# The Negligible Role of C−H Stretch Excitation in the Physisorption of CH₄ on Pt(111)

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ABSTRACT: We report a molecular beam study of the effect of vibrational excitation on the physisorption of methane on a Pt(111) surface. Our experiments use a continuous molecular beam of CH₄, prepared in its antisymmetric C−H stretch mode ν_3 by infrared laser pumping via rapid adiabatic passage. Physisorbed CH₄(ads) is detected on a Pt(111) surface by reflection absorption infrared spectroscopy. At a surface temperature of 77 K, the desorption lifetime of CH₄(ads) is observed to be 0.4 ± 0.2 s. Trapping probabilities for the incident CH₄ are measured by the King and Wells beam reflectivity method with and without vibrational excitation. Vibrational excitation of the incident CH₄ with one quantum of ν_3 vibration does not produce a measurable effect (less than 0.2% change) on the trapping probability, in sharp contrast to the dissociative chemisorption process. The effect of resonant vibrational excitation of physisorbed CH₄(ads) on its dissociation rate was also investigated.
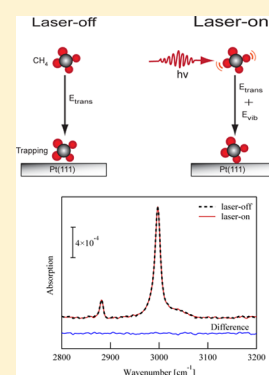
INTRODUCTION

The trapping of a gas-phase molecule into a weakly bound physisorbed state on a solid surface plays a central role in condensation processes as well as the initial step of chemisorption reactions via a precursor-mediated mechanism. It is well-established that the trapping probability decreases with increasing incident translational energy because any excess energy beyond the physisorption well depth needs to be transferred to surface degrees of freedom during the surface impact for trapping to occur. In the simplest case, the initial trapping probability depends only on the incident translational energy normal to the surface (normal energy scaling with $E_t \cdot \cos^2\theta$) as described by the Baule model.[1] Madix et al.[2,3] have measured trapping probabilities for Ar and CH₄ on Pt(111) and concluded that in these two systems normal energy scaling is obeyed.

The role of vibrational excitation of the incident molecule on the physisorption (trapping) probability is not yet well-understood, and experimental results reported to date in the literature differ for different molecules and surfaces. Sibener et al.[4] studied the condensation coefficients of molecular beams of CCl₄ and SF₆ on their respective condensed phases at cryogenic temperatures. They observed a (small) decrease in the trapping probability with increasing rotational and vibrational excitation at low incident translational energy consistent with simple models of the trapping process.[5] On the other hand, Wodtke et al.[6] studied the trapping of the diatomic NO in $v = 0$ and 2 on a Au(111) surface at 300 and 480 K. Using quantum state resolved detection of surface scattered NO by resonant multiphoton ionization they concluded that there was no measurable difference between the trapping probabilities for NO($v = 0$) and NO($v = 2$) for incident kinetic energies in the

range of 0.1−0.75 eV. The fact that trapping was found to be insensitive to NO vibrational states was interpreted as being due to weak mechanical coupling between the high-frequency NO stretch and the low-frequency lattice vibrations of the Au(111) crystal. Bisson et al.[7] studied the chemisorption of SiH₄ on a Si(100) surface and found that vibrational excitation of the incident SiH₄ increased the dissociation probability both in the direct and the precursor-mediated pathway, which implies that trapping into the precursor state is not significantly reduced by SiH₄($v = 2$) excitation. Hundt et al.[8] studied the effect of vibrational excitation on the sticking of water on ice and observed no detectable difference in the trapping probability between water molecules without vibrational excitation and those with one quantum of antisymmetric stretch excitation.

We have previously combined infrared laser pumping in a molecular beam for reactant preparation with surface analysis techniques for product detection to perform quantum state resolved reactivity studies of methane dissociation on Ni and Pt surfaces.[9] Here, we report the application of the same methods to study the effect of vibrational excitation in the physisorption of CH₄ on a Pt(111) surface both for vibrational excitation of the incident CH₄ and the physisorbed CH₄(ads). The result reveals that the role of vibrational energy in the physisorption process is substantially different from that in the dissociative chemisorption process.
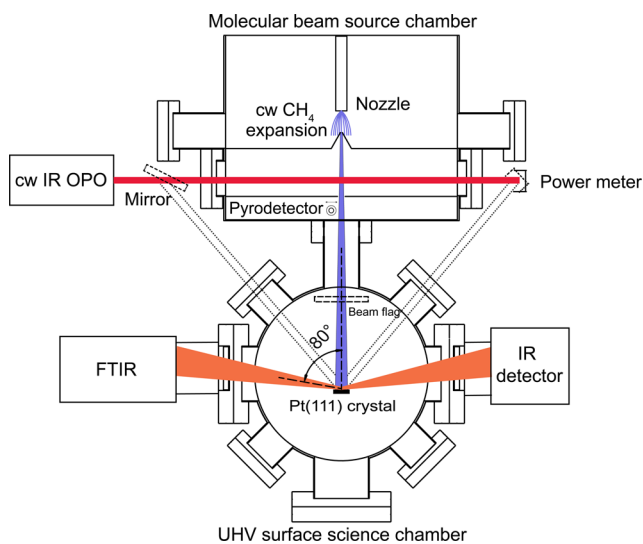
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■ EXPERIMENTAL SECTION

The experimental setup (Figure 1) is described in detail in a separate publication.[10] Briefly, we use a triply differentially

Figure 1. Schematic of the gas−surface experimental setup combining IR pumping of incident gas-phase reactants or adsorbed surface-bound species (dashed lines) with in situ RAIRS detection of adsorption products.

pumped molecular beam source for state-specific infrared laser preparation of methane molecules incident on a single crystal surface in an ultrahigh vacuum (UHV) surface science chamber to measure state-resolved sticking coefficients. Adsorbed species produced by the incident molecular beam can be detected online by a Fourier transform infrared spectrometer (FTIR, Bruker Vertex V70) using reflection absorption infrared spectroscopy (RAIRS). Surface-scattered species are detected by a quadrupole mass spectrometer.

In the experiment described here, a continuous molecular beam of methane (CH_4, 99.9995%), generated by a 30 μm diameter pinhole nozzle, collided with a single crystal surface Pt (111) at normal incidence angle with an average translational energy of 9 kJ/mol.

A tunable, single-mode, continuous-wave optical parametric oscillator (cw-OPO, Lockheed Martin Acculight Argos 2400-

SF) was used to excite either the incident CH_4 molecules in the molecular beam before surface impact or the physisorbed CH_4 molecules on the Pt(111) surface. For rovibrational state-specific excitation of the gas-phase CH_4 reactants, we locked the OPO idler frequency to a Dopper-free Lamb-dip (1 MHz line width)[11] detected via IR absorption in a room-temperature gas cell filled with about 50 μbar of methane. Suitable focusing of the OPO IR beam (typically 1 W single mode) onto the molecular beam leads to complete population transfer between the initial and final rovibrational states connected by the IR radiation via rapid adiabatic passage.[12] A room-temperature pyroelectric detector was used to detect the vibrationally excited CH_4 and to characterize the excited fraction in the molecular beam. For the vibrational excitation of the adsorbed CH_4 molecules on the Pt(111) surface, we aligned the OPO beam at 45° incidence onto the Pt(111) surface and tuned the OPO idler frequency to the band center of RAIRS absorption lines for the physisorbed CH_4.

For sticking coefficient measurements by the molecular beam reflectivity method of King and Wells,[13] a mica beam flag (10 × 10 mm^2) is used to block/unblock the molecular beam in the UHV chamber about 50 mm from the Pt(111) surface.

A Pt single crystal (10 mm in diameter, 2 mm thick) cut within 0.1° of the (111) direction was obtained from Surface Preparation Laboratories, Leiden. The Pt(111) surface was cleaned by sputter−anneal cycles, typically 10−15 min Ar$^+$ sputtering followed by 2 min annealing at T_s = 1200 K under a vacuum better than 5 × 10^{-10} mbar, until no contamination (carbon, oxygen, etc.) could be detected by Auger electron spectroscopy. The Pt(111) surface was mounted between 0.35 mm diameter tungsten wires that are clamped at either end to a pair copper cold fingers in contact with a liquid nitrogen reservoir.[14] Heating of the Pt(111) surface was accomplished by passing up to 25 A of current through the W wires using a regulated dc current supply connected to a PID temperature controller. Cooling was done via thermal contact through the W wires with the liquid nitrogen reservoir. Without heating the surface temperature dropped from 300 K to a final equilibrium temperature of 87 K in 10 min. Sample temperatures as low as 77 K could be achieved by pumping on the liquid N_2 reservoir or by bubbling Helium gas through the liquid N_2 for cooling by Helium transpiration.[15] The surface temperature was measured by a Chromel−Alumel (K-type) thermocouple inserted into a Ø 0.5 mm hole in the side of the sample.
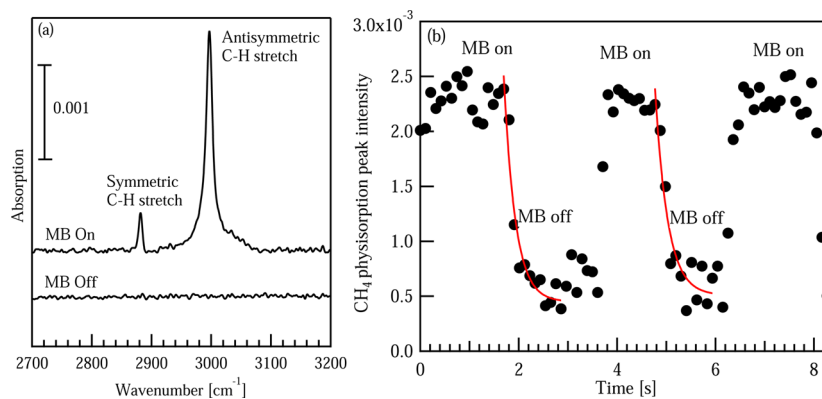
Figure 2. (a) RAIRS detection of physisorbed methane, CH_4(ads), during exposure of the Pt(111) surface, T_s = 77 K, to a molecular beam of CH_4 with incident translational energy E_{trans} = 9 kJ/mol. (b) Variation of RAIRS CH_4(ads) peak intensity of CH_4 (antisymmetric C−H stretch) when the molecular beam was switched on/off in 2 s intervals. Fitting an exponential decay to the data points indicates a desorption time of 0.25 ± 0.07 s.

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■ RESULTS

Figure 2a shows a RAIRS spectrum recorded during exposure of the Pt(111) surface at T_s = 77 K to a molecular beam of CH_4 (E_{trans} = 9 kJ/mol; $\langle E_{vib} \rangle$ = 0.1 kJ/mol; incident CH_4 flux, 0.8 ML/s). We observe absorption bands at 2997 and 2882 cm^{-1} corresponding to the antisymmetric (ν_3) and symmetric (ν_1) C−H stretch normal modes of physisorbed CH_4,[16] respectively, which are red-shifted relative to the gas phase frequencies of CH_4 (ν_3 = 3019 cm^{-1} and ν_1 = 2916 cm^{-1}). The symmetric C−H stretch mode ν_1, which is infrared-inactive for CH_4 in the gas phase, is observed in the RAIRS spectrum because of the reduced symmetry of the adsorbed CH_4. The line shape of the absorption peak due to the ν_3 fundamental of CH_4(ads) is Lorenzian with a full width half-maximum width of 11.4 cm^{-1}. This width includes contributions due to vibrational energy relaxation, vibrational dephasing (due to substrate phonons), and possibly inhomogeneous broadening due to different adsorption sites and isotopes. The relative importance of the different processes cannot be determined from our data, which was obtained at a single surface temperature. We can set a lower limit for the vibrational lifetime of about 440 fs if the line width was solely determined by the vibrational energy relaxation from the adsorbate to the substrate.

When the molecular beam is blocked from reaching the Pt(111) surface, the CH_4 bands disappear within less than 1 s from the RAIRS spectrum, indicating the transient nature of physisorption of CH_4 on Pt(111) at T_s = 77K, consistent with peak desorption temperatures for CH_4 from Pt(111) in the range of 66−73 K for the first layer and near 50 K for the overlayer.[17−19] Exposure of the Pt(111) surface to a continuous molecular beam of CH_4 leads to an equilibrium between adsorption and desorption with a coverage that depends on incident beam flux and surface temperature.

To measure the CH_4 desorption lifetime, we performed time-resolved RAIRS measurements with the highest time-resolution (0.1 s/scan at 4 cm^{-1} spectral resolution) of our FTIR instrument to record the time evolution of the physisorbed methane absorption signal when the molecular beam was switched on and off by manually opening and closing a valve in the second stage of the molecular beam source chamber. (The valve closing time of 5 ms was significantly faster than the desorption time scale.) As shown in Figure 2b, the methane physisorption signal increased to a constant level within about 0.3 s as the molecular beam exposure was turned on and decayed with a time constant of 0.25 ± 0.07 s as the molecular beam exposure was stopped. The decay time was determined by fitting a single exponential decay to the falling edge of the RAIRS signal. Note that the 0.1 s time-resolution of the FTIR acquisition was insufficient to accurately follow the fast transient methane trapping and desorbing processes; mass spectrometric measurements with higher time resolution using the King and Wells method[13] will be presented below.

For an equilibrium between adsorption and desorption rate, we expect the methane coverage to grow with increasing incident methane flux at constant surface temperature. Indeed, as shown in Figure 3, the CH_4(ads) RAIRS signal and therefore the surface coverage increased as the incident methane flux was increased at a fixed surface temperature T_s = 77.0 ± 0.4 K. Note that the RAIRS signal approaches a constant level with increasing incident flux, indicating the saturation of the first layer of CH_4(ads) on Pt(111). The saturation coverage for CH_4 on Pt(111) has previously been reported as 0.33 ML[18] where
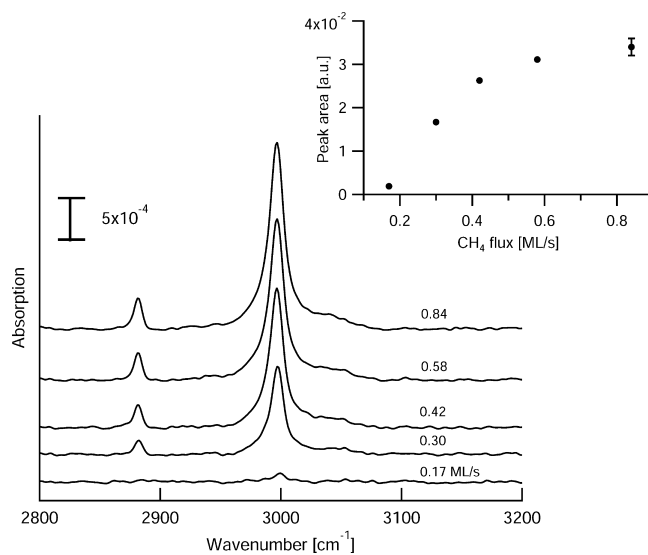
Figure 3. RAIRS signal versus incident CH_4 molecular beam flux demonstrating the formation of a saturation coverage layer of CH_4(ads) on Pt(111). The inset shows how the RAIRS absorption peak area (antisymmetric C−H stretch) converges to the saturation coverage with increasing incident flux. T_s = 77.0 ± 0.4 K. The error bar indicates the standard deviation of four measurements. The incident CH_4 flux was varied by changing the nozzle stagnation pressure between 0.3 and 1.6 bar.

1 ML corresponds to 1.5×10^{15} atoms/cm^2 for the Pt(111) surface.

We measured the initial trapping probability as well as the desorption lifetime (τ) of CH_4 on Pt(111) at T_s = 77 K using the King and Wells method.[13] Figure 4 shows the CH_4 partial
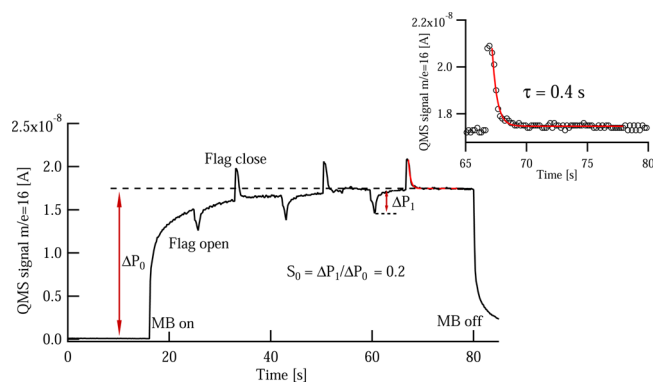
Figure 4. King and Wells beam reflectivity measurements of the initial trapping probability (S_0) and desorption lifetime (τ) for CH_4 physisorption on Pt(111) at T_s = 77 K. The solid line in the inset is a fit of the data points with a single exponential decay function.

pressure variation, detected by a quadrupole mass spectrometer in the UHV chamber tuned to m/z = 16, when the King and Wells beam flag is opened and closed. The initial trapping probability is determined to be S_0 = 0.2 from the relative pressure drop when the flag is opened and the molecular beam impinges on the clean Pt(111) surface. The subsequent partial pressure rise indicates the approach to equilibrium between CH_4 adsorption and desorption rate with increasing methane coverage. When the King and Wells flag blocks the molecular beam from reaching the surface there is a rise in the 16 amu partial pressure signal due to desorption of the layer of

physisorbed CH_4 on the Pt(111) surface. We determine the desorption lifetime to be τ = 0.4 s at T_s = 77 K from an exponential fit to the QMS data in reasonable agreement with the 0.25 s from RAIRS measurements. On the basis of the desorption kinetics, $\tau = \nu_0^{-1} \exp[D/(RT_S)]$, where $\nu_0 = 1 \times 10^{13}$ Hz is the pre-exponential factor, D = 18.3 kJ/mol[17] the physisorption well depth of CH_4 on Pt(111), and T_s (K) the surface temperature. We calculate τ = 0.27 s at T_s =77 K, consistent with our measured lifetime.

Effect of C−H Stretching Excitation on the Trapping of CH_4 on Pt(111). To probe for the effect of vibrational excitation on the trapping probability of CH_4 on Pt(111), we compare the CH_4(ads) coverage (detected via the RAIRS signal) resulting from identical incident beams of CH_4 with and without laser preparation of the ν_3 state.

Adiabatic passage via IR laser pumping was used to excite CH_4 in the molecular beam via the ν_3−R(1) transition at 3038.49 cm^{-1} to the antisymmetric C−H stretch normal mode. Bleaching experiments described previously[20] using a second IR laser that excites from the same initial state into a different final state showed that 95% of the CH_4 molecules were transferred from the initial state (v = 0, J = 1) to the excited state (v = 1, J = 2). We measured the relative population of the initial J = 1 state to be 30% by comparing the pyroelectric detector signal obtained for excitation out of different initial rotational states populated in the molecular beam. Combining these numbers, we estimated that about 28% of the CH_4 molecules in the beam incident on the Pt(111) surface were excited to the v = 1, J = 2 state.

To detect the influence of vibrational excitation on the trapping probability it was essential to work under conditions where the CH_4(ads) coverage on the Pt(111) surface was not saturated; otherwise a change in trapping probability due to the vibrational excitation may not lead to a change in coverage detected by the RAIRS signal. We therefore reduced the incident CH_4 flux to less than 60% of the flux needed to achieve the saturation coverage shown in Figure 3.

We then recorded RAIRS spectra of the Pt(111) surface at T_s = 77 K exposed to a molecular beam of pure CH_4 with and without IR laser pumping of the incident CH_4. The average incident translational energy in both experiments was E_t = 9 kJ/mol. Without IR laser pumping the thermal vibrational energy content of the molecular beam is estimated to be $\langle E_{vib} \rangle$ = 0.1 kJ/mol. IR pumping of the ν_3 vibration adds 36 kJ/mol of vibrational energy. Figure 6 shows a comparison of the resulting RAIRS spectra obtained under identical molecular beam conditions with and without laser excitation. We detect no measurable change in the CH_4(ads) coverage upon excitation of 28% of the incident CH_4 to the ν_3 vibrational state, which indicates that the addition of 36 kJ/mol vibrational energy in the ν_3 mode causes no measurable effect in the trapping probability. We obtain an upper limit for the effect from the change of relative peak area (2916−3159 cm^{-1}) between the laser-on (0.01788 absorption unit cm^{-1}) and laser-off (0.01785 absorption unit cm^{-1}) RAIRS spectrum to be less 0.2%.

Effect of C−H Stretching Excitation of Physisorbed CH_4 on Pt(111). We also used RAIRS to probe for effects of vibrational excitation of the physisorbed CH_4(ads) on the Pt(111) surface. Upon absorption of an IR photon, a physisorbed CH_4 molecule might either react with the metal surface and dissociate, or desorb from the Pt(111) surface, or simply dissipate its vibrational energy into the metal surface
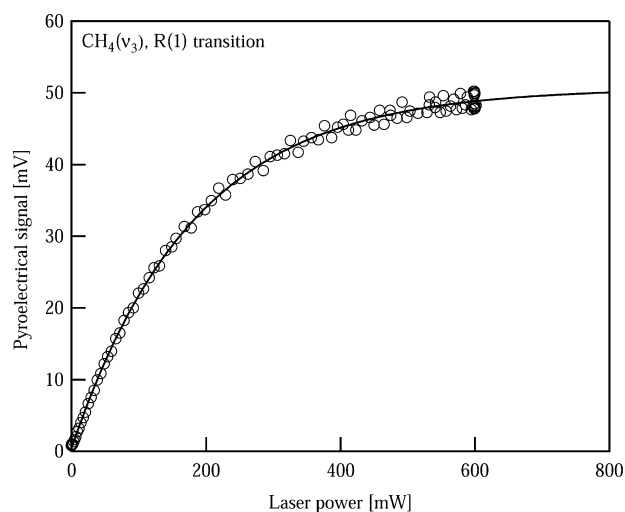

Figure 5. Laser power dependence of the pyroelectric detector signal detecting the amount of ν_3 excited $CH_4(\nu_3)$ in the molecular beam prepared via IR pumping via the R(1) transition.
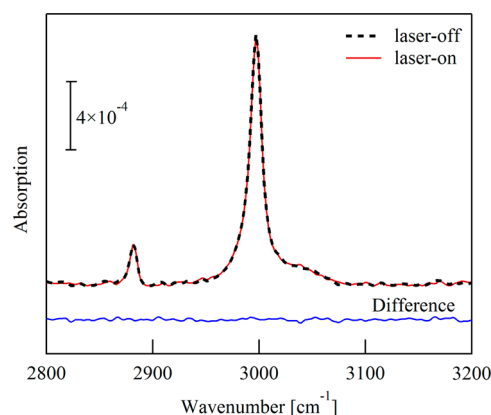
**Figure 6.** Comparison of RAIR spectra of CH_4(ads) on Pt (111) at T_s = 77 K resulting from an incident molecular beam of methane with (solid line) and without laser excitation (dashed line) of ν_3 mode. Both traces were acquired under identical molecular beam conditions as given in Figure 5. The calculated difference spectrum shows no change in the coverage of CH_4(ads) due to ν_3 excitation of approximately 28% of the incident methane indicating that ν_3 excitation has no detectable effect on the trapping probability on Pt(111) at T_s = 77 K.

leading to surface heating. To probe for these processes, we irradiated the physisorbed methane on the Pt(111) surface with cw infrared light from the OPO. The incident IR was p-polarized in order to excite the surface vibrations efficiently according to the metal surface-selection rule.[21] The laser power was chosen low enough (100 mW, beam 3.8 mm diameter) to minimize surface heating to avoid thermal desorption and maintain a significant coverage of physisorbed CH_4 as monitored by RAIRS. The OPO frequency was tuned to overlap with either the antisymmetric (ν_3) or the symmetric (ν_1) C−H stretch of the physisorbed CH_4 in the RAIRS spectrum, as shown in Figure 7.

Figure 8 compares RAIR spectra taken before and after 35 min of IR irradiation of a layer of physisorbed methane generated by continuous exposure of the Pt(111) at 77 K to an incident beam of CH_4. The data shows that IR irradiation of CH_4(ads) on Pt(111) yields no detectable methyl (CH_3) coverage resulting from vibrationally activated dissociation via
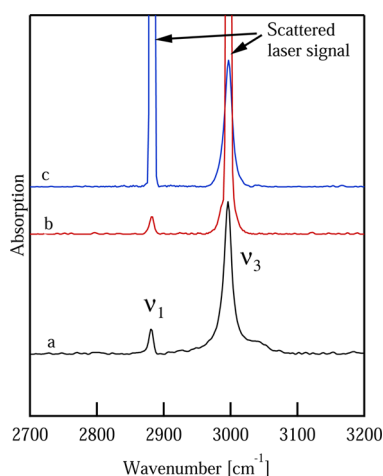
Figure 7. Tuning the OPO idler frequency to excite either the symmetric C–H stretch ν_1 or the antisymmetric C–H stretch mode ν_3 of CH_4(ads). (a) RAIRS signal due to the C–H stretch modes ν_1 and ν_3 of CH_4(ads). (b) IR excitation of the ν_3 mode. Scattered IR light used for excitation of CH_4(ads) is detected as the off-scale peaks overlapping the RAIRS signal of either the ν_3 mode (b) or the ν_1 mode (c).
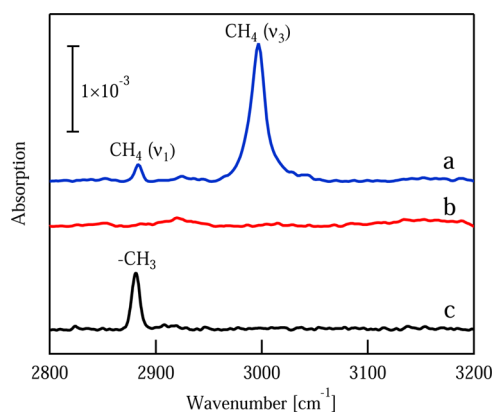
Figure 8. Probing for evidence of vibrational-induced dissociation of physisorbed CH_4 on Pt(111): (a) RAIRS signal of physisorbed CH_4(ads) on Pt(111) at 77 K created by exposure to a molecular beam of pure CH_4; (b) RAIRS scan showing the absence of any chemisorbed methyl (CH_3(ads)) products after 35 min IR irradiation (∼1 W/cm²) on a layer of CH_4(ads); (c) RAIRS scan of chemisorbed methyl (CH_3(ads)) on Pt(111) produced by the dissociative chemisorption of CH_4, displayed as a reference.

CH_4(ads, ν_3) → CH_3(ads) + H(ads). Any adsorbed methyl groups CH_3(ads) would be detected as a peak near 2883 cm⁻¹, as shown in trace c of Figure 8, which was recorded following deposition of a high-energy beam of CH_4 on the Pt(111) surface. Excitation of the ν_1 band of physisorbed CH_4 also caused no measurable effect (data not shown). We can therefore exclude vibrationally activated dissociation of the physisorbed CH_4 via ν_3 or ν_1 excitation as a feasible process.

For the vibrational-induced desorption of physisorbed CH_4 on Pt(111), as shown in Figure 7, a band area decrease of about 30% for the ν_1 band and 44% for the ν_3 band in the RAIRS spectra was observed upon the surface vibrational excitation relative to that without excitation. We believe the decreases were most likely due to the heating effect during surface IR irradiation. For better measurements, the surface needs to be cooled to even lower temperatures so that the direct laser

heating effect is negligible for the trapping probability of CH_4 on Pt(111).

■ DISCUSSION

Our experiments show that ν_3 excitation of CH_4 adding 36 kJ/mol of vibrational energy to the incident gas-phase methane molecules has no measurable effect on the trapping probability into the physisorbed state on Pt(111) with a well depth of ∼18 kJ/mol.[17] This behavior stands in sharp contrast to the chemisorption process in which the dissociative sticking coefficient is strongly enhanced by ν_3 excitation as well as for other vibrations. In CH_4 chemisorption, the ν_3 vibrational energy assists the incident molecules to surmount the reaction barrier and increases the reactivity by up to several orders of magnitude, resulting in vibrationally mode- and bond-specific dissociation.[9,22,23] While one might expect that vibrational excitation reduces or suppresses the trapping probability in the shallow physisorption well, our experiments show that vibrational energy appears to play the role of a spectator in the trapping event.

A similar insensitivity of trapping to vibrational excitation was observed in several previous studies for different molecules on a range of surfaces including metals, semiconductors, and insulators. Wodtke et al.[6] found that 44 kJ/mol vibrational energy in NO($v = 2$) had no measurable effect on the trapping of NO on Au(111). Bisson et al.[7] reported that the dissociative chemisorption of SiH_4 on Si(100) is activated by Si–H stretching overtone excitation (52 kJ/mol) for both a direct and a precursor-mediated pathway, implying that vibrational excitation does not inhibit trapping of SiH_4 on Si(100) in the precursor-mediated pathway. Recently, Hundt et al.[8] observed that OD-stretch (34 kJ/mol) excitation of the incident heavy water D_2O molecules caused no significant change in the sticking probability of D_2O on the D_2O-ice surface.

Trapping of molecules into the physisorbed state requires dissipation of a sufficient amount of incident translational energy of motion along the surface normal so that the scattered molecules are unable to escape the physisorption well. Excess translational energy can strongly suppress the trapping probability of CH_4 and other alkenes at metal surfaces.[24] For example, the trapping probability of CH_4 on Pt(111) at 50 K is suppressed from 0.7 to almost zero as the incident normal translational energy is increased from 3 to about 20 kJ/mol.[2] Vibrational energy of the incident molecule should influence trapping if sufficient coupling exists between the vibrational and translational degrees of freedom (V–T coupling) during the molecule–surface collision event. However, molecular dynamics simulations have shown that mainly low-frequency bending and rotation motions rather than high-frequency stretching modes are involved in the V–T coupling during the colliding of CH_4 molecules with Pt(111) surface.[24] This is consistent with the experimental observation reported by Sibener and Lee:[4] thermal excitation of the rotational and low-frequency vibrational degrees of freedom in a beam of CCl_4 or SF_6 was found to decrease the trapping probability on its correspondent condensed phases.

In fact, on the basis of the principle of detailed balance, one might have predicted the lack of a vibrational effect in trapping from previous unsuccessful attempts to probe for the direct vibrational-induced desorption of physisorbed molecules from insulator[25] and metal[26] surfaces. The measurements have shown negligible desorption yields and a lack of isotope selectivity. For example, a vibration-induced desorption study[25]

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of an adsorbed mixture of CH_4 and CD_4 on NaCl(100) showed that both isotopologues desorbed simultaneously from the surface upon vibrationally resonant excitation of the internal vibrational modes of either physisorbed CH_4 or CD_4. The lack of isotope selectivity in addition to the observation of a laser fluence threshold for the desorption yield suggests a vibrational resonant heating mechanism in which the substrate temperature is raised because of vibrational energy transfer from internal adsorbate vibrations to surface vibrations (phonons) leading to thermal desorption. This lack of direct vibrationally induced desorption is consistent with the insensitivity of trapping to vibrational excitation observed here, which together suggest that the high-frequency C−H stretching vibrational motion is a spectator in the direct trapping−desorbing processes of methane at the Pt(111) surface.

Our unsuccessful attempts to achieve vibrationally induced dissociation of physisorbed CH_4 on Pt(111) might be explained by the fact that 36 kJ/mol vibrational energy added via one-quanta excitation of the C−H stretching is insufficient to surmount the ~90 kJ/mol[27] dissociation barrier, calculated for the direct dissociation process. However, if a precursor-mediated pathway exists, the physisorbed methane has sufficient time to explore the PES and find pathways with significantly lower reaction barrier for example on defect sites. Alternatively, fast vibrational energy transfer from the physisorbed molecule to electron−hole pair excitations of the metal surface may effectively outcompete the dissociation process. To further investigate these possibilities, we will perform trapping and dissociation measurements for higher vibrationally excited states via excitation of overtone and combination bands (e.g., $2\nu_3$ and $\nu_1 + \nu_3$).

CONCLUSIONS

State-resolved measurements of CH_4 physisorption on Pt(111) at $T_s = 77$ K show that one quantum of ν_3 antisymmetric C−H stretching excitation has no detectable effect (<0.2% change) on the CH_4 trapping probability. Vibrational excitation of physisorbed CH_4 to the symmetric or antisymmetric C−H stretch modes ν_1 and ν_3 does not induce dissociation on the Pt(111) surface. On the basis of similar observations for trapping of other molecules on metal, semiconductor, and insulator surfaces as well as the lack of experimental evidence for vibrationally resonant desorption, we suggest that the absence of vibrational effects is due to a lack of coupling between the internal vibrational degrees of freedom and the desorption coordinates. Measurements with multiquantum vibrational excitation (e.g., overtone excitation) may provide further insight into the role of vibrational excitation in physisorption. Comparing Wodtke's experiments[6] to their theory, Tully and co-workers were able to reproduce the experimental data for NO($v = 0$) and NO($v = 2$) trapping on Au(111) with electronically nonadiabatic theory.[28] These simulations predict the trapping probability to be strongly reduced for highly vibrational excited state ($v = 15$) because of the highly nonadiabatic behavior, i.e., vibrational energy transfer into electronic excitations. On the other hand, simulations assuming electronic adiabaticity predict that the trapping probability should increase with increasing vibrational energy because of the increasing bond length (or transient dipole) which results in an increasing average binding energy of NO at the surface. Therefore, experiments with multiquantum vibrational excitation experiments could be useful for detecting evidence for electronic nonadiabaticity in the transfer of vibrational energy between methane at transition-metal surfaces.

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Notes

The authors declare no competing financial interest.

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