Chapter 3

CO adsorption on Pd model catalysts

The adsorption of carbon monoxide on metal surfaces is probably one of the most studied systems in surface science. CO is a very suitable probe molecule to characterize the different binding sites on catalytic surfaces. The CO/Pd system has been studied by several groups using different surface science techniques [20,42,56-59]. In the group of Goodman at the Texas A&M University PM-IRAS was used to investigate the adsorption of CO on Pd(111) from UHV to millibar pressures in a wide temperature range [10]. Recently, PM-IRAS has been used to investigate Pd supported nanoparticles [60].

The adsorption of CO on Pd(111) and on alumina supported Pd nanoparticles has been characterized in our group using SFG spectroscopy, both under UHV and under more relevant conditions [42,43,59,61,62]. One of the major instrumental disadvantages of SFG is the limited vibrational range of acquisition. Adsorbed species which may be present below 1600 cm^{-1} can not be detected due to instrumental limitations. Another problem is that three-fold hollow sites are underestimated by SFG and thus a direct quantitative analysis of SFG spectra is rather complicated. The slow acquisition time (typically 20-30 minutes per spectrum) and the high cost are further drawbacks of the SFG technique. Recently, a PM-IRAS experimental setup was build up in our group in order to overcome the limitations encountered using SFG spectroscopy. The PM-IRAS technique represents a complementary tool to SFG to perform UHV and high pressure vibrational studies on heterogeneous catalytic surfaces.

The operation of the new PM-IRAS setup was first tested using CO as probe molecule on Pd(111). Previous PM-IRAS and SFG studies on the same system will be used as a

reference for the present measurements. The limitations of SFG spectroscopy previously discussed will be addressed by PM-IRAS.

This chapter is organized as follow:

The first two sections are concerned with the adsorption of CO on Pd(111) under UHV and under high pressure, respectively. CO adsorption was also investigated on a more defective single crystal surface, i.e. Pd(111) surface strongly sputtered. Annealing effects on the CO structures are discussed, as well as a comparison with previous data obtained with SFG. In the closing section some initial results of PM-IRAS investigation on high pressure CO adsorption on Pd nanoparticles are shown. The possibility of CO dissociation on both Pd surfaces is also discussed.

3.1 CO adsorption on Pd(111) at low pressure

Carbon monoxide absorption on metal surfaces is a simple system characterized by a rich behaviour, which can still provide new information on the mechanism of adsorption and interaction between adsorbates. The structure of CO adsorption on Pd(111) surfaces has been extensively studied [20,42,56,57,59]. In particular, LEED experiments identified seventeen distinct ordered structures ranging in coverage from 1/3 to 3/4 ML (monolayer) [63].
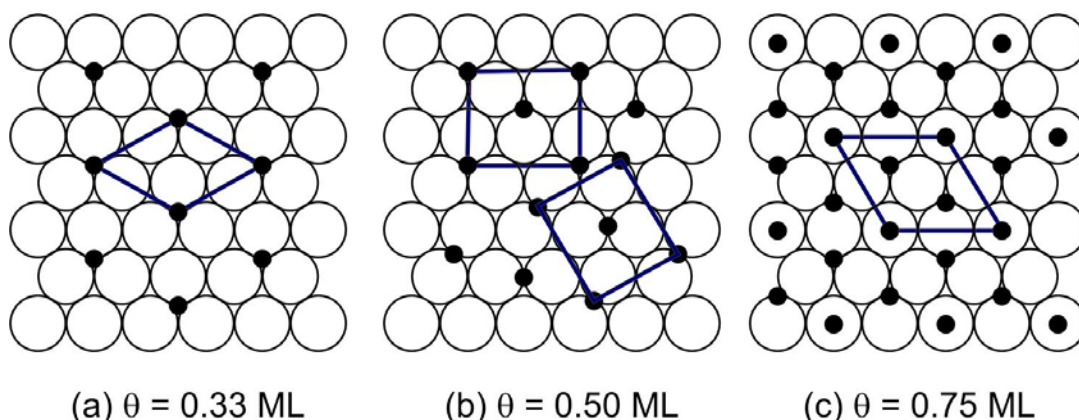

Figure 3.1: Schematic representation of ordered CO overlayers on Pd(111). (a) $\theta_{CO} = 0.33$ ML. (b) $\theta_{CO} = 0.50$ ML. (c) $\theta_{CO} = 0.75$ ML.

An STM study [57] revealed that at a CO coverage of $\theta_{CO} = 0.33$ ML the dominant ordered CO phase corresponds to a $(\sqrt{3}x\sqrt{3})R30°$-1CO structure, where CO occupies primarily fcc hollow sites (Figure 3.1a). When the CO coverage increases to $\theta_{CO} = 0.50$ ML, CO is in a c(4x2)-2CO geometry. In the past this phase was assigned to CO adsorbed on bridge sides, but more recent studies suggested a combination of fcc and hcp sites [64,65]. *Rose et al.* [57] suggested that the c(4x2)-2CO phase coexist in two different geometries where CO occupies either bridge or fcc and hcp hollow sites (Figure 3.1b). The saturation coverage is reached at $\theta_{CO} = 0.75$ ML (Figure 3.1c), where CO occupies atop and 3-fold hollow sites. This (2x2)-3CO phase is characterized by three CO atoms per unit cell, one CO molecule atop and two CO molecules on 3-fold sites

The vibrational frequencies of the C-O bond stretching depend on the different adsorption sites of CO on Pd(111), i.e. IR spectra present distinct features at different coverages. The PM-IRAS spectra in Figure 3.2 show the shift in frequency of the C-O stretching mode depending on coverage. The different adsorption sites (linear on-top, bridge, hollow) are also depicted at the top of Figure 3.2.
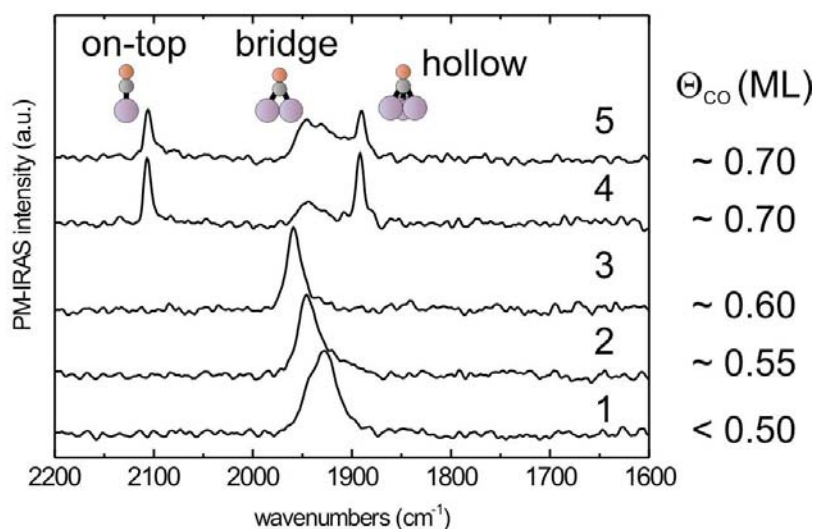

Figure 3.2: PM-IRAS spectra acquired at 10^{-6} mbar CO exposure on Pd(111) at 100 K. Spectrum 5 was acquired after increasing the CO pressure to 10^{-5} mbar at 100 K. Approximate coverages are also indicated.

Initially, for coverages below $\theta_{CO} = 0.50$ ML, CO adsorbs preferentially on 3-fold hollow sites with stretching frequencies from 1830 to 1900 cm^{-1} (spectrum not shown). At

about 1/2 ML coverage, a single peak around 1925-1930 cm^{-1} is observed, which can be attributed to CO adsorbed on bridge and/or hollow sites (Figure 3.2, spectrum 1). Above this coverage the peak continues to shift towards higher frequencies and CO occupies mainly bridge sites (peak around 1950 cm^{-1}; Figure 3.2, spectra 2 and 3). When the coverage approaches 3/4 ML a new CO structure is formed which is characterized by more than one single vibrational feature. The spectrum 4 in Figure 3.2 in 10^{-6} mbar CO corresponds to an approximate coverage of $\theta_{CO} = 0.70$ ML, and shows linear atop (2106 cm^{-1}), bridge (~1945 cm^{-1}) and 3-fold (1890 cm^{-1}) bonded CO. At saturation coverage only linear atop and hollow sites are occupied. Increasing the CO exposure at 100 K to 10^{-5} mbar (Figure 3.2, spectrum 5) did not produce any changes in the vibrational features, i.e. it was not possible to reach a perfect ordered (2x2)-3CO structure under these conditions. At low temperature the CO mobility is quite low, thus at this temperature less ordered structures are easily formed. As reported by *Rupprechter at al.* [42], more ordered structures can be achieved when CO is dosed at higher temperature and then cooled to 100 K in 10^{-6} mbar CO.

Figure 3.3a shows a comparison between a perfect (2x2)-3CO structure (PM-IRAS spectrum 1 and corresponding LEED picture) and a disordered CO structure (PM-IRAS spectrum 2 and corresponding LEED picture). Spectrum 1, corresponding to a coverage of $\theta_{CO} = 0.75$ ML, was obtained by cooling the sample in 10^{-6} mbar CO from 700 K to 100 K, as described in [42]. The peak at 2110 cm^{-1} corresponds to CO sitting on top, and the feature at 1895 cm^{-1} is due to CO on 3-fold hollow sites. The full-width-half-maximum (FWHM) of the on-top and three-fold peaks is 5 and 6 cm^{-1}, respectively. The highly ordered (2x2)-CO structure can be also recognized in the corresponding LEED picture. In Figure 3.3b and Figure 3.3c XPS spectra in the C1s and Pd3d region of the (2x2)-CO structure on Pd(111) are reported (traces 4), as well as spectra of the clean surface (traces 3). The spectra were recorded at constant pass energy of 20 eV. The peak integral in the C1s region was quantified and compared to the peak integral of Pd3d$_{5/2}$. The calculated C1s area is 1.75% of the corresponding Pd3d$_{5/2}$ area, and this ratio corresponds to a CO coverage of 0.75 ML. Assuming identical sensitivity factors for CO and CH$_x$ and CH$_x$O species, the quantitative analysis of XPS spectra reported in this work was carried out by using the (2x2)-3CO structure of CO on Pd(111) at 0.75 ML as reference.
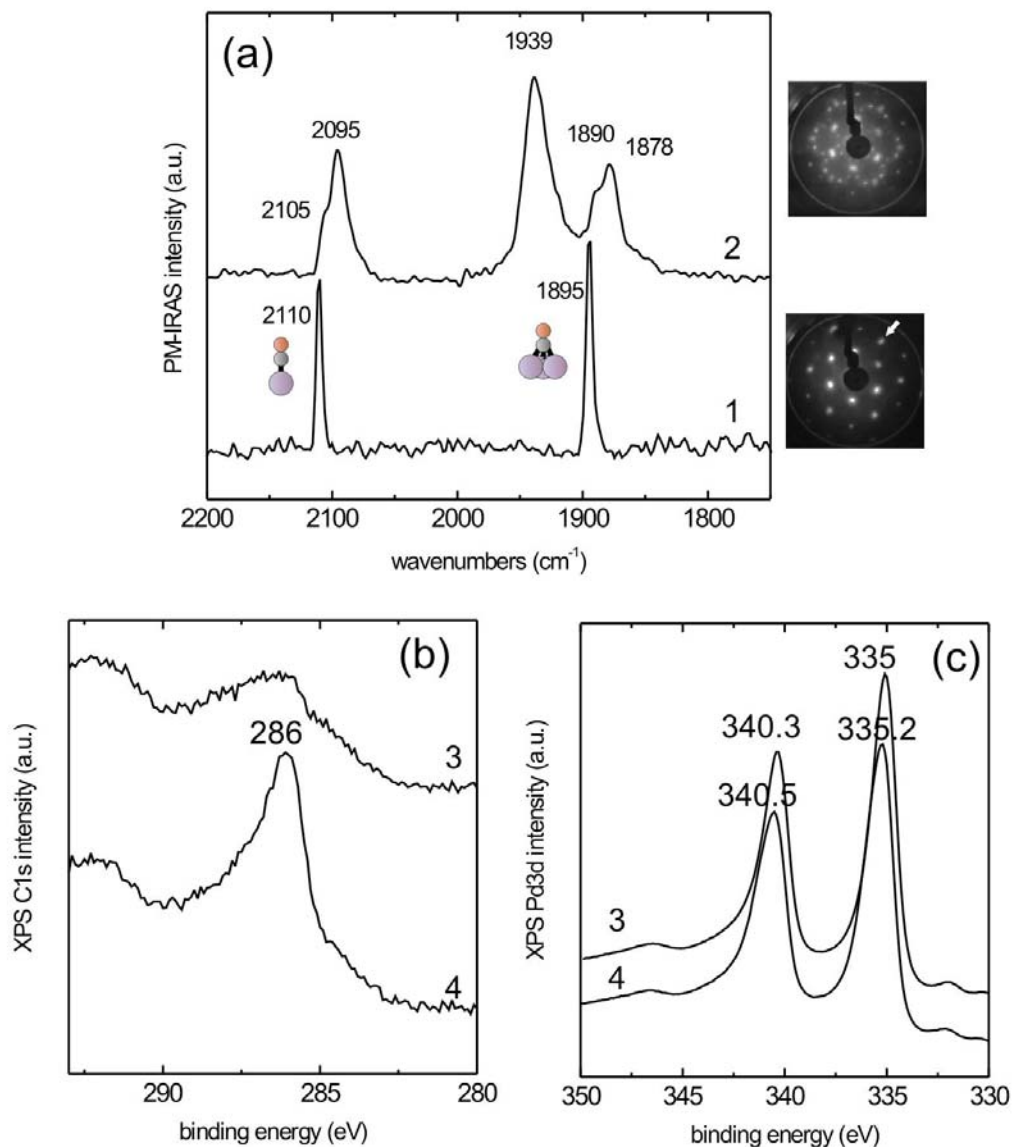
Figure 3.3: (a) PM-IRAS spectra of CO structures on Pd(111). The two surface overlayers were obtained as follow: spectrum 1) 10^{-6} mbar CO from 700 to 100 K; spectrum 2) 10^{-6} mbar CO at 100 K. LEED pictures corresponding to the two different structures are also reported. The white arrow on the lower LEED picture points on a Pd(111) reflex. XPS spectra in the C1s (b) and Pd3d (c) regions of a clean Pd(111) surface (traces 3) and of a (2x2)-3CO overlayer (traces 4). The two "bumps" observed in trace 3 (clean surface) in (b) are Pd-satellite peaks due to the non-monochromatic X-ray source used (see section 2.2) and do not originate from adsorbed species. The small shift of +0.2 eV observed in the Pd3d region (b) is due to CO adsorbed on the surface (trace 4).

When CO is directly introduced at low temperature, disordered CO structures are more likely to be formed, as in the case shown in spectrum 2 of Figure 3.3a, which is characterized by three main broad peaks centred at 2095 cm^{-1} (CO atop), at 1939 cm^{-1} (CO bridge-bonded), and at 1878 cm^{-1} (CO 3-fold coordinated). Shoulders are also observed at 2105 and 1890 cm^{-1}. This particular vibrational spectrum could correspond to the superposition of CO-domains of different coverage, i.e. a (2x2)-structure and a structure of a smaller CO coverage, explaining also the presence of bridge-bonded CO. The superposition of CO-domains of different coverage can also be recognized in the LEED picture corresponding to spectrum 2, where a "flowered" structure typical of ~0.6 ML coverage is superimposed to the (2x2) structure achieved at the maximum coverage of 0.75 ML.

For the (2x2)-3CO overlayer obtained at maximum coverage (Figure 3.3a, spectrum 1), the total peak area of the feature due to CO adsorbed on-top is about 80% of the peak area related to CO on three-fold hollow sites. The ratio 1.2:1 (three-fold:on-top) seems to disagree with the structure at 0.75 ML coverage [20], where the number of three-fold sites is double the number of on-top sites. This apparent discrepancy could be due to the different environments for CO molecules adsorbed on-top or three-fold, which could influence the dynamic dipole moments for the vibrational transitions. The intensity of IRAS spectra, in fact, can not be directly related to the real surface coverage, as it is proportional to the square of the dynamic dipole moment of the oscillator. Also the dipole-dipole interaction could affect the intensity, attenuating the features associated with CO on three-fold sites, where each molecule is surrounded by a higher number of equivalent dipoles [66,67]. Further discussion will be given in the section dedicated to CO adsorbed at high pressure.

CO was also adsorbed on a defective Pd(111) surface. In order to introduce defects on a smooth surface, a Pd(111) sample was sputtered at low temperature (2 KeV Ar^{+} at 100 K) without following annealing.

When CO is adsorbed on a strongly sputtered surface (Figure 3.4, spectrum 1), a new feature is observed in the bridge region at about 1980 cm^{-1}. The peak at 2105 cm^{-1} corresponding to linear on-top CO is, instead, compatible with the adsorption on a perfect surface. When the surface is heated to 300 K in CO and cooled again to 100 K (spectrum 2), no appreciable changes are observed, so this thermal treatment did not allow a better reordering of the CO structure. This defect-related species was already observed by

Unterhalt at al. using SFG [59], where it was shown that defects created by Ar$^+$-bombardment are stable up to about 550 K.
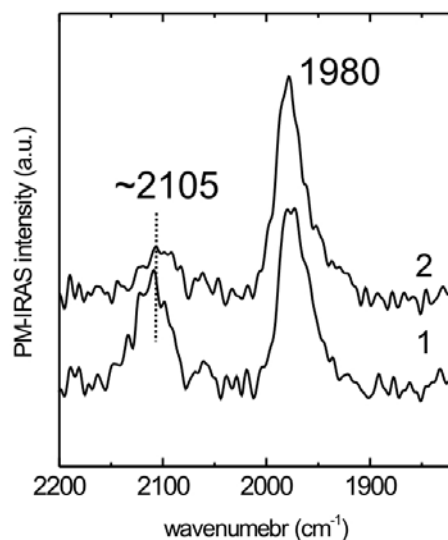

Figure 3.4: PM-IRAS spectra of CO adsorbed at 100 K on strongly sputtered Pd(111): spectrum 1) 10^{-5} mbar CO at 100 K; spectrum 2) after annealing to 300 K. Spectra recorded at 100 K.

3.1.1 Annealing in UHV

As already mentioned, (PM-)IRAS spectra of CO adsorbed on Pd(111) are strongly influenced by the sample preparation conditions. Figure 3.5 shows the dependence of these vibrational features on the annealing temperature. Spectrum 1 was obtained by directly exposing the sample to 10^{-5} mbar CO at 190 K. This CO overlayer is characterized by a prominent feature at ~1960 cm^{-1} (bridge bonded CO), and a broad weak feature at 2089 cm^{-1} (linear bonded CO) (θ_{CO} ~0.6 ML). For spectra 2 and 3 the sample was annealed to 300 and 500 K in 10^{-5} mbar CO, respectively, than cooled in presence of the gas to 100 K for acquisition. By increasing the annealing temperature, the feature related to on-top CO gradually shifts to higher frequency and increases in intensity, while the peak at lower wavenumbers splits in two components. In spectrum 3 three peaks are recognized at 2110 cm^{-1} (on-top), 1938 cm^{-1} (bridge), and 1895 cm^{-1} (three-fold hollow) (θ_{CO} ~0.7 ML). The changes due to this annealing/cooling treatment observed in Figure 3.5 reflect the formation

of more ordered and more densely packed CO structures. During the annealing treatment CO gains probably sufficient mobility to reorder on the surface, and while cooling back to lower temperature its coverage increases, facilitating a phase transition from bridge/on-top to bridge-hollow/on-top configuration.
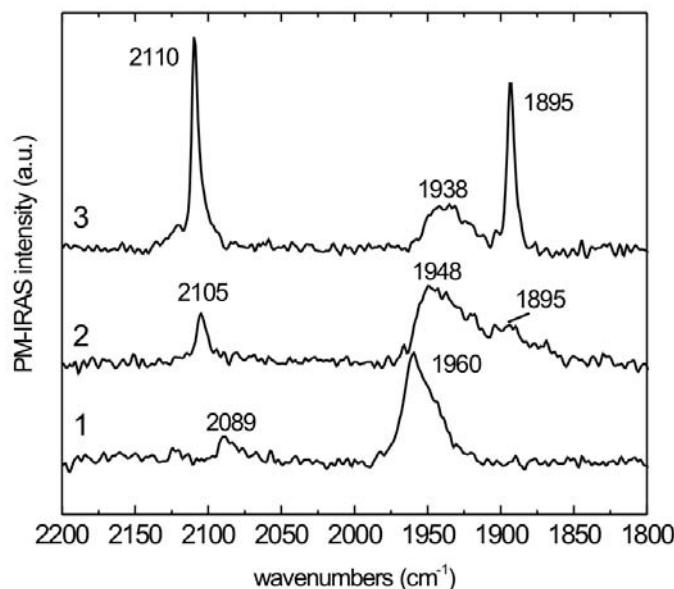

Figure 3.5: Annealing effect on the ordering of CO surface overlayers on Pd(111) shown by PM-IRAS. (1) 10^{-5} mbar CO dosed at 190 K. (2) After flash in CO to 300 K. (3) After flash in CO to 500 K. All spectra were acquired in CO at 100 K.

3.2 CO adsorption on Pd(111) at high pressure

The CO/Pd(111) system was also investigated under more relevant conditions. Studies in ultra-high vacuum or at low pressure (below 10^{-4} mbar) are not always representative of more realistic catalytic systems. High pressure may induce surface reconstructions or produce new surface structures that were absent under UHV, as observed by STM during high pressure CO exposure at 300 K on Pt(111) [68]. This fact underlines the need of surface-sensitive techniques which are able to investigate a catalytic system from UHV up to high pressure regimes and to understand discrepancies which may occur under these different environments. PM-IRAS and SFG are recently developed *in-situ* vibrational

spectroscopy techniques which can be used to investigate heterogeneous catalytic systems under more relevant conditions, i.e. under mbar pressure.
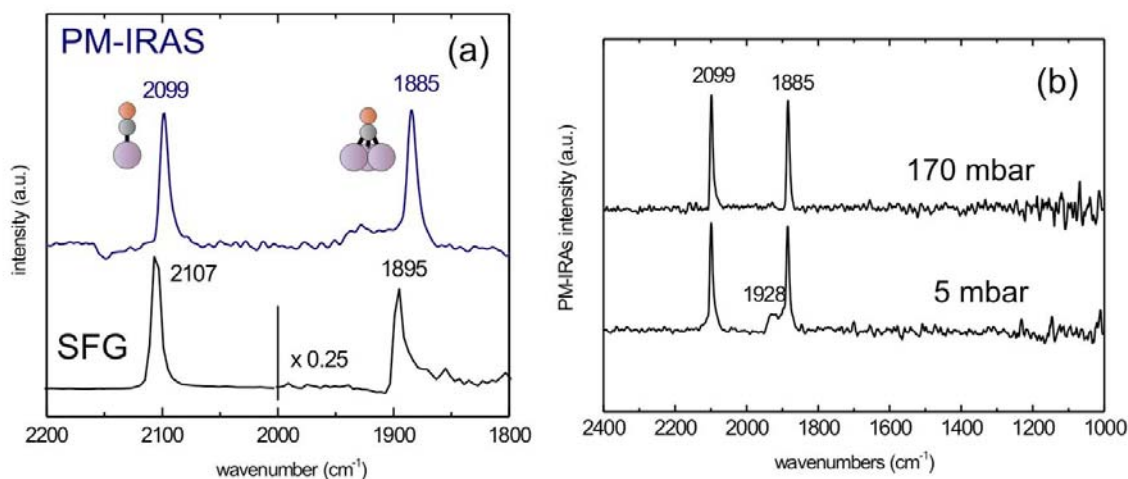

Figure 3.6: (a) (2x2)-CO structure on Pd(111) measured by PM-IRAS (170 mbar) and SFG (100 mbar). Both spectra were acquired at 190 K. (b) High pressure CO adsorption detected by PM-IRAS, showing the extended spectral range available with this technique.

In Figure 3.6a, high pressure spectra of CO on Pd(111) detected by PM-IRAS and SFG are reported. The good agreement between the two spectra confirms the possibility of using PM-IRAS to investigate systems under elevated pressure. Furthermore, PM-IRAS enables investigation over the spectral window ~2400-1000 cm^{-1} (Figure 3.6b), which can be routinely adjusted depending on the system under investigation by simply changing the photoelastic modulation frequency. Instrumental limitations of the SFG setup does not allow investigation below 1600 cm^{-1} [42], and its underestimation of multiple-coordinated sites leads to dominant on-top (~2110 cm^{-1}) features. However, as already discussed, the IRAS intensity as well does not reflect the real adsorbate concentration. Further on, saturation of the signal intensity occurs often before the saturation coverage is reached [20]. However, for low coverage the IRAS intensity can be correlated with the number of adsorbed molecules.

In a recent study [69], the line shape and signal intensity of CO adsorbed on Pd model catalysts were analyzed and compared to corresponding (PM-)IRAS spectra. As already

discussed, the CO structure at saturation coverage ($\theta_{CO} = 0.75$ ML) on Pd(111) contains two hollow-bonded CO molecules and one linear-bonded CO molecule, and the hollow/on-top ratio is therefore 2:1. However, the measured hollow/on-top ratio for the PM-IRAS spectrum in Figure 3.6a is about 0.8:1. According to recent DFT calculations [69], the higher sensitivity of IRAS towards on-top CO is related to a higher dynamic dipole moment for linearly bounded CO, suggesting a hollow/on-top ratio of about 1.4:1. Nevertheless, the difference between the experimentally measured hollow/on-top ratio and the calculated hollow/on-top ratio can not be completely explained.
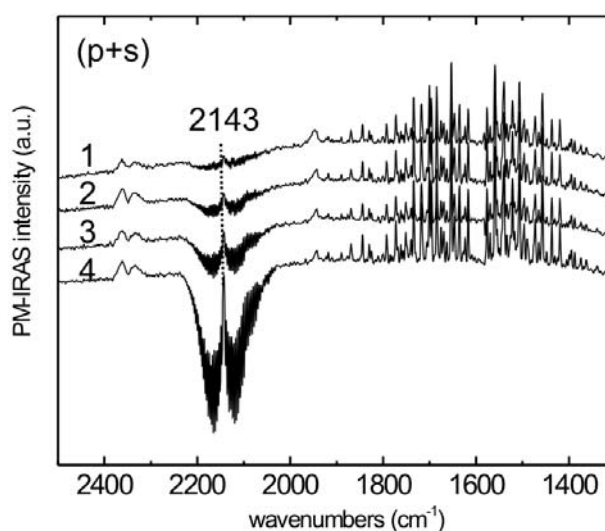

Figure 3.7: Gas phase spectra of CO adsorbed on Pd(111) under high pressure. The spectra were acquired under the following conditions: spectrum 1) 10 mbar; spectrum 2) 20 mbar; spectrum 3) 65 mbar; spectrum 4) 65 mbar at 250 K.

The difference in frequency observed between PM-IRAS and SFG spectra of Figure 3.6a could be related to different contributions of CO domains of coverage slightly smaller than 0.75 ML, influencing the (2x2) domain size [59]. This discrepancy could also be attributed to a not perfect calibration of the PM-IRAS spectrometer. In Figure 3.7 (p+s) spectra of CO under mbar pressure are reported. The rotovibrational contours of CO gas are evident on the left hand side of the spectra. The zero point in the CO gas phase is at 2143 cm^{-1} (see arrow), as reported in the literature, so an erroneous calibration of the instrument could be excluded. Another gas phase contribution can be recognized between 1900 and

1400 cm^{-1} which is attributed to water, (atmospheric water). The presence of water during high pressure experiments constitutes a problem, especially during long time exposures at low temperatures. This problem was pointed out by *Rupprechter et al.* [70] during high pressure CO adsorption on Pt(111). In that work it was observed that coadsorbed water induced a 15 cm^{-1} redshift of the on-top CO frequency. High pressure experiments should therefore be carried out above the desorption temperature of water (~160 K for Pt and ~175 K for Pd). The spectra in Figure 3.7 were recorded at a sample temperature of 150 K, that means below the desorption temperature of water. Nevertheless the last spectrum (trace 4) in Figure 3.7 was acquired at 250 K, but water is still present. Summarising, the lower frequencies observed in the PM-IRAS spectrum in Fig. 3.6 with respect to the corresponding SFG spectrum is not due to an erroneous calibration of the IRAS setup, but it is most probably related to the presence of CO domains of coverage slightly lower than 0.75 ML. In fact, a broad and small feature is observed at ~1910-1920 cm^{-1} (PM-IRAS spectrum in Fig. 3.6a), which can be attributed to the presence of bridge-bonded CO.

Isothermal CO adsorption on Pd(111) was performed at 190 K and 300 K for increasing pressure, as shown in Figure 3.8a[1] and Figure 3.8b. At low temperature and under low pressure, (Figure 3.8a, spectrum 1), CO predominantly occupies bridge sites (peak at 1960 cm^{-1}), while the feature related to on-top position (peak at 2088 cm^{-1}) is weak. A disordered (or flowered) (2x2)-CO structure is obtained under high pressure at 190 K (spectra 2-4), with peaks centred at 2090, 1945 and 1875 cm^{-1}, correspondingly to CO adsorbed on-top, bridge and hollow. Increasing the pressure has no effect on the peak frequency, while the on-top and hollow features become slightly more intense. The CO coverage is evidently not strongly influenced by the increased pressure. Most probably, under mbar pressure, the saturation coverage was reached. Also an increase in the temperature to 250 K (spectrum 5) has no influence. It is noteworthy that no high pressure induced species can be observed. In the isothermal CO growth at 300 K (Figure 3.8b), a shift to higher frequency and a higher peak intensity are evident when the pressure is increased from 10^{-5} mbar (spectrum 6) up to almost atmospheric pressure (spectrum 11). At 10^{-5} mbar (spectrum 7), a peak around 1930 cm^{-1} indicates a coverage below 0.5 ML, due to CO bridge and/or hollow bonded. At increasing pressure, this peak become sharper, its intensity increases and a blue-shift of +14

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[1] The spectra of Figure 3.8.a are the corresponding surface spectra of the (p+s) gas phase spectra shown in Figure 3.7.

cm^{-1} is reached under atmospheric pressure (spectra 9-11). The CO structure reached under these conditions corresponds to a CO coverage below 0.6 ML and the peak at 1952 cm^{-1} is related to CO on bridge sites. At $\theta_{CO} \geq 0.6$ ML, CO is preferentially bridge bonded (~1950-1960 cm^{-1}) with a smaller contribution of linear on-top CO (~2090 cm^{-1}), as observed in Fig. 3.5 (trace 1) and in [42].
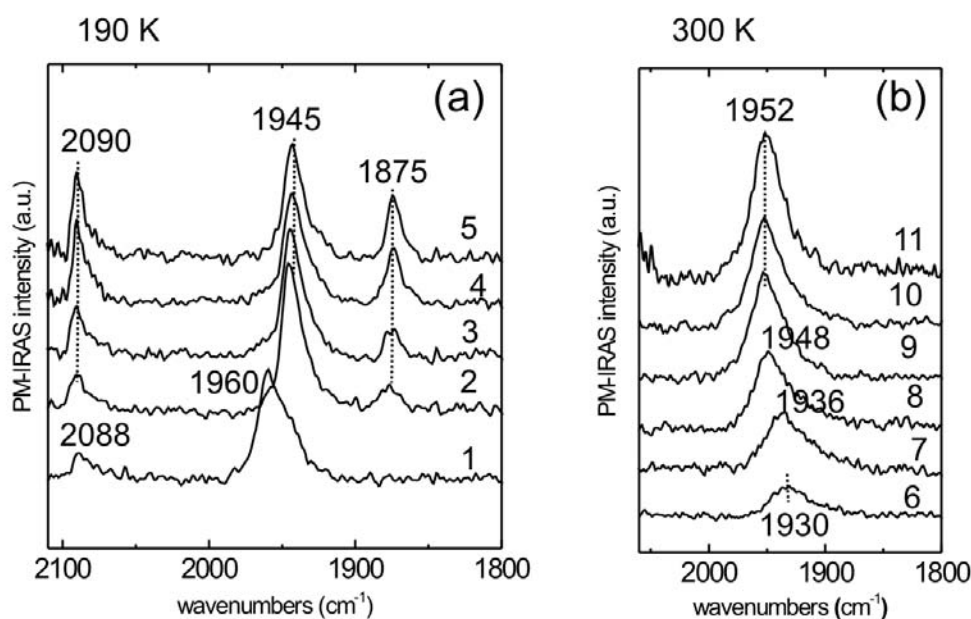

Figure 3.8: (a) PM-IRAS spectra of CO adsorbed on Pd(111) at 190 K. The spectra were acquired under the following conditions: spectrum 1) 10^{-4} mbar; spectrum 2) 10 mbar; spectrum 3) 20 mbar; spectrum 4) 65 mbar; spectrum 5) 65 mbar at 250 K. (b) PM-IRAS spectra of CO adsorbed on Pd(111) at 300 K. The spectra were acquired under the following conditions: spectrum 6) 10^{-5} mbar; spectrum 7) 10^{-4} mbar; spectrum 8) 1 mbar; spectrum 9) 100 mbar; spectrum 10) 250 mbar; spectrum 11) 1150 mbar.

Elevated pressure studies on CO adsorption on Pd(111) presented in this work are in good agreement with previous PM-IRAS studies performed in the group of Goodman [10]. In order to verify the correlation between the behaviour of the Pd(111) surface at low and high adsorbate pressures, isobaric PM-IRAS experiments were performed by Goodman and co-workers [10] at different CO pressures. Comparison of the different data revealed that the structure of the CO overlayers was almost unchanged within the 10^{-6}-600 mbar region. The high pressure data reported in [10] were used to extend the previously reported phase diagram [56] for the transition from the bridging CO overlayer structure to the three-fold

hollow/atop structure below 13 mbar. A Clausius-Clapeyron activation energy of 44.3 ± 1.6 kJ/mol was derived from the slope of the equilibrium (bridging – 3-fold/atop) phase transition diagram for CO on Pd(111) [10]. A value close to 39.8 kJ/mol was derived for the phase transition from bridging to 3-fold hollow CO structures using TPD results [56].

3.3 CO adsorption on Pd/Al$_2$O$_3$/NiAl(110)

The Pd/Al$_2$O$_3$/NiAl(110) system represents a further step towards the complexity of real heterogeneous catalysis, because some aspects of the conventional high surface area supported catalysts can not be simply mimicked in surface science studies on single crystal model catalysts. In fact, when compared with the Pd(111) single crystal, Pd clusters supported on oxides present a higher degree of heterogeneity due to their three-dimensional shape. Pd clusters on alumina grow in a truncated cubo-octahedral shape, thus presenting top-facets with a (111) orientation, and side-facets with (100) and (111) orientation. These crystalline particles exhibit also several defects, such as steps, edges, kinks and corners. According to the metal surface selection rules (MSSR, see chapter 2.1.1), CO adsorbed on the side facets should produce only a small signal, as the molecule is tilted with respect to the surface normal. The IR signal of CO adsorbed on Pd particles should behave similar to a Pd(111) surface.

Recently, PM-IRAS was applied in our group to investigate the Pd/Al$_2$O$_3$/NiAl(110) system. Initial results will be discussed in this work and will demonstrate that PM-IRAS can also be applied to three-dimensional nano-clusters.

Figure 3.9 shows PM-IRAS data for CO adsorption on Pd/Al$_2$O$_3$/NiAl(110) at increasing pressure between 250 and 175 K. As the temperature is decreased to 175 K in 10 mbar CO the topmost spectrum (trace 4) in Figure 3.9 shows three complex bands centred at about 2102, 1990 and 1890 cm^{-1}. The features at ~2102 cm^{-1} and 1890 cm^{-1} could be assigned to CO adsorbed on atop and hollow sites of (111) facets, respectively. The IR band at ~2102 cm^{-1} present an asymmetry towards lower frequency, which could be due to the contribution of CO adsorbed on the (100) side-facets. The band at ~1990 cm^{-1} is related to CO adsorption on steps and/or particle edges [71].
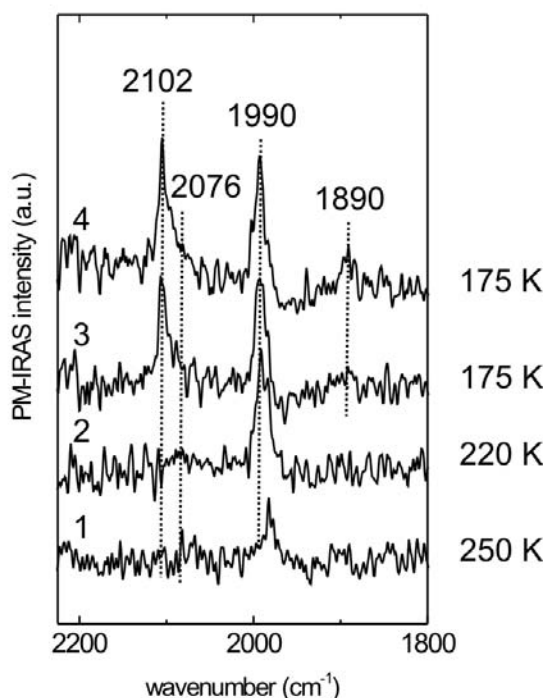
Figure 3.9: PM-IRAS data for CO adsorption on Al_2O_3 supported Pd nanoparticles between 10^{-4} and 10 mbar CO and at temperatures between 250 and 175 K. The spectra were acquired as follows: spectrum 1) 10^{-4} mbar CO were dosed at 300 K, then the sample was cooled in CO to 250 K and the corresponding spectrum acquired at 250 K; spectrum 2) CO pressure was kept to 10^{-4} mbar and the sample temperature was decreased to 220 K; spectrum 3) the pressure was kept constant until a temperature of 175 K was reached and then the pressure increased to 1 mbar; spectrum 4) the pressure was increased to 10 mbar CO at 175 K.

3.4 Is there C-O bond scission under high pressure?

The first study on supported metal nanoclusters by PM-IRAS was performed at the Texas A&M University, in the group of Goodman [60]. CO adsorption was investigated at elevated pressure and temperature on $Pd/SiO_2/Mo(112)$. According to a combined PM-IRAS and AES (Auger electron spectroscopy) study, *Ozensoy et al.* [60] stated that CO dissociates on the Pd clusters at 185 mbar and at temperature > 600 K. For comparison, in the same work CO adsorption was also investigated under similar condition on Pd(111)

single-crystal surface, without any indication of C-O bond scission (i.e. carbon deposition was not observed by AES spectroscopy).

Despite these results, CO dissociation on Pd surfaces is still an open question and great care has to be taken in the interpretation of experimental results. It is known that CO adsorbs molecularly on Pd(111) under UHV. Anyway, partial CO dissociation at high pressure can not be completely ruled out, even on a single-crystal surface. Under mbar pressure, in fact, disproportionation of CO can occur with subsequent formation of carbon (through the Boudouard reaction: $2CO \rightarrow C + CO_2$), as observed on Pt(111) [72,73]. Recently, a combined high-pressure XPS and SFG spectroscopy study [74,75] was applied in our group to investigate the possibility of CO dissociation on Pd(111) in a pressure range from 10^{-6} to 1 mbar and at temperatures between 200 and 400 K. Even under mbar pressure, CO vibrational SFG spectra were comparable with the previous structure reported under UHV [42,43] and no carbon deposition was detected by *in-situ* HP-XPS (the highest pressure applied was ~0.1 mbar), i.e. no evidence for CO dissociation was observed under the given conditions.

Different studies on supported Pd are in disagreement. *Matolin et al*. [76] have observed C deposition on supported Pd particles from CO dissociation or disproportionation [77], while other authors have not observed that [74,78].

Considering the debate nature of this topic, the CO/Pd system was revisited under different conditions, using PM-IRAS and XPS, which could give information about the nature of the adsorbed species and the possible formation of carbonaceous deposits.

Pre- and post-reaction XPS was applied to investigate the CO/Pd(111) system at 0.1 mbar gas exposure and at 300 K. The post-reaction XPS did not show any carbon formation (data not shown). Also *in-situ* XPS data by *Kaichev et al.* [74] did not observe any carbon deposition deriving from CO dissociation under 0.1 mbar CO exposure.
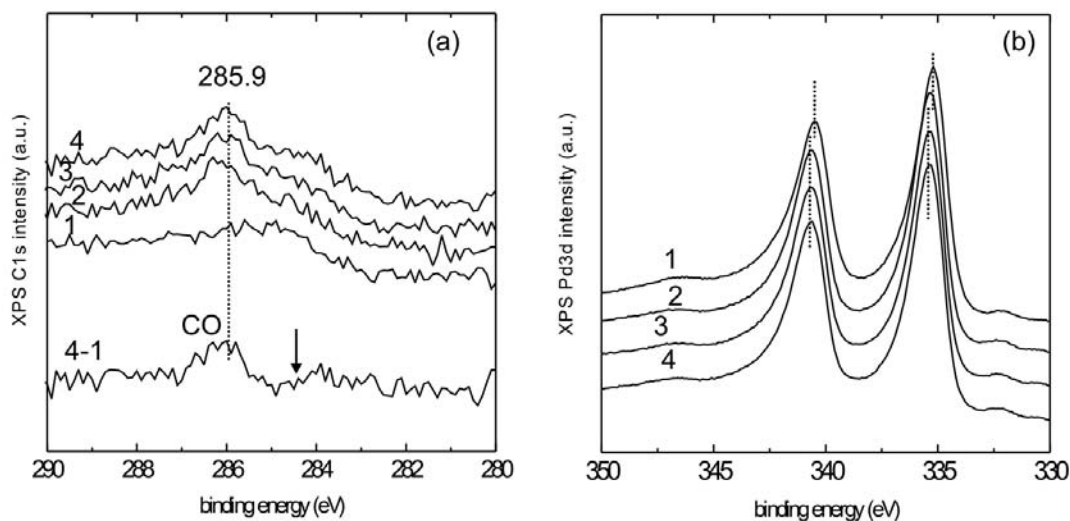
Figure 3.10: XPS spectra of Pd/Al$_2$O$_3$/NiAl(110) in the C1s (a) and Pd3d (b) region: spectrum 1) Pd particles after deposition and stabilization; spectrum 2) after 5 minutes in 10^{-6} mbar CO; spectrum 3) after 60 minutes in 10^{-6} mbar CO; spectrum 4) after 120 minutes in 10^{-6} mbar CO. In the C1s region (a) the difference spectrum (4 - 1) is also shown. CO was dosed at 300 K and all the spectra were acquired at the same temperature.

Figure 3.10 shows a series of XPS spectra of 10^{-6} mbar CO adsorbed at 300 K on Pd particles supported on alumina for increasing CO exposure time. The feature at 285.9 eV in the XPS spectra (Fig. 3.10a) corresponds to adsorbed CO (coverage CO = 0.50 ML). Carbon deposits deriving from CO dissociation should appear at ~284.5 eV (see arrow in Fig. 3.10a), but no C related feature can be observed, even after 2 hours CO exposure (trace 4 in Figure 3.10a). The corresponding XPS spectra in the Pd3d region are also reported (Figure 3.10b). A shift of about + 0.2 eV is observed for traces 2, 3, and 4 with respect to trace 1 of the clean Pd surface. This small shift is due to the adsorption of CO on the surface. From these *in-situ* XPS data it is possible to conclude that under UHV (or low pressure regime) CO does not dissociate on Pd clusters supported on alumina.

The adsorption of CO on Pd particles was also investigated under mbar pressure using PM-IRAS. In the experiment shown in Figure 3.11a, CO was dosed at 300 K and PM-IRAS spectra were acquired in 100 mbar and 200 mbar CO, traces 1 and 2, respectively. Two major features are observed at about 2093 and 1982 cm^{-1}, corresponding to CO adsorbed on-top and on steps and/or particle edges. No frequency shift is observed increasing the CO

pressure from 100 to 200 mbar (traces 1 and 2, respectively). The peak area instead increases with the CO pressure, due to a higher CO coverage. The sample was then heated to 500 K in presence of 200 mbar CO and then cooled to 300 K. A new spectrum was acquired (trace 3). After this anneal-cool cycle partial changes are observed in the corresponding PM-IRAS spectrum (trace 3). The peak associated with CO adsorbed on defect sites shifts to ~1988 cm^{-1}, its FWHM slightly increases and its area decreases of less than 30% (with respect to trace 2) (Fig. 3.11b).
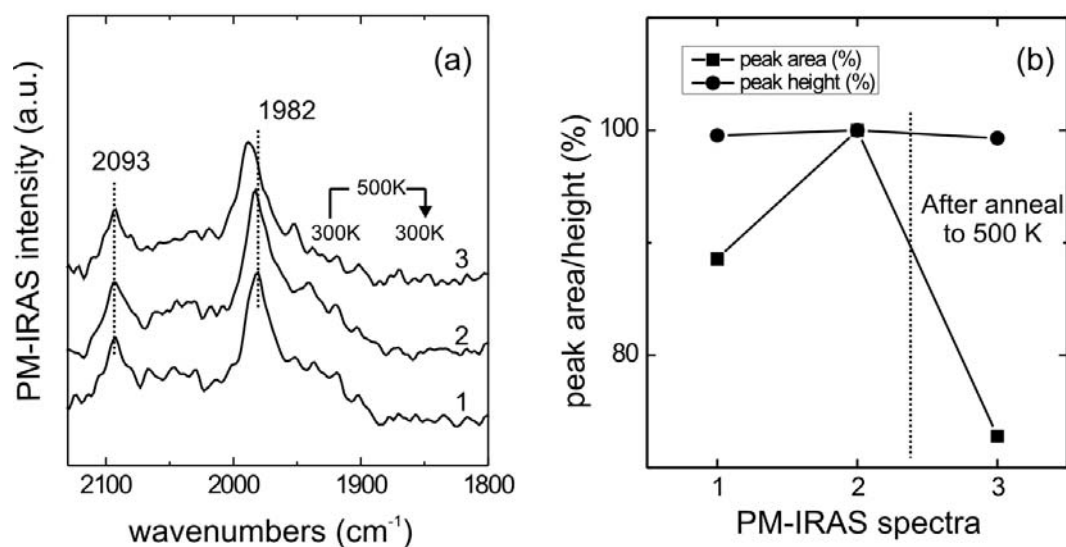

Figure 3.11: (a) PM-IRAS spectra of mbar CO adsorbed on Pd clusters at 300 K: 1) 100 mbar CO at 300 K; 2) 200 mbar CO at 300 K; 3) after heating in 200 mbar CO to 500 K and cooling back in CO to 300 K. (b) The integral and the height of the PM-IRAS peak at ~1980 cm^{-1} for the three different conditions are also reported.

As in the case of Pd(111) single crystal, PM-IRAS spectra did not report any high pressure (and high temperature) induced species on alumina supported particles.

The carbon deposit observed in the post-reaction AES on the Pd/SiO$_2$/Mo(112) [60] may originate from disproportionation of CO following the Boudouard reaction $2CO \rightarrow C + CO_2$, which can be facilitated under high pressure and high temperature on steps and edges of Pd particles. Unfortunately, the authors did not report the exact amount of carbon deposition observed in the post-reaction AES spectrum. It is very demanding to perform measurements at elevated pressure under precisely controlled conditions. As a consequence, carbon may also originate from carbonyls impurity present in the CO gas. As mentioned (section 2.6), at elevated pressure CO cleanliness has to be carefully controlled and

impurities have to be removed by passing CO over a carbonyl adsorber cartridge and a cold trap filled with *l-N$_2$*. Therefore, the decrease in IR intensity observed in the PM-IRAS spectra during annealing-cooling cycles of high pressure CO on silica-supported Pd nanoparticles and the carbon deposit observed in the post-reaction AES spectrum [60] are not sufficient evidences of C-O bond scission. The possibility that CO can dissociate on Pd model catalysts under relevant conditions remains an open question.

Summarizing, under UHV and at pressure up to 0.1 mbar, XPS and PM-IRAS data indicated that CO adsorb molecularly on both systems, Pd(111) and Pd/Al$_2$O$_3$/NiAl(110), and no carbon traces were detected. The *in-situ* PM-IRAS spectra at elevated pressure showed a "regular" CO adsorption for Pd(111) single crystal and alumina supported nanoparticles. These data are in good agreement with previous HP-XPS and SFG studies on Pd model catalysts [42,43,74,123], where no indications of CO dissociation or carbonyl formation were found under the given conditions.

3.5 Summary

The applicability of PM-IRAS to investigate the adsorption of CO on Pd model catalyst surfaces from UHV to elevated pressures has been shown. The advantages of standard IRAS spectroscopy, i.e. high resolution and high sensitivity, can be extended to higher pressure. Moreover, some drawbacks of the SFG technique can be solved by PM-IRAS. In fact, PM-IRAS is not limited to a certain spectral range and has a faster acquisition time per spectrum than SFG.

The problem of the underestimation of multiple-coordinated sites by SFG has been discussed and compared to PM-IRAS data. For CO structures at saturation coverage, the experimentally measured hollow/atop ratio by PM-IRAS and the calculated hollow/atop ratio are still different. Nevertheless, PM-IRAS data are more consistent with the predicted values.

PM-IRAS measurements on the CO/Pd(111) system are in good agreement with previous SFG data and spectra reported by Goodman and co-workers. Initial results of elevated pressure CO adsorption on alumina supported Pd nanoparticles have been reported,

showing the possibility of investigating complex model catalysts under relevant conditions by PM-IRAS.

The possibility of C-O dissociation on Pd model catalysts surfaces has been addressed. PM-IRAS and XPS measurements on Pd(111) and Pd/Al$_2$O$_3$/NiAl(110) have shown that CO does not dissociate under UHV conditions and at lower CO pressures (up to 0.1 mbar). PM-IRAS *in-situ* spectra of millibar pressure CO adsorption on Pd(111) and on Pd/Al$_2$O$_3$/NiAl(110) did not report any high pressure species or adsorbate induced surface reconstructions. Great care has to be taken during high pressure experiments to avoid contamination. Moreover, high pressure measurements have to be carefully analysed in order to avoid misinterpretation.

The data reported are not exploring the complete pressure range from UHV up to mbar CO pressure for the both Pd systems, Pd(111) and alumina-supported Pd particles, therefore more experiments would be required in order to give a clear answer if CO can dissociate under relevant conditions on Pd model catalysts.