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Cutting a chemical bond with demon's scissors: Mode- and bond-selective reactivity of methane on metal surfaces

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ABSTRACT

In this paper we discuss several aspects of methane reactive sticking on Pt(111) in the light of supersonic molecular beam experiments (including state-resolved measurements) and quasi-classical trajectory calculations based on an accurate reaction specific reactive force field constructed from Density Functional Theory (DFT) data. With the aim of understanding the origin of the full bond selectivity recently achieved experimentally and to predict how selectivity depends on the collision conditions, we discuss in detail, the role of initial translational and (mode-specific) vibrational energy of CH_4 and all its deuterated isotopomers, as well as surface temperature effects. Last but not least, the systematic and detailed theoretical analysis presented here serves as an illustration of the possibilities and usefulness of accurate reaction specific reactive force fields built from DFT data. This approach allows investigating dynamical aspects of the interaction of polyatomic molecules on surfaces through quasi-classical trajectory calculations accounting for the full dimensionality of the system (including both molecular and surface degrees of freedom): something that a few years ago was just a dream for the gas–surface dynamics community.

1. Introduction

James Clerk Maxwell, the great Scottish physicist, conceived an imaginary creature capable of realizing some processes unlikely to happen in reality, e.g., turning a cup of well mixed milk tea into two layers with the milk on top and the tea at bottom. Such an imaginary creature is now named as Maxwell demon and usually used by physicists to describe some thought experiments. Chemists resort seldom to such a demon to describe whatever processes in chemical reactions. Nevertheless, we will show that the bond-selective reactivity in the dissociative adsorption of methane isotopomers on some metal surfaces looks quite like the action of a Maxwell demon.

The dissociative adsorption of light hydrocarbons on transition-metal surfaces is a key step in various technologically important processes, e.g., catalytic steam reforming, and growth of graphene by chemical vapor deposition [1–5]. A large number of experimental results are now available for methane dissociation on Ni and Pt surfaces and this makes such systems the benchmarks for reactions of polyatomic molecules on metal surfaces. Reactive scattering experiments using supersonic molecular beams with resolved initial states have revealed unambiguously mode- and bond-selective reactivity of methane on Ni and Pt surfaces [6–10]. Many chemical reactions can take place only when an activation energy is provided, e.g., the cleavage of one C–H bond in a methane molecule upon its collision with a Pt(111) surface requiring at least ~ 0.8 eV. The very characteristic feature of the mode-selective reactivity is that the activation efficiency depends not only on the amount of energy but also on the way in which it is imparted to the molecule. It was shown experimentally that the energy deposited into a vibrational mode (in particular, a stretching mode) is more efficient for dissociating a methane molecule on Ni(111) than depositing the same amount into the translational degree of freedom (DOF) of the center of mass of the molecule [6,8]. Furthermore, Beck et al. [7] have shown that a roughly equal amount of energy deposited into two vibrational modes, one stretching a single C–H bond of CH_2D_2 and the other stretching both of them, results in a higher dissociation probability of the molecule on Ni(100) for the former.

All the partially deuterated isotopomers of methane have the same electronic structure. Thus, the activation energy is the same for cleaving a C–H or a C–D bond. Therefore, from the point of view based purely on energetics, achieving a selective scission of one of the two types of bonds seems to be possible only for Maxwell demon. Nevertheless, the different masses of H and D atoms result in different stretching modes for C–H and C–D bonds. By exciting precisely a mode stretching a C–H bond with a laser, the groups of Utz and Beck have succeeded in achieving the full selective cleavage of a C–H bond of some deuterated methane isotopomers upon its collision with Ni(111) [10] or Pt(111) surfaces [11], respectively.

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Before the experiments revealing the mode- and bond-selective reactivity of methane on Ni and Pt surfaces, there were two competing theoretical models, based on very different assumptions, to account for the methane dissociative adsorption on metal surfaces. One is a statistical model based on the assumption that the adsorbate–surface collision complex allows for very fast energy redistribution between different DOFs [12–14]. Due to the fast randomization of energies associated with different DOFs, only the total amount of energy of the molecule matters and the statistical model does not predict any mode- or bond-selective reactivity. The inadequacy of such an assumption has been revealed unambiguously by the experimental finding of mode- and bond-selective reactivity of methane on Ni and Pt surfaces.

Another model relies on the dynamical description of reacting systems. As surface reactions are concerned, the dissociative adsorption of a diatomic molecule on a solid surface has been studied most extensively with the hydrogen dissociation on various metal surfaces as one prototypical reaction [15–19]. The two basic ingredients of a dynamic model are 1) a potential energy surface (PES) and 2) a method for describing the dynamics of the reacting system. The degree of difficulty for studying a given system is determined by the complexity and some key characteristics of its PES, e.g., dimensionality, landscape, barrier height, etc. Within the approximation of a rigid substrate, the PES for the dissociation of a diatomic molecule on a solid surface is a six-dimensional (6D) one. Now, various methods exist for constructing reliable 6D PES for the dissociative adsorption of diatomic molecules on solid surfaces (see e.g., Refs. [20] and [21] as well as references therein). However, many successful methods for constructing PES of diatomic molecules, in particular those based on interpolation, can be hardly extended to deal with PES of higher dimensionality. Therefore, building a reliable PES which accounts for all the DOFs of methane and also those of the surface atoms on an equal footing is already a theoretical challenge.

Early investigations on the dissociation dynamics of methane on metal surfaces have been carried out with quantum dynamics methods. Such methods are computationally very demanding and the state-of-the-art ones can only afford an explicit description of about a dozen of DOFs. For quantum dynamics investigations, it is necessary to simplify the description of the system in order to reduce the DOFs to be considered explicitly. Some early studies have been made with a drastically simplified model, i.e., quasi-diatomic model which treats the methyl group as a single entity [22–26]. The quasi-diatomic model has some obvious drawbacks. First, the vibration spectrum of such a model has nothing to do with the true spectrum of methane. Hence, this excludes any attempt to study mode-selective reactivity. Since there is only one cleavable bond in this model, it is also out of the question to study bond-selective reactivity. To alleviate the severe limitations of the quasi-diatomic model, Jackson and Nave have proposed a more elaborate model, called reaction path Hamiltonian (RPH) [27,28]. In this model, the stretching of one C–H bond along the minimum energy path is fully described while all the other DOFs perpendicular to the reaction coordinate are modeled by a harmonic approximation. The improvement provided by this model with respect to the quasi-diatomic model is that it gives the correct vibration spectrum of an isolated methane molecule within the harmonic approximation and thus allows for investigating the mode-selective reactivity. It is worthwhile to note that the reaction path Hamiltonian inherits also some characters of the quasi-diatomic model. Since only the stretching of one C–H bond is fully described and the stretching of the other three C–H bonds is described with a parabolic potential which does not allow for bond breaking, the RPH is a model with only one cleavable C–H bond like the quasi-diatomic model and thus prevents studying the bond-selective reactivity.

Recently, Guo's group has constructed a 12D PES for CH_4/Ni(111) in order to carry out a quantum dynamics study [29]. The strategy for reducing the number of DOFs was applied directly in the dynamics calculation by imposing the C_{3v} symmetry to the methyl group. Because of this symmetry constraint, the three C–H bonds of the constrained methyl group are stretched or compressed simultaneously. In principle, these three bonds can be broken at the same time but such a simultaneous cleavage of three C–H bonds costs much energy and does not take place without the supply of a huge amount of energy. The imposed C_{3v} symmetry modifies the vibration spectrum of the molecule with in principle all the modes being affected except the totally symmetric one. This renders impossible the study of mode-selective reactivity for some modes, i.e., those most affected by the symmetry constraint. Moreover, imposing the C_{3v} symmetry predestines the cleavable C–H bond and thus excludes the possibility to study bond-selective reactivity. Both the RPH proposed by Jackson and Nave and the model studied by Guo's group can be qualified as models with one-active C–H bond. To the best of our knowledge, quantum dynamics calculations have been performed only for such models with only one-active C–H bond until now. It is to note also that in the quantum dynamics studies reported so far, the translational DOFs of methane parallel to the surface were not considered explicitly (to reduce the total number of DOFs) and dynamics calculations were performed only for the incidence of the molecule at a top site. The effect of the impact points at the surface was accounted for by an ad hoc post-treatment [26,27,29,28].

Experiments showed that surface temperature has a significant effect on the sticking probability of methane on metal surfaces, in particular for the molecule at low incident energies [30–32]. Accounting for the surface temperature the effect from first principles requires explicit consideration of the DOFs of surface atoms in dynamics calculations. This is far beyond of the capability of any state-of-the-art quantum dynamics method and appears out of reach of such methods even in the foreseeable future. In all the previous quantum dynamics studies, the surface temperature effect has been treated with some ad hoc approximations [27].

Once an approach for determining the interatomic forces is prescribed, quasi-classical molecular dynamics (QCMD) simulations can be carried out also for studying surface reaction dynamics. In the case that a preconstructed PES is available, the straightforward calculation of interatomic forces allows fast molecular dynamics (MD) simulations to be performed within the framework of quasi-classic method. As already pointed out above, some of the established interpolation methods to construct a PES for diatomic molecules interacting with surfaces [33], cannot be easily extended to consider polyatomic molecules or the surface degrees of freedom. Reactive force fields (RFFs) provide an alternative approach capable of dealing with, in principle, much more DOFs. For the dissociative adsorption of hydrogen on Pd(111), we have shown that a carefully parameterized RFF allows for describing adequately the effect of surface temperature by dealing with the DOFs of the substrate on an equal footing of the adsorbate DOFs [34,35]. Recently, we have also demonstrated the feasibility of constructing accurate PES by using RFFs for methane dissociation on Ni and Pt surfaces [36]. These RFFs render now possible full-dimensional MD simulations of the dissociative adsorption of methane on Ni(111) and Pt(111) surfaces, including even the DOFs of the substrate.

QCMD simulations can be performed also with an ab initio molecular dynamics (AIMD) method in which the interatomic forces are calculated on the fly from highly time-consuming electronic-structure calculations. AIMD has been applied by Groß and co-workers to study hydrogen dissociative adsorption on Pd surfaces [37,38]. But, for the dissociation of methane on a metal surface, AIMD simulation becomes much more complicated since the dissociation probability is lower by several orders of magnitude than that for hydrogen dissociation on a transition metal surface and a huge number of trajectories are needed to obtain statistically meaningful results ($\sim 10^6$ in the region of low incident energies). Nevertheless, Nattino et al have reported recently some results for CHD_3/Pt(111) of AIMD calculations performed in the region of high incident energies where the dissociation probability is relatively high [39].

In this feature article, we will summarize the key characteristics of the reactive force fields we developed for describing methane dissociative adsorption on a metal surface. We show also how our approach allows for addressing an important issue unexplored theoretically until recently, i.e., simulating bond-selective reactivity and predicting new possible