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Citation: *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **35**, 05C201 (2017); doi: 10.1116/1.4980145

View online: <http://dx.doi.org/10.1116/1.4980145>

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Review Article: Dynamics of methane dissociation on transition metals

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(Received 6 March 2017; accepted 30 March 2017; published 14 April 2017)

One of the many contributions of Harold Winters to surface science was his pioneering ultrahigh vacuum study on the kinetics of the technologically important dissociation of CH₄ on transition metals in the 1970s. He observed a dramatic activation of the dissociation with surface temperature alone and a huge isotope effect and suggested a simple dynamical model to rationalize his results. Since that time, our general understanding of the dynamics of gas-surface dissociations has exploded due to experimental advances (e.g., molecular beam and eigenstate resolved studies) and theoretical advances (quantum or classical dynamics on *ab initio* potential energy surfaces). This review tries to highlight how our understanding of the dynamics of CH₄ dissociation on transition metals has matured since Harold's pioneering experiments and original model. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1116/1.4980145>]

I. INTRODUCTION

Although Harold Winters is best known for his many and various contributions to surface science related to plasma-surface interactions, he also pioneered studies of activated adsorption of CH₄ on transition metal surfaces in the mid 1970s. This had long been a subject of intense interest, even predating the advent of clean surface science, because of its central role in the steam reforming of natural gas to produce syngas, principally a mixture of H₂ + CO. This is one of the most important industrial catalytic processes and has been of commercial viability for over 70 years. The initial and generally rate-limiting step in the steam reforming reaction is the dissociative chemisorption of CH₄ on a supported metal catalyst, i.e., the breaking of one of the C-H bonds of CH₄ by the transition metal. Since the thermal rate for this dissociation is quite low, there is a high barrier to this process and energy must be supplied to affect this dissociation. This has traditionally been discussed in terms of so-called "C-H bond activation." Harold performed the first study of this activated dissociation on an atomically clean transition metal in the early days of clean UHV surface science and suggested a simple dynamical model to rationalize his results.^{1,2}

Since Harold's pioneering work, our general understanding of the dissociation dynamics of molecules on clean surfaces has blossomed and matured, due to both experimental and theoretical advances over the past four decades.³⁻⁵ For example, theory describing the dissociation of simple diatomic molecules such as H₂ on metal surfaces is now in

almost quantitative agreement with the experiment.⁶ However, the dissociation of polyatomic molecules such as CH₄ opens up entirely new challenges to our understanding of dissociation dynamics, e.g., the role of different vibrational modes in promoting dissociation, whether bond specific activation is possible, the importance of lattice coupling in the dissociation, etc.⁷ In fact, ever refined measurements of CH₄ dissociation on transition metal surfaces and the dynamical theory to understand them have become perhaps the central focus of the gas-surface dynamics community today. This mini-review attempts to show how our understanding of CH₄ dissociation on transition metals has evolved over the past 40 years since Harold's early experiments. We will present this in a more or less historical fashion, discussing experiments and the theories that evolved to understand them. We discuss Harold's (and other) kinetic studies of CH₄ dissociation in Sec. II, molecular beam experiments of the dissociation in Sec. III, and finally the current era of eigenvalue resolved dissociation dynamics and theory in Sec. IV. Finally, we present a short summary and outlook in Sec. V.

II. KINETIC STUDIES

The kinetic rate of dissociation simply convolutes the collision rate at a gas-surface interface with the dissociation probability at the surface S , $k(T_s, T_g) = k_{col}(T_g)\langle S(T_s, T_g) \rangle$. While k_{col} depends only on the gas pressure and temperature T_g , S can depend on both T_g and surface temperature T_s if they are not in equilibrium. Figure 1(a) shows Harold's initial measurement of the CH₄ and CD₄ initial dissociation

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probability (S_0) on an atomically clean W filament as a function of surface temperature T_s , while the gas temperature T_g is held constant at 300 K.¹ He developed a simple but elegant way to do this type of experiment by carefully measuring the decay of CH_4 pressure in a closed volume when exposed to a heated W filament, while getting all more active background and product gases that could contribute to a pressure change or contamination at the surface. There were two intriguing aspects to this result. First, the dissociation probability increased nearly 2 orders of magnitude with T_s , and second, there was a dramatic isotope effect. The pronounced isotope effect led Winters to suggest that CH_4 dissociation occurred via tunneling of an H atom through a barrier along a C-H stretch vibrational coordinate. Because of the strong dependence of S_0 on T_s , he suggested that a CH_4 collision complex that was in thermal equilibrium with the surface

formed the vibrationally excited molecular species prior to dissociation.²

At roughly the same time, Ehrlich and collaborators showed that CH_4 dissociation on Rh field emitter tips could be enhanced by increasing T_g at a fixed T_s .⁸ Because this experiment also exhibited a large kinetic isotope effect, they attributed this to a dominant role of vibrational excitation in the activation. However, they did not invoke tunneling but rather a nontraditional unimolecular decomposition of a collision complex to rationalize their experiments.

Since both these early interpretations implied a pivotal role of CH_4 vibration in enhancing dissociation, several early attempts were made to promote dissociation directly via laser vibrational excitation.^{9,10} These attempts were unsuccessful, and it was later pointed out that under the conditions of the experiments, enhancements of the dissociation rate were not likely to be observable.¹¹ Section IV discusses how modern laser technology has made this approach highly successful and led to entirely new dynamic insights.

Over the succeeding years, there have been many other measurements of $S_0(T_s, T_g)$ for CH_4 dissociation on “clean” transition metal surfaces. A few measured $S_0(T_s, T_g = 300 \text{ K})$ in the manner of Harold’s early measurements, e.g., Pt(110)¹² and Ni(100),¹³ and both showed considerable T_s dependence as well. However, most emphasis has been on measuring isothermal rates that require $T_s = T_g = T$ since these rates and the activation barriers determined from them are the important ones for catalysis. Isothermal rates and barriers have been measured for Ni(111),^{14,15} Ni(100),^{13,14} Ni(110),¹⁴ and Ru(0001).¹⁵ The isothermal condition is generally achieved by using very high CH_4 gas pressures so that it is exceedingly hard to keep the surface atomically clean during the measurements. It is likely that only the later isothermal measurements by Chorkendorff and collaborators fully satisfied this difficult constraint. Since all these kinetic measurements exhibited large isotope effects, the importance of tunneling in the kinetics led to an acrimonious discussion, largely based on whether parameters for one dimensional tunneling models were appropriate.^{16–19}

III. MOLECULAR BEAM EXPERIMENTS

Far more detailed information on the dissociation dynamics is available from molecular beam experiments than kinetic studies since these unravel some of the thermal averaging inherent in the kinetics. Seeded supersonic molecular beams allow independent control of the incident translational energy E_i , angle of incidence to the surface θ_i , average CH_4 vibrational temperature T_v , and surface temperature T_s . Such measurements can give $S_0(E_i, \theta_i, T_v, T_s)$, which provide a more stringent test of the proposed dynamical theory. The first molecular beam studies of CH_4 dissociation on W(110) by Rettner *et al.*²⁰ showed a dramatic nearly exponential increase of 4 orders of magnitude in S_0 with the component of translational energy normal to the surface, $E_n = E_i \cos^2 \theta_i$. They also observed the large isotope effect characteristic of the kinetic experiments. Rettner *et al.* proposed that this dissociative chemisorption was dominated by a one-dimensional

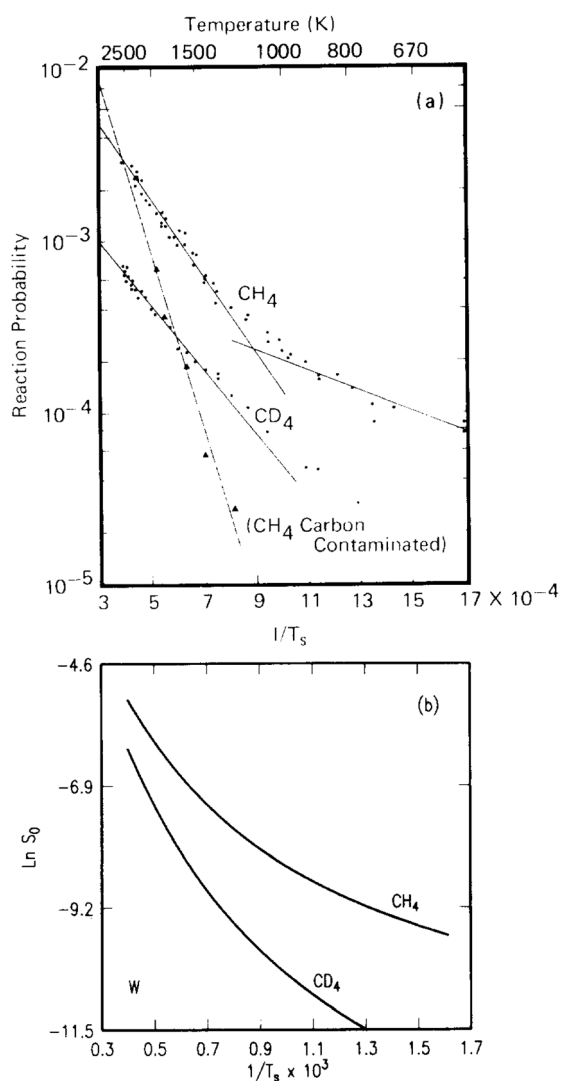


FIG. 1. Arrhenius plot of the variation of CH_4 and CD_4 dissociation probabilities (S_0) on W with surface temperature T_s (in Kelvin): (a) from the original experiments of Winters and (b) from the dynamical model of lattice coupling via momentum transfer during direct dissociation. Reprinted with permission from Luntz and Harris, Surf. Sci. **258**, 397 (1991). Copyright 1991 Elsevier.

tunneling mechanism, albeit via some unspecified direct dissociation process involving dissociation on the direct impact with the surface. Later, they showed that increasing T_v at constant E_n also enhanced the dissociation and defined a vibrational efficacy for this increase, arguing that average vibrational energy was nearly as effective as translational energy in activating dissociation.¹¹ However, one significant ambiguity in this interpretation is that not all vibrational modes of CH_4 may be equivalent in enhancing dissociation. Resolving this important issue and its implications are the focus of Sec. IV.

Qualitatively, similar molecular beam results have also been obtained for CH_4 dissociation on $\text{Ni}(111)$,^{21,22} $\text{Pt}(111)$,²³ $\text{Ni}(100)$,^{24,25} and $\text{Ru}(0001)$,^{26,27} including the nearly exponential increase in S_0 with E_n and a strong dependence on T_v , so that the dissociation dynamics appears similar on all the transition metal surfaces. When both the detailed molecular beam and the isothermal rates were measured for the same system, averaging $S_0(E_i, \theta_i, T_v, T_s)$ over the thermal distributions gave excellent agreement with the isothermal kinetic rates and apparent barriers derived from them.^{13,27} There was also a large T_s dependence of S_0 for $\text{Pt}(111)$, and this is shown in Fig. 2. This T_s dependence is incompatible with that anticipated from a precursor-mediated or long-lived collision complex mechanism for the dissociation. Furthermore, the dramatic E_n dependence of S_0 also indicates a direct dissociation on the initial impact. Therefore, the more detailed molecular beam experiments are not compatible with the early one-dimensional model originally proposed by Winters to rationalize the T_s dependence in CH_4 dissociation.

Borrowing ideas already well developed for describing the dissociation of diatomic molecules at surfaces, Luntz and Harris²⁸ proposed that the dissociation of CH_4 could be described qualitatively as direct dissociation dynamics of a quasidiatomic R–H governed by a potential energy surface (PES) $V(z, d)$, where z is the distance of R–H from the surface and d is the vibrational coordinate for a local R–H

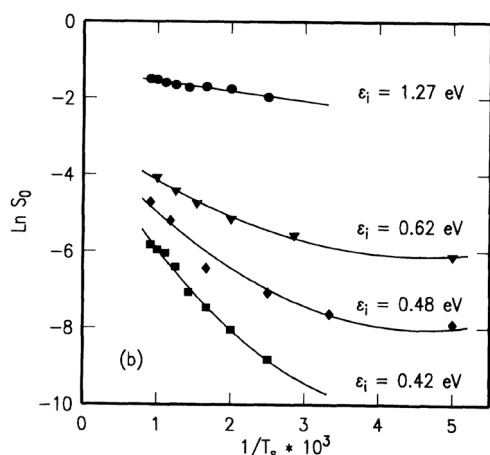


Fig. 2. Dissociation probability (S_0) (plotted logarithmically) for CH_4 dissociation on $\text{Pt}(111)$ as a function of inverse surface temperature in Kelvin at different normal incident energies E_n . Reproduced with permission from ■, Phys. Rev. Lett. **67**, 652 (1991). Copyright 1991 APS (Ref. 52).

vibrational mode. This two dimensional dynamical model then naturally accounts for a E_n and T_v dependence of S_0 . To rationalize the dependence of S_0 on T_s , they argued that the translational coordinate z could exchange energy with a lattice coordinate q via a coupling of the form $V(z-q, d)$ to account for momentum exchange to the surface during the dissociation itself. Averaging over a thermal distribution of phonon modes describing q produced a marked T_s dependence of S_0 . Using a reasonable but arbitrary PES, $V(z-q, d)$ gave reasonable agreement with a wide variety of experiments. Figure 1(b) shows the calculations of this model relative to the original experiment of Winters. The qualitative agreements between the experiment and the model show that a dramatic T_s dependence of the dissociation is possible even in direct dissociation. This model or subsequent slight modifications of it qualitatively rationalized the kinetic and molecular beam experiments to date at that time. It solved the dynamics on the PES using quantum wave-packet dynamics for all three nuclear coordinates. Therefore, if tunneling was important, it was included automatically. The T_s dependence was originally discussed in terms of thermally assisted tunneling.²⁸ However, it was later realized that the same T_s enhancement of S_0 would occur in classical dynamics as well. The 3D dynamical model was also soon generalized to include a rotational degree of freedom²⁹ since density function theory (DFT) calculations implied tight orientation constraints in the transition state.³⁰

IV. EIGENSTATE RESOLVED STUDIES OF METHANE DISSOCIATION

While the molecular beam experiments showed that both the vibrational and translational energies of the incident CH_4 are efficient for activating the dissociation on transition metals, these experiments could not distinguish between a statistical mechanism where the sum of translational kinetic energy and total vibrational energy from all the internal modes of methane contributes and the possibility of *mode specificity* where certain modes have a significantly larger effect than others independent of their vibrational energy. A nonstatistical dissociation mechanism opens the possibility for vibrational bond selectivity^{31,32} where excitation of a local bond mode provides control over which molecular bond is broken in the dissociation reaction. These and other important questions about the reaction dynamics of methane chemisorption can be addressed using quantum state-specific preparation of the incident methane by infrared laser pumping, a technique that has been applied to the study of methane chemisorption by at least three research groups in the last 20 years.^{33–35}

In these state-resolved reactivity measurements, infrared laser radiation is used to excite surface incident methane in a molecular beam to a specific rovibrational eigenstate before the surface collision and dissociation on a clean single crystal surface in an ultrahigh vacuum. Reactive sticking coefficients are determined by quantifying the resulting coverage of the chemisorbed dissociation products [either $\text{C}(\text{ads})$ or $\text{CH}_3(\text{ads})$] using surface analytical methods such as Auger

electron spectroscopy or infrared reflection absorption spectroscopy (RAIRS).

The first eigenstate resolved experiments^{33–35} measured the increase in CH₄ reactivity due to state specific vibrational excitation with one or two quanta of the ν_3 antisymmetric C–H stretching normal mode and compared it with the amount of translational energy ΔE_{trans} needed to obtain the same increase in reactivity for CH₄($v=0$) in the vibrational ground state. This comparison of translational and vibrational activation yields a vibrational efficacy $\eta(\nu_i)$ for each vibrational state ν_i defined as

$$\eta(\nu_i) = \frac{\Delta E_{\text{trans}}}{h\nu_i},$$

where $h\nu_i$ is the vibrational energy of mode ν_i . The vibrational efficacy $\eta(\nu_i)$ is found to depend on the vibrational state ν_i , the type of transition metal (Ni or Pt), and the crystallographic orientation of the single crystal surface (100 or 111) with values ranging from 0.4 to 1.4. A $\eta(\nu_i)$ value different from 1 indicates a nonstatistical dissociation mechanism for which the reactivity is not controlled by the total available energy but depends on how this energy is distributed between translation and different vibration degrees of freedom.

State specific preparation of different vibrational modes and comparison of their effect on the dissociation probability on the same surface were done to probe for *vibrational mode specificity* in methane chemisorption. For example, preparation of the totally symmetric ν_1 mode of CH₄ by stimulated Raman pumping³⁶ revealed a tenfold larger increase in reactivity on Ni(100) than what was observed for the isoenergetic ν_3 mode.³³ Figure 3 shows a comparison of the mode specificity and vibrational efficacies for CH₄

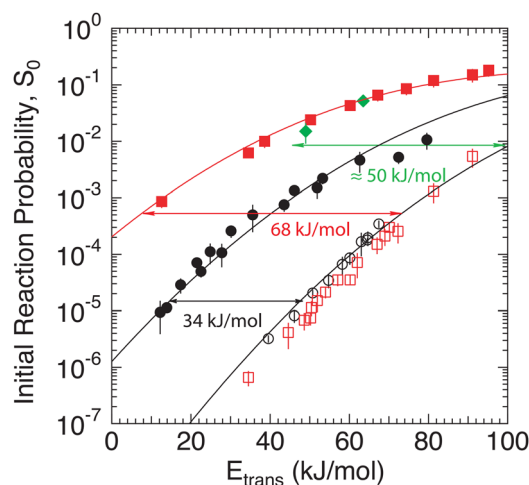


Fig. 3. (Color online) Quantum state-resolved reaction probabilities for CH₄ dissociation on a Ni(100) surface for three different eigenstates at a surface temperature of 475 K. Open symbols denote the laser-off data $S_0^{\text{laser-off}}$ from the study by Juurlink *et al.* (circles) (Ref. 33) and Schmid *et al.* (squares) (Ref. 35). Solid symbols denote the state-resolved data for one and two quanta of ν_3 excitation, $S_0^{\nu_3}$ (circles) (Ref. 33), $S_0^{2\nu_3}$ (squares) (Ref. 35), and one quantum of ν_1 excitation $S_0^{\nu_1}$ (diamonds) (Ref. 36). Reproduced with permission from Juurlink *et al.*, Prog. Surf. Sci. **84**, 69 (2009). Copyright 2009 Elsevier (Ref. 53).

dissociation on Ni(100). It also shows the nearly exponential increase in S_0 with the E_n characteristic of the earlier molecular beam experiments (laser off experiments). The mode specificity between the ν_1 and ν_3 modes of CH₄ was predicted by theoretical models of methane chemisorption^{37,38} to be due to differences in surface induced vibrational energy redistribution caused by the interaction of the vibrating molecule with the metal surface.

For partially deuterated methane, both the groups of Utz and Beck were able to demonstrate that methane chemisorption can be made *bond selective* by bond specific vibrational excitation. Killelea *et al.*³⁹ used a selective recombination reaction with subsurface D-atoms to show that excitation of the unique ν_1 C–H stretch mode of CHD₃ strongly favors the breaking of the C–H bond in the dissociation on Ni(111). Chen *et al.*^{7,40} used RAIRS to detect the methyl products formed by the dissociative chemisorption of partially deuterated methane (CH₃D, CH₂D₂, and CHD₃) on Pt(111) to show that in each case, the addition of a single quantum of C–H stretching vibration is sufficient to change the C–H/C–D cleavage branching ratio from near statistical to fully bond selective. These results provide clear evidence that methane dissociation is far from statistical and that the dissociating molecule retains a clear memory of the quantum state that it was initially prepared in.

Vibrational excitation by linearly polarized infrared light can be used to align the vibrating methane molecules in the laboratory frame. Yoder *et al.*⁴¹ used this technique to probe for steric effects in the dissociative chemisorption of methane (CH₄ and CHD₃) on Ni(100), Ni(111), and Ni(110). Their study⁴² showed that the dissociation is favored by up to a factor of two when the C–H stretching amplitude is aligned parallel to the plane of the surface rather than along the surface normal.

Vibrational activation is not limited to intramolecular vibrations and also the vibrational motion of the surface atoms can have a strong effect on the chemisorption probability as discussed previously. This was again demonstrated in a recent combined experimental/theoretical study of Campbell *et al.*⁴³ that probes the surface temperature (T_s) dependence of the state-resolved CH₄ reactivity on Ni(111). The study reveals a strong surface temperature dependence of the CH₄(ν_3) reactivity close to the dissociation threshold (Fig. 4). In contrast to the mechanical model of lattice coupling in the study by Luntz and Harris,²⁸ DFT calculations for CH₄ dissociation on Ni(111) show a significant lowering of the barrier height with puckering of an atom out of the surface.⁴⁴ This implies that the dominant effect of thermal motion of the Ni surface atoms in and out of the surface plane is to modulate the dissociation barrier height and thereby broaden the translation energy dependence of the reactivity with increasing T_s . At $T_s = 90$ K, where this barrier height modulation due to surface atom motion is negligible, the state resolved reactivity $S_0(\nu_3)$ drops precipitously near the calculated minimum dissociation barrier. Similar DFT calculations for CH₄ dissociation on Pt(111) indicate that both the mechanical effect and the barrier height modulation are important for that system.⁴⁵

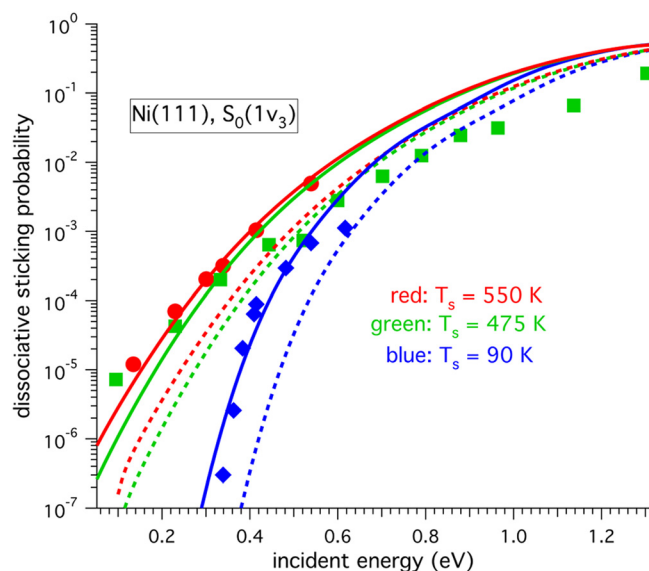


FIG. 4. (Color online) Dissociative sticking probability for $\text{CH}_4(\nu_3)$ on Ni(111) as a function of incident energy and surface temperature. Solid symbols are experimental data from the study by the Utz group, and dashed and solid lines are the theoretical data from the study by the group of Bret Jackson. Reproduced with permission from Jackson and Nave, *J. Chem. Phys.* **138**, 174705 (2013). Copyright 2014 AIP Publishing (Ref. 54).

In summary, these eigenstate resolved measurements not only uncover the detailed reaction dynamics, including the effects of mode specificity, bond selectivity, steric dependence of methane chemisorption, and surface atom motion, but also provide experimental data that can serve as stringent tests for theoretical models for methane/surface reactions since averaging over rotational and vibrational states is not needed. Theoretical data from the study by several groups^{38,46–48} have used DFT to calculate PES for up to 15 molecular degrees of freedom for the dissociation reaction of methane on transition metals and performed either classical or quantum dynamics calculations and compared their results with the available eigenstate resolved reactivity data.

Bret Jackson and his group have developed a first principles model for methane chemisorption based on a reaction path Hamiltonian (RPH) approach³⁸ which treats all 15 molecular degrees of freedom explicitly. In their model, DFT is used to accurately calculate the minimum energy (reaction) path across the PES from reactants to products. The PES is assumed to be harmonic in the 14 degrees of freedom normal to the reaction path, and the normal coordinates of CH_4 are calculated for each point along the reaction path leading to a vibrationally adiabatic curve for each vibrational mode. The calculations show that the frequency of the ν_1 mode decreases much more than the others along the reaction path, an effect described as *mode softening* which leads to the reduction in the adiabatic barrier height for the ν_1 mode. Jackson *et al.* treat the dynamics of the reaction quantum mechanically by propagating wave packets on the PES including nonadiabatic transitions, which can convert vibrational energy into translation along the reaction path. Jackson's first principles quantum dynamics simulations reproduce the experimentally observed mode specificity and

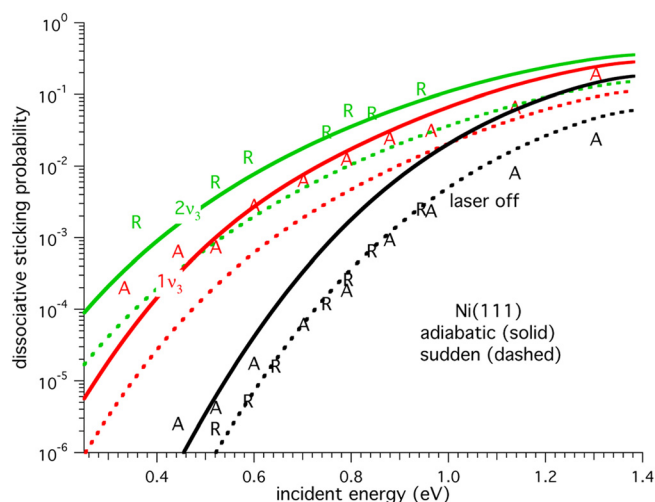


FIG. 5. (Color online) Comparison of the prediction of the RPH model for methane dissociation on Ni(111) at 475 K with state resolved experimental data. The symbols are experimental data from the study by the groups of Utz (A) and Beck (R). Reproduced with permission from Jackson *et al.*, *J. Chem. Phys.* **141**, 054102 (2014). Copyright 2014 AIP Publishing (Ref. 55).

bond selectivity and yield semiquantitative agreements with state resolved experiments without any adjustable parameters. The effect of surface motion is treated by a sudden model where values of the lattice displacement are randomly sampled, and quantum calculations are implemented for these fixed lattice configurations.⁴⁹ Figure 5 shows a comparison of predictions of the RPH model with eigenstate resolved reactivity measurements for CH_4 dissociation on Ni(111).⁵⁰

On the other hand, Geert-Jan Kroes and his group use *ab initio* molecular dynamics (AIMD) calculations^{46,51} to simulate methane dissociation on Ni and Pt surfaces. Here, the PES is calculated by DFT “on-the-fly” only for regions that are sampled by the reaction dynamics. The PES includes all the molecular degrees of freedom as well as the surface

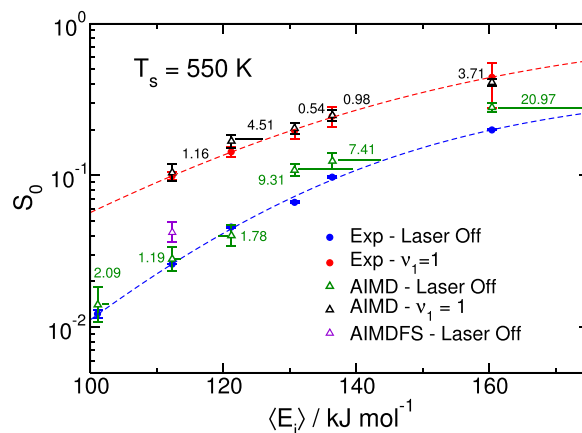


FIG. 6. (Color online) Calculated (using AIMD) and experimental reaction probabilities for CHD_3 dissociation on Ni(111) (Ref. 46) where ν_1 is the unique C-H stretching mode of CHD_3 . AIMDFS designates the calculated AIMD results for a frozen surface. Reproduced with permission from Nattino *et al.*, *J. Phys. Chem. Lett.* **7**, 2402 (2016). Copyright 2016 American Chemical Society.

atoms of the metal. Classical mechanics is used to calculate the motion of all the atoms. This method uses a semiempirical PES since the mixing of two different exchange-correlation functionals in the DFT is adjusted to match state-resolved experimental benchmark data. The optimized mixed functional is then used to predict the methane reactivity with chemical accuracy for a wider range of conditions. Figure 6 shows a comparison with experimental data for the dissociation of CHD₃ on Ni(111).⁴⁶

V. SUMMARY AND OUTLOOK

One of the less celebrated achievements of Harold Winters was his pioneering UHV study on the kinetics of the technologically important dissociation of CH₄ on transition metals in the 1970s. The continued study of this dissociation process with ever refined experimental techniques over the past four decades (molecular beam and eigenstate resolved experiments) has provided great impetus in developing more sophisticated theories and understanding the formation and breaking of bonds at surfaces. Most importantly, experimental studies of this dissociation dynamics forced the theory to confront novel aspects of polyatomic dissociation such as mode and bond selectivity and to include important coupling of the dissociation to the lattice degrees of freedom. At this point in time, first principles dynamical theory is in semi-quantitative agreement with the most refined experiments. Even more detailed experiments on CH₄ dissociation dynamics will undoubtedly continue to push the theory forward. Thus, the initial study by Harold was an important seed for the entire field of gas-surface reaction dynamics. This review has tried to highlight how our understanding of this important dissociation has evolved since Harold's initial pioneering experiments. On a personal note, one of us (ACL) very much misses Harold as a colleague, friend, and collaborator.

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