Quantum state resolved molecular beam reflectivity measurements: CH_4 dissociation on Pt(111)

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The King and Wells molecular beam reflectivity method has been used for a quantum state resolved study of the dissociative chemisorption of CH_4 on Pt(111) at several surface temperatures. Initial sticking coefficients S_0 were measured for incident CH_4 prepared both with a single quantum of ν_3 antisymmetric stretch vibration by infrared laser pumping, and without laser excitation. Vibrational excitation of the ν_3 mode is observed to be less efficient than incident translational energy in promoting the dissociation reaction with a vibrational efficacy η^{ν_3} = 0.65. The initial state resolved sticking coefficient $S_0^{\nu_3}$ was found to be independent of the surface temperature over the 50kJ/mol to 120kJ/mol translational energy range studied here. However, the surface temperature dependence of the King and Wells data reveals the migration of adsorbed carbon formed by CH_4 dissociation on the Pt(111) surface leading to the growth of carbon particles.

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I. INTRODUCTION

Quantum state resolved sticking coefficient measurements for the dissociative chemisorption of methane on several transition metal surfaces have permitted highly detailed studies of this important gas/surface reaction[1-4]. Observations include mode specificity[5-9], bond selectivity[10-12], and steric effects[13,14] all of which demonstrate the non-statistical reaction dynamics of methane chemisorption. First principles theory combined with classical and quantum dynamics simulations are able to reproduce at least qualitatively many of the experimental observations[15-22]. Several techniques have been developed to measure sticking coefficients with quantum state resolution, for example by detecting the surface bound products using Auger electron spectroscopy[5,6,23,24], reflection absorption infrared spectroscopy[7,11,15,21], or titration of the adsorbates to make molecules that desorb and can be detected in the gas phase mass spectrometrically[9,12,22,25]. Whilst these have proved to be powerful techniques for determining quantum state resolved sticking coefficients, they share a common disadvantage in that calibrations are necessary to quantify the adsorbate coverage and number of molecules incident on the surface, both of which need to be known to accurately determine the sticking coefficient.

In their study of nitrogen on tungsten[26], King and Wells (K&W) introduced an alternative method for determining the sticking coefficient which is self-calibrated, by comparing the partial pressures obtained by scattering the molecular beam from an inert surface and the reactive surface of interest. Madix et al. used this technique extensively for studying the physisorption of CH_4[27,28] and other small alkanes on Pt(111)[29-32] and Pd(111) surfaces[33,34], as well as to obtain sticking coefficients for the dissociative chemisorption of methane on Pt(111)[35]. Other groups have also applied it to study the dissociative chemisorption of CH_4 on Pt(110)-(1x2)[36], Ru(0001)[37] and Ni(100)[38] as well as studying chemisorption in other systems, see for example references 39-45.

More recently, the K&W technique has been used for quantum state resolved sticking coefficient measurements to study sticking of molecules prepared in an initial rovibrational quantum state. No difference between laser-on and laser-off sticking was detected for the physisorption of CH_4 on Pt(111)[28] or for D_2O on ice[46] which demonstrated that the trapping probability into a physisorbed state is insensitive to vibrational excitation of the incident molecule. Utz et al. have used K&W to investigate the dissociative chemisorption of methane on Ni(111) with quantum state resolution[16]. Here we report the first application of the K&W technique to the dissociative chemisorption of CH_4 on Pt(111), a system where vibrational excitation enhances the reactivity less strongly than for CH_4 on Ni(111)[15,47].

The remainder of the paper is organized as follows. In Section II, we give a general overview of the experimental setup and methods used, before focussing on the application of the K&W technique to obtaining quantum state resolved sticking coefficients. We then present and discuss the results before the final section summarizes the key points.

II. EXPERIMENTAL METHODS

The experimental apparatus has been described in detail previously[48] and only the most relevant features will be presented here. The setup consists of a differentially pumped molecular beam source attached to an ultrahigh vacuum (UHV) surface science chamber, with a base pressure of $5x10^{-11}$ mbar. The first and second differential pumping stage can be isolated by a separation valve which when closed prevents the molecular beam from entering the UHV chamber. An inert beam flag made from Teflon is attached to a computer controlled stepper motor located at the entrance of the UHV chamber which, when shut, stops the molecular beam hitting the surface. For a diagram of the molecular beam path, the reader is directed to Figure 2 in reference 48.

The Pt(111) single crystal sample is mounted between two tungsten wires which allow resistive heating of the surface to above 1200K, and cooling of the surface to 80K using liquid nitrogen. For the measurements presented here, the surface was held at temperatures of 500K, 650K and 800K. Between each experiment the Pt(111) surface was cleaned using Ar^+ sputtering and annealing cycles. The cleanliness was confirmed using Auger electron spectroscopy (AES), with the carbon level on the surface before the measurements below the 1% detection limit.

The molecular beam is produced by expanding a 1% CH_4 in H_2 mix through a nozzle with a 50µm diameter hole, with backing pressures between 1.4bar and 2bar. The nozzle can be heated resistively to temperatures above 800K, with temperatures between 298K and 700K used in the experiments presented here. The velocity of the molecular beam was measured by time of flight (TOF) methods, using a fast chopper wheel in conjunction with an on-axis quadrupole mass spectrometer (QMS).

For the laser-on measurements, a fraction of the incident CH_4 molecules was prepared in a single rovibrationally excited quantum state (ν_3=1, J=2) with one quantum of ν_3 antisymmetric stretch vibration using a continuous wave optical parametric oscillator (OPO). The OPO frequency was stabilized to the R(1) $\nu_3 \leftarrow v$=0 transition at 3038.490 cm^{-1} by locking to a Lamb-dip created in an absorption cell containing approximately 30μbar of CH_4. We use state preparation by rapid adiabatic passage (RAP) to maximize the excited fraction (f_{exc}) of the incident molecular beam. RAP uses controlled frequency tuning of the excitation field to achieve complete population transfer from an initial to a final quantum state[49]. A room temperature pyroelectric detector was used to determine the f_{exc} of CH_4 in the molecular beam prepared by the laser.

III. STATE RESOLVED KING AND WELLS MEASUREMENTS

The initial sticking coefficients for the dissociative chemisorption of CH_4 on Pt(111) averaged over all the quantum states populated in the molecular beam were obtained using K&W measurements[26] using an off-axis QMS monitoring the methane parent mass at 16 amu. Data from a typical measurement is presented in the left hand panel of Figure 1 for an incident translational energy (E_{trans}) of 105kJ/mol and surface temperature (T_S) of 800K. The time axis has been shifted so that t=0s corresponds to the time when the K&W flag is moved and the molecular beam hits the clean Pt(111) surface. At t =-60s the separation valve is opened and the molecular beam containing 1% CH_4 in H_2 enters the UHV chamber and scatters off the inert beam flag. The partial pressure detected by the QMS signal at 16 amu corresponds to the total flux of molecules scattered from the flag. The resulting drop in the QMS signal at t=0s is due to the molecules that don't scatter but dissociate on the clean Pt(111) surface. This pressure drop decreases with time because the initially clean Pt(111) gets passivated by the build-up of a layer of dissociation products. After 8s, the beam flag is closed and the QMS signal corresponds again to CH_4 scattering from the flag. Finally, the molecular beam is switched off at t =60s by closing the separation valve. The time dependence of the K&W trace $S(t)$ can be calculated from the QMS data using

$$S(t) = \frac{\Delta P(t)}{P} \qquad (1)$$

where P is the partial pressure rise when the separation valve is opened and $\Delta P(t)$ the decrease in partial pressure at time t after the flag is opened. These quantities are shown as red arrows in the left hand panel of Figure 1.

The right hand panel of Figure 1 presents typical examples of $S(t)$ obtained for laser-off (black) and laser-on (red) measurements, with an incident E_{trans}=105kJ/mol, with the laser-off trace at T_S=800K corresponding to the data presented in the left hand panel of the figure. A clear difference is seen between the laser-on and laser-off reactivities, showing the promotional effect of vibrational energy (E_{vib}) on the dissociative sticking coefficient. As will be discussed in more detail in the following section, $S(t)$ is governed by two different processes. For this reason the laser-on ($S_0^{\mathrm{laser-on}}$) and laser-off ($S_0^{\mathrm{laser-off}}$) sticking coefficients at t=0s were obtained by fitting the time dependence of the K&W trace using

$$S(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} \tag{2}$$

where $A_1 + A_2 = S_0$ and k_i account for the rate the sticking coefficient decreases. The fits to the laser-off and laser-on data obtained using Equation (2) are shown in the right hand panel of Figure 1 as dashed green and blue lines respectively.

The value of $S_0^{\mathrm{laser-on}}$ in these measurements does not correspond to the quantum state resolved sticking coefficient for ν_3, $S_0^{\nu_3}$, but rather is an averaged reactivity over all the quantum states populated in the molecular beam when the preparation laser is on. Similarly, $S_0^{\mathrm{laser-off}}$ is the averaged reactivity over all quantum states populated by heating of the expansion nozzle. While the rotational degrees of freedom are strongly cooled in the supersonic expansion there is very limited cooling of the thermally excited vibrations so that the vibrational temperature of the molecular beam is usually assumed to be equal to the nozzle temperature. For high nozzle temperatures $S_0^{\mathrm{laser-off}}$ cannot be neglected in comparison with $S_0^{\mathrm{laser-on}}$. Since the preparation laser transfers population only from the *v*=0 state, the thermally excited population is unchanged by the laser excitation and drops out of the difference between the two averages. As long as f_{exc} prepared by the laser is known, the state resolved sticking coefficient $S_0^{\nu_3}$ can be calculated from the following expression[1,8]

$$S_0^{\nu_3} = \frac{S_0^{\mathrm{laser-on}} - S_0^{\mathrm{laser-off}}}{f_{\mathrm{exc}}} + S_0^{v=0} \tag{3}$$

where $S_0^{v=0}$, the sticking coefficient for molecules in the vibrational ground state, *v*=0 needs to be known to calculate the state resolved reactivity $S_0^{\nu_3}$. At low incident E_{trans}, the contribution from $S_0^{v=0}$ is usually neglected in Equation (3)[8,11,12,21]. However, if E_{trans} is high, close to the minimum barrier for dissociation, setting $S_0^{v=0} = S_0^{\text{laser-off}}$ may be a better approximation and this was applied when calculating $S_0^{\nu_3}$ using Equation (3)[16,24]. The value of $S_0^{\nu_3}$ obtained using this approximation will be an upper limit.

IV. RESULTS AND DISCUSSION

The initial sticking coefficients measured for the dissociative chemisorption of CH_4 on Pt(111) are presented in Figure 2, for T_S=500K (black), 650K (red) and 800K (blue) for CH_4 prepared in ν_3 (open squares) and without laser excitation (filled squares). At these surface temperatures, any hydrogen in the molecular beam that dissociates rapidly recombinatively desorbs[50-53], not affecting the measurement of $S(t)$. Within experimental error, the values of $S_0^{\nu_3}$ obtained are independent of the temperature of the surface. For the laser-off measurements, the sticking coefficient for T_S=500K is lower for E_{trans} less than 90kJ/mol, whereas increasing T_S at higher energies does not change $S_0^{\text{laser-off}}$ significantly. This is consistent with previous experiments performed by Utz *et al.* for the dissociative chemisorption of CH_4 on Ni(111)[22,25], where it was found that $S_0^{\nu_3}$ increased more as T_S was increased when the total energy (E_{trans} + E_{vib}) was lower than the barrier height, and $S_0^{\nu_3}$ changed less when the total energy was greater than the barrier height.

To quantify the extent to which adding a single quantum of ν_3 promotes the dissociation of CH_4, the dependence of S_0 on E_{trans} was fit using an S-shape reactivity curve[1,54]

$$S_0(\mathrm{E_{trans}}) = \frac{A}{2}\left[1 + \mathrm{erf}\left(\frac{\mathrm{E_{trans}} - \mathrm{E_0}}{W}\right)\right] \tag{4}$$

where A is the asymptote of the fit, $\mathrm{E_0}$ is the average activation barrier height for the dissociative chemisorption, and W is the width of the distribution of barrier heights. The fits to the laser-off (solid line) and ν_3 (dashed line) data obtained using Equation (4) with A=1 and W=72.5kJ/mol are shown in Figure 2. Whilst calculations have shown that W changes with surface temperature[55,56], the average value obtained from fitting the data when W was allowed to vary was used so that vibrational efficacies (η^{ν_3}) could be determined using[54]

$$\eta^{\nu_3} = \frac{\mathrm{E_0^{laser-off}} - \mathrm{E_0^{\nu_3}}}{\mathrm{E_{vib}}} \tag{5}$$

For the data presented here, η^{ν_3}=0.65±0.03 at all T_S. This is also in good agreement with η^{ν_3}=0.7 reported previously for T_S=150K[21]. These results suggest that η^{ν_3} does not depend strongly on T_S for the dissociative chemisorption of CH_4 on Pt(111).

Whilst η^{ν_3} and S_0 obtained here are independent of T_S, $S(t)$ strongly depends on T_S. Figure 3 shows the K&W traces obtained for T_S=500K (black), 650K (red) and 800K (blue) at E_{trans}=120kJ/mol without laser excitation. For all T_S, the sticking coefficient is observed to be highest at t=0s, corresponding to when the CH_4 collides and dissociates on the clean Pt(111) surface. For the next 2s, $S(t)$ decreases at a similar rate as the adsorbates (carbon atoms) block vacant sites on the surface. The coverage of adsorbed carbon on the surface can be determined by integrating the K&W trace over the dose of incident molecules. As the flux of the molecular beam is the same for each measurement, the carbon coverage on the surface at each T_S up to t=2s will be the same, and corresponds to approximately 4% of a monolayer (ML). However, $S(t > 2s)$ is significantly different, with the sticking coefficient decreasing more slowly at T_S=800K than at T_S=500K. As is suggested from the shape of the traces in Figure 3, and apparent from the trace in the right hand panel of Figure 4, the coverage of carbon on the surface can be greater than 1ML, i.e. there can be more than one carbon atom per platinum atom. At these surface temperatures, scanning tunnelling microscopy measurements have shown that the carbon migrates on the surface to form carbon particles[57], leading to graphene formation at surface temperatures higher than 800K[57,58] (carbon migration into the bulk has only been observed at T_S greater than 1150K[59]). This is further supported by high resolution electron energy loss spectroscopy measurements which show only evidence of larger carbon clusters when adsorbed carbon atoms are rehydrogenated after annealing to T_S greater than 500K[60]. In the K&W measurements presented here, the molecular beam footprint is a similar size to the surface, so there is not a significant fraction of the surface available for the carbon to migrate into. Additionally, AES measurements show that the carbon remains localized in the area that the molecular beam hits the surface on the timescale of the experiments. This suggests that the carbon particles that are formed have a height of more than one carbon atom.

The effect of the carbon migration and formation of carbon particles is to create vacant sites on the Pt(111) surface, where the incident CH_4 in the molecular beam can continue to dissociate. The rate of the growth of these particles, through either carbon atom migration or particle migration across the surface, increases with T_S, freeing up vacant sites more quickly at higher T_S causing $S(t)$ to drop more slowly at T_S=800K than at T_S=500K. As this process is not included in the Langmuir model which is usually used to describe the dissociative chemisorption of CH_4 on transition metal surfaces[21,25], the model could not be used to fit the data presented here. As the shape of $S(t)$ is determined by two different processes, the fast, initial dissociation of CH_4 and slower growth of carbon particles on the surface, the data were fit using the sum of two exponentials, as given in Equation (2).

An alternative mechanism for creating vacant sites on the surface would be through recombination of the surface bound carbon with molecules in the incident molecular beam. Any recombination leading to the desorption of products with a mass different from 16 amu would be detected as sticking via the partial pressure drop in the methane K&W experiment, but would lead to a decrease in carbon coverage and to the creation of vacant sites. One possibility is the recombination of surface bound carbon with oxygen contaminant if present in the incident molecular beam to produce CO. During the measurements, we therefore also monitored the QMS signal at mass 28 but failed to detect any evidence for this recombinative desorption, suggesting this is not responsible for the formation of vacant sites. The formation of carbon particles on the surface is therefore the most likely explanation for the shape of the K&W traces that is observed.

To further explore the carbon migration, we performed measurements at T_S=800K and E_{trans}=105kJ/mol, where we repeatedly opened and shut the K&W beam flag. The resulting K&W trace is shown in the left hand panel of Figure 4. At t=0s, the flag was opened for the first time, and the first 15s of $S(t)$ shows the same double exponential decay as in Figure 3. After 15s, the flag was shut and opened again at t=30s. Each time the K&W signal shows the same trend, with an initial fast decrease in $S(t)$ due to CH_4 dissociation products passivating the surface followed by a slower drop cause by carbon particle growth at longer times. The fact that $S(t = 30s) > S(t = 15s)$ indicates that carbon migration and particle growth must have continued on the surface whilst the flag was shut in order to increase the number of vacant sites on the surface leading to an increase $S(t)$ when the flag is opened again. Figure 4 shows that this can be repeated several times, with a double exponential decay observed each time the flag is opened. It follows that $S(t)$ in these measurements cannot be converted directly to a coverage dependent sticking coefficient as the carbon coverage does not uniquely define the number of vacant sites on the surface. For comparison, the right hand panel of Figure 4 shows the K&W trace recorded under the same conditions without opening and shutting the flag. Here, $S(t)$ is limited by carbon particle growth at longer times and no increase in sticking coefficient is observed.

V. SUMMARY

We have measured laser-off and rovibrationally quantum state resolved (ν_3=1, J=2) sticking coefficients for the dissociative chemisorption of CH_4 on Pt(111) at surface temperatures of 500K, 650K and 800K using the K&W beam reflectivity method. Over the incident translational energy range of 50kJ/mol to 120kJ/mol we find that $S_0^{\nu_3}$ is independent of the surface temperature, and that $S_0^{\mathrm{laser-off}}$ has a weak dependence on surface temperature at incident energies of less than 90kJ/mol. The vibrational efficacy η^{ν_3} was determined to be 0.65±0.03 at the three surface temperatures considered here.

The King and Wells data show a surface temperature dependence indicating that for $T_s > 500$ K the chemisorbed carbon atoms formed by CH_4 dissociation on Pt(111) are mobile and diffuse to form carbon particles. This T_s dependent process continuously creates free sites for methane dissociation preventing the passivation of the Pt(111) surface by the dissociation products.

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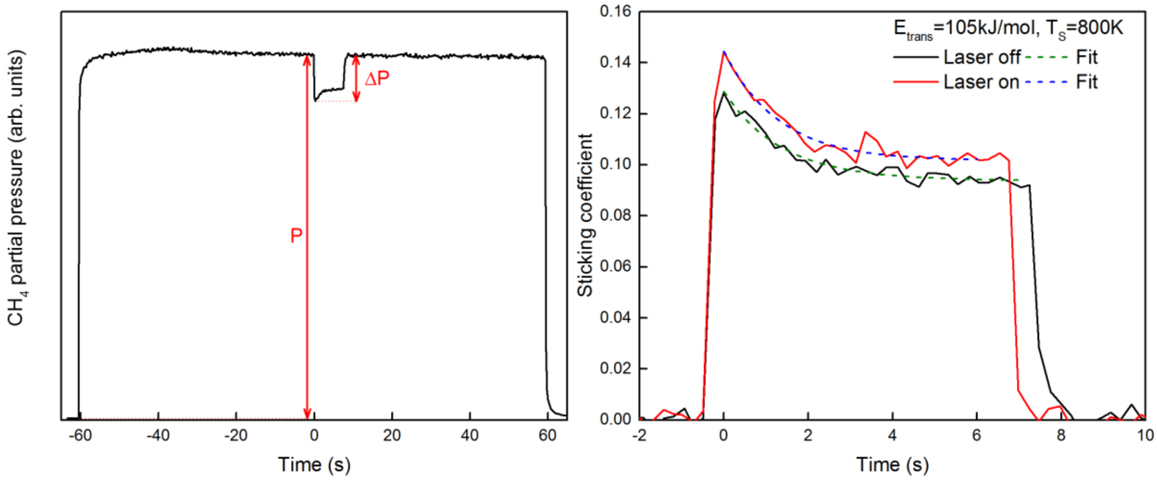

FIG 1: Left panel. K&W QMS signal for the dissociative chemisorption of CH$_4$ on Pt(111) at a surface temperature of 800K and translational energy of 105kJ/mol without laser excitation. The time axis has been shifted so that t =0s corresponds to the time when the inert beam flag was opened and the molecular beam hit the surface. Right panel. Time dependence of the K&W trace with (red) and without (black) laser excitation for the same conditions. The dashed blue and green lines correspond to the fits to the laser-on and laser-off data respectively, obtained using Equation (2).

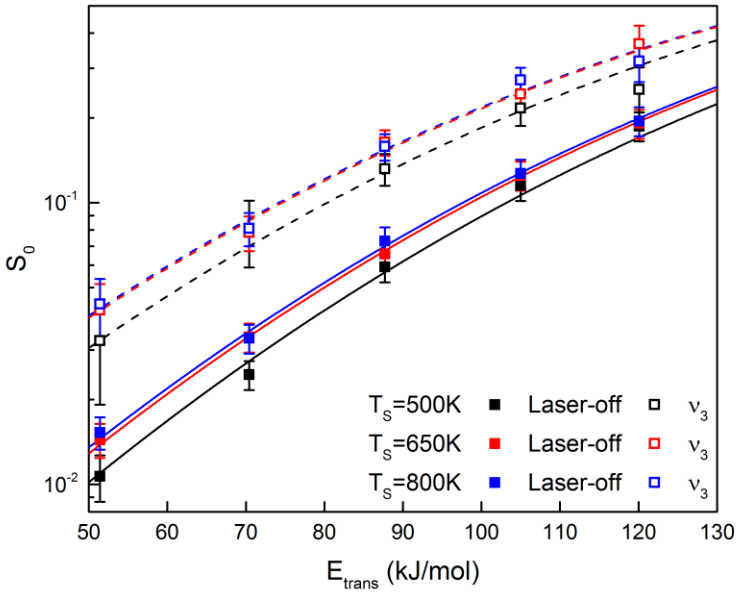

FIG 2: The initial sticking coefficients measured for the dissociative chemisorption of CH$_4$ on Pt(111) without laser excitation (solid squares), and for molecules excited with a single quantum of antisymmetric stretch (open squares) at surface temperatures of 500K (black), 650K (red) and 800K (blue). The solid and dashed lines are S-shape curve fits to the laser-off and state resolved ν_3 data respectively, obtained using Equation (4). The error bars represent 68% confidence limits.

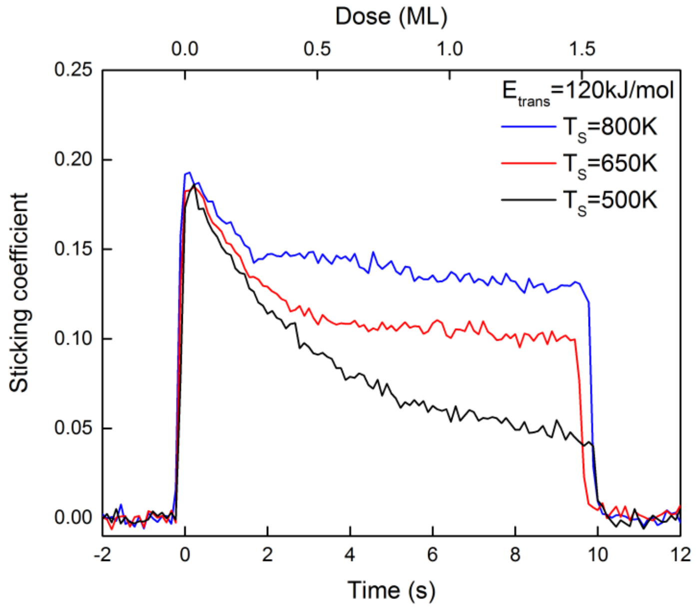

FIG 3: Time dependence of the K&W trace for the dissociative chemisorption of CH_4 on Pt(111) without laser excitation at a surface temperature of 500K (black), 650K (red) and 800K (blue) for a translational energy of 120kJ/mol.

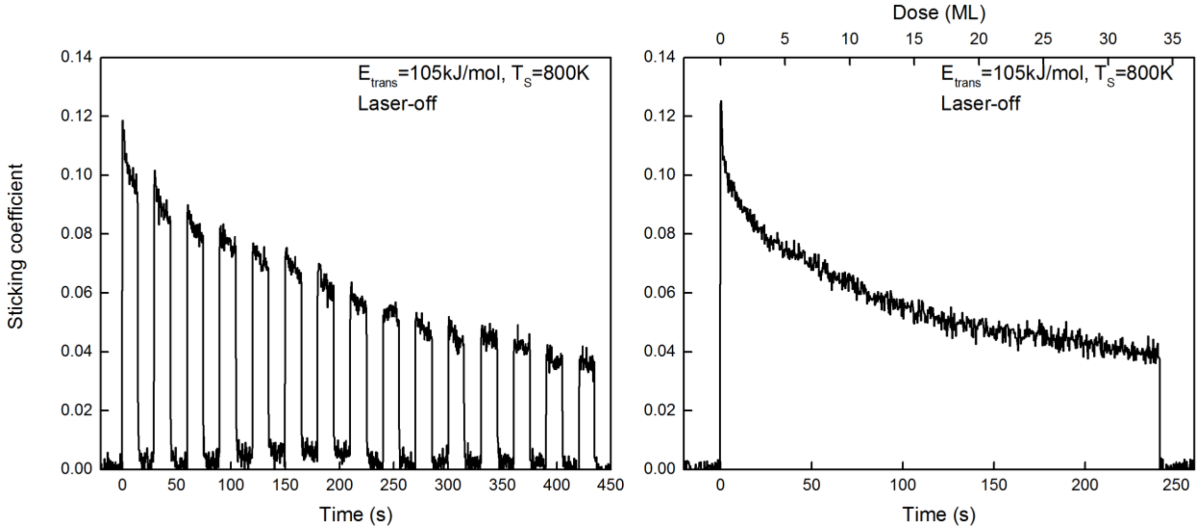

FIG 4: Left panel. Time dependence of the K&W trace for the dissociative chemisorption of CH_4 on Pt(111) without laser excitation for a translational energy of 105kJ/mol at a surface temperature of 800K. The K&W beam flag was open and shut alternately every 15s. Right. Time dependence of the K&W trace under the same conditions, but with the K&W beam flag open continuously.

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