# Rotational Dynamics of Desorption: Methane and Ethane at Stepped and Kinked Platinum Surfaces 

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#### Abstract

When the interactions between surfaces and adsorbates are studied, molecular rotations are often neglected. In this work, we carefully analyse the rotational dynamics of methane and ethane molecules desorbing from two different platinum surfaces by means of first-principles molecular dynamics simulations. With respect to its rotational symmetry, methane - a benchmark system for adsorption dynamics - constitutes a spherical top and ethane is a symmetric top. We focus upon the achiral $\operatorname{Pt}\{110\}-(1 \times 2)$ surface, which exhibits both mirror symmetry and a stepped geometry, and upon the chiral $\operatorname{Pt}\{531\}$ surface, which exhibits kink sites and lacks reflection symmetry. For methane, neither a strong nor directed angular momentum is induced by either of the two surfaces, whereas for ethane we find an increased directionality for the molecular rotation upon desorption from $\operatorname{Pt}\{531\}$ compared to $\operatorname{Pt}\{110\}-(1 \times 2)$. The principle of microscopic reversibility implies that such results (in time reversal) will also be relevant to the process of adsorption, which would therefore be sensitive to the initial rotational state of incoming molecules.


## Introduction

A detailed understanding of fundamental chemical processes such as chemisorption facilitates the optimisation of industrially relevant reactions and inspires the design of novel experiments. A rigorous analysis of the translational, vibrational and rotational motion, as well as the energetics of the adsorbate molecules and surface atoms, is therefore necessary. While existing studies examine structure, energetics and vibrational changes upon adsorption, the rotations of adsorbing or desorbing molecules are usually omitted or only considered in passing; there only exists a small amount of experimental work looking at rotational effects on adsorption. ${ }^{1,2}$ In this study, we will therefore focus on the rotations of the two smallest simple hydrocarbons, methane and ethane, upon their desorption from platinum surfaces. With regard to their rotational properties both molecules are highly symmetric, methane being a spherical top and ethane a prolate symmetrical top. Both molecules have attracted considerable attention as small hydrocarbons of industrial importance, particularly for their involvement in hydrocarbon rearrangement and conversion reactions catalysed by transition metals. ${ }^{3-6}$ Inspired by this key role in large-scale chemical reactions, they have also often served as model systems in surface science, and methane in particular is regarded as a benchmark system for surface adsorption and desorption dynamics. ${ }^{4,7,8}$ The bond and mode-selective chemistry of methane interacting with various metals is of profound interest for a deeper understanding of reaction probabilities and reactivity in general. ${ }^{9-13}$

Both molecules undergo dissociative adsorption on platinum. We employ ab initio molecular dynamics (MD) simulations initialised from the transition state of this dissociation reaction at the surface and analyse the subsequent desorption trajectories. This approach enables us to simulate only reactive trajectories and directly link any results to a dissociation event. Due to the principle of microscopic reversibility, any findings gathered from these desorption trajectories translate to information about the adsorption behaviour as well. This study follows the methodology used in our previous work, ${ }^{14}$ but now focuses on hydrocarbons interacting with a reactive transition metal.

Furthermore, we compare the desorption from the achiral $\operatorname{Pt}\{110\}-(1 \times 2)$ surface and from the chiral $\operatorname{Pt}\{531\}$ surface to investigate potential chiral effects on the rotational motion induced by the chirality of the surface. We do not expect asymmetric rotation to be as pronounced in these systems compared to formic acid desorption from $\mathrm{Cu}\{531\}$, because the molecules here exhibit rather higher symmetry. Nevertheless, it will be instructive to examine our results carefully for any such effects, as will become apparent. Moreover, an analysis of desorption processes from both $\operatorname{Pt}\{110\}-(1 \times 2)$ and $\operatorname{Pt}\{531\}$ also represents a comparison between a stepped and a kinked surface, which is known to be an important distinction with regard to catalytic activity and molecule-surface interaction mechanisms. ${ }^{15-17}$

## Methods

All DFT calculations were performed with the CASTEP code (Version 18.1) ${ }^{18}$ using the PBE exchange-correlation functional, ${ }^{19}$ ultrasoft pseudopotentials, ${ }^{20}$ and a cut-off energy of 500 eV for the plane-wave basis. To account for long-range molecule-surface interactions, the Tkatchenko-Scheffler dispersion force correction scheme ${ }^{21}$ was used. Transition state searches were initially performed with the LST-QST ${ }^{22}$ algorithm as implemented in CASTEP. The candidate transition state structures were then refined with hybrid eigenvector-following ${ }^{23-25}$ in the OPTIM code in conjunction with CASTEP energies and gradients until the root-meansquare (RMS) gradient was smaller than $0.001 \mathrm{eV}_{\AA^{-1}}$. Finite-displacement calculation of molecular vibrations revealed the expected normal modes and a single imaginary frequency, representing the reaction coordinate. The same amount of kinetic energy for each trajectory was distributed equally among these modes, i.e. $\mathrm{k}_{B} \mathrm{~T}$ in each normal mode and $\mathrm{k}_{B} \mathrm{~T} / 2$ in the reaction coordinate $(T=300 \mathrm{~K})$ based on the equipartition theorem and zero potential energy. The phase of each vibrational mode was chosen randomly, thus enabling the generation of different initial velocities for MD trajectories with the same amount of assigned kinetic energy. MD simulations were performed using an NVE ensemble (constant number N of
particles, volume V, and total energy E) and a time step of 0.5 fs . A total of 32 trajectories were computed per surface, of duration 200 fs each. For more computational details and further explanations of the methodology we refer to previous work. ${ }^{14}$

The angular momentum of the molecule, $\mathbf{L}$, is calculated as

$$
\begin{equation*}
\mathbf{L}=\sum_{i=1}^{K}\left(\mathbf{r}_{i} \times \mathbf{v}_{i}\right) m_{i} \tag{1}
\end{equation*}
$$

where $K$ is the number of atoms, $\mathbf{r}_{i}$ and $\mathbf{v}_{i}$ are the position and velocity vectors of atom $i$ (both relative to the centre of mass), and $m_{i}$ is its atomic mass. The magnitude of the angular momentum is given in atomic units (a.u.) in the following, i.e. in multiples of $\hbar$. The principal axes of the moment of inertia are defined by the eigenvectors of the moment of inertia tensor, which is obtained from the positions of all atoms in the molecule, again with respect to the centre of mass. The diagonal elements of the moment of inertia tensor are defined as $I_{x x}=\sum_{i} m_{i}\left(r_{i}^{2}-x_{i}^{2}\right)$ and similarly for $I_{y y}$ and $I_{z z}$, using the Cartesian coordinates $x_{i}, y_{i}$ and $z_{i}$ of atom $i$. Off-diagonal elements are given by $I_{x y}=-\sum_{i} m_{i} x_{i} y_{i}$ etc.

## Results

## Geometry Optimisation and Transition State Search

## Methane on $\operatorname{Pt}\{531\}$ and $\operatorname{Pt}\{110\}-(1 \times 2)$

To determine the transition state (TS) necessary for initialising the MD simulations, the adsorption geometries of methane and methyl on $\operatorname{Pt}\{531\}$ and $\operatorname{Pt}\{110\}-(1 \times 2)$ first had to be determined. The dissociation of methane on $\operatorname{Pt}\{110\}-(1 \times 2)$ has previously been described as a C-H bond cleavage along the close-packed ridge. ${ }^{11,26}$ This result has been confirmed by our own calculations, see Fig. 1 for methane, methyl and transition state geometries. $\operatorname{On} \operatorname{Pt}\{531\}$, the adsorption geometries had not been studied before. Based on the results for $\operatorname{Pt}\{110\}$ $(1 \times 2)$, the $\mathrm{C}-\mathrm{H}$ bond cleavage was assumed to take place across a first-layer Pt atom towards
a nearest-neighbour second-layer Pt atom. Different possible geometries were sampled and the most energetically favourable methane and methyl adsorption geometries along with their corresponding transition state are shown in Fig. 2. Even though methane adsorbs more strongly to the $\operatorname{Pt}\{531\}$ surface than to the $\operatorname{Pt}\{110\}-(1 \times 2)$ surface, the energetic barriers for the dissociation reaction are similar on both surfaces (relative to the energies of either the dissociated or intact adsorbed species) and the adsorption energy at the transition state is positive in both cases (i.e. less stable than the intact molecule in the gas phase), see Table 1. The energetic barrier referenced to the potential for infinite distance between the gas-phase molecule and the surface varies significantly, however, from $\operatorname{Pt}\{531\}$ to $\operatorname{Pt}\{110\}-(1 \times 2)$. Both for methane and ethane adsorption, this barrier is much smaller for the kinked than for the stepped surface. This is very much in line with experimental and computational findings of increasing reaction barriers of adsorption with increasing coordination numbers of the relevant surface atoms, i.e. going from kinked to stepped to terraced surfaces. ${ }^{27-29}$


Figure 1: Adsorption geometries for methane dissociation on $\operatorname{Pt}\{110\}-(1 \times 2)$.

## Ethane on $\operatorname{Pt}\{531\}$ and $\operatorname{Pt}\{110\}-(1 \times 2)$

The dissociation of ethane on $\operatorname{Pt}\{110\}-(1 \times 2)$ was investigated previously by AngHEL et al., ${ }^{30}$ who identified two different reaction pathways, both of which were revisited with our computational setup here. In the first pathway, ethane's C-C bond is approximately

Table 1: Adsorption energies upon dissociative adsorption on Pt surfaces.

| Molecule | Surface | Adsorption state | $\boldsymbol{E}_{\text {ads }}[\mathrm{eV}]$ |
| :--- | :---: | :---: | :---: |
| $\mathrm{CH}_{4}$ | $\operatorname{Pt}\{110\}-(1 \times 2)$ | intact | -0.207 |
|  |  | dissociated | -0.342 |
|  |  | TS | 0.527 |
| $\mathrm{CH}_{4}$ | 531 | intact | -0.371 |
|  |  | dissociated | -0.774 |
|  |  | TS | 0.108 |
| $\mathrm{CH}_{3} \mathrm{CH}_{3}$ | $\operatorname{Pt}\{110\}-(1 \times 2)$ | intact | -0.414 |
|  |  | dissociated | -0.627 |
|  | $\operatorname{Pt}\{531\}$ | TS | 0.218 |
|  |  | intact | -0.641 |
|  |  | dissociated | -1.100 |
|  |  | TS | -0.167 |



Figure 2: Adsorption geometries for methane dissociation on $\operatorname{Pt}\{531\}$.
aligned with the $[1 \overline{1} 0]$ direction (the close-packed ridge), while the C-H bond cleavage occurs perpendicular to [110], with motion of the departing hydrogen atom along the [100] direction. This pathway will therefore be called the [100] pathway. In the second pathway, the C-H bond is broken approximately along the [110] direction and is therefore labelled as the [1 $\overline{1} 0]$ pathway. We found the [100] pathway to yield more favourable adsorption geometries for both intact and dissociated ethane, see Fig. 3 and Table 1.

Based on these results and the findings for methane on $\operatorname{Pt}\{531\}$, we assumed the dissociation of ethane on $\operatorname{Pt}\{531\}$ to take place across a topmost Pt atom again. Several geome-
tries were sampled, of which the pathway shown in Fig. 4 involved the most energetically favourable adsorption geometries, see Table 1.

The location of the $H$ atom immediately after dissociation, as shown in Figs. 3 and 4 depends upon the transition state involved and is likely to change to other, possibly more favourable positions on the surface on a longer timescale (via surface diffusion) but this migration is not of interest in the present study.


Figure 3: Adsorption geometries for ethane dissociation on $\operatorname{Pt}\{110\}-(1 \times 2)$. The [100] adsorption pathway is shown.


Figure 4: Adsorption geometries for ethane dissociation on $\operatorname{Pt}\{531\}$.

## Molecular Dynamics Simulations of Methane and Ethane Desorption

## Methane on $\operatorname{Pt}\{531\}$ and $\operatorname{Pt}\{110\}-(1 \times 2)$

Molecular dynamics runs were started from the transition state (as described in the Methods section) and 200 fs of molecular motion were simulated for 32 different trajectories per surface. Figs. 5 and 6 show the evolution of the angular momentum and the $z$-component of the angular momentum for all these trajectories. The angular momentum is very similar in magnitude on both surfaces and does not change significantly over time, i.e. $\mathrm{L}(t=0 \mathrm{fs}) \approx$ $\mathrm{L}(t=200 \mathrm{fs})$. A very similar result is found for $\mathrm{L}_{z}$ when the average is taken across all trajectories. Some subtle distinctions emerge when we analyse sub-populations of trajectories. The adsorption energies of methane on Pt are sufficiently small to allow for desorption of all methane molecules during the trajectory without having to initialise with additional energy along the surface normal, in contrast to our study of formic acid on copper. Consequently, Fig. 7 shows that the distance between the centre of the molecule (approximated as the methane carbon atom) and the topmost Pt atom does indeed increase over time for all trajectories on both surfaces. On $\operatorname{Pt}\{531\}$ this distance is much smaller and exhibits a larger spread of final values than on $\operatorname{Pt}\{110\}-(1 \times 2)$, and for some trajectories even levels off around $3 \AA$ rather than desorbing further from the surface. This result indicates incomplete desorption, which is more pronounced in some trajectories than in others. The different desorption processes become even clearer if the distance between the re-associating hydrogen atom and the topmost Pt atom, shown in Fig. 8, is also taken into account. On $\operatorname{Pt}\{531\}$ a few trajectories exhibit a very small distance at the end of the simulation, which is very similar to the one found for the adsorbed but intact methane molecule as shown in Fig. 2 $(2.1 \AA)$. Other trajectories exhibit rather large Pt-H distances of $4 \AA$ or more.

The total angular momentum is unaffected by these differences in desorption behaviour, but the mean final $\mathrm{L}_{z}$ on $\operatorname{Pt}\{531\}$ of trajectories with a large Pt-C distance ( $>4.0 \AA$, shown in red in Figs. 6b, 7 and 8) is zero, and the mean of trajectories with low Pt-C distance
$(<3.6 \AA$, shown in blue in Figs. 6b, 7 and 8$)$ is +3.0 a.u., see left panel of Fig. 6b. This distinction is based on the Pt -C distance, which is unaffected by intramolecular rotations of the molecule and therefore more meaningful as an indicator of distance for the whole molecule. The thresholds are chosen as half a standard deviation above and below the mean. Even when only trajectories that have desorbed fully are considered in the average, there is still no significant $\mathrm{L}_{z}$ component induced by the chiral surface structure.

For $\operatorname{Pt}\{110\}-(1 \times 2)$ the behaviour is different. The trajectories desorb more uniformly (especially clear from the Pt-C distance). If anything, lower Pt-C distances ( $<5.1 \AA$, shown in red in Figs. 6b, 7 and 8) correlate with higher absolute $\mathrm{L}_{z}$ values, positive or negative. Higher Pt-H distances ( $>5.3 \AA$, shown in blue in Figs. 6 b, 7 and 8 ) correlate with low absolute $\mathrm{L}_{z}$ values(right panel of Fig. 6b). This result can be explained by a higher translational energy and higher translational velocity component parallel to the surface normal in trajectories with good desorption, which leads to a lower $L_{z}$ because $\mathbf{L}$ and $\mathbf{v}$ are perpendicular (see Eq. (1)).


Figure 5: Time evolution of the angular momentum magnitude, L, of a methane molecule desorbing from $\operatorname{Pt}\{531\}$ (left) and $\operatorname{Pt}\{110\}-(1 \times 2)$ (right). The value of L for individual trajectories is shown in black, the mean in red, and the standard deviation in grey. The same colour scheme is applied throughout this paper for depictions of the mean and standard deviation.

(a) All trajectories shown in black. Red lines indicate the mean values for each surface, while an error range of one standard deviation is indicated in grey.

(b) Trajectories with a high Pt-C distance at 200 fs are shown in red, those with a low Pt-C distance are shown in blue (see text), intermediate cases that don't fall in either of these categories remain black.

Figure 6: Time evolution of the $z$-component of the angular momentum, $\mathrm{L}_{z}$, of a methane molecule desorbing from $\operatorname{Pt}\{531\}$ (left) and $\operatorname{Pt}\{110\}-(1 \mathrm{x} 2)$ (right).

Table 2: Vibrational frequencies in $\mathrm{cm}^{-1}$ of phonon modes obtained for the transition states of methane on $\operatorname{Pt}\{531\}$ and $\operatorname{Pt}\{110\}-(1 \times 2)$ compared to for gas-phase methane. Literature values are also provided alongside an assignment of the mode. ${ }^{31}$ Frequencies in bold indicate importance for the analysis, see text. Asterisks indicate a computational artefact due to our periodic setup, these frequencies should actually be zero. Abbreviations: frust. - frustrated, rot - rotation, trans - translation, sym. - symmetric, deg. - degenerate, deform - deformation

| No. | $\operatorname{Pt}\{\mathbf{5 3 1}\}$ | $\operatorname{Pt}\{\mathbf{1 1 0 \}} \mathbf{- ( \mathbf { 1 } \times \mathbf { 2 } )}$ | gas-phase | literat. | assignment |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $\operatorname{Pt}\{531\}$ | $\operatorname{Pt}\{110\}-(1 \times 2)$ |
| 1 | $\mathbf{3 4}$ | 110 | 0 | 0 | frust. rot | frust. trans $x$ |
| 2 | 135 | 124 | 0 | 0 | frust. trans $x$ | frust. trans $y$ |
| 3 | $\mathbf{2 2 0}$ | $\mathbf{2 5 8}$ | 0 | 0 | frust. rot | frust. rot |
| 4 | 262 | $\mathbf{3 3 3}$ | $215^{*}$ | 0 | frust. trans $y$ | frust. rot |
| 5 | $\mathbf{4 8 7}$ | $\mathbf{4 7 5}$ | $263^{*}$ | 0 | frust. trans $z$ | frust. trans $z$ |
| 6 | 854 | 834 | $280^{*}$ | 0 | frust. rot | frust. rot |
| 7 | 915 | 919 | 1289 | 1306 |  |  |
| 8 | 1225 | 1186 | 1296 | 1306 | deg. deform |  |
| 9 | 1396 | 1402 | 1301 | 1306 |  |  |
| 10 | 1425 | 1417 | 1524 | 1534 | deg. deform |  |
| 11 | $\mathbf{2 1 5 7}$ | $\mathbf{1 7 2 0}$ | 1527 | 1534 |  |  |
| 12 | 2977 | 2980 | 2983 | 2917 | sym. stretch |  |
| 13 | 3062 | 3060 | 3094 | 3019 |  | deg. stretch |
| $\mathbf{1 4}$ | 3118 | 3129 | 3101 | 3019 |  |  |
| $\mathbf{1 5}$ | -755 | -850 | 3106 | 3019 |  |  |



Figure 7: Time evolution of the distance between the topmost Pt atom and the methane carbon atom on $\operatorname{Pt}\{531\}$ (left) and $\operatorname{Pt}\{110\}-(1 \times 2)$ (right), including a magnification of the first 25 fs. Colour coding is the same as used in Fig. 6b.


Figure 8: Time evolution of the distance between the topmost Pt atom and the methane re-associating hydrogen atom on $\operatorname{Pt}\{531\}$ (left) and $\operatorname{Pt}\{110\}-(1 \times 2)$ (right), including a magnification of the first 15 fs . Colour coding is the same as used in Fig. 6b.

Some of the features of the individual trajectories can also be attributed to the phase initialisation of the vibrational modes. In Table 2 all vibrational frequencies of the transition state on each surface are listed alongside the calculated gas-phase and literature values for a single unperturbed methane molecule. Mode 15 , which corresponds to stretching the $\mathrm{C}-\mathrm{H}$ bond that is broken, is the only imaginary mode, identifying both structures as first-order transition states. All modes that influence the angular momentum or the movement of the molecule during the first few fs are highlighted in bold in Table 2.

On $\operatorname{Pt}\{531\}$, the sign of $\mathrm{L}_{z}(t=0)$ is determined by a well-defined, yet essentially arbitrary, phase relationship of modes 1 and 3. A large initial $L_{z}$ (either distinctly positive or negative; $\left.\left|L_{z}\right|>0.6\right)$ is observed only when the initial signs of the two modes are different. Similarly, $\mathrm{L}_{z}(t=0)$ on $\operatorname{Pt}\{110\}-(1 \times 2)$ is determined by a combination of the initial phases of modes 3 and 4. A large initial $\mathrm{L}_{z}$ is observed only when the initial signs of both normal mode vectors are the same.

A close inspection of the first 30 fs of Fig. 7 and the first 15 fs of Fig. 8 reveals a bifurcation of the set of trajectories with respect to the $\mathrm{Pt}-\mathrm{C}$ and the $\mathrm{Pt}-\mathrm{H}$ distance (see
also the insets in these figures). Both bifurcations are also connected to the initial phase of certain modes, but in this case the same mode is involved on both surfaces. Which Pt-C distance curve is initially followed by an individual trajectory is determined by mode 5 on both surfaces, which looks much like a Pt-C stretching mode, with the displacements of the four hydrogen atoms being rather small compared to the displacement of the carbon atom towards or away from the topmost Pt atom. A very similar connection is found between the bifurcated $\mathrm{Pt}-\mathrm{H}$ distance plot and mode 11, which involves a significant displacement of the dissociating hydrogen atom along the surface normal, towards or away from the topmost Pt atom. Note that mode 11 is identical to the $\nu_{1}$ mode that was identified by SACCHI et al. ${ }^{9,32}$ as connected to the reaction probability of the dissociation of methane on $\operatorname{Pt}\{110\}-(1 \times 2)$.


Figure 9: Vector representation of $\mathbf{L}$ (blue) and $\mathbf{I}_{\mathbf{A}}, \mathbf{I}_{\mathbf{B}}, \mathbf{I}_{\mathbf{C}}$ (red, green, orange) for methane on $\operatorname{Pt}\{531\}$ and $\operatorname{Pt}\{110\}-(1 \times 2)$ at different times in the trajectories. A randomly selected methane molecule is included for clarity.

Methane is a spherical top because it has $\mathrm{T}_{d}$ symmetry, and its three principal axes of the
moment of inertia tensor all have the same eigenvalue, i.e. methane has the same inertia for rotations about any one of these three axes. Therefore, there is no particular axis along which the angular momentum is predestined to evolve during the desorption process, and any set of orthogonal axes would serve equally well as principal axes because $\{x, y, z\}$ form a basis for a T irreducible representation. In Fig. 9, the angular momentum vector, L, is depicted for each trajectory along with the three principal axes, $\mathbf{I}_{\mathbf{A}}, \mathbf{I}_{\mathbf{B}}, \mathbf{I}_{\mathbf{C}}$ of methane calculated based on the instantaneous geometry at 20, 60 and 200 fs of simulation time for both surfaces. The principal axes are shown with unit length and $\mathbf{L}$ is shown in units of 10 a.u. Initially, the three principal axes have a relatively well-defined shared direction for all trajectories, especially on $\operatorname{Pt}\{531\}$, because they were started from the same initial geometry of a surface-bound transition state, which is certainly not a spherical top. Nevertheless, the angular momentum vectors are already distributed across a full hemisphere even after this very short simulation time. This distribution continues to spread across the whole sphere as the simulation time increases, while the principal axes also lose their shared directions, and eventually are also scattered randomly across the whole sphere, as expected due to the degeneracies in a spherical top. Indeed, there is no evidence for alignment of $\mathbf{L}$ with any particular axis in the reference frame of the principal axes. There is also no significant difference between the evolution of these vectors and their directional relationships on $\operatorname{Pt}\{531\}$ and $\operatorname{Pt}\{110\}-(1 \times 2)$.

## Ethane on $\operatorname{Pt}\{531\}$ and $\operatorname{Pt}\{110\}-(1 \times 2)$

Due to the higher adsorption energy of ethane on the two Pt surfaces, the addition of 0.8 eV of translational energy parallel to the surface normal was necessary to achieve clear desorption for all trajectories. We have applied this method previously (see elsewhere for more details of the physical justification ${ }^{14}$ ). Otherwise, the same approach as for methane was used to study the desorption of ethane with MD simulations.

The mean angular momentum of ethane, shown in Fig. 10, does not change much over time upon desorption from $\operatorname{Pt}\{531\}$. It only exhibits a small drop of approximately a sixth


Figure 10: Time evolution of the angular momentum magnitude, L, of an ethane molecule desorbing from $\operatorname{Pt}\{531\}$ (left) and $\operatorname{Pt}\{110\}-(1 \times 2)$ (right).


Figure 11: Time evolution of the $z$-component of the angular momentum, $\mathrm{L}_{z}$, of an ethane molecule desorbing from $\operatorname{Pt}\{531\}$ (left) and $\operatorname{Pt}\{110\}-(1 \times 2)$ (right).
of its magnitude after the first 50 fs , which is recovered steadily in an upward trend until the end of the simulation, when the angular momentum levels off at a very similar level to $t=0$. In contrast, the angular momentum of molecules desorbing from $\operatorname{Pt}\{110\}-(1 \times 2)$ exhibits a downward trend over the course of the trajectories, which results in an overall difference of approximately 4.7 a.u. between the two surfaces at the end of the simulation time.

The mean of the $z$-component of the angular momentum is very close to zero throughout the simulation time for both surfaces, see Fig. 11. On $\operatorname{Pt}\{531\}$, individual trajectories also exhibit very little change in their respective $L_{z}$ value over time, so that the standard deviation remains constant, whereas on $\operatorname{Pt}\{110\}-(1 \times 2)$ the $\mathrm{L}_{z}$ of individual trajectories shows some tendency towards zero as well, thereby reducing the standard deviation of the average $\mathrm{L}_{z}$.


Figure 12: Time evolution of the distance between the topmost Pt atom and the ethane re-associating hydrogen atom on $\operatorname{Pt}\{531\}$ (left) and $\operatorname{Pt}\{110\}$ - $(1 \times 2)$ (right).

Following the vibrational analysis for methane, a similar analysis of the initial phases of the ethane vibrational modes hightlighted the importance of two particular vibrations on each surface, again indicated in bold in Table 3. Mode 3 of ethane on $\operatorname{Pt}\{531\}$ and mode 4 on $\operatorname{Pt}\{110\}-(1 \times 2)$ determine the initial sign of $\mathrm{L}_{z}$, both corresponding to an approximate asymmetric stretch vibration of the $\mathrm{Pt}-\mathrm{C}-\mathrm{C}$ bonds. The bifurcation of the set of $\mathrm{Pt}-\mathrm{H}$ distance curves, shown in Fig. 12, is connected to mode 18 on both surfaces. This mode is strongly

Table 3: Vibrational frequencies in $\mathrm{cm}^{-1}$ of phonon modes obtained for the transition states of ethane on $\operatorname{Pt}\{531\}$ and $\operatorname{Pt}\{110\}$ - $(1 \times 2)$ compared to for gas-phase ethane. Literature values are also provided alongside an assignment of the type of mode. ${ }^{31}$ Frequencies in bold indicate importance for the analysis, see text. Asterisks indicate a computational artefact due to our periodic setup, these frequencies should actually be zero.

| No. | $\mathbf{P t}\{\mathbf{5 3 1}\}$ | $\mathbf{P t}\{\mathbf{1 1 0 \}} \mathbf{- ( \mathbf { 1 } \times \mathbf { 2 } )}$ | gas-phase | literature | Assignment |
| :--- | :---: | :---: | :---: | :---: | :---: |
| 1 | 52 | 52 | 0 | 0 | frust. translation $x$ |
| 2 | 135 | 109 | 0 | 0 | frust. translation $y$ |
| 3 | $\mathbf{1 9 4}$ | 187 | 0 | 0 | frust. rotation |
| 4 | 244 | $\mathbf{2 0 9}$ | $148^{*}$ | 0 | frust. rotation |
| 5 | 387 | 311 | $180^{*}$ | 0 | frust. rotation |
| 6 | 437 | 418 | $247^{*}$ | 0 | frust. translation $z$ |
| 7 | 484 | 469 | 414 | 289 | H-C-C-H torsion |
| 8 | 734 | 741 | 820 | 822 |  |
| 9 | 967 | 937 | 833 | 822 | $\mathrm{CH}_{3}$ rock |
| 10 | 978 | 972 | 991 | 995 | $\mathrm{C}-\mathrm{C}$ stretch |
| 11 | 1050 | 1028 | 1183 | 1190 |  |
| 12 | 1182 | 1159 | 1195 | 1190 | CH 3 rock |
| 13 | 1217 | 1207 | 1366 | 1379 | $\mathrm{CH}_{3}$ sym. deform |
| 14 | 1381 | 1336 | 1382 | 1388 | $\mathrm{CH}_{3}$ sym. deform |
| 15 | 1415 | 1411 | 1453 | 1468 | $\mathrm{CH}_{3}$ deg. deform |
| 16 | 1454 | 1434 | 1471 | 1468 |  |
| 17 | 1467 | 1443 | 1476 | 1469 | $\mathrm{CH}_{3}$ deg. deform |
| 18 | $\mathbf{2 1 5 1}$ | $\mathbf{2 1 6 6}$ | 1481 | 1469 |  |
| 19 | 2971 | 2838 | 2977 | 2896 | $\mathrm{CH}_{3}$ sym. stretch |
| 20 | 2978 | 2983 | 2984 | 2954 | $\mathrm{CH}_{3}$ sym. stretch |
| 21 | 3016 | 2996 | 3031 | 2969 | $\mathrm{CH}_{3}$ deg. stretch |
| 22 | 3042 | 3043 | 3038 | 2969 |  |
| 23 | 3074 | 3064 | 3056 | 2985 | $\mathrm{CH}_{3}$ deg. stretch |
| 24 | -718 | -715 | 3061 | 2985 |  |
|  |  |  |  |  |  |



Figure 13: Time evolution of the distance between the topmost Pt atom and the ethane carbon atom, to which hydrogen is re-associating, on $\operatorname{Pt}\{531\}$ (left) and $\operatorname{Pt}\{110\}-(1 \times 2)$ (right).
perturbed compared to the gas-phase molecule ( $\Delta \nu \approx 670 \mathrm{~cm}^{-1}$ ) and involves almost zero displacements for atoms aside from the dissociating hydrogen, which moves parallel to the surface normal towards and away from the topmost Pt atom. However, the Pt-C distance of ethane on both Pt surfaces does not exhibit a bifurcation, and thus, no connection to a particular vibrational mode can be established. The overall desorption of ethane is more robust than for methane, with most trajectories achieving a Pt-H distance of $4 \AA$ or more, but requiring the addition of translational energy.

Ethane is a prolate symmetrical top because its principal axis along the C-C bond has a smaller eigenvalue than the other two axes, which share the same eigenvalue, lie in the plane orthogonal to the C-C bond, and can be arbitrarily chosen within that plane because they form a basis for $\mathrm{E}_{u}$ in $\mathrm{D}_{3 d}$. This relationship to the geometry of the ethane molecule is especially easy to discern in Figs. 14a and 14d with the unique axis, $\mathrm{I}_{A}$, shown in orange along the direction of the $\mathrm{C}-\mathrm{C}$ bond and the other two axes, $\mathrm{I}_{B}$ and $\mathrm{I}_{C}$, shown in green and red, perpendicular to $\mathrm{I}_{A}$.

The angular momentum vectors are initially distributed over a large range of directions


Figure 14: Vector representation of $\mathbf{L}$ (blue) and $\mathbf{I}_{\mathbf{A}}, \mathbf{I}_{\mathbf{B}}, \mathbf{I}_{\mathbf{C}}$ (orange, red, green) for ethane on $\operatorname{Pt}\{531\}$ and $\operatorname{Pt}\{110\}-(1 \times 2)$ at different times of the trajectories. A randomly selected ethane molecule is included for clarity.
on both surfaces. On $\operatorname{Pt}\{531\}$, however, they align increasingly along one particular direction in space, i.e. in the frame of reference of the unit cell and the surface, quite distinctly visible in Figs. 14a to 14c. To describe this effect quantitatively, a measure for the degree of clustering of a set of vectors around its vector mean is needed. If all of the vectors lie within a narrow cone around the mean, the angle between each individual vector and the ensemble mean will vary between 0 and a small maximum, e.g. $15^{\circ}$. Conversely, if they are scattered in a wide range around the mean, the angle between each individual vector and the mean will vary between 0 and $180^{\circ}$. The mean of all these angles therefore reports on how wide or narrow the clustering of the vectors around their mean is, the closer to 0 the narrower, i.e. well-aligned along the mean, the closer to $90^{\circ}$ the wider, i.e. unaligned. At 20 fs , the
mean of these angles is $70^{\circ}$ and reduces to $60^{\circ}$ after 60 fs and $42^{\circ}$ at the end of the simulation time. A similar alignment is not found for ethane desorbing from $\operatorname{Pt}\{110\}-(1 \times 2)$; instead the angular momentum vectors just continue to scatter in all directions as the simulation time increases.

## Discussion/Comparison

Even though all trajectories were started from a transition state for a C - H bond cleavage of a small hydrocarbon on the same Pt surfaces, there are some important differences in the results for methane and ethane. Firstly, the observed angular momentum of ethane is much larger (approximately 2.5 times in magnitude) than for methane. This difference is due to the higher molecular mass and therefore higher moment of inertia, which can give rise to angular momentum at the beginning of the trajectory through surface-perturbed molecular vibrations. Note that the additional angular momentum cannot be attributed to the additional translational energy supplied to the desorbing ethane molecules, since the extra velocity is applied to the whole molecule and has no angular component.

Furthermore, for methane there is no significant difference in $L$ between the chiral and the achiral surface, whereas for ethane opposite trends are observed, which result in an absolute difference in angular momentum of 4.7 a.u. at the end of the simulation time. Even though neither methane nor ethane exhibit a significant non-zero mean $\mathrm{L}_{z}$, there is another small difference between the chiral and the achiral surface observed for ethane: the $\mathrm{L}_{z}$ of individual trajectories are either constant over time $(\operatorname{Pt}\{531\})$ or tend to zero, i.e. showing a decreasing standard deviation over time $(\operatorname{Pt}\{110\}-(1 \times 2))$. The most striking effect is the increase in directionality of the angular momentum vectors of ethane on $\operatorname{Pt}\{531\}$, which is not seen on $\operatorname{Pt}\{110\}-(1 \times 2)$, or for methane on either surface. These three effects together reveal a small influence of the chiral surface on ethane, inducing a slightly directed angular momentum in the movement of ethane molecules desorbing from $\operatorname{Pt}\{531\}$. The fact that we
could not observe any directed rotational effects upon desorption - and in time-reversal also upon adsorption - is in line with experimental state-resolved studies of methane dissociation on Ni, where no such influences could be established either. ${ }^{1,2}$

Compared to the influence of a chiral surface on the rotations of formic acid, ${ }^{14}$ our findings for methane and ethane on Pt are much less pronounced. The lack of a non-zero $\mathrm{L}_{z}$ is a major difference from the effect observed for formic acid. We postulate that the magnitude of chiral information transfer from the surface to rotational motion of the desorbing molecule is connected to the geometry of the transition state, in particular the direction of the reforming bond and its geometric relation to the center of mass of the entire molecule. If the two atoms of the re-forming bond, A (the re-associating atom) and B (still connected to the main molecular fragment), and the center of mass, CMS, all lie on the same line, as they do in methane to a very good approximation, the angle between A-B and A-CMS is zero. For ethane, this angle is approximately $13^{\circ}$, whereas for formic acid it is approximately $32^{\circ}$. This difference could be the crucial geometric factor determining whether there will be a significant $\mathrm{L}_{z}$, which is then perhaps magnified by the chiral surface or reduced by the achiral surface from which the molecule is desorbing.

## Conclusion

We have analysed the desorption of methane and ethane from $\operatorname{Pt}\{531\}$ and $\operatorname{Pt}\{110\}-(1 \times 2)$. After identification of the most energetically favourable reaction pathway for dissociative adsorption on both surfaces, we performed MD simulations of desorption and analysed the time evolution of rotational properties for desorbing molecules, as well as the influence of the various vibrational modes. Methane desorbs with only a small angular momentum from both surfaces, with no significant mean $\mathrm{L}_{z}$, and without a preferred rotational axis. Initial values of $\mathrm{L}_{z}$ for individual trajectories correlate with the initial phase of two vibrational modes in the transition state. Initial desorption is linked to the phase of two other individual modes at the start of the trajectories. No pronounced difference between the chiral and the achiral
surfaces is observed for methane on $\operatorname{Pt}$. The desorption of ethane from $\operatorname{Pt}\{531\}$ and $\operatorname{Pt}\{110\}$ $(1 \times 2)$ gives rise to a larger angular momentum, but also with no significant non-zero $\mathrm{L}_{z}$. The angular momentum vectors, however, exhibit an increasing directionality over time on Pt $\{531\}$. Together with other small differences between the results for the chiral and the achiral surface, we propose a small chiral effect on the rotation of ethane desorbing from Pt. As for methane, there are connections between the initial $\mathrm{L}_{z}$ values of individual trajectories and the initial desorption behaviour to the phase of one particular mode. Hence, this study has revealed further insight into the adsorption and desorption of small hydrocarbons on metal surfaces and their molecular vibrations and rotations.

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## TOC Graphic



