Incident Angle Dependence of CHD$_3$ Dissociation on the Stepped Pt(211) Surface

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Supporting Information

ABSTRACT: The dissociation of methane on transition metal surfaces is not only of fundamental interest but also of industrial importance as it represents a rate-controlling step in the steam-reforming reaction used commercially to produce hydrogen. Recently, a specific reaction parameter functional (SRP32-vdW) has been developed, which describes the dissociative chemisorption of CHD$_3$ at normal incidence on Ni(111), Pt(111), and Pt(211) within chemical accuracy (4.2 kJ/mol). Here, we further test the validity of this functional by comparing the initial sticking coefficients ($S_0$), obtained from ab-initio molecular dynamics calculations run using this functional, with those measured with the King and Wells method at different angles of incidence for CHD$_3$ dissociation on Pt(211). The two sets of data are in good agreement, demonstrating that the SRP32-vdW functional also accurately describes CHD$_3$ dissociation at off-normal angles of incidence. When the direction of incidence is perpendicular to the step edges, an asymmetry is seen in the reactivity with respect to the surface normal, with $S_0$ being higher when the molecule is directed toward the (100) step rather than the (111) terrace. Although there is a small shadowing effect, the trends in $S_0$ can be attributed to different activation barriers for different surface sites, which in turn is related to the generalized co-ordination numbers of the surface atom to which the dissociating molecule is adsorbed in the transition state. Consequently, most reactivity is seen on the least co-ordinated step atoms at all angles of incidence.

1. INTRODUCTION

The dissociation of molecules on stepped and corrugated transition metal surfaces can be considered to model the reaction at defect sites on transition metal catalysts. Calculations have shown that for the dissociation of methane, less co-ordinated surface atoms typically have lower activation barriers, which can influence the dynamics of the collision of the molecule with the surface. For the dissociation of methane on “flat” low-index transition metal surfaces, the sticking coefficient, $S_0$, typically increases with increasing incident energy because of the significant activation barrier, although Utz et al. reported an increase in $S_0$ with decreasing incident energy on Ir(111), which they attributed to precursor-mediated dissociation. Normal energy scaling, where the reactivity is proportional to the incident translational energy directed normal to the surface, has been seen for methane dissociation on Ni(111), Pt(111), and Pd(111). For the corrugated Pt(110)-(1 × 2) surface, deviations from normal energy scaling were observed, both for molecules without vibrational energy and for molecules prepared in the antisymmetric stretch overtone state. When the methane velocity was directed parallel to the rows in the Pt(110)-(1 × 2) surface, normal energy scaling was seen, but when the incident energy was perpendicular to the rows, Madix et al. reported a scaling of $E\cos^2\theta$, where $E$ is the incidence energy and $\theta$ is the polar angle of incidence. Bisson et al. attributed this slower decrease in $S_0$ to a shadowing effect, as at larger values of $\theta$, methane preferentially collided with a ridge atom where the activation barrier to the reaction is the lowest.

Previous experimental work by Gee et al. also reported that $S_0$ for methane dissociation on stepped Pt(533) does not follow normal energy scaling. They found that the sticking coefficients fell more slowly as the incident methane was directed toward the (100) step than the (111) terrace. By assuming that the reactivity on the (111) terrace is the same as on an extended Pt(111) surface, they could separate the total sticking coefficient into a contribution from the (100) step and the (111) terrace. The authors found that the reactivity on each facet of the surface fell faster than would be predicted by normal energy scaling.

In the current work, we present a combined experimental—theoretical study of the dependence of $S_0$ on the angle of incidence of CHD$_3$ with respect to a Pt(211) surface. The Pt(211) surface is stepped, consisting of three-atom wide (111) terraces separated by one-atom high (100) steps, as
shown schematically in Figure 1A. There are three different types of atoms on this surface, which we refer to as step (red), terrace (blue), and corner (green) to be consistent with the notation used in previous studies. The (111) terrace consists of red, blue, and green atoms, and the (100) step consists of adjacent red and green atoms, the shaded area in panel B. The y-axis is parallel to the step edges, the x-axis along the direction of the corrugation, and the z-axis perpendicular to the macroscopic (211) plane. Panel B. Depiction of the polar angle $\theta_i$ and the azimuthal angle $\phi_i$ which define the direction of the incoming CHD$_3$. 

The three-atom wide (111) terraces consists of green, blue, and red atoms, and the one-atom high (100) step consists of the adjacent red and green atoms (the shaded area in panel B). The direction of incidence $\theta_i \phi_i$ corresponds to changing the angle of incidence with respect to the (100) steps and the (111) terraces ($\phi_i = 0^\circ$, see Figure 1). During the depositions, the surface was held at a temperature of 650 K using a proportional, integral, differential (PID) controller and was cleaned between measurements by Ar$^+$ sputtering and annealing. The surface cleanliness was confirmed by Auger electron spectroscopy.

The molecular beam was formed by expansion of a 1.5% CHD$_3$ seeded in H$_2$ gas mix through a 50 $\mu$m-diameter hole in a stainless steel nozzle and a 2 mm-diameter skimmer. The nozzle was resistively heated to 500 K, and the resulting velocity was determined using time-of-flight methods, described in detail in Section S1 of the Supporting Information. For the 2016 experiments, this gave a normal incident energy of 96.8 kJ/mol, and for the 2018 experiments, it was 98.5 kJ/mol. Different-sized apertures in a chopper wheel (diameter 2, 1, and 0.5 mm) were used to collimate the molecular beam to ensure that all molecules hit the surface for all angles of incidence. (We direct the interested reader to Figure S7 in ref 4 for a schematic of the molecular beam path in the machine).
The initial sticking coefficients were determined using the King and Wells (K&W) method.\textsuperscript{3,27,28} An off-axis quadrupole mass spectrometer (QMS) was used to monitor the partial pressure of mass 19 in the UHV chamber, with a typical trace presented in Figure 2A. Initially, the separation valve between the molecular beam source and the UHV chamber was shut, and there is correspondingly no significant mass 19 QMS signal. The separation valve is then opened at $t = -120$ s. At this point, the molecular beam is scattered from an inert beam and the QMS signal is a measure of the total number of molecules entering the UHV chamber. The beam flag is opened at $t = 0$ s, and the drop in the QMS signal corresponds to the number of molecules sticking to the surface. At $t = 15$ s, the beam flag is shut, and the separation valve is shut at $t = 90$ s. The time dependence of the sticking coefficient can then be found using

$$ S(t) = \frac{\Delta P(t)}{P} $$

where $\Delta P$ is the change in partial pressure when the beam flag is open and $P$ is the partial pressure increase when the separation valve is opened. Their values are shown in Figure 2A. $S(t)$ is fit using a double exponential decay\textsuperscript{28} to obtain the initial sticking coefficient $S_0$ as shown in Figure 2B. The baseline of the K&W trace when the flag is shut ($t < 0$ s, $t > 15$ s) is not zero, as the QMS current was seen to increase when the beam flag is opened under conditions where no reactivity was observed. This has been accounted for in the analysis of both sets of experimental data, and the correction gives rise to the apparent nonzero baseline when the beam flag is closed.

We present a comparison of the sticking coefficients measured at normal incidence ($\theta_i = 0^\circ$, $\phi_i = 0^\circ$) at a surface temperature of 650 K from the 2016 (red), 2018 A (blue), and 2018 B (black) experiments in Figure 3. The 2018 A angle of incidence data presented in Section 4 were recorded in the same way as the unscaled 2018 A data shown as a blue-filled circle at an incident energy of 98.5 kJ/mol, which is larger than the sticking coefficients obtained from the 2016 experiments (the full unscaled data set is shown in the Supporting Information in Figure S5). After the data were recorded, a systematic error was found in the angular 2018 A data because of an unstable backing pressure in the molecular beam expansion. Once this was rectified, the data point at 98.5 kJ/mol was repeated, and the sticking coefficient that was obtained (black, 2018 B) is in agreement with the original 2018 A data set at $\theta_i = 0^\circ$, $\phi_i = 0^\circ$. This scaling then accounts for the systematic error in the acquisition of the 2018 A data, and the slightly different normal incident energies obtained at the 500 K nozzle temperature used to record the two sets of data. As will be shown in Section 4, this brings the two sets of experiments into excellent agreement for $\theta_i > 0^\circ$, $\phi_i = 0^\circ$, which were recorded in both 2016 and 2018.

3. THEORETICAL METHODS

The methods used in the calculations have also been described in detail previously,\textsuperscript{4,29} and so only the most relevant details will be presented here. In brief, either 500 or 1000 quasi-classical AIMD trajectories were run for CHD$_3$ colliding with Pt(211) for $\nu_1 = 1$ or laser-off conditions, respectively, using the Vienna ab-initio simulation package (VASP) version 5.3.5.\textsuperscript{30–33} We call the AIMD trajectories quasi-classical because zero point energy was imparted to the vibrational modes of CHD$_3$. The first Brillouin zone was sampled using a $4 \times 4 \times 1$ Γ-centered grid with a cutoff energy of 350 eV for
the plane wave basis set. Projector augmented wave pseudopotentials have been used to represent the core electrons. The Pt(211) surface has been modelled using a 4 layer ($1 \times 3$) supercell slab with each slab separated from its first periodic replica by 13 Å of vacuum. To facilitate convergence, a Fermi smearing was used with a broadening parameter of 0.1 eV. Extensive tests of the parameters used in the calculations have been performed, the results of which can be found in the Supporting Information of ref 4.

The specific reaction parameter exchange correlation functional (SRP32-vdW) used in the present work is defined as

$$SRP32-vdW = (1 - 0.32)E^{PBE}_X + 0.32E^{RPBE}_X + E^{vdW}_C$$

where $E^{PBE}_X$ and $E^{RPBE}_X$ are, respectively, the PBE and RPBE exchange functionals and $E^{vdW}_C$ is the van der Waals correlation functional of Dion et al. Previous work has shown that this weighted average produces chemically accurate results for the dissociation of CHD$_3$ on Pt(211) under normal incidence conditions.

The initial conditions used for the trajectory calculations were sampled to replicate the molecular beam scattering experiments performed in 2016 with the velocity of the molecules sampled from the experimental time of flight measurements and rotated by $\phi_i$ and $\theta_i$. For the "laser-off" trajectories, the vibrational populations of the molecules were sampled using a Boltzmann distribution at the 500 K nozzle temperature used to create the molecular beam expansion. Although it was not possible to perform state-resolved reactivity experiments, as the difference between the reactivity of the laser excited molecules could not be separated from the reactivity of the molecules without vibrational excitation, state-resolved calculations were performed where all the molecules were prepared with a single quantum of C−H stretch vibration in the $j = 2$, $K = 1$, $v_1 = 1$ rovibrational state. The initial positions and velocities of the surface atoms were randomly sampled from calculations run to equilibrate the slab at a surface temperature of 650 K.

At the start of the trajectory, the CHD$_3$ is positioned 6.5 Å above the surface with $x$ and $y$ chosen to randomly sample all positions on the Pt(211) slab. As in previous work, the kinetic energy of the molecules was increased by 2 kJ/mol to compensate for the potential energy shift due to the unconverted vacuum space. The trajectories were propagated with a time step of 0.4 fs using the velocity-Verlet algorithm until the CHD$_3$ dissociated on the Pt(211) surface, scattered back into the gas phase or was trapped on the Pt(211) surface. The molecule was considered to have reacted if one of the bonds in the molecule was greater than 3 Å, whereas if the center of mass (COM) of the molecule was 6.5 Å away from the surface, with the COM velocity directed away from the surface, it was considered to have been scattered. If neither outcome was reached within the maximum 1 ps timeframe that the trajectory was propagated for, the molecule was considered to be trapped on the surface.

The sticking coefficients were calculated from the AIMD calculations using

$$S_0 = \frac{N_{\text{react}}}{N_{\text{tot}}}$$

where $N_{\text{react}}$ is the number of trajectories that dissociate and $N_{\text{tot}}$ is the total number of trajectories. The statistical error bars were found as

$$\sigma = \sqrt{\frac{S_0(1 - S_0)}{N_{\text{tot}}}}$$

and represent 68% confidence limits. The other probabilities and errors presented in Section 4 are calculated with analogous expressions, unless the probability is 0 or 1, in which case the error is calculated as

$$\sigma = 1 - 0.32^{1/N_{\text{tot}}}$$

which also represent 68% confidence limits.

4. RESULTS AND DISCUSSION

Figure 4 presents a comparison of $S_0$ measured experimentally for $\phi_i = 0^\circ$, $\theta_i \geq 0^\circ$ (red circles) and for $\phi_i = 0^\circ$ for both positive and negative $\theta_i$ (open blue circles) with those from K&W experiments at an incident energy of 96.8 kJ/mol (red circles) and scaled sticking coefficients from experiments at an incident energy of 98.5 kJ/mol (blue open circles) for $\phi_i = 0^\circ$. The dashed black line shows a $\cos^2 \theta_i$ distribution, and the arrows denote the angles of incidence perpendicular to the (100) step and the (111) terrace.
Furthermore, the sticking coefficients are seen to follow normal energy scaling for $\theta_i > 0^\circ$, but not for $\theta_i < 0^\circ$.

While no experimental data are available for $\phi_i = 90^\circ$, AIMD calculations were run with the results (squares) compared with those for $\phi_i = 0^\circ$ (circles) in Figure 5. The sticking coefficients fall as quickly with $\theta_i$ for $\phi_i = 90^\circ$ as is seen to occur rotating toward the (111) terrace ($\theta_i < 0^\circ$) for $\phi_i = 0^\circ$ for molecules both under laser-off conditions (blue) and prepared in the $\nu_i = 1, J = 2$, and $K = 1$ rovibrational state (red). This suggests that for angles where the molecules collide with the (111) terrace, only the polar angle of incidence ($\theta_i$) appears to be important and not the azimuthal angle ($\phi_i$). The dashed black line in Figure 5 shows $S_i(0^\circ)\cos\theta_i$ scaled to the $\nu_i = 1$, $\theta_i = 0^\circ$, $\phi_i = 90^\circ$ sticking coefficient, illustrating that for $\phi_i = 90^\circ$, the reactivity drops more quickly than would be predicted by normal energy scaling. This is in contrast to the Pt(110)-(1×1) surface where the reactivity was found to obey normal energy scaling when the molecules were directed parallel to the ridge atoms.20

Figure 6 shows the position of the COM of the molecules at the point where the dissociating bond becomes longer than the transition state value for C–H cleavage (red) and C–D cleavage (blue) for a range of $\theta_i$ for $\phi_i = 0^\circ$ for the laser-off trajectories (left column) and for $\nu_i = 1$ (right column). The dashed lines in each plot indicate the direction that the CHD$_3$ approaches the surface. As the angle of incidence changes from normal to the (111) terrace ($\theta_i \approx -20^\circ$) to normal to the (100) step ($\theta_i \approx 40^\circ$), the reaction site shifts from the terrace and step atoms toward the (100) step, reflecting the change in position on the surface where the normal incidence energy is the highest. Most of the reactivity is seen to occur at the top of the step atoms, which is the site with the lowest activation barrier for the dissociation of methane on Pt(211).1,28

The fraction of molecules that dissociate on the step (red) and terrace (blue) atoms in the AIMD calculations are presented in Figure 7 for $\phi_i = 0^\circ$ (panels A and B) and $\phi_i = 90^\circ$ (panels C and D) under laser-off conditions (panels A and C) and for molecules prepared with a quantum of C–H stretch vibration (panels B and D). The site of reaction was taken to be the surface atom closest to the COM of the CHD$_3$ when the dissociating bond became larger than the transition state value. It should be noted that no dissociation was seen on the corner atoms at any angle of incidence. Dissociation on the step atoms dominates the reactivity at all angles of incidence under both laser-off conditions and for $\nu_i = 1$, which is consistent with previous work at lower incident energies and a surface temperature of 120 K for CH$_4$ dissociation on Pt(211) at $\theta_i = 0^\circ$. The highest reactivity observed on the terrace atoms is seen for $\theta_i < 0^\circ$ at $\phi_i = 0^\circ$, which could be due to the kinetic energy of the incoming molecule normal to the (111) terrace being higher and the probability of the molecule hitting the terrace atoms being larger.

To decide whether the differences in reactivity at different angles of incidence can be attributed to a shadowing effect, we identified the surface atom closest to the site of methane impact for both reactive and nonreactive trajectories. The results are shown in Figure 8 for the step (red), terrace (blue), and corner (green) atoms for $\phi_i = 0^\circ$ (panels A and B) and $\phi_i = 90^\circ$ (panels C and D) for the trajectories run sampling laser-
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shown that adsorption energies tend to scale linearly with the

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activation barriers for the dissociation at different positions on

the Pt(211) surface.

Activation barriers are typically found to scale linearly with

adsorption energies for the dissociation of molecules on transition metal surfaces.43-46 In turn, Calle-Vallejo et al. have

shown that adsorption energies tend to scale linearly with the
generalized co-ordination number of the surface atom to which
the molecule adsorbs46,47 which, unlike co-ordination

numbers, also takes into account the co-ordination number of
the nearest neighbors of the atom of interest. It follows that
activation barriers would be expected to scale linearly with the
generalized co-ordination number. On Pt(211), the generalized co-ordination number follows the order, step atoms
(5.58) 46 < terrace atoms (7.33) < corner atoms (8.75),46 with the
activation barriers following the same trend.48 This would
predict that most reactivity would occur on the step atoms and
least on the corner atoms, as observed in the AIMD calculations presented here, at all angles of incidence. It is also
interesting to note that all atoms in the Pt(211) surface have a
different generalized co-ordination number to those on an
extended Pt(111) surface (7.50)48 and Pt(100) surface
(6.67) 46 despite the Pt(211) surface consisting of one-atom

9B, where the site-specific reaction probability on the terrace
atoms is at its maximum at \( \theta_i = -20^\circ \), which corresponds
to the direction of incidence being normal to the (111) terrace.
The same is not seen in the laser-off sticking coefficients in
Figure 9A; but as the total reactivity is lower, the statistics are
less good in this analysis. An asymmetry is seen in the reactivity
around the angle where \( S_0(\text{site}) \) is the largest for both the step
and terrace atoms for \( \phi_i = 0^\circ \). This asymmetry cannot be due
to shadowing and is therefore likely to be due to different
activation barriers for the dissociation at different positions
on the Pt(211) surface.

Disentangling the reactivity on each site of the surface from
the shadowing effect, we calculated site-specific sticking
coefficients for each site as

\[
S_i(\text{site}) = \frac{N_{\text{react}}(\text{site})}{N_{\text{total}}(\text{site})}
\]

(6)

where \( N_{\text{react}}(\text{site}) \) is the number of reactive trajectories for step or terrace atoms and \( N_{\text{total}}(\text{site}) \) is the number of trajectories for
which that site is the site of impact. \( S_i(\text{site}) \) are presented in
Figure 9 for the step (red) and terrace (blue) sites for \( \phi_i = 0^\circ \) (panels A and B) and \( \phi_i = 90^\circ \) (panels C and D) for laser-
off conditions (panels A and C) and for \( \nu_i = 1 \) (panels B and D)
Calculations for \( \phi_i = 0^\circ \) (panels A and B) and \( \phi_i = 90^\circ \) (panels C and D).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7}
\caption{Fraction of molecules that dissociate on the step atoms (red) and on the terrace atoms (blue) calculated for the laser-off (panels A and C) and \( \nu_i = 1 \) (panels B and D) trajectories for \( \phi_i = 0^\circ \) (panels A and B) and \( \phi_i = 90^\circ \) (panels C and D). No dissociation was observed on the corner atoms.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8}
\caption{Fraction of all trajectories that impact nearest the step (red), terrace (blue), and corner (green) atoms for the laser-off (panels A and C) and \( \nu_i = 1 \) (panels B and D) calculations for \( \phi_i = 0^\circ \) (panels A and B) and \( \phi_i = 90^\circ \) (panels C and D).}
\end{figure}
The fraction of C–H cleavage seen in the AIMD calculations is presented in Figure 10 for dissociation on the step (red) and terrace (blue) atoms for \( \phi_i = 0^\circ \) (panels A and B) and \( \phi_i = 90^\circ \) (panels C and D). The fraction of C–H cleavage is found to be 0.25 for both sites within error bars, as would be expected for a statistical 3:1 branching ratio for C–DI:C–H cleavage. More C–H bond cleavage is seen for the \( \nu_1 = 1 \) trajectories, with a slightly higher degree of bond selectivity being observed for dissociation on the terrace atoms than on the step atoms at all angles of incidence, although this difference is within the error bars of the calculations for individual incidence conditions. At a surface temperature of 150 K and at lower incident energies, the branching ratio for the dissociation of CHD\(_3\), CH\(_2\)D\(_2\), and CH\(_3\)D on Pt(111) has been shown to be statistical under laser-off conditions, whereas when a quantum of C–H stretch was added to the molecule, only C–H cleavage was observed. Increasing the surface temperature (to 650 K) lowers the effective activation barrier to the dissociative chemisorption due to the thermal motion of the atoms in the surface, which when combined with a higher incident translational energy is likely to make CHD\(_3\) dissociation less bond selective for \( \nu_1 = 1 \), as is seen to be the case in the AIMD calculations.

5. SUMMARY

Sticking coefficients have been measured and calculated for CHD\(_3\) dissociation on a Pt(211) surface at a temperature of 650 K for different angles of incidence at a fixed incident energy (\( \approx 97 \text{ kJ/mol} \)). The measured sticking coefficients, obtained by the K&W method, are in good agreement with those from AIMD calculations using the SRP32-vdW functional, further demonstrating the quality of the functional for describing methane dissociation on Pt(211). An asymmetry is seen in the polar incident angle distribution in both the calculated and experimental sticking coefficients, with a more rapid drop in reactivity for incidence toward the (111) terraces compared to toward the (100) steps. At all incident angles, the calculations show that preparing the CHD\(_3\) with one quantum
of C–H stretch vibration increases the reactivity and favors C–H bond cleavage over C–D bond cleavage. A shadowing effect is seen, which favors impact on the step sites compared to the terrace sites as the polar angle of incidence is increased toward normal incidence to the steps, although this by itself does not account for the difference in reactivity seen at the two sites. The reactivity on the terrace atoms is seen to be the highest at angles of incidence where the energy normal to the (111) terrace is the highest, but reactivity on the step atoms dominates at all angles of incidence where the activation barrier for dissociation is the lowest. The site of dissociation is seen to shift around the step atoms as the angle of incidence is increased, reflecting the change of position where the normal energy is the highest and the difference in activation barrier heights at the different sites of the Pt(211) surface.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b05887.

Determination of the experimental velocity distribution, comparison of different sets of experimental data, contribution of trapped trajectories to reaction, and Pt(211) as a Pt(311) surface (PDF)

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Notes

The authors declare no competing financial interest.

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