Final Scientific/Technical Report

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Title:	Theory of the reaction dynamics of small molecules on metal surfaces
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Abstract:

The objective of this project has been to develop realistic theoretical models for gas-surface interactions, with a focus on processes important in heterogeneous catalysis. The dissociative chemisorption of a molecule on a metal is a key step in many catalyzed reactions, and is often the rate-limiting step. We have explored the dissociative chemisorption of H_2, H_2O and CH_4 on a variety of metal surfaces. Most recently, our extensive studies of methane dissociation on Ni and Pt surfaces have fully elucidated its dependence on translational energy, vibrational state and surface temperature, providing the first accurate comparisons with experimental data. We have explored Eley-Rideal and hot atom reactions of H atoms with H- and C- covered metal surfaces. H atom interactions with graphite have also been explored, including both sticking and Eley-Rideal recombination processes. Again, our methods made it possible to explain several experiments studying these reactions. The sticking of atoms on metal surfaces has also been studied. To help elucidate the experiments that study these processes, we examine how the reaction dynamics depend upon the nature of the molecule-metal interaction, as well as experimental variables such as substrate temperature, beam energy, angle of impact, and the internal states of the molecules. Electronic structure methods based on Density Functional Theory are used to compute each molecule-metal potential energy surface. Both time-dependent quantum scattering techniques and quasi-classical methods are used to examine the reaction or scattering dynamics. Much of our effort has been directed towards developing improved quantum methods that can accurately describe reactions, as well as include the effects of substrate temperature (lattice vibration).

This Final Report covers nearly 29 years of work, and 80 publications. Here, we divide the work into five general areas: H_2-metal interactions, gas-surface sticking, Eley-Rideal reactions, H-graphite/graphene interactions, and the dissociative chemisorption of methane on metals. For each topic we provide a brief overview and discuss the key findings. Details can be found in earlier Progress Reports. We conclude with a discussion of our most recent work, taking place since our last Progress Report (Feb. 2015).

In 1987 our group published the first time dependent quantum dynamics studies of the dissociative chemisorption of H_2 on a metal surface [1]. We followed this 2-DOF (degree of freedom) study with several others that used mixtures of quantum with classical mechanics to include additional molecular DOFs [12, 15, 16]. These new (at that time) wave packet methods were also used to explore the rotationally and vibrationally inelastic scattering of H_2 from metal surfaces [5,6,8]. We examined how the probability for dissociative chemisorption or ro-vibrational excitation varied with collision energy, vibrational state and isotope (H_2 vs HD vs D_2). We also examined how features of the potential energy surface (PES) modified the dynamics, using model potentials, though little was known about the "true" PESs at that time. Another result of this early work was to show that these quantum wave packet methods worked well for these processes, and several groups adapted them around this time, many working on H_2 dissociation, slowly adding additional molecular DOF as computer power increased. We moved on to more difficult problems, though we have done some H_2 studies since, in collaboration with other groups [32, 63].

The other focus of our earliest work was to develop quantum mechanical models for gas-surface sticking, where a particle collides with a surface and traps in the attractive well by exciting one or more phonons (quantized lattice vibrations) [2-4,7, 9-11]. Using our quantum wave packet methods to treat an incident He, Ne or Ar atom, we expanded the total wavefunction in a basis set describing several phonon excitations and de-excitations. This allowed for a fully quantum description of sticking, including quantization of the gas-metal bound states. Of interest was the variation of the sticking probability with collision energy, particle mass, well depth, phonon coupling and surface temperature. Agreement with available experimental data was reasonable for these studies, again using model potentials.

Starting around 1988, several experimental groups began to report observations of Eley-Rideal (ER) reactions. In an ER reaction, a particle entering from the gas phase reacts with another particle adsorbed on a surface. While this mechanism had long been proposed as likely to be important in some catalytic and etching reactions, these were the first molecular beam studies of the dynamics. Working with Mats Persson (Chalmers, Liverpool), we developed the first quantum models for ER processes, studying H(g) + H/metal, H(g) + Cl/metal and H(g) + H/Si reactions, first with only 2 molecular DOFs [13,14,17,18]. We later extended this to a full dimensional treatment for a flat metal surface [19-

21,23,25-31]. This latter approach was improved using discrete Bessel transform methods [33], in collaboration with Didier Lemoine (Lille, Toulouse), and applied to several reactions under experimental study [33,37,40-44]. There were several major findings. First, we showed that the 2-DOF models used by us (and later others) gave misleading results, and it was necessary to compute a proper 3D scattering cross section. Second, for the H(g) + H/metal reactions, we showed that the cross section for a direct ER reaction was actually very small, while the cross section for adsorbate-mediated trapping was large. Thus, the incident H scattered from the adsorbed H, trapping on the metal. However, relaxation of the trapped H was slow, due to the small H-to-metal atom mass ratio, and this trapped "hot" H atom eventually reacted with an adsorbed H to give H_2 before fully relaxing. We showed that the product H_2 resulting from these "hot-atom" reactions was highly excited, vibrationally, just as for the more direct ER reaction. Around this time we began to use DFT (Density Functional Theory) to compute our PESs, eventually developing a full 6-DOF PES for H atom recombination on Cu(111)[28]. Quasiclassical trajectory (QCT) studies on this PES gave excellent agreement with experiment with regard to the rotational and vibrational state distributions in the desorbing H_2 product [30], supporting our earlier hypothesis regarding hot-atom reactions. Similar DFT-based studies of H(g) + Cl/Au [42,43,48] helped to elucidate this reaction, though strong phonon or electron hole pair damping of the product HCl was necessary to explain the experiments. We predicted that a sizable ER cross section was possible for the H(g) + H/graphite reaction [31, 37], and this was later confirmed by experiment [40,41]. QCT studies on large moving slabs of Ni(100) helped us to better understand the effects of lattice motion on ER reaction, trapping and hot atom relaxation [34,39]. Studies involving many adsorbates [39] helped us develop kinetic models for these reactions that were useful in interpreting some experiments [36]. Overall, our work has significantly impacted and helped to define the field of ER and hot-atom reactions.

During the period of our ER studies, we began to examine the interactions of H with graphite and graphene. This is relevant to processes occurring in fusion reactors and interstellar space, and to the modification of the electronic properties of graphene. Our earliest DFT study showed that chemisorption of H involved a significant puckering of the carbon lattice [35] (278 citations!). Subsequent studies of H(g) + H/gr ER reactions using our DFT-based PES showed that the ER cross section was large, as noted [37,40,41]. Subsequent work has examined H chemisorption and physisorption [45,47,49,53,54,60,62,71]. One chemisorption study examined H adsorption on various edge and defect sites, relevant to H-storage experiments [45]. Several other studies focused on chemisorption on a terrace carbon [47,49,53], where there are two complications arising from the need to pucker the carbon lattice. First, this results in a barrier. Second, the slower lattice atoms might not be able to move/pucker on the timescale of an H atom collision. We constructed DFT-based models that eventually included 121 moving lattice atoms [53], which was used in a QCT study of sticking. We concluded that while initial

(bare surface) sticking cross sections were small, the chemisorption of H lead to lower barrier chemisorption pathways at sites adjacent to the chemisorbed H. Finally, we have made several studies of H physisorption at low energy and temperature [54,60,62,71], using a rigorous fully quantum treatment based on the reduced density matrix [50,54]. These studies used DFT-based PESs and phonon couplings, and surface corrugation was included. This latter effect is important, as trapping can be enhanced by diffraction. Our approach compared favorably with a more traditional quantum basis set approach [60], and we made several, as yet untested, predictions regarding diffraction–mediated trapping of H on graphene [62,71].

The bulk of our work since 2007 has focused on the dissociative chemisorption of methane on metal surfaces [51,52,55-59,61,64-70,72-75,78-80], the rate-limiting step in the steam reforming of natural gas. Our DFT studies of methane dissociation on Ni(111) found that at the transition state the molecule is almost directly over a metal atom, and when this atom vibrates in and out of the plane of the surface, the barrier to dissociation increases and decreases, respectively [51,52]. Quantum scattering calculations including several key methane DOFs, as well as the motion of the metal atom over which the reaction occurs, showed that the reaction probability was significantly larger than for a static lattice, and strongly increased with temperature [51,52]. Studies of how lattice motion effected methane dissociation led to the development of sudden models, where quantum calculations were implemented for several frozen lattice configurations, sampled at the substrate temperature [56,58]. These approaches reproduced the quantum results, and because motion of the heavy metal atom was not explicitly included in the wave function, the computations were two orders of magnitude faster. Subsequent DFT studies found that lattice motion modifies the energetics of methane dissociation in a similar fashion on Ni(100), Pt(100), Pt(111) and the stepped Pt(110)-(1x2) surface [55,57].

Significant progress in modeling methane reactions and understanding bond-selective and mode-specific chemistry has been made using a formulation based on the Reaction Path Hamiltonian (RPH). Assuming that the PES is harmonic with respect to displacements away from the reaction (or minimum energy) path, we use DFT to compute a reasonably accurate PES that includes all 15 molecular DOF. We computed the RPH for methane dissociation on Ni(100), and derived close-coupled equations for the total wavefunction by expanding in the adiabatic vibrational states of the molecule [59]. This was then used to compute full 15-DOF dissociative sticking probabilities for methane dissociation on Ni(100), using sudden models to average over surface impact sites and to introduce the effects of lattice motion [61]. These were the first calculations containing all relevant DOF from first principles that could be compared directly with experiments (receiving an *Editor's Choice Award* from *J. Chem. Phys.*). We demonstrated how the efficacies for vibrational enhancement are related to transitions from higher to lower energy vibrationally adiabatic states, with the excess energy going into motion along the reaction path, which

corresponds to bond breaking at the transition state. Agreement with experiment was good, in terms of both the magnitude of the reactivity over a broad range of incident energies, and the efficacies of the different vibrational modes for promoting reaction. More importantly, our approach made it possible to follow the flow of energy within the molecule as it dissociates, providing a detailed understanding of how translational, vibrational and lattice energy contribute to dissociative sticking. Our next study [65] applied this approach to methane reactions on Ni(111), motivated by experiments from the Utz (Tufts) and Beck (EPFL) groups. In particular, Utz' most recent measurements of methane dissociative sticking probabilities over a wide range of surface temperatures allowed for the first real test of our models for introducing the effects of lattice motion. Our methods were able to accurately describe the observed variation in reactivity with collision energy and vibrational state, over several orders of magnitude, as well as the variation with temperature [65,78]. We were able to explain why this variation was strong at some energies and weak at others. We also examined the dissociative chemisorption of CH_4 on Pt(110)-(1x2), where the missing-row reconstruction leads to a very large surface corrugation, making this a model for actual (rough) catalysts [66]. We found that the edge sites were the most reactive, as expected, and that the phonon coupling was far more complicated than for smooth Pt surfaces, involving the motion of several lattice atoms. However, we showed that the net effects of lattice motion were not any larger than on smoother surfaces, due to cancellations as the metal atoms vibrated out of phase. We were also able to model and explain the variation in reactivity with nozzle temperature due to contributions to sticking from vibrationally excited molecules [65,66].

QCT methods and *ab initio* molecular dynamics (AIMD) are important tools for these complex systems, and it is important to understand their limitations. We applied QCT methods to our RPH to examine methane reactions on Ni(100) and Ni(111), and found that classical methods did a good job at describing the reactions of vibrationally excited molecules, but that they overestimated the reaction probability of molecules in the ground vibrational state [68]. This was due to an unphysical flow of the substantial (about 1.2 eV) zero point energy (ZPE) into other molecular DOFs. As part of a four-way collaboration, we are working with the Kroes (Leiden) group to use AIMD to study CHD_3 dissociation on Pt(111) and Ni(111), while the Utz and Beck groups do the corresponding experiments. Part of the motivation is to test DFT functionals, but our first studies [70,72] told us many important things. First, there is little translational steering, so our sudden models for impact site averaging are likely reasonable. However, there is little rotational steering, and our rotationally adiabatic approximation is probably inaccurate. We thus developed a way to correct our quantum RPH model to describe rotationally sudden behavior [72]. The agreement with experiment was greatly improved for the ground state reactivity on Ni(111).

Nearly all theoretical studies of dissociative chemisorption focus on zero-coverage sticking probabilities, but in the experiments, and on real catalytic surfaces there can be significant reactant and product coverages. Experimental studies of CH_4 dissociation on Pt(111) by the Beck group show that the saturation coverage of the product CH_3 on the surface increases with both the translational energy and vibrational excitation of the incident molecule, suggesting a coverage dependent barrier to dissociation. We used DFT to examine how the dissociation barrier is modified by the presence of chemisorbed H and CH_3 fragments, and found that this barrier increases with the surface coverage of reaction products [67]. Using our DFT results, we developed kinetic models that were able to reproduce and explain the saturation behavior observed in the experimental uptake curves [67].

We explored both mode- and bond-selective chemistry more closely in a study of CHD_3 dissociative chemisorption on Ni(111) [74]. In addition to reproducing the experimentally observed strong enhancement in C-H cleavage selectivity with excitation of the ν_1 stretch, we were able to explain it in terms of mode softening, and how the vibrationaly nonadiabatic coupling keeps vibrational energy localized on the reactive bond. Examining both CH_4 and CHD_3 reactions on Ni surfaces, we argued that this behavior, in combination with how symmetry effects the vibrationally non-adiabatic couplings, should lead to larger efficacies for promoting reaction for symmetric stretches over antisymmetric stretches, even though these two types of vibration typically have similar energies.

In the year and a half since our last Progress Report, we have completed three projects. The dissociative chemisorption of H_2O, HOD and D_2O on Ni(111) was explored using our RPH approach [75], motivated by recent experimental results from the Beck group. Mode-selective chemistry was observed, as for methane, with both stretch modes strongly enhancing reactivity. The effects of lattice motion were more complicated than for methane, with several types of motion able to modify the barrier to reaction. Reasonable agreement with experiment required a rescaling of the barrier height, but this is not unexpected given the nature of DFT. Second, we contributed to two studies that used statistical models to examine the scattering and sticking of H atoms on graphene surfaces [76,77]. Our contributions to this work involved modeling the lattice dynamics of a large graphene cluster. Third, we finished a detailed study of the dissociative chemisorption of methane on Pt(111), using a newly developed PES for this surface [79]. Detailed comparison were made with these reactions on Ni(111), using a new PES for this surface also (larger supercells than in earlier work). We also developed an improved model for describing the motion of the atoms on the surface of the metal [79]. Overall, these modifications led to a much better agreement with experiments on both metals, as well as recent AIMD studies. While reaction probabilities were larger on Pt due to lower barrier heights, the Ni reactions exhibited more vibrational enhancement due to the larger vibrationally nonadiabatic couplings.

We have made significant progress on five new projects [80-84]. Working with the Utz experimental group, we have been trying to understand why the symmetric and antisymmetric stretch states of CH_2D_2 have similar reactivities on Ni(111) [81]. This is different from what has been observed for the dissociation of other isotopologues of methane on several metals. Using our RPH approach, we have shown that these two states become mixed in the entrance channel due to the molecule's interaction with the surface. Our results are in excellent agreement with the experiment over all energies measured [81]. A second project, also being written up, explores the reactions of CH_4 molecules excited to the $2\nu_3$ (antisymmetric stretch) state, on Ni(111) [82]. Anharmonicity splits this state into three components, with A_1, E and F_2 symmetry. The Beck group has measured the probability for dissociative chemisorption for these three states, and they are, surprisingly, different. We have been able to reproduce and understand this behavior using our RPH model. We can describe these different states using linear combinations of normal modes, within our RPH approach. States containing more stretch character are more reactive [82].

We have begun to look at the dissociative chemisorption of CO_2 on smooth Ni(100) and the stepped Ni(711) [83]. The Jurrlink group (Leiden) has experiments planned for the latter surface, and other data exists for the former. We find that the coupling to the lattice motion on Ni(100) is far more complex for this reaction than for methane. Initial scattering studies suggest that the incident CO_2 initially traps in a bent physisorbed molecular state, thermalizes, then dissociates [83]. Vibrational enhancement is minor. The lattice effects for sticking on Ni(711) appear to be even more complicated, involving the motion of many metal atoms. Similar behavior has been observed for methane dissociation on the stepped Pt(211) and Ni(211) surfaces [84], as again, the motion of several atoms can modify the barrier height. It is likely that reactions on real catalysts take place on steps and other defect sites, and we are exploring how the dynamics, lattice effects and mode specificity differ on these sites. Scattering calculations on Pt(211) are only now starting. In a recently submitted invited Perspective in *J. Phys. Chem. Lett.*, we have presented these new results for the lattice coupling, comparing with the behavior observed for other molecules on other metals [80]. The strong lattice motion effects found for methane dissociation are likely to be important in a great many gas-surface reactions.

Finally, we note that this DOE-funded work has been summarized in several book chapters and review articles [22,26,44,64,69,73], and that we have engaged in a few minor projects not part of any major initiative (and not discussed here) [24,38,46].

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