

Quantum Theory of Dissociative Chemisorption on Metal Surfaces

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ABSTRACT

Recent theoretical progress in gas–surface reaction dynamics, a field relevant to heterogeneous catalysis, is described. One of the most fundamental reactions, the dissociative chemisorption of H₂ on metal surfaces, can now be treated accurately using quantum mechanics. Density functional theory is used to compute the molecule–surface interaction, and the motion of the hydrogen atoms is simulated using quantum dynamics, modeling all six molecular degrees of freedom. Theory is in good quantitative agreement with molecular beam experiments, offering useful interpretations, and allowing reliable predictions. The success of the approach calls for extensions to larger systems, such as dissociative chemisorption of polyatomic molecules.

Reactions at surfaces often correspond to rather complicated multistep processes, which hampers their theoretical modeling. For improved understanding of the overall reaction, a bottom-up approach has frequently been employed, involving atomistic studies of elementary reaction steps at well-defined single crystal surfaces. This approach has recently resulted in some remarkable successes. One study combined atomistic experimental and theoretical methods to establish that at elevated oxygen pressures, CO can be oxidized on ruthenium in a mechanism in which CO reacts with oxygen incorporated in the oxidized ruthenium surface.¹ In another example, the

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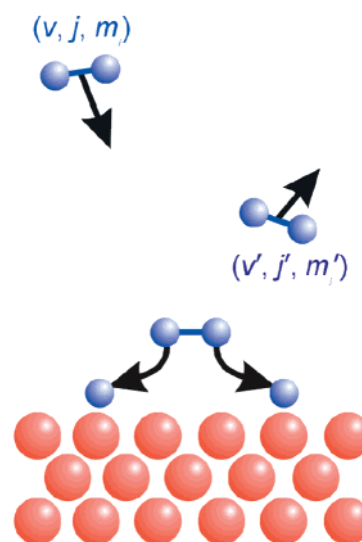


FIGURE 1. Schematic representations of the most important processes that can be probed in the scattering of a diatomic molecule from a reactive surface. A molecule approaching the surface in a specific initial internal state characterized by the vibrational quantum number v , the rotational angular momentum quantum number j , and the magnetic rotational quantum number m_j , can either react (dissociative chemisorption) or scatter back to the gas phase in a final rovibrational state (v', j', m_j') .

full step from combined atomistic experimental and theoretical studies to the rational design of an improved catalyst was taken for the steam reforming process (which converts methane and water to hydrogen and carbon-monoxide).²

The understanding of complex chemical reactions is based on even more fundamental studies of elementary reaction steps. The detailed study of such elementary molecule–surface reactions, such as the dissociative chemisorption reaction^{3–11} (see Figure 1), constitutes the mission of the field of molecule–surface reaction dynamics. One aim of the field is to answer questions that are related to the topic of chemical control:¹² can reaction be promoted by changing the internal quantum state of a reacting molecule, or by changing its orientation or alignment relative to the surface? Analogous questions are asked in gas-phase reaction dynamics.^{12,13} Another aim revolves around a goal that is central to chemistry, that

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is, the accurate determination of potential energy surfaces (PESs), which summarize information on the interatomic interactions that determine the outcome of chemical reactions. The progress made by electronic structure theories in computing the interaction of a molecule with a metal surface (a notoriously difficult problem) can be monitored by careful comparisons of experimental and theoretical dynamics studies.^{9,10} Finally, by carrying out studies on well-defined crystallographic metal surfaces, researchers in the field can aim to provide quantitative data for reaction rates at facets of nanosized metal particles present in supported catalysts. Such data can be used in mesoscopic kinetic simulations of sustained catalytic reactions on industrially used catalysts.¹⁴

To gain deeper insight into reaction mechanisms, benchmark systems are needed for which experimental as well as theoretical studies can be performed with similar accuracy and microscopic resolution. In this review the dissociative chemisorption of H₂ on metal surfaces is discussed. A great advantage of this system for theoretical studies is that in the modeling of the reaction, the neglect of phonons represents a good approximation, resulting in a shift of the reaction probability vs collision energy curve of only a few hundredths of an eV.¹⁵ Experiments¹⁶ and theoretical calculations¹⁵ have shown that above threshold, the effect of increased surface temperature can be modeled in a simple way. The comparisons between theory and experiment that we will present below suggest that accurate results can be obtained while also neglecting electron–hole pair excitation (see also ref 17). The H₂ + metal surface system is, therefore, ideal for testing the usefulness of electronic structure methods for computing molecule–metal surface interactions.

As we will show, the availability of a wide range of experimental data^{3–6,18–23} has led to a breakthrough in the quantum mechanical description of the dissociative chemisorption of H₂ on metal surfaces. The dissociative chemisorption and the most important scattering processes, which are depicted schematically in Figure 1, can now be modeled with unprecedented accuracy. In the next section, we will describe the theoretical improvements that have been made over the past decade. The success of these improvements will be illustrated by comparisons to experiment. We will focus on two systems, one of which is an example of a nonactivated reaction (H₂ + Pd(100)), and the other, of an activated reaction (H₂ + Cu(100)). We conclude with a brief outlook in which we address the challenges posed by the system that we believe will become a new benchmark for quantum reaction dynamics studies, that is, the dissociative chemisorption of a polyatomic molecule (methane) on metal surfaces.

Theory. Until the mid-1990s, dynamical calculations had to rely on highly approximate models for the molecule–surface interaction derived, for instance, from calculations on molecule–metal clusters^{8,24} or effective medium theory.²⁵ Restrictions on computational resources meant that only a few molecular degrees of freedom could be modeled in calculations treating the dissociation dynamics quantum mechanically.^{7,8,25–27} Nevertheless,

these calculations played, and continue to play, an important role in the prediction and interpretation of experimental trends. The rich knowledge gained from such calculations has been reviewed elsewhere.²⁸

In 1994, the first paper appeared that presented an accurate and detailed determination of the molecule–surface interaction for H₂–metal surface systems.²⁹ This and later studies used density functional theory (DFT)^{30,31} for two reasons: First, periodic boundary conditions can be implemented in DFT using either a three-dimensional supercell³² or a two-dimensional slab³³ approach. This allows a good description of the delocalized electronic structure and bonding properties of metal surfaces. With present-day computational resources, the size of the periodic unit can be taken large enough to allow the calculation of a converged value of the energy of an isolated molecule interacting with a metal surface. Second, the use of the so-called generalized gradient approximation (GGA) to the exchange correlation energy^{34,35} now also allows a considerably accurate determination of molecule–surface interaction energies.³⁶ The problem of how to treat the exchange correlation energy is central to DFT, which states that the ground-state energy of a system is determined by its electron density, but it has not yet provided an exact method for calculating this energy from the density.

Figure 2 presents aspects of the potential energy surfaces (PESs)^{37,38} for the two systems that are here considered in most detail. Following a convention in surface science, energies are expressed in electronvolts (1 eV = 96.485 kJ/mol). The H₂ + Pd(100) system is a classic example of a nonactivated system, the PES being barrierless at some sites (like the bridge site, Figure 2A,B), although having a barrier at others (like the top site, Figure 2C,D). At moderate collision energies, dissociation is feasible if the molecule is lying parallel to the surface, so that both atoms can form bonds to the surface upon dissociation, but not if the molecule is standing upright (Figure 2B,D). The H₂ + Cu(100) system is a classic example of an activated system, dissociation proceeding over a potential barrier above all sites (Figure 2E–H). As previously found for H₂ + Cu(111),²⁹ the barrier to dissociation varies considerably with surface site and orientation of the molecule.

The reaction of H₂ on Pd(100) is much more exothermic, and the associated barrier height is much lower (or zero) than for the H₂ + Cu(100) system. This difference can be explained from the position of the center of the metal d band relative to the Fermi level.^{24,39} The center of the d band lies farther below the Fermi level in Cu, resulting in a greater filling of the molecule–surface and atom–surface antibonding levels at the barrier and in the exit channel, respectively.³⁹

For an accurate treatment of the dynamics of H₂ reacting on a metal surface, it is necessary to use quantum mechanics and to treat all six molecular degrees of freedom. Comparisons of quantum dynamical, quasi-classical, and classical results for H₂–metal surface systems have shown that neither of the two classical approaches yields

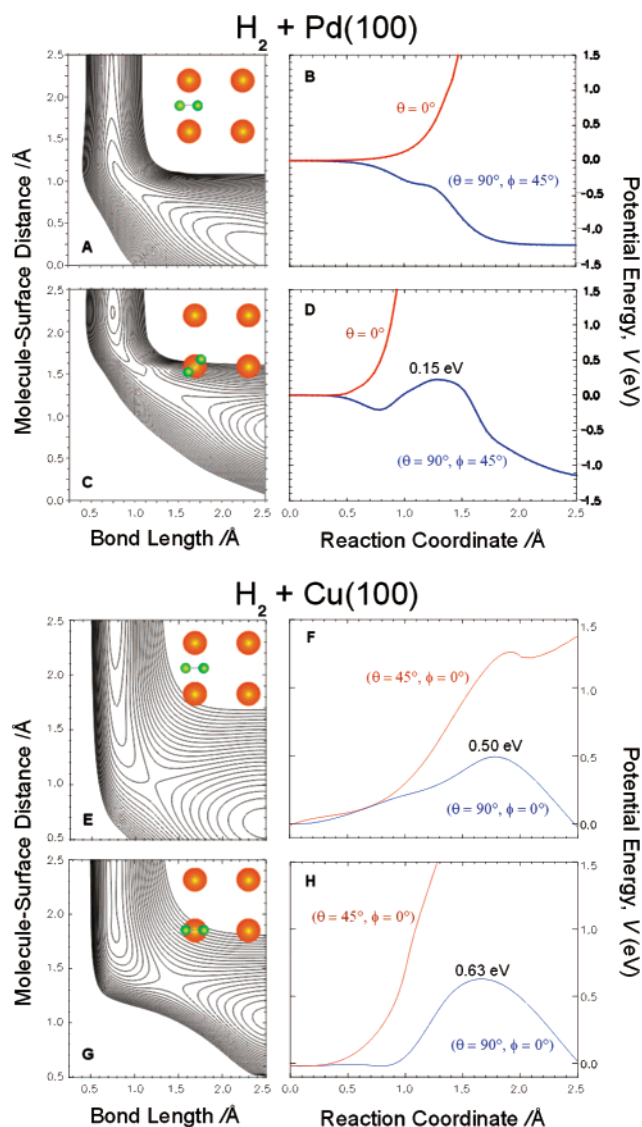


FIGURE 2. PESs for $\text{H}_2 + \text{Pd}(100)$ (A–D) and $\text{H}_2 + \text{Cu}(100)$ (E–H). Two-dimensional cuts through the PES are shown for the molecule being parallel to the surface, for the bridge-to-hollow (A) and top-to-hollow (C) configurations for $\text{H}_2 + \text{Pd}(100)$, and for the bridge-to-hollow (E) and top-to-bridge (G) configurations for $\text{H}_2 + \text{Cu}(100)$. The configurations are visualized in the insets, viewing the system from above. The contour lines are for potential energies 0.1 eV apart. For each cut, the potential along the reaction path is shown on the right as a function of the reaction coordinate for the molecule in a parallel ($\theta = 90^\circ$) and in a tilted ($\theta \neq 90^\circ$, ϕ is the azimuthal angle of orientation of the molecular axis) geometry.

a quantitatively accurate description of the nonactivated $\text{H}_2 + \text{Pd}(100)$ reaction⁴⁰ and that it is not a priori clear which of the two classical approaches will yield the best description of a given $\text{H}_2 + \text{metal}$ system.¹⁷ The requirement of a quantum mechanical treatment of the dynamics at present rules out the application of classical *ab initio* molecular dynamics methods, such as the well-known Car–Parrinello method, to H_2 –metal surface reactions.⁴¹

Classical trajectory⁴² and quantum dynamics¹⁰ calculations have shown that all six molecular degrees of freedom of H_2 need to be treated to obtain accurate results for the reaction probability, which is diminished substantially

when the molecular rotations and the translations parallel to the surface are included in the dynamical model. Fixed-site calculations, in which the molecule’s translational motion along the surface is not treated, often yield a qualitatively correct description of the influence of the molecule’s initial vibrational and rotational state and of the molecule’s initial orientation relative to the surface, on reaction.¹¹ If an appropriate average is performed over results for different sites, such calculations may even yield reaction probabilities that agree well with six-dimensional results, as shown for the activated dissociation of H_2 on $\text{Cu}(111)$.¹¹ However, the accuracy of this approach is not guaranteed for activated dissociation (as shown for $\text{H}_2 + \text{Cu}(100)$ ⁴³), and it is not expected to work for nonactivated dissociation in which the potential can steer the molecule to sites where dissociation is favorable.⁹ Another established shortcoming of the fixed-site model is that it is incapable of yielding a correct simultaneous description of vibrational excitation and vibrational enhancement of reaction of H_2 on $\text{Cu}(111)$.⁴⁴ Furthermore, the fixed-site model cannot describe reactions for which the reaction probability depends on the component of the collision energy parallel to the surface, as observed for the $\text{H}_2 + \text{Pd}(100)$ reaction discussed here.⁴⁰

The quantum dynamical treatment of reactions of H_2 on (100) metal surfaces was facilitated by the use of the symmetry associated with the surface unit cell, which allows large computational savings for reaction at normal incidence.^{40,45} Other important innovations include a new algorithm for propagating coupled-channel equations⁴⁶ within a reaction path formulation⁹ and the use of an efficient time-propagation method⁴⁷ within the time-dependent wave-packet method.⁴⁸

In the first six-dimensional quantum dynamical calculation, the dissociation of H_2 on $\text{Pd}(100)$ was studied⁹ using a coupled-channel method in which the time-independent Schrödinger equation is rewritten and solved as a set of coupled differential equations in a “scattering coordinate”. The coupled-channel method yields results for all initial states present in the scattering basis set, which is advantageous for simulating beam experiments in which many states of H_2 are populated in the beam. The first studies on activated dissociation ($\text{H}_2 + \text{Cu}(100)$ ¹⁰ and $\text{H}_2 + \text{Cu}(111)$ ¹¹) both used a time-dependent wave packet method in which the time-dependent Schrödinger equation is solved.⁴⁸ The wave packet method allows for larger scattering basis sets but yields results for only one initial state per calculation.

Nonactivated Dissociation: $\text{H}_2 + \text{Pd}(100)$. Computed reaction probabilities⁹ are compared with experimental results¹⁸ in Figure 3A. The quantitative agreement with experiment is quite reasonable for the PES³⁷ for which the majority of dynamics results (as presented below) were obtained. There is also good qualitative agreement between experiment and theory in that with increasing collision energy, the reaction probability first decreases and then increases again. Good quantitative agreement between theory and experiment has been achieved in later

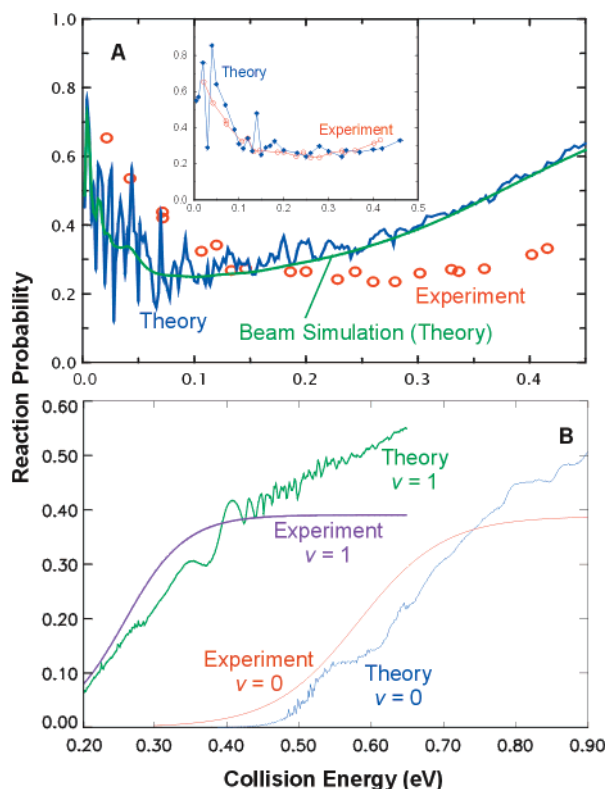


FIGURE 3. Reaction probabilities as functions of normal incidence energy for $\text{H}_2 + \text{Pd}(100)$ and $\text{Cu}(100)$. Theoretical results⁹ for H_2 incident in its rovibrational ground state ($v = 0, j = 0$), and for H_2 incident in a distribution of (v, j) states representative of a molecular beam experiment are compared to results of a molecular beam experiment,¹⁸ for $\text{Pd}(100)$ (A). The inset also shows the comparison of the molecular beam results¹⁸ to theoretical results for H_2 ($v = 0, j = 0$) from calculations employing a PES based on a larger set of DFT calculations.⁴⁹ The computed reaction probability³⁸ for H_2 normally incident on $\text{Cu}(100)$ in its rovibrational ground state ($v = 0, j = 0$), and first excited vibrational state ($v = 1, j = 0$) is compared to fits²⁰ based on data from molecular beam and associative desorption experiments (B).

calculations based on a more elaborate PES (see inset to Figure 3A⁴⁹).

The calculations have also settled a long-standing debate about the mechanism responsible for the high surface reactivity at lower energies by establishing the effectiveness of so-called “steering”: For molecules that approach with low kinetic energies, the forces exerted by the surface steer the molecule to sites and orientations that are favorable to reaction. Figure 4A shows how, at the low collision energy of 0.01 eV, a molecule that is initially ($t = 0$ fs) unfavorably oriented for dissociation can be reoriented to a favorable geometry by the time it hits the surface ($t = 160$ fs) so that it can react ($t = 215$ fs).⁴⁰ Figure 4B shows that at the higher energy of 0.12 eV, there is not enough time for the forces exerted by the surface to redirect or reorient the molecule by the time it hits the surface ($t = 60$ fs) so that the molecule hits the surface end-on, and is scattered back ($t = 165$ fs) after hitting the surface with its other end ($t = 80$ fs). Initially rotating molecules are likewise less easily steered into favorable orientations than nonrotating molecules, which explains

why rotationally excited ($v = 0, j = 4$) H_2 is less reactive than nonrotating ($v = 0, j = 0$) H_2 ⁵⁰ (Figure 4C). A theoretical prediction that lower reaction probabilities should be measured on $\text{Pd}(100)$ in a pure (rotationally hot) beam⁹ rather than in a seeded (rotationally cold) beam was confirmed in experiments on the analogous $\text{H}_2 + \text{Pd}(111)$ system.⁴

Another consequence of steering is that at low energies, $\text{Pd}(100)$ exhibits the same surface reactivity toward H_2 dissociation as $\text{Rh}(100)$,⁴⁹ whereas static energy considerations and simple chemical intuition (chemical activity of the d band)³⁹ would suggest Rh to be more reactive: dissociation of H_2 on $\text{Rh}(100)$ is barrierless for a much larger fraction of surface sites.⁴⁹ This demonstrates that electronic structure theory alone cannot accurately predict the surface reactivity; a subsequent dynamical calculation is required to model the influence of dynamic effects, such as steering.

The reactivity of H_2 can also be significantly enhanced by exciting the vibration of the molecule prior to the collision⁵¹ (Figure 4C) as a result of conversion of vibrational energy to dissociative motion. In the nonactivated $\text{H}_2 + \text{Pd}(100)$ system, this is caused by a decrease in the force constant associated with the vibrational motion perpendicular to the reaction path,⁵¹ but in the late barrier $\text{H}_2 + \text{Cu}$ system, it is attributed to an increase in the reduced mass associated with that mode.²⁸ In Figure 4D vibrational and rotational temperatures of hydrogen desorbing from $\text{Pd}(100)$ are plotted as a function of surface temperature. These temperatures are meant as parameters characterizing the mean energy in the corresponding degree of freedom upon desorption. Earlier experiments¹⁹ had yielded very large values that were later questioned by the quantum calculations.⁵¹ More refined experiments²³ have now confirmed the theoretical results, showing that theory is now able to make quantitative predictions for reaction that may even lead to a reconsideration of experiments. Figure 4D also shows good agreement between theory and experiment for rotational temperatures.

Activated Dissociation: $\text{H}_2 + \text{Cu}(100)$. Reaction probabilities computed using a new PES³⁸ are compared with reaction probabilities fitted²⁰ to experiment in Figure 3B. In evaluating the comparison, one should keep in mind that the fit to experiment is somewhat uncertain,²⁰ being based on a limited set of experimental results, and being mostly an extrapolation of molecular beam results above 0.5 eV. Agreement between experiment and theory is very satisfying for both vibrationless and vibrationally excited H_2 , especially if one takes into account that the accepted uncertainty in the DFT/GGA determination of barrier heights is on the order of 0.1 eV. This comparison and that of the previous section for $\text{H}_2 + \text{Pd}(100)$ shows that the first principles approach here described is now mature enough to enable reliable quantitative comparisons with experiments for hydrogen dissociation on metal surfaces.

Six-dimensional quantum dynamics calculations for $\text{H}_2 + \text{Cu}(100)$ have also been useful for the interpretation of experimental results and have led to exciting new predic-

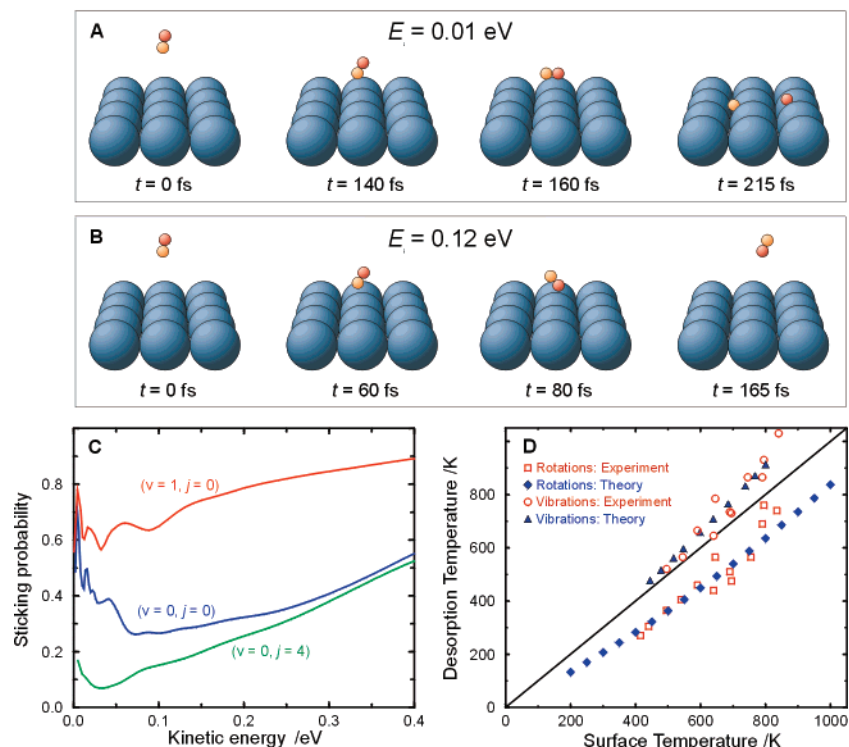


FIGURE 4. Computational^{50,51} and experimental results are shown for $\text{H}_2 + \text{Pd}(100)$. Snapshots of classical trajectories of H_2 molecules impinging on $\text{Pd}(100)$ that illustrate the steering effect are shown for an initial kinetic energy of 0.01 eV (A) and 0.12 eV (B) for otherwise identical initial conditions (see the text for further explanation).⁴⁰ The computed reaction probability is shown as a function of normal incidence energy for the rovibrational ground state ($\nu = 0, j = 0$), for a rotationally excited state ($\nu = 0, j = 4$), and for the vibrationally excited state ($\nu = 1, j = 0$) (C). Theoretical predictions for the rotational and vibrational temperatures are compared with experimental measurements²³ on hydrogen associatively desorbing from $\text{Pd}(100)$ (D).

tions. For instance, the much enhanced reactivity of vibrationally excited ($\nu = 1$) H_2 (Figure 3B), which is in agreement with experiment,²⁰ can be attributed to the barrier being late for $\text{H}_2 + \text{Cu}$.^{28,52} In the mechanism invoked, the vibration perpendicular to the reaction path, which corresponds to the H_2 vibration before reaction, remains excited. However, part of its energy flows into the reaction coordinate, because its vibrational frequency is lowered at the barrier as a result of a mass effect.²⁸ Recent calculations⁵³ refine this interpretation by showing that above the top site, vibrationally excited H_2 can react by losing an entire vibrational quantum of energy. This effect makes the top site the preferred reaction site for $\nu = 1$ H_2 at low collision energies (see Figure 5A), even though the barrier to reaction is higher at this site than at the bridge site (compare Figure 2, panels E and G), which is the preferred reaction site for $\nu = 0$ H_2 .⁵³ According to the calculations,⁵³ the predicted difference in site-reactivity between $\nu = 0$ and $\nu = 1$ H_2 can be confirmed by experiments using existing techniques, by measuring the rotational quadrupole alignment parameter $A_0^{(2)}$ of molecules desorbing associatively from $\text{Cu}(100)$ in the ($\nu = 0, j = 4$) and ($\nu = 1, j = 4$) states (see Figure 5B).⁶

A very rigorous test of the first principles approach is obtained in comparisons of state-to-state probabilities for scattering. A comparison with state-of-the-art molecular beam experiments is shown in Figure 5C,D for scattering of ($\nu = 1, j = 1$) H_2 from $\text{Cu}(100)$.⁵ Good agreement

was obtained for the probability that H_2 remains in the same rovibrational state (Figure 5C). However, Figure 5D demonstrates discrepancies between theory and experiment for rotational excitation into the ($\nu = 1, j = 3$) state. These discrepancies are a challenge for both theory and experiment. A possible source of error in the theory is an inaccurate description of the anisotropy of the molecule–surface interaction in the region in which the molecule is yet to reach the barrier. This rather subtle aspect of the PES can be ameliorated by employing improved methods to fit the DFT data, as are currently being developed.^{54,55} Another possible improvement consists of using more accurate density functionals, the development of which is being pursued actively.^{56,57} The accepted accuracy of DFT for reaction barrier heights is in the range 0.1–0.2 eV, and because in many instances a higher accuracy would be preferable in modeling activated processes, the development of such functionals is important to the description of such reactions.

Outlook. The success of the theoretical approach described here for dissociative chemisorption of hydrogen calls for extensions of the approach to even more challenging systems, such as dissociative chemisorption of heavier diatomic molecules, and of polyatomic molecules. We expect that a quantum dynamical treatment will be required for processes involving the breaking of an X–H bond, whether in a diatomic or a polyatomic molecule (as discussed below). Accurate treatments of the direct

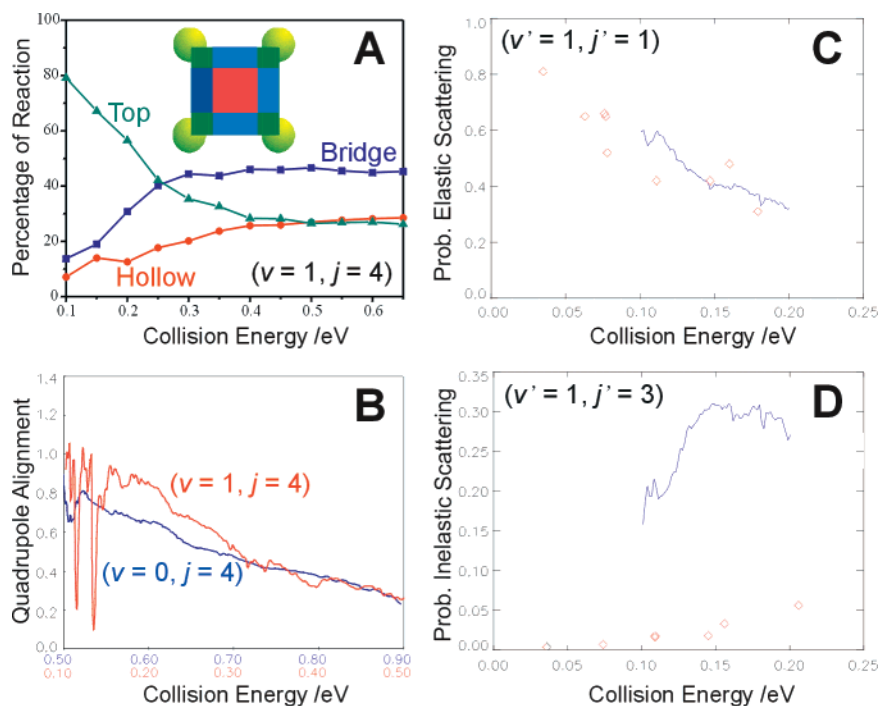


FIGURE 5. Quantum dynamics results are shown for $\text{H}_2 + \text{Cu}(100)$ for site-specific reaction and for rotationally elastic and inelastic scattering. A plot of the percentage of reaction at the high-symmetry sites shows that in its $(\nu = 1, j = 4)$ initial state, H_2 reacts preferentially at the top site at low collision energies⁵³ (A). The theoretical prediction that $\nu = 0$ and $\nu = 1$ H_2 react at different sites (bridge and top, respectively)⁵³ at low energies can be confirmed experimentally by establishing that in associative desorption, $(\nu = 1, j = 4)$ H_2 displays a higher rotational quadrupole alignment $A_0^{(2)}$ than $(\nu = 0, j = 4)$ H_2 , at desorption energies at which the reaction probability is low, that is, close to 0.05 (the lower end of the energy scale in Figure 5B).⁵³ Note: $A_0^{(2)} = \langle 3 \cos^2 \Theta - 1 \rangle$, Θ being the angle between j and the surface normal. Probabilities measured in supersonic molecular beam experiments (red diamonds) for elastic scattering of H_2 $(\nu = 1, j = 1)$ to the final $(\nu' = 1, j' = 1)$ state (C) and rotational excitation to the $(\nu' = 1, j' = 3)$ (D) state are compared to six-dimensional quantum dynamics results (blue curves).⁵

dissociative chemisorption of a heavy diatomic molecule on a metal surface (which also requires the treatment of phonons) should be feasible with classical ab initio molecular dynamics simulations in which the forces are calculated on the fly, for example, in the Car–Parrinello method,⁴¹ and the use of such methods has already resulted in useful insights in the mechanisms of complex molecule–surface reactions.⁵⁸ However, the classical dynamics method (as implemented in Car–Parrinello⁴¹) requires many trajectories to be run for the accurate determination of reaction probability vs collision energy curves, which is necessary to validate theoretical approaches by rigorous comparisons to energy-resolved results of molecular beam experiments. Nevertheless, we expect that with the ever increasing computational resources, such calculations will become feasible in the next decade.

An important question that can be addressed for polyatomic molecules is which vibrational modes of the molecule are effective in promoting reaction. Figure 6 shows results of the first beam–surface experiments that provided direct experimental evidence for vibrational activation by a specific vibrational mode for $\text{CH}_4 + \text{Ni}(100)$.⁵⁹ The dissociative chemisorption of CH_4 involves the breaking of a C–H bond, which requires a quantum dynamical treatment. Reduced dimensionality quantal calculations treating CH_4 as a pseudodiatomic RH ($\text{R}=\text{CH}_3$) and modeling one C–H (R–H) stretch vibration^{60,61} reproduce the reactivity of vibrational ground-state CH_4 reasonably

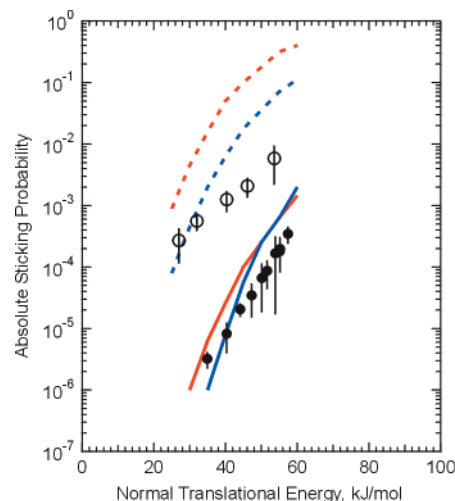


FIGURE 6. Experimental results⁵⁹ for the dissociative chemisorption of CH_4 on $\text{Ni}(100)$, for CH_4 in its vibrational ground state (filled circles with error bars) and its $\nu_3 \nu = 1$ C–H stretching eigenstate (open circles) are compared to theoretical results (solid lines for the vibrational ground state, dashed lines for the vibrationally excited state). The red curves are results for $\text{Ni}(100)$ of reduced dimensionality quantum dynamics calculations, which treated the motion of the molecule toward the surface and one C–H stretch vibration within the surface mass model for phonon motion.⁶⁰ The blue curves are results of quantum dynamical calculations additionally treating two of the molecule's rotational modes for $\text{Ni}(111)$.⁶¹

well (Figure 6). However, the theory for vibrationally excited CH_4 disagrees with the experimental results for

CH₄ with its ν_3 asymmetric stretch vibration excited with one quantum prior to the collision (Figure 6). This lack of agreement and results of DFT calculations on CH₄ + Ni(111) indicating the need for modeling the bending vibrations of CH₄,⁶² point to the desirability of a quantum dynamical model treating all molecular motions.

We expect that at first, progress in the quantum dynamical treatment of polyatomics reacting on surfaces will be made by developing reduced dimensionality models treating more than one vibrational mode of the molecule, as is already being done for gas-phase reactions of CH₄ with atoms.⁶³ Ultimately, the promising quantum dynamical approaches for many-degree-of-freedom systems that are now being developed^{64,65} will also facilitate calculations in which all degrees of freedom of the polyatomic molecule are treated. These calculations will lead to a deeper understanding of reaction mechanisms, as the six-dimensional quantum dynamics calculations have already done for dissociation of H₂ on metals.

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