Activated adsorption of methane on Pt(1 1 1)—an \textit{in situ} XPS study

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\textbf{Abstract.} We have investigated the activated adsorption of methane on Pt(1 1 1) by the combination of a supersonic molecular beam and \textit{in situ} high-resolution X-ray photoelectron spectroscopy at the German synchrotron radiation facility BESSY II. On exposing the surface to a methane beam with kinetic energies between 0.30 and 0.83 eV, CH\textsubscript{3} is formed as a stable species at 120 K; upon heating, at around 260 K the adsorbed methyl partly dehydrogenates to CH and partly recombines to methane, which desorbs. Upon adsorption at 300 K, CH is directly formed as a stable surface species. To verify the chemical identity of CH as an intermediate, we have also investigated the thermal evolution of a saturated ethylene layer. Upon heating, at \(~\)290 K partial ethylene desorption and the formation of ethylidyne is clearly observed in the spectra, as expected from the literature. From the binding energies and also from the vibrational signature of the C 1s spectra, an unequivocal assignment of the various surface species is possible. Measurements of the sticking coefficients of methane show that the saturation coverage at 120 K depends on the kinetic energy of the molecule; furthermore, the sticking coefficient for vibrationally excited molecules is strongly enhanced.
1. Introduction

Methane is one of the most important natural resources of the future. In the methane steam reforming process, a mixture of methane and water reacts over a metal catalyst to form synthesis gas, a mixture of carbon monoxide and hydrogen (see, e.g., [1] and references therein). This synthesis gas is essential for the ammonia synthesis (Haber–Bosch process) or the production of higher hydrocarbons (Fisher–Tropsch synthesis).

In order to understand heterogeneously catalysed reactions in detail, the various steps involved, such as adsorption, reaction and desorption, need to be studied. For methane steam reforming, efforts have been undertaken to study in particular the adsorption behaviour of methane under various conditions using different surface science techniques. We will concentrate here on the adsorption on Pt(1 1 1) surfaces, which is the subject of our study. For surface temperatures below 73 K, only physisorption is reported on Pt(1 1 1) [2]–[7]. For methane applied at high pressures and high surface temperatures, dissociative adsorption can be observed in bulb experiments [8]. Luntz and Bethune [9] have investigated the activated dissociative adsorption of methane on Pt(1 1 1), under ultrahigh vacuum conditions using a supersonic molecular beam system, to vary and control the kinetic energy of the impinging methane molecules. The energy can be changed by seeding with He and/or by changing the nozzle temperature. This, however, not only changes the kinetic energy, but also the vibrational excitation of the molecules [10].

In order to stay close to the technically relevant conditions and to avoid contaminations, such as CO, caused by the high local pressure of the molecular beam, surface temperatures above 500 K, i.e., above the desorption temperatures of possible contaminants, have been used for most investigations of initial sticking coefficients [8, 9, 11], scattering properties [12, 13] or surface reactions [14]. Using infrared absorption spectroscopy, Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD), Oakes et al [15] investigated CH₄ dissociation at 150 K, determining CH₃ (methyl) as the adsorbed product, with the initial sticking coefficients depending on surface temperature. X-ray photoelectron spectroscopy (XPS) measurements of
methane adsorption have been performed in the past, generating methyl either by radiation damage \[3, 7\] or by electron irritation \[2\] of physisorbed methane layers. The corresponding C 1s spectra display some fine structure or asymmetric line shapes. This originates from vibrational splitting of the XPS signal, due to excitation of vibrational modes in the photoemission final state. This splitting is most clearly resolved in gas phase spectra of methane \[16]–\[19\]. For larger adsorbed hydrocarbons on various surfaces, vibrational splitting has also been recently reported \[20]–\[24\].

In order to get a more detailed survey of the situation on Pt(1 1 1), we are using a combination of a supersonic molecular beam and in situ high-resolution XPS to characterize and quantify the chemical species present on the surface for different adsorption conditions. To follow their thermal evolution in situ, we apply temperature-programmed XPS (TPXPS) \[25\]. In situ measurements with the necessary resolution on a reasonable timescale require synchrotron radiation as excitation source. Using this approach, vibrationally resolved XP spectra of the adsorbed methyl species from activated methane adsorption on Pt(1 1 1) have recently been reported by Fuhrmann et al \[26\]. As a main result, the vibrational fine structure has been analysed in detail, including isotopic studies. Furthermore, no dependence of the adsorbed species on the kinetic energy of the impinging methane molecules was found.

This study is significantly extended in the current contribution. Quantitative analysis of the XPS spectra additionally allows one to determine the kinetics of the activated adsorption as a function of kinetic energy and vibrational excitation of the impinging methane molecules. From the time-dependent measurements not only can the sticking coefficients be obtained, but also the saturation coverages. Furthermore, we also address the influence of the surface temperature on the adsorption process, adding the additional information about the adsorbed species, which was found to change with temperature due to dehydrogenation processes \[26\]. In order to calibrate the adsorbate coverages and to verify our species assignment, ethylene adsorption and its thermal dehydrogenation on Pt(1 1 1) are studied. In addition, TPD is used to confirm the recombinative desorption of part of the adsorbed methyl species as methane.

2. Experimental procedure

All XPS measurements were performed at the BESSY II synchrotron radiation facility in Berlin, Germany, in a transportable UHV chamber, which has already been described elsewhere \[27\]. Briefly, it consists of three separate chambers: (1) an analysis chamber, equipped with a hemispherical electron energy analyser (Omicron EA 125 U7 HR). Synchrotron radiation from beamline U49/2-PGM1 enters at an angle of 50° with respect to the analyser lens system in the plane of linear light polarization. All C 1s spectra were obtained at a photon energy of 380 eV, with the overall resolution set to 200 meV, requiring about 8 s per 6 eV wide spectrum. The reproducibility of binding energy values within this study is ±30 meV. (2) In the molecular beam chamber, a collimated supersonic beam is produced by expanding CH\(_4\) through a 100 μm diameter Mo nozzle into the first of three successive differential pumping stages. The molecular beam enters the analysis chamber at an angle of 45° with respect to the analyser lens system; it runs through the focal point of the analyser in order to allow for in situ measurement of adsorption processes. A flag, mounted on a pneumatic feedthrough in the second stage, allows for fast (<0.1 s) switching of the beam. Methane (99.995% purity; Messer), additionally cleaned by a cooling trap (230 K), was used. The kinetic energy was varied by heating the nozzle up to 1273 K and/or using He as seeding gas, with seeding ratios between 1.25 and 10% methane in He.

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By varying the nozzle temperature, the occupation of the CH₄ vibrational states can also be varied [10]. The kinetic energies were measured in a similar setup [28] using time-of-flight methods. In this setup, also TPD experiments of methane (CH₄, m/e = 16) and of hydrogen (m/e = 2) were recorded with a quadrupole mass spectrometer. (3) Finally, a preparation chamber contains low energy electron diffraction (LEED) optics, an ion gun and a quadrupole mass spectrometer. The sample holder is mounted on a xyz-manipulator with rotational feedthrough, which also allows for variation of the polar angle orientation of the sample. Alternative to the supersonic molecular beam, gas can also be dosed into the analysis and preparation chambers by a conventional dosing system with a capillary array doser, which in this work was used for oxygen dosing (purity 99.998%; Messer) for sample cleaning and ethylene dosing.

The Pt(1 1 1) sample (diameter 10 mm) is spot-welded to Ta wires and can be heated resistively up to 1500 K (for sample cleaning) and cooled by an LN₂ cryostat to 95 K. During XPS, the sample is heated radiatively by a filament positioned at the back in order to avoid disturbing magnetic fields caused by resistive heating. The temperature is measured by a K-type thermocouple spot-welded to the edge of the sample. A linear temperature ramp can be applied by a programmable temperature controller (Eurotherm). The sample was cleaned by repeated cycles of Ar⁺ ion bombardment (1 kV), heating in oxygen (1.3 × 10⁻⁷ mbar, 300–800 K and approx. 2 K s⁻¹ ramp) and annealing to 1300 K. After the sample was bulk-cleaned, carbon contaminants on the surface could be removed efficiently by a single cycle of heating in oxygen and annealing. Sample cleanness was controlled before each experiment by XPS.

All XPS measurements in this study have been performed with the sample surface normal facing the molecular beam; therefore, the electron emission angle was 45° with respect to the surface normal.

3. Results and discussion

3.1. Activated adsorption and peak assignment

3.1.1. Methane. Recent experiments in our group have shown [26] that in the kinetic energy range between 0.09 and 0.83 eV (obtained by seeding and/or varying nozzle temperatures), always the same adsorbed species, namely CH₃, is formed on the surface at 120 K. In figure 1(a) a typical C 1s spectrum after exposing the surface at 120 K to a methane beam with a kinetic energy of 0.60 eV is shown. The spectrum is dominated by the contributions from CH₃; in addition, there is a small signal due to CH, formed by radiation damage (see below). In order to analyse the spectrum, it was fitted using five asymmetric peaks with Doniach–Sunjic line shapes (for a detailed description see [26]). The three peaks at 282.54, 282.94 and 283.33 eV (indicated as blue lines) are assigned to CH₃; they show a uniform shift to higher binding energies with increasing coverage by a total of 140 meV [26]. Independent of coverage, they exhibit the same intensity ratio and a constant peak separation; therefore, this unique structure is attributed to vibrational excitations of C–H stretching modes in the photoemission process, and not to different chemical species on the surface [26]. The energetic separation between the adiabatic and the first exited peak is 400 ± 4 meV, which is in good agreement with data for the gas phase [16]–[18], [29]. The S-factor, i.e., the ratio of the area of the first excited peak to the adiabatic peak [30], is determined to be 0.50 [26]. Further details about the vibrational fine structure, peak fitting and isotope effects can be found in [26]. The energetic position of the adiabatic peak of CH₃ is in good agreement with previous results [3, 7].
The remaining two peaks at 283.61 and 284.03 eV in figure 1(a) (green lines) are assigned to CH, formed from adsorbed CH\textsubscript{3} by radiation damage due to the highly intense synchrotron radiation. The influence of radiation is even more evident in the data shown in figure 1(b) which have been collected after exposing the surface to the photon beam for 24 min. As can be clearly seen, exposure to radiation leads to an increase of the CH signal at the expense of a CH\textsubscript{3} signal. The
existence of two peaks, now separated by about 420 ± 10 meV, is again attributed to a vibrational fine structure due to excitation of the C–H mode in the photoemission process; the corresponding S-factor is 0.16 [26]. The integrated peak area of the C 1s signal in figure 1(b) is 16% smaller than that in figure 1(a). One possible explanation would be the differences in photoelectron diffraction for CH₃ and CH (see [31] and references therein). Alternatively, photon stimulated desorption (PSD) could also cause this effect. For methane physisorbed at 55 K, PSD has been reported by Matsumoto et al [3]; to the best of our knowledge, this has not been investigated for CH₃. Being aware of the formation of CH due to radiation damage, we have exposed the surface to radiation only during the XPS measurements and changed the sample position frequently.

3.1.2. Ethylene. In order to perform a quantitative analysis of the data, the intensities obtained from the fitting procedure need to be converted into coverages. Since no LEED pattern was obtained for CH₃ at any coverage, the calibration was performed by comparison to spectra obtained for ethylene on Pt(1 1 1), where the saturation coverage at 140 K is reported to be 0.25 ML [32].

Ethylene was dosed onto Pt(1 1 1) at 120 K using the multicapillary array doser at a background pressure of 1.7 × 10⁻⁸ mbar. The XPS measurements were performed in the same geometry as used for methane. In figure 2(a), the spectrum measured after an exposure of 1.5 L is shown. The inset shows the total C 1s signal during exposure, reaching saturation at 0.9 L. According to the literature [32], the spectrum in figure 2(a) should correspond to an ethylene coverage of 0.25 ML, assuming no influence of the slightly different surface temperature [33]. The corresponding normalized peak area in figure 2(a) has therefore been used to calibrate the coverages obtained in this study. As already mentioned, the possibility that photoelectron diffraction may influence the recorded intensities from different species [31] has to be taken into account. Additionally, small variations in the determined coverage of the order of ±0.02 ML can be caused by slightly different experimental geometries for different beamtimes.

The spectrum in figure 2(a) can be fitted using three asymmetric peaks. By assuming a symmetric adsorption geometry with the C–C axis parallel to the surface, as has been proposed in the past [34, 35], one would expect that the two C atoms are equivalent, which results in only one C 1s peak in the XP spectra. Within the uncertainty of our experiment, this should even be true if the molecule were slightly tilted, as alternatively proposed in a LEED study [36]; a resulting small binding energy shift between the two C atoms could be obscured by the width of the spectral features. The three observed peaks are therefore again attributed to vibrational fine structure, due to excitation of the C–H stretching vibration in the photoemission process. Additional contributions caused by excitation of the C–C vibration cannot be resolved (compare, e.g., ethylene on Ni(1 0 0) [37] or on Rh(1 1 1) [20]) and contribute to the asymmetric line shape. With increasing coverage, the peaks are uniformly shifting to higher binding energies by 160 meV (not shown), due to adsorbate–adsorbate interactions. The binding energies at saturation are 283.16, 283.54 and 283.89 eV. The separation of the adiabatic and the first excited peak of 388 meV is slightly larger than the value of 368 meV obtained in gas phase measurements [29]. The S-factor obtained from figure 2(a) and other spectra during the uptake is determined to be 0.36. The comparison of the S-factors in our data for CH₃ (methyl, see above), CH₂ (in ethylene) and CH (methylidyne, see above) yields values of 0.50, 0.36 and 0.16, respectively, which nicely scale with the number of C–H bonds as expected [29], yielding 0.17 ± 0.02 per C–H bond.
Figure 2. (a) C 1s spectrum of a saturated ethylene layer on Pt(1 1 1) at a surface temperature of 120 K. Violet lines indicate deconvoluted components (see text for details). The inset shows the time-dependent increase of the ethylene coverage, as determined from quantitative analysis of the C 1s data taken during exposure. (b) C 1s spectrum obtained after heating the saturated ethylene layer to 300 K. (c) C 1s spectrum obtained after heating to 400 K. In both spectra, contributions from further intermediates are shown as coloured lines (see legend for details).

3.2. Thermal evolution

3.2.1. Methyl. In order to study the thermal evolution of the adsorbed CH₃ species, temperature-programmed photoelectron spectroscopy (TPXPS) has been performed. Up to 500 K, the crystal was heated radiatively by a filament positioned in the back. At a linear heating ramp of 0.5 K s⁻¹, an XP spectrum was collected in situ every 10 K. Higher temperatures were obtained by direct resistive heating; in that case the spectra were collected after the heating.
The C 1s spectra after exposure of Pt(1 1 1) to methane at 120 K show characteristic changes associated with changes in the adsorbed species [26]: In figure 3(a), spectra for a surface with an initial methyl coverage of about 0.16 ML are shown in a colour-coded density plot, for the temperature range from 200 to 450 K. Each horizontal line corresponds to a C 1s spectrum at the temperature indicated; the spectral intensity is translated into a colour scale, ranging from black for low intensities to yellow for high intensities, as indicated by the scale bar. Upon heating to 220 K, only minor changes in the spectra are observed. Around 250 K, the dominating CH$_3$ peak at ~282.6 eV (note that its binding energy is slightly higher than in figure 1(a) due to the higher coverage) begins to decrease and simultaneously the CH peak at ~283.6 eV gains intensity, indicating dehydrogenation of methyl at this temperature. It is interesting to note at this point that the spectra unequivocally show the formation of the same product, namely CH, on the surface by radiation damage and by thermal treatment, as is deduced from the identical binding energy and S-factor obtained in both cases. To visualize this identity, the spectrum of the CH species obtained at 400 K is added to figure 1(c).

Figure 4 shows the results of a quantitative analysis of the TPXPS experiment from figure 3(a), starting with the methyl coverage of about 0.16 ML obtained from activated methane
adsorption using a kinetic energy of 0.83 eV. Below 250 K, only a small decrease of the CH₃ signal and a slight increase of the CH signal are observed; both changes are attributed to beam damage. Between 250 and 280 K, temperature-induced dehydrogenation takes place: the CH₃ signal drops to zero and simultaneously the CH signal increases to 0.04 ML. The fact that the CH coverage is much smaller than the initial CH₃ coverage, which is most evident from the total C 1s intensity in figure 4, indicates that parallel to dehydrogenation, recombinative desorption of CH₄ occurs. This methane formation from CH₃ + H was also observed by TPD (see below). It is interesting to note that the amount of CH formed on the surface during heating of a methyl layer prepared at 120 K is always close to 0.04 ML, independent of initial methyl coverage (if larger than 0.04 ML). This could be due to the fact that hydrogen atoms from the dehydrogenation process block adsorption sites for further dissociation products, making recombinative methane desorption energetically favourable. This interpretation is supported by the observation that higher CH coverages of >0.1 ML can be prepared by repeating adsorption and annealing cycles up to 300 K to desorb part of the hydrogen. Also, applying the methane beam at temperatures above 300 K results in higher CH or carbonaceous species coverages, as will be shown below.

In the temperature range between 280 and 450 K, the situation on the surface remains unchanged. Starting at around 450 K, dehydrogenation of CH takes place, forming carbonaceous species on the surface. In TPD spectra of hydrogen (data not shown), a desorption peak is found around 500 K, in agreement with this XPS result.

From the quantitative analysis of the TPXPS data in figure 4, desorption of a carbon containing species was indicated around 270 K. Indeed, TPD experiments performed in a separate molecular beam system show recombinative methane desorption with a maximum rate around 265 K, as shown in figure 5. This is in good agreement with results reported by Oakes et al [38]. The different initial CH₃ coverages were prepared by offering always the same CH₄ dose to the sample³ and by varying the kinetic energy by changing the nozzle temperature—with increasing beam energy one expects increasing surface coverage due to the activated nature of methane.

³ These experiments were performed in a different setup; therefore, the fluxes are not comparable with the ones used throughout this paper. The doses in all cases, however, result in methyl coverages above 0.04 ML.
adsorption (see also below). The observation that the amount of methane desorption, i.e. the peak area in figure 5, increases with increasing kinetic energy of the impinging molecules, is in line with this expectation and the observation of a fixed residual CH coverage obtained from TPXPS. The inset in figure 5 shows the integrated amounts of H₂ desorption above 320 K, which were determined in the same experiment. The data show that the amount of desorbing H₂ with its maximum desorption rate around 500 K, which reflects the amount of CH formed on the surface, is more or less the same for the four initial methyl coverages studied. This result is in best agreement with the observation discussed above that at 120 K the amount of CH formed on the surface is 0.04 ML, independent of the initial CH₃ coverage.

3.2.2. Ethylene. The thermal formation of only CH is in contrast to conclusions by Oakes et al [15] and Fairbrother et al [39], who additionally propose the formation of ethylidyne (CCH₃) from methyl on Pt(1 1 1) by heating to 300 K; the discrepancy could result from a dependence of the reaction pathway on the methyl coverage [39]. We have, therefore, also investigated the thermal evolution of ethylene on Pt(1 1 1) by TPXPS, because for this system, the formation of ethylidyne upon heating is widely accepted [32]. The measurements were performed for a saturated ethylene layer with a coverage of 0.25 ML prepared at 120 K, at a heating rate of 0.2 K s⁻¹. The corresponding measurements in the interesting temperature range from 200 to 450 K are shown in figure 3(b), again in a colour-coded density plot. Up to ~240 K, the spectra are dominated by an adiabatic C₂H₄ peak at 283.3 eV. Starting at 240 K, this peak looses intensity and a new peak at 284.0 eV starts to grow. This process is completed at ~320 K; above this temperature only the new species is present on the surface. The corresponding spectrum at 400 K is shown...
Figure 6. Thermal evolution of ethylene on Pt(1 1 1), as determined from quantitative analysis of the data in figure 3b. For ethylene (C₂H₄), intensities for the two vibrational components are plotted separately, while for ethylidyne (CCH₃), the sum of the two contributions is shown. In addition, dashed lines display a calculated deconvolution of the high binding energy C₂H₄ component, if an additional intermediate is assumed (see text for details).

In figure 2(c), according to the literature [32, 38], the new species is assigned to ethylidyne. If we now compare the binding energies of ~283.6 and ~284.0 eV of the adiabatic peaks of the species formed by heating the methyl layer (figure 3(a)) and the ethylene layer (figure 3(b)), respectively, we immediately conclude that they represent different surface species; this supports our above assignment of the CH species formed by dehydrogenation of CH₃. The formation of CH is also plausible from the observation that the same species is formed by radiation damage. In addition, we observe no coverage-dependent shift of the CH binding energy. Furthermore, CH has been predicted as the most stable C1 fragment on Pt(1 1 1) [40]; also, its proposed formation for methane decomposition on Pt(1 1 0) [41] supports our assignment. In recent reflection absorption infrared spectroscopy (RAIRS) studies, CH was found as dehydrogenation product of CH₃ and CH₂, also confirming these findings [42, 43]; CH was found to be stable up to 500 K [43], in good agreement with our results of figure 4.

In figure 6, the quantitative analysis of the thermal evolution of ethylene on Pt(1 1 1) is shown. The data obtained from the spectra in figure 3(b) reveal a decrease of the measured total carbon coverage by about 40%, in this case from 0.26 to 0.15 ML, during the conversion to ethylidyne. This decrease is due to molecular desorption of ethylene, which has been reported to occur at around 280 K to an amount of about 56% of the saturated layer [33].

The detailed inspection of figures 3(b) and 6 shows that in the temperature range around 290 K, where the conversion from C₂H₄ to CCH₃ occurs, there are indications for an additional surface species. This is concluded from a variation of the intensity ratio of the peaks assigned...
as first excited and adiabatic peak of ethylene at low temperatures, in that temperature range. It is most evident in the spectrum at 300 K, which is shown in figure 2(b); here, the intensity of the peak at the position of the first excited state (grey line) is even higher than the one of the adiabatic ethylene peak. Note, that the positions of both peaks have shifted to lower binding energies by about $\sim 100$ meV during the thermal treatment (as compared to figure 2(a)), inverting the coverage-dependent behaviour observed during uptake of ethylene. The binding energy of this new species is thus $\sim 283.5$ eV, quite similar to CH and the first vibrationally excited peak of C$_2$H$_4$. To analyse this species in more detail, we have plotted the intensity of the adiabatic peak and the peak at the position of the first excited peak of C$_2$H$_4$ separately in figure 6, as dark violet and grey lines. In addition, we have also included the expected intensity of the first excited peak, determined by using a constant ratio of 0.36 to the adiabatic peak, as dashed light violet line. Up to $\sim 230$ K, the solid grey and the dashed light violet lines coincide, indicating that the peak at 283.5 eV is solely due to the first vibrationally excited state of C$_2$H$_4$. Starting at $\sim 230$ K, a significant difference is observed, which is included as a blue dashed line in figure 6; it represents the coverage of the additional species that is formed in that temperature range. Most likely, it is an intermediate species, formed in the process of the conversion of the symmetric ethylene molecule, bound via di-$\sigma$ bonding parallel to the surface (see discussion above), to the ethylidyne molecule, assumed to be oriented with the C–C axis normal to the surface [38]. Ethylidene (CHCH$_3$) has been proposed as an intermediate, by comparison with infrared spectra either from the thermal products of the respective iodide molecules [44, 45] or from organometallic clusters [46]. Therefore, we propose that the peak at 283.5 eV with its maximum at around 290 K represents the major C 1s binding energy of the ethylidene species on Pt(1 1 1); the expected additional fine structure cannot be resolved in the co-adsorption situation with overlapping peaks.

In the following, we will analyse the line shape of the signal attributed to ethylidyne. As seen in figure 2(c), the XPS signal contains only two obvious contributions at 283.96 and 284.36 eV, which are separated by a binding energy difference typical for vibrational splitting. This implies that the two non-equivalent carbon atoms in CCH$_3$ either have the same binding energy or are separated by the same binding energy difference as the vibrational splitting of the CH$_3$ group in ethylidyne. From the quantitative analysis of the deconvoluted spectra, we obtain an intensity ratio of 0.21. Within a margin of error, this value is consistent with an $S$-factor of 0.25 that is expected, if we assume that the adiabatic peak contains intensity from two carbon atoms and apply the simple rule of thumb of an $S$-factor $\sim 0.17$ per C atom (see above). This is in particular true, if one considers that the contribution of the two carbon atoms might be different due to photoelectron diffraction; indeed, the intensity ratio changes to 0.12 for normal emission. We thus conclude that both carbon atoms in ethylidyne exhibit the same C 1s binding energy on Pt(1 1 1). The alternative explanation, namely that the two peaks represent the two different C atoms, appears very unlikely to us, due to an intensity difference of a factor of nearly five, which is much too high to be explained by photoelectron diffraction. We want to mention that our result is in contrast to that observed for ethylidyne on Rh(1 1 1) or Pd(1 1 1), where two distinct C 1s peaks, separated by 0.6 eV were observed; only one of them shows vibrational splitting [20, 21, 23]. This difference could be due to, e.g., a different adsorption site for the CCH$_3$ species, leading to a different electron distribution within the molecule. Interestingly, a much smaller peak separation of only 180 meV between the two C 1s peaks has been observed on Rh(1 1 1), if ethylidyne was coadsorbed with CO, causing an adsorption site change of the CCH$_3$ molecule [23].
3.3. Vibrationally assisted sticking of methane

As mentioned in section 2, the kinetic energy of the molecular beam can be varied by changing the nozzle temperature and/or using He as seeding gas. Using higher nozzle temperatures will excite vibrational states in the methane molecule while changing the seeding ratio will change only the kinetic energy [10]. It has been shown, e.g., for methane on Ni(1 0 0) [47, 48] at a surface temperature of about 475 K, that vibrational energy can help to overcome the activation barrier in the dissociation process, i.e. it can increase the initial sticking coefficient quite remarkably.

In order to study this effect also for Pt(1 1 1), in particular at a surface temperature of 120 K, where the stable methyl intermediate is formed, we have investigated the activated adsorption of methane by generating two beams with the same kinetic energy, but a different degree of vibrational excitation: a beam with kinetic energy of 0.45 eV was produced either by using a seeding ratio (CH₄ in He) of 10% with the nozzle at 973 K or a seeding ratio of 1.25% with the nozzle at 573 K. The corresponding C 1s XP spectra after equivalent CH₄ doses⁴ are shown in figure 7 as red and black curves, respectively. For a high seeding ratio and low nozzle temperature, i.e., low vibrational excitation, only little adsorption is found (black curve). For a lower seeding ratio and higher nozzle temperature, i.e., higher vibrational excitation, a significant (more than 15 times higher) CH₃ signal is observed, corresponding to ∼0.10 ML. This clearly demonstrates the influence of the vibrational excitation on the activated formation of CH₃ on Pt(1 1 1) in addition to the influence of kinetic energy. From our data, the separation of the individual contributions of the two channels (kinetic versus vibrational energy) is not possible. However, such an approach has been successfully demonstrated by using selective excitations of the vibrational channel by a separate laser [48].

⁴ Note that the methane flux was by a factor of four higher for the lower seeding ratio; therefore, the dosing time in that case was a factor of four lower, yielding the same exposure in both cases.
3.4. Sticking coefficients and saturation coverage

We now turn to the adsorption of methane as a function of energy of the incoming methane molecule and as a function of surface temperature. Figure 8(a) shows the surface coverage with C-containing species versus time at 300 K for increasing kinetic energy of the impinging CH$_4$ molecules. The kinetic energy was changed by varying the nozzle temperature between 773 and 1073 K at a fixed seeding ratio of 5% CH$_4$ in He. At 300 K, CH is the stable species on the surface. The data in figure 8(a) clearly show that the initial sticking coefficient, which is given by the initial slope of the uptake curves, increases with increasing kinetic energies, as expected for activated adsorption [15]. The surface coverage seems to converge towards the same saturation value of $\sim 0.18$ ML, if the data curves are extrapolated to larger adsorption times; only the curve for $E_{\text{kin}} = 0.71$ eV reaches this value in figure 8(a). This observation is in agreement with results of Larsen and Chorkendorff [49] for CH$_4$ on Ni(1 1 1) at sample temperatures above 350 K, who could model their data with the same saturation coverage independent of particle energy, using a first-order adsorption process.

Figure 8(b) shows the same experiment performed at a surface temperature of 120 K for increasing kinetic energy of the impinging CH$_4$ molecules. The kinetic energy was changed by varying the nozzle temperature between 773 and 1273 K at a fixed seeding ratio of 5% CH$_4$ in He, or by varying the seeding ratio between 2.5 and 5% of CH$_4$ in He or using a pure methane beam at a fixed nozzle temperature of 1273 K. At the surface temperature of 120 K, CH$_3$ is formed on the surface independent of the energy of the methane molecules [26], with small amounts of CH (due to radiation damage). The data in figure 8(b) show the total C coverage; for the lowest and highest kinetic energies, the individual contribution of CH$_3$ is included in addition (dashed lines), indicating that the amount of CH (due to radiation damage) at the highest coverages is on the order of 0.01 ML and the overall behaviour does not change. For the initial sticking coefficient (i.e., the initial slope of the curves), again an increase with increasing kinetic energy is observed. Interestingly, the curves for $E_{\text{kin}} = 0.58$ and 0.71 eV show almost identical behaviour, both in slope and saturation coverage. Since the beam with $E_{\text{kin}} = 0.58$ eV has been produced with a higher nozzle temperature (1273 versus 1073 K for the beam with $E_{\text{kin}} = 0.71$ eV), this is attributed to the enhanced sticking coefficient for vibrationally excited methane molecules (see above).

Inspection of figure 8(b) reveals that in contrast to the situation at 300 K, the saturation coverage at 120 K depends on the kinetic energy of the impinging molecules. For the highest kinetic energy used (0.83 eV), a total coverage of about 0.17 ML is reached. A possible explanation for this observation could be that at 120 K, all the hydrogen atoms from the dissociation are still adsorbed on the surface, in contrast to the experiments at 300 K. The higher impact energy could lead to some displacement of hydrogen, which is not possible at low energies, allowing more methyl fragments to adsorb. Alternatively, the sticking coefficient for a given kinetic energy could be significantly lowered by the presence of hydrogen, leading to a lower apparent saturation coverage. In other words, using significantly higher doses than used here might lead to a higher surface coverage with CH$_3$ also for the lower kinetic energies. A possible influence on the adsorption behaviour by contaminating species can be excluded for two reasons. Firstly, except for some small amounts of CO, which are not correlated to the observed behaviour, no contamination could be observed in XPS. Secondly, it is possible to observe an additional uptake on a surface apparently saturated at a given kinetic energy (e.g., as obtained in figure 8(b)) by using methane molecules with higher kinetic energy (data not shown).
Figure 8. (a) Adsorption behaviour of methane on Pt(1 1 1) at 300 K for different kinetic energies of the molecules, generated by varying the nozzle temperature for a fixed seeding ratio of 5% methane in helium. Shown is the total coverage, as determined from a quantitative analysis of the C 1s spectra. (b) Adsorption behaviour of methane on Pt(1 1 1) at 120 K for different kinetic energies of the molecules, generated by varying the nozzle temperature and the seeding ratio of methane in helium. The dashed lines show the CH₃ signals only, while the solid lines represent the total C 1s intensity, including the radiation damage product CH. (c) Total surface coverages versus adsorption time, derived from quantitative analysis of C 1s spectra for methane adsorption at different surface temperatures ranging from 120 to 400 K. The adsorption was always performed using a seeded beam with 5% CH₄ in He and a nozzle temperature of 1073 K.
In addition to 120 and 300 K, we have also measured the sticking coefficient at other temperatures for a kinetic energy of 0.71 eV, obtained by a seeding ratio of 5% methane in He at a nozzle temperature of 1073 K. The corresponding data are shown in figure 8(c) for surface temperatures between 120 and 400 K. The data are obtained from separate experiments as the ones in figures 8(a) and (b) and, thus, the curves for 120 and 300 K are not identical to the data shown there; the deviations are in the range of the estimated error bars. Interestingly, for 240 K the lowest carbon coverage is obtained, even showing a small decrease after a maximum. At this surface temperature, which is close to the rate maximum of recombinative desorption of methane from Pt(1 1 1) around 260 K, a spectral change with adsorption time is observed (spectra not shown). Starting with spectra typical for CH$_3$, the conversion to CH by dehydrogenation is observed. The hydrogen formed in this process remains at the surface; it obviously blocks adsorption sites for additional C-containing species, which leads to a saturation coverage of $\sim 0.10$ ML.

The adsorption behaviour at 280 and 300 K leads to the same saturation coverage of $\sim 0.17$ ML, albeit at a different slope. This is probably due to a higher dissociation probability at the higher surface temperature or due to different amounts of coadsorbed hydrogen present at the surface, which partially desorbs in that temperature range. In both cases CH is the stable C-containing species on the surface, identified by its binding energy and the characteristic vibrational splitting of the C 1s signal [26]. The observation that the saturation coverages at 280 and 300 K are not much higher than at 120 K, although different adsorbates are found on the surface, could be explained by the relatively high coverage reached at this kinetic energy already at 120 K, as seen in figure 8(b).

For 400 K, a significantly higher total C coverage was observed. The hydrogen desorption [38] and, thus, the generation of free adsorption sites could cause this increase. Additionally, at this temperature already the complete dehydrogenation to C takes place to some extent, as can be observed by spectral changes with increasing adsorption time (data not shown). This is in agreement with the starting CH dissociation observed in the TPXPS data in figure 4, considering the heating rate applied there. Experiments using a surface temperature of 500 K (data not displayed) show the same behaviour and lead to even higher carbon coverages. At this temperature, carbon was found as the only detectable species on the surface.

We now will address the energy dependence of the initial sticking coefficient in more detail. Due to the fact that we cannot determine the absolute impingement rate of methane on the surface, only relative initial sticking coefficients could be derived from the initial slopes (in ML s$^{-1}$) of the curves shown in figures 8(a) and (b), which all have been measured using the same methane flux. As a word of caution, we have to mention here that a coverage can only be given reliably, if it is above $\sim 0.01$ ML; this, however, represents already 5–10% of the saturation coverage and prevents the accurate determination of the initial sticking coefficient in the true zero-coverage limit. Besides the expected increase of the initial sticking coefficient with increasing kinetic energy and vibrational excitation, we observe different values for the same molecular beam properties but different surface temperatures in figure 8. While a behaviour like this has been reported by Oakes et al before [15], the relative changes are, however, inverted: whereas these authors observe an increase in the initial sticking coefficient by going from a surface temperature of 150 to 550 K, we initially observe a decrease by going from 120 to 300 K. This is evident from the initial slopes in the curves displayed in figures 8(a) and (b). By analysing the data of figure 8(c), we find that both results are not in contradiction. On changing the surface temperature from 300 to 400 K, the initial slope, indeed, increases again. We explain the smaller values in the temperature range around 300 K by the simultaneous recombinative desorption of
methane, which reduces the effective surface coverage and, thus, reduces the observed initial slope.

Finally, when using higher nozzle temperatures to increase kinetic energy and vibrational excitation of the incoming CH₄ molecules, one has to consider the possibility of dissociation in the nozzle, which would yield an increasing contribution of cracking fragments to the impinging flux. Since the sticking coefficient of methane is small, but the sticking coefficients of fragments are expected to be high (close to unity), one would obtain apparently higher surface coverages, due to the additional adsorption channel; this would yield an apparent increase of the initial sticking coefficient and, thus, a change in curvature of curves for the initial sticking coefficients versus kinetic energy in case of fixed seeding ratio. This, however, is not observed in our data. Since also no other reaction products, like higher hydrocarbons, could be observed on the surface, we are confident to exclude thermal cracking up to 1273 K.

4. Summary

Using a combination of supersonic molecular beams and in situ high-resolution XPS, we have investigated the activated adsorption of methane on Pt(1 1 1) at surface temperatures between 120 and 500 K. By heating the nozzle and/or seeding with He, the kinetic energy of the methane molecules was varied from 0.30 to 0.83 eV. By heating the nozzle up to 1273 K, in addition vibrational excitation of the methane molecules is achieved.

At a surface temperature of 120 K, independent of kinetic energy of the incoming methane molecule, the adsorbed surface species is methyl (CH₃). In the C 1s spectra, a fine structure is resolved that is attributed to vibrational excitations in the photoemission process; the vibrational splitting for CH₃ is 400 meV with an S-factor (i.e., the ratio of the first excited to the adiabatic peak) of 0.50. The thermal evolution of the adsorbed layer was studied by TPXPS: at ~260 K, CH₃ partly dehydrogenates to CH and partly recombines with H to form gaseous CH₄; the latter is also observed in a separate TPD experiment. Above a certain initial CH₃ coverage prepared at 120 K, the amount of CH formed during heating is always 0.04 ML. Measurements with increasing kinetic energies show an increase in the initial sticking coefficient, as expected for activated adsorption. Furthermore, a strong increase in the initial sticking coefficient is also observed for vibrationally excited molecules. Interestingly, the saturation coverage of CH₃ at 120 K also increases with beam energy.

At a surface temperature of 300 K, CH is directly formed as a stable surface species. The C 1s spectra exhibit vibrational splitting by 420 meV and an S-factor of 0.16. The sticking coefficient at 300 K increases again with kinetic energy of the methane molecules, as expected, and the saturation coverage of CH converges to the same value for different energies. It is important to note that the formation of CH can be induced not only by surface temperature, but also by the highly intense photon beam. Thus, great care has been taken to minimize the influence of beam damage.

In addition, we have also investigated the adsorption and thermal evolution of ethylene on Pt(1 1 1). The reason was twofold: (1) from the known saturation coverage of 0.25 ML, we are able to calibrate the CH₃, CH and C coverages. (2) In previous studies, ethylidyne was reported as a reaction product upon heating a methyl layer. From the known reaction route from ethylene to ethylidyne, we were able to confirm our proposed reaction pathway from CH₃ to CH, by comparison. The ethylene C 1s spectra exhibit a vibrational splitting of 388 meV with an S-factor of 0.25. Comparison of the S-factors in our data for CH₃ (methyl), CH₂ (in ethylene)
and CH (methylidyne) yields values of 0.50, 0.36 and 0.16, respectively, which nicely scale with the number of C–H bonds as expected [29], yielding 0.17 ± 0.02 per C–H bond.

Upon heating, we observe the reaction of ethylene to ethylidyne at ~290 K; simultaneously ~40% of ethylene desorbs. A detailed inspection of the C 1s data in this temperature range reveals the existence of an intermediate species with a binding energy very close to that for CH; by comparison with literature, this species can be identified as ethylidene.

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