

## Ab Initio Molecular Dynamics Calculations versus Quantum-State-Resolved Experiments on $\text{CHD}_3 + \text{Pt}(111)$ : New Insights into a Prototypical Gas–Surface Reaction

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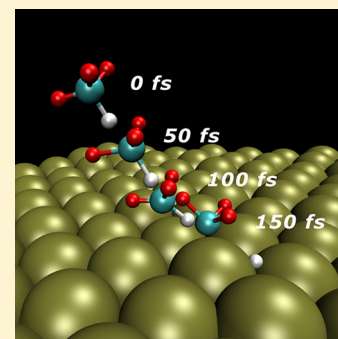
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**S** Supporting Information

**ABSTRACT:** The dissociative chemisorption of methane on metal surfaces is of fundamental and practical interest, being a rate-limiting step in the steam reforming process. The reaction is best modeled with quantum dynamics calculations, but these are currently not guaranteed to produce accurate results because they rely on potential energy surfaces based on untested density functionals and on untested dynamical approximations. To help overcome these limitations, here we present for the first time statistically accurate reaction probabilities obtained with ab initio molecular dynamics (AIMD) for a polyatomic gas-phase molecule reacting with a metal surface. Using a general purpose density functional, the AIMD reaction probabilities are in semiquantitative agreement with new quantum-state-resolved experiments on  $\text{CHD}_3 + \text{Pt}(111)$ . The comparison suggests the use of the sudden approximation for treating the rotations even though  $\text{CHD}_3$  has large rotational constants and yields an estimated reaction barrier of 0.9 eV for  $\text{CH}_4 + \text{Pt}(111)$ .

**SECTION:** Surfaces, Interfaces, Porous Materials, and Catalysis



The steam reforming process, in which methane and water react over a Ni catalyst, is the main commercial source of molecular hydrogen. The dissociation (or dissociative chemisorption) of  $\text{CH}_4$  on the catalyst into  $\text{CH}_3(\text{ad}) + \text{H}(\text{ad})$  is a rate-determining step of the full process.<sup>1</sup> Moreover, dissociation of methane on metal surfaces is of fundamental interest.<sup>2–13</sup> Already from early molecular beam experiments, it is known that vibration is very effective in promoting reactivity.<sup>3,4,14</sup> More recently, it has been shown that the reaction is mode-specific, that is, the degree to which energizing the molecule promotes reaction depends on whether the energy is put in translation or vibration and even on which vibration it is put in (vibrational mode specificity).<sup>5–8</sup> These observations, which have been explained qualitatively on the basis of different models,<sup>9,15</sup> rule out the application of fully statistical models. For some vibrational modes, the vibrational efficacy, which measures how effective putting energy into vibration is at promoting reaction relative to increasing the incidence energy ( $E_i$ ), is even larger than one.<sup>7,10</sup> In addition, the dissociation of partially deuterated molecules shows bond selectivity; for instance, in  $\text{CHD}_3$ , the CH bond can be selectively broken upon excitation to an appropriate initial vibrational state.<sup>11,12</sup> Finally, dissociative chemisorption of methane on metal surfaces represents a current frontier in the theoretical description of the dynamics of reactions of gas-phase molecules on metal surfaces,<sup>15–24</sup> with much current efforts now being aimed at achieving an accurate description of this

reaction through high-dimensional quantum dynamics calculations.<sup>16,23,24</sup>

A wealth of experiments exist for the methane +  $\text{Pt}(111)$  system.<sup>3,8,12,17,25–29</sup> There has been considerable debate<sup>2,25</sup> concerning the importance of tunneling in this and similar systems. Recent calculations<sup>17,23,30</sup> suggest only a minor role for tunneling under the conditions addressed by us. Research on Ni<sup>31</sup> and on Pt<sup>17</sup> surfaces suggests that the dissociation of methane should proceed through a direct mechanism under both thermal and hyperthermal conditions on these surfaces. This suggests the possibility to accurately model experiments relevant to both kinetics and dynamics with a unified approach. Harrison and coworkers have indeed shown<sup>17</sup> that a dynamically biased semiempirical statistical model yields an accurate description of a large range of experiments. However, this model cannot describe that, as also observed for  $\text{CH}_4 + \text{Pt}(111)$ ,<sup>8,26,27</sup> the extent to which putting energy into vibration promotes reaction depends on which vibrational state is excited. The model also does not yield the minimum reaction barrier height ( $E_b$ ), which would be useful for testing new electronic structure methods that are potentially more accurate than the present state-of-the-art method for computing

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potential energy surfaces (PESs) for molecule–metal surface reactions (density functional theory (DFT) at the generalized gradient approximation (GGA) level).<sup>32</sup> The DFT-GGA method is known to yield  $E_b$  with an accuracy no better than 5 kcal/mol for gas-phase reactions,<sup>33</sup> with GGA functionals both underestimating and overestimating  $E_b$  for gas–metal surface reactions,<sup>34</sup> while adsorption energies on metal surfaces exhibit similar lack of accuracy.<sup>35</sup> An accurate value of  $E_b$  is also relevant to accurately modeling the steam reforming reaction over a Pt(111) surface as kinetics calculations of rates of heterogeneously catalyzed processes require reaction barrier heights as input parameters.<sup>1</sup>

Within the appropriate level of dynamical theory and if an accurate PES is available, dynamics calculations can in principle solve all of the above problems and yield a consistently accurate description of all experiments described above. Dynamics calculations and their comparison to supersonic molecular beam experiments directly test whether the PES contains an accurate description of  $E_b$  and of the couplings of the molecule's and surface atoms' vibrations to the reaction coordinate. The quasi-classical trajectory (QCT) method (trajectory method with zero-point energy (ZPE) imparted to all molecular vibrational modes) is cheap to use, but with this method, artificial energy flow between vibrations of similar frequency can occur even in the isolated molecule.<sup>22</sup> This could hamper the accurate calculation of vibrational efficacies and explains that vibrational efficacies computed with the QCT method for  $\text{CH}_4 + \text{Ni}(111)$  are too low when compared with experiments and results of quantum dynamics (QD) calculations.<sup>15,22</sup> It would therefore be best to use QD to describe methane dissociation on metal surfaces. Ideally, such calculations would treat all molecular degrees of freedom (DOFs) and the relevant surface DOFs without approximations. This is currently not possible, and the high-dimensional (i.e., modeling motion in many DOFs) QD calculations published so far rely on untested dynamical approximations<sup>16,22–24</sup> and PESs based on untested density functionals.<sup>16,22–24</sup>

To help overcome these two shortcomings, we have performed ab initio molecular dynamics (AIMD) calculations and molecular beam experiments on the dissociation of  $\text{CHD}_3$  on Pt(111) at normal incidence, comparing sticking (dissociation) probabilities of hyperthermal and CH stretch excited  $\text{CHD}_3$ . The use of AIMD bypasses the need to fit a high-dimensional PES as forces are calculated on the fly with DFT and allows motion to be described in all molecular DOFs as well as of the surface atoms, which should also be relevant. The minimum energy barrier to dissociative adsorption is considerably lowered if the surface atom below the dissociating molecule moves out of the surface plane,<sup>36</sup> and the reaction shows a high surface temperature dependence.<sup>3,37–40</sup> Our goal is to test the validity of the dynamical approximations and the density functionals used in earlier high-dimensional QD<sup>16,22–24</sup> and QCT<sup>15,18,22</sup> calculations on dissociation of methane on metal surfaces. Our calculations can help pave the way toward chemically accurate quantum dynamical calculations on reactions of methane on metal surfaces, as accomplished earlier for  $\text{H}_2 + \text{Cu}(111)$ .<sup>41</sup>

The AIMD calculations that we present use the QCT method. The usual QCT pitfalls (problems due to the absence of ZPE conservation and to neglect of tunneling effects) are avoided by performing the calculations for average total molecular energies  $\langle E_{\text{tot}} \rangle$  well above  $E_b^c$  (the ZPE-corrected

value of  $E_b$ ; see Table 1) and by avoiding reduced-dimensionality calculations.<sup>22</sup> The primary reason that we

**Table 1. Values of  $E_b$  and of  $E_b^c$  Given in eV for Dissociation of  $\text{CH}_4$  and  $\text{CHD}_3$ <sup>a</sup>**

$E_b$	$E_b^c(\text{CH}_4)$	$E_b^c(\text{CHD}_2\text{-D})$	$E_b^c(\text{CD}_3\text{-H})$
0.805	0.700	0.729	0.683

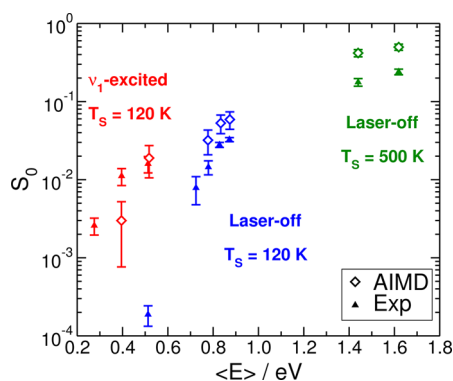
<sup>a</sup>The barrier geometry that we consider is computed from the minimum-energy transition state configuration from ref 48.

consider  $\text{CHD}_3$  is that this allows us to also accurately study the effect of initial vibrational energy on the reactivity with the QCT method for the case that the  $\nu_1$  CH stretch is pre-excited with one quantum. In  $\text{CHD}_3$ , the  $\nu_1$  CH stretch is mostly localized on one bond and has a frequency that is off-resonance with other vibrations, so that artificial intramolecular vibrational energy redistribution is minimized.<sup>42</sup> Compared to earlier QD and QCT calculations with a claim to high accuracy, advantages of the present AIMD calculations are that dynamical approximations,<sup>15,16,22–24</sup> artificial energy flow between  $\text{CH}_4$  vibrations of similar frequency,<sup>15,18,22</sup> and errors in PES fitting<sup>15,16,18,22–24</sup> are avoided, while the comparison of calculated laser-off reaction probabilities with experiment probes the quality of the density functional used more directly than other calculations.<sup>18</sup>

Previously, Sacchi et al. used AIMD to investigate the reaction of methane on Ni. However, they modeled the dynamics for the reverse associative desorption reaction, starting from the transition state toward the reactants ( $\text{CH}_4 + \text{clean surface}$ ), invoking detailed balance in order to extract qualitative information regarding the relative efficacies of vibrational modes for promoting the forward dissociation reaction.<sup>19–21</sup> The present work is the first study using AIMD as a quantitative tool to compute probabilities for methane dissociation on a metal surface.

The GGA-level PBE density functional<sup>43,44</sup> has been used in the calculations. This makes our calculations relevant to earlier high-dimensional QD and QCT calculations on dissociation of methane on Ni and Pt surfaces. In these calculations, either the PW91 functional<sup>45</sup> was used,<sup>15,16,18</sup> or the PBE functional, which was designed to reproduce PW91 energies,<sup>43</sup> was used.<sup>18,23,24</sup> Boltzmann distributions of vibrational states are used to describe the experimental gas temperature of the simulated laser-off beams. On the other hand, only molecules in the ( $\nu_1 = 1$ ) initial state are considered when simulating laser-on beams, as appropriate. The initial conditions of each molecule are chosen such that normal vibrational coordinates and momenta sample classical microcanonical distributions. The initial molecular angular momentum is set to zero, and the initial  $E_i$  of the molecule samples velocity distributions as recorded experimentally using time-of-flight techniques.

We find semiquantitative agreement between the theoretical and experimental dissociation probabilities (Figure 1). The calculations overestimate the experimental laser-off reactivity. The results therefore strongly suggest that the PBE functional used underestimates the  $E_b$  value for methane + Pt(111) by approximately 0.1 eV, this value being the energy with which the theoretical curve needs to be shifted in order to obtain agreement with experiment near the reaction threshold, while the  $E_b$  value obtained with the RPBE functional (1.06 eV<sup>46</sup>) is probably too high by 0.15 eV. These results are consistent with the finding that the PBE density functional typically over-



**Figure 1.** Sticking probability as a function of  $\langle E_i \rangle$ . Triangles are experimental, and diamonds are AIMD results. Red symbols represent  $\nu_1$ -excited beams, and blue symbols laser-off beams, both on a 120 K surface. Green symbols are for laser-off beams on a 500 K surface.

estimates and the RPBE functional usually underestimates the reactivity in activated dissociation of  $H_2$  on metal surfaces.<sup>41,47</sup> The value that our calculations suggest for  $E_b^\ddagger$  for  $CH_4$  dissociating on Pt(111) (0.80 eV, i.e., our PBE value (Table 1) plus 0.1 eV) is consistent with an experimental estimate of this quantity ( $0.60 \pm 0.20$ ) eV. This estimate can be calculated<sup>17</sup> on the basis of calorimetry<sup>28</sup> and associative desorption experiments.<sup>29</sup> The agreement further improves if one considers that the barrier sampled in the desorption experiments (0.6 eV) is about 0.15 eV lower than the one sampled in adsorption (0.8 eV) due to lattice relaxation,<sup>48</sup> that is, the puckering of the Pt atom on which the methyl is adsorbed before desorption of methane.

Both experiment and theory show a large increase in the sticking probability when the CH stretch mode is excited. Jiang et al. justified the observed enhancement in the  $CHD_3 + Ni(111)$  reactivity after pre-excitation of the  $\nu_1$  mode by considering the large projection that this mode has on the reaction coordinate at the transition state.<sup>15</sup> This argument, which is not specific to gas–surface reactions<sup>49</sup> and considered valid under the assumption that vibrational energy remains localized on the CH stretch, is expected to be valid for our system as well. Note that the theory underestimates the experimental vibrational efficacy because the energy shift between the laser-off and the  $\nu_1$ -excited reaction probability curves is lower for the AIMD results than that for the experiments. One reason for this<sup>50</sup> could be that the barrier obtained with the PBE functional occurs at a too small value of the length of the breaking bond, as also found for  $H_2 + Cu(111)$ .<sup>41</sup>

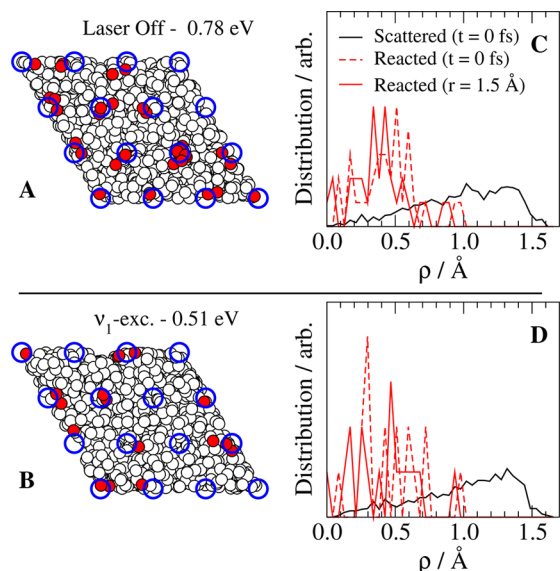
The ratio between CH and CD bond cleavage is, within the error bars of the calculations, equal to the statistical value of 1:3 for laser-off beams, but only CH cleavage is observed when the CH stretch is pre-excited (Table 2). This is in qualitative agreement with experiments, which were however done for lower  $E_{tot}$ , for which reaction probabilities could not be computed with AIMD. The reaction of vibrationally pre-excited  $CHD_3$  is bond-selective because at the low  $E_i$  investigated, vibrationless methane cannot react, so that the reaction should come from the vibrationally pre-excited normal mode, which in the present case is localized on the CH stretch.

Insight into the microscopic details of the reaction and the validity of common dynamical approximations can be extracted from the collected dynamical data. For instance, we observe that dissociating molecules impact close to the top site

**Table 2. Experimental and Calculated Branching Ratios for Different States and  $E_{tot}$  (eV)<sup>a</sup>**

	state	$E_{tot}$	%CD cleavage	% CH cleavage	% error bars
AIMD	laser-off	0.92	81.3	18.7	6.9
	laser-off	1.00	77.4	22.6	5.7
	laser-off	1.07	76.3	23.7	5.5
	$\nu_1 = 1$	0.77	0.0	100.0	24.9
	$\nu_1 = 1$	0.89	0.0	100.0	6.5
experiment	laser-off	0.55	71.4	28.6	
	$\nu_1 = 1$	0.65	<1	>99	

<sup>a</sup>Error bars represent 68.3% confidence intervals.

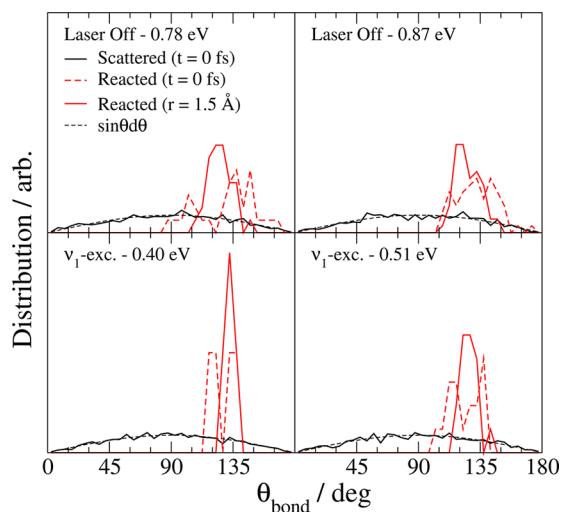


**Figure 2.** (A,B) Initial lateral displacement of the molecules in the supercell for two collision energies; red and white circles represent reacted and scattered molecules, respectively; blue open circles are the top sites in the supercell. (C,D) Impact parameter distributions for the collisions of the reacting molecules with the closest first layer atoms, evaluated at the beginning of the trajectories (dashed red line) and when the dissociating bond length reaches the lowest-energy transition-state value (solid red line). For comparison, the initial distributions of the scattered trajectories are plotted in black.

(equilibrium position of a first layer atom, Figure 2), consistent with minimum-energy paths for adsorption. The impact parameter distributions for collisions of normally incident  $CHD_3$  with top layer surface atoms confirm this and show that there is little steering toward reactive sites; the distributions do not shift much to lower impact parameters upon the approach of the reacting molecules to the transition state. This gives support to the use of sudden approximations,<sup>16,23,24</sup> which assume that observables of interest can be computed by averaging results of calculations performed for fixed values of the coordinate(s) that remain almost unchanged, to describe the lateral motion of the molecule. We have also studied the effect of surface motion on the reaction, looking at the vertical displacement of the surface atom closest to the incident molecule.<sup>40</sup> Here, our AIMD results confirm the validity of a result obtained earlier with models using a much more simplified treatment of surface motion,<sup>24,37,38,40</sup> that is, that at low  $E_i$  reaction occurs only if the closest surface atom is above the surface plane and moves toward the projectile, thereby lowering the barrier and increasing the relative velocity.



Angular distributions show that the initially nonrotating reacting molecules have their reactive bond initially pointing obliquely down to the surface, forming an angle with the surface normal in the range of  $90 < \theta < 180^\circ$  (Figure 3). During



**Figure 3.**  $\theta$  distributions evaluated at the beginning of the trajectories (dashed red line) and when the dissociating bond length reaches the lowest-energy transition-state value (solid red line) for reacting trajectories for four collision energies. For comparison, the distributions computed for the CH bonds of scattered trajectories are plotted in black. The dashed black lines correspond to  $\sin \theta$ , which is the distribution sampled when generating the initial orientations of the molecules.

the subsequent approach to the barrier, there is little rotational steering (distributions only become a little bit narrower), and the distributions at the transition state are centered around values that are close to the orientation at the minimum-energy barrier in the static calculations ( $\approx 132.60^\circ$ ).<sup>36</sup> Molecules with small moments of inertia (high rotational constants, about  $3 \text{ cm}^{-151}$ ) like  $\text{CHD}_3$  would be expected to easily reorient toward the minimum-energy barrier orientation when approaching the transition state. On the basis of this argument, some of the earlier QD calculations<sup>23,24</sup> employed the rotationally adiabatic approximation, which means that perfect steering of the reacting molecules was assumed along the reaction path. Our calculations show that this approximation is not valid for  $\text{CHD}_3(\nu_1 = 1)$  because the initial distribution of the reacting molecules does not resemble a  $\sin \theta$  distribution at all (the validity of this approximation for the laser-off reaction will be discussed elsewhere). In contrast, our result that the  $\theta$  distributions at  $t = 0$  and at the transition state are narrow and similar supports the use of the sudden approximation for the polar angle  $\theta$ . In light of the fairly large rotational constants of  $\text{CHD}_3$  and our current findings, the sudden approximation is probably applicable to any direct gas–surface reaction of a polyatomic molecule under conditions similar to those studied here. No correlation has been found between the reactivity and the azimuthal orientation of the dissociating bond (described by the  $\phi$  angle), in agreement with observations of a flat PES with respect to  $\phi$  in the static calculations.<sup>36</sup>

In summary, the AIMD method has been used for the first time to obtain quantitative results for the direct reaction of a polyatomic gas-phase molecule colliding with a metal surface, in the form of statistically accurate reaction probabilities. The comparison of the AIMD results with new quantum-state-

resolved experiments on the reaction of  $\text{CHD}_3$  with  $\text{Pt}(111)$ , which is a prototypical example of such reactions, suggests that the AIMD method using the general purpose PBE functional is capable of a semiquantitative description of this category of reactions. Somewhat surprisingly, even though methane has large rotational constants, our calculations suggest that a sudden approximation to the rotations should yield an accurate description of this reaction. This suggests a general applicability of the rotational sudden approximation to direct reactions of polyatomic molecules with surfaces for hyperthermal energies. The AIMD calculations also reproduce the observed bond selectivity in the dissociation of CH stretch pre-excited  $\text{CHD}_3$ , and they suggest that the PBE functional underestimates the reaction barrier height by  $\sim 0.1 \text{ eV}$  for  $\text{CH}_4 + \text{Pt}(111)$ . The latter finding and similar observations for  $\text{H}_2 + \text{Cu}(111)$  and  $\text{Ru}(0001)$  suggest that the PBE and PW91 functionals, which were used in earlier high-dimensional QD and QCT calculations on methane dissociation on Ni and Pt surfaces, underestimate the barriers for these systems by a similar amount.

## ■ ASSOCIATED CONTENT

### Supporting Information

Supporting text describing the experimental and theoretical methods and discussing the pitfalls of the QCT method, the effect of vibrationally excited states on laser-off reactivity, and the effect of surface motion on the reaction. Molecular beam parameters (Table S1). Convergence tests of the electronic structure calculations with respect to the minimum energy barrier  $E_b$  (Table S2). The analysis of the contribution of thermally excited vibrational states to the theoretical laser-off reactivity (Table S3). A figure showing the average normal mode energies for freely vibrating CH stretch excited  $\text{CHD}_3$  (Figure S1). A figure showing the estimated tunneling contribution for  $\text{CH}_4$  on  $\text{Ni}(100)$  at the surface temperature of 120 K (Figure S2). A figure showing the effect of surface atom motion on the reactivity (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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