

Assessing a microcanonical theory of gas-surface reactivity: Applicability to thermal equilibrium, nonequilibrium, and eigenstate-resolved dissociation of methane on Ni(100)

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A simple, three-parameter microcanonical theory of gas-surface reactivity is shown to predict experimental dissociative sticking probabilities for methane dissociative chemisorption on the Ni(100) surface over roughly ten orders of magnitude variation in both pressure and sticking—even at quantum state resolved levels of detail. Facile energy randomization within the transiently formed gas-surface collision complexes is postulated to make the pooled energy from 15 local degrees of freedom statistically available to surmount the barrier to dissociation. The apparent threshold energy for C–H bond cleavage of CH₄ incident on Ni(100) is 67 kJ/mol, down from 432 kJ/mol in the gas phase. © 2003 American Institute of Physics. [DOI: 10.1063/1.1570393]

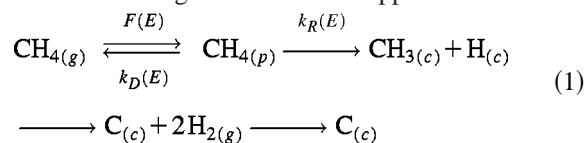
I. INTRODUCTION

Activated dissociation of molecules on a metal surface is essential to many catalytic processes and achieving a quantitative understanding of dissociative chemisorption is one of the most important goals of surface science research directed toward advancing heterogeneous catalysis. Industrial catalytic processes, such as ammonia synthesis or steam reforming of methane, that are rate-limited by dissociative chemisorption and run at sufficiently high temperatures [e.g., 750 K at 30 bar¹] that the surface coverage of adsorbates remains vanishingly small should be ideally suited for analysis and simulation based on the detailed experimental findings of ultrahigh vacuum surface science. Although this premise has largely held true for ammonia synthesis,² it has been more difficult to demonstrate for the nickel catalyst surfaces relevant to industrial steam reforming of methane because of the diversity of experimental results,³ and the lack of a comprehensive theory.⁴ In this paper, we implement a microcanonical theory of gas-surface reactivity to show, for the first time, that recent experimental measurements of methane dissociative sticking probabilities on the Ni(100) surface using nonequilibrium molecular beams^{5,6} and intermediate pressure (approximately mbar) thermal equilibrium bulbs⁷ are in broad accord with one another and can be theoretically treated using a unified kinetic model that provides a quantitative connection to electronic structure theory predictions of the properties of the reactive transition state. Importantly, our analysis indicates that the apparent threshold energy for methane dissociative chemisorption on Ni(100) is 67 kJ/mol, in quantitative accord with *ab initio* quantum chemistry calculations but 15%–45% smaller than calculations based on the currently popular and widely applied generalized gradient approximation density functional theory.

Methane is the principal component of natural gas and has the highest H/C ratio and highest C–H bond strength of any closed shell hydrocarbon. Beyond methane's importance

as a clean and abundant energy resource through direct combustion, steam reforming of methane on supported nickel catalysts is a primary industrial source of both hydrogen and synthesis gas, the latter being a versatile mixture of CO and H₂ that can be catalytically transformed into many valuable chemical commodities such as methanol, gasoline, and higher hydrocarbons.¹ Commercial steam reforming catalysts consist of 10 nm–100 nm diam Ni single crystals formed by high temperature aggregation on Al₂O₃, MgO, or magnesium aluminum spinel supports. Accordingly, surface science studies of the most stable and closely packed Ni surfaces, the Ni(111) and Ni(100) facets that are predominantly exposed on a working Ni catalyst, are most relevant to steam reforming. The possible role of steps as the “active sites” in steam reforming has been discounted in intermediate pressure thermal equilibrium bulb studies⁸ and it is believed that terrace sites on the low index Ni surfaces are indeed responsible for methane dissociative chemisorption under industrial steam reforming conditions. Here, we analyze methane dissociative chemisorption on Ni(100), the system for which the experimental literature is most extensive and includes supersonic molecular beam studies that have independently investigated the effects of changing the surface temperature, incident methane isotope, translational energy, vibrational and rotational energies by varying the molecular beam nozzle temperature,⁵ and methane rovibrational eigenstate by direct laser pumping.⁶ The exceptional range of experimental results currently available for the CH₄/Ni(100) system makes it the most rigorous proving ground for theories of gas-surface reactivity involving polyatomic molecules.

Surface science studies of methane dissociative chemisorption are performed at sufficiently high surface temperatures that the following kinetic scheme applies:



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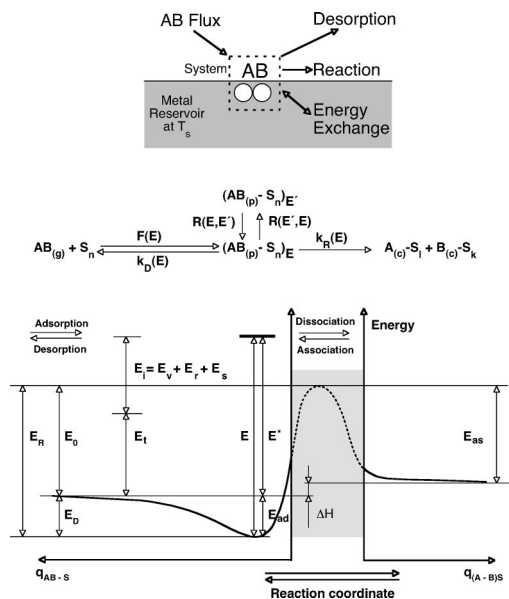


FIG. 1. Schematic depiction of the kinetics and energetics of activated dissociative chemisorption. Zero-point energies are implicitly included within the potential energy curve along the reaction coordinate. The total energy of the physisorbed gas/surface collision complex, $E = E_t + E_v + E_r + E_{ad} + E_s$, is assumed to be randomized by the collision and actively exchangeable unless subject to conservation laws. The energies summing to E above are the translational, vibrational, rotational, and adsorption energies of the incident AB molecule, and the surface energy of several surface oscillators vibrating at the mean substrate phonon frequency. See the text for further details.

Methane incident on the surface from the gas phase will form a transient gas/surface collision complex consisting of a molecule, in the neighborhood of the physisorption potential well minimum, that interacts with a few immediately adjacent surface atoms (see Fig. 1). These collisionally formed “physisorbed complexes” or “local hot spots” are energetic and transient intermediate species that are not in thermal equilibrium with the surrounding substrate. Physisorbed complexes formed at some total energy E [i.e., $\text{CH}_{4(p)}$ in Eq. (1) where surface coordination numbers are suppressed] can go on to desorb or react dissociatively with the surface to yield chemisorbed fragments. The initial C–H bond cleavage of methane is rate limiting and a single carbon atom is left on the surface for every methane dissociated. Initial dissociative sticking coefficients, S , are derived from the ratio of the deposited C coverage, typically measured by Auger electron spectroscopy, to the incident fluence of methane molecules, extrapolated backwards to zero accumulation of C on the surface. Unfortunately, methane dissociative sticking coefficients on the Ni surfaces relevant to steam reforming have proven to be particularly difficult to accurately determine, presumably in part, because the surface temperature must be limited to $T_s \leq 550$ K in order to prevent product carbon from diffusing into the Ni bulk and escaping detection.⁸

II. MICROCANONICAL UNIMOLECULAR RATE THEORY

Figure 1 provides a conceptual illustration of our general model for gas-surface reactivity based on the ideas that: (a) adsorbate chemistry is a local phenomenon, (b) the active

system energy of an adsorbed molecule and a few immediately adjacent surface atoms suffices to fix microcanonical rate constants for surface kinetic processes such as desorption and dissociation,^{9,10} and (c) energy exchange between the local adsorbate-surface complexes and the surrounding substrate can be treated via a Master equation to describe the system/heat reservoir coupling.¹¹ For the $\text{CH}_4/\text{Ni}(100)$ experiments investigated here, the net energy transfer due to phonon-mediated energy exchange between the short-lived physisorbed $\text{CH}_4/\text{Ni}(100)$ surface collision complexes and the surrounding substrate should be negligible.¹¹ Consequently, we can employ a microcanonical unimolecular rate theory (MURT) in which collisionally formed physisorbed complexes (PC) undergo only competitive unimolecular decay via desorption or reaction [i.e., the Fig. 1 PC “system” can be effectively treated as adiabatically isolated and the $R(E', E)$ can be set to 0]. Unless subject to conservation laws, the PC-MURT assumes that all the local energy of a physisorbed complex formed at energy E is efficiently and randomly mixed by the gas-surface collision and microcanonical equilibrium is maintained over the lifetime of the complex, presumably by intramolecular vibrational energy redistribution (IVR). A detailed analysis and discussion of these assumptions can be found in Ref. 11, Sec. IV D. Rice–Ramsperger–Kassel–Marcus (RRKM) theory is used to provide unimolecular rate constants for desorption, $k_D(E)$, and reaction, $k_R(E)$. The local cluster of surface atoms contributing to the physisorbed complex is assumed to be capable of freely exchanging its vibrational energy within the complex. The cluster is simply represented by several surface oscillators whose number, s , is a free parameter that must be fixed by theoretical simulation of experimental data.

Applying the Fig. 1 kinetics of Eq. (1) to the coverage of physisorbed complexes at energy E in increment dE , $\theta_p(E, t)dE$, yields

$$\frac{d\theta_p(E, t)}{dt} = F(E, t) - \{k_R(E) + k_D(E)\}\theta_p(E, t), \quad (2)$$

where $F(E, t) = F_0(t)f(E)$ is the flux distribution of physisorbed complexes formed at E , $F_0(t)$ is the net flux of methane incident on the surface in monolayers/s, and $f(E)$ is the normalized probability distribution for creating a physisorbed complex at E . Assuming a constant methane flux made incident on an initially clean surface, application of the steady state approximation [i.e., setting Eq. (2) = 0; $F_0(t) = F_0$] allows us to define the reactive flux at E as

$$\begin{aligned} \frac{d\theta_c(E)}{dt} &= k_R(E)\theta_p^{ss}(E) \\ &= \frac{k_R(E)}{k_R(E) + k_D(E)}F(E) = S(E)F(E), \end{aligned} \quad (3)$$

where $\theta_c(E)$ is the coverage distribution of the chemisorbed C formed via dissociation at E and $S(E)$ is the microcanonical sticking coefficient. This leads to the operational definition of the experimentally realized sticking coefficient,

$$S = \frac{1}{F_0} \frac{d\theta_c}{dt} = \frac{1}{F_0} \int_0^\infty \frac{d\theta_c(E)}{dt} dE = \int_0^\infty S(E) f(E) dE. \quad (4)$$

RRKM expressions for the microcanonical rate constants are

$$k_D = \frac{W_D^\ddagger(E - E_D)}{h\rho(E)} = \frac{W_D^\ddagger(E^*)}{h\rho(E^* + E_{ad})}, \quad (5)$$

$$k_R = \frac{W_R^\ddagger(E - E_R)}{h\rho(E)} = \frac{W_R^\ddagger(E^* - E_0)}{h\rho(E^* + E_{ad})},$$

where W_i^\ddagger is the sum of states for transition state i , h is Planck's constant, ρ is the physisorbed complex density of states, and E_0 is the apparent threshold energy for dissociative chemisorption. Substituting into Eq. (4), and noting that the zero of the E^* energy scale occurs for methane at infinite separation from the surface and at rest, it is convenient to write

$$S = \int_0^\infty S(E^*) f(E^*) dE^*, \quad (6)$$

where

$$S(E^*) = \frac{W_R^\ddagger(E^* - E_0)}{W_R^\ddagger(E^* - E_0) + W_D^\ddagger(E^*)}, \quad (7)$$

and

$$f(E^*) = \int_0^{E^*} f_t(E_t) \int_0^{E^* - E_t} f_v(E_v) \int_0^{E^* - E_v - E_t} f_r(E_r) \times f_s(E^* - E_t - E_v - E_r) dE_r dE_v dE_t, \quad (8)$$

where $f(E^*)$ is the probability distribution for creating a physisorbed complex at E^* . The $f(E^*)$ is formed by convolution over the distribution functions for the flux weighted translational energy, vibrational energy, and rotational energy

of the incident methane, along with the surface energy distribution for s oscillators vibrating at the mean Ni phonon frequency, $\nu_s = \frac{3}{4} k_b T_D / h$, of 235 cm^{-1} .

Once the transition state characteristics have been defined through iterative simulation of varied experimental data or by electronic structure theory calculations, any experimental sticking coefficient can be predicted using Eq. (6) to average the microcanonical sticking coefficient over the probability for creating a physisorbed complex at E^* under the specific experimental conditions of interest. Note that $S(E^*)$ is simply the ratio of the available exit channels through the reactive transition state to the total number of exit channels available through either the reactive or desorptive transition states. The statistical premise that all exit channels at total energy E^* have equal *a priori* probability of being accessed returns the same result. Given that at reactive energies the physisorbed complex density of states is already huge [$\rho(E^* \geq E_0) > 10^5 \text{ states/cm}^{-1}$] and the number of available exit channels is vast [e.g., $W_D^\ddagger(E^* \geq E_0) > 10^6 \text{ states}$], statistical behavior is anticipated, especially when IVR rates are high.¹¹

Molecular beam studies of methane dissociative chemisorption on Ni(100) find that the dissociative sticking coefficient scales with the translational energy directed along the surface normal, $E_n = E_t \cos^2 \vartheta$. Normal energy scaling of the dissociative sticking is consistent with conservation of parallel molecular momentum, presumably due to negligible corrugation of the interaction potential across the Ni(100) surface. Discounting parallel molecular translational energy as a spectator or inactive form of energy over the course of the reactive gas-surface collisions, we assume that only normal translation will contribute to E_t in the above-mentioned expressions (i.e., set $E_t = E_n$ alone).

In the absence of definitive guidance from electronic structure calculations, and in the spirit of developing a surface kinetics theory with a minimum number of adjustable

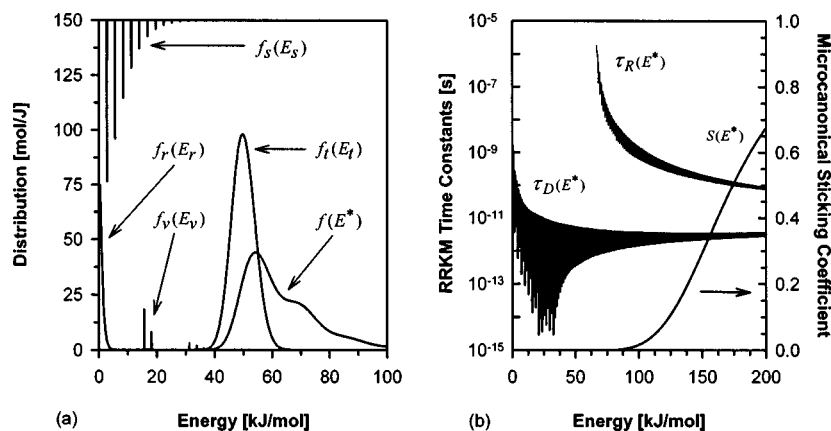


FIG. 2. (a) Energy distributions associated with a molecular beam of CH_4 incident normal to Ni(100) under conditions typical for dissociative sticking experiments; $\langle E_t \rangle = 50 \text{ kJ/mol}$, $T_n = 750 \text{ K}$ (nozzle temperature), $T_s = 475 \text{ K}$. The rotational, vibrational, and surface distributions are scaled such that their maximum value is 75 units and the surface energy distribution is inverted for clarity. The CH_4 translational energy and the physisorbed complex energy distributions are normalized. (b) Unimolecular time constants ($k(E^*)^{-1}$) for desorption and reaction of the physisorbed complexes ($E_0 = 67 \text{ kJ/mol}$ parameter set). At reactive energies the time constant for desorption is $\sim 2 \text{ ps}$. The microcanonical sticking coefficient, $S(E^*) = \tau_D(E^*) / [\tau_D(E^*) + \tau_R(E^*)]$, is plotted on a linear scale.

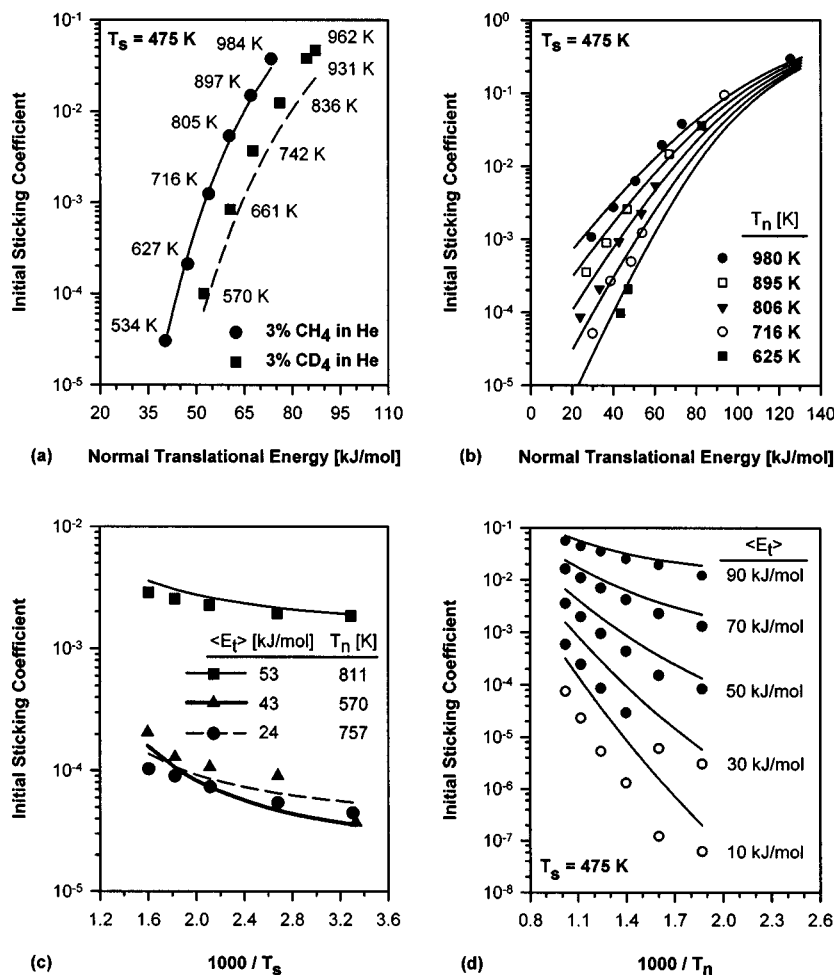


FIG. 3. Dissociative sticking for methane molecular beams incident normal to Ni(100) under widely varied experimental conditions. The points are experimental data (Ref. 5) and the lines are theoretical predictions of the PC-MURT based on $E_0=67$ kJ/mol, $v_D=100$ cm⁻¹, and $s=2$. (a) Variation of S with $\langle E_t \rangle$ at fixed 3% methane seeding in He. The molecular beam nozzle temperature, T_n , is given beside each data point. (b) Scans of S vs $\langle E_t \rangle$ at various T_n accomplished by varying the % CH₄ seeding in He and H₂. (c) Arrhenius-styled plots of CH₄ S vs $10^3/T_s$. (d) Arrhenius-styled plots of CH₄ S vs $10^3/T_n$.

parameters, we assume the transition states for desorption and dissociation are loose and share as many common mode frequencies with each other (and the physisorbed complex) as possible. The transition state for desorption is taken to occur when methane is freely rotating and vibrating in the gas phase, far from the surface. The dissociation transition state is characterized by the nine vibrational modes of methane in the gas, s vibrational modes of the surface oscillators, four vibrational modes at a single lumped frequency v_D representative of the three frustrated rotations and vibration along the surface normal of methane at the dissociation transition state, and one of the triply degenerate antisymmetric C–H stretching vibrations [$v_3(\text{CH}_4)=3020$ cm⁻¹] of methane is sacrificed as the reaction coordinate. Although the theory does not require specification of the physisorbed complex to calculate sticking coefficients, it is possible to estimate the individual rate constants $k_D(E^*)$ and $k_R(E^*)$ by assuming the physisorbed complex has $\phi=(13+s)$ modes at the frequencies of the dissociation transition state. In the end, our PC-MURT has only three adjustable parameters, E_0 , v_D , and s that will be fixed here by comparative simulation to varied experimental data.

Figure 2 provides an overview of the energy distributions and kinetics relevant to calculating a dissociative sticking coefficient for CH₄ incident on Ni(100) under conditions typical of molecular beam experiments. Collisions during the supersonic expansion through the molecular beam nozzle

lead to a CH₄ $f_t(E_t)$ characterized by a low translational temperature, T_t , (~ 25 K) superimposed on a common stream energy. The beam expansion also cools the rotations but vibrations are inefficiently cooled, if at all. Following standard practice,³ we assume the molecular beam nozzle temperature sets the vibrational temperature of the beam molecules at $T_v=T_n$ and the rotational temperature as $T_r=0.1 T_n$. Figure 2(a) shows the probability distribution to create a physisorbed complex at E^* , $f(E^*)$, along with the energy distributions required to assemble $f(E^*)$ by convolution [Eq. (8)]. The rotational and vibrational states are treated semiclassically and quantum mechanically, respectively. The Beyer–Swinehart algorithm is used to calculate density and sums of states. Figure 2(b) provides time constants for desorption and reaction for the physisorbed complexes as well as the microcanonical sticking coefficient, $S(E^*)$. The $S(E^*)$ is an “S”-shaped curve with limiting values of 0 and 1. Averaging $S(E^*)$ over the $f(E^*)$ experimental conditions of Fig. 2(a) according to Eq. (6) yields a predicted experimental sticking coefficient of $S=1.3\times 10^{-3}$. In molecular beam experiments, $f(E^*)$ is typically scanned over a range of E^* where dissociative chemisorption is possible by: (a) varying the mean translational energy, $\langle E_t \rangle$, and T_t of the molecular beam by seeding in various carrier gases and/or by changing T_n , (b) varying T_n to exert control over T_v and T_r , or (c) varying T_s . In the simpler thermal equilibrium bulb

experiments, a thermal gas impinges on the surface from all possible angles simultaneously and all temperatures are the same.

III. CHEMISORPTION FROM NONEQUILIBRIUM MOLECULAR BEAMS

The most extensive and well-characterized molecular beam study of methane dissociative chemisorption on Ni(100) was reported by Chorkendorff and co-workers.^{3,5} The key experimental data are reproduced in Fig. 3 and show how the dissociative sticking coefficient varies as a function of isotope, mean normal translational energy $\langle E_n \rangle$, T_n , and T_s over a wide range of experimental conditions. In these experiments, as pointed out in Fig. 11 of Ref. 3, the temperature of the methane gas did not fully equilibrate to the temperature of the heated tip of the molecular beam nozzle prior to expansion (i.e., $T_g < T_n$; with lags up to ~ 100 K). Using Chorkendorff's detailed characterization of the terminal translational temperature of pure He beams as a function of experimentally measured T_n in his apparatus and his equations relating pre-expansion gas temperature, T_g , to post-expansion mean translational energy in seeded beams,³ we have calculated T_g 's for the seeded molecular beams and report these values as corrected T_n 's in Fig. 3.

The PC-MURT parameters were optimized by simulation of the Chorkendorff [Figs. 3(a)–3(c)] experiments for methane beams seeded in He alone (i.e., at 3%, 10%, 25%, and 50% methane) because only pure He beams have been fully characterized in Chorkendorff's apparatus and it was important to be confident of the accuracy of the corrected T_n values. Using these 39 experimental data points, the (E_0, v_D, s) PC-MURT parameter space was searched to find a global minimum in the average relative discrepancy (ARD) between theoretical simulations of the sticking and the experimental data. Achieving an ARD of 27%, the best fit parameters were $E_0 = 67$ kJ/mol, $v_D = 100$ cm⁻¹, and $s = 2$. The resulting theoretical predictions for all the Chorkendorff experiments are shown as the lines of Fig. 3.

Data not involved in optimizing the PC-MURT parameters include the Fig. 3(b) data at $\langle E_n \rangle$ greater than 80 kJ/mol involving CH₄ seeded in H₂ beams, and the data of Figs. 3(b) and 3(c) at $\langle E_n \rangle$ less than 30 kJ/mol involving 100% CH₄ beams. The Fig. 3(d) data reported experimentally were derived from vertical cuts of the Fig. 3(b) data by drawing empirical smooth curves through the measured S data at constant T_n values and interpolating/extrapolating along these curves to estimate an $S(1/T_n)$ at specific values of $\langle E_n \rangle$. In Fig. 3(d) the experimentally interpolated points are marked as closed circles and the extrapolated points are the open circles. The largest discrepancies between theoretical predictions and experiment occur for the extrapolated sticking data of Fig. 3(d) and two of the three high $\langle E_n \rangle$ H₂ seeded beams of Fig. 3(b). Overall, the agreement between the theoretical predictions of the PC-MURT and experiment is unprecedentedly good.

In an important experimental advance, Utz and co-workers⁶ employed an infrared laser to selectively excite the ν_3 antisymmetric C–H stretching vibration of CH₄ in a molecular beam impinging on Ni(100) and measured the dis-

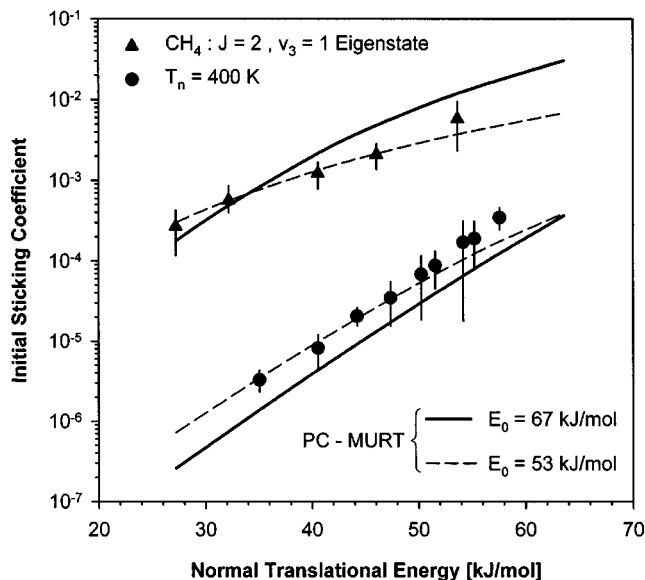


FIG. 4. Dissociative sticking for a CH₄ molecular beam incident on Ni(100) at $T_s = 475$ K. Experimentally derived data (Ref. 6) are for a molecular beam with $T_n = 400$ K, and for a hypothetical beam of molecules prepared in a single $J = 2, v_3 = 1$ rovibrational eigenstate by infrared laser excitation at a photon energy of $h\nu = 34.3485$ kJ/mol.

sociative sticking coefficient as a function of $\langle E_n \rangle$. From these elegant experiments it was possible to calculate the sticking coefficient for a hypothetical beam of CH₄ molecules prepared in a single rovibrational eigenstate. The Utz experimental results are summarized as the points of Fig. 4 along with lines giving predictions of the PC-MURT. Our theory was used to predict the Utz experiments based on the Fig. 3 derived parameter set above ($E_0 = 67$ kJ/mol) and based on another parameter set ($E_0 = 53$ kJ/mol, $v_D = 260$ cm⁻¹, and $s = 2$) that best fit the Utz data under the constraint that $s = 2$, a value that could be firmly established based on earlier simulations of the $S(1/T_s)$ data of Fig. 3(c).

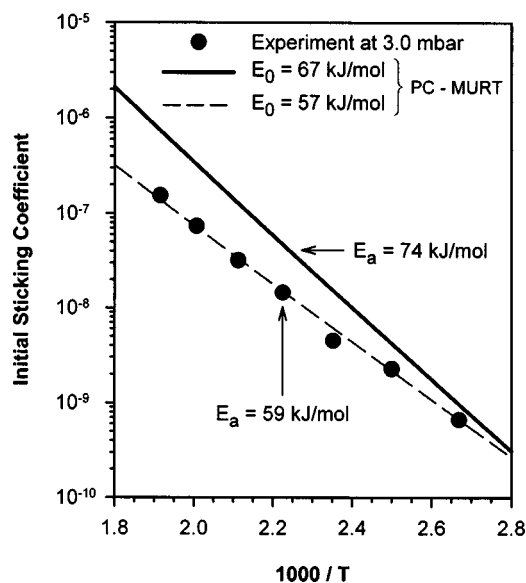


FIG. 5. Arrhenius plot of S vs $10^3/T$ for CH₄ on Ni(100) under thermal equilibrium conditions. Experimental data are from Nielsen *et al.* (Ref. 7).

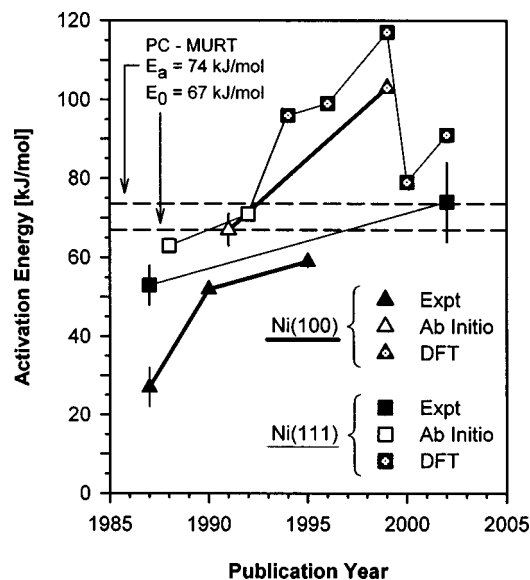


FIG. 6. Activation energies for CH_4 dissociative chemisorption, E_a , derived experimentally (Refs. 16, 17, 7, 8) and apparent threshold energies, E_0 ($=E_a$ at 0 K), derived from *ab initio* (Refs. 18, 13, and 12) or density functional theory (Refs. 19, 20, 14, 15, and 21) electronic structure calculations are compared to the predictions of the PC-MURT.

The statistical PC-MURT model predicts the Utz data quite well, particularly for the $E_0=53$ kJ/mol parameter set. However, we discount the global validity of the $E_0=53$ kJ/mol parameter set because it very poorly (\sim order of magnitude worse) predicts the Chorkendorff molecular beam sticking of Fig. 3 and the thermal equilibrium sticking of Fig. 5. Unfortunately, the ARD for the ($E_0, v_D, s=2$) PC-MURT parameter space based on a limited range of experimental data (e.g., the Utz experiments alone) typically exhibits a relatively shallow valley around its minimum. Consequently, the $E_0=67$ kJ/mol parameter set, based on the more varied and extensive data of Fig. 3 and derived from a more steeply defined minimum in ARD, is more reliably determined and is uniquely able to “adequately” predict all the data of Figs. 3–5.

IV. CHEMISORPTION AT THERMAL EQUILIBRIUM

At roughly ten orders of magnitude higher pressure than the molecular beam experiments, dissociative sticking coefficients for CH_4 on Ni(100) under thermal equilibrium conditions have been measured in thermal bulb studies most recently by Nielsen *et al.*⁷ Figure 5 compares the equilibrium sticking coefficients to the predictions of the PC-MURT. Although a specifically optimized PC-MURT parameter set ($E_0=57$ kJ/mol, $v_D=375$ cm^{-1} , and $s=2$) can describe the limited thermal equilibrium data very well, the $E_0=67$ kJ/mol parameter set is far better at simultaneously predicting all the data of Figs. 3–5. The Fig. 5 relative deviation between the $E_0=67$ kJ/mol PC-MURT predictions and experiment increases monotonically from 46% to 385% as the temperature is increased. This increasing deviation with temperature may be caused by known experimental difficulties associated with fully equilibrating the methane gas temperature to that of the surface or having some product carbon

evade detection by diffusing into the nickel bulk.^{7,8} Both these difficulties tend to reduce the experimentally calculated sticking and become more pronounced at higher temperature so that artificially low thermal activation energies, E_a , are extracted. Figure 6 shows that measured activation energies have monotonically increased as experimental refinements have been implemented over time. Embedded within the timeline of this trend, the most recent Ni(100) sticking data of Fig. 5 might be subject to further upwards revision and this would tend to bring experiment into closer agreement with the $E_0=67$ kJ/mol predictions of the PC-MURT. Our predicted E_a for Ni(100) is very reasonable because it matches the current experimental estimate⁸ for Ni(111) of 74 ± 10 kJ/mol and *ab initio* electronic structure calculations predict that E_a for the close packed Ni(111) surface¹² should be only 4 ± 4 kJ/mol higher than for the more open Ni(100) surface.¹³

Fractional energy uptakes, f_j , defined as the fraction of the mean energy of the physisorbed complexes undergoing reaction that derives from the j th degrees of freedom of the reactants (e.g., molecular translation, rotation, vibration, and surface) can be calculated for thermal equilibrium and nonequilibrium dissociative chemisorption using the PC-MURT.¹¹ For thermal dissociative chemisorption of CH_4 on Ni(100) at 500 K, the mean energy of the reacting complexes is $\langle E^*(T) \rangle_R = 0.97$ eV and the fractional energy uptakes are predicted to be $f_t=14\%$, $f_r=20\%$, $f_v=40\%$, and $f_s=26\%$ using the $E_0=67$ kJ/mol parameter set. For this equilibrium scenario relevant to catalysis, the incident gas molecules supply the preponderance of energy used to surmount the barrier to chemisorption, $f_g=f_t+f_v+f_r=74\%$, but the surface contribution at $f_s=26\%$ remains substantial.

V. COMPARISON WITH ELECTRONIC STRUCTURE THEORY

Figure 6 reviews how experimentally determined activation energies and theoretically predicted apparent threshold energies for CH_4 dissociative chemisorption on Ni(100) and Ni(111) surfaces have evolved over time. Siegbahn and co-workers¹³ calculated $E_0=67 \pm 4$ kJ/mol for CH_4 on Ni(100) using *ab initio* quantum chemistry methods, in quantitative agreement with our PC-MURT finding based on analysis of the varied experimental data above. We assume this consensus value of $E_0=67$ kJ/mol for CH_4 dissociation on Ni(100) is correct (cf. 432 kJ/mol to cleave a C–H bond of gas-phase methane). The generalized gradient approximation density functional theory (GGA-DFT) prediction for Ni(100) is 54% larger at $E_0=103$ kJ/mol.¹⁴ Similarly, GGA-DFT calculations of E_0 for Ni(111) are 11%¹⁵ to 65%¹⁴ larger than the 71 kJ/mol value of the most sophisticated *ab initio* calculation.¹² It is worth pointing out that accurate determination of E_0 is crucial in surface kinetics because dissociative sticking depends exponentially on this parameter. For example, the GGA-DFT value of E_0 for CH_4 on Ni(100) would underestimate the thermal sticking coefficient at 500 K by four orders of magnitude. Our analysis here suggests that threshold energies for catalytic reactions on metals are calculated more accurately using *ab initio* theory rather than GGA-DFT.

The PC-MURT's ability to quantitatively predict and compare the results of disparate equilibrium and nonequilibrium experiments to one another and to the predictions of electronic structure theory opens up important new opportunities to rigorously test and refine our understanding of reactive transition states and kinetics at surfaces. Improving such understanding is central to advancing catalysis and scientifically designing new catalysts. More generally, because the gas-surface interface provides a window into the world of condensed phase reactivity, the conceptual simplicity of the PC-MURT provides some welcome encouragement that theories of chemical reactivity at any interface need not be overly complicated.

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