Ethylene adsorption on Pd(111) studied using infrared reflection–absorption spectroscopy

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Abstract

The adsorption of ethylene has been studied on clean and hydrogen-covered Pd(111) using reflection–absorption infrared spectroscopy and molecular beam methods. Using a correlation diagram, in which vibrational frequencies are plotted versus a $\sigma\pi$ parameter proposed by Stuve and Madix, shows that ethylene is substantially rehybridized on Pd(111) having a $\sigma\pi$ parameter intermediate between those of ethylene on Ni(111) and Ru(001). In contrast, when ethylene adsorbs on hydrogen-covered Pd(111), only π-bonded species are detected. An additional species appears exhibiting a characteristic frequency of 957 cm^{-1} when Pd(111) is cooled to ~80 K and the system pressurized with ~10^{-5} Torr of ethylene. This species also appears on a CO-saturated Pd(111) surface. Molecular beam measurements show that its coverage reaches ~1.3 ML indicating that it is due to ethylene adsorbed in the second and subsequent layers. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The adsorption of ethylene has been extensively studied on noble metal surfaces since these catalyze the hydrogenation of unsaturated carbon–carbons bonds [1]. Two major species are found on close-packed (1 1 1) surfaces, consisting of ethylidyne that generally forms at or above 300 K, and more weakly bound molecular species that are present at lower temperatures. The adsorption of ethylene has perhaps been the most extensively studied on Pt(1 1 1), where both di-σ- and π-bonded species have been identified using second-harmonic generation [2] and infrared spectroscopy [3,4]. The di-σ-bonded species forms following adsorption on clean Pt(1 1 1) at low temperatures and π-bonded ethylene appears as the system is pressurized. Similar chemistry is found on Pd(1 1 1), which is also an excellent hydrogenation catalyst, although there are subtle differences between platinum and palladium. For example, ethylidyne forms more slowly on Pd(1 1 1) than on Pt(1 1 1) [5]. This allows us to examine molecularly adsorbed ethylene on Pd(1 1 1) without any ethylidyne species forming. In addition, near-edge X-ray absorption fine structure (NEXAFS) [5] and high-resolution electron energy loss (HREELS) [6]

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spectroscopies suggest that ethylene is π-bonded on Pd(1 1 1), although recent density functional calculations [7] have led to the suggestion that both π- and di-σ-species should have approximately the same stabilities on the surface. The adsorption of small hydrocarbons is of additional interest on palladium since this is of potential use as a hydrodechlorination catalyst [8]. Since vibrational spectroscopy appears to be a more sensitive gauge of the extent of rehybridization of small unsaturated hydrocarbons on transition metal surfaces [9,10] than photoelectron spectroscopy or NEXAFS, we have reexamined the adsorption of ethylene on Pd(1 1 1), both in ultrahigh vacuum and under pressures of ethylene. In addition, since hydrogen is also present on the surface during hydrogenation reactions, we have further examined the effect of hydrogen on the adsorption of ethylene.

2. Experimental

Infrared data were collected using a system that has been described previously [11]. A palladium single crystal was mounted in a modified $2.75''$ six-way cross equipped with infrared-transparent, KBr windows. It could be resistively heated to 1200 K, or cooled to 80 K using liquid nitrogen. Infrared spectra were collected using a Bruker Equinox infrared spectrometer and a liquid-nitrogen-cooled, mercury cadmium telluride detector. The complete light path was enclosed and purged with dry, CO_2-free air. Data were typically collected for 1000 scans at 4 cm^{-1} resolution.

Molecular beam data were collected in another ultrahigh vacuum chamber that has been described in detail elsewhere [12] where coverages were measured from the change in background pressure after the sample had been moved to intercept the beam in a so-called King and Wells experiment [13].

The Pd(1 1 1) sample was cleaned using a standard procedure which consisted of heating at 1000 K in $\sim 4 \times 10^{-8}$ Torr of oxygen and then annealing at 1200 K in vacuo to remove any remaining oxygen. Since the carbon KLL Auger feature is effectively obscured by a strong palladium peak,

Auger spectroscopy is insensitive to the presence of small amounts of surface carbon. A sensitive gauge of carbon coverage was to saturate the surface with oxygen and to perform a temperature-programmed desorption experiment. The presence of surface carbon is manifest by the desorption of CO. As the surface becomes depleted of carbon, the CO yield decreases and the yield of oxygen increases correspondingly. The complete absence of carbon is indicated by the desorption of only O_2.

Ethylene (Matheson), CO (Linde, Research Grade) and hydrogen (Gas Tech, CP Grade) were transferred to glass bottles and attached to the gas-handling systems of the vacuum chambers. Ethylene was further purified by several freeze-pump-thaw cycles. CO was transferred to a glass bottle and any less volatile impurities, particularly iron carbonyl, were condensed into a liquid-nitrogen cooled cold finger. C_2D_4 (Cambridge Isotopes, 98% D) and deuterium (Linde, CP Grade) were used as received. The cleanliness of all reactants was monitored mass spectroscopically.

3. Results

It has been shown previously that the reflection–absorption infrared spectrum (RAIRS) of ethylene (5 L, 1 L = 1×10^{-6} Torr s) adsorbed on clean Pd(1 1 1) at a sample temperature of 80 K displays a single intense feature at $\sim$1100 cm^{-1}, with a weaker C–H stretching mode apparent at 2914 cm^{-1} [14]. The 1100 cm^{-1} feature was assigned to a CH_2 wagging mode, and is substantially shifted from the gas-phase value of 948 cm^{-1} [15], suggesting that ethylene has undergone substantial rehybridization on the surface. This will be discussed in greater detail below. Fig. 1(a) shows the corresponding spectrum for ethylene adsorbed on a hydrogen pre-saturated Pd(1 1 1) surface (formed using a hydrogen exposure of 5 L [14]), where the spectrum is completely different to that found on clean palladium, so that adsorbed hydrogen appears to have a profound effect on the state of adsorbed ethylene. The spectrum now displays a sharp C–H stretching mode at 3012 cm^{-1} and a broad feature at $\sim$935 cm^{-1}. The
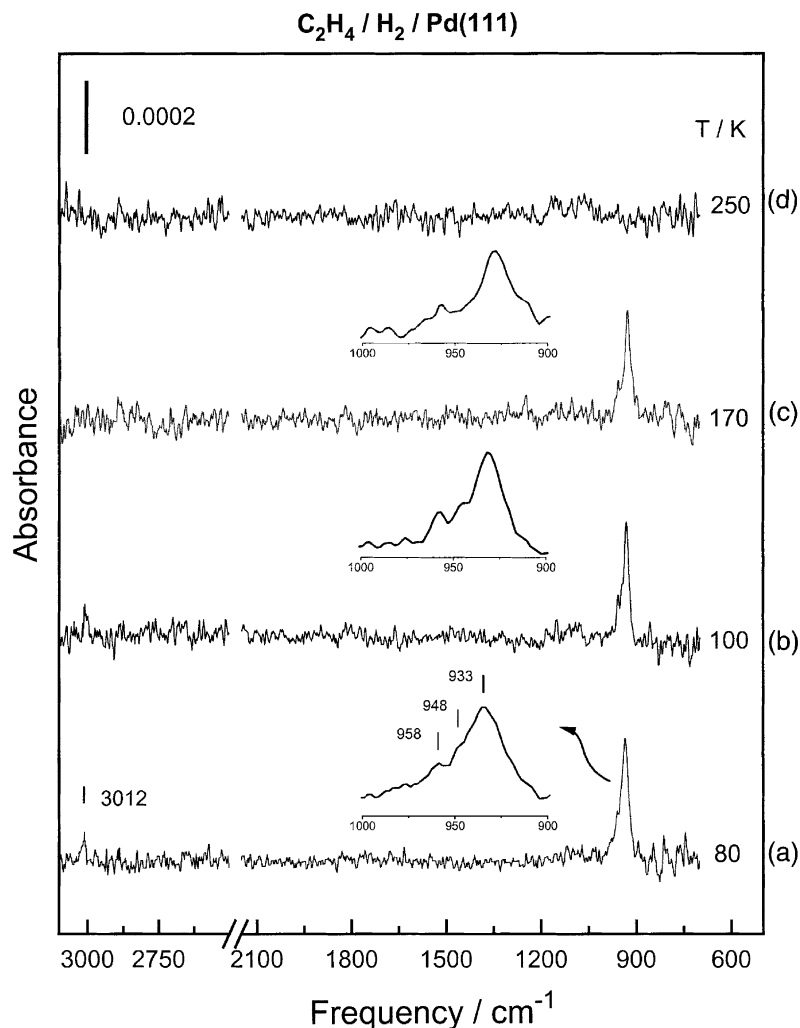
Fig. 1. RAIRS of 5 L of ethylene adsorbed on a surface predosed with 5 L H_2 ($\Theta(H) = 1.0$) at 80 K and annealed to various temperatures. The annealing temperatures are displayed adjacent to the corresponding spectrum.

935 cm^{-1} peak has been expanded and is displayed as an inset adjacent to each feature. This reveals that the feature comprises three peaks at 933, 948 and 958 cm^{-1}. Fig. 1(b)–(d) show the effect of annealing the sample in vacuo, where the annealing temperatures are displayed adjacent to the corresponding spectrum. The spectrum is only slightly changed on heating to 100 K, but, after warming to 170 K, both the 3012 and 948 cm^{-1} features are absent, while the 933 and 958 cm^{-1} peaks persist. These are both removed when the sample is warmed to 250 K. This implies that two

ethylenic species are present on H/Pd(1 1 1), one more weakly bound displaying infrared features at 948 and 3012 cm^{-1}, and another with vibrational modes at 933 and 958 cm^{-1}. Note that, assuming that the features between 933 and 958 cm^{-1} are due to CH_2 wagging modes, ethylene on hydrogen-covered Pd(1 1 1) is substantially less distorted than on the clean surface.

It was found on Pt(1 1 1) that, although di-σ-bonded ethylene formed on the clean surface in ultrahigh vacuum [3], π-bonded ethylene appeared when the sample was pressurized [4]. This

experiment was repeated for Pd(1 1 1) and the results displayed in Fig. 2. Fig. 2(a) reproduces the 1100 and 2910 cm^{-1} features found previously [14] and Fig. 2(b)–(d) show the effect of pressurizing the surface with ethylene at a sample temperature of 80 K. The 1100 and ∼2910 cm^{-1} features persist as the surface is pressurized up to 5×10^{-5} Torr, confirming the continued presence of distorted ethylene on the surface, while an intense feature appears at 957 cm^{-1} accompanied by a much less intense C–H stretching mode at 3090 cm^{-1}. These

frequencies are very close to those assigned to π-bonded ethylene on Pt(1 1 1) (with vibrations at 954 and 3090 cm^{-1} respectively). The frequency of 957 cm^{-1} is also extremely close to that of 958 cm^{-1} for ethylene on hydrogen-covered Pd(1 1 1) (Fig. 1) but is not accompanied by the more intense 933 cm^{-1} mode and is therefore assigned to a different surface species. In addition a peak is detected at 1437 cm^{-1} at higher ethylene pressures. This ethylenic species adsorbs reversibly on the surface and is completely removed, either by
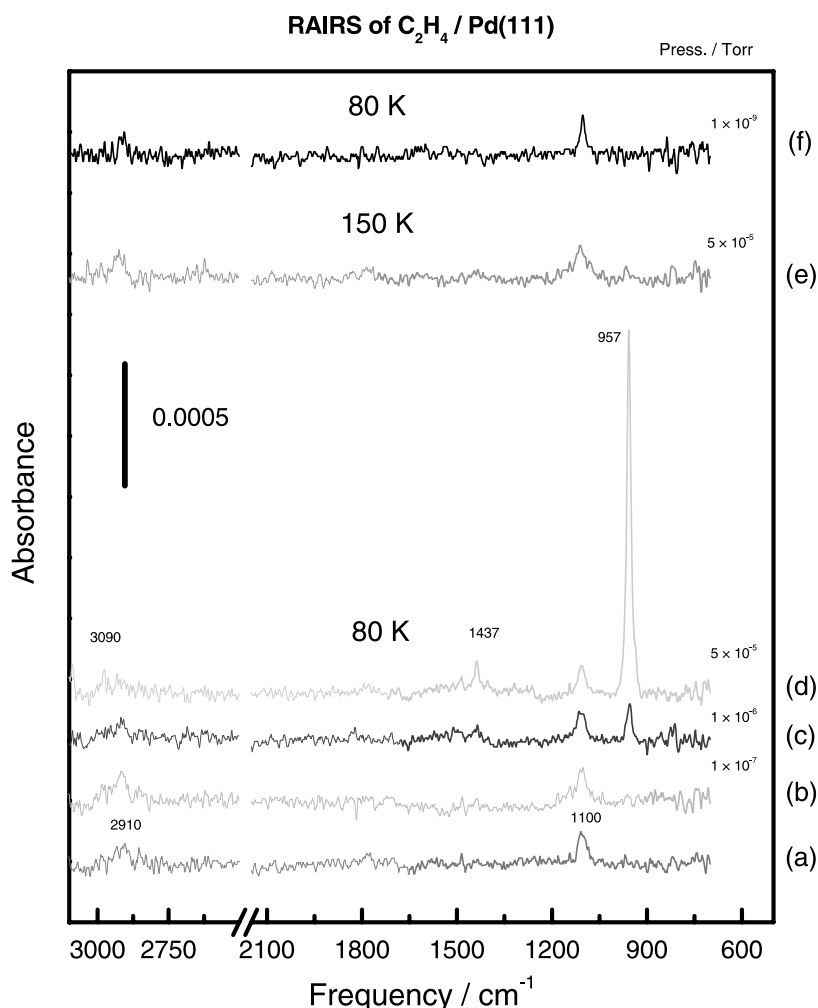

Fig. 2. RAIRS of (a) 5 L of ethylene adsorbed on clean Pd(1 1 1) at 80 K and (b–d) as a function of ethylene pressure. Ethylene pressures are marked adjacent to the corresponding spectrum. Spectrum (e) shows the effect of heating a sample pressurized to 5×10^{-5} Torr of ethylene to 150 K and (f) evacuating below 1×10^{-9} Torr.

heating a pressurized surface to 150 K (Fig. 2(e)) or by evacuating to $<1 \times 10^{-9}$ Torr (Fig. 2(f)). The most striking aspect of the spectrum measured by pressurizing with $\sim 5 \times 10^{-5}$ Torr of ethylene is the large intensity of the CH_2 wagging mode, which has a peak absorbance of $\sim 1 \times 10^{-3}$ compared to $\sim 1.4 \times 10^{-4}$ for the 1100 cm^{-1} peak due to a saturated ethylene overlayer ($\Theta(C_2H_4) = 0.33$ [16], where coverages are referenced to the palladium atom site density on the (1 1 1) surface). This implies that either the ethylene that displays the peak at 957 cm^{-1} has an extremely high absorption cross section, or its coverage is extremely high.

Assuming that its absorption cross section is similar to that for ethylene on clean Pd(1 1 1) yields a coverage of approximately 3 ML and would imply that this state is due to multiple layers of ethylene. This point will be addressed further below.

These experiments were repeated using C_2D_4 and the results are displayed in Fig. 3. Fig. 3(a) shows the spectrum for d_4-ethylene adsorbed on hydrogen-covered Pd(1 1 1) at 80 K displaying a feature at ~ 704 cm^{-1}, which corresponds to the ~ 933 cm^{-1} feature shown in Fig. 1. The frequency of this mode for gas-phase ethylene is shifted by a ratio of 1.32 due to deuteration and the shift from
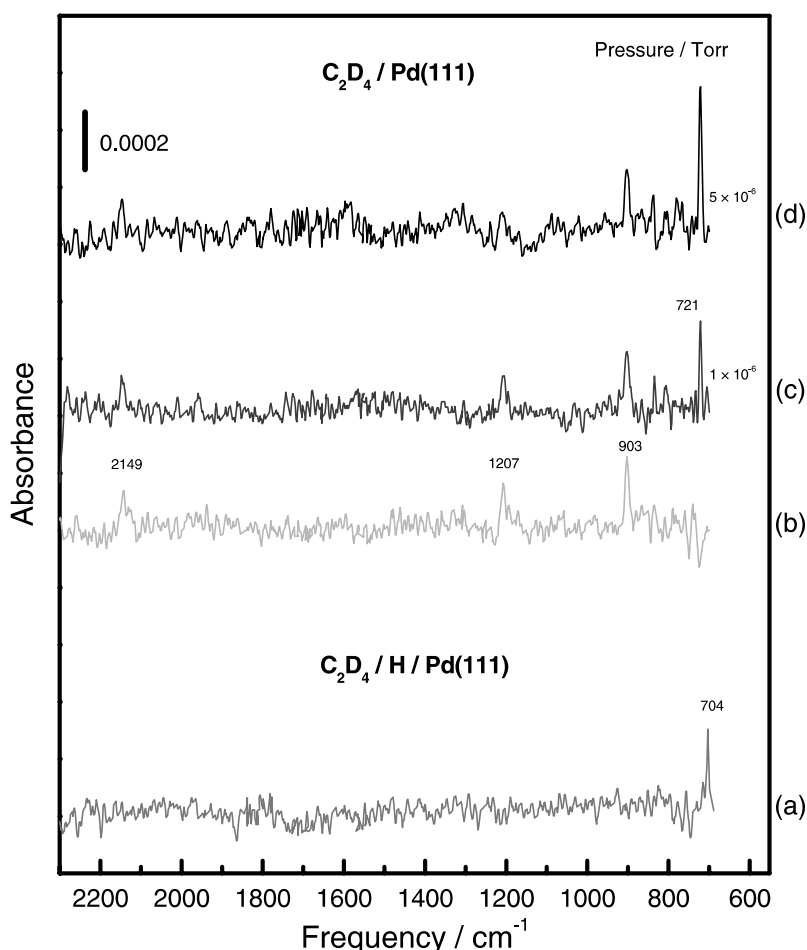

Fig. 3. RAIRS of (a) 5 L of C_2D_4 adsorbed on hydrogen pre-covered Pd(1 1 1) (hydrogen exposure 5 L, $\Theta(H) = 1.0$) at 80 K, and (b) C_2D_4 adsorption (5 L) at 80 K on clean Pd(1 1 1) and (c,d) the effect of pressurizing clean Pd(1 1 1) with C_2D_4 where C_2D_4 pressures are marked adjacent to the corresponding spectrum.

933 to 704 cm^{-1} is consistent with this. The spectrum for d$_4$-ethylene adsorbed on clean Pd(1 1 1), Fig. 3(b), displays peaks at 2149, 1207 and 903 cm^{-1}. The effect of pressurizing with ethylene is shown in Fig. 3(c) and (d), where a 721 cm^{-1} feature grows with increasing pressure corresponding to the intense 957 cm^{-1} feature detected for normal ethylene (Fig. 2(c)–(e)). Again, the intensity of the 721 cm^{-1} feature is substantially larger than that for C$_2$D$_4$ adsorbed at 80 K. If the absorption cross section for this state is similar to that for other adsorbed ethylenic species, the ethylene must form multilayers on the surface. Note, however, that the vapor pressure of ethylene at 80 K is 7.3×10^{-4} Torr [17] and should therefore not condense onto the surface. It was also found that the heat of adsorption of the species giving rise to the 954 cm^{-1} feature on Pt(1 1 1) [18], assigned to π-bonded ethylene, was 40 ± 10 kJ/mol, substantially higher than the sublimation energy of ethylene, $\Delta H_{sub} = 18.3$ kJ/mol [19]. It may, however, adsorb due to an interaction between ethylene and a polarized chemisorbed species which may cause it to bond more strongly. From previous molecular beam results, weakly adsorbed ethylene has been suggested to be present on top of an ethylene-saturated Pt(1 1 1) surface [20] and the presence of second-layer propylene on Pt(1 1 1), identified spectroscopically, has recently been reported [21]. If this is the case, similar ethylenic species should be observed on other chemisorbed overlayers. In order to probe this effect, we have examined the adsorption of ethylene on a CO-saturated surface. The strong infrared signal of CO will, in addition, show whether CO is being displaced from the surface or, since the CO stretching frequency is sensitive to adsorption site, will allow any changes in the substrate structure to be measured. The results of this experiment are illustrated by the infrared spectra displayed in Fig. 4. Fig. 4(a) shows the infrared spectrum of a saturated overlayer of CO ($\Theta(CO) = 0.75$ [22]) adsorbed on Pd(1 1 1) by cooling from 300 to 80 K in the presence of CO, and is in good agreement with that found by others [23]. The feature at $\sim$2106 cm^{-1} is due to CO adsorbed on the atop site while the doublet at 1894 and 1956 cm^{-1} is due to CO in the face-centered cubic (fcc) and hexagonal-close packed

(hcp), threefold hollow sites, respectively [24]. This surface was then pressurized with ethylene with the sample held at 80 K, and the infrared spectra recorded, but using the spectrum of the CO-covered surface as a background. The spectra are shown in Fig. 4(b)–(d) as a function of ethylene pressure. It is clear that the intense 957 cm^{-1} feature also appears on CO-saturated Pd(1 1 1) along with the 1437 cm^{-1} feature detected on ethylene-covered Pd(1 1 1), as well as the C–H stretching mode at 3096 cm^{-1}. This confirms the possibility that ethylene can adsorb, when pressurized, on a pre-covered surface. Changes are also observed in the CO vibrational spectrum. For example, the intensity of both the atop and fcc CO decreases substantially with increasing ethylene pressure, while the intensity of the hcp CO increases. This implies that the CO overlayer is being substantially perturbed by the presence of the ethylene. Fig. 4(e) shows the effect of evacuating the cell to $<1 \times 10^{-9}$ Torr. All of the ethylene is removed from the surface while the CO atop site population remains diminished and the fcc population enhanced. This is emphasized by the data in Fig. 4(f) which shows the RAIRS spectrum of the surface after heating to 600 K to desorb all CO. However, the total CO coverage remains the same indicating that no CO has been displaced from the surface.

It is evident that the species characterized by peaks at 957, 1437 and 3090 cm^{-1} appears when ethylene- and CO-covered surfaces are pressurized by ethylene when the sample is held at 80 K. The saturation peak absorbance of the 957 cm^{-1} feature is $\sim 10^{-3}$ on an ethylene-covered surface and $\sim 6 \times 10^{-4}$ for a surface covered by CO. These values are substantially larger than for other di-σ- and π-bonded ethylene species found on the Pd(1 1 1) surface. This immediately suggests that the coverage of this species is relatively high and, in particular, far too high to be assigned to a species adsorbed on the metal surface. Note, however, that the peak absorbance of the CH$_2$ wagging mode can be of the order of 10^{-3} for a monolayer of adsorbed ethylene, as exemplified by the adsorption of ethylene on Ag(1 1 1) [25]. In addition, we have previously suggested that it is possible to adsorb species onto the surface in the presence of a carbonaceous overlayer, where these
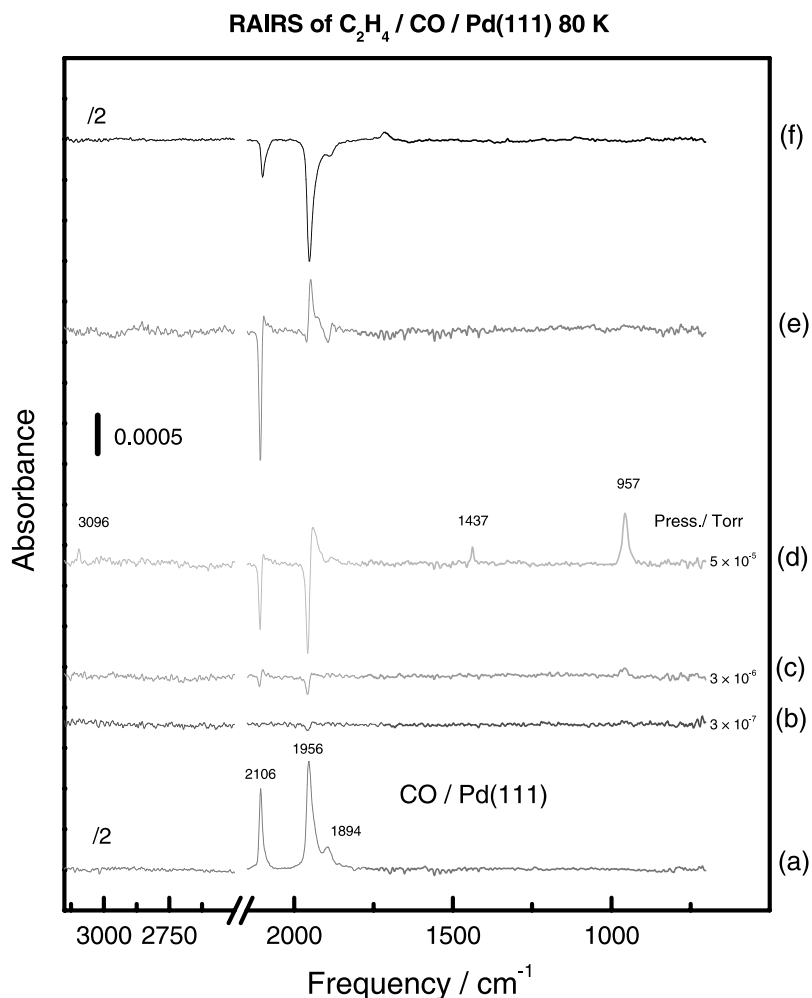
RAIRS of C$_2$H$_4$ / CO / Pd(111) 80 K

Fig. 4. RAIRS of (a) CO/Pd(1 1 1) (Θ(CO) = 0.75) at 80 K, (b–d) following adsorption of ethylene on CO-saturated Pd(1 1 1) as a function of ethylene pressure using the CO saturated surface as a background, where the ethylene pressures are marked adjacent to the corresponding spectrum, and (e) the spectrum found following evacuation to 1×10^{-9} Torr and (f) after heating to 600 K.

have been detected using infrared spectroscopy and by molecular beam methods [12,26]. In order to measure the coverage of this species, we have carried out molecular beam experiments on a Pd(1 1 1) surface at 80 and 150 K. The results for these experiments are shown in Fig. 5 which plots the reversibly adsorbed ethylene coverage as a function of ethylene flux at 80 (■) and 150 K (▲). After saturating the ethylene overlayer (Θ_{sat}-(C$_2$H$_4$) = 0.33), some additional ethylene is adsorbed with an incident flux of ∼0.1 to 10 ML/s at a sample temperature of 150 K (▲) where the

saturation coverage in this case is ∼0.5. When the sample temperature is lowered to 80 K (■), the coverage similarly increase to ∼0.5 ML for an incident flux of ∼0.4 ML/s, and then increases when the flux reaches ∼1.5 ML/s to a coverage of ∼0.85 corresponding to the increase in infrared signal seen in Fig. 2. The coverage continues to increase with increasing pressure so that at a flux of ∼10 ML/s, the coverage is ∼1.3. Note that this coverage exceeds the saturation coverage of CO on Pd(1 1 1) (Θ_{sat} ∼ 0.75 ML [22]). This rules out the possibility of ethylene adsorbing into the
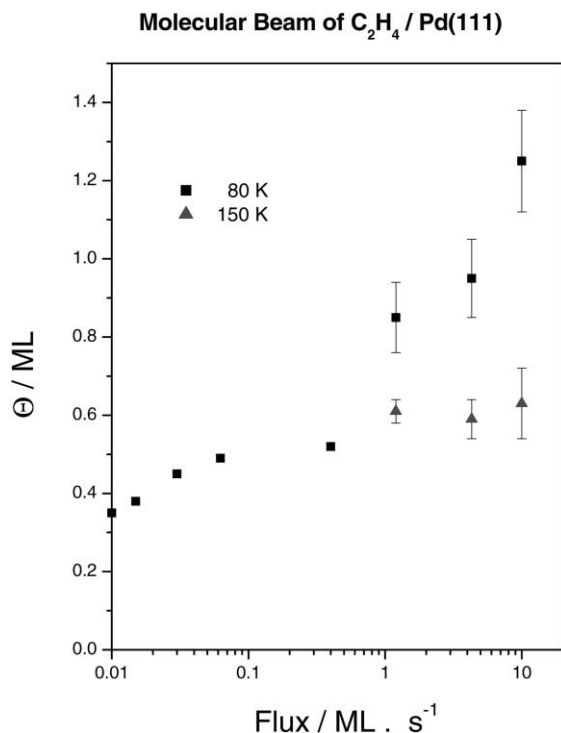
Fig. 5. The coverage of ethylene on Pd(1 1 1) as a function of ethylene pressure measured using the King and Wells method at a sample temperature of 150 K (▲) and at 80 K (■).

first-layer, even with its C=C axis oriented perpendicularly to the surface.

A slight increase in the absorbance of the 1100 cm^{-1} feature is seen in the infrared data of Fig. 2, where this peak has an absorbance of ∼1.2 ± 0.1×10^{-4} when ethylene is chemisorbed in ultra-high vacuum (Fig. 2(a)), and increases to ∼1.4 ± 0.1×10^{-4} when pressurized to 1×10^{-7} Torr (Fig. 2(b)). It is clear from the data of Fig. 5 that some additional ethylene can adsorb onto a surface pressurized with ethylene at 150 K. This additional ethylene is not due to the species that gives rise to the 957 cm^{-1} feature since the infrared spectrum of a Pd(1 1 1) surface pressurized to 5×10^{-5} Torr of ethylene and heated to 150 K (Fig. 2(e)) displays only features at 1100 and 2910 cm^{-1} due to di-σ-bonded ethylene. If the additional ethylene were π-bonded, based on the data shown in Fig. 1, it should appear at ∼930 cm^{-1} with an intensity at least equal to that of the 1100 cm^{-1} feature.

Adsorption isotherms for this additional ethylene are displayed in Fig. 6 for temperatures between 200 and 280 K. In this case, $\Delta\Theta$ represents the additional coverage of ethylene adsorbed onto the surface. Analysis of these data, using a procedure described previously [12], yields a heat of adsorption of 8 ± 2 kJ/mol.

4. Discussion

Ethylene adsorbs on clean Pd(1 1 1) and exhibits vibrational frequencies at 1100 and 2914 cm^{-1} [14]. Assuming that ethylene adsorbs with its molecular plane parallel to the Pd(1 1 1) surface [5,27], the symmetry is lowered to C_{2v}, from D_{2h} in the gas-phase. This symmetry is maintained even if the carbons rehybridize from sp^2 to sp^3, as long as the carbon–carbon bond remains parallel to the surface. Gas-phase A_g and B_{1u} irreducible representations in D_{2h} correlate with A_1 in C_{2v} symmetry [28]. Only modes of A_1 symmetry are active in RAIRS [29] so that, in principle, ethylene adsorbed with C_{2v} symmetry should exhibit four peaks.

These features shift as ethylene rehybridizes and there have been two major approaches to using vibrational spectra to estimate the degree of ethylene rehybridization on transition-metal surfaces from these shifts. The first has been to define a σπ parameter as proposed by Stuve and Madix [9]. This defines two vibrational bands: Band I referring to the higher, and Band II to the lower of the $v(CC) + \delta(CH_2)$ pair. The σπ is defined such that it is 0 for ethylene and 1 for 1,1-dibromoethane. However, it was found, particularly for large values of the σπ parameter, that C_2H_4 and C_2D_4 vibrational frequencies yielded different values of the parameter. Another approach has been to use correlation diagrams in which the degree of rehybridization is represented by the C–C force constant [10]. We have taken an analogous, but slightly different, approach and plotted a correlation diagram using the σπ parameter to represent the extent of ethylene hybridization. Such a plot is shown in Fig. 7. In this case, following a suggestion by Cooper and Raval [30], the vibrational frequencies of $Os_2(CO)_8C_2H_4$ have been used to
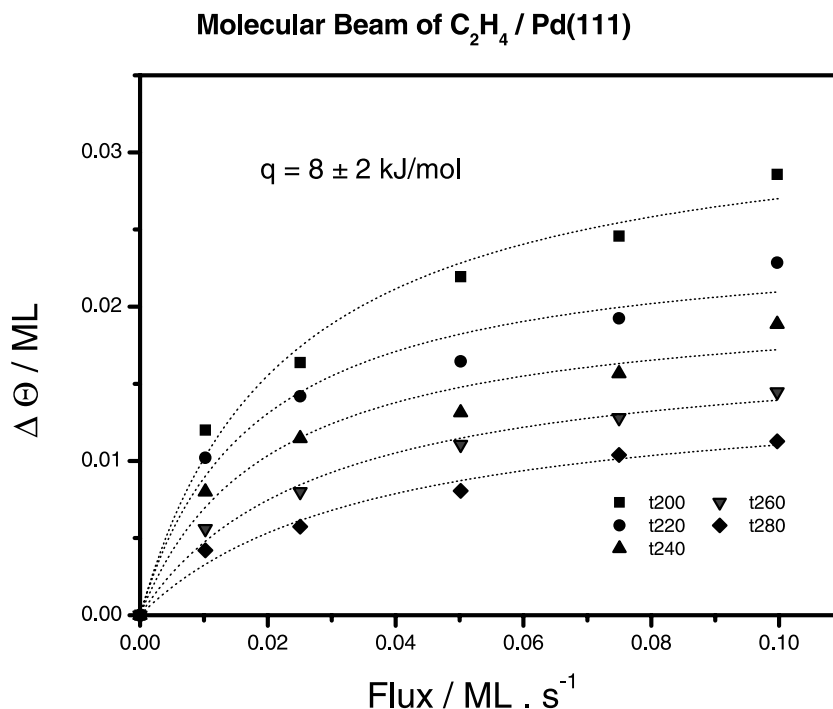
Molecular Beam of C_2H_4 / Pd(111)

Fig. 6. Adsorption isotherms measured using the King and Wells method for ethylene on Pd(1 1 1) at various temperatures: (■) 200 K, (●) 220 K, (▲) 240 K, (▼) 260 K and (◆) 280 K.

represent di-σ-bonded ethylene, since this is likely to more faithfully mimic sp³-hybridized ethylene coordinated to a transition-metal surface. The dotted lines in this figure represent linear interpolations between gas-phase ethylene ($\sigma\pi = 0$) and the osmium cluster ($\sigma\pi = 1$), for modes of A_1 symmetry. These lines cross at two points, at $\sigma\pi \sim 0.4$ and 0.8. Since the modes are all of A_1 symmetry, as their frequencies approach each other, they interact. The extent of this interaction depends on the strength of the coupling between the modes and the resultant normal mode is a linear combination of the individual modes, resulting in the so-called non-crossing rule. Thus the C–C stretching ($\nu(CC)$) and CH_2 scissor ($\delta(CH_2)$) modes mix as the σπ parameter increases from 0 to 0.4 and is the reason that calculation of the σπ parameter requires the use of both frequencies to assess the degree of ethylene hybridization. Also shown plotted onto this figure are the measured vibrational frequencies for Band I (◆) and Band II (▼) for ethylene on various surfaces measured by

HREELS taken from the assignments in Ref. [10]. This illustrates the operation of the non-crossing rule where the measured frequencies are significantly perturbed from the linear interpolations (the dotted line). The vibrational wavefunction for Band I can be represented as $\alpha\Psi(\nu(CC))-\beta\Psi(\delta(CH_2))$, and the vibrational frequency moves to higher values compared to the linear interpolation. The Band II wavefunction is $\gamma\Psi(\nu(CC))+\delta\Psi(\delta(CH_2))$, where vibrational frequencies move to lower values. The magnitudes of α, β, γ and δ depend on the degree of hybridization where $\alpha \sim 1$, $\beta \sim 0$, $\gamma \sim 0$, $\delta \sim 1$ for $\sigma\pi = 0$ and $\alpha \sim 0$, $\beta \sim 1$, $\gamma \sim 1$ and $\delta \sim 0$ for $\sigma\pi = 1$. The shift to higher frequencies for Band I relative to the linear interpolation is approximately equal to the corresponding downward shift for Band II, as expected. However, as the σπ parameter approaches ~ 0.8, the coupling between Band I and Band II decreases so that Band I has primarily $\delta(CH_2)$ character ($\alpha \sim 0$, $\beta \sim 1$). Now, however, the C–C stretching mode frequency approaches that of the
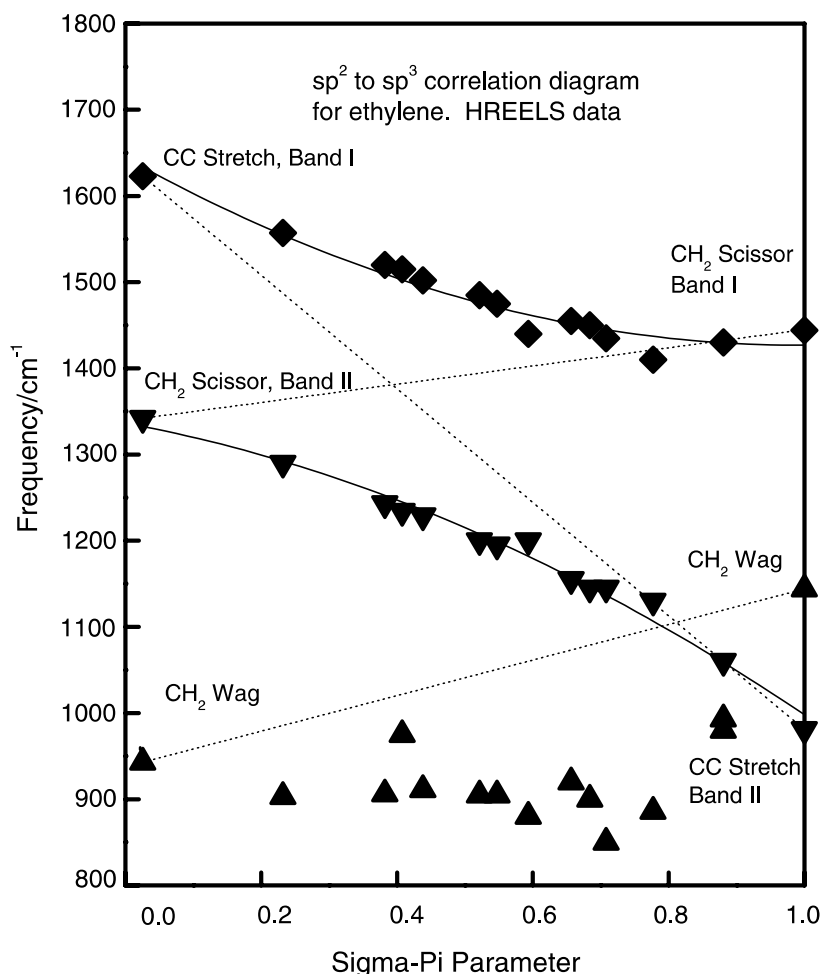
Fig. 7. Correlation diagram of the CH_2 wagging mode ($\omega(CH_2)$, ▲), carbon–carbon stretching mode ($v(C–C)$, ◆) and CH_2 scissor mode ($\delta(CH_2)$, ▼) plotted versus the $\sigma\pi$ parameter using HREELS data taken from Ref. [10].

$\omega(CH_2)$ (wagging) mode so that, at these higher values of the $\sigma\pi$ parameter, this mixing should be taken into account. Ideally, in constructing such a correlation diagram, independent structural information on the degree of hybridization should be available. In the absence of this, we will continue to use the $\sigma\pi$ parameter to represent this quantity, understanding that, at higher values, this will be affected by mixing with the $\omega(CH_2)$ mode.

Significantly less information is available for the RAIRS spectra of ethylene adsorbed on transition-metal surfaces. This is partially due to the difficulty in collecting these data since absorbances are typ-

ically 10^{-4} or less. Indeed, initial studies of ethylene on Ru(0 0 1) were able to detect no signal [31] while subsequent experiments revealed the presence of features at 1130, 1435 and 2950 cm^{-1} with peak absorbances of 10^{-4} [32]. The advantage, however, of RAIRS is that only totally symmetric dipole active modes are detected, while additional impact scattered modes can appear in HREELS. Also, because of the higher resolution of RAIRS, frequencies can be more accurately measured and similar frequencies resolved. A correlation diagram has been plotted using the available RAIRS data in Fig. 8, which also includes data for ethylene-con-
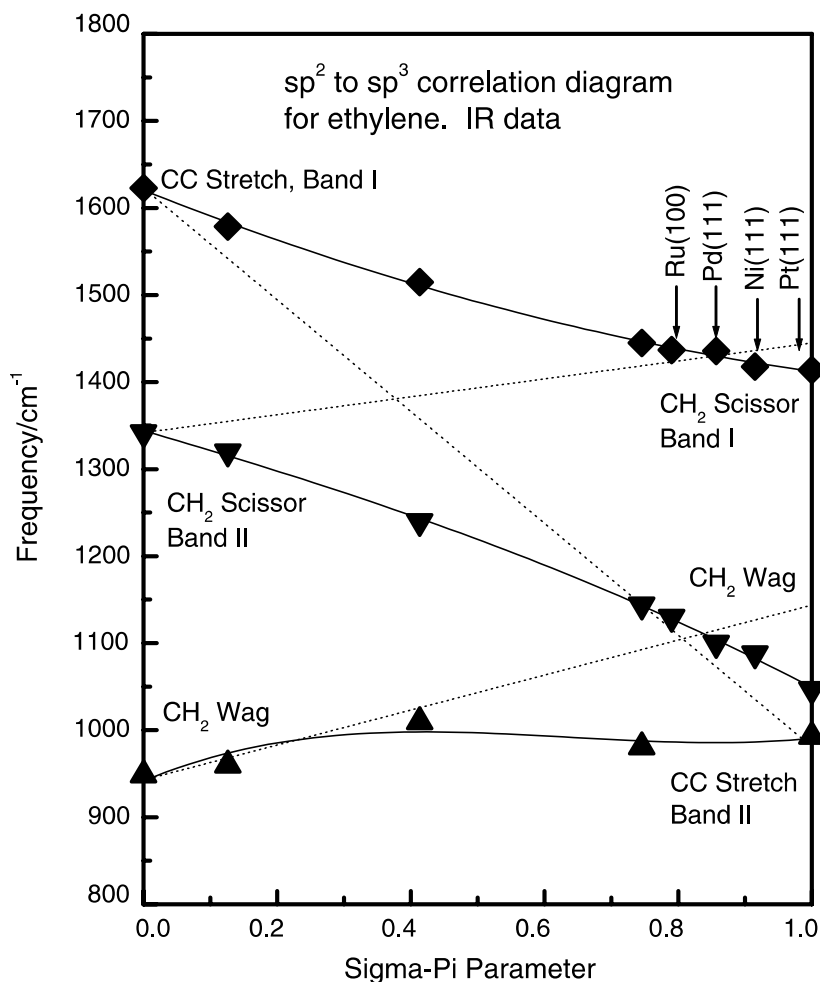
Fig. 8. Correlation diagram of the CH₂ wagging mode (ω(CH₂), ▲), carbon–carbon stretching mode (v(C–C), ◆) and CH₂ scissor mode (δ(CH₂), ▼) plotted versus the $\sigma\pi$ parameter using infrared data. The data used for the plot are summarized in Table 1.

taining organometallics. In addition, the $\sigma\pi$ parameter has been calculated in this case assuming that ethylene on Pt(1 1 1) has a $\sigma\pi$ parameter of unity (while the value from HREELS data is 0.92 [9]). The vibrational frequencies used to construct this curve are summarized in Table 1 and the data for ethylene adsorbed on single crystal surfaces are indicated. The curves for Bands I and II are essentially identical to those measured using HREELS data (Fig. 7). It is striking that the data for the organometallic and adsorbed species all fall on the same smooth lines. The data for Band II and the ω(CH₂) mode at high values of $\sigma\pi$ parameter

have been plotted following the non-crossing rule. The modes at frequencies of ∼990 cm⁻¹ and between 1000 and 1150 cm⁻¹ are therefore due to combinations of v(CC) and ω(CH₂) modes. An additional advantage to plotting the data in this way is that $\sigma\pi$ parameters can be estimated even if both Bands I and II are not detected in the weak RAIRS spectra. For example, the infrared spectrum for ethylene adsorbed on clean Pd(1 1 1) exhibits a peak at 1100 cm⁻¹ (Fig. 2). Reference to Fig. 8 implies that this corresponds to a $\sigma\pi$ parameter of ∼0.87. The corresponding Band I frequency is predicted to be at ∼1425 cm⁻¹ and the

Table 1
Infrared frequencies in cm^{-1} of ethylene clusters, or ethylene adsorbed on close-packed faces of transition metals, measured using infrared spectroscopy

System	$\sigma\pi$ parameter	Vibrational frequency (cm^{-1})		
$C_2H_{4(g)}$ [15]	0	943	1623	1342
$(C_2H_4Ag)^+BF_4^-$ [37]	0.13	960	1579	1320
Zeise's salt [37]	0.41	1010	1515	1240
C_2H_4/Ru(0 0 1) [32]	0.79		1437	1130
C_2H_4/Ni(1 1 1) [30]	0.91		1418	1088
C_2H_4/Pt(1 1 1) [3]	1.00	1047	1414	993
$C_2H_4(CO)_8Os_2$ [38]	0.74	1144	1445	981

These data were used for plotting the graph shown in Fig. 8. Shown also is the $\sigma\pi$ parameter calculated assuming that ethylene on Pt(1 1 1) is sp^3 hybridized ($\sigma\pi$ parameter = 1).

low-frequency mode at ~985 cm^{-1}. These are not detected in the spectrum of ethylene on Pd(1 1 1)([12] and Fig. 2(a)). However, the spectrum for C_2D_4/Pd(1 1 1) (Fig. 3(b)) clearly shows Band I at 1207 cm^{-1}, as well as Band II at 903 cm^{-1}. This is in accord with RAIRS data on other surfaces where the relative intensity of Band I is larger for d$_4$-ethylene than for C_2H_4 [3]. The corresponding frequencies on Ni(1 1 1) are 1418 cm^{-1} for C_2H_4 and 1188 cm^{-1} for C_2D_4, leading to a frequency ratio of 1.19. The $\sigma\pi$ parameter for ethylene on Ni(1 1 1) (0.91, Table 1) is close to the proposed value of 0.87 for C_2H_4/Pd(1 1 1), suggesting that a similar isotope shift should apply to ethylene on Pd(1 1 1). This predicts a Band I frequency of ~1436 cm^{-1}. This value is plotted in Fig. 8 and also results in a $\sigma\pi$ parameter of 0.87. This conclusion appears to contradict previous HREELS [6], photoelectron spectroscopic [26] and NEXAFS data [5] which indicate that ethylene adsorbed on clean Pd(1 1 1) is not substantially distorted from the gas-phase geometry. These results have also been questioned recently as a result of theoretical studies [7] which suggest a combination of π- and di-σ-adsorbed ethylene as the most stable surface composition. In addition, they also appear to differ from the value of $\sigma\pi$ measured from HREELS data of 0.43.

The results of Fig. 1 indicate that the ethylene structure is strongly affected by the presence of hydrogen on the surface since features are detected at 933 and 3012 cm^{-1} on hydrogen-covered

Pd(1 1 1) (Fig. 1). Note that these frequencies are lower than those for the ethylenic species that forms at higher pressures with a CH$_2$ frequency of 957 cm^{-1}, a value which is very close to the gas-phase value of 949 cm^{-1}, and assigned to π-bonded ethylene on Pt(1 1 1) [4]. The data of Fig. 1 reveal that the 933 cm^{-1} peak comprises several features. The components at 948 and 3012 cm^{-1} disappear on heating to 170 K. This temperature coincides with the sharp desorption state seen in temperature-programmed desorption of C_2H_4/H/Pd(1 1 1), at ~120 K [12]. These vibrational frequencies are very close to those of gas-phase ethylene (Table 1) and are assigned to undistorted, weakly bound (π-bonded) ethylene. From the peak desorption temperature of 114 K, a Redhead analysis [33] yields a desorption activation energy of 28 kJ/mol.

The spectrum formed by heating to 170 K reveals two features at 933 and 958 cm^{-1}. These disappear on heating to 250 K coincident with the broad ~230 K ethylene desorption peak [12]. Ethane is also formed in the same temperature range, indicating that the second ethylenic species hydrogenates by reaction with adsorbed hydrogen [12]. The most intense 933 cm^{-1} peak is assigned to a ω-CH$_2$ mode. A similar structure in this feature has been detected for ethylene on atomic-oxygen covered Ag(1 1 0) [34] and ascribed to the appearance of the gas-phase B$_{2g}$ mode (943 cm^{-1}) [15]. This correlates with a B$_1$ mode as the symmetry is reduced to C$_{2v}$ [27] and this irreducible representation transforms as x (which is oriented along the C–C axis [15]). This implies that the π-bonded ethylene might be slightly tilted so that one carbon is somewhat farther away from the surface than the other. The presence of two types of π-bonded ethylene is rather interesting. One possible explanation for this effect is that one ethylenic species interacts directly with a surface hydrogen via one of its p-orbitals. It has been suggested that ethylene hydrogenation takes place by hydrogen from the bulk reacting with the double bond [35]. A similar effect could occur if ethylene adsorbed with one carbon interacting with adsorbed hydrogen. This would certainly account for the tilted geometry and for the appearance of the 958 cm^{-1} along with the 933 cm^{-1}, A$_1$ modes. It may, of course, also be due to ethylene adsorbed at different sites.

The detection of π-bonded ethylene on hydrogen-covered Pd(1 1 1) may also account for the π-bonded species detected by other techniques referred to above. It is extremely difficult to remove final traces of hydrogen from Pd(1 1 1) since the bulk absorbs substantial amounts of hydrogen. Great care was taken to remove all hydrogen in these experiments, while the presence of some residual hydrogen in other experiments may have lowered the hybridization of adsorbed ethylene.

We turn our attention now to the nature of the species formed by pressurizing Pd(1 1 1) with ethylene which exhibits an intense $\omega(CH_2)$ peak at 957 cm^{-1} (Fig. 2). As noted above, the absorbance of this peak is substantially larger than that typically found for ethylene on transition-metal surfaces. Similar intense peaks are also found when a CO-saturated surface is pressurized with ethylene (Fig. 4). Both cases could be due to the formation of an extremely compressed overlayer in which the ethylene has a large absorption cross section. However, the molecular beam data of Fig. 5 show an increase in ethylene coverage under a flux of ~1 ML/s when the sample is held at 80 K, corresponding to the growth of the 957 cm^{-1} ethylene feature in RAIRS (Fig. 2). The coverage continues to increase with increasing pressure up to a value of ~1.3 adsorbed ethylene molecules per exposed palladium atom. It is extremely unlikely that such a large ethylene coverage could be accommodated in the first monolayer and must therefore be assigned to ethylene adsorbing in second and possibly subsequent layers. The infrared spectra of monomeric and dimeric ethylene in argon matrices have been recorded, where the monomer exhibits frequencies of 948 and 1441 cm^{-1} [36]. When a dimer is formed, the 948 cm^{-1} mode frequency increases to 950 cm^{-1} while the 1441 cm^{-1} mode decreases to 1438 cm^{-1} [36]. The detection of peaks at 957 and 1437 cm^{-1} when the surface is pressurized by ethylene (Fig. 2) is consistent with the shifts found in argon matrices.

5. Conclusions

Ethylene rehybridizes when adsorbed on clean Pd(1 1 1) exhibiting a σπ parameter intermediate between those of ethylene on Ni(1 1 1) and Pt(1 1 1). However, the presence of pre-adsorbed hydrogen has a substantial effect on adsorbed ethylene where it is π-bonded on hydrogen-covered Pd(1 1 1). Previous temperature-programmed desorption experiments have shown that π-bonded ethylene on Pd(1 1 1) reacts with adsorbed hydrogen to form ethane. An additional ethylene species is found when CO/Pd(1 1 1) and C_2H_4/Pd(1 1 1) are pressurized with ethylene characterized by an intense peak at ~957 cm^{-1}. Molecular beam experiments, however, reveal that this species can attain coverages up to ~1.3 adsorbed ethylene species per palladium atom on the (1 1 1) surface so that this species is ascribed to ethylene adsorbed in second and subsequent layers.

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