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The dynamical origin of non-normal energy scaling and the effect of surface temperature on the trapping of low molecular weight alkanes on Pt(111)

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Abstract

Molecular classical dynamical simulations of alkanes trapping on platinum surfaces were performed to examine the origin of non-normal energy scaling for molecular adsorption. Conversion of normal to parallel translational energy at normal incidence and conversion of parallel translational energy into normal translational energy at glancing angles are the primary mechanisms which produce non-normal energy scaling of alkanes trapping on cold Pt(111). In addition, a tendency to convert rotational energy gained in the first gas–surface collision into normal translational energy for collisions at glancing incidence further increases the degree of non-normal energy scaling. Increasing surface temperature is shown to have little effect on energy transfer processes in the first bounce but increasing influence on subsequent bounces. Despite difficulties in defining trapping at high surface temperatures, simulations indicate that the initial trapping probability of ethane on Pt(111) does not fall by more than a factor of two over the surface temperature range of 100–700 K. © 1997 Elsevier Science B.V.

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1. Introduction

When atomic or molecular trapping is found to scale monotonically with $E_T \cos^2 \theta_i$, where E_T is the incident kinetic energy and θ_i is the angle of incidence the gas–surface potential has been characterized as “flat”, since for such conditions interconversion of normal and parallel momentum is not expected, and trapping is dominated by loss of momentum normal to the surface. Such scaling is referred to as “normal energy scaling.” However,

in many cases normal energy scaling is not observed experimentally, and corrugation of the gas–surface potential has been suggested to account qualitatively for this result [1–19]. The degree of corrugation in the scattering potential in these systems is often assessed by scaling the initial trapping probabilities with $E_T \cos^n \theta_i$, where n is allowed to vary from 0 to 2. While a few systems have been found which do not scale according to this functionality [15–19], the molecular trapping probabilities reported to date for most species conform to such scaling [1–14]. Systems which scale with n near zero are often assumed to have a highly corrugated gas–surface potential, and such scaling is referred to as “total energy scaling.”

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Deviations from normal energy scaling may have several possible origins [20–22]; namely, (1) interconversion of incident normal translational energy and parallel translational energy [19,23,24], (2) excitation of parallel surface phonon modes [25], (3) excitation–deexcitation of rotational motion [26–37], (4) slow thermalization with the surface from increased surface temperature [5,38–42], and (5) microstructural roughness [15–17,19,43–45]. In this paper we examine these effects for alkane adsorption on platinum surfaces using stochastic trajectory simulations. In these simulations we employed a potential function that provides excellent agreement between simulated initial trapping probabilities for ethane on Pt(111) and leads to successful *prediction* of experimentally observed trapping probabilities for ethane and propane on Pt(110)-(1×2) and propane on Pt(111) [19,23,43] for a wide range of incident energies and angles, giving us confidence in the utility of the platinum–alkane potential function.

2. Simulation methods

Classical molecular dynamics, employing a stochastic technique which has been described previously [46,47], were used to simulate ethane and propane trapping on Pt(111). In this study we present only a brief description of the computations. A more detailed description of the potentials and calculation methods used in this study is given elsewhere [23]. Periodic boundary conditions were imposed in the plane of the surface to create an infinite slab in the x and y directions. Friction, random and constraint forces were applied to the bottom layer of the slab to mimic the effect of the missing bulk platinum atoms. A slab composed of three layers with 36 platinum atoms in each layer was used for the Pt(111) simulations. The platinum atoms were chosen to vibrate about their equilibrium positions, which were taken to be the bulk-terminated positions for Pt(111). The surface potential was represented by nearest neighbor and next-nearest neighbor harmonic force constants. These slab parameters accurately reproduce the bulk platinum Debye temperature of 234 K [48].

Ethane and propane molecules were considered to be pseudo-diatomic and -triatomic, respectively. For the collisional energies used in this study vibrational excitation of modes associated with the methyl groups would be negligible [19,23,43]. The ethane–platinum gas–surface potential results from the two methyl groups, connected by a Morse potential, each interacting with each surface platinum atom via a second pairwise additive Morse potential. The Morse potential parameters for the methyl–Pt interaction were determined by quantitatively reproducing the experimental initial trapping probabilities and scattered angular distribution of ethane incident on Pt(111) at a surface temperature (T_s) of 95 K for a wide range of incident energies and angles [23]. The Morse potential well depth ϵ (2.53 kJ mol^{-1}) was adjusted to yield the independently measured energy of adsorption of 28 kJ mol^{-1} [1]. The propane–platinum gas–surface potential [43] was taken to result from the interaction of two methyl groups and a methylene group with each surface platinum atom via the same pairwise additive methyl–platinum Morse potential determined from the ethane/Pt(111) study [23]. This set of Morse potential parameters accurately *predicts* the experimentally determined values of the adsorption probabilities of methane/Pt(111) [11], ethane/Pt(111) [1], ethane/Pt(110)-(1×2) [19], propane/Pt(111) [4] and propane/Pt(110)-(1×2) [17].

The well depth of the methyl–methyl pseudo diatomic Morse potential of ethane was set equal to the C–C bond energy ($\epsilon = 347 \text{ kJ mol}^{-1}$), and the methyl–methyl distance was set equal to the center of mass methyl–methyl distance of ethane ($r_o = 1.7 \text{ \AA}$). The range parameter for the methyl–methyl interaction was set to match the ethane C–C vibrational frequency of 1000 cm^{-1} ($\sigma = 2.0 \text{ \AA}^{-1}$) [49]. Propane methyl–methylene interactions were described by these same parameters. In addition, a harmonic C–C–C bending force constant of 275 cm^{-1} was used for propane [49,50]. Excitation of this mode was determined to have little effect in the trapping of propane on Pt(111) and Pt(110)-(1×2) [43].

Classical stochastic trajectories governed by the interactions described above were integrated by a modified Beeman algorithm with a time step of

2 fs [51]. The initial momenta of the surface atoms were chosen at random for each trajectory from a Boltzmann distribution at a prescribed surface temperature. Ethane and propane molecules were initially located outside the range of the gas–surface interaction at 9.5 and 11 Å above the platinum slab. The initial x and y center-of-mass positions and orientation of ethane and propane were chosen randomly. Because molecules generated in molecular beams are expected to have significant rotational cooling, the initial rotational temperature was taken to be near zero, 10 K. Trajectories were integrated until one of the three following conditions occurred: (1) The molecule scattered from the surface and escaped to a height greater than 9 Å. These trajectories were classified as scattered. (2) The ethane total energy (kinetic plus potential) fell below a specific value designated as the criterion for trapping, the trajectory was designated as trapped. For this study the trapping criterion was set at -20 kJ mol^{-1} , which is over $-10k_{\text{B}}T_{\text{s}}$ per methyl group for $T_{\text{s}}=95 \text{ K}$; this criterion has been previously established as more than sufficient for trapping [52]. (3) If neither of (1) or (2) occurred after the 15 000 integration steps (30 ps) the trajectory was terminated and classified as uncertain. The number of uncertain trajectories was always small, typically about 1.5% of the total, and were hence excluded from the analysis. Unless otherwise stated, all computed trapping probabilities were obtained from a sample of 2000 trajectories for ethane and 2500 trajectories for propane, giving a statistical uncertainty of ± 0.02 .

3. Discussion and analysis

To investigate the possible origins of non-normal energy scaling for the trapping of ethane and propane on platinum surfaces, the partitioning of energy of each single trajectory after colliding with the surface was analyzed in detail for the first two bounces. After the molecule collided with the surface once and rebounded to either the scatter height (for scattered molecules) or the classical turning point away from the surface [23], the kinetic energy in helicopter and cartwheel rotational motion, in-plane and perpendicular transla-

tional motion, and the potential energies were individually evaluated and stored. The total amount of energy lost to surface phonons was calculated by subtracting the sum of the five aforementioned energies from the initial incident kinetic (translational and rotational) energy. If a given trajectory continued for a second surface collision, the same energy calculations were repeated at either the scatter height or outward turning point following that collision. In addition, if a trajectory proceeded beyond more than two surface collisions, the energy in the various modes of motion was calculated when the trajectory was terminated. The number of surface collisions a trajectory experienced was also stored as information. Once all the trajectories were finished, the appropriate average values of the energies were calculated.

3.1. Non-normal energy scaling of alkanes/Pt(111)

The measured scaling function for the adsorption probability of ethane on Pt(111), $E_{\text{T}} \cos^{0.6} \theta_{\text{i}}$, compares well to the results of the simulations, which give $E_{\text{T}} \cos^{0.7} \theta_{\text{i}}$. The simulations also show that the adsorption probability is determined to within 10% by the fate of the first collision with the surface [23], so that the main cause for non-normal energy scaling in the trapping of ethane on Pt(111) must arise from the first gas–surface encounter. Indeed, the calculated values of the apparent trapping probabilities of ethane on Pt(111) after the first bounce scale with $n=1.0$ (see Fig. 1), a value only slightly higher than the energy scaling exponent obtained when multiple bounces are considered ($n=0.7$). Table 1 lists the average change in rotational kinetic energies (cartwheel+helicopter), parallel translational energy, perpendicular translational energy and surface phonon energy after the first bounce for ethane incident on Pt(111) with different initial translational energies and angles. In each case there is exactly 10 kJ mol^{-1} of initial normal translational energy, E_{n} . Perfect normal energy scaling would require that the initial trapping probabilities, α , for all these incident conditions would all be equal – a result clearly not observed either experimentally or theoretically [1,23]. The nearly equal amount of energy stored in surface phonons after the first

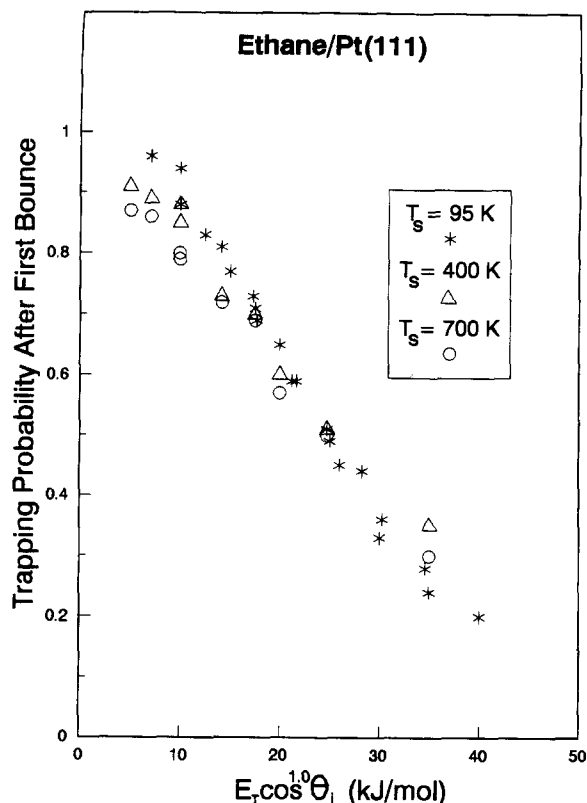


Fig. 1. The apparent trapping probabilities after the first bounce of ethane on Pt(111) plotted as a function of $E_T \cos^{1.0} \theta_i$. The asterisks, triangles and circles represent the simulations at surface temperatures of 95, 400 and 700 K, respectively.

Table 1

Table of average change in energies after the first bounce from ethane incident at Pt(111) with a surface temperature of 95 K

Incident condition	Rot.	Par.	Perp.	Phonon	α
10 kJ mol ⁻¹ , 0°	5.8	2.8	-18.4	9.8	0.93
20 kJ mol ⁻¹ , 45°	7.1	-1.3	-16.2	10.4	0.78
40 kJ mol ⁻¹ , 60°	9.2	-6.7	-13.6	11.1	0.52

All average energies shown are in kJ mol⁻¹. Positive numbers indicate a gain, negative numbers a loss. Perpendicular energy is the sum of normal kinetic energy and the potential energy interaction with the surface.

bounce for all three incident conditions (10.4 ± 0.7 kJ mol⁻¹) is expected for normal energy scaling, indicating that energy transfer to phonons does not affect the non-normal energy scaling of

ethane. In addition, the extent of rotational excitation increases with angle of incidence at constant E_n , making α potentially even more dependent on incident angle than expected for normal energy scaling. Furthermore, at a surface temperature of 95 K, less than 10% of the total trajectories scatter after two or more bounces; thus chattering collisions due to excessive rotational excitation on the first bounce and deexcitation on subsequent bounces are not the primary source of the non-normal energy scaling of ethane either. The modest gain in parallel translational energy at normal incidence (2.8 kJ mol⁻¹) and the losses at 45° and 60° (-1.3 and -6.7) suggests that non-normal energy scaling behavior results after the first gas-surface collision from the interconversion of normal and parallel translational energy. This interconversion arises from the surface potential roughness. At low angles of incidence (near the surface normal) perpendicular momentum is converted to parallel momentum in the surface collision, and at higher angles of incidence the converse occurs.

Although the number of trajectories that produce scattering from multiple bounces (more than one) for this system was calculated to be less than 10% of the total number of trajectories, the simulations indicate that molecules incident at glancing angles are more susceptible to multiple bounce scattering than those at normal incidence, further lowering the energy scaling exponent. Because molecules at glancing incidence are rotationally more excited in the cartwheel motion after the first bounce, scattering on subsequent bounces due to a chattering collision occurs more frequently. Hence, relative to perfect normal energy scaling, the trapping of ethane on Pt(111) is enhanced at normal incidence due to a conversion of normal to parallel momentum and reduced at glancing incidence by the converse process, producing non-normal energy scaling; multiple bounce chattering collisions further contribute to this effect as a secondary influence.

3.2. Surface temperature

The understanding of changes in energy accommodation of alkanes due to increasing surface

temperature is crucial for the interpretation of precursor-mediated dissociation data obtained from molecular beam experiments. The current approach for analyzing such information is to assume that the trapping probability is independent of the surface temperature and to calculate the rate parameters governing the branching ratio between desorption and surface reaction from the temperature dependence of the dissociative sticking probability [53]. Contrary to the notion of quasi-trapping [38], this approach makes a clear distinction between the regimes of trapping and desorption.

However, in recent experiments of Ar trapping on Pt(111), Mullins et al. measured trapping probabilities from velocity distributions and reported changes in the energy scaling of the trapping probability with increasing surface temperatures [5]. Subsequent theoretical studies of Ar scattering from Pt(111) [38,39] by Head-Gordon et al. and Smith et al. have suggested that the parallel velocity component is slower to accommodate at higher surface temperatures, such that the surface residence time of the rare gas atoms is comparable to the accommodation time of the parallel velocity component, producing what are called “quasi-trapped” atoms, which complicates the concept of scattering and desorption [38]. As a result, the increased apparent corrugation suggested from energy scaling observed by Mullins et al. was attributed to quasi-trapped species. In order to provide some guidance to the assumption of the independence of the trapping probability on surface temperature, we have simulated the effect of surface temperature on the trapping probability for ethane trapping on Pt(111).

The simulations clearly suggest that surface temperature has a small effect on the first gas–surface collision. To begin with, the probability that ethane becomes trapped in the potential well after the first bounce remains constant to within 10% between surface temperatures of 95 and 700 K for all incident angles and energies studied (Fig. 1). This result agrees qualitatively with simple hard cube models which consider only a single bounce and indicate only minor reductions in trapping due to increasing surface temperature [54,55]. Although small changes do occur in the partitioning of

energy after the first bounce with increasing temperature, producing greater rotational and parallel excitation and less phonon excitation, the net effect is to produce nearly the same degree of scattering. Furthermore, the energy scaling exponents, n , which best represent the trapping probability after the first bounce remain constant at unity for all three surface temperatures examined. This result indicates that the increased dynamical corrugation produced by perpendicular vibration of the platinum atoms at elevated surface temperatures does *not* significantly affect the first gas–surface collision. Propane incident at Pt(111) for surface temperatures of 95, 400 and 700 K also exhibits a similar trend; the energy scaling exponent for trapping after the first bounce remains constant at 1.2. Hence, in terms of the first bounce alkanes scattering from Pt(111) exhibit negligible changes in energy scaling resulting from increasing surface temperature.

On subsequent bounces, however, molecules are increasingly scattered with increasing temperatures, leading to a slight dependence of α on the surface temperature (Table 2). The increase in multiple bounce scattering occurs for two reasons: first, higher surface temperatures are clearly more likely to produce energy transfer from the surface

Table 2

The number of trajectories which scatter after either one or two or more bounces at three surface temperatures for several different incident angles and total energies

Ethane on Pt(111)				
T_s	1 Bounce	2+ Bounces	1 Bounce	2+ Bounces
	20 kJ mol ⁻¹ $\theta_i=0$		20 kJ mol ⁻¹ $\theta_i=45$	
95 K	698	52	383	56
400 K	796	194	545	265
700 K	865	537	567	689
	35 kJ mol ⁻¹ $\theta_i=0$		35 kJ mol ⁻¹ $\theta_i=45$	
95 K	1516	87	973	183
400 K	1391	193	985	348
700 K	1406	334	1004	629

The number of initial trajectories at each surface temperature, incident energy and angle is 2000 trajectories. The **total** number of scattered trajectories for particular incident conditions and surface temperature is the sum of the entries in the one and 2+ bounce columns.

to the molecule; second, the decrease in energy lost to phonons on the first bounce due to the higher temperature makes the molecule more susceptible to scattering from the surface on subsequent bounces, since more energy is retained after the first bounce.

The substantial increase in multiple bounce scattering of ethane from Pt(111) at 700 K suggests desorption prior to accommodation. Indeed, the surface residence time of accommodated species suggested from the binding energy of ethane on Pt(111) [1] at 700 K is approximately 24 ps, which is on the order of the duration of a single trajectory simulation (30 ps). These findings appear consistent with the results from Head-Gordon et al. [38] and suggest that quasi-trapping of ethane is occurring at a surface temperature of 700 K. Simulations of propane trapping on Pt(111) at 700 K exhibit analogous behavior and suggest quasi-trapping of propane at this temperature.

Moreover, unlike simulations at lower surface temperatures, at 700 K the calculated initial trapping probability considering all bounces shows a decrease by a factor of about 0.5 compared to the apparent trapping probability computed after four bounces (Fig. 2). Since at 700 K ethane molecules desorbing thermally require about 20 bounces or more (24 ps), during the first four bounces scattering will occur predominantly by the direct reconversion of incident kinetic energy into normal momentum. Conversely, after many collisions with the surface, partially accommodated ethane molecules will more likely be ejected upon colliding with an energetic surface atom. Hence, whereas both ejection mechanisms contribute to the net probability of adsorption at the higher temperature for all bounces, the apparent trapping probability after four bounces is primarily determined by the fraction of molecules which directly scatter. The calculated results thus suggest that the effect of surface temperature on the initial trapping probability due to increased scattering during the first four bounces is small, but that there is a larger effect of surface temperature due to the desorption of quasi-trapped species (Fig. 2). However, even with this effect included, the calculated initial trapping probabilities decrease by no more than a factor of two at a surface temperature of 700 K

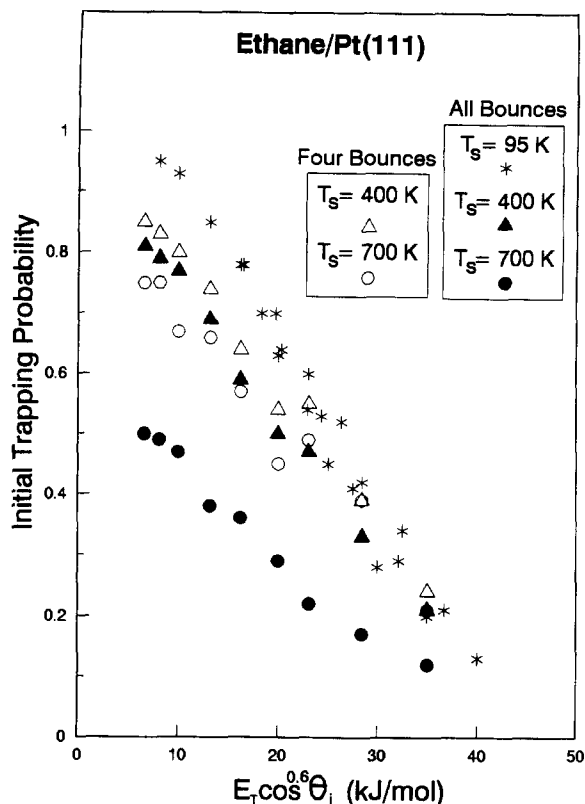


Fig. 2. The apparent trapping probabilities after the fourth surface bounce and the calculated initial trapping probabilities of ethane on Pt(111) plotted as a function of $E_T \cos^{0.6} \theta$. The open triangles and open circles represent the apparent values after four bounces at surface temperatures of 400 and 700 K, respectively. The asterisks, solid triangles and solid circles represent the calculated values at temperatures of 95, 400 and 700 K, respectively.

over the range of incident conditions studied. The simulations also indicate that the reduction does not appear to be linear with surface temperature (Table 2), as would be expected if desorption dictates the decrease in the initial trapping probability observed at higher surface temperatures.

4. Summary and conclusions

We have employed stochastic trajectory calculations of alkanes trapping on platinum surfaces to examine the origin of non-normal energy scaling

of these systems. The three main conclusions from this study are:

(1) Non-normal energy scaling of alkanes on Pt(111) results primarily from the interconversion of perpendicular and parallel translational energy after the first gas–surface collision.

(2) Because glancing beams are more susceptible to chattering collisions after the first bounce, multiple bounce scattering of alkanes from Pt(111) also increases the degree of non-normal energy scaling.

(3) Decreases in trapping from increasing surface temperature result primarily from multiple bounce gas–surface collisions. Over the surface temperature range of 100–700 K, the initial trapping probability of ethane on Pt(111) is estimated to decrease by no more than a factor of two.

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