An effusive molecular beam technique for studies of polyatomic gas–surface reactivity and energy transfer

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An effusive molecular beam technique is described to measure alkane dissociative sticking coefficients, \( S(T_g, T_s; \theta) \), on metal surfaces for which the impinging gas temperature, \( T_g \), and surface temperature, \( T_s \), can be independently varied, along with the angle of incidence, \( \theta \), of the impinging gas. Effusive beam experiments with \( T_g = T_s = T \) allow for determination of angle-resolved dissociative sticking coefficients, \( S(T; \theta) \), which when averaged over the \( \cos(\theta)/\pi \) angular distribution appropriate to the impinging flux from a thermal ambient gas yield the thermal dissociative sticking coefficient, \( S(T) \). Nonequilibrium \( S(T_g, T_s; \theta) \) measurements for which \( T_g \neq T_s \) provide additional opportunities to characterize the transition state and gas–surface energy transfer at reactive energies. A resistively heated effusive molecular beam doser controls the \( T_g \) of the impinging gas striking the surface. The flux of molecules striking the surface from the effusive beam is determined from knowledge of the dosing geometry, chamber pressure, and pumping speed. Separate experiments with a calibrated leak serve to fix the chamber pumping speed. Postdosing Auger electron spectroscopy is used to measure the carbon of the alkyl radical reaction product that is deposited on the surface as a result of alkane dissociative sticking. As implemented in a typical ultrahigh vacuum chamber for surface analysis, the technique has provided access to a dynamic range of roughly \( 6 \) orders of magnitude in the initial dissociative sticking coefficient for small alkanes on Pt(111). © 2011 American Institute of Physics. [doi:10.1063/1.3577076]

I. INTRODUCTION

The kinetics of polyatomic molecules reacting at metal surfaces are challenging to characterize because the states of both the incident molecules,¹,² and the surface,³ can sharply influence the gas–surface reactivity.⁴,⁵ In this paper, an effusive molecular beam technique is described to characterize the dissociative chemisorption of alkanes on metal surfaces. Alkanes are naturally abundant polyatomic molecules, and there has been sustained interest in finding low temperature, energy efficient, catalytic means to transform alkanes into more valuable chemical feedstocks such as hydrogen, olefins, and alcohols.⁶ Currently, the industrial supply of hydrogen derives predominately from the steam reforming of methane⁷ over supported Ni nanocatalysts wherein the rate limiting step is considered to be the dissociative chemisorption of methane.⁸ A detailed understanding of the dissociative chemisorption kinetics of alkanes is sought that may ultimately provide means to predict and possibly improve the rates of catalytic processes involving alkanes.

A number of techniques are available to explore alkane reactivity at surfaces. Thermal dissociative sticking coefficients, \( S(T) \), for light alkanes can be measured on single crystal metal surfaces prepared in ultrahigh vacuum (UHV) by exposing a heated surface to alkanes at several torr pressure such that the gas within a mean free path length of the hot surface comes in to thermal equilibrium with the surface through gas–gas and gas–surface collisions. This “thermal bulb” technique was developed by Yates⁹ and Goodman¹⁰ and further refined by Chorkendorff and et al.¹¹ It typically provides access to \( S(T) \) values less than \( 10^{-6} \). King and Wells¹² developed a versatile, self-normalizing, collimated molecular beam technique that is well suited for measurement of nonequilibrium dissociative sticking coefficients greater than about \( 10^{-2} \). Dosing alkanes on to a surface using supersonic molecular beams, followed by Auger electron spectroscopy (AES) measurement of the C content of the chemisorbed alkyl reaction products left behind on the surface provides access to an extended range¹³ of nonequilibrium dissociative sticking coefficients greater than about \( 10^{-7} \). Importantly, supersonic molecular beams provide opportunities to explore multidimensional gas–surface reaction dynamics as a function of the molecule’s translational and internal energies, and the surface temperature.¹⁴ With laser-pumped supersonic molecular beams, it has even become possible to measure rovibrational eigenstate-resolved dissociative sticking coefficients for CH₄ and SiH₄.¹⁵ Why then consider making measurements with thermal effusive molecular beams? The answer lies in the ability to measure a broad range of dissociative sticking coefficients \( (10^{-1} \geq S \geq 10^{-7}) \), including quasithermal equilibrium and nonequilibrium ones, with a single, relatively inexpensive, apparatus under conditions where the energy distributions of the incident molecules are particularly well-defined and suitable for theoretical modeling. The rotational cooling

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and asymmetric mode-specific vibrational cooling\textsuperscript{16–18} of molecules that can occur during the supersonic expansion of supersonic molecular beams\textsuperscript{19} are avoided through the use of thermal effusive beams. The rotational and vibrational coolings of molecules in supersonic beam studies of dissociative sticking are rarely, if ever, spectroscopically characterized sufficiently to unambiguously define the internal energy content of the molecules, which plays a crucial role in determining dissociative sticking coefficients.\textsuperscript{20} In contrast, there is no ambiguity about the energy distributions of molecules incident on the surface in effusive molecular beam studies of dissociative sticking—the energy distributions are flux-weighted thermal distributions. By comparing dissociative sticking from effusive molecular beams with that from supersonic molecular beams [where rotational energy is effectively frozen out (e.g., $T_{\text{rot}} \sim 20 \text{ K}$)], there are opportunities to address the role of rotational energy in gas–surface reactivity.

Effusive molecular beam studies allow for the measurement of dissociative sticking coefficients, $S(T_g, T_s; \theta)$, on surfaces for which the impinging gas temperature, $T_g$, and surface temperature, $T_s$, can be independently varied, along with the angle of incidence, $\theta$, of the impinging gas.\textsuperscript{4,5} Effusive beam experiments with $T_g = T_s = T$ can determine angle-resolved dissociative sticking coefficients, $S(T; \theta)$, which when averaged over a $\cos(\theta)/\pi$ angular distribution yield the thermal dissociative sticking coefficient, $S(T)$, appropriate to reaction with a thermal ambient gas. Measurements of $S(T; \theta = 0^\circ) = S_\theta(T)$ for gas incident along the surface normal can provide a close approximation to $S(T)$. Nonequilibrium $S(T_g, T_s; \theta)$ measurements for which $T_g \neq T_s$ afford additional opportunities to characterize the transition state and gas–surface energy transfer at reactive energies. Microcanonical unmolecular rate theory,\textsuperscript{20–22} analysis of recent alkane $S_\theta(T)$ and $S_\theta(T_g, T_s)$ measurements,\textsuperscript{4,5} for methane, ethane, and propane on Pt(111) sufficient to extract transition state and gas–surface energy transfer parameters. The experimentally derived threshold energies, $E_0$, for alkane dissociative chemisorption were uniformly lower than predictions based on density functional theory (DFT) electronic structure theory calculations [e.g., $E_{0, \text{DFT}} = 48 \text{ kJ/mol}$, $34 \text{ kJ/mol}$, $21 \text{ kJ/mol}$ for methane, ethane, and propane on Pt(111), respectively].\textsuperscript{5} An Evans–Polanyi relation between the experimental activation energy for $S_\theta(T)$ and the alkane desorption energy, $E_D$, was found, $E_d = 72.9 \text{ kJ/mol} - 0.94 E_D$, which is strongly suggestive that van der Waals interactions, which are not accounted for in traditional DFT calculations, play an essential role in defining the alkane reaction kinetics.\textsuperscript{4,5} Furthermore, the nonequilibrium $S_\theta(T_g, T_s)$ measurements for which $T_g \neq T_s$ demonstrate that reactivity and gas–surface energy transfer are intimately mixed for alkanes larger than methane. In the current paper, we elaborate on the experimental details of making these kinds of alkane dissociative sticking measurements using a resistively heated effusive molecular beam douser mounted in a typical UHV chamber for surface analysis.

The formalism described for measuring dissociative sticking coefficients using effusive molecular beams should be transferable to other kinds of polyatomic gas/surface systems that exhibit activated dissociative chemisorption, such as alkynes on Cu(111),\textsuperscript{23} CH$_3$OH on Pt(111),\textsuperscript{24} and SiH$_4$ on Si(100).\textsuperscript{15,25} Analytical techniques employed to monitor reactivity for these examples of activated dissociative chemisorption of polyatomic molecules have ranged from Auger electron spectroscopy,\textsuperscript{23} optical ellipsometry,\textsuperscript{23} surface differential optical reflectivity,\textsuperscript{15} secondary ion mass spectrometry,\textsuperscript{15} to mass spectrometry of volatile reaction products.\textsuperscript{24} Other surface analytical techniques that could be employed to monitor the products of dissociative chemisorption include He beam reflectivity,\textsuperscript{26,27} work function measurements,\textsuperscript{28} reflection absorption infrared spectroscopy,\textsuperscript{29} and x-ray photoelectron spectroscopy.\textsuperscript{30} Here, we determine alkane/Pt(111) dissociative sticking coefficients using effusive molecular beams and Auger electron spectroscopy to monitor the C derived from the chemisorbed reaction products.

II. MEASURING DISSOCIATIVE STICKING COEFFICIENTS WITH AN EFFUSIVE MOLECULAR BEAM

A. Overview

In alkane effusive molecular beam experiments, dissociatively chemisorbing alkane molecules are assumed to yield alkyl radicals whose C remains on the surface, independent of any secondary chemistry.\textsuperscript{31} The effusive beam is aimed at the center of the surface, along the direction of the surface normal. The initial dissociative sticking coefficient, $S(T_g, T_s; \theta)$, is determined from effusive beam experiments by Auger electron spectroscopy measurements of the carbon coverage, $\theta_C$, deposited on the surface at an angle $\theta$ from the beam center axis after dosing for a time $\tau$ with a known beam flux based on knowledge of the chamber pressure, $p$, and pumping speed, $C_p$. The heated gas which misses or does not react with the sample surface in its first collision is assumed to become thermalized to the chamber wall temperature, $T_s$, through collisions before being removed by the chamber pump or striking the sample surface again. For $S(T_g, T_s; \theta) \leq 0.1$, modest $\theta_C$ accumulation, and practical dosing geometries, the following expression:

$$S(T_g, T_s; \theta) = \frac{1}{R} \int \frac{\theta_C \sigma}{n F_{\text{bkg}} \tau} - S_{\text{bkg}}(T_s, T_s) \, d\theta$$

applies, where $\sigma$ is the atom area density of the sample surface [e.g., $1.50 \times 10^{15} \text{ cm}^{-2}$ for Pt(111)], $n$ is the number of carbons in the alkane, $F_{\text{bkg}} = p/\sqrt{2\pi m k_B T_s}$ is the background flux from the thermalized gas load that strikes the surface, $R$ is the ratio of the direct flux, $F_{\text{dir}}$, from the effusive molecular beam that strikes the surface to the background flux, and $S_{\text{bkg}}(T_s, T_s)$ is the dissociative sticking coefficient for the ambient background gas at the chamber temperature that strikes the surface. With the beam orifice at a distance $d$ away from the center of the sample surface, the ratio $R$ varies spatially across the surface as

$$R = \frac{F_{\text{dir}}}{F_{\text{bkg}}} \approx C_p \sqrt{2 m \cos^2(\theta) j(\theta)} \frac{W}{\sqrt{\pi k_B T_s} d^2},$$

where $\theta$ is the angle away from the beam center axis for flux that hits the surface at a radial distance $x$ from the surface.
center \([\theta = \tan^{-1}(x/d)]\). The flux angular function, \(j(\theta)\), and transmission coefficient, \(W\), for effusion from an aperture of finite wall thickness are given analytically elsewhere.\(^{32–34}\) These quantities tend to \(\cos(\theta)\) and 1, respectively, in the limit of a vanishingly thin aperture wall. We restrict our attention to effusive beams working in the transparent regime of operation for which the aperture Knudsen numbers are \(Kn_D = \Lambda/D \geq 1\) and \(Kn_L = \Lambda/L \gg 1\), where \(\Lambda\) is the mean free path of the gas and \(D\) and \(L\) are the diameter (dia.) and length (wall thickness) of the nozzle aperture, respectively.\(^{32,35}\)

**B. Analysis of effusive molecular beam sticking experiments**

Following Pauly’s review,\(^{32}\) the rate of effusion from an effusive molecular beam nozzle operating in the transparent regime is

\[
\frac{dN}{dr} = \int \frac{d^2N}{d\Omega dr} d\Omega
= \frac{p_n A_n}{2\pi mk_BT_n} \int \frac{j(\theta)\cos^3(\theta)}{\pi} d\Omega = \frac{p_n A_n W}{2\pi mk_BT_n}.
\]

where \(T_n\) is the nozzle temperature, \(d\Omega\) is an increment of solid angle, and the integration is over the forward hemisphere of solid angle. The direct flux from the effusive beam that strikes the surface when it is in the dosing position, centered and in front of the beam nozzle, varies as

\[
F_{\text{dir}} = \frac{d^2N}{dA dr} = \frac{d^2N}{d\Omega dr} dA = \frac{p_n A_n}{2\pi mk_BT_n} \frac{j(\theta)\cos^3(\theta)}{\pi} \frac{d^2}{dA d\theta},
\]

given that \(d\Omega = dA \cos(\theta)/r^2\), where \(dA\) is an increment of area on the sample surface, \(r = d/\cos(\theta)\), and \(\theta = \tan^{-1}(x/d)\).

Under steady-state conditions, equilibrium is established between the rate of effusion, \(dN/dr\), of gas coming into the chamber through the source’s nozzle hole with area \(A_n\) and the removal of (i) some of the gas that initially strikes the surface and dissociatively sticks and (ii) the remaining gas that has been thermalized through gas–wall collisions and which is pumped with the chamber pumping speed, \(C_c\). The throughput balance is

\[
C_c p = \frac{d(pV)}{dr} = k_BT_n \frac{dN}{dr}
\times \left[1 - \int_{\text{Surface}} S(T_g, T_s; \theta) \frac{j(\theta)\cos^3(\theta)}{W\pi d^2} dA\right],
\]

where \(p\), \(V\), and \(T_c\) are the chamber pressure, volume, and temperature, respectively. The pumping speed of the chamber, \(C_c = C_p + C_s\), is the sum of that from the chamber pump, \(C_p\), and the sample surface, \(C_s\). The pumping speed of the clean sample surface of area \(A\) is

\[
C_s = S_{\text{bkg}}(T_c, T_s) \sqrt{\frac{k_BT_c}{2\pi m A}}.
\]

The background flux of molecules striking the surface is spatially unvarying and given by

\[
F_{\text{bkg}} = \frac{p}{\sqrt{2\pi mk_BT_c}} = \frac{1}{C_c} \frac{k_BT}{2\pi m} \frac{dN}{dr}
\times \left[1 - \int_{\text{Surface}} S(T_g, T_s; \theta) \frac{j(\theta)\cos^3(\theta)}{W\pi d^2} dA\right].
\]

after substituting for the chamber pressure, \(p\), of Eq. (5). The ratio \(R\) varies spatially across the surface as

\[
R = \frac{F_{\text{dir}}}{F_{\text{bkg}}} = \frac{C_c \sqrt{2\pi mk_BT_n}}{k_BT c W A_n}
\times \left[1 - \int_{\text{Surface}} S(T_g, T_s; \theta) \frac{j(\theta)\cos^3(\theta)}{W\pi d^2} dA\right]^{-1}.
\]

The background sticking coefficient \(S(T_g, T_s; \theta)\) can be isolated after integrating Eq. (10) over a dosing period \(\tau\) that deposits a coverage \(\theta_{\text{dir}}\) that is sufficiently small that there are negligible coverage-dependent changes in the dissociative sticking coefficients during dosing such that Eq. (1) results. The background sticking coefficient \(S_{\text{bkg}}(T_c, T_s)\) is characterized independently by dosing the surface with gas from a nondirectional leak valve rather than from a directed effusive beam. Equation (1) gives \(S(T_g, T_s; \theta)\) as a function of the position/angle \([n, b, \theta = \tan^{-1}(x/d)]\) across the surface where \(\theta_{\text{dir}}\) is measured. Typically, the dissociative sticking along the direction of the surface normal \(S(T_g, T_s; \theta = 0^\circ) = S_n(T_g, T_s)\) is determined based on the \(\theta_{\text{dir}}\) deposited at the center of the sample surface. Worth noting is that by translating the center of the sample surface laterally, away from being directly underneath the effusive beam’s centerline axis, it is possible to perform experiments where \(S(T_g, T_s; \theta)\) can be measured over an extended range of angles.
For most practical implementations of the effusive beam technique as described below and for dissociative sticking coefficients $S(T_s, T_i; \theta) \leq 0.1$, the surface integral in Eq. (5) and Eqs. (7)–(9) is negligible as is the pumping speed of the surface, $C_s$, in Eq. (6). In such cases, Eq. (2) is an adequate approximation to Eq. (8).

If sufficiently high $\theta_C$ is accumulated during dosing, dissociative sticking coefficients are typically found to obey a coverage dependence such as $S(\theta_i) = S_0[1 - (\theta_C/\theta_{C,max})]$, where $S_0$ is the initial dissociative sticking coefficient and $\theta_{C,max}$ is a constant. For sufficiently small $\theta_C$ accumulations, the dissociative sticking coefficient may be approximated as coverage independent, $S(\theta_i) \sim S_0$, and Eq. (1) applies well. For dosing leading to higher $\theta_C$ accumulations where $S(\theta_i)$ is discernibly coverage dependent, Eq. (10) should be integrated with the explicit coverage dependence built in to the $[S(T_s, T_i; \theta), S_{kg}(T_s, T_i)]$ coefficients, which gives more complicated expressions from which the initial values for $S(T_g, T_i; \theta)$ may ultimately be extracted.

III. INSTRUMENTATION FOR $S_n(T_g, T_s)$ MEASUREMENTS FOR LIGHT ALKANES ON Pt(111)

A. Vacuum system and sample

Experiments were performed in an UHV surface analysis chamber with a base pressure of $1 \times 10^{-10}$ Torr, shown schematically in Fig. 1. The chamber was pumped by a Pfeiffer TMH-261 210 L/s turbomolecular pump and a 240 L/s ion pump with an integrated Ti sublimation pump (TSP). When alkanes were dosed into the chamber, the ion pump and TSP were separated from the main chamber by a gate valve in order to maintain a constant chamber pumping speed based on the turbomolecular pump alone. The chamber is equipped with a Phi 15–255 GAR double-pass cylindrical mirror analyzer for AES, a 0–2 keV ion sputter gun, a residual gas analyzer, a twice-differentially pumped quadrupole mass spectrometer for thermal programmed desorption (TPD), a thin-walled 100 μm dia. aperture calibrated leak from Vacuum Technology Inc., and a variable temperature, effusive molecular beam doser. Gas pressures in the chamber were measured using a Stabil-Ion Bayard-Alpert gauge from Granville-Phillips with ±6% accuracy as well as a MKS model 615 bakeable Baratron capacitive manometer gauge with a model 670 signal conditioner. A 0–1 Torr range MKS model 122BA Baratron on the gas handling manifold was positioned directly behind the calibrated leak for use in chamber pumping speed measurements. This manifold Baratron could also be valved so as to monitor the gas manifold pressure, leading to the effusive molecular beam nozzle during dosing.

A Pt single crystal of 10 mm dia. × 1.5 mm thickness with a surface oriented to within 0.1° of the (111) face was obtained from Surface Preparation Laboratory, Zaandam, The Netherlands. The Pt(111) surface was mounted to a resistively heated sample holder adapted from Menzel’s design. The sample was spot welded between a pair of 0.010 in dia. 75% W/25% Re wires that were resistively heated using a Xantrex XFR 12–100 programmable dc power supply. The sample temperature was monitored by a K-type thermocouple spot welded directly to the back side of the crystal. A Eurotherm 906S-EPC proportional/integral/derivative (PID) controller read the thermocouple and controlled the sample temperature by driving the Xantrex power supply. The sample was cooled by its connection to a continuous flow cryostat from Oxford Instruments. The sample mount provided access to a Pt(111) surface temperature range from 20–1250 K with LHe cooling and 90 to 1250 K with LN2 cooling. Sample temperatures were calibrated by TPD based on fitting the leading edge of the zeroth-order TPD peak of multilayers of several different gases, as described elsewhere.

The Pt(111) surface was initially prepared by repeated cycles of Ar+ ion sputtering at 800 K and annealing for 5 min at 1200 K. To remove C contaminants, the sample was oxidized by repeated sample annealing at 800 K in a 5 × 10−9 Torr O2 atmosphere, followed by flashing to 1150 K. In all cleaning procedures, the surface temperature is maintained below 1275 K to avoid a reconstruction of the Pt(111) surface that occurs at 1320 K. The sample was considered clean and ready for alkane dosing when no contaminants, including Si and Ca, were detectable by AES. Carbon accumulation after alkane dosing was monitored by AES. Gases used for dosing and C calibration were research grade methane (99.999%), ethane (99.995%), and propane (99.993%) and CP grade ethylene (99.5%), which were purchased from Matheson Tri-Gas and used without further purification.

B. Effusive molecular beam

Figure 2 provides a schematic diagram of the effusive molecular beam doser used in measurements of alkane $S_{al}(T_g, T_i; \theta)$ on metal surfaces. The doser’s gas exposed interior components are all made of type 304 stainless steel (304 SS). The central dosing tube is a 0.25 in. outer diameter.
temperature. The effusive beam nozzle reaches a temperature less than 160 W of dc power at less than 4 A current. A chamber base pressure of \( \lesssim 1 \times 10^{-10} \) Torr is maintained during effusive molecular beam dosing of propane as a function of nozzle temperature while maintaining a total chamber pressure of 10 Torr.

In dissociative sticking coefficient experiments using the effusive molecular beam, it is assumed that the gas temperature of the effusing molecules matches beam’s nozzle temperature as read by the thermocouple spot welded to the end of the nozzle. To verify that \( T_n = T_g \) holds well, propane pyrolysis experiments were conducted in which residual gas analysis (RGA) was performed while flowing propane through the heated effusive doser at different nozzle temperatures while maintaining transparent flow. Figure 3 shows that the relative ion currents from the RGA at different masses are constant as a function of \( T_n \) until the onset of propane pyrolysis is reached at a temperature of 960 K. At the pyrolysis onset, the relative intensities of the ion currents begin to change as is most evident for the ion currents at the lowest masses. These observations are in good accord with a recent gas phase study of propane pyrolysis, which observed less than 0.6% propane decomposition at 913 K but 5.6% at 963 K and 15.6% by 1003 K. On the basis of these pyrolysis experiments, we estimate that the measured \( T_n \) and \( T_g \) agree to within \( \pm 10 \) K.

C. Auger electron spectroscopy of carbon deposition on Pt(111)

Postreaction determination of the C coverage accumulated on the surface after alkane dosing was made by AES so that dissociative sticking coefficients could be determined.
AES spectra were obtained over the 70–600 eV range in order to additionally monitor for other species that could possibly adsorb (e.g., O from CO). Alkane exposures were chosen such that C coverages of θ_C = 0.1–0.4 ML were deposited where one monolayer is 1 ML = 0.64 × 10^15 cm^{-2}. The lower coverage limit was chosen such that reactivity at defect sites did not dominate the measurements, and the upper limit was chosen to ensure the measurements still allowed for a reasonable calculation of the initial sticking coefficient appropriate to the majority of surface sites. It was preferable to analyze undifferentiated, rather than differentiated, AES spectra for signal to noise reasons and also because the C peak in AES can change its shape and energetic position as a function of the C coverage or state (e.g., carbide versus graphitic C) in ways that render analysis of differentiated AES spectra less quantitative. Consequently, θ_C was determined by fitting the undifferentiated AES spectrum using the CASAXPS program and comparing the relative intensities of the integrated Pt237 and C272 peaks. The AES peaks are labeled traditionally according to their elemental source and energetic position in electronvolts within differentiated AES spectra. Shirley background subtraction over the interval from 210 to 280 eV was applied to the undifferentiated AES spectra and was found to give more consistent analytical results than either a linear or Tougaard subtraction. Peak fitting was initially optimized for a clean Pt(111) AES spectrum. A convolution of 30% Lorentzian and 70% Gaussian was used to fit the Ar219, Pt237, Pt248, and the C272 peaks using the Marquardt nonlinear least squares fitting routine. Peak positions were constrained to 221 eV (Ar219), 233 eV (Pt237), and 248 eV (Pt248), but the C272 peak position was not constrained. FWHM constraints were applied to Ar219 (11.7 eV), Pt237 (12.5 eV), Pt248 (11.2 eV), and the C272 (15 eV) peaks. Integrated peak area ratios were also constrained and set for Int(Pt248)/Int(Pt237) to 0.48 and for Int(Ar219)/Int(Pt237) to 0.15. Fitting parameters were verified by dosing ethylene to give standard C coverages. For AES using a 3 keV incident electron beam, the carbon coverage in units of Pt(111) monolayers was given by θ_AE = 0.61 Int(C272)/Int(Pt237). A saturated monolayer of ethylene formed at T_e = 300 K gave a C coverage of 0.46 ML, whereas extended dosing of ethylene at T_e = 1000 K gave a saturated monolayer of graphene with a C coverage of 2.57 ML. The alkane deposition and C calibration experiments were performed at T_e ≤ 1050 K, which ensured that there was negligible C diffusion into the bulk of the Pt(111) sample. In the alkane dissociative sticking coefficient experiments, postdosing AES spectra were taken at T_e = 500 K with an electron beam energy of 3 keV.

Figure 4 shows the buildup of carbon coverage as measured by AES when ethylene was dosed on Pt(111) as a background gas at a surface temperature of 1014 K. The dissociative sticking coefficient for ethylene can be written as S(θ) = (1/n) dθC/dε, where ε = F_bkg τ is the exposure in ML of collisions and n = 2 carbon atoms are deposited for every ethylene that dissociatively chemisorbs. Figure 4 experimental data, θ_C(ε), is compared to a simulation with a globally fitted form of S(θ) = S_0 [1 - (θ_C / θ_C,max)] and its linear approximation. First-order Langmuirian kinetics have been observed previously for ethylene on Pt(111). The inset shows that for the 0.1–0.4 ML range of θ_C (the range typically accumulated in alkane dissociative sticking experiments) the experimental variation of θ_C with ε is linear, indicating a constant sticking coefficient. Experimental sticking coefficients calculated as S = θ_C/(2ε) are typically not in precise accord with the local value of the globally fitted S(θ) functional form nor its initial value (e.g., S = 0.80, S(0.3ML) = 0.72, S_0 = 0.82 describe the Fig. 4 inset data). Alkane dissociative sticking coefficients exhibited similar global coverage dependencies, but there were no discernable coverage variations in the sticking coefficients calculated with θ_C in the 0.1–0.4 ML range.

D. Chamber pumping speed

In dissociative sticking coefficient studies using effusive beams, it is important to have accurate knowledge of the chamber pumping speed, C_p, which scales the ratio of the direct to indirect flux, R = F_{dir}/F_{bkg}, in Eq. (2), which, in turn, inversely scales the direct dissociative sticking coefficient, S(T_s; T_e; θ), of Eq. (1).

The chamber pumping speed is the sum of the pumping speeds derived from the turbomolecular pump and from the Pt(111) surface, C_p = C_p(def + C_bkg). Additional pumping speed for some molecules might be encountered due to condensation on, or reaction with, unpassivated chamber walls, but this has not been found to be a problem for alkanes ranging in size from methane to nonane. The Pfeiffer TMH-261 turbomolecular pump has a rated pumping speed of 210 L/s.
for N₂ at its inlet but the pumping speed at the chamber is reduced to ~170 L/s due to the series conductance \(^5\) of the tubing and gate valve attaching the turbopump to the chamber. The pumping speed of the clean Pt(111) surface is given by Eq. (5) which amounts to \(C_c = S_{\text{bar}}(T_c, T_s) A \times 15.7 \text{ L s}^{-1} \text{ cm}^{-2}\) for methane at \(T_c = 300\) K. Given that \(C_c \propto 1/\sqrt{m}\) and \(S_{\text{bar}}(T_c, T_s) < 0.1\) for all the light alkanes under study here, the 1 cm dia. Pt(111) surface area \(A = 0.79\) cm\(^2\) yields a pumping speed of \(C_c < 1.2\) L/s which is negligible in comparison to \(C_p\). Pumping speeds for turbo-molecular pumps are typically specified by the manufacturer for N₂ and occasionally for a few other gases. \(^6\) It is prudent and typically necessary to directly measure the chamber pumping speeds for the gases involved in dissociative sticking studies.

The chamber pumping speed was measured using a thin walled orifice style of calibrated leak purchased from Vacuum Technology Inc. The calibrated leak with a nominal diameter of 100 \(\mu\)m has a NIST-traceable leak rate of \(C_l = 8.10 \times 10^{-4}\) Torr L/s for N₂ at \(T = 296\) K with an accuracy of ±11% at \(10^{-1}\) Torr, ±7% at \(10^{-2}\) Torr, and ±15% at \(10^{-3}\) Torr. To determine the chamber pumping speed, a continuous flow of gas was admitted to the vacuum chamber via the calibrated leak and the pressures behind the leak and within the chamber were measured. Application of the throughput balance, \(0 = C_l p_l - C_c p\), where the pressure directly behind the calibrated leak, \(p_l\), is approximated by the manifold pressure, \(p_m\), measured by the Baratron adjacent to the leak yields a practical determination of \(C_c\),

\[
C_c = \frac{C_l p_m}{p}.
\]  

(11)

The Baratron was positioned as close as possible to the calibrated leak with sufficient calculated conductance that \(p_m\) approximates \(p_l\) to 0.15%. The chamber pressure was measured using the Stabil-Ion Bayard-Alpert ion gauge. The conductance of an orifice style calibrated leak varies as \(1/\sqrt{m}\) and so with a N₂ calibration it is possible to calculate the leak rate for other gases under molecular flow conditions. \(^5\) Figure 5(a) experiments confirm that the conductance of the calibrated leak varies as \(C_l \propto \sqrt{1/m}\) for a number of gases of different masses. In these experiments the gas manifold leading up to the calibrated leak was filled with a test gas and the valve above the Baratron was closed before the valve separating the leak valve to the chamber was opened (see Fig. 1). The pressure \(p_m\) was monitored as a function of time as gas escaped from the trapped volume through the calibrated leak. The time constant for evacuation of the trapped volume \(V\) between the calibrated leak and valve above the Baratron is given by \(\tau = V/C_l\). The \(\sqrt{m}\) variation observed for \(\tau\) confirms that \(C_l\) varies as \(\sqrt{1/m}\). Figure 5(a) also shows simple exponential decays of the pressure \(p_m\) inside the trapped volume over the pressure range from 1 Torr to \(\sim 10^{-4}\) Torr, which indicates constant leak rates for the different gases. The 100 \(\mu\)m dia. calibrated leak should remain in molecular flow with a Knudsen number \(K_{nD} \geq 1\) which limits the highest \(p_m\) pressure in the Fig. 5(a) experiments to less than 0.15 Torr for the bulkiest gas, neopentane, which has the shortest mean free path. Once \(K_{nD}\) drops below one and transitional flow begins, the orifice flow is gradually enhanced. The transitional flow enhancement \(^5\) is calculated to reach about 30% at \(p_m = 1\) Torr for neopentane.

Figure 5(b) shows the chamber pumping speed for N₂ determined according to Eq. (11) as a function of the chamber pressure \(p\) measured using the Stabil-Ion Bayard-Alpert ion gauge. The falling off of \(C_c = C_l p_m / p\) at pressures below \(p \sim 8 \times 10^{-3}\) Torr and \(p_m \sim 1.7 \times 10^{-3}\) Torr is tentatively attributed to artificially enhanced \(p\) due to electron stimulated desorption (ESD) at the ion gauge. \(^6\) In Fig. 5(a) experiments, the simple exponential decay of the Baratron measured pressure \(p_m\) as N₂ exited the trapped volume through the calibrated leak indicates a constant leak rate and consistent pressure measurement even for \(p_m < 1.7 \times 10^{-3}\) Torr. The pumping speed of the turbomolecular pump is expected to be pressure invariant \(^6\) near \(10^{-3}\) Torr and so that leaves...
the ion gauge measurements of $p$ as the suspicous factor in the downturn of the calculated chamber pumping speed at the lowest pressures. Although the Stabil-Ion Bayard-Alpert ion gauge is designed for pressure metrology to within $\pm 6\%$, the gauge is likely sensitive to ESD effects at pressures in the neighborhood of $5 \times 10^{-9}$ Torr.$^{36}$ For some larger alkanes, downturns in the calculated pumping speeds were observed at pressures closer to $p \sim 10^{-8}$ Torr. Consequently, we restricted our pumping speed measurements to chamber pressures $p \geq 3 \times 10^{-8}$ Torr where ESD effects should be negligible and to manifold pressures $p_m \leq 10^{-1}$ Torr or pressures such that the calibrated leak was assuredly operating under transparent flow conditions. In this way, the average chamber pumping speed for $N_2$ determined from the data of Fig. 5 was 172 L/s.

1. Ion gauge relative sensitivity factors

Ion gauges are calibrated to read out accurate pressures for $N_2$. For other gases, the true pressure is given by the ion gauge readout pressure divided by the gas’s relative sensitivity factor, $R_g = \text{Sen}_g / \text{Sen}_{N_2}$, where $\text{Sen}_g$ and $\text{Sen}_{N_2}$ are the ion gauge sensitivities for the particular gas $g$ and $N_2$, respectively.$^{49,50}$ Ion gauge relative sensitivity factors for the different effusive beam gases were experimentally determined by comparing the Stabil-Ion Bayard-Alpert ion gauge pressure readings at 4 mA emission current with the absolute pressure readings of the chamber’s bakeable Baratron. Relative sensitivity factors were found to be $R_g = 1.6$, $2.6$, $3.7$, and $4.3$ for methane, ethane, propane, and isobutane, respectively, in close accord with literature values.$^{49,50}$ Relative sensitivity factors for the gases were measured over a range of pressures accessible to both the ion gauge and the bakeable Baratron, $5 \times 10^{-5}$ Torr $\leq p \leq 1 \times 10^{-3}$ Torr. Changing the ion gauge emission current from 4 to 1 mA was not observed to influence the relative sensitivity factors of the gases over the pressure regime investigated.$^{51}$

E. Background dissociative sticking coefficients, $S_{bkg}(T_g, T_s)$

The initial background sticking coefficient can be calculated for modest accumulations of $\theta_C$ as [cf., Eqs. (10) and (1)]

$$S_{bkg}(T_g, T_s) = \frac{\theta_C \sigma}{nF_{bkg} \tau} = \frac{\theta_C \sigma}{n \tau} \frac{\sqrt{2 \pi m k_B T_g}}{p}, \tag{12}$$

where the impinging background flux is $F_{bkg} = p / \sqrt{2 \pi m k_B T_g}$ and $\tau$ is the duration of the gas exposure. To avoid any possibility that hot filaments might crack alkanes in the gas phase and the alkyl fragments produced might eventually land on the sample surface, the chamber ion gauge and RGA were turned off when alkanes were dosed during dissociative sticking experiments. Typically, alkanes were dosed through the nondirectional calibrated leak (100 $\mu$m orifice) that was aimed at a chamber wall rather than the front surface of the sample. In some instances, the gas was introduced through the effusive doser (500 $\mu$m orifice) with the sample rotated 180° away such that the beam did not strike the front surface of the sample. In advance of dissociative sticking experiments, working curves for dosing were measured to relate the chamber pressure $p$ to the manifold pressure $p_m$ behind the calibrated leak or effusive beam doser when gas was introduced in to the chamber. In this way, the chamber pressure $p$ could be known during dosing in dissociative sticking experiments based on the $p_m$ measured by the manifold Baratron. Relatively high pressures, $5 \times 10^{-5}$ Torr $\leq p \leq 1$ Torr, could be measured directly during dosing using the bakeable Baratron.

In our experience, how the alkane chamber pressure $p$ was established during dosing had no discernable effect on $S_{bkg}(T_g, T_s)$ values calculated according to Eq. (12). Experiments in which the turbomolecular pump was valved off and a stagnant pressure of alkane was established in the chamber for a time gave the same result as when the turbomolecular pump was actively pumping the chamber and an alkane gas load was introduced to establish a steady-state dynamic pressure of alkane. More importantly, when the effusive beam doser was heated over the range from 300 to 700 K and the beam was directed away from the surface, methane $S_{bkg}(T_g, T_s)$ values did not vary with the initial temperature of the dosed molecules. This is in accordance with idea that molecules from a hot effusive beam doser that initially miss the sample surface typically suffer sufficient collisions with the chamber walls that they thermalize to the chamber temperature before they have another opportunity to strike the sample surface. Gas–surface energy transfer has been observed to increase with alkane size and complexity.$^{3,5}$ Consequently, collisional thermalization of higher alkanes to the chamber wall temperature should be even more efficient than that of methane.

F. Directed dissociative sticking coefficients, $S_d(T_g, T_s)$

The dissociative sticking coefficient along the direction of the surface normal $S(T_g, T_s; \theta = 0\degree) = S_d(T_g, T_s)$ is theoretically interesting and is the easiest angle-resolved $S(T_g, T_s; \theta$) to measure in effusive molecular beam experiments. During dosing, the effusive beam is aimed at the center of the sample surface, along the direction of the surface normal, such that the beam flux is highest for $S_d(T_g, T_s)$ measurements. Furthermore, Madix et al. supersonic molecular beam experiments$^{52}$ for light alkanes on Pt(111) established that the alkane dissociative sticking coefficients scale with the normal component of the translational energy of incident molecules, $E_n = E_v \cos^2(\theta)$, and the dissociative sticking increases with $E_n$. A consequence of this normal energy scaling is that $S_d(T_g, T_s) \geq S(T_g, T_s; \theta)$. Measurements of $S_d(T_g, T_s)$ made according to the formalism of Sec. II A and application of Eq. (1) are shown in Fig. 6. Our interest is to use the directed flux to extract dissociative sticking coefficients $S_d(T_g, T_s)$ as a function of both $T_g$ and $T_s$, despite the additional sticking from the background flux that has been thermalized to the chamber wall temperature. The background dissociative sticking coefficient $S_{bkg}(T_g, T_s)$ is measured in separate experiments with gas randomly impinging on the surface. During directed effusive beam experiments at the working distance of $d = 1$ cm separating the effusive doser and the sample surface, the ratio of the direct to background flux
is given by Eq. (8) which amounts to $R = 15.6$ at $\theta = 0^\circ$ for the light alkanes. For heated beam experiments with $T_g > T_s$, typically $S_n(T_g, T_s) > S_{bk, bkg}(T_g, T_s)$ because the dissociative chemisorption of light alkanes is activated [e.g., CH$_4$ in Fig. 7(a)]. Consequently, in alkane heated beam experiments, the fraction of the accumulated carbon coverage $\theta_C$ [used in Eq. (1)] that can be attributed to dissociative sticking from the thermalized background gas is typically much less than $1/R$.

To determine $S_n(T_g, T_s)$ from effusive beam experiments according to Eq. (1), it is important to know the ratio of the direct to background flux, $R = F_{dir}/F_{bkg}$, the background flux, $F_{bkg} = p/\sqrt{2 \pi m k_B T_c}$, the dosing time, $\tau$, and the accumulated carbon coverage $\theta_C(\theta = 0^\circ)$. The background flux is fixed by the chamber pressure $p$, which in turn can be related to the manifold pressure $p_m$ read by the Baratron. After establishing working curves $p(p_m)$ for the effusive beam doser operating at a particular $T_g$, $S_n(T_g, T_s)$ experiments were performed with the ion gauge turned off. For dissociative sticking coefficients $S \leq 0.1$, a negligible fraction of the effusive beam gas introduced into the chamber dissociatively sticks to the sample surface. The ratio of the direct to background flux, $R$, is adequately represented by Eq. (2) under our dosing conditions, because the surface integral term, representing the fraction of the effusive beam molecules that directly strike the surface and dissociatively chemisorb in

$$R_{Eq.(2)}/R_{Eq.(8)} \geq 1 - \frac{1}{W} \int_{\text{surface}} S(T_g, T_s; \theta) \frac{j(\theta) \cos^3(\theta)}{\pi d^2} dA$$

$$= 1 - \frac{1}{W} \int_0^{\theta_{\text{max}}} S(T_g, T_s; \theta) j(\theta) \sin(\theta) d\theta$$

Starting

FIG. 6. (Color online) Evolution of the carbon coverage buildup on Pt(111) at $T_s = 700$ K when dosed by an effusive beam at $T_g = 700$ K from a heated nozzle with a 0.0197 in. dia. orifice and 0.003 in. orifice wall thickness at a distance of 1 cm away from the surface. The exposure from background gas is typically much less than that from the directed effusive beam. The line passing through the origin was fitted to the direct component of the total C coverage for data with $\theta_C \geq 0.1$ ML. The line’s slope yields $S_{dir}$.

FIG. 7. (Color online) Alkane dissociative sticking coefficients on Pt(111) for the impinging gas temperatures indicated (Ref. 5). The solid points (expts) and lines (ME-MURT simulations) are for normally directed effusive molecular beams. The open points (expts) and dashed lines (ME-MURT simulations) are for ambient gas impingement. (a) Methane/Pt(111); (b) Propane/Pt(111) for which the $S_n(T)$ points from direct effusive beam experiments are additionally labeled by encirclement.
from Eq. (13), numeric integration finds that 36% of the effusive flux initially strikes the surface and \( R_{\text{Eq}(2)}/R_{\text{Eq}(8)} \) \( \geq 1 - S_d(T_g, T) \times 0.36 \). Again, \( R_{\text{Eq}(2)} \approx R_{\text{Eq}(8)} \) is a good approximation for \( S_d(T_g, T) \leq 0.1 \). If higher sticking coefficients are to be investigated using effusive beam methods, there will be increasing need to self-consistently solve the Eq. (10) carbon deposition kinetics to extract accurate dissociative sticking coefficients.

The ratio of the direct to background flux for methane during effusive beam dosing in our apparatus for \( \theta = 0^\circ \), appropriate to \( S_b(T_g, T) \) measurements, is \( R(\theta = 0^\circ) = 15.6 \), according to Eq. (2), with \( C_c = 210 \) L/s, \( W = 0.27 \), and \( d = 1 \) cm. This ratio stays fairly constant for the higher alkanes, because \( R \propto C_c / \sqrt{m} \) in Eq. (2) and the pumping speed of the turbomolecular pump,\(^{48}\) and hence \( C_c \), falls off with mass as roughly \( 1 / \sqrt{m} \). To confirm the analytic expressions given by Pauly\(^{32}\) for the nozzle transmission \( W \) and angular function \( j(\theta) \) a second effusive beam nozzle was recently made with a 0.003 in. end wall thickness and 0.0197 in. (0.50 mm) dia. orifice. The second nozzle geometry gives \( W = 0.87, j(\theta) \sim \cos^3(\theta) \), and \( R(\theta = 0^\circ) = 4.9 \). Values of \( S(T_g, T; \theta) \) for methane on Pt(111) measured with both effusive beam nozzles were identical to within experimental error.

Centering the sample surface underneath the effusive beam was be done by AES mapping of the carbon deposition profile after dosing the surface with a heated methane beam. The direct flux varies across the surface as \( F_{\text{dir}} \propto j(\theta) \cos^3(\theta) \) and light alkane \( S(T_g, T; \theta) \) are also peaked around the surface normal\(^{22}\) because of their normal energy scaling. Consequently, the carbon deposition profile due to direct dissociative sticking of an alkane should always be at least as sharp as \( \cos^3(\theta) \).

Figure 6 provides an example of effusive molecular beam measurements sufficient to determine the \( \text{CH}_4/\text{Pt}(111) \) dissociative sticking coefficient \( S_b(T_g = 700 \) K, \( T = 700 \) K) from the directed beam flux that strikes the surface and the resulting carbon accumulation. Although these data were taken with the second nozzle geometry with 0.003 in. orifice wall thickness and relatively modest R, the carbon deposition from dissociative sticking of the directed beam was overwhelming larger than that of the thermalized background gas load (i.e., \( \sim 160 \)-fold). A linear fit to all the direct \( C \) data yields a line passing through zero exposure at \( \theta_C = 0.004 \) ML with slope \( S_{\text{dir}} = S_b(T_g = 700 \) K, \( T = 700 \) K) \( = 4.9 \times 10^{-5} \). An exponential fit to these data, assuming \( \theta_C,_{\text{max}} = 2.7 \) ML, yields \( S_{\text{dir}} = 5.3 \times 10^{-5} \). Given that there was no unusual behavior observed at low coverages (e.g., enhanced sticking at defects), it was expedient to fit the alkane dissociative sticking data to a line passing through the origin for data with 0.1ML \( \leq \theta_C \leq 0.4 \) ML (i.e., coverages in the linear regime well above the Auger detection limit of \( \sim 0.01 \) ML). This last procedure provided the line shown in Fig. 6 and gave \( S_{\text{dir}} = 5.2 \times 10^{-5} \).

**IV. REPRESENTATIVE RESULTS: CH\(_4\) AND C\(_3\)H\(_8\) ON Pt(111)**

Figure 7 shows some representative effusive molecular beam measurements of dissociative sticking coefficients for methane and propane on Pt(111).\(^{5}\) A master equation-microcanonical unimolecular rate theory (ME-MURT) model\(^{20,22}\) sufficed to analyze the experimental dissociative sticking data and extract transition state and gas–surface energy transfer parameters. Statistical error bars for the experimental data were typically \( \pm 20\% \) based on two to seven replicate measurements for each dissociative sticking coefficient reported.

In Fig. 7(a), the lowest \( S_{\text{bkg}}(T_c = 300 \) K, \( T) \) determined for ambient gas dosing of methane on Pt(111) was \( S_{\text{bkg}}(T_c = 300 \) K, \( T = 400 \) K) \( = 1.3 \times 10^{-7} \). The ME-MURT theoretical prediction for \( S_{\text{bkg}}(T_c = 300 \) K, \( T = 400 \) K) of \( 5.5 \times 10^{-9} \) is considerably lower as is an Arrhenius extrapolation based on the high \( T_c \) measurements of \( S_{\text{bkg}}(T_c = 300 \) K, \( T_c \)). Although RGA analysis did not discern C containing contaminants in the research grade (99.999\%) methane used in the effusive beam experiments, it seems likely that impurities in the gas are beginning to discernibly augment the \( S_{\text{bkg}}(T_c = 300 \) K, \( T_c \)) values which are less than \( \sim 10^{-6} \). There are means described in the literature for further purification of methane\(^{9,11}\) that have allowed thermal bulb dissociative sticking coefficient measurements to be measured down to \( S(T) \sim 10^{-9} \). We speculate that similarly small dissociative sticking coefficients could be measured with the effusive beam apparatus with enhanced purification of the dosing gases.

The \( S_b(T_c, T) \) with \( T_c = T = T \) are quasithermal \( S_b(T) \) dissociative sticking coefficients which are a close approximation and formal upper bound to the thermal dissociative sticking coefficients \( S(T) \) as can be seen from the ME-MURT simulations of Fig. 7. The normal energy scaling of the dissociative sticking coefficients for the light alkanes on Pt(111) (Ref. 52) requires that \( S_b(T) > S(T) \). The difference between \( S_b(T) \) and \( S(T) \) decreases as the alkane complexity increases because (i) the relative role of translational energy in surmounting the activation barrier for reaction diminishes as the number of molecular vibrational modes increases and (ii) the gas–surface energy transfer efficiency increases with alkane complexity.\(^{4,5}\) The energy distributions of the gas–surface collisions incurred during effusive molecular beam measurements of \( S_b(T) \) are very similar to those incurred in high pressure thermal catalysis, and \( S_b(T) \) should provide a sufficiently accurate approximation to \( S(T) \) for most purposes. No special model is required to analyze the \( S_b(T) \) data and Arrhenius parameters can be easily extracted. With more extensive measurement of \( S(T; \theta) \), it is possible to directly calculate \( S(T) \) by averaging \( S(T; \theta) \) over the angular flux distribution of an ambient gas impinging on a surface at thermal equilibrium,

\[
S(T) = \int \frac{\cos(\theta)}{\pi} S(T; \theta) d\Omega. \tag{15}
\]

In summary, the effusive molecular beam technique provides a convenient means to measure alkane quasithermal \( S_b(T) \) that closely approximate the thermal \( S(T) \) appropriate to high pressure catalysis, to measure \( S(T; \theta) \) sufficient to directly calculate \( S(T) \), and to also measure nonequilibrium \( S(T_c, T_c; \theta) \) that can provide extended information about the reactive transition state, reaction scaling laws, and gas–surface energy transfer.\(^{4,5}\)
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