictions and the experimental observations is excellent. Measurements of the collision-induced dissociation cross section with neon (Ne) as the incident projectile are also in excellent agreement with the model predictions. The physical picture that emerges is straightforward. The Ar or Ne atom collides with CH_4, transfers some fraction of its energy in a collision that is well described as an impulsive, bimolecular event, and then reflects from the surface. The

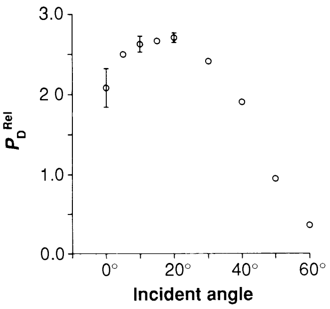


Fig. 6. Relative cross section for dissociation of chemisorbed CO induced by collision with an incident Xe atom at 148 kcal/mole as a function of the Xe incident angle measured from the surface normal. The surface temperature is 420 K. Error bars are 95% confidence limits based on a series of at least five measurements.

subsequent CH_4-surface collision is the same as in translational activation. The CH_4 molecule rams into the surface with its newly acquired normal energy, deforms, and dissociates. Therefore, translational activation and collision-induced activation are completely consistent with each other. They are simply different methods for providing energy to deform CH_4, but the mechanism for dissociation is the same.

Although the Ar-CH_4 collision is well described as a bimolecular and impulsive translationally elastic event, the title of this section does refer to the function of the inert gas atom as that of a hammer. This description implies that the physisorbed CH_4 suffers a nonimpulsive collision, as illustrated in Fig. 5B. So, to find a hammer, consider krypton (Kr) as the incident particle. The experimentally determined cross sections for dissociation of CH_4 induced by the impact of a Kr atom are significantly greater than those calculated from the dissociation probability integrated over impact parameter (*28*). This disagreement is a result of the breakdown in the hard-sphere collision part of the model. Because Kr is so massive compared to CH_4, the fraction of the Kr energy transferred to CH_4 upon the first and impulsive collision is small. Although this collision accelerates CH_4 into the surface, the Kr atom still has much energy remaining in the forward direction so it follows CH_4 into the surface and it hits the CH_4 molecule a second time. Upon this second collision, the Kr atom literally squashes the CH_4 molecule between itself and the surface. The Kr atom now plays an intimate role in the transition state of the dissociating CH_4, resulting in a higher dissociation probability than that for an unhindered CH_4-surface collision. In this case the incident Kr atom really does function like a hammer!

The energy to move the carbon atom of CH_4 in close proximity to the Ni surface is the origin of the barrier to the dissociative chemisorption of CH_4. This simple notion that barriers to adsorbate dissociation can be associated largely with the energy required to move the adsorbate closer to the surface is readily extended to the dissociative chemisorption of CO on Ni(111). Carbon monoxide binds to Ni through the carbon with the CO bond axis perpendicular to the macroscopic surface plane. The CO molecule is held in this configuration fairly rigidly because of a very strong anisotropic interaction with the Ni. As the surface temperature is raised, CO desorbs. No dissociation of CO is observed. However, the dissociation of adsorbed CO can be effected by collision with an incident xenon (Xe) atom (*29*). In addition, it appears very likely that the barrier to dissociation is again the energy associated with tilting the CO so as to push the repulsive oxygen end of the molecule close enough to the Ni surface to form a Ni–O bond, thereby cleaving the $C\equiv O$ bond. This reaction coordinate is suggested by the dependence of the cross section for collision-induced dissociation on the incident angle of the Xe. As shown in Fig. 6, the cross section is small at normal incidence but increases as the incident angle increases and then decreases again at very glancing incidence. Excitation of the low-frequency $Ni{-}C\equiv O$ bending mode apparently aids the Xe atom in tilting the molecule to a horizontal configuration because the magnitude of the cross section increases at higher surface temperatures. Collision-induced dissociative chemisorption of H_2O on Ni(111) has also been recently observed (*29*). For the dissociative chemisorption of CH_4, CO, and H_2O on Ni(111), thermodynamics requires that both atoms of the adsorbate bond to be broken form new bonds with the surface. The energy required to position both atoms of the adsorbate near the surface may well be a general phenomenon associated with a barrier to dissociative chemisorption.

A New Mechanism for Desorption: Collision-Induced Desorption

Consider again the schematic potential energy surface in Fig. 1. It is clear from this diagram that there is an alternative pathway available to a physisorbed adsorbate once energy has been transferred to it by collision with an incident atom. This alternative pathway is desorption, and in the case of Ar atoms incident on CH_4 physisorbed on Ni(111), it competes effectively against collision-induced dissociation. Collision-induced desorption can occur when the extent of deformation of the CH_4 is not sufficient for dissociation or when the orientation of the CH_4 or the site on which CH_4 is deformed is not energetically favorable for dissociation. In these cases, the deformed CH_4 releases its energy by pushing itself off the surface and into the gas phase. The dynamics of collision-induced desorption are studied by measuring the desorption cross section as a function of the energy and incident angle of the Ar atoms. These results coupled with classical molecular dynamics simulations establish the mechanism for collision-induced desorption and explain the complicated dependence of the cross section on the variable parameters to arise from just two straightforward but competing dynamical effects (*30, 31*).

First, for desorption to occur, the physisorbed CH_4 must be hit by the incident Ar atom. The probability of collision is given by the geometric collision cross section, Σ_C, which is defined as the surface area per CH_4 inside of which Ar cannot strike without colliding with CH_4. Two types of collision, direct and mirror collisions, contribute to Σ_C. In a direct collision, the Ar hits the CH_4 on its incoming trajectory, whereas mirror collisions take place on the outgoing Ar trajectory after the Ar has suffered a collision with the surface. Because the Ar-CH_4 interaction extends far above the surface plane, Σ_C is a strongly increasing function of the Ar angle of incidence for both types of collisions. This important trend is general to the cross section for collision of an incident particle with any isolated adsorbate on a smooth surface. The exact dependence of Σ_C on the incident angle is an intrinsic function of the shape of the Ar-CH_4 interaction potential.

Upon the Ar-CH_4 collision, the efficiency of kinetic energy transfer to CH_4 motion normal to the surface determines the subsequent fate of the CH_4 with respect to desorption. For the small impact-parameter collisions that are most effective at transferring energy, the fraction of Ar energy transferred to CH_4 normal kinetic energy decreases as the incident angle increases, thereby decreasing the fraction of collisions that result in CH_4 having sufficient kinetic energy in the normal direction to desorb. The magnitude of the fraction of desorbing collisions is also determined by the extent of energy accommodation that occurs upon the CH_4-surface collision. Thus it is the normal kinetic energy of CH_4 as it rebounds from the surface that must be greater than its binding energy in order for desorption to occur.

It is concluded that the competition between the increase in the collision cross section and the decrease in the energy transferred to

CH_4 motion in the normal direction with increasing angle are the two sole important components in determining the dependences of the cross section for collision-induced desorption on energy and incident angle. Collision-induced desorption near the threshold energy for desorption occurs as a result of a direct and impulsive, bimolecular collision of the incident particle with the adsorbate (*30, 31*).

Molecular Beams as Synthetic Tools: Adsorbed Methyl Radicals and Benzene from Methane

Having established this link between high-pressure processes and UHV surface science, we now know how to bypass the high pressure requirement simply by raising the energy of the incident molecule (translational activation) or collisionally inducing dissociation (collision induced activation). We have used both methods to carry out a high-pressure reaction at low pressure: the synthesis of benzene (C_6H_6) from CH_4 (*32*). The low-pressure conditions have allowed us to use high-resolution electron energy loss spectroscopy to identify the adsorbed intermediates and to determine the mechanism of this reaction.

The synthesis is most easily effected by using collision-induced dissociation to activate the CH_4. The products of collision-induced activation of CH_4 physisorbed on Ni(111) at 47 K are an adsorbed methyl radical and an adsorbed hydrogen atom (*7, 18, 28*). Once the adsorbed CH_3 species are so synthesized, their reactivity is probed by monitoring the vibrational spectrum as a function of surface temperature. Above 150 K, the CH_3 radicals dissociate to form adsorbed CH and more adsorbed atomic hydrogen. The adsorbed CH then recombines to form adsorbed C_2H_2, an acetylenic type of species, as the surface temperature is raised to 230 K. At 370 K, the adsorbed acetylene trimerizes to form adsorbed C_6H_6, and at 410 K the atomically adsorbed hydrogen recombines and desorbs as H_2. At a slightly higher temperature, 425 K, some of the chemisorbed C_6H_6 dehydrogenates to form gas-phase H_2 and partially hydrogenated carbon rings on the surface while some of the C_6H_6 desorbs intact, as detected by a quadrupole mass spectrometer in a thermal desorption experiment. Although the maximum desorption yield for C_6H_6 is 1.5%, the gas-phase hydrocarbon selectivity of this synthesis for benzene production is 100%. This procedure represents the first synthesis of C_6H_6 from CH_4 over a single catalyst and suggests the use of molecular beams as a synthetic tool. These data also provide mechanistic information useful to the possible extrapolation of this synthesis from UHV environments to more practical conditions.

An additional bonus from utilizing these rediscovered and new mechanisms for dissociative chemisorption is that they have allowed novel adsorbates such as CH_3 and CH to be synthesized under low-pressure conditions (*7*). Adsorbed CH_3 and CH radicals have long been invoked as reaction intermediates in a wide variety of hydrocarbon-surface reactions carried out both in an UHV environment and under high-pressure conditions. Despite their importance as proposed reaction intermediates, this result represents the first time that these species have been produced cleanly on a single-crystal metal surface and unambiguously identified by vibrational spectroscopy because up to now there has been no simple way to synthesize them. Methane and ethane, natural candidates for the clean production of these species, are completely unreactive with most metal surfaces under low-pressure conditions of the adsorbing gas. However, it is now clear both why methane is unreactive at low pressures and how such activation can be achieved. The variability of the collision energy afforded by molecular beams makes them a tool with which novel adsorbates can be synthesized.

Implications of Collision-Induced Chemistry and Desorption

As we have discussed, molecular beam techniques have led to the discovery of two new kinds of mechanisms for dissociative chemisorption and desorption and a more recent observation of a new mechanism for absorption, collision-induced absorption (*33*). These are mechanisms that could not have been detected unambiguously in an isotropic environment of an ambient gas above a surface. In addition, the control and variability of the energy and direction of the incident particles afforded by beam techniques have allowed the dynamics of both mechanisms to be probed and understood.

But perhaps more important than the physics behind these processes is the fact that they have been observed. Knowledge of their existence is significant for understanding the complex environment of high-pressure processes such as heterogeneous catalysis, chemical vapor deposition, or etching reactions because collision-induced chemistry and desorption likely play important roles in high-pressure environments. This is because under these conditions, a surface is covered with adsorbate, and the adsorbate-covered surface is continually bombarded by gas-phase molecules. With the observation of these processes, no mechanism for a high-pressure reaction can now be considered complete without an assessment of the role of collision-induced chemistry and desorption as potential major steps. These observations are cause for reexamination of the mechanisms of heterogeneous catalytic reactions in which the effect of inert gas on reaction rates has been noted (*34*). Collision-induced chemistry and desorption are additional contributors to the pressure gap in the reactivity of heterogeneous catalysis. They are additional reasons why surface chemistry at high pressures is often very different from surface chemistry at low pressures.

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