

Direct dissociative chemisorption of alkanes on Pt(111): Influence of molecular complexity

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(Received 16 February 1999; accepted 6 October 1999)

The direct dissociative chemisorption of ethane, propane, *n*-butane, isobutane, and neopentane on Pt(111) was investigated as a function of the initial translational energy, E_T , polar angle of incidence, θ_i , initial vibrational temperature, and surface temperature using supersonic molecular beam techniques. For each alkane, the initial probability for direct dissociative chemisorption scales with the initial normal energy of the alkanes, $E_n = E_T \cos^2 \theta_i$, and is independent of both the surface temperature and initial vibrational energy of the alkanes under the experimental conditions employed. Above initial normal energies of approximately 125 kJ/mol, at constant E_n , the dissociation probability decreases with increasing chain length of the C₂–C₄ linear alkanes; however, the dissociation probability of neopentane is greater than that of isobutane, and both isobutane and neopentane are more reactive than *n*-butane. By assuming that cleavage of primary C–H bonds is the dominant reaction pathway for all of the alkanes investigated here, the trends in reactivity are best explained by considering the differences in the steric factors for primary C–H bond cleavage for these alkanes. Secondary C–H bond cleavage does appear to contribute to the reactivity of propane and *n*-butane but only at the highest energies examined. Additionally, the reaction probabilities of each of these alkanes were estimated using a statistical model recently proposed by Ukrainstev and Harrison [J. Chem. Phys. **101**, 1564 (1994)]. Assuming cleavage of only primary C–H bonds, the trends in reactivity for ethane, propane, *n*-butane, and isobutane were qualitatively reproduced by the statistical model; however, except for ethane, which was used to obtain the necessary parameters for the theory, there was poor quantitative agreement, and the predictions for neopentane were significantly lower than the measured values. The model also predicts that the dissociation probability is enhanced by increasing the energy in all vibrational modes, which is inconsistent with the experimental results. Thus, we believe that direct alkane dissociation would be better described using a dynamical rather than statistical approach. © 2000 American Institute of Physics. [S0021-9606(00)70801-4]

I. INTRODUCTION

The dissociative chemisorption of alkanes onto transition metal surfaces is the first step in a variety of heterogeneously catalyzed reactions of considerable technological and economic importance. In fact, it is believed that dissociative chemisorption is the rate-limiting step in many metal-catalyzed reactions that convert hydrocarbons to chemicals of greater value. For example, the dissociative adsorption of ethane has been shown to be one of the slowest elementary steps in the oxidative dehydrogenation of ethane on platinum gauze catalysts.¹ Thus, in order to successfully predict the overall surface reactivity of saturated hydrocarbons, it is essential to develop a fundamental understanding of alkane dissociative chemisorption. The focus of the present molecular beam study is the direct dissociation of a homologous series of alkanes onto Pt(111). Since a number of investigations^{2–10} suggest that all linear and branched alkanes dissociate by a single C–H bond cleavage, we view this investigation as an opportunity to probe how alkane size and structure affect reactivity.

Molecular beam techniques have been extremely useful

for investigating the roles of translational and vibrational energy in direct alkane dissociation^{2,10–23} and in the subsequent development of models^{24–28} to account for the observed behavior. In studies of the direct dissociative adsorption of alkanes, reaction probabilities have been shown to increase substantially with increasing beam translational energy.^{2,10–23} In addition, at low translational energies, below about 70 kJ/mol, both the vibrational energy of the reactants^{2,11,12,16,23} and the thermal energy of the surface¹⁶ promote the direct dissociation of methane on several transition metal surfaces. However, neither increasing the vibrational energy of the alkanes nor of the surface has been found to produce a measurable enhancement in the direct dissociation probability of any perhydro-alkane at high translational energies (> 100 kJ/mol).^{17–20} These observations indicate that at high incident energies the appreciably populated, lower frequency vibrational modes of the alkane and surface remain effectively uncoupled from the reaction coordinate for direct dissociation. Since C–H bond stretching is the most likely reaction coordinate, it was proposed that the populations of excited states of C–H stretch modes were too low to produce an observable effect at the vibrational temperatures employed.^{17,19} Recently, detectable vi-

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brational enhancements in the direct dissociation of CD_4 and C_2D_6 on Ir(110) were reported,¹⁹ and found to be most consistent with excitation of C–D stretching motion. Hence, the emergent picture of direct dissociation at high E_T is one in which translational energy and only C–H stretching modes measurably affect the reaction probability.

An investigation of the direct dissociation of a series of alkanes should provide some insights on the role of molecular size and structure. A few similar investigations have been reported,^{13,14,21} but the results are controversial. For example, in the first studies of direct dissociation of methane, ethane, propane, and *n*-butane on Ni(100) (Ref. 13) and Ir(110) (Ref. 14), it was found that higher translational energies were required to produce the same initial reaction probabilities for hydrocarbons of increasing chain length. This effect was attributed to energy dissipation out of the reaction coordinate due to impulsive energy transfer to surface phonons. More recently, however, in experiments of the direct dissociative chemisorption of methane, ethane, propane, and cyclopropane on Ir(110),²¹ reaction probabilities were reported to be essentially independent of molecular weight, prompting those authors to suggest that energy losses to the lattice are unimportant, and that the dissociation probabilities are simply dictated by bond energetics. However, at the highest kinetic energies used in that study the reaction probabilities for ethane and propane *do* appear to diverge. Thus, the influence of alkane complexity on the probability of direct dissociative chemisorption remains a question that is not yet settled.

Recently, we have reported quantitative predictions of the trapping probabilities for a series of alkanes on several platinum surfaces.^{29–33} In order to achieve such accuracy with the simulations, it was necessary to realistically describe the surface corrugation (potential), the internal structure of the alkanes, and the vibrational properties of the solid; each physical property plays an important role in dictating the adsorption dynamics. In contrast, a theoretical calculation that quantitatively *predicts* the probability for direct alkane dissociation has never been reported. This is mainly due to the fact that limited information exists on the multi-dimensional potential energy surfaces for dissociation. Furthermore, given the complexity of quantum dynamical calculations, it is understandable that fewer than four degrees of freedom have been included in dynamical models for methane dissociative adsorption.^{25–28} For example, the direct dynamical model of Luntz and Harris²⁶ only includes coordinates for the molecule–surface separation, the H–CH₃ bond length, and the displacement of a surface atom. More recently, the molecular orientation of the pseudo-diatom R–H was also incorporated into a direct dynamical model for methane dissociation on Ni(111).²⁸ Although these models are simple, they qualitatively reproduce (within an order of magnitude) most of the experimental features for methane dissociation, suggesting that, perhaps, including the “important” degrees of freedom is enough to capture much of the essential physics. However, effects due to molecular complexity, which influence the dissociation of large alkanes,^{13,14} cannot be rigorously predicted by the reduced-dimensionality models. The only possible effect that could

be predicted *a priori* by the three-dimensional model is greater lattice recoil for alkanes of increasing molecular weight.

A recent statistical model proposed by Ukrainstev and Harrison²⁴ has the advantage of easily including many gas–surface degrees of freedom in the calculation of dissociation probability. Hence, the statistical model can predict, in advance, how the dissociation probability might change for alkanes of increasing size and with different structures. The statistical model assumes that all vibrational modes of the molecule are able to provide energy to the reaction channel for direct dissociation. This assumption can be tested by comparing the model calculations with experimental measurements for the direct dissociative adsorption of a variety of alkanes.

In this study, we have used molecular beams to investigate the direct dissociative adsorption of ethane, propane, *n*-butane, isobutane, and neopentane on Pt(111) as a function of initial translational energy, initial vibrational temperature, angle of incidence, and surface temperature. Above an energy threshold of about 125 kJ/mol, differences in the dissociation probabilities of these molecules are clearly observed. The reaction probabilities decrease with increasing chain length for the linear alkanes, but increase with molecular size for isobutane and neopentane. The trends in reactivity for the alkanes investigated here are best explained by considering steric effects and assuming preferential cleavage of primary C–H bonds. Secondary C–H bond cleavage does appear to contribute to the reactivity of propane and *n*-butane but only at the highest energies examined. Calculations using the statistical model of Ukrainstev and Harrison²⁴ qualitatively reproduce the trend in reactivity for the C₂–C₄ alkanes; the agreement is poor for neopentane, although it is still within an order of magnitude for all energies.

II. EXPERIMENTAL DETAILS

The molecular beam scattering apparatus employed in this study has been described in detail previously.^{34,35} All experiments were performed on a Pt(111) crystal cleaned by well-established procedures^{34,35} which produced the expected $p(1 \times 1)$ hexagonal LEED pattern. Carbon monoxide temperature programmed desorption measurements indicate the defect concentration on this Pt(111) surface to be 3.7%.²² Once calcium was removed by sputtering, only oxygen cleaning was used to remove carbon contamination that accumulated during the adsorption experiments. Sputtering was only occasionally necessary to remove calcium that migrated to the surface from the bulk. When impurity concentrations were less than the sensitivity of AES (< 0.01 ML), the surface was assumed to be clean.

Alkane translational energies were varied from around 110 to 520 kJ/mol by seeding into either helium or hydrogen and varying the nozzle temperature. Research grade alkanes (ethane, Matheson 99.99%; propane, Matheson 99.99%; *n*-butane; Matheson 99.99%; isobutane, Matheson 99.9%; neopentane, Scott Speciality Gases 99.0%) were used in all of the experiments without further purification. Mass spectrometric analysis of the beam using modulation and synchronous detection showed no impurities in the alkane

beams. Even though trace impurities may be present in the beam gases employed ($< 1\%$), the adsorption of such contaminants, even with unit sticking probability, does not affect the measurements of the initial dissociation probabilities for the alkanes under study, since the lowest alkane adsorption probabilities reported here are 0.05. For example, assuming 1% impurities with $S_0=1$ and a total beam flux of $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$, the coverage of contaminants which would develop during the initial pressure drop in the King and Wells trace could only be as high as about 0.0003 monolayer for the 0.3 s typically required to complete the initial pressure drop. Such a small level of contamination would have no effect on measurements of the initial alkane adsorption probability for S_0 values of 0.05 and higher.

Translational energies were measured by modulating the beam at frequencies near 650 Hz and monitoring the primary mass fragment of each alkane (ethane, $m/q=28$; propane, $m/q=29$; *n*-butane, $m/q=43$; isobutane, $m/q=41$; neopentane, $m/q=57$) with the rotatable mass spectrometer in a phase-sensitive detection mode. The phase difference between the signals detected at the front and back of the chamber was used to calculate the alkane flight time across the chamber. For the translational energies used in these experiments, and for the nozzle conditions employed, the beam velocity distributions are expected to be very narrow,³⁶ reaching velocity spreads only as high as about 5%. To achieve high translational energies, the nozzle temperature, T_N , was increased as high as 760 K. Even at the highest nozzle temperature, the composition of the beams, according to mass spectrometric analysis, was identical to the compositions of beams generated from a room temperature nozzle source, which indicates that the alkanes did not decompose in the nozzle at high temperatures. It is also important to note that the beams generated at the highest temperatures were seeded into hydrogen, which inhibits dehydrogenation.

The vibrational temperature of the alkanes in the beam was altered by changing the temperature of the gas in the nozzle source. Supersonic molecular beams were generated by expanding a gas mixture of less than 20% alkane in *helium* or *hydrogen* through a nozzle with a diameter D of 55 μm at total pressures p from 760 to 1140 Torr, which yields pD ranging from 4.2 to 6.3 Torr cm. For similar expansion conditions (source pressure, nozzle diameter, and alkane concentration), but using *argon* as the beam diluent, significant vibrational cooling has been reported by Mayer *et al.*³⁷ for methyl formate, pentanol, and *n*-pentane, and by Amirav *et al.*³⁸ for large aromatic hydrocarbons ($\text{C}_{14}\text{H}_{10}$, $\text{C}_{18}\text{H}_{12}$, $\text{C}_{22}\text{H}_{14}$, $\text{C}_{32}\text{H}_{14}$). However, when *helium* is used as the carrier gas, laser-induced fluorescence spectroscopy indicates that vibrational cooling is negligible even for low-frequency modes for large hydrocarbons at source pressures of around 1 atm ($pD=11.4$ Torr cm), and only becomes significant at source pressures higher than 10 atm ($pD=114$ Torr cm).³⁸ The authors suggest that velocity slip between the large hydrocarbons and light carrier gases results in inefficient vibrational energy transfer during the expansion. Since we have only used hydrogen and helium as seed gases, it is reasonable to assume that for the range of pD we employed vibrational relaxation is negligible for all of the

beams used in our experiments, and that the vibrational temperature of the alkanes is equal to the nozzle temperature.

Direct sticking probability (DSP) measurements were conducted with the stationary mass spectrometer using the reflectivity method of King and Wells.³⁹ A moveable, gold-plated flag was placed in front of the Pt(111) crystal which blocks the beam. The flag was assumed to be inert to reaction over the entire range of kinetic energies studied. Since carbon accumulation is known to passivate surfaces toward direct collisional activation of alkanes, even if there is some initial reactivity, the flag must be inert to reaction with the molecules in the beam, since the experimental results were reproducible over long periods of time, separated by weeks. A reference background partial pressure of alkane is produced when the beam strikes the flag, since none of these alkanes adsorb on the gold-plated surface. Rapid removal of the flag from in front of the crystal results in a transient decrease in the alkane partial pressure due to adsorption onto the Pt(111) surface, which provides an absolute measurement of the adsorption probability in the zero coverage limit, S_0 . Alkane partial pressures in the UHV scattering chamber were measured by monitoring the intensity of the largest alkane mass fragment. The error in determination of adsorption probability using this method is about ± 0.02 . For alkane beams seeded in hydrogen it was necessary to perform experiments at surface temperatures of 500 K and higher in order to avoid significant amounts of hydrogen accumulation on the surface. It is noted that trapping-mediated reaction on Pt(111) was not observed for ethane and propane at any incident condition, and that the trapping-mediated reaction of the larger alkanes only occurs to an appreciable extent for $E_T < 100 \text{ kJ/mol}$.²² Thus, contributions from trapping-mediated reaction are negligible in measurements of S_0 at $E_T > 100 \text{ kJ/mol}$ and $T_s > 500 \text{ K}$.

III. RESULTS

Shown in Fig. 1 is the initial probability of direct dissociative adsorption for C_2H_6 , C_3H_8 , *n*- C_4H_{10} , *i*- C_4H_{10} , and neo- C_5H_{12} as a function of the initial normal energy, $E_n = E_T \cos^2 \theta_i$, at $T_2=500 \text{ K}$, where E_T is the initial translational energy of the alkane and θ_i is the angle of incidence with respect to the surface normal. For each alkane, the initial probability of direct dissociative adsorption increases monotonically with E_n . This is not surprising, since normal energy scaling has been observed for all alkanes directly dissociating on most transition metal surfaces,^{2,10-17,19-23} including previous measurements reported for CH_4 ,^{15,16} C_2H_6 ,¹⁷ and neo- C_5H_{12} (Ref. 22) dissociation on Pt(111). The dependence of S_0 on the initial normal energy indicates that molecular translation directed along the surface normal is highly effective at promoting direct alkane dissociation, whereas parallel translation remains uncoupled from the reaction coordinate. Interestingly, the initial probability of *molecular* adsorption exhibits a much weaker dependence on the incident angle for each of these alkanes,^{33,40,41} indicating that parallel momentum conversion to surface vibrations and other molecular motions influences molecular trapping. Although parallel momentum exchange is significant in nonre-active collisions, it appears to have a negligible effect on the

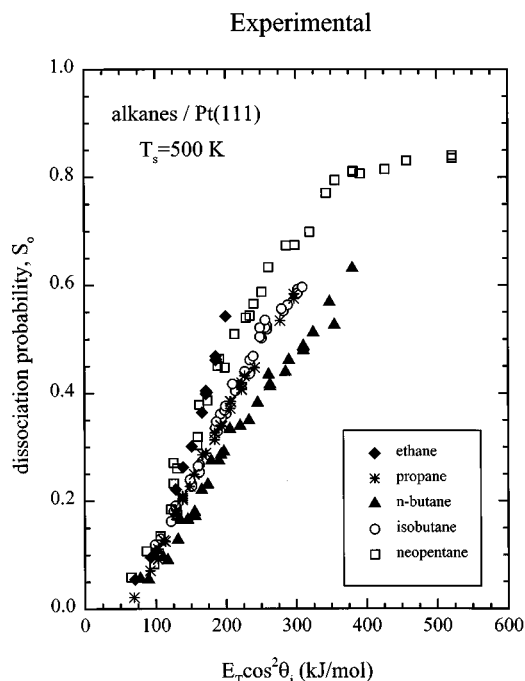


FIG. 1. Initial probability of direct dissociative chemisorption of ethane (\blacklozenge), propane ($*$), *n*-butane (\blacktriangle), isobutane (\circ), and neopentane (\square) on Pt(111) as a function of initial normal translational energy, $E_T \cos^2 \theta_i$, at a surface temperature of 500 K. Incident angles ranging from 0° to 45° were used in these measurements for each alkane. Energy is given in units of kJ/mol.

direct dissociative adsorption of alkanes. Further, dissociation probabilities shown in Fig. 1 exhibited no measurable surface temperature dependence for $500 < T_s < 1000$ K, also in agreement with other investigations.^{2,10-15,17-22}

Increasing the initial vibrational energy of the alkanes with the nozzle temperatures employed (Table I) does not lead to an observable enhancement in the probability of direct dissociation beyond that produced by translational energy for any of these alkanes within the experimental error limits (± 0.02) over the entire range of E_n . Assuming that vibrational relaxation in the molecular beams is negligible for our experimental conditions,³⁸ the average vibrational energy of the alkanes is computed from a Boltzmann distribution characterized by the nozzle temperature. As seen in Table I, the nozzle temperatures used for each alkane produced a wide range of initial vibrational energies. The neopentane data have been replotted in Fig. 2 to explicitly show the variation in T_N for a representative set of data points. Notice that the reaction probabilities measured at the same

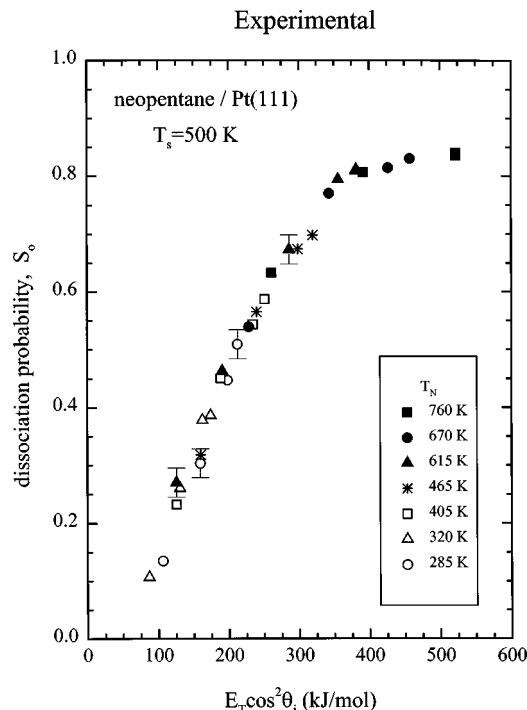


FIG. 2. Initial probability of direct dissociative chemisorption of neopentane on Pt(111) as a function of initial normal translational energy, $E_T \cos^2 \theta_i$, at a surface temperature of 500 K. As indicated in the figure legend, the various symbols correspond to beams generated at the specified nozzle temperatures. Filled symbols are for vibrationally hot beams and open symbols are for the colder beams.

E_n but differing E_v are identical within the error limits of the measurement (Fig. 2). For example, at an incident E_n of 200 kJ/mol there is no difference in S_0 for neopentane having vibrational energies of 10.5 and 55.0 kJ/mol (Fig. 2). Many of the overlapping data points in Fig. 1 were also measured at the same E_n but different T_N . Thus, vibrational modes that are appreciably populated under these experimental conditions must be relatively uncoupled from the reaction coordinate during the time scale for direct dissociation for all of these alkanes. Tables with the populations of vibrationally excited states for methane and ethane at similar temperatures as those used here are documented in Refs. 17 and 19. At these temperatures, C-H stretch modes are too weakly populated for them to enhance the reaction probability.¹⁷⁻²⁰

Below normal translational energies of about 125 kJ/mol, when S_0 is less than 0.10, the reaction probabilities at a constant energy are indistinguishable for different alkanes. Similar observations were made by Kelly *et al.*²¹ for the direct dissociation of methane, ethane, and propane on Ir(110) for kinetic energies up to 105 kJ/mol. However, above normal translational energies of 125 kJ/mol there are distinct differences in the direct dissociation probabilities of the alkanes under study (Fig. 1), and these differences become more discernible with increasing energy. Specifically, at a constant E_n , S_0 decreases in the order $C_2H_6 \sim \text{neo-C}_5H_{12} > C_3H_8 \sim i\text{-C}_4H_{10} > n\text{-C}_4H_{10}$. Similar differences in reactivity were most likely undetectable in the experiments of Kelly *et al.*²¹ since their comparisons were limited to $E_n < 105$ kJ/mol.

TABLE I. Total energy in all excited states of all vibrational modes for each alkane for the lower and upper limits of nozzle temperature employed.

	Nozzle temperature, T_N (K)		$\langle E_v \rangle$ (kJ/mol)	
	Lower	Upper	Lower	Upper
ethane	770	920	24.2	36.2
propane	385	665	8.5	31.4
<i>n</i> -butane	285	710	7.4	54.0
isobutane	435	710	19.0	54.7
neopentane	285	760	10.5	83.8

IV. DISCUSSION

A. Energy dissipation

The general trend of reactivity of the linear alkanes on Pt(111) agrees qualitatively with previous measurements of alkane direct dissociation on Ni(100) (Ref. 13) and Ir(110) (Ref. 14). Specifically, we observe here that linear hydrocarbons of increasing molecular weight require higher translational energies to exhibit the same initial dissociation probability on Pt(111). In contrast, the dissociation probabilities of isobutane and neopentane do not continue this trend, indicative of more complex structural effects. Previously, it was suggested that the apparent dissociation barriers increase with molecular weight due to greater energy dissipation out of the reaction coordinate and to the surface.^{13,14} It was shown that the $S_0(E_n)$ curves for the linear alkanes could be reasonably well collapsed to a universal curve when the energy axis was rescaled to $E_n - \Delta$, where Δ is the energy loss to the surface predicted by the hard-cube model.⁴² Although these were logical arguments, the increases in S_0 for isobutane and neopentane (Fig. 1) relative to *n*-butane (at a fixed kinetic energy) clearly defy such a simple explanation. A different interpretation is required to explain the observed behavior for all of the alkanes investigated.

Internal excitation of alkane vibrations is expected to be significant at the high energies which produce direct dissociation. For example, in recent trajectory calculations of alkane trapping on Pt(111),³³ collisional excitation of C–C–C bending modes is appreciable even for incident energies less than 100 kJ/mol; excitation of the skeletal torsional mode of *n*-butane is very facile at these energies. Since our measurements indicate that alkane vibrations remain uncoupled from the reaction coordinate for direct dissociation, it is conceivable that collisional excitation of low-frequency vibrations reduces the energy available for bond cleavage. However, to produce the differences in reactivity for the alkanes investigated here, the collisional energy transfer to vibration would need to be significantly different for each alkane. For example, the initial normal energies required to produce $S_0 = 0.5$ for both neopentane and *n*-butane differ by more than 100 kJ/mol (Fig. 1). This energy difference is certainly much greater than any difference in vibrational excitation for these species. Thus, even if vibrational excitation influences the reaction probability, it cannot solely account for the trends in reactivity of the alkanes currently under study.

B. Selective bond scission

To better understand the observed trends in reactivity, it is useful to review what is known about selective bond scission in alkane dissociation. It is very reasonable to assume that cleavage of a single C–H bond is the initial reaction step in the direct dissociation of each of the alkanes we have investigated. First, several experiments indicate that C–H bond cleavage is more energetically favorable than C–C bond cleavage in the trapping-mediated dissociation of linear and branched alkanes on transition metal surfaces.^{3–7} Additionally, results based on direct spectroscopic identification^{2,9,10} and kinetic isotope effects^{8,19,20} strongly support the notion that a single C–H bond breaks in the direct dis-

sociation of noncyclic alkanes. In particular, using reflection-absorption infrared spectroscopy, Chesters *et al.* have observed that ethyl¹⁰ and neopentyl⁹ groups, respectively, are formed at low surface temperatures in the direct dissociative adsorption of ethane and neopentane on Pt(111). There is also a strong possibility that certain C–H bonds are selectively broken, i.e., 1° vs. 2° or 3° C–H bonds. In trapping-mediated dissociation,^{3–5} the activation energies for C–H bond scission appear to decrease in the order suggested by bond energetics, i.e., 1° > 2° > 3°. However, contrary to predictions based on bond energetics, a single molecular beam investigation employing propane isotopes indicates that 1° C–H bond cleavage is highly favored over 2° C–H bond cleavage in the direct dissociation of propane on Ir(110).⁸ Apparently, steric effects favor cleavage of 1° C–H bonds in direct alkane dissociation.

C. Theoretical descriptions

In order to fully understand how molecular size and structure influences alkane reactivity, it would be most desirable to have detailed dynamical information on the dissociation process. Unfortunately, a complete dynamical description would require complicated multi-dimensional calculations which account for the “inactive” degrees of freedom in the molecules. More tractable approaches for computing dissociation probabilities are the reduced dimensionality dynamical models^{25–28} and the statistical model of Ukrainstev and Harrison.²⁴ Since the dynamical and statistical models offer fundamentally different viewpoints of the dissociation process, we consider interpretations of our current results from each perspective.

The original surface mass model of Luntz and Harris²⁶ includes three degrees of freedom which describe the alkane–surface separation, the displacement of a surface atom, and the bond distance of the pseudo-diatom R–H, where R represents an alkyl group. Assuming a similar potential hypersurface for each alkane, the three-dimensional (3D) model could only predict greater lattice recoil for alkanes of increasing molecular weight, which our current results indicate is not the primary cause of differences in the reactivity of large alkanes. Recently, steric effects have been empirically accounted for in dynamical calculations by computing the dissociation probabilities of methane using the 3D model and then averaging these values over a Gaussian distribution of barrier heights.²⁷ Although this approach has produced better agreement with experimental measurements, it does not differentiate between the possible steric effects, i.e., molecular orientation, impact site, etc.

Dynamical calculations which explicitly include the molecular orientation of the R–H diatom have recently been reported by Jackson *et al.*²⁸ for the dissociative adsorption of methane on Ni(111). The orientational dependence of the potential energy function that they used was based on *ab initio* calculations of the transition state configuration for methane dissociation on Ni(111),⁴³ which indicated that the saddle point region of the reactive methane–Ni(111) potential is narrow with respect to the polar orientation of the molecule. Consequently, at high kinetic energies the dissociation probability of methane is very sensitive to the initial

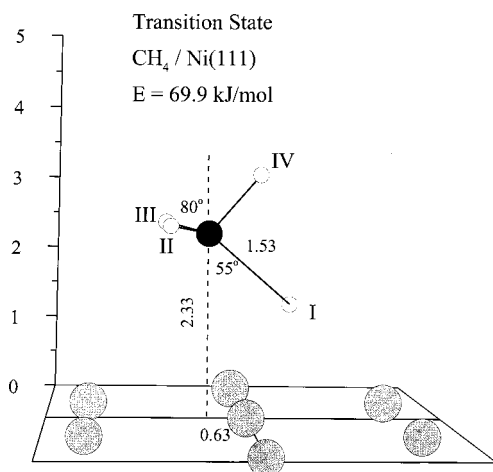


FIG. 3. Geometry of the transition state configuration of methane on Ni(111) as reported in Refs. 42–45. Distances are given in angstroms.

orientation of the diatom ($R-H$), differing by as much as a factor of 2 for molecules with different initial bond alignments.²⁸ For larger alkanes, we expect that the reactive gas–surface potentials are similar to that for methane, and that the probability for dissociation also depends on the bond alignment during the gas–surface collision. Moreover, if primary C–H bond cleavage is the dominant reaction pathway for large alkanes, the probability of an alkane encountering the surface in a reactive orientation would depend significantly on the molecular structure of the alkane.

The transition state configuration for methane dissociation on Ni(111), predicted in several, independent theoretical investigations,^{43–46} may provide justification for assuming that primary C–H bond cleavage is the favored reaction pathway for large alkanes. In the computed transition state geometry (Fig. 3), the reactive C–H bond is stretched to a length of 1.53 Å and forms an angle of 55° with the surface normal, two of the nonreacting C–H bonds are in a plane which is tilted by 80° from the surface normal, and the remaining C–H bond is directed away from the surface. Also, the C_{3v} axis of the nonreacting methyl group is rotated by 30° from the reactive bond due to deformation of the molecule. For a large alkane, if a CH_2 or CH group is placed in this transition state configuration, one or more of the nonreacting CH_x groups of the alkane would be very close to the surface, at a distance where the gas–surface repulsion is large (positions II and III, Fig. 3). In contrast, if a methyl group of an alkane ($R-CH_3$) adopts this transition state configuration, the repulsive gas–surface interaction would be minimized when the larger, inactive side-group (R) is in the position farthest from the surface (position IV, Fig. 3).

Repulsive energies were computed for propane on Pt(111) for molecular configurations consistent with 1° and 2° C–H bond cleavage. The pairwise-additive Morse potential which was used in these calculations treats the CH_x groups of propane as single interaction centers and uses the same parameters for both CH_2 –Pt and CH_3 –Pt atom interactions. Since this single potential energy function quantitatively simulates the molecular adsorption dynamics of

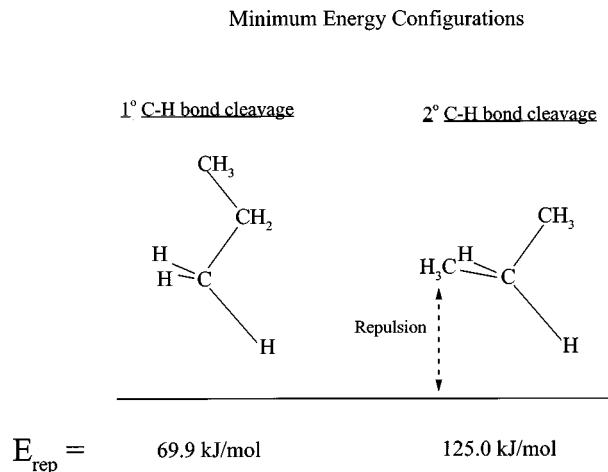


FIG. 4. Minimum energy configurations for (a) primary C–H bond cleavage and (b) secondary C–H bond cleavage of propane on Pt(111), based on the computed transition state geometry for methane dissociation on Ni(111) (Refs. 42–45). The repulsive energies indicated for these configurations were computed using a Morse potential as described in the text and in previous work (Ref. 33).

ethane, propane, *n*-butane, isobutane, and neopentane on Pt(111),³³ it is believed to be an accurate representation of the *physical* alkane–Pt(111) interaction. Indeed, the most energetically favorable configurations for both primary and secondary C–H bond cleavage of propane are those which maximize the distance between the surface and the inactive, alkyl side groups (Fig. 4). For the minimum energy configuration for primary C–H bond cleavage [Fig. 4(a)], the distance between the carbon atom of the “reacting” CH_3 group and the surface plane was set at 1.02 Å in the model calculations in order to yield a repulsive energy of 69.9 kJ/mol, i.e., exactly the energy at the transition state for methane dissociation on Ni(111).⁴³ For a distance of 1.02 Å between the CH_2 group and the surface, the repulsive energy was determined to be 125.0 kJ/mol for the minimum energy configuration for secondary C–H bond cleavage [Fig. 4(b)]; this energy is 55.1 kJ/mol greater than that for primary C–H bond cleavage. Thus, based on the transition state configuration computed for methane dissociation, 2° or 3° C–H bond cleavage of alkanes is expected to be less energetically favorable than 1° C–H bond cleavage due to greater repulsion between the surface and the inactive alkyl side groups.

The trends in reactivity for the alkanes investigated here may arise from differences in the steric factors for direct, primary C–H bond cleavage, i.e., the probability of a 1° C–H bond being appropriately oriented at the surface at impact. In order to test this idea, a nonreactive molecular dynamics (MD) model was used to compute “steric factors” for each alkane, which were then compared to the relative dissociation probabilities of the molecules under investigation. For simplicity, the steric factor⁴⁷ was defined as the probability (P) of a CH_3 group of the alkane being closest to the surface at impact, i.e., the classical inner turning point of the molecular center of mass. The MD model used for this analysis is the same as that mentioned above; the CH_x groups of the alkanes are treated as point masses, and a single, pairwise CH_x –Pt Morse potential was used for all alkanes.³³ For

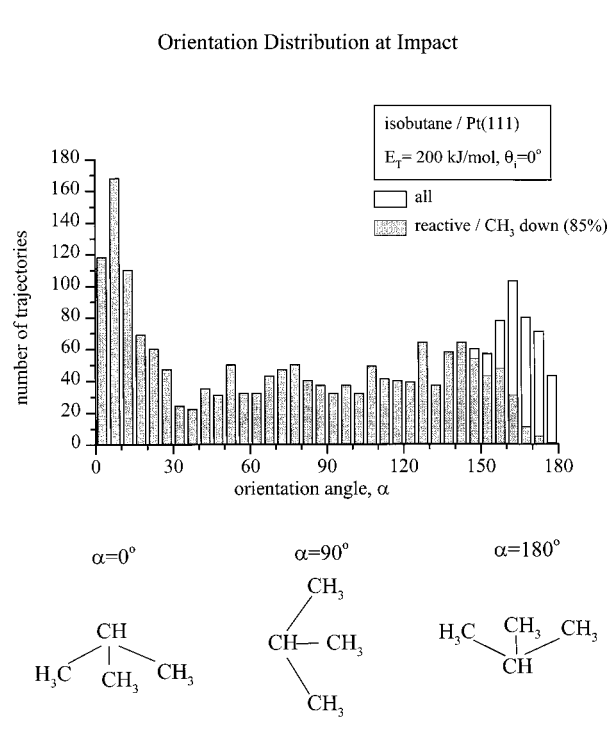


FIG. 5. Distribution of orientation angles at the inner turning point for isobutane initially with 200 kJ/mol translational energy and at normal incidence with Pt(111). White bars are for all trajectories and shaded bars are only for molecules that reached the inner turning point with a methyl group closest to the surface. Sample configurations of isobutane are shown in the lower panel to indicate that the orientation angle α is defined as the angle between the C_{3v} axis and the surface normal.

a fixed initial energy and angle of the alkanes, each molecule-specific steric factor was computed from 2000 trajectories, each initiated at random molecular orientations, impact sites, and vibrational phase of the surface atoms.

To better illustrate how the steric factors were determined from this analysis, the distribution of orientation angles at the inner turning point is shown in Fig. 5 for all trajectories (white bars) of isobutane initially with 200 kJ/mol translational energy, and for only those molecules which impact with a methyl group closest to the surface (shaded bars). The orientation angle for isobutane is defined as the angle between the C_{3v} axis and the surface normal. At $E_T = 200$ kJ/mol, the steric factor is found to be 0.85 for isobutane, i.e., 85% of the isobutane molecules impact with a methyl group closest to the surface, which corresponds to nearly all of the isobutane orientations for $\alpha < 160^\circ$ (Fig. 5).

Interestingly, the orientational distributions at impact with the surface are predicted to be nonrandom for all of the alkanes investigated here. This behavior originates from the sudden rotational excitations experienced by molecules traversing the *repulsive* part of the potential. In general, most molecules only rotate through a small angle ($< 10^\circ$) before reaching the inner turning point since the repulsive interaction occurs on a very short time scale. However, the angular displacements are significant (up to 50°) for molecules which experience a large torque. Consequently, the distribution of orientations at the inner turning point is more highly populated with orientations for which the torque on the molecule

Influence of Steric Factors

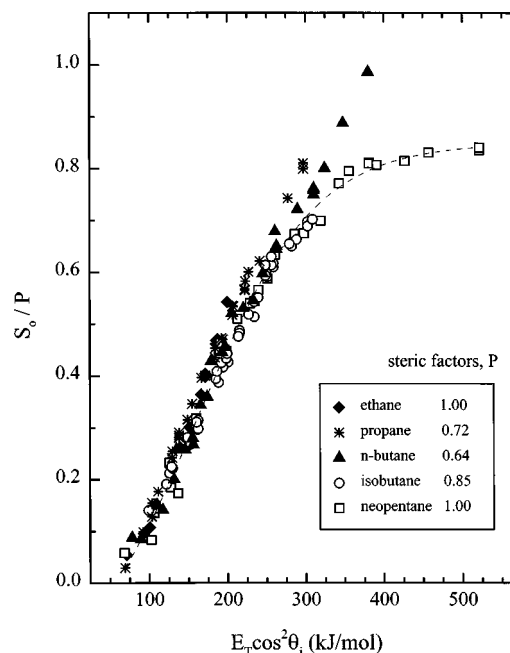


FIG. 6. Initial probability of direct dissociative chemisorption S_0 divided by the steric factors P reported in the text.

is balanced, and is depleted at orientations which initially subject the molecules to a large torque. For example, isobutane has a tendency to reach the inner turning point with its symmetry axis parallel to the surface normal (Fig. 5). Both the orientational distributions and the steric factors were found to be independent of the initial translational energy for $E_T = 75$ to 350 kJ/mol; this is also a consequence of the short time over which the repulsion is operative. In contrast, the steering effect previously reported by Gross *et al.*⁴⁸ for H_2 dissociative adsorption diminishes with increasing incident kinetic energy, and is only important at energies less than about 20 kJ/mol. In H_2 steering, the attractive forces of the reactive gas-surface potential guide impinging molecules along low-energy pathways for dissociation. Indeed, the gentle steering produced by a reactive gas-surface potential is fundamentally different from the sudden molecular reorientation caused by the physical gas-surface repulsion. Finally, it is noted that steric factors evaluated from random molecular orientations differed by only up to 20% from those at the inner turning point; however, the latter do provide a more consistent description of the experimental trends.

The energy independence of the steric factors greatly simplifies the present analysis, since a unique steric factor for each molecule can be defined for all energies. The steric factors were determined to be the following; 1.0 for ethane and neopentane, 0.85 for isobutane, 0.72 for propane, and 0.64 for *n*-butane. Remarkably, the steric factors decrease in essentially the same order as the reaction probabilities of the alkanes. In fact, for energies less than about 275 kJ/mol the reaction probabilities of all of these alkanes nearly collapse onto a universal curve (Fig. 6) when scaled by the steric factors given above, i.e., $S_0^1 = S_0/P$, where P is the steric factor. However, at energies greater than 275 kJ/mol the re-

action probabilities of propane and *n*-butane exceed those predicted by the steric factors for primary C–H bond cleavage. This may indicate that secondary C–H bond cleavage also contributes to the reactivity of propane and *n*-butane at high energies. Overall, the trends in reactivity for the alkanes under investigation appear to be primarily attributable to the differences in the steric factors for primary C–H bond cleavage.

D. Description and application of the statistical model

The statistical model²⁴ for direct dissociative adsorption circumvents the difficulties inherent in dynamical calculations, and it is important to assess its utility as a semi-empirical predictive model of the reactivity for a homologous series of reactants. As will be discussed, the applicability of the statistical model necessitates a very different physical interpretation of the reaction process compared to that inferred from dynamical considerations.

The statistical model for direct dissociative adsorption is based on the Rice–Ramsperger–Kassel–Marcus (RRKM) theory for unimolecular reactions. There are two related, yet distinct, assumptions in RRKM theory. The first considers that the states of the energized reactants can be represented by an equilibrium microcanonical ensemble, i.e., for a given energy each state is equally probable. The other assumption is that each member of the ensemble has an equal opportunity of reacting. These criteria for statistical behavior will be met if the rate of intramolecular vibrational energy redistribution (IVR) in the energized reactant is much faster than any reaction rate, since under this condition the reactants can explore all of the available phase space, including the regions that connect the reactants and products. It is important to note that the normal translational energy must be involved in the energization process according to this theory.

In order to describe direct dissociative adsorption, the RRKM postulates were applied to a “collision complex” composed of the alkane and a local cluster of surface atoms.²⁴ Since gas–surface collisions occur at random impact conditions, the ensemble of collision complexes sample a relatively large region of configurational phase space prior to intramolecular energy exchange. If, in addition, vibrational excitation is efficient in alkane–surface collisions, then the distribution of states of the collision complex might be nearly ergodic. However, if appreciable reaction probabilities only occur for specific molecule–surface configurations, it is unlikely that every trajectory will have an equal opportunity to react during the collision time. Furthermore, even if a microcanonical ensemble gives a close approximation to the actual distribution of states, statistical decay from this population via reaction or desorption requires that intramolecular energy exchange throughout the collision complex be very rapid, occurring on a time scale that is less than the characteristic time for a gas–surface collision ($\sim 10^{-13}$ s). Estimates of typical IVR times in gas-phase alkyl radicals are very close to but not shorter than gas–surface collision times.^{49,50} For example, Rabinovitch and co-workers⁵⁰ have shown that the time for intramolecular energy exchange in excited sec-butyl radicals is at most 2×10^{-13} s. Nonetheless, in order to invoke a purely statistical description of

alkane chemisorption, the IVR rates may need to be much faster than the values indicated in gas-phase results.

We now briefly review the statistical model of Ukrainstev and Harrison and describe our application of this approach for the molecules we have investigated. For a formal derivation of the statistical theory of direct dissociative chemisorption the reader is referred to the original Ref. 24, and to more general texts on RRKM theory.^{49,51–54} An expression for the initial probability of dissociative chemisorption was formulated by considering that the collision complex can decompose through one of two channels, desorption (*D*) or reaction (*R*). Desorption indicates that the alkane molecule and surface-cluster separate, and reaction means that an alkane C–H bond is broken. The general expression for the initial probability of dissociative chemisorption derived from the statistical model is the following;

$$S_0(E) = \frac{\alpha_R W_R(E - E_R)}{\alpha_R W_R(E - E_R) + W_D(E - E_D)}, \quad (1)$$

where α_R is the reaction path degeneracy and E_R and E_D and $W_R(E - E_R)$ and $W_D(E - E_D)$ are the energy barriers and sum of states of the activated complex for reaction and desorption, respectively. For these systems, the reaction path degeneracy is equal to the number of equivalent bonds that can break in a particular alkane molecule. The energy E is referenced to the bottom of the physisorption well and, as such, is given by $E = E_n + E_i + E_D$, where E_n is the normal translational energy of the alkane and E_i is the total internal energy of the complex, both of which are assumed available for reaction. The total internal energy is given by $E_i = E_v + E_r + E_z$, where E_v are E_r are the initial vibrational and rotational energies of the alkane and E_z is the thermal energy of the surface cluster.

The semi-classical approximation of Whitten and Rabinovitch⁵² is used to compute the sum of states, leading to the following working formula for the dissociation probability for a reactant with ν “active” degrees of freedom in the collision complex;

$$S_0(E) = \left[1 + \frac{\omega_D (E_n + E_i + a_D E_{z,D})^{\nu-1}}{\alpha_R \omega_R (E_n + E_i + a_R E_{z,R} - E_0)^{\nu-1}} \right]^{-1}, \quad (2)$$

where $a_D E_{z,D}$ and $a_R E_{z,R}$ are the products of the Whitten–Rabinovitch *a*-factors and the zero-point energies of the activated complexes for desorption and reaction, respectively. The values of the empirical *a*-factors are increasing functions of the total freely exchangeable energy of the complexes,^{1,52} and determine the fraction of the zero-point energy to be used in computing the sums of states for the desorption and reaction complexes at a given total energy. The frequencies of modes associated with the reaction coordinates for desorption and reaction are given by ω_D and ω_R . Generally, ω_R is taken to be a normal mode of the reactant. In principle, this expression contains only three adjustable parameters: (1) ω_D , the vibrational frequency associated with the reaction coordinate of the activated complex for desorption, (2) E_0 , the critical energy required to break a specified bond in the alkane, and (3) ν , the number of active degrees of freedom of the complex. The active degrees of freedom (DOF) are motions that can freely exchange energy prior to dissocia-

TABLE II. Parameters used in the statistical calculations as defined in the text. The number of active degrees of freedom, ν , is $\nu=3N+1$, where N is the number of atoms in an alkane. The ω_R are asymmetric CH_3 stretching frequencies and are taken from Refs. 56 and 57. The reaction path degeneracy, α_R , is the number of 1° C–H bonds in an alkane, and are assumed to be the only reactive bonds. The parameters not shown in the table are E_0 and ω_D , which were set at 56.0 kJ/mol and 130 cm^{-1} , respectively, for each alkane.

	Ethane	Propane	<i>n</i> -butane	Isobutane	Neopentane
Active DOF, ν	25	34	43	43	52
$\omega_R(\text{cm}^{-1})$	2985	2977	2968	2958	2975
α_R	6	6	6	9	12

tion. The frequency ω_D corresponds to a perpendicular vibration of the alkane in the physisorption well and has typical values ranging from 50 to 200 cm^{-1} . The initial rotational energy of the molecule and normal translational energy are considered as exchangeable energies of the collision complex, and are assigned frequencies of ω_D for the sums of states calculations. They contribute four degrees of freedom to the total number of active DOF. All $3N-6$ vibrational degrees of freedom of the N -atom alkane are assumed to be active in contributing to dissociation, and the cluster of surface atoms contributes s degrees of freedom, yielding for the total number of active degrees of freedom $\nu=3N-6+4+s$. For methane dissociation on Pt(111),²⁴ s was set equal to three to correspond to the vibrations of three surface atoms in the direction perpendicular to the surface, since, based on the observation that the reaction probability scales with normal energy, parallel modes are considered inactive.²⁴

In a molecular beam experiment, the measured probability for dissociative adsorption is an average over the translational and internal energy distribution of the beam molecules and surface-cluster. Since a molecular beam has a narrow velocity distribution, a delta function is used to approximate the translational energy distribution. A Gaussian distribution is used to represent the internal energy distribution of the collision complex. Thus, the values of $S_0(E_n)$ are computed by averaging $S_0(E_n+E_i)$ over the internal energy distributions as specified by the surface temperature and vibrational and rotational temperatures for each measurement. Consistent with Ukrainstev and Harrison,²⁴ the vibrational temperature is assumed to correspond to the temperature of the nozzle, and since substantial rotational cooling occurs in a supersonic expansion the rotational temperature is taken as 10% of the nozzle temperature. The average internal energy and variance of the Gaussian distribution are computed using heat capacity data⁵⁵ and spectroscopic data^{56,57} for the vibrational frequencies of the alkanes and surface. It has been pointed out by Engstrom and co-workers⁵⁸ that the frequencies of the transition state for dissociation might differ from those for the isolated alkane molecule, and, hence, could be treated as adjustable parameters. Lacking detailed information on the transition state configurations for each of these alkanes, the vibrational frequencies^{56,57} of the gas-phase molecules were used in the computations.

The parameters ν and ω_D were maintained at values consistent with Ukrainstev and Harrison,²⁴ $\nu=3N+1$ and $\omega_D=130\text{ cm}^{-1}$. We assume that only primary C–H bond cleavage contributes to direct dissociation and set ω_R at the values of asymmetric stretching frequencies of CH_3 groups

for each molecule.^{56,57} The best fit of the ethane data was found using the parameters specified above with $E_0=56.0\text{ kJ/mol}$. Since primary C–H bond energies are approximately the same in these alkanes,⁵⁹ the same value of E_0 was used in all the calculations of S_0 for the larger alkanes in order to examine the effect of increasing the number of vibrational degrees of freedom. Table II lists all of the parameters used in the computations.

E. Predictions of the statistical model

The predictions of the statistical model are shown in Fig. 7 for each of the alkanes investigated with each point simulated at the values of E_T and T_N used in the experiments. Additionally, the computed values of S_0 for each molecule are compared with the experimental data (Fig. 8).

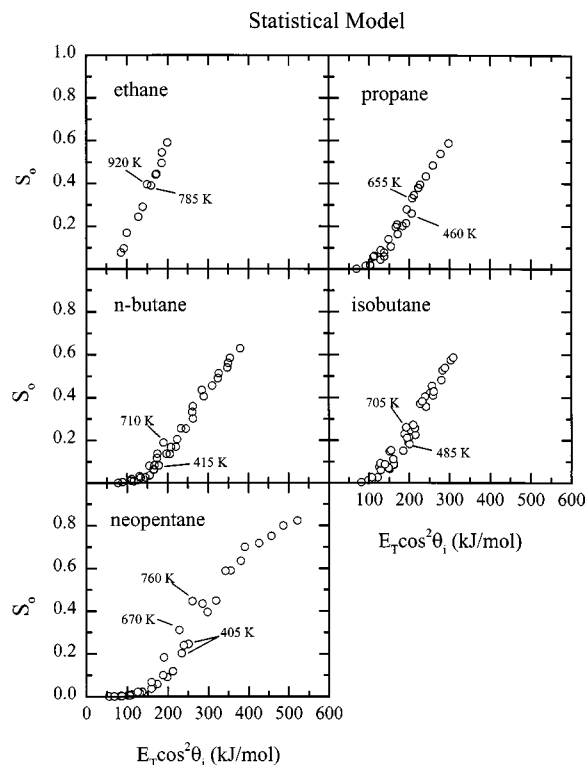


FIG. 7. Predictions of the initial probability of direct dissociative chemisorption of ethane, propane, *n*-butane, isobutane, and neopentane on Pt(111) using the statistical model described in the text. The data is shown as a function of initial normal translational energy, $E_T \cos^2 \theta_i$, and the surface temperature is constant at 500 K. The parameters used in the model calculations are given in Table II for each molecule.

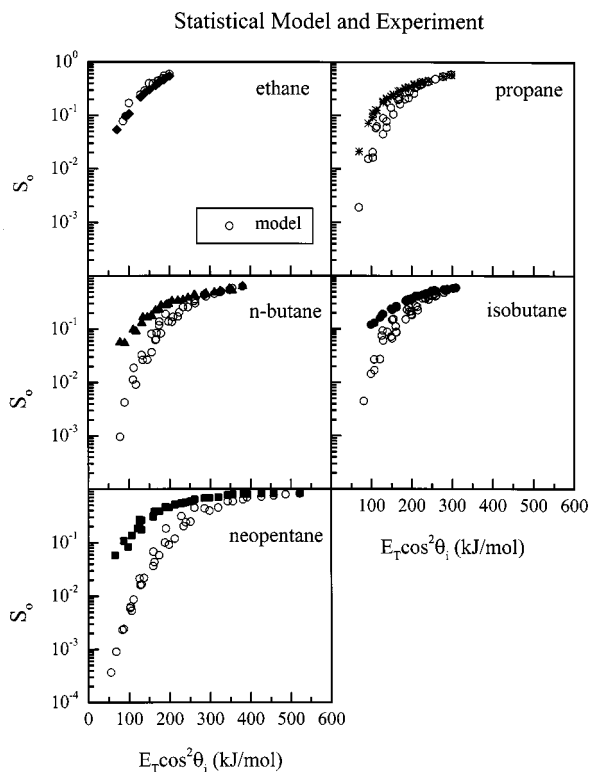


FIG. 8. Comparison of the dissociation probabilities predicted using the statistical model (\circ) along with the experimental data for ethane (\blacklozenge), propane ($*$), *n*-butane (\blacktriangle), isobutane (\bullet), and neopentane (\square). The data is shown as a function of initial normal translational energy, $E_T \cos^2 \theta_i$, and the surface temperature is constant at 500 K. The parameters used in the model calculations are given in Table II for each molecule.

Qualitatively, the overall agreement illustrated in Fig. 8 is *very* good. However, there is significant spread in the graph of S_0 versus E_n (Figs. 7 and 8) for points simulated with similar normal translational energies but different initial vibrational energies, since the model predicts a vibrational enhancement from all modes; this effect is *not* observed experimentally. Also, as E_n decreases, $S_0(\text{stat})$ falls below $S_0(\text{exp})$ (Fig. 8), and, consequently, the model consistently underestimates the dissociation probability for all molecules but ethane at all but the highest energies. The steep rise in the dissociation probability with E_n predicted by the model is highly sensitive to the energy dependence of the term $a_R E_{zR}$ in Eq. (2), i.e., the product of the Whitten–Rabinovitch factor and the total zero-point energy of the reaction complex. Since increasing the incident energy from 100 to 500 kJ/mol is accompanied by a sizeable increase ($\sim 30\%$) in $a_R E_{zR}$ for all molecules, a more significant energy dependence of the reaction probability is predicted than if the sum of states for the reaction complex were evaluated using a constant fraction of the zero-point energy for all total energies. However, since the Whitten–Rabinovitch approximation has been shown to yield accurate sums of energy states for various molecules,⁵² the strong energy dependence of $S_0(\text{stat})$ compared with $S_0(\text{exp})$ is probably not due to an error in the sum of states calculation, but is simply an additional manifestation of the problems associated with using the statistical treatment to describe direct alkane dissociation.

To better illustrate the *trends* predicted by the statistical

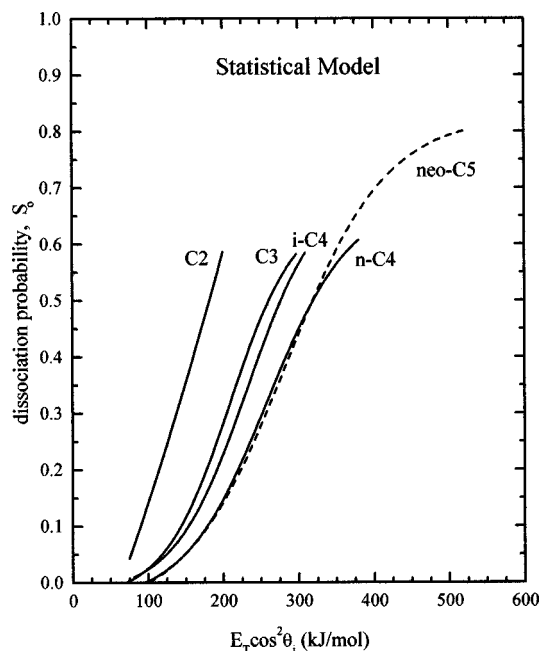


FIG. 9. Sigmoidal curves fit to the statistical predictions. The data is shown as a function of initial normal translational energy, $E_T \cos^2 \theta_i$, and the surface temperature is constant at 500 K. The parameters used in the model calculations are given in Table II for each molecule.

model, the computed values of S_0 for each molecule shown in Fig. 7 were simply fit by sigmoidal curves which are shown in Fig. 9 without the experimental data. Remarkably, the predictions are in good *qualitative* agreement with the experimental trends in S_0 for ethane, propane, *n*-butane, and isobutane. However, the prediction is poor for neopentane, its values for S_0 lying very close to those of *n*-butane.

The best agreement between the model and experimental trends resulted by assuming that only primary C–H bond cleavage occurs in direct alkane dissociation. For example, by using the same activation energies for 1°, 2°, and 3° C–H bonds, the statistical model predicts nearly identical values of S_0 for isobutane and *n*-butane, which is contrary to the experimental results. In addition, if the activation energies for 2° and 3° C–H bond cleavage are reduced by any amount from the value used for 1° C–H bonds, the trends predicted by the statistical model deviate even more from experiment. Thus, along with previous experimental findings for propane,⁹ the predictions from the statistical model support the idea that 1° C–H bond cleavage is the dominant reaction pathway in the direct dissociation of the alkanes investigated. The differences in reactivity predicted by the model for these alkanes are primarily attributable to two factors; (1) the number of active degrees of freedom, and (2) the reaction path degeneracy α_R , i.e., the number of 1° C–H bonds. The higher value of S_0 for isobutane compared with *n*-butane is due entirely to isobutane having more reactive bonds ($\alpha_R = 9$ vs. 6). In addition, the sums of states for both the desorption and reaction complexes are much greater for the larger alkanes. *However, since all energy above the vacuum zero is available for desorption, whereas only energy in excess of the barrier height is available for reaction, the sum of states for desorption increases more substantially with al-*

kane size than that for reaction. Thus, increasing the degrees of freedom favors desorption over reaction, since less of the total phase space corresponds to reactive conditions, and lowers S_0 at a given E_n . However, even with the increased value of α_R , the predicted values of S_0 for neopentane are much lower than the experimental values, indicating that the effect of increasing the degrees of freedom is overestimated for neopentane by this approach.

F. Dynamical versus statistical interpretation

The statistical model assumes that, during the time scale of a single gas-surface collision, energy in any molecular mode of motion can flow into and activate a C-H bond due to rapid energy exchange among all molecular vibrations. Under this assumption, all forms of energy (translational, vibrational, surface) are equally effective in promoting dissociation. However, in our experiments, only translational energy directed along the surface normal enhances the probability for dissociation, and neither initial vibrational energy nor surface temperature measurably affects the reaction probability. Thus, it appears that direct alkane dissociation cannot appropriately be explained in terms of a strong coupling model in which all internal vibrational modes are able to provide energy to the reaction coordinate during the collisional lifetime. Rather, the probability for direct alkane dissociation depends only on the energy in specific motions; namely, perpendicular translation, and possibly C-H stretching.

In addition, since the statistical model is based on a unimolecular decomposition that is independent of spatial orientation, the steric conditions of the gas-surface collision are not properly accounted for in the model. Moreover, the basis of the RRKM theory is that prior to reaction each trajectory has sufficient time to explore all of the momentum and position coordinates that are consistent with a given energy. Thus, in applying the RRKM postulates to a theory of direct dissociative adsorption, it is implied that every trajectory can explore all of the configurational space during a single gas-surface collision. In reality, molecules will only sample a limited range of configurations during the collision time. Moreover, for direct gas-surface reactions with stringent steric requirements, a significant fraction of trajectories will be essentially prohibited from accessing the dissociation channel, suggesting that it is particularly unreasonable for a theoretical treatment to neglect the influence of bond alignment in the direct dissociative adsorption of large molecules.

Although the predictions of the statistical model are in qualitative agreement with the trends in reactivity for the C_2 to C_4 alkanes, we believe that this agreement arises because the competing effects which determine the probability for dissociation in the statistical model, the sums of states and reaction path degeneracies, qualitatively change in the same way as the geometrical factors for these alkanes. The fact that the effect of initial vibrational energy predicted by the model disagrees with our measurements is convincing evidence that the assumptions of the statistical model oversimplify the actual physical mechanism for direct alkane dissociation. The discrepancies between the calculations of the

model and the experimental results for neopentane lend further support to this conclusion.

As discussed in Sec. IV C, the trends in reactivity for the alkanes investigated here are best explained by considering how geometrical factors for each molecule determine the distributions of favorable orientations for primary C-H bond cleavage. Our conclusion is based on previous findings from both *ab initio* and dynamical calculations of CH_4 dissociation on Ni(111) which indicate that the reaction probability is very sensitive to the initial bond alignment.^{28,43-46} In addition, experimental findings for propane dissociation on Ir(110) indicate that 1° C-H bond cleavage is favored over 2° C-H bond cleavage.⁸ Furthermore, preferential cleavage of primary C-H bonds on Pt(111) is consistent with the transition state configuration for C-H bond cleavage predicted for methane dissociation on Ni(111).⁴³⁻⁴⁶ Finally, this conclusion appeals to our intuitive notion that a gas-surface reaction is a highly directional process.

V. SUMMARY AND CONCLUSIONS

Supersonic molecular beam techniques were employed to measure the translational and vibrational energy dependence of the direct dissociative chemisorption probabilities of ethane, propane, *n*-butane, isobutane, and neopentane onto a Pt(111) surface. For each alkane, the dissociation probability scales with initial normal energy and is insensitive to changes in the initial vibrational energy of the reactants and the surface temperature. Differences in the reaction probabilities of different alkanes are observed for initial normal energies exceeding approximately 125 kJ/mol. Specifically, the dissociation probability at a constant normal energy decreases in the following order; $C_2H_6 \sim \text{neo-}C_5H_{12} > C_3H_8 \sim i-C_4H_{10} > n-C_4H_{10}$.

Based on previous experimental⁸ and theoretical studies,⁴³⁻⁴⁶ we contend that primary C-H bond cleavage is the preferred reaction pathway for the alkanes investigated here. Secondary C-H bond cleavage only appears to contribute to the reactivity of propane and *n*-butane at the highest energies examined. Overall, the trends in reactivity for these alkanes are best explained by considering the differences in the steric factors for primary C-H bond cleavage. This interpretation is also consistent with the results of previous studies of direct alkane dissociation on both Ni (Ref. 13) and Ir (Refs. 14 and 21) surfaces. Since in those studies only linear alkanes were examined, mass and steric effects were not separable,^{13,14} and the effect was attributed to mass effects. The arguments presented in the present study are believed to be general for alkane direct dissociation on different transition metal surfaces.

A statistical model²⁴ for direct dissociative chemisorption was used to estimate the alkane reaction probabilities. The best agreement between the model predictions and experimental results was found by assuming preferential cleavage of 1° C-H bonds. With this assumption, the model qualitatively reproduces the trends in reactivity for ethane, propane, *n*-butane, and isobutane. However, the model significantly underestimates the dissociation probability of neopentane, and predicts that increasing the initial energy in all vibrational modes facilitates reaction, which is contrary to

our experimental measurements. Given the discrepancies between the predictions of the statistical model and the experimental results, we favor a dynamical interpretation of our current results based on preferred orientations for dissociation. Thus, we believe that direct alkane dissociation would be better described by a dynamical rather than statistical approach.

ACKNOWLEDGMENTS

The authors are grateful to Katja Street and Professor Michael Chesters for providing their RAIRS data on neopentane dissociative adsorption prior to publication. We are also grateful for the financial support for this work provided by the Department of Energy, Chemical Sciences Division, Office of Basic Energy Sciences (Grant No. DE-FG03-86ER13468).

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