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Molecular simulation of temperature-programmed desorption

Kristen A. Fichthorn [a,b,*], Kelly E. Becker [a], Radu A. Miron [b,1]

[a] *Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, United States*
[b] *Department of Physics, The Pennsylvania State University, University Park, PA 16802, United States*

Abstract

We use accelerated molecular dynamics to probe the thermal desorption of *n*-alkanes from the Au(1 1 1) and C(0 0 0 1) surfaces. Studying an alkane series ranging from CH_4 to $C_{16}H_{34}$, we find that the desorption prefactor increases with increasing chain length for the short chains until a certain chain length is reached when it becomes essentially constant and independent of chain length. We can understand the dependence of the preexponential factor on alkane chain length in terms of conformational changes within the alkane molecules. For the shorter molecules, the desorption temperatures probed in experimental temperature-programmed desorption studies lie below those for which torsional motion is activated. Thus, the short alkanes can be treated as rigid rods, and the loss in translational and rotational entropy upon adsorption leads to a preexponential factor that increases with increasing chain length. As the alkane chain length increases, the binding energy and the experimental desorption temperatures also increase. Thus, torsional motion is activated to an extent that increases with increasing chain length. This torsional activation increases the entropy of adsorption and counteracts the entropy decrease due to a loss of translation and rotation. This leads to a virtually constant prefactor for sufficiently long chains. Our findings are consistent with experimental data for the thermal desorption of alkanes from the Au(1 1 1), Pt(1 1 1), MgO(1 0 0) and C(0 0 0 1) surfaces.

Keywords: Temperature-programmed desorption; *n*-alkanes; Thermal desorption

1. Introduction

The thermal desorption of adsorbed species from solid surfaces is an important process that occurs in heterogeneous catalysis. A fundamental understanding of this phenomenon will enable a correct description of catalysis kinetics. Much of our knowledge of thermal desorption has come from experimental temperature-programmed desorption (TPD) studies. In this technique, molecules are adsorbed onto a solid surface to a fixed coverage θ and at a temperature T_0 for which desorption is insignificant. Subsequently, the surface temperature T is ramped linearly with time t (*i.e.*, $T = T_0 + \beta t$, where β is the heating rate). As the temperature increases, desorption occurs and the desorption rate goes through a maximum at a peak temperature of T_p. Assuming that the desorption rate constant k has the Polanyi–Wigner form suggested by transition-state theory (TST), *i.e.*,

$$k = \nu \exp\left(\frac{-E_d}{k_B T}\right), \qquad (1)$$

the desorption activation energy E_d and the preexponential factor ν can be estimated from analysis of T_p for various heating rates. The values of E_d and ν characterize the binding energy of the molecule to the surface and the entropy change involved with adsorption, respectively. Despite the extensive use of TPD to determine rate data, interpretation of this experiment can still be controversial. There have been many studies on how to interpret TPD experiments, with analyses ranging from Redhead's original approach [1], which employs rate equations, to kinetic Monte Carlo simulations [2–6], in which individual atoms and molecules are taken into account. However, none of these approaches is without drawbacks and, in all cases, assumptions must be made that may not be accurate.

From a theory perspective, the most accurate model for thermal desorption is one in which we follow the molecular dynamics of each atom and molecule in an adlayer. With an

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* Corresponding author at: Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, United States.
Tel.: +1 814 863 4807; fax: +1 814 865 7846.
E-mail address: fichthorn@psu.edu (K.A. Fichthorn).

[1] Present address: SDA Software Design Ahnert GmbH, Berlin, Germany.

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accurate description of the inter- and intra-molecular interactions of the adsorbed species, as well as the interactions between the adsorbates and the solid surface, we can integrate Newton's equations of motion to obtain molecular trajectories and to track desorption events. From these direct molecular dynamics (MD) simulations, one could, in principle, obtain desorption rates and even model entire TPD experiments. The inherent difficulty with direct MD simulation of desorption, however, is the time scale involved. While MD simulations typically probe the nanosecond time scale, thermal desorption, as characterized in experimental studies, typically occurs over time scales on the second range or longer. Thus, direct MD simulation of thermal desorption is not feasible under typical experimental conditions.

With developments in *accelerated* MD simulations [7–11] for rare event dynamics, it is possible obtain rate constants for thermal desorption. Below, we review our recent studies in this area [12,13]. Our work to date has focused on understanding the thermal desorption of *n*-alkanes from Au(1 1 1) and C(0 0 0 1). These systems are good examples of the difficulties in interpreting TPD data. Although the desorption energies of these chain-like molecules on Au(1 1 1) [14] and graphite [15–17] surfaces are similar and similar forces are involved, the preexponential factors determined by TPD experiments differ by approximately six orders of magnitude for Au(1 1 1)[14] and the basal plane of graphite [15,16]. Moreover, while TPD studies of alkane desorption from C(0 0 0 1) [17] reveal that the preexponential factor increases with increasing chain length for alkane chains ranging from methane (CH_4) to decane ($C_{10}H_{22}$), similar studies of desorption from Au(1 1 1) [14] and studies of alkanes ranging between C_7H_{16} and $C_{44}H_{90}$ on graphite [15,16] report a constant preexponential factor that is independent of chain length. Do these discrepancies reflect significant differences between alkane adsorption on these surfaces or is the analysis of TPD problematic for these systems? Below, we convey the insight that our simulations have yielded into these issues [12,13].

2. Methods

We consider the desorption of a single *n*-alkane molecule on Au(1 1 1) or C(0 0 0 1). In our study of alkane desorption from Au(1 1 1) [12], we considered a series of molecules ranging from methane (CH_4) to dodecane ($C_{12}H_{26}$). In this study, we adopt the united-atom (UA) model for *n*-alkanes [18–20], in which CH_N ($N = 2$–4) groups are modeled as single interaction centers. We describe the UA–Au interaction using a Lennard–Jones (12–6) potential, with parameters adjusted to match the desorption energy of *n*-hexane from Au(1 1 1) [14] and we model the Au(1 1 1) surface as a five-layer slab with 64 atoms per layer. In our study of alkane desorption from graphite [13], the alkane molecules range in length from *n*-pentane (C_5H_{12}) to *n*-hexadecane ($C_{16}H_{34}$). An all-atom representation is used, in which we explicitly model each carbon and hydrogen atom in an alkane based on the OPLS force field [21]. The interaction between the carbon and hydrogen atoms in the alkane and the graphite surface is modeled using a modified Steele's potential [22] with parameters designed to fit experimental binding energies for *n*-alkanes on graphite [15].

Rare events, such as thermal desorption can be described using transition-state theory (TST). In TST, the desorption rate constant k_{TST} is a canonical average of the flux of molecules from the adsorbed state through the dividing surface defining the transition-state to the gas phase above the surface. It can be written as [23]:

$$k_{\mathrm{TST}} = \frac{1}{2}\left(\frac{2k_{\mathrm{B}}T}{\pi m}\right)^{1/2} \frac{\int_{\mathbf{R}} \delta[F(\mathbf{R})]\, \mathrm{e}^{-U(\mathbf{R})/k_{\mathrm{B}}T}\, \mathrm{d}\mathbf{R}}{\int_{\mathbf{R}} \mathrm{e}^{-U(\mathbf{R})/k_{\mathrm{B}}T}\, \mathrm{d}\mathbf{R}}, \tag{2}$$

where the integrals span the entire configuration space ranging from the surface to the transition-state, $\delta[x]$ is the Dirac delta function of x, $F(\mathbf{R})$ is defined to be zero over the transition-state dividing surface, $U(\mathbf{R})$ is the potential energy and m is the mass of the alkane molecule. Since alkane adsorption is not an activated process, there is no clear transition-state between an adsorbed molecule and a free molecule in the gas phase. Thus, the transition-state is chosen so that trajectories that cross the transition-state dividing surface have a high probability of continuing on to the product (free molecule) state. This corresponds to a plane at a height above the surface where the alkane–surface interaction is negligible [12,13].

Although in principle the integrals in Eq. (2) can be evaluated by direct MD simulation of alkane molecules desorbing from the surface, this is not possible in practice because thermal desorption occurs over much longer time scales than can be probed with conventional MD. We use umbrella sampling [24] to "boost" MD trajectories into the transition-state region so that Eq. (2) can be evaluated. In this procedure, we recognize that the canonical average in Eq. (2) can be expressed as:

$$k_{\mathrm{TST}} = \frac{1}{2}\left(\frac{2k_{\mathrm{B}}T}{\pi m}\right)^{1/2} \frac{\int_{\mathbf{R}} \delta[F(\mathbf{R})] W(\mathbf{R})\, \mathrm{e}^{-U(\mathbf{R})/k_{\mathrm{B}}T}/W(\mathbf{R})\, \mathrm{d}\mathbf{R}}{\int_{\mathbf{R}} W(\mathbf{R})\, \mathrm{e}^{-U(\mathbf{R})/k_{\mathrm{B}}T}/W(\mathbf{R})\, \mathrm{d}\mathbf{R}}, \tag{3}$$

where $W(\mathbf{R})$ is a weighting function. In our studies, we use a weighting function of the form:

$$W(\mathbf{R}) = \exp\left[\left(\frac{s-1}{s}\right)\frac{U(\mathbf{R})}{k_{\mathrm{B}}T}\right]. \tag{4}$$

Substituting Eq. (4) into Eq. (3), we see that in using this weighting function, we run the simulation at a high temperature sT where desorption occurs on conventional MD time scales. The desorption rate constant at the desired temperature T becomes the ratio of the average of $1/W$ at the transition-state to the average of $1/W$ over the entire configurational space probed with a simulation temperature of sT. Representing the transition-state dividing surface as a thin box of width b, the rate constant is thus given by:

$$k_{\mathrm{TST}} = \frac{1}{2}\left(\frac{2k_{\mathrm{B}}T}{\pi m}\right)^{1/2} \frac{1}{b} \frac{\left\langle \delta[F(\mathbf{R})]/W \right\rangle_{sT}}{\left\langle 1/W \right\rangle_{sT}}, \tag{5}$$

where the averages in the numerator and denominator are obtained at a temperature of sT [24].

It should be noted that there is a restricted range of s values for which this acceleration scheme is both correct and effective. A high value of s yields a highly accelerated system. However, if s is too high, the simulation will not sample the low-energy configurations characteristic of thermal desorption at experimental temperatures. We ensure that the system spends time in the low-energy configurations through the examination of energy histograms [13]. With proper acceleration, the energy range covered by the accelerated simulation includes that covered by the MD simulation plus higher energies (near the transition-state) that direct MD simulation cannot probe effectively.

The simulation protocol proceeds as follows: at the beginning of a simulation, the molecule is placed near the surface and equilibrated. Subsequently, the averages in Eq. (5) are evaluated. When the molecule has passed through the desorption box, it is placed back on the surface with a different orientation and re-equilibrated. Desorption rate constants are obtained for each molecule as an average over as few as 500 desorptions (for the smaller molecules) and as many as 3700 desorptions for hexadecane. For each molecule, we obtained rate constants in a temperature range that brackets the peak temperatures observed in experimental TPD studies [14,16]. The simulated desorption rates k_{TST} are plotted on an Arrhenius plot. From the slope of the best-fit line, the desorption energy E_d is calculated and the prefactor ν is determined from the intercept.

3. Results and discussion

3.1. Au(1 1 1) [12]

Desorption activation energies and preexponential factors for alkanes on the Au(1 1 1) surface are shown in Table 1, where we see that E_d and ν both increase with increasing chain length. Recent TPD studies of alkane chains ranging from methane (CH_4) to decane ($C_{10}H_{22}$) on MgO(1 0 0) [25], Pt(1 1 1) [17] and C(0 0 0 1) [17] also indicate that the preexponential factor increases with increasing chain length. The increase of the preexponential factors with increasing chain length reflects a growing difference between the entropies of the rigid-rod-like adsorbed molecules and the free molecule, transition-state species, which are rendered exactly in MD simulations. Motions that are free at the transition-state (*e.g.*, translation and rigid-body rotation) are hindered significantly on the surface and to an extent that increases with increasing chain length. This leads to the increasing prefactors.

Table 1
TST prefactors ν and barriers E_d for the desorption of alkanes from Au(1 1 1)

Alkane	ν (s^{-1})	E_d (kJ/mol)
CH_4	$(1.5 \pm 0.2) \times 10^{12}$	11.1 ± 0.2
C_2H_6	$(1.3 \pm 0.1) \times 10^{13}$	21.7 ± 0.4
C_4H_{10}	$(4.3 \pm 0.6) \times 10^{13}$	40 ± 1
C_6H_{14}	$(3.7 \pm 0.6) \times 10^{14}$	62 ± 2
C_8H_{18}	$(2.5 \pm 0.4) \times 10^{15}$	82 ± 2
$C_{10}H_{22}$	$(1.0 \pm 0.6) \times 10^{16}$	98 ± 4
$C_{12}H_{26}$	$(2.8 \pm 0.6) \times 10^{16}$	121 ± 5

Table 1 indicates that the prefactors for the larger molecules are significantly greater than the typically assumed value of 10^{13} s^{-1}. In their experimental TPD study of alkane desorption from Au(1 1 1), Wetterer et al. utilized prefactors of 10^{13} s^{-1} in the analysis of their data [14]. We consider the ramifications of this assumption by simulating TPD for our alkane series. To simulate TPD, we solve the first-order rate equation for the n-alkane fractional coverage θ as a function of time t, applying a linear temperature ramp with the experimental [14] heating rate of $\beta = 2.0$ K/s and using the TST rate parameters in Table 1 to characterize the rate, *i.e.*,

$$\frac{d\theta}{dt} = -k_{\mathrm{TST}}\theta, \tag{6}$$

and

$$\frac{dT}{dt} = \beta. \tag{7}$$

The Redhead equation for first-order desorption is used in many experimental studies to relate the peak temperature T_p to rate parameters ν_{TPD} and E_{TPD} through the expression:

$$\frac{E_{\mathrm{TPD}}}{k_B T_p} = \ln\left(\frac{\nu_{\mathrm{TPD}} T_p}{\beta}\right) - 3.64. \tag{8}$$

Using Eq. (8), we extract TPD binding energies E_{TPD} from the simulated TPD spectra by assuming that $\nu_{\mathrm{TPD}} = 10^{13}$ s^{-1}. By simulating TPD with the correct (TST) rate parameters and (incorrectly) analyzing the results assuming that $\nu_{\mathrm{TPD}} = 10^{13}$, we mimic the corresponding experimental study [14]. The resulting TPD activation energies are shown along with the TST values in Fig. 1, where we also include the experimentally determined desorption energies for alkanes on Au(1 1 1) [14]. The experimental and simulated TPD activation energies agree

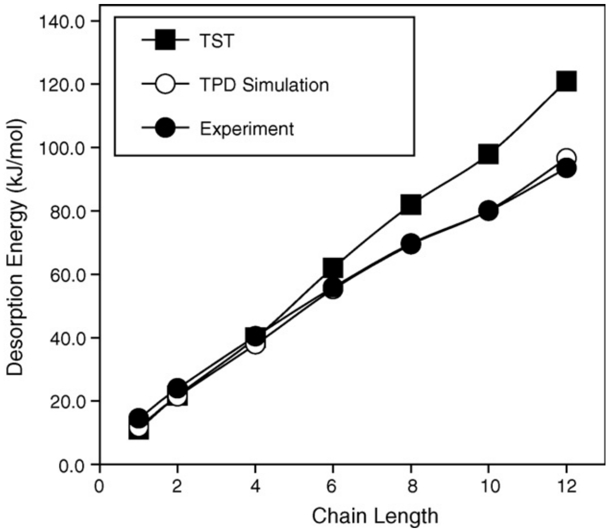

Fig. 1. Comparison of desorption activation energies obtained from accelerated MD simulation (TST), from simulation and analysis of TPD assuming a preexponential factor of 10^{13} and from experiment [14].

within 3 kJ/mol. Thus, our results show that the assumption of a constant prefactor can lead to incorrect estimates of the activation energy. In Fig. 1, we see that the TPD desorption energies are less than the "true" TST values by up to 24 kJ/mol for dodecane. Our studies also indicate that analyses of surface kinetics must be extremely thorough to ascertain the correct rate parameters. Despite vast differences between the TST and TPD rate parameters, the TPD peak temperatures arising from them are the same. If rate parameters can be corroborated by methods other than TPD, then a sufficiently wide temperature range should be probed to determine them uniquely.

3.2. C(0 0 0 1) [13]

Activation energies and preexponential factors for the desorption of alkanes from the basal plane of graphite are shown in Table 2. Here, we see that the activation energy increases with increasing chain length for this series. While the activation energies for the shorter chains (pentane–dodecane) are in good agreement with experimental values [15–17], we significantly overestimate the experimental desorption energies [15,16] for tetradecane and hexadecane. The origins of the discrepancy for these longer molecules is unclear—although a significant difference between our simulations and the TPD experiments is that we probe the low-coverage limit of a single molecule, while the experiments probe desorption from a monolayer. It is possible that coverage effects are important for these long alkane molecules and we will address coverage effects in a future study [26].

In Table 2, we see that the preexponential factor initially increases with increasing chain length, then levels off to a constant, average value of about $10^{18.3}$ for molecules longer than octane. In experimental TPD studies of alkane molecules containing between 7 and 44 carbons on C(0 0 0 1) [16], Paserba and Gellman found a constant, average prefactor of $10^{19.6}$. They explicitly determined preexponential factors for heptane ($\nu = 10^{18.7}$) and dodecane ($\nu = 10^{20.3}$). Our prefactors are in somewhat better agreement with those found by Tait et al. [17], who also probed alkane desorption on C(0 0 0 1) and found $10^{17.7}$ for hexane, $10^{16.5}$ for octane and $10^{17.8}$ for decane. We note that differences between our prefactors and those found experimentally are comparable to variations among the prefactors found by the two experimental groups.

To understand the relatively constant values of the preexponential factors for the longer molecules in this study and in the experiments [16,17], we recognize that there are two competing effects which determine the dependence of the prefactor on chain length. One is the effect of increasing molecular size and the other is the effect of increasing temperature. It is instructive to consider these effects separately and then examine how their combination ultimately affects the dependence of the prefactor on chain length.

Table 2
TST prefactors ν and barriers E_d for the desorption of alkanes from C(0 0 0 1)

Alkane	E_d (kJ/mol)	$\log_{10}(\nu)$ (s^{-1})
C_5H_{12}	49 ± 2	15.1 ± 0.7
C_6H_{14}	62 ± 2	16.1 ± 0.7
C_7H_{16}	73 ± 3	16.7 ± 0.7
C_8H_{18}	84 ± 2	17.1 ± 0.5
$C_{10}H_{22}$	108 ± 4	18.3 ± 0.8
$C_{12}H_{26}$	116 ± 4	17.7 ± 0.6
$C_{14}H_{30}$	142 ± 5	18.3 ± 0.7
$C_{16}H_{34}$	163 ± 5	19.0 ± 0.7

In our study of the desorption of short *n*-alkanes from Au(1 1 1), we discussed that there is an increasing loss in (mostly rotational) entropy upon adsorption with increasing chain length which leads to a corresponding increase in the preexponential factor [12]. A recent developed statistical mechanical model by Tait et al. [25] describes a similar increase that they observed experimentally in the prefactors of short alkane molecules on MgO(1 0 0). They treat an alkane as a rigid rod at both the surface and the transition-state. At the transition-state, the molecule is allowed to rotate and translate freely, while rotation and translation normal to the surface is prohibited for an adsorbed molecule. In our simulations of alkane desorption from graphite, we also see an increase in prefactor with chain length for pentane–decane. We confirmed [13] that pentane–octane spend more than 90% of their time in the *trans* configuration at experimentally relevant temperatures and can be treated as rigid rods. Thus, the analysis of Tait et al. [25] applies.

Unlike the short alkanes, we find that the longer molecules (dodecane, tetradecane and hexadecane) spend the majority of their time in the *gauche* conformation at experimentally relevant temperatures [13]. Although we still expect these molecules to lose a considerable amount of rotational entropy, as well as translational degrees of freedom when they adsorb on C(0 0 0 1) (hence the large prefactors for these molecules), torsional motion is activated for these molecules and they can no longer be treated as rigid rods. For these molecules, the temperature effect becomes important in determining the value of the preexponential factor.

Increasing the temperature has the effect of decreasing the prefactor. This can be seen as separate from the molecular size effect by examining the temperature dependence of k_{TST} for pentane over a wide temperature range that includes higher temperatures than those probed in TPD experiments. As we see in Fig. 2, an Arrhenius plot for pentane is not linear over a wide temperature range. While the prefactor for the lower temperature range probed in TPD experiments (130–180 K) is $10^{15.1}$, the prefactor for the higher temperature range (300–400 K) is $10^{12.0}$. We can link this nonlinearity to the extent that the molecule is in the *trans* conformation on the surface [13]. Over the lower temperature range, pentane is in the *trans* conformation over 98% of the time, while the molecule is more likely to assume one of its *gauche* conformers over the higher temperature range.

We note that the torsion barriers for a free alkane molecule are not strongly dependent on chain length. To a lesser extent, we also expect this to be true for adsorbed alkanes although because of the alkane–surface interaction, torsions are more likely near the chain ends than in the middle of the chain [13]. Since the binding energies of the alkane chains increase with

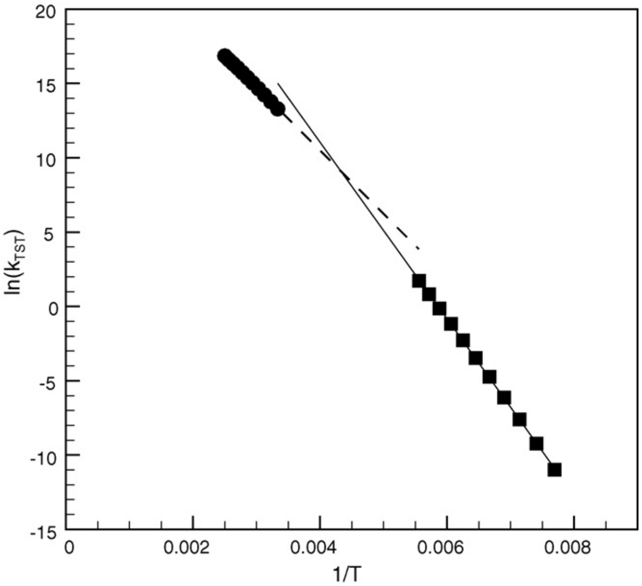

Fig. 2. Arrhenius plot of TST rate constants *vs.* $1/T$ for pentane. The solid line represents the best-fit line for the low temperature range (130–180 K). The dashed line represents the best-fit line for the high temperature range (300–400 K).

increasing chain length, the TPD peak temperatures also increase, enabling torsion. Our studies indicate that molecules larger than decane are mostly in their *gauche* states to an extent that increases with increasing chain length over experimental temperature ranges [13]. This increasing occupation of *gauche* states produces a concomitant increase in the adsorption entropy. Torsions that could only be treated as vibrations for the shorter molecules become hindered or free internal rotations for the longer molecules and there are more conformational degrees of freedom. The increase in the entropy of adsorption lowers the entropy difference between the adsorbed molecule and the transition-state and decreases the prefactor.

As we progress through an alkane series of increasing chain length, the increasing molecular size causes the prefactor to increase due to a loss in translational and rotational entropy on the surface. However, the increase in the alkane binding energy and, hence, TPD peak desorption temperature with increasing chain length causes the prefactor to decrease due to a gain in the entropy associated with torsion. For temperatures (chain lengths) where conformational changes are significant, these two effects can counteract each other, yielding a nearly constant prefactor that becomes independent of alkane chain length.

4. Conclusions

In summary, we conducted single molecule simulations of alkane desorption from two different surfaces. To be able to model desorption events at experimentally relevant temperatures, it was necessary to use an accelerated MD scheme. Progressing through an alkane series ranging from CH_4 to $C_{16}H_{34}$, we find that the activation energy for desorption increases with increasing chain length. For this series, the desorption prefactor increases in magnitude with increasing chain length until a certain chain length is reached when it becomes constant. For alkanes on C(0 0 0 1), these trends are consistent with experimental data [16,17]. Although our finding of an increasing prefactor for the shortest alkanes on the Au(1 1 1) surface is at odds with experimental data [14], we showed that our predicted TPD peak temperatures are the same as those found experimentally. Further, if we assume that the prefactor is constant with a value of 10^{13}, we obtain the experimental values for the activation energy in simulated TPD spectra. We note that prefactors that increase with increasing chain length have been found recently in experimental studies of the desorption of short alkanes from Pt(1 1 1) [17], MgO(1 0 0) [25], as well as C(0 0 0 1) [17]. Thus, it is likely that this trend generally holds for short alkane physisorption on solid, single crystal surfaces.

We can understand the dependence of the preexponential factor on alkane chain length by examining conformational changes within the alkane molecules. For the shorter molecules, the TPD peak desorption temperatures lie below those for which torsional motion is activated and the molecules can be treated as rigid rods, consistent with the model developed by Tait et al. [25]. For longer chain molecules, torsions are activated to an extent that increases with increasing chain length, causing a greater increase in entropy of the adsorbed molecule than what would be expected for a rigid rod. The corresponding decrease in the entropy difference between the free molecule transition-state and the adsorbed molecule counteracts the increase in the entropy difference gained from increased molecular size. This leads to a prefactor that increases with chain length until conformational changes within the molecule become activated, at which point the prefactor levels off to a constant value. In future work, we aim to determine the effects of coverage on conformational changes and ordering within the layer and their effects on desorption.

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