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Effusive Molecular Beam Study of C$_2$H$_6$ Dissociation on Pt(111)

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The dissociative sticking coefficient for C$_2$H$_6$ on Pt(111) has been measured as a function of both gas temperature (T_g) and surface temperature (T_s) using effusive molecular beam and angle-integrated ambient gas dosing methods. A microcanonical unimolecular rate theory (MURT) model of the reactive system is used to extract transition state properties from the data as well as to compare our data directly with supersonic molecular beam and thermal equilibrium sticking measurements. We report for the first time the threshold energy for dissociation, $E_0 = 26.5 \pm 3$ kJ mol^{-1}. This value is only weakly dependent on the other two parameters of the model. A strong surface temperature dependence in the initial sticking coefficient is observed; however, the relatively weak dependence on gas temperature indicates some combination of the following (i) not all molecular excitations are contributing equally to the enhancement of sticking, (ii) that strong entropic effects in the dissociative transition state are leading to unusually high vibrational frequencies in the transition state, and (iii) energy transfer from gas-phase rovibrational modes to the surface is surprisingly efficient. In other words, it appears that vibrational mode-specific behavior and/or molecular rotations may play stronger roles in the dissociative adsorption of C$_2$H$_6$ than they do for CH$_4$. The MURT with an optimized parameter set provides for a predictive understanding of the kinetics of this C−H bond activation reaction, that is, it allows us to predict the dissociative sticking coefficient of C$_2$H$_6$ on Pt(111) for any combination of T_s and T_g even if the two are not equal to one another.

Introduction

Understanding the dissociation dynamics of polyatomic molecules on metal surfaces remains a significant challenge. An important class of polyatomics is represented by the alkanes for which C−H bond activation represents the first step in dissociative chemisorption.[1−3] A significant body of work by Madix and co-workers has probed the adsorption dynamics of alkanes on metal surfaces.[4−6] Using the King and Wells method, they have been able to investigate the regime in which the initial dissociative sticking coefficient S is >0.02 for a range of alkanes. They have also investigated the trapping probability for molecular adsorption ζ. The initial trapping probability of molecular ethane on Pt(111) at 95 K has been shown by Arumainayagam et al.[7] to decrease from 0.91 to 0.13 as the translational energy increases over the range of 6−40 kJ mol^{-1}. The trapping probability decreases by less than a factor of 2 as the surface temperature T_s increases from 100 to 700 K.[5] Molecular rotation, in particular, rotation to normal translational energy transfer, is found to play an important role in the trapping dynamics.[5]

The need to perform experiments for which $S > 0.02$ has led the Madix group to concentrate on molecular beam experiments with translational energies of 60−520 kJ mol^{-1}. At these high energies, Madix and co-workers have stated that excitation of low frequency vibrational modes does not enhance the reactivity of ethane with Pt(111); however, high frequency stretching and deformation modes likely do play a role.[5] This is consistent with observations on Ir(110)−(1 × 2).[8] The role of vibrational excitation in the dissociation of methane and whether certain modes contribute more toward dissociation than

others has recently received a great deal of attention. Vibrational energy enhances the reactive sticking coefficient of CH$_4$ on Ni[9−17] and Pt[18−20] surfaces. On Pt(111) Bernasek and co-workers[19] and on Ni surfaces the groups of Utz[12−14] and Beck[15−17] have recently explored the vibrational mode specificity of methane dissociation. From these studies, it appears that not all modes are equivalent; however, these differences were not found to be kinetically relevant to the thermally state-averaged sticking for the CH$_4$/Pt(111)[20] or CH$_4$/Ni(100)[22] systems. We expect that the vibrational efficacy η_v is not constant.[21,22] It should vary with parameters such as the translational energy and T_s. In particular, as the sticking coefficient increases toward its limiting value, the efficacy will likely drop.

Normal energy scaling is observed for dissociative chemisorption of C$_2$H$_6$ on Pt(111).[23] For normal translational energy $80 \le E_n \le 400$ kJ mol^{-1}, changes in surface temperature (500 K $\le T_s \le$ 1000 K) have little to no effect on S_0.[24] A weak but detectable T_s dependence in the sticking of ethane on Pt(110)−(1 × 2) has been observed by Harris et al.[25] who have also made measurements in the $S_0 > 0.02$ regime.

A microcanonical unimolecular rate theory (MURT) model of gas/surface reactivity can *quantitatively* describe the dissociation of CH$_4$ on Pt(111).[20,21,26] Similarly, good quantitative descriptions have also been demonstrated for CH$_4$/Ni(100),[22,27,28] CH$_4$/Ir(111),[29] and SiH$_4$/Si(100).[30] MURT is able to explain and make quantitative predictions about the translational energy, vibrational energy, and T_s dependence of S, as well as the isotope effect. This good agreement demonstrates that the MURT captures the essence of the activated dissociative chemisorption dynamics in these instances and, therefore, the MURT formalism works.

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We specify three variables (angle of incidence measured from the normal ϑ, gas temperature T_g, and surface temperature T_s) of an effusive molecular beam. By analyzing the data obtained with a MURT,[21,22,26] we obtain three transition state parameters: s the effective number of surface oscillators involved in the collision complex, ν_D a mean vibrational frequency, and E_0 the threshold energy for reaction. The mean vibrational frequency represents a lumped mean of four vibrational modes—three frustrated rotations as well as the vibration normal to the surface of the C₂H₆ molecule at the transition state. Consequently, by setting three experimental variables, we obtain three transition state parameters that allow us to predict with startling accuracy[20–22,26–30] the reaction rates for arbitrary conditions, either equilibrium or nonequilibrium, quantum-state averaged, or quantum-state resolved. This parameter set contains only one more element than an Arrhenius analysis, which has no predictive capacity for nonequilibrium or quantum-state-resolved measurements. This number is significantly fewer than the catalog of error function parameters for each quantum state necessitated by a dynamical model[31] to describe thermal equilibrium sticking.[22] Furthermore, the presence of strong and systematic deviations from MURT predictions—as opposed to random fluctuations—provides conclusive evidence for when kinetically relevant deviations from statistical behavior arise and lays a benchmark for determining when dynamical restrictions significantly affect reaction rates. As we will argue below, the case of dissociative C₂H₆ chemisorption on Pt(111) is one in which dynamical constraints play an important role in the dissociation dynamics.

During the data analysis, it has become apparent that the values of s and ν_D are coupled but that they are largely independent of E_0. Our value of E_0 can be compared directly with the results of electronic structure theory and the transition state barrier derived therefrom. In addition, MURT allows us to calculate S as a function of T for a gas in equilibrium with the surface and thereby derive the thermal activation energy E_a appropriate to dissociative sticking in thermal bulb experiments.

In the MURT model,[21,22,26] we assume that C₂H₆ dissociative chemisorption can be described microcanonically within the following scheme

$$C_2H_{6(g)} \underset{k_D(E^*)}{\overset{F(E^*)}{\rightleftharpoons}} C_2H_{6(p)} \xrightarrow{k_R(E^*)} C_2H_{5(c)} + H_{(c)} \qquad (1)$$
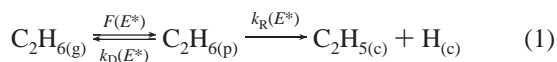
The zero of energy E^* ($= E_n + E_v + E_r + E_s$) occurs at 0 K with infinite separation between the surface and C₂H₆. Ethane incident on the surface forms a transient gas/surface collision complex consisting of the molecule and a few adjacent surface atoms. This local hot spot is an energetic, transient intermediate species, which is *not* in thermal equilibrium with the remainder of the substrate. Energy in this transiently formed physisorbed complex (PC or C₂H₆(p) in eq 1) is assumed to be microcanonically randomized in an ensemble-averaged sense either through the collision process itself or through rapid intramolecular vibrational energy redistribution (IVR). A PC formed with total energy E^* subsequently either competitively desorbs or reacts with RRKM rate constants $k_D(E^*)$ and $k_R(E^*)$.

By applying the steady-state approximation to the coverage of C₂H₆(p), we obtain

$$S = \int_0^\infty S(E^*)f(E^*)\, dE^* \qquad (2)$$

where

$$S(E^*) = \frac{W_R^{\ddagger}(E^* - E_0)}{W_R^{\ddagger}(E^* - E_0) + W_D^{\ddagger}(E^*)} \qquad (3)$$

is the microcanonical sticking coefficient, $W_i^{\ddagger}$ is the sum of states for transition state i, E_0 is the apparent threshold energy for dissociation, and

$$f(E^*) = \int_0^{E^*} f_n(E_n) \int_0^{E^* - E_n} f_v(E_v)$$
$$\int_0^{E^* - E_n - E_v} f_r(E_r) f_s(E^* - E_n - E_v - E_r)\, dE_r\, dE_v\, dE_n \qquad (4)$$

is the flux distribution function for creating a physisorbed complex at E^*. One strength of the MURT analysis is that once the transition state characteristics have been defined by fits to experimental data or by electronic structure theory calculations, the dependence of an experimental sticking coefficient for any dynamical variable (T_s, E_n, E_v, etc.) can be predicted on the basis of eq 2 by averaging the microcanonical sticking coefficient over the probability for creating a physisorbed complex at E^* under the specific experimental conditions of interest.

Experimental Section

Experimental procedures have been described in detail elsewhere[20] and will only be summarized here. The Pt(111) crystal, oriented to within 0.2°, was cleaned using standard procedures involving Ar⁺ sputtering and annealing in O₂. Repeated cycles of Ar⁺ sputtering were performed at 800 K, oxidation at 800 K in an O₂ atmosphere of 5×10^{-8} Torr, and annealing to 1250 K. Research purity ethane (99.995%) was purchased from Matheson Tri-Gas and used without further purification. A lack of impurities was confirmed by mass spectrometry measured in the experimental apparatus with a doubly differentially ion pumped quadrupole mass spectrometer (QMS). This QMS was also used for temperature programmed desorption (TPD) measurements. Ethane exposures were chosen to deposit ∼0.04−0.15 ML C on the surface in any given run. The lower limit was selected so that activity at defect sites (estimated to be ∼0.002 ML as determined by CO titration) does not dominate, and the upper limit was chosen in order to make our measurements an adequate approximation of the initial sticking coefficient on majority sites. In other words, sticking measurements were made in the regime for which the coverage is linearly dependent on the exposure. All coverages are reported in monolayers (ML) calculated with respect to the number of surface Pt atoms.

Carbon coverage was determined by Auger electron spectroscopy. All Auger data was collected at 500 K after a brief annealing to 700 K. This procedure ensured desorption of any extraneous CO and that the decomposition of hydrocarbon fragments to C was complete.[32] We recorded integral Auger spectra from 200 to 300 eV using a 3 keV beam energy, encompassing both the Pt₂₃₇ and C₂₇₂ lines. The program CasaXPS was used to perform a Shirley background subtraction on the interval from 210 to 280 eV and to fit the peaks to a mixed Gaussian/Lorentzian line shape. The calibration of the absolute value of C coverage was obtained by measuring the Auger signal from a saturation graphite layer.

The main chamber was pumped by a 210 L s⁻¹ turbomolecular pump, a 240 L s⁻¹ ion pump, and a cryogenically cooled Ti sublimation pump (TSP). The base pressure was in the upper 10^{-11} Torr range. The ion gauge, ion pump, and TSP filaments were turned off during dosing of the crystal to prevent alkanes from being cracked and forming potentially reactive

radicals or ions. Gas pressure in the chamber was measured either with an ion gauge or with a bakeable Baratron (MKS model 615 with Type 670B signal conditioning electronics). Gas pressure in the gas handling manifold was measured with an MKS model 122B Baratron.

To ensure that Auger measurements reflected the true amount of C deposited from ethane, several control experiments were performed. These control experiments demonstrated that (i) no C-containing contaminants were released from either the gas handling system or main vacuum chamber due to competitive adsorption, outgassing, or leaks, (ii) no C deposition resulted from decomposition of CO or CO_2 emanating from background gas, (iii) no high-sticking coefficient impurity in the gas bottle (such as ethylene) substantially contributed to the measured C deposition, (iv) O_2 from the background was not removing deposited C from the surface, (v) the heated W wire on the effusive nozzle did not result in an additional background contribution to the C deposition, and (vi) C diffusion into the bulk of the Pt crystal was not influencing the coverage data.

The pressure during dosing was maintained low enough that no equilibration of the gas to T_s occurred. A lack of pressure dependence in the sticking coefficients determined by angle-integrated ambient gas dosing was confirmed for pressures below 1 Torr.

We report the sticking coefficient of ethane incident on a Pt(111) crystal measured either (1) from a variable temperature molecular beam or (2) from an isotropic ambient gas exposure. The procedure for calculating S and the background subtraction for experiments of type (1) are the same as that reported previously.[20] In both cases, T_s can be chosen arbitrarily in the range 30 K $\leq T_s \leq$ 1200 K. The temperature of the nozzle used to form the molecular beam was varied over the range 295 K $\leq T_N \leq$ 680 K. Time-of-flight measurements confirmed that the translational temperature of the molecules in the beam corresponded to the T_N. Because of the low pressure in experiments of type (2), which we refer to as angle-integrated experiments, the gas temperature was fixed at T_g = 295 K.

The sticking coefficient S is calculated from the carbon coverage θ_C and the incident flux Z_W by

$$S = \frac{\theta_C \sigma_{Pt}}{Z_W t} \tag{5}$$

where t is the time and $\sigma_{Pt} = 1.50 \times 10^{15}$ cm^{-2} is the areal density of Pt(111). For the molecular beam experiments, the value θ_C was corrected for a contribution due to molecules that have left the nozzle, bounced off of the crystal then equilibrated with the chamber walls before striking the crystal again.

To characterize the degree of agreement between the predictions of the MURT analysis (theory) and experimental data (exp), we introduce the average relative discrepancy as defined by

$$ARD = \left\langle \frac{|S_{theory} - S_{exp}|}{\min(S_{theory}, S_{exp})} \right\rangle \tag{6}$$

Results

Dissociative Chemisorption Data and MURT Analysis. The results for both our effusive molecular beam and angle-integrated experiments are presented in Figure 1. Also presented in Figure 1 are solid lines, which represent the predicted values of S derived from the MURT analysis for the effusive molecular beam experiments, and a dashed line, which depicts the MURT prediction for the angle-integrated data. The heavy dashed line
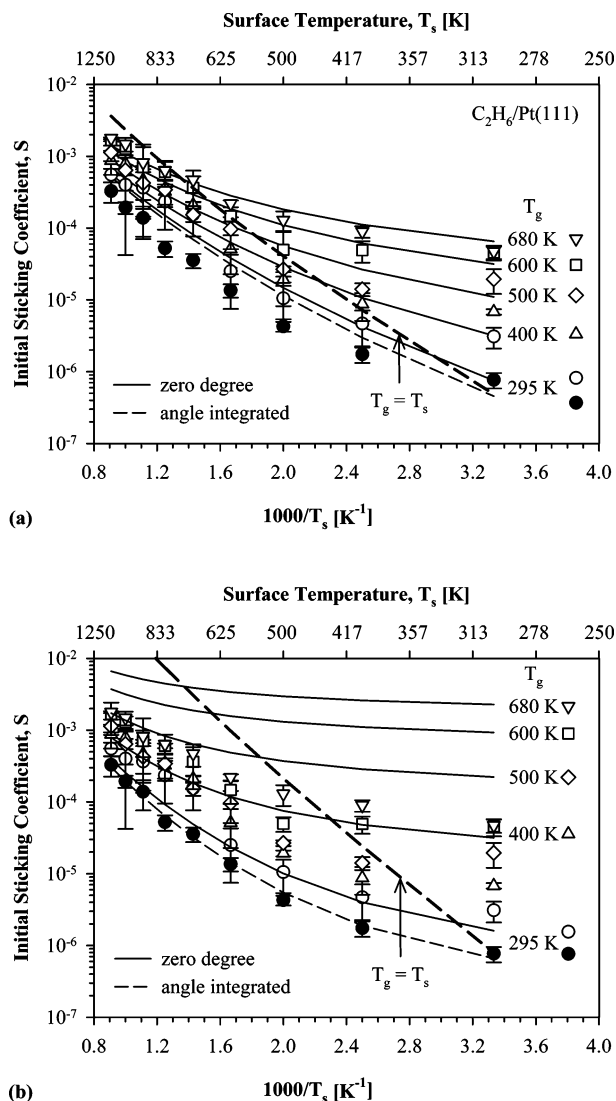
Figure 1. Measurements for C_2H_6 dissociation on Pt(111) (symbols) as a function of gas and surface temperatures are compared with the predictions of the PC-MURT (lines) for transition state parameter sets (a) {E_0 = 24 kJ mol^{-1}, ν_D = 215 cm^{-1}, s = 10}, yielding ARD = 53%, and (b) {E_0 = 29 kJ mol^{-1}, ν_D = 90 cm^{-1}, s = 2}, yielding ARD = 556% for all data, and ARD = 13% for the angle-integrated data alone. The heavy dashed lines represent the predictions for thermal equilibrium ambient gas experiments when $T_g = T_s$.

represents the MURT prediction for a thermal equilibrium experiment in which $T_g = T_s$.

Optimization of the MURT parameters relative to our *molecular beam data* in Figure 1a resulted in an ARD of 53% for all the chemisorption data and an optimized parameter set of {E_0 = 24 kJ mol^{-1}, s = 10, ν_D = 215 cm^{-1}}. This parameter set yields a fit of the room-temperature angle-integrated sticking data that systematically overestimates the value of S.

In Figure 1b, the *angle-integrated data* are used to optimize the MURT parameters. The ARD of the angle-integrated data is just 13% with {E_0 = 29 kJ mol^{-1}, s = 2, ν_D = 90 cm^{-1}}. However, if all chemisorption data are included, then the ARD is 556%. This parameter set systematically overestimates the effect of T_g. In other words, this parameter set predicts that the internal excitation of the ethane should have a much stronger effect on S than is observed.

MURT Analysis of Prior Data. We can now compare our results with prior results for the C_2H_6/Pt(111) system. The first case that we treat is angle-integrated sticking data. In Figure 2,

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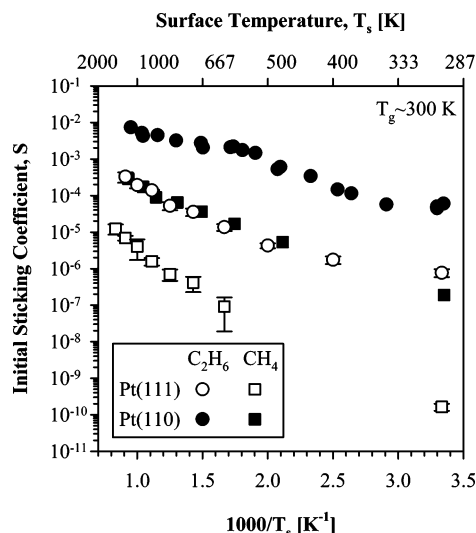
Figure 2. Comparison of alkane dissociative sticking as a function of surface structure and T_s measured for low pressure, $T_g \approx 300$ K ambient gas impinging on (a) Pt(111) (open symbols, this work and ref 20) and (b) Pt(110) (filled symbols, ref 33).

Figure 3. Comparison of PC-MURT predictions of sticking of C$_2$H$_6$ for the data set {$E_0 = 24$ kJ mol^{-1}, $\nu_D = 215$ cm^{-1}, $s = 10$} to the bulb experiment of Rodriguez and Goodman[35] on Pt(111) measured at 1 Torr total pressure.

we compare the C$_2$H$_6$ dissociative sticking data obtained here on Pt(111) with the data we obtained previously[20] for the dissociative chemisorption of CH$_4$ on Pt(111). The Pt(111) data is also compared with the dissociative sticking data obtained on the Pt(110)−(1 × 2) surface by Luntz and Winters.[33] In all cases, the data were recorded with $T_g \approx 300$ K and for variable T_s. For both methane and ethane, the Pt(110)−(1 × 2) surface is significantly more active. This is consistent with a previous comparison performed by Johnson and Weinberg.[34] MURT analysis of the ethane/Pt(110) sticking data, assuming that only E_0 differs from Pt(111), yields $E_0 = 11.5$ kJ mol^{-1}. Comparison to the barriers calculated by Johnson and Weinberg is complicated by the fact that they analyzed their data assuming thermalized precursor mediated chemisorption. Madix and co-workers[5,23] and Luntz and Winters[33] concluded, and we concur, that dissociative chemisorption of ethane on Pt(111) and Pt(110) is a direct process. For both surfaces in this low-energy, low-sticking (<0.01) regime, ethane is significantly more reactive than methane. At translational energies significantly above the threshold energy for reaction, between roughly 60 and 120 kJ mol^{-1}, however, there is little difference between the methane and ethane sticking coefficients.[5]

Next, we compare the predictions of the MURT analysis with bulb experiments performed by Rodriguez and Goodman.[35] These experiments were performed at a total pressure of 1 Torr. This pressure is somewhat problematic because subsequently Nielsen et al.[36] found that a pressure of at least 2.25 Torr is required to ensure that the gas temperature equilibrates to the surface temperature in the kinetically relevant volume surrounding the crystal. Furthermore, the pressure is not sufficiently low enough to ensure that the mean free path is long compared with the size of the chamber and, therefore, that the gas temperature is equal to the temperature of the chamber walls. Consequently, we expect these data to fall between the two limiting cases of {$T_g = 300$ K, T_s variable} and $T_g = T_s$. These comparisons are made in Figure 3. While the effective activation energy derived from the data of Rodriquez and Goodman (37 kJ mol^{-1}) is close to the MURT prediction for the $T_g = T_s$ thermal equilibrium limit (32 kJ mol^{-1}), the absolute value of the sticking coefficient is nearly 3 orders of magnitude lower than predicted. Note that Chesters and co-workers[37,38] also found that the data of Rodriguez and Goodman were similarly low by orders of
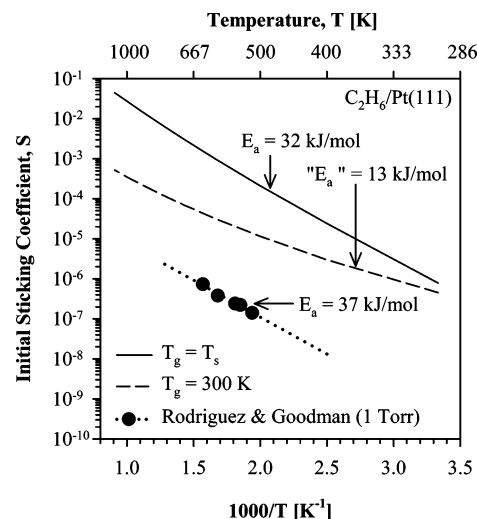
magnitude compared with their prediction. It would be quite interesting for this bulb experiment to be repeated.

Finally, we compare to two sets of supersonic molecular beam data. These experiments were performed under nominally the same experimental conditions apart from the nozzle temperature, which was substantially different in the two cases. One set of data was taken by Schoofs et al.[39] and the second by Chesters and co-workers.[37,38] Two important aspects of these data sets are that (i) they exhibit clear evidence for vibrational enhancement of the sticking because lower nozzle temperatures lead to less sticking in the low translational energy regime and (ii) they asymptotically approach the same values for high translational energy where their nozzle temperatures differ very little.

To understand and interpret these data, we compare them with the predictions of our MURT analysis, which appears as lines in Figure 4. In Figure 4a, we used the MURT parameter set {$E_0 = 24$ kJ mol^{-1}, $\nu_D = 215$ cm^{-1}, $s = 10$}, whereas {$E_0 = 29$ kJ mol^{-1}, $\nu_D = 90$ cm^{-1}, $s = 2$} is used in Figure 4b. With ARDs of only 20% and 106% for the data of Schoofs et al.[39] and Newell et al.,[37,38] respectively, the parameter set with $s = 2$ clearly describes the supersonic molecular beam data better. In both cases, MURT predicts the shape of the data points from both groups. The supersonic beam data are certainly consistent with a threshold energy for dissociation in the range of 24−29 kJ mol^{-1}.

Discussion

Our combination of effusive beam sticking experiments and a MURT analysis has allowed us to describe in great detail the dissociation dynamics of CH$_4$ on Pt(111).[20] This gives us confidence that our experimental procedures, which are virtually the same for CH$_4$ and C$_2$H$_6$, are correct. Furthermore, the quantitative descriptions provided by MURT for CH$_4$/Ni(100),[22,27,28] CH$_4$/Ir(111),[29] and SiH$_4$/Si(100)[30] demonstrate that this theoretical formalism is robust. With this foundation, we now turn to an interpretation of the results for C$_2$H$_6$ dissociation on Pt(111).

Rodriguez and Goodman[35] performed site blocking experiments, which suggested that an ensemble of 2−3 surface atoms is required to dissociate ethane on Pt(111). Similarly, we have found that 2−3 surface atoms are required for methane dissociation on Pt(111).[20] It has been suggested from supersonic
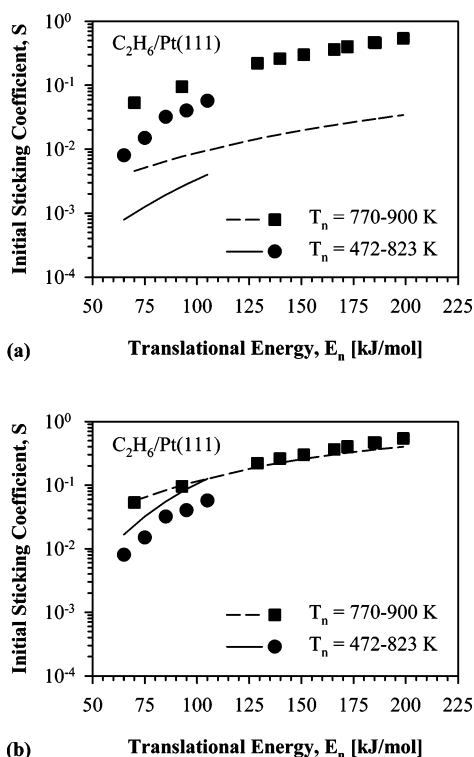
Figure 4. Comparison of PC-MURT predictions (lines) based on this work (a) $\{E_0 = 24$ kJ mol^{-1}, $\nu_D = 215$ cm^{-1}, $s = 10\}$ and (b) $\{E_0 = 29$ kJ mol^{-1}, $\nu_D = 90$ cm^{-1}, $s = 2\}$ to the supersonic molecular beam experiments performed by Madix and co-workers (squares)[39] and by Chesters and co-workers (circles).[37]

molecular beam scattering[37−39] that vibrational energy is important for dissociative sticking but that not all vibrational modes contribute equally to the reaction. We discuss below how MURT analysis of our effusive molecular beam sticking data as well as the supersonic molecular beam data relate to these propositions.

Figure 1 demonstrates that both T_g and T_s affect the dissociative sticking coefficient of ethane on Pt(111) over the ranges 300 K $\leq T_s \leq$ 1200 and 295 K $\leq T_g \leq$ 680 K. An unconstrained optimization of the MURT parameters leads to a very good quantitative fit to the data. While the threshold energy for reaction $E_0 = 24$ kJ mol^{-1} is quite reasonable, the number of surface oscillators involved in the reactive complex $s = 10$ is clearly too high. From the standpoint of making quantitative predictions for $S_0(T_g, T_s)$ in the region of parameter space covered by the experiments, this is not problematic and thermal predictions should also be quantitatively accurate. From the standpoint of a physical interpretation of the dissociation dynamics, the $s = 10$ result clearly calls into question one or more of the assumptions that have been made in the MURT analysis.

If we constrain the optimization such that only the $T_g = 300$ K, angle-integrated data is fitted, we obtain a physically reasonable value of $s = 2$ and $E_0 = 29$ kJ mol^{-1}. From the range of threshold energies, we are able to set a value of $E_0 = 26.5 \pm 3$ kJ mol^{-1}. Looking at the result of the fit in Figure 1b, it is clear that this parameter set systematically overestimates the dissociative sticking coefficient for $T_g \neq T_s$. Again our conclusion is that one or more of the assumptions made in the MURT analysis is in error.

Other determinations of the threshold energy include 74 kJ mol^{-1} as determined by Hirschl et al.[40] using density functional theory (DFT) and 56 kJ mol^{-1} as determined by Weaver et al.,[24]

who applied an earlier statistical, local hot spot model[41] to describe their data. When we use Weaver's parameter set and compare with their supersonic molecular beam sticking data for C_2H_6/Pt(111), we find an ARD of 4416%. This group did not scan for optimal s and ν_D parameters, and the large ARD calls into question the reported value of the threshold energy. Other experiments have been unable to ascertain a value of E_0 that can be compared with a potential energy surface obtained by DFT. Apparent activation energies of 37.2 ± 3.3 and 34.6 ± 2 kJ mol^{-1} have been reported by Rodriguez and Goodman[35] and Newell et al.,[37] respectively. However, neither of these values was obtained under equilibrium conditions nor do they relate directly to the threshold energy for dissociation.

We turn now to an examination of the assumptions in the MURT model. There must be an oversimplification of the transition state used in the MURT model, which does not correctly account for (i) internal molecular energy and mode selective chemistry, (ii) entropic effects (i.e., stiffening or weakening of transition state vibrational frequencies), or (iii) energy transfer out of the collision complex. First, we examine whether all vibrational modes contribute equally to dissociation.

Both Madix and co-workers[5] and Chesters and co-workers[37,38] have suggested that only high-frequency vibrational modes contribute to dissociation. However, the MURT analysis with the $s = 2$ parameter set and with all vibrational modes contributing equally correctly predicts the effects of translational energy and vibrational temperature on their sticking data. Therefore, in this high translational energy regime with virtually no rotational excitation, it appears that all vibrational modes of ethane are contributing equally. Furthermore, this analysis shows that the differences between these two data sets can be explained primarily as a result of the different vibrational temperatures and that the Madix data becomes increasingly insensitive to vibrational temperature changes as the translational energy increases.

For our low kinetic energy effusive beam data, however, it does not appear that all rovibrational modes are contributing equally. The $s = 2$ data set overestimates the effect of T_g on the sticking coefficient. It does so by overpredicting the rovibrational contribution to sticking. The MURT model can successfully fit the effusive beam data. It does this by selecting the $s = 10$ parameter set. A parameter set in which the number of surface oscillators is 10 is essentially attempting to overemphasize the contribution of surface energy while deemphasizing the contribution of molecular energy to overcome the barrier to reaction. This parameter set attempts to describe the T_s and T_g dependence by ascribing the effect primarily to the surface and reducing the importance of molecular excitations. If all rovibrational modes do not contribute equally, then this is precisely the behavior we expect of the model.

Thus, there is a kinetically significant degree of rovibrational mode specificity in the dissociative sticking coefficient for data taken with effusive beams C_2H_6 incident on Pt(111) but not for supersonic beams. We posit two possible explanations for this effect that account for (i) the supersonic beams that have high translational energy but essentially no rotational excitation and (ii) the effusive beams that are slower but have thermally populated rotational levels.

First, high translational energy collisions may lead to distortions in the molecule upon impact that engender efficient intermode coupling and energy randomization. At sufficiently low translational energy, this may no longer be the case and mode specificity arises. Vibrational efficacies differing from unity and depending on the vibrational mode in the dissociative

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sticking coefficient of CH_4 have been observed by Utz and co-workers[13,14] and Beck and co-workers[16,17] on Ni surfaces as well as by Bernasek and co-workers[19] on Pt(111). In none of these cases has the mode specificity been shown to make a kinetically significant contribution to thermally averaged dissociative sticking coefficients. A greater importance of mode specificity for C_2H_6 compared with CH_4 might be related to the fact that the barrier to CH_4 dissociation is significantly higher (52.5 vs 26.5 kJ mol^{-1}) and, therefore, that only collisions with high enough energy to distort the molecule and cause intermode coupling contribute significantly to CH_4 dissociation. On the other hand, the MURT performed well in predictions of SiH_4 dissociation on Si(100) where the threshold energy for dissociation is even lower,[30] 19 kJ mol^{-1}. Thus, there may be some evidence for greater mode specificity at lower translational energy; however, this evidence is not overwhelming.

Second, we consider the effects of rotational excitation. Molecular dynamics simulations of ethane have shown that the interconversion of normal energy and cartwheeling (out-of-plane) rotation plays an important role in the molecular trapping dynamics.[5] Rotation is unique among molecular excitations in that it not only contributes to the energy of the system but also plays a role in determining the orientation of the molecule at impact. This dual role has been demonstrated both for gas-phase[42,43] and surface-catalyzed[44,45] dissociation reactions. The inhibition of dissociation at low J is related to the inability of the system to follow the minimum energy pathway to dissociation. The enhancement of reactivity at high J is related to the coupling of rotational energy into the dissociation coordinate via bond elongation. The latter process is quite effective for H_2 dissociation on Cu(111), in which the only vibrational mode couples directly to rotation and the dissociation coordinate.

It is unlikely that rotation can as efficiently couple into dissociation for C_2H_6 as it does for H_2. A centrifugal distortion of the C−C bond does not help with the dissociation of the C−H bond, which is the first step taken in the dissociative chemisorption of C_2H_6. Rotational anisotropy (cartwheeling vs helicoptering), which is known to play a role in molecular ad/desorption,[46,47] is also expected to be more pronounced for the rodlike C_2H_6 than for the spherical CH_4 or for H_2. Rotational states appear to be well-behaved and contribute statistically to CH_4 dissociation on Pt(111).[20,26] For H_2 dissociation on Cu(111), rotational alignment does play a role, albeit not extremely large, in the dissociation dynamics as is evinced by the small degree of rotational alignment that is measured for H_2 desorbed from Cu(111)[48] and Pd(100).[49] Note that the C_2H_6/Pt(111) supersonic molecular beam experiments, which are well-described by the $s = 2$ parameter set, have virtually no rotational excitation. The higher temperature effusive molecular beam experiments, which are not well fit by this data set, have a fully thermal set of rotational excitations. Our analysis suggests that rotational excitation of C_2H_6 is detrimental to dissociation on Pt(111) and that rotational energy is not making a statistical contribution to the dissociation probability. Further experiments in which the sticking coefficients of individual rovibrational states of C_2H_6 are probed are clearly warranted.

The second suspect assumption of the MURT analysis is a fairly loose transition state in which one grouped frequency describes the behavior of the frustrated translation along the surface normal as well as the three frustrated rotations of ethane in the transition state and all other vibrational frequencies correspond to the values of gas-phase ethane. This pragmatic assumption essentially states that there are no strong entropic effects in the transition state or, more accurately, that there are

no dynamical constraints that affect some degrees of freedom more strongly than others. However, it is known that not all types of C−H bonds react equally well.[5] On Pt(111), the dissociation of primary C−H bonds is more facile than secondary or tertiary C−H bonds. Weaver et al.[5] conclude from this and other aspects of their molecular beam data that steric effects are important for determining the sticking coefficients of alkanes on Pt(111). Such steric effects would be reflected in particularly high values in one or more of the vibrational frequencies associated with the transition state. An ab initio electronic structure theory calculation can be used to estimate these frequencies, but alas, none are available for ethane/Pt(111). When these frequencies are available, we will incorporate them into our MURT analysis, which will remove the uncertainty of our assumed relatively loose transition state and will unambiguously reveal the importance of steric effects in determining the sticking coefficient.

The third assumption concerns energy transfer out of the reactive complex. Direct measurement of energy transfer from the transition state complex to the rest of the solid is experimentally inaccessible. We can only begin to address these effects after we have a clear understanding of the effects of the initial molecular excitation and the vibrational frequencies in the transition state.

Conclusions

The dissociative sticking coefficient of ethane on Pt(111) depends on both the gas temperature and the surface temperature. We report a threshold energy for dissociation $E_0 = 26.5 \pm 3$ kJ mol^{-1} that can be directly related to a barrier height derived from a potential energy surface. Just as on Pt(110)−(1 × 2), for energies where the sticking coefficient is low (<0.01), the dissociation of C_2H_6 is orders of magnitude more probable than the dissociation of CH_4. Vibrational energy is important for overcoming the barrier to dissociation and there may be indications that not all vibrational states contribute equally to the sticking coefficient. Rotational excitation appears to have an adverse effect on the dissociative sticking coefficient. Entropic factors in the transition state may also be playing an important role in the dissociation dynamics. These are clear indications that dynamical corrections are kinetically relevant for determining ethane dissociative sticking coefficients and that even the thermal dissociation dynamics are not adequately described by a statistical model. Our results indicate that a more detailed understanding of the dissociation dynamics of ethane on metal surfaces will require (i) improved bulb, effusive molecular beam, and supersonic molecular beam studies to confirm quantitatively the value of the sticking coefficient under a variety of conditions, (ii) rovibrational state resolved sticking measurements that directly probe the mode specificity of the sticking coefficient, and (iii) knowledge of the vibrational properties in the transition state as can be derived from ab initio calculations.

References and Notes

(1) Weinberg, W. H. *Langmuir* **1993**, *9*, 655.
(2) Larsen, J. H.; Chorkendorff, I. *Surf. Sci. Rep.* **1999**, *35*, 163.

(3) Choudhary, T. V.; Aksoylu, E.; Goodman, D. W. *Catal. Rev.* **2003**, *45*, 151.

(4) Arumainayagam, C. R.; Madix, R. *J. Prog. Surf. Sci.* **1991**, *38*, 1.

(5) Weaver, J. F.; Carlsson, A. F.; Madix, R. *J. Surf. Sci. Rep.* **2003**, *50*, 107.

(6) Kao, C.-L.; Madix, R. *J. Surf. Sci.* **2004**, *557*, 215.

(7) Arumainayagam, C. R.; Schoofs, G. R.; McMaster, M. C.; Madix, R. J. *J. Phys. Chem.* **1991**, *95*, 1041.

(8) Verhoef, R. W.; Kelly, D.; Mullins, C. B.; Weinberg, W. H. *Surf. Sci.* **1993**, *291*, L719.

(9) Lee, M. B.; Yang, Q. Y.; Ceyer, S. T. *J. Chem. Phys.* **1987**, *87*, 2724.

(10) Holmblad, P. M.; Wambach, J.; Chorkendorff, I. *J. Chem. Phys.* **1995**, *102*, 8255.

(11) Larsen, J. H.; Holmblad, P. M.; Chorkendorff, I. *J. Chem. Phys.* **1999**, *110*, 2637.

(12) Juurlink, L. B. F.; McCabe, P. R.; Smith, R. R.; DiCologero, C. L.; Utz, A. L. *Phys. Rev. Lett.* **1999**, *83*, 868.

(13) Juurlink, L. B. F.; Smith, R. R.; Killelea, D. R.; Utz, A. L. *Phys. Rev. Lett.* **2005**, *94*, 208303.

(14) Smith, R. R.; Killelea, D. R.; DelSesto, D. F.; Utz, A. L. *Science* **2004**, *304*, 992.

(15) Schmid, M. P.; Maroni, P.; Beck, R. D.; Rizzo, T. R. *J. Chem. Phys.* **2002**, *117*, 8603.

(16) Beck, R. D.; Maroni, P.; Papageorgopoulos, D. C.; Dang, T. T.; Schmid, M. P.; Rizzo, T. R. *Science* **2003**, *302*, 98.

(17) Maroni, P.; Papageorgopoulos, D. C.; Sacchi, M.; Dang, T. T.; Beck, R. D.; Rizzo, T. R. *Phys. Rev. Lett.* **2005**, *94*, 246104.

(18) Luntz, A. C.; Bethune, D. S. *J. Chem. Phys.* **1989**, *90*, 1274.

(19) Higgins, J.; Conjusteau, A.; Scoles, G.; Bernasek, S. L. *J. Chem. Phys.* **2001**, *114*, 5277.

(20) DeWitt, K. M.; Valadez, L.; Abbott, H. L.; Kolasinski, K. W.; Harrison, I. *J. Phys. Chem B* **2006**, *110*, 6705.

(21) Bukoski, A.; Blumling, D.; Harrison, I. *J. Chem. Phys.* **2003**, *118*, 843.

(22) Abbott, H. L.; Bukoski, A.; Harrison, I. *J. Chem. Phys.* **2004**, *121*, 3792.

(23) McMaster, M. C.; Madix, R. *J. Surf. Sci.* **1992**, *275*, 265.

(24) Weaver, J. F.; Krzyzowski, M. A.; Madix, R. J. *J. Chem. Phys.* **2000**, *112*, 396.

(25) Harris, J. J. W.; Fiorin, V.; Campbell, C. T.; King, D. A. *J. Phys. Chem. B* **2005**, *109*, 4069.

(26) Bukoski, A.; Abbott, H. L.; Harrison, I. *J. Chem. Phys.* **2005**, *123*, 094707.

(27) Bukoski, A.; Harrison, I. *J. Chem. Phys.* **2003**, *118*, 9762.

(28) Abbott, H. L.; Bukoski, A.; Kavulak, D. F.; Harrison, I. *J. Chem. Phys.* **2003**, *119*, 6407.

(29) Abbott, H. L.; Harrison, I. *J. Phys. Chem. B* **2005**, *109*, 10371.

(30) Kavulak, D. F.; Abbott, H. L.; Harrison, I. *J. Phys. Chem. B* **2005**, *109*, 685.

(31) Luntz, A. C. *J. Chem. Phys.* **2000**, *113*, 6901.

(32) Fuhrmann, T.; Kinne, M.; Whelan, C. M.; Zhu, J. F.; Denecke, R.; Steinrück, H.-P. *Chem. Phys. Lett.* **2004**, *390*, 208.

(33) Luntz, A. C.; Winters, H. F. *J. Chem. Phys.* **1994**, *101*, 10980.

(34) Johnson, D. F.; Weinberg, W. H. *Science* **1993**, *261*, 76.

(35) Rodriguez, J. A.; Goodman, D. W. *J. Phys. Chem.* **1990**, *94*, 5342.

(36) Nielsen, B. Ø.; Luntz, A. C.; Holmblad, P. M.; Chorkendorff, I. *Catal. Lett.* **1995**, *32*, 15.

(37) Newell, H. E.; Oakes, D. J.; Rutten, F. J. M.; McCoustra, M. R. S.; Chesters, M. A. *Faraday Discuss.* **1996**, *105*, 193.

(38) Oakes, D. J.; Newell, H. E.; Rutten, F. J. M.; McCoustra, M. R. S.; Chesters, M. A. *Chem. Phys. Lett.* **1996**, *253*, 123.

(39) Schoofs, G. R.; Arumainayagam, C. R.; McMaster, M. C.; Madix, R. *J. Surf. Sci.* **1989**, *215*, 1.

(40) Hirschl, R.; Eichler, A.; Hafner, J. *J. Catal.* **2004**, *226*, 273.

(41) Ukraintsev, V. A.; Harrison, I. *J. Chem. Phys.* **1994**, *101*, 1564.

(42) Mayne, H. R.; Minick, S. K. *J. Phys. Chem.* **1987**, *91*, 1400.

(43) Blackwell, B. A.; Polanyi, J. C.; Sloan, J. *J. Chem. Phys.* **1978**, *30*, 299.

(44) Darling, G. R.; Holloway, S. *Rep. Prog. Phys.* **1995**, *58*, 1595.

(45) Rettner, C. T.; Michelsen, H. A.; Auerbach, D. J. *J. Chem. Phys.* **1995**, *102*, 4625.

(46) Jacobs, D. C.; Kolasinski, K. W.; Madix, R. J.; Zare, R. N. *J. Chem. Phys.* **1987**, *87*, 5038.

(47) Jacobs, D. C.; Kolasinski, K. W.; Shane, S. F.; Zare, R. N. *J. Chem. Phys.* **1989**, *91*, 3182.

(48) Gulding, S. J.; Wodtke, A. M.; Hou, H.; Rettner, C. T.; Michelsen, H. A.; Auerbach, D. J. *J. Chem. Phys.* **1996**, *105*, 9702.

(49) Wetzig, D.; Dopheide, R.; Rutkowski, M.; David, R.; Zacharias, H. *Phys. Rev. Lett.* **1996**, *76*, 463.