Towards Bond Selective Chemistry from First Principles: Methane on Metal Surfaces

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Controlling bond-selective chemical reactivity is of great importance and has a broad range of applications. Here, we present a molecular dynamics study of bond selective reactivity of methane and its deuterated isotopologues (i.e., $CH_{4-x}D_x$, $x = 0,1,2,3,4$) on Ni(111) and Pt(111) from first principles calculations. Our simulations allow for reproducing the full C-H bond selectivity recently achieved experimentally via mode-specific vibrational excitation and explain its origin. Moreover, we also predict the hitherto unexplored influence of the molecular translational energy on such a selectivity as well as the conditions under which the full selectivity can be realized for the *a priori less active* C-D bond.

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Bond selective chemistry is of great importance for many technological applications, including heterogeneous catalysis, surface and nanostructure functionalization, etc. For instance, achieving high selectivity is one of the major goals in catalysis because this allows for producing preferentially the desired products [1]. Therefore, elucidating and controlling the factors that promote the cleavage of a specific bond of a polyatomic molecule is of great fundamental importance and tremendous practical usefulness. This is certainly why bond-selective reactivity on surfaces has attracted so much attention during the last decade, with the partially deuterated isotopologues of methane (i.e., $CH_{4-x}D_x$, $x = 1,2,3$) being the usual benchmark molecules for experiments [2–8]. The challenge of bond selectivity with $CH_{4-x}D_x$ is the ability of selecting the cleavage of the C-H or C-D bond, despite their same activation energy. Thus, a branching ratio of C-H (or C-D) cleavage similar to the fraction of C-H (or C-D) bonds in the molecule corresponds to a statistical (or weak) selectivity, whereas full selectivity is attained if only one type of bond (C-H or C-D) is cleaved.

Initial-state-resolved measurements using supersonic molecular beams have provided unambiguous evidence for vibrational-mode- and bond-specific reactivity of CH_4 and its deuterated isotopologues on both Ni(111) and Pt(111) surfaces. Full C-H bond selectivity was achieved by exciting a C-H stretching mode before the collision, in sharp contrast with the statistical selectivity observed under laser-off experimental conditions (i.e., most molecules in the vibrational ground state, GS) [4,7]. Since such selectivity has been hitherto studied for a single initial total energy of the molecules for each case of Ni(111) [4] and Pt(111) [7], it is, for instance, not known how the bond selectivity varies as a function of the molecular translational energy. Moreover, until now, full selectivity has been achieved only for the cleavage of the C-H bond, which is *a priori*, more active than the C-D one [9]. Whether and how fully selective cleavage of the less active C-D bond can be realized remains an open issue. This deserves in-depth investigations, particularly in view of the counterintuitive results of a recent cross beam experiment showing that exciting a stretching vibrational mode can sometimes even be unfavorable for cleaving the targeted bond [10]. This illustrates the complexity of surface reaction dynamics involving polyatomic molecules and the risk of making unreliable predictions even based on educated intuition.

Molecular dynamics (MD) is a powerful tool to investigate reactzion dynamics at surfaces. However, an accurate and computationally affordable method for describing surface reaction dynamics of polyatomic molecules including surface atom degrees of freedom (DOF), has been long-time expected (see, e.g., [11,12]). Thus, to our knowledge, no MD simulation dealing with bond selective reactivity for methane on surfaces has been reported. On one hand, quantum MD (QMD) methods have not yet gone beyond the only-one-active-bond approximation (see, e.g., [13–19]) which prevents investigating bond selectivity because at least two active (i.e., cleavable) bonds are required. On the other hand, the very low dissociation probability of methane on metal surfaces ($\sim 10^{-4}$–10^{-2}) [20] hampers extensive classical *ab initio* MD (AIMD) simulations [21,22] in which the interatomic forces are calculated on the fly from density functional theory (DFT) [23,24]. Finally, for polyatomic molecules, the use of the divide and conquer strategy employing an analytical or numerical potential energy surface (PES) (successful for diatomic molecules [25–27]), is hindered by the difficulty of building accurate PESs of dimensionality much higher than 6.

In this work, we report the results of a quasiclassical MD (QCMD) study of the dissociative adsorption of $CH_{4-x}D_x$ ($x = 0,1,2,3,4$) on Ni(111) and Pt(111), based on two accurate system-specific reactive force fields (RFF) parametrized from DFT total energy data. Through simulations treating all the molecular and surface DOFs on an equal footing, we have obtained C-H bond selectivities and vibration-mode-specific reactivities in excellent agreement with experiments. Moreover, we have investigated the so far barely explored influence of the molecular translational energy on the bond selectivity and predict the conditions under which full C-D selectivity can be also attained even for the statistically most unfavorable case of CH_3D.

In order to describe the methane-surface interaction, we carried out first DFT calculations for $CH_4/Ni(111)$ and $CH_4/Pt(111)$ which were then used to parametrize the RFFs. The (111) surfaces have been modeled by a five layer slab and a (3×3) unit cell with a vacuum space between consecutive slabs corresponding to six metal layers (see the Supplemental Material [28]). The procedure used to generate the RFFs is similar to that successfully implemented recently by some of us for H_2/Pd [29]. The analytical expression of the RFFs and the optimum parameters obtained for both systems can be found in the Supplemental Material [28]. Each input database contains $\sim 10^4$ DFT total energies for (i) equilibrium and distorted configurations of both CH_4 and the surface far from each other, most of them extracted from AIMD calculations, (ii) configurations visited during our own search of saddle points of the PESs reported previously [30], with and without surface relaxation, (iii) configurations of methane over various high symmetry surface sites and different molecular orientations, (iv) configurations selected from QCMD calculations based on the preliminary versions of the RFFs, and (v) configurations visited by a few AIMD trajectories for various initial molecular translational energies and vibrational states.

A full description of the procedure to generate the RFFs and the tests of accuracy (including the comparison of the geometries and energies of various saddle points predicted by the RFFs and DFT calculations) will be presented elsewhere [31]. Here we simply mention that DFT results are well reproduced by our RFFs, with discrepancies being, in the interatomic distances at transition states $\lesssim 0.1$ Å, and in activation energies $\lesssim 10\%$. In addition, the RFF vibrational spectra of CH_4 and all its deuterated isotopologues in vacuum are in excellent agreement with the experimental ones: the same level ordering and numerical discrepancies smaller than ~ 100 cm^{-1} (i.e., ~ 0.01 eV). This is particularly important for our present purpose to study mode- and bond-selective reactivities. Ascertained also by other stringent tests of accuracy [31], our RFFs provide a description of the DFT energetics of methane reactive and unreactive scattering from both Ni(111) and Pt(111), with errors similar to the uncertainties of DFT (with semilocal approximations) itself [32].

The QCMD calculations to evaluate the reactive initial sticking probability S_0 as a function of the incident translational energy E_i (at normal incidence and for initially nonrotating molecules) are described in the Supplemental Material [28]. For comparison with the experiments, our simulations for Ni(111) and Pt(111) were carried out for surface temperatures 475 and 150 K, respectively, with the help of a Berendsen thermostat and the metal atoms of the two top layers are mobile.

Figure 1(a) shows that the theoretical C-H branching ratios are in excellent agreement with the available experimental data for all the partially deuterated isotopologues of methane on Pt(111) [7]. For CHD_3, CH_2D_2, and CH_3D initially in their vibrational GS, the branching ratio is close to the statistical one. In contrast, the fully selective cleavage of the C-H bond is achieved when a C-H stretching mode is excited before the collision of the molecules with the surface. Interestingly, such a drastic change of bond selectivity is found in spite of keeping constant the initial

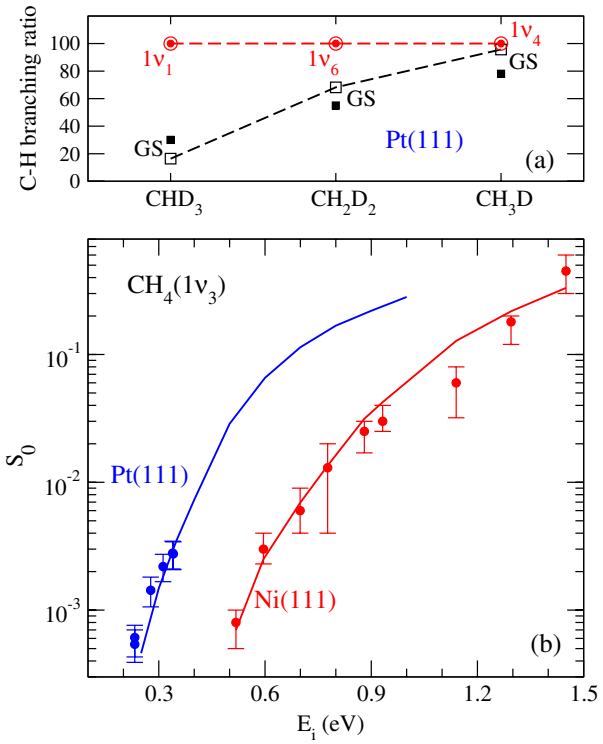

FIG. 1 (color online). (a) Branching ratio of C-H bond cleavage for $CH_{4-x}D_x/Pt(111)$ ($x = 1,2,3$). Open symbols represent the theoretical results of this work and filled symbols the experimental data from [7]. Circles: vibrationally excited molecules (vibration mode indicated near the corresponding data) for $E_i = 0.25$ eV; squares: molecules in the vibrational GS (under laser-off conditions in the case of experiments) for $E_i = 0.55$ eV. Dashed lines connecting theoretical results are plotted to guide the eyes. (b) Experimental (symbols) and theoretical (lines) reactive initial sticking probability, S_0, for $CH_4(1\nu_3)$ on Pt(111) and on Ni(111) as a function of the translational energy E_i at normal incidence. Experimental data taken from Refs. [8] (Pt) and [3] (Ni).

total energy (vibrational plus translational) of the molecules (vibrationally excited molecules have lower translational energies) [7].

Since the bond selectivity is achieved through a specific-mode vibrational excitation, there is a strong interplay between bond- and mode-specific features of reactivity [2]. Therefore, an appropriate description of mode-specific reactivity (in particular, for vibrationally excited states) is a prerequisite for a reliable theoretical study of bond selectivity. Our approach provides indeed such a description. In Fig. 1(b), we compare the S_0 values we have obtained for $CH_4(1\nu_3)/Pt(111)$ and $CH_4(1\nu_3)/Ni(111)$ with available experimental data and the agreement is also excellent. Our results account for the higher reactivity of Pt(111) with respect to Ni(111) due to a lower activation energy barrier in the former case by ~ 0.2 eV (present work and Ref. [30]). In addition, the E_i dependence of the experimental S_0 data for both surfaces is well reproduced and the theory-experiment agreement is quantitative [33]. This indicates that contrary to the usual belief of many years [13,15,34], and in line with recent investigations [35], methane dissociative adsorption is largely dominated by a classical over-the-barrier mechanism (even at low impact energies and low-surface temperatures).

Varying the number of H and D atoms in the methane isotopologues entails strong changes in the molecular vibrational modes which, in turn, determine the optimum conditions to achieve bond selectivity. Thus, bond selectivity and isotopic effects are coupled with each other. In Fig. 2, we present our results of S_0 (E_i) for $CH_{4-x}D_x$ on Pt(111) (for $x = 0,1,2,3,4$, and molecules in their vibrational GS). The reactivity of the deuterated isotopologues decreases when the number of D atoms x increases. The difference in S_0 we obtained for CH_4 and CD_4 is qualitatively the same as that obtained experimentally [36], in spite of the higher surface temperature in the experiments (i.e., 800 K). Unfortunately, the experimental E_i dependence of S_0 for partially deuterated isotopologues (i.e., $x = 1,2,3$) has not been reported for Pt(111). However, it is important to mention that the ordering of the S_0 (E_i) curves we have obtained for different values of x is the same as that found experimentally for tungsten surfaces [37]. All these results point to a reactivity of the C-H bond higher than that of the C-D bond. Since vibrations significantly affect reactivity, it is natural to look for a possible correlation between the ordering of the S_0 (E_i) curves shown in Fig. 2, and the ZPE values of $CH_{4-x}D_x$ which decrease when x increases. To shed further light on this issue, we calculated also the sticking curve for an *artificial* CD_4 molecule (hereafter referred to as CD_4^*) whose ZPE is set equal to that of CH_4. In the inset of Fig. 2, $S_0(CH_4)/S_0(CD_4^*)$ (red curve) is plotted as a function of E_i and a constant value close to 1 (i.e., $\sim$1.2) is observed. This shows clearly that the difference in ZPE between CH_4 and CD_4 is the main responsible for the isotopic effect observed in Fig. 2 and a detailed discussion of such effect will be presented elsewhere. It is interesting to note also that $S_0(CH_4)/S_0(CD_4)$ (black curve) decreases strongly from values as high as $\sim$20 at low E_i ($\sim$0.5 eV) to nearly 1 at high E_i. These results show that the role of vibrational energy on reactivity is more prominent at low translational energies and becomes relatively less important when E_i increases.

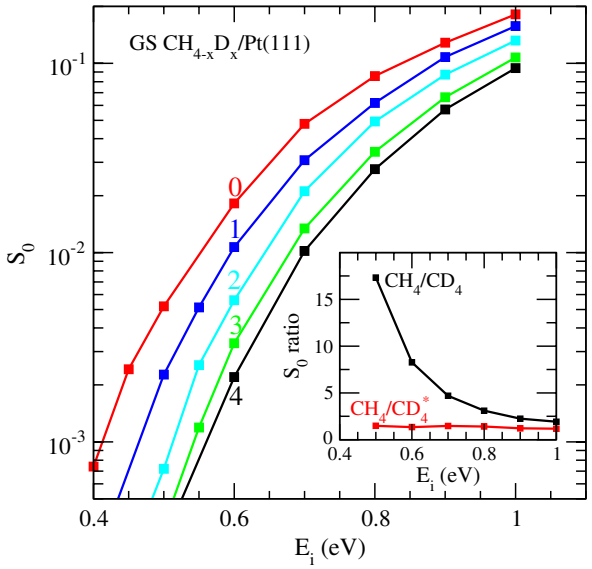

FIG. 2 (color online). Reactive initial sticking probability S_0 of $CH_{4-x}D_x$ molecules ($x = 0,1,2,3,4$) in the vibrational ground state (GS) on Pt(111) as a function of initial perpendicular translational energy E_i. Inset: ratios $S_0(CH_4)/S_0(CD_4)$ and $S_0(CH_4)/S_0(CD_4^*)$ (see text) as a function of E_i.

In Fig. 3, we report the theoretical branching ratios of the C-H bond cleavage on Pt(111) for $CH_{4-x}D_x$ ($x = 1,2,3$) in different initial vibrational states as a function of E_i. Our results show that the high C-H selectivity observed in Fig. 1(a) for $CHD_3(1\nu_1)$, $CH_2D_2(1\nu_6)$, and $CH_3D(1\nu_4)$, decreases with increasing E_i. Although no experimental report of such an E_i dependence has been made yet for methane interacting with surfaces, it is interesting to mention that a similar *loss* of selectivity has been observed in bimolecular reactions [38,39]. When E_i increases, the branching ratios of C-H and C-D bond cleavage tend to approach the corresponding statistical values. The loss of bond selectivity with increasing E_i reflects the fact that translational energy is not bond selective. At high translational energies the molecules approach closer to the surface and vibrational softening is strongest: the typical Morse-like effective C-X (X = H or D) interaction potential far from the surface, tends to become purely repulsive close to the surface when the atoms start forming new bonds with the metal. Thus, when E_i increases, the bond most likely to be cleaved (more and more irrespective of the vibrational energy initially stored in it) is that most involved in the molecule-surface interaction, i.e., the one

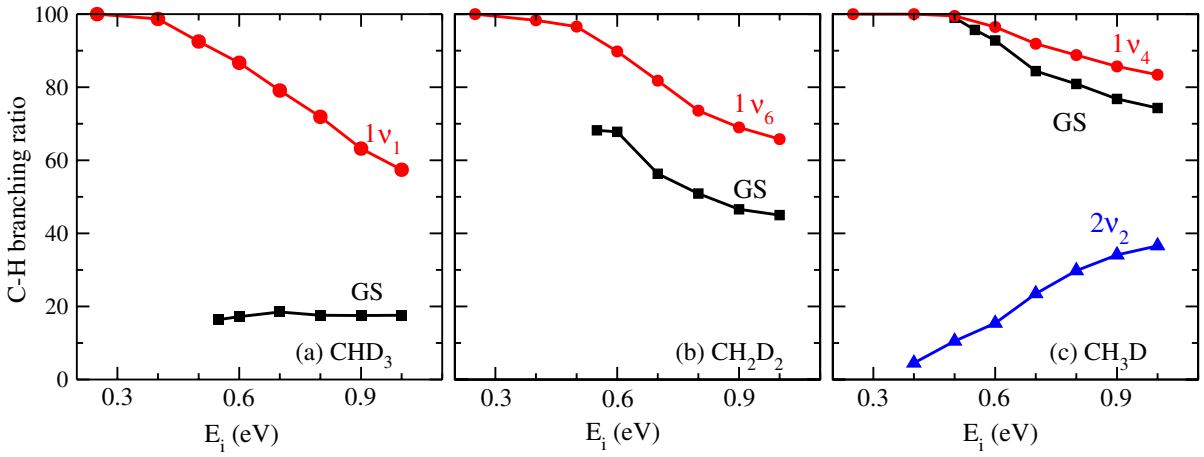

FIG. 3 (color online). C-H branching ratio as a function of E_i for $CH_{4-x}D_x/Pt(111)$ for various initial vibrational states. (a) $x = 3$, (b) $x = 2$, and (c) $x = 1$.

most favorably oriented for dissociation near the point of closest approach to the surface. Then, the loss of bond selectivity induced by stretching at high E_i can be explained, on one hand, by the nonselective character of the translational energy and, on the other hand, by the decreasing role of the initial vibrational energy when E_i increases (inset of Fig. 2 and [40]). This shows, in addition, that the mode-specific high selectivity observed experimentally [Fig. 1(a)] is due, to a large extent, to the low translational energies considered. Under such conditions, the vibrational energy initially deposited in a stretching mode promotes more efficiently the corresponding bond(s) scission than the non bond-selective translational energy.

To the best of our knowledge, full selectivity of a C-D bond in a partially deuterated isotopologue of methane on Ni(111) and Pt(111), has not been experimentally achieved so far. Hence, it is interesting to investigate the possibility of such a selective cleavage, in particular, for the most statistically unfavorable case, i.e., CH_3D. Therefore, we have computed $S_0(E_i)$ for $CH_3D(1\nu_2)$ and $CH_3D(2\nu_2)$ on Pt(111) (ν_2 being the localized C-D stretching mode of CH_3D). In both cases, an increased C-D bond selectivity is observed. Though full C-D selectivity cannot be reached for $CH_3D(1\nu_2)$ (results not shown), our simulation predicts that the full C-D selectivity can be achieved with the first overtone of ν_2, i.e., $CH_3D(2\nu_2)$, for $E_i \lesssim 0.4$ eV [see the blue curve in Fig. 3(c)]. Under such a condition, the effect of mode-specific vibrational excitation prevails over the nonselective translational energy. Finally, we just mention that all the aspects of the bond selective reactivity for methane isotopologues on Pt(111) reported in details here were also observed on Ni(111).

In summary, we have carried out thorough quasiclassical molecular dynamics simulations to study various aspects of bond- and mode-selective reactivities of methane and its deuterated isotopologues on Ni(111) and Pt(111). Based on two accurate reactive force fields parametrized from DFT data, our simulations reproduce the high C-H bond selectivity recently achieved experimentally by exciting C-H stretching modes of partially deuterated isotopologues of methane as well as the mode-selective reactivity of vibrationally excited CH_4 on both Pt(111) and Ni(111). Moreover, our simulations reveal that the very high bond selectivity observed experimentally can be reached only at relatively low initial translational energies and it strongly decreases with increasing E_i due to the decreasing role of the vibrational energy with respect to that of the non-bond-selective translational energy. We predict also that the full selectivity of the less active C-D bond can be achieved at sufficiently low translational energies even in the statistically less favorable case of CH_3D. We hope our predictions provide some impetus to further experimental investigations on bond selectivity in a wider range of incident energies and also to the attempts for achieving experimentally the full C-D bond selectivity. With its accuracy demonstrated in this work, and its high computational efficiency, the present methodology that combines precise system-specific RFFs with quasiclassical molecular dynamics provides a very useful strategy for studying gas-surface reaction dynamics with increasing complexity.

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