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On the Coverage-Dependent Adsorption Geometry of Benzene Adsorbed on Pd{111}: A Study by Fast XPS and NEXAFS

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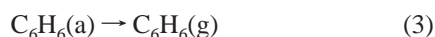
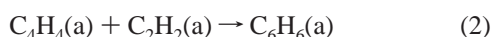
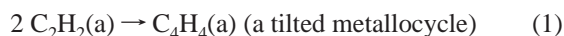
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Fast XPS data obtained during benzene uptake on Pd{111} are consistent with those obtained during benzene desorption, and both are in accord with the corresponding NEXAFS results. At low coverage the molecule lies flat, is strongly adsorbed, and is characterized by a relatively low C 1s binding energy. At higher coverage, a second form of benzene is also present. This species is strongly tilted with respect to the metal surface. It is characterized by a relatively high C 1s binding energy and a narrower π^* resonance: both attributes are in keeping with its observed weaker adsorption strength. The coverage-dependent change in adsorption geometry from flat to tilted benzene, originally suggested in order to account for the kinetics of acetylene trimerization on Pd{111}, is unequivocally demonstrated.

Introduction

The chemisorption of benzene on well-defined transition metal surfaces has received much attention, as an inspection of the recent literature reveals (see for example refs 1–8 and references therein). In part, this reflects the experimental convenience of working with a stable organic adsorbate that is also considered to be “catalytically relevant”. One key issue concerns the adsorption geometry of the aromatic ring with respect to the surface, both parallel and tilted configurations being reported, depending on the particular instance. In the case of Pd{111}, the question acquires a particular significance which is genuinely relevant to catalysis. It is known that this surface is very efficient for the trimerization of acetylene to benzene over a wide range of conditions ranging from ultrahigh vacuum⁹ to atmospheric pressure.¹⁰ The reaction mechanism and the identity of the critically important surface intermediate have been established with a high degree of confidence,¹¹ the most recent evidence being provided by a time-resolved XP study of the reacting system.¹² It is well established¹¹ that benzene formation occurs by the following sequence of steps:



We have demonstrated that on Pd{111} step (3), product desorption, is rate determining for the appearance of gaseous benzene.¹³ This is by no means universally true: in the case of Cu{110} it is very clear that step (1) is rate limiting.¹⁴ On

Cu{110}, during temperature-programmed reaction, the reactively formed benzene desorbs in a single peak.¹⁴ In contrast, on Pd{111} desorption of the benzene product occurs in *two* well-defined peaks⁹ centered at ~ 200 K and ~ 500 K. It is plausibly postulated¹¹ that the low-temperature peak is due to desorption of a weakly adsorbed tilted form of benzene formed on an initially crowded surface. As the temperature rises and coverage decreases, the remaining benzene molecules adopt a more stable flat-lying conformation, eventually desorbing at higher temperature to yield the ~ 500 K peak. This model is at least consistent with early NEXAFS data¹⁵ which indicate that at high coverages benzene does adsorb on Pd{111} in a tilted configuration. However, the tilted \rightarrow flat transition as a function of temperature and coverage has always been a matter of inference. It has never been directly demonstrated and its occurrence (or nonoccurrence) is critically important to a correct interpretation of the reaction kinetics of benzene formation from acetylene under UHV conditions^{9,11,13} and to an understanding of the benzene/*n*-hexane selectivity behavior of Pd/Au acetylene trimerization catalysts operated at atmospheric pressure.¹⁶ Even if this general view regarding a coverage-driven flat \rightarrow tilted transition is correct, another issue needs to be resolved. Is there just one tilted benzene conformation or does the adlayer traverse a continuous series of molecular tilt angles as the coverage varies? Here, we address and resolve both these questions.

Experimental Methods

Measurements were carried out at the SuperESCA beamline of the ELETTRA (Trieste) synchrotron radiation source using a Pd{111} single-crystal sample prepared by standard procedures and maintained under ultrahigh vacuum ($\sim 1 \times 10^{-10}$ Torr). Quoted benzene exposures are given in Langmuirs ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}^{-1}$) and are uncorrected for ion-gauge sensitivity. The crystal was held at 100 K during benzene dosing in order to avoid desorption of weakly bound adsorption states. Temperature-programmed desorption data were acquired by

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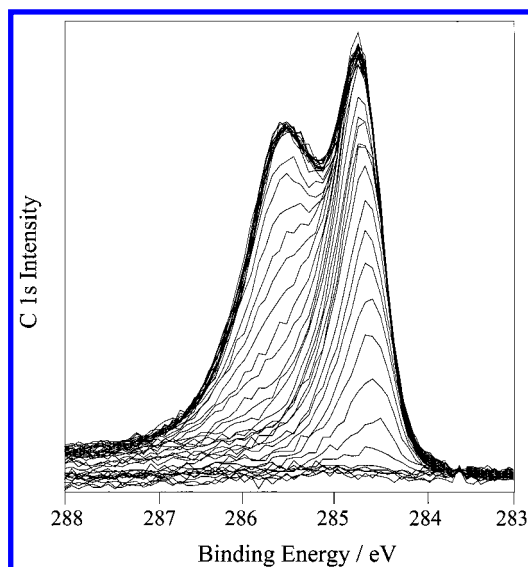


Figure 1. C 1s fast-XP spectra of C₆H₆ uptake on Pd{111} at 100 K.

application of a linear heating ramp ($\sim 0.4 \text{ K s}^{-1}$) to the benzene-covered sample. Benzene (Aldrich 99%) was purified by repeated freeze–pump–thaw cycles prior to dosing the sample by backfilling the vacuum chamber.

Carbon 1s and Pd 3d XP spectra, referenced to the Fermi level, were acquired at a photon energy of 400 eV and energy resolution of $\sim 100 \text{ meV}$. Individual spectra were acquired approximately every 10 s during fast XP measurements. The background-subtracted spectra were fitted using a Doniach–Sunjic function convoluted with a Gaussian, a common line shape being used for all carbon peaks. NEXAFS spectra were acquired at the C K-edge in both total yield and Auger modes (VSW CLASS150 Hemispherical Analyzer), however only the higher-quality total yield data are reported here. The NEXAFS data were recorded at photon incidence angles of $\theta = 0^\circ$ (normal incidence), 20° , 40° , 60° , and 80° , and normalized with respect to the incident beam intensity before division by the appropriate clean surface spectra.

Results and Discussion

Benzene Adsorption Monitored by Fast XPS. The adsorption of benzene on the clean Pd{111} surface was monitored by fast XPS, and Figure 1 shows a sequence of background-subtracted C 1s XP spectra obtained during continuous exposure of the sample to 5×10^{-8} Torr of benzene over a period of $\sim 1000 \text{ s}$. Nondissociative benzene adsorption was observed under all conditions. At low coverages benzene adsorption generates a single low binding energy (BE) peak at $\sim 284.7 \text{ eV}$. This feature saturates at $\sim 1 \text{ L}$, then broadens toward higher BE, with the eventual emergence of a new feature at $\sim 285.5 \text{ eV}$. The high BE feature increased continuously with benzene exposure and did not saturate, indicating multilayer formation. Figure 2 shows the coverage-dependent (and time-dependent) population of these two features as derived from the fitted, integrated peak intensities.

It is important to note that for all benzene coverages each spectrum was readily fitted using only two components with identical C 1s line shapes. These line shapes were obtained from measured reference spectra for chemisorbed CO and C₂H₂ for each of which only one type of carbon is present in the adsorbed layer; fitting parameters are given in Table 1. Inclusion of additional components did not improve the overall quality of fit, thus confirming the existence of no more than two

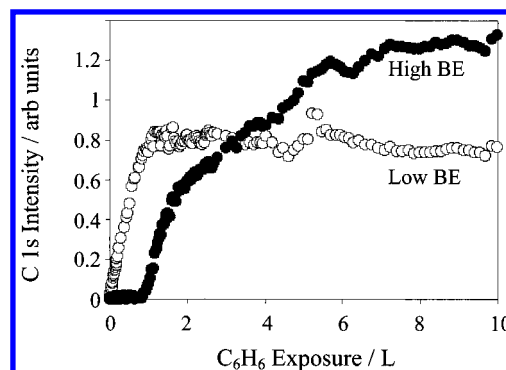


Figure 2. Fitted, integrated C 1s peak intensities of C₆H₆ uptake on Pd{111} at 100 K.

TABLE 1: Fitted Benzene Peak Parameters

Peak Parameter	eV
η^6 -C ₆ H ₆ BE	284.7
η^1 -C ₆ H ₆ BE	285.5
Lorentzian fwhm	0.12
Gaussian fwhm	0.52
asymmetry factor	0.19

chemically distinct benzene environments on the Pd{111} surface. We can thus rule out the possibility of a continuously evolving benzene adlayer in which either (i) the molecular conformation (e.g., tilt angle) or (ii) the number of chemically distinct types of benzene changes with increasing coverage.

It is clear from Figure 2 that population of the high BE state commences only after the low BE state has been saturated: this occurs at $\sim 1 \text{ L}$ C₆H₆ which corresponds to a surface coverage of $\sim 0.16 \text{ ML}$ or a C/Pd atom ratio of ~ 1 . Beyond this point additional benzene is incorporated entirely into the high BE state, initially rapidly and then more gradually at higher exposures. Even at 100 K most of the molecules associated with the high BE state were stable only in the presence of the 5×10^{-8} Torr ambient pressure of benzene. Evacuation resulted in immediate disappearance of $\sim 75\%$ of the high BE benzene, which we therefore associate with molecules present in a condensed multilayer. The remaining 25% of the high BE benzene must reside in the chemisorbed contact layer. The fact that the chemisorbed and multilayer components of the high BE benzene are indistinguishable in XPS suggests that this chemisorbed species must interact relatively weakly with the metal surface. As we shall see, the NEXAFS results are in good accord with this view.

Orientation of Adsorbed Benzene as a Function of Coverage. The adsorption geometries of the two benzene states were examined by recording C 1s NEXAFS spectra as a function of benzene coverage and photon incidence angle θ , Figure 3 a–b. Exposures below 1 L which populate only the low BE state give rise to the spectra shown in Figure 3a, which exhibit four peaks at 286.5, 289.6, 294.4, and 301.3 eV. These are, respectively, assigned as transitions from the C 1s orbital to e_{2u} and b_{2g} molecular orbitals of π^* symmetry and to e_{1u} and $e_{2g} + a_{2g}$ orbitals of σ^* symmetry. The spectra display a pronounced angular dependence on the polarization vector angle, in particular the π^* resonance at 286.5 eV is almost absent at normal incidence with maximal intensity observed for grazing photon incidence. This is consistent with a high degree of molecular orientation with benzene adopting a planar (η^6) geometry. Thus the low-coverage low BE XP state populated at $< 1 \text{ L}$ clearly corresponds to flat-lying benzene.

A similar, though much less pronounced, trend is apparent in the NEXAFS spectra from a saturated benzene adlayer, Figure

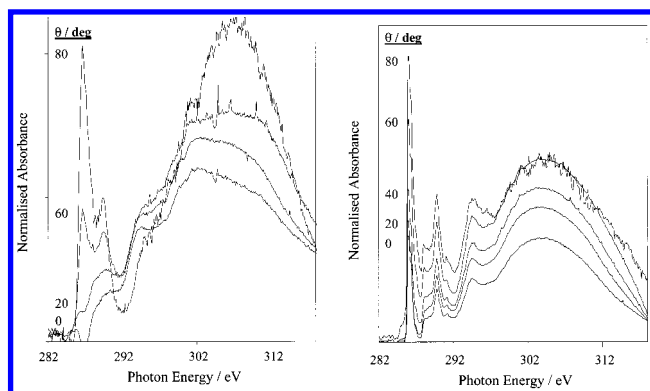


Figure 3. C 1s NEXAFS of (a) 1 L C₆H₆ and (b) 6 L C₆H₆ on Pd{111} at 100 K as a function of incident photon angle.

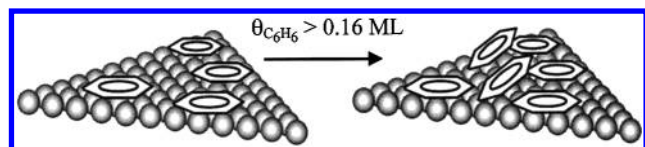


Figure 4. Schematic of low-temperature C₆H₆ adsorption on Pd{111}.

3b. Note that these data were recorded in the absence of the multilayer state: they refer only to molecules present in the chemisorbed contact layer. The same sets of four peaks are apparent, in addition to a weak feature at 288.4 eV which has been previously assigned to either a Rydberg resonance¹⁷ or a transition to a CH* valence orbital.¹⁸ Even for normal incidence the principal π^* resonance possesses significant intensity, which is enhanced at grazing incidence, indicating that at least some benzene molecules are now tilted away from the surface. Note that this resonance is appreciably sharper than for the lower-density benzene adlayer, presumably reflecting the weaker interaction of tilted molecules with the Pd surface: stronger coupling of the π^* orbital to the Pd conduction band reduces final state lifetime leading to greater peak broadening for the flat-lying benzene. Thus the high BE, weakly chemisorbed state which starts to fill for exposures > 1 L must be associated with tilted benzene, most likely η^1 -adsorbed.

An indication of the different degrees of tilt within (i) the purely flat-lying and (ii) the mixed configuration saturated adlayer may be obtained by fitting the 286.5 eV π^* resonance intensity versus incident photon angle data to the appropriate theoretical function.¹⁹ In following this procedure, all intensities were normalized with respect to the tilt-invariant “magic angle” of $\theta = 54.7^\circ$. The results indicate that for low coverages, the molecules are aligned within $10^\circ \pm 10^\circ$ of the Pd{111} surface, whereas at high coverages the *average* tilt angle increases to $\sim 40^\circ \pm 10^\circ$. Clearly, this is a lower limit on the actual tilt angle of the molecules in the saturated mixed layer that constitute the minority ($\sim 25\%$) tilted component.

Taken together, the fast XPS and NEXAFS data give a clear, consistent picture according to which benzene initially adsorbs in a planar geometry on Pd{111}, Figure 4, surface crowding resulting in subsequent adsorption into a tilted configuration. This provides the first direct experimental validation of the hypothesis proposed many years ago²⁰ in order to account for the observed kinetics of benzene desorption in the Pd{111}-catalyzed trimerization of acetylene. Our findings regarding the number of distinct benzene species, their adsorption geometries, their relative adsorption strengths, and the variation in populations of the two states as a function of temperature and coverage are in excellent agreement with the observed catalytic behavior.^{13,21}

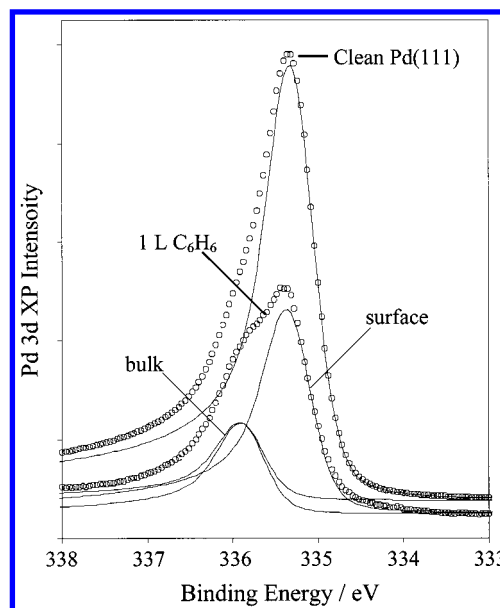


Figure 5. Pd 3d XPS spectra from clean and C₆H₆-saturated Pd{111} surfaces showing quenching of clean Pd surface state. Deconvoluted surface and bulk components (—) are also shown.

A comment on the different C 1s XP binding energies of flat-lying and tilted benzene is in order. As always, this shift reflects a combination of different initial state and final state effects. It is difficult to predict the relative importance of the former which is associated with the different bonding modes (predominantly π -bound versus σ -bound, respectively). However the direction of the shift ($BE(\eta^6) < BE(\eta^1)$) suggests that final state effects are important here. One would expect the stronger adsorbate–substrate interaction of η^6 flat-lying benzene to result in greater core-hole screening by electrons in the metal, and hence a reduced BE. This interpretation is consistent with the NEXAFS results in that the π^* resonance associated with η^6 flat-lying benzene is relatively broader. It is interesting to note that benzene adsorption attenuates the clean Pd{111} surface state emission at 335.3 eV, relative to the emission from bulk Pd at 336 eV (Figure 5). This quenching signifies Pd–benzene bond formation, consistent with the π^* resonance broadening observed by NEXAFS.

Benzene Desorption Monitored by Temperature-Programmed Fast XPS and NEXAFS. To complete the picture, we studied the thermal desorption of a saturated benzene overlayer by means of fast XPS; complementary NEXAFS data were also obtained. Figure 6 shows a sequence of C 1s XP spectra acquired during sample heating over the range 100–700 K. There was no evidence for benzene decomposition over this temperature regime. In this experiment the Pd crystal was maintained under a background pressure of $\sim 5 \times 10^{-8}$ Torr benzene, until just prior to heating. This procedure was followed in order to maximize occupancy of the multilayer and chemisorbed tilted states. It can be seen that heating to ~ 120 K induced the gradual desorption of the high BE multilayer to leave a smaller signal due to chemisorbed tilted benzene. Photoemission from the low BE state associated with planar benzene remains unchanged in intensity until ~ 300 K, at which point desorption commences.

These changes are more readily apparent from the data illustrated in Figure 7, which shows the thermal evolution of the fitted, integrated peak intensities for benzene-precovered Pd{111} as a function of temperature. In this experiment, for the sake of clarity, the multilayer state was “pumped off” prior to starting the heating ramp. It is clear that the high BE state

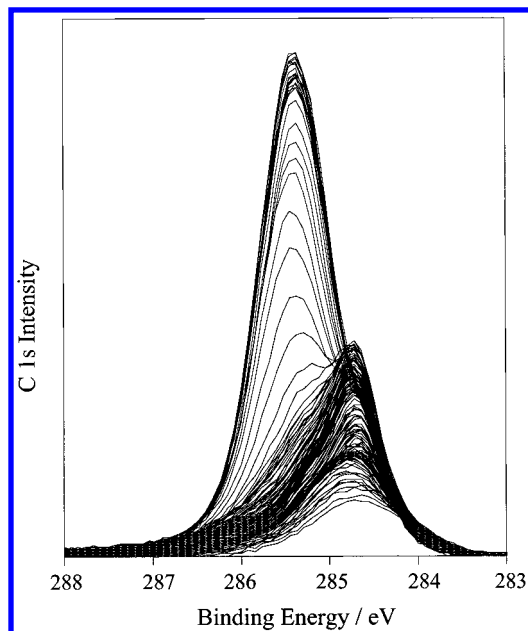


Figure 6. C 1s fast-XP spectra obtained from a C_6H_6 -saturated Pd{111} surface as a function of surface temperature.

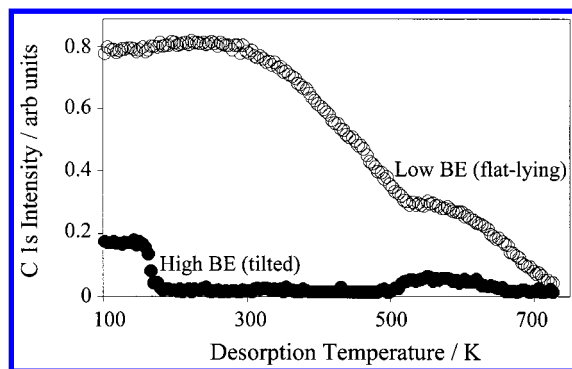


Figure 7. Fitted, integrated C 1s peak intensities derived from a C_6H_6 -saturated Pd{111} surface as a function of temperature, showing η^1 - C_6H_6 (●) and η^6 - C_6H_6 (○) components.

η^1 -species is stable up to 150 K, beyond which it rapidly desorbs over a narrow window of ~ 20 K, leaving a surface covered with flat-lying η^6 -benzene. This observation confirms our assignment of the high BE state to a weakly bound η^1 -benzene species. η^6 flat benzene is stable up to 250 K, beyond which point it desorbs in two distinct stages. About 60% of the flat benzene is lost in the interval 250–500 K. Then, as coverage decreases and repulsive lateral interactions with nearest neighbor molecules are eliminated, the remaining flat-lying benzene molecules are more strongly adsorbed, desorbing between 500 and 700 K. All these changes are entirely consistent with earlier conventional mass-spectrometric TPD studies of benzene on Pd{111}, and with related Monte Carlo simulations of lateral interactions within the evolving benzene adlayer.²² Thus at high benzene coverages there is a substantial decrease in adsorption strength associated with population of a low-temperature state only stable below 200 K; at lower coverages a more strongly bound state exists. These strong and weak adsorption states are readily assigned to the low BE (flat-lying) and high BE (tilted) benzene species, respectively.

Notice that as the remaining flat benzene is removed above 500 K, emission due to a high BE state re-appears (Figure 7). The associated species possesses the same C 1s BE and line shape as tilted benzene. At first sight this seems surprising, as it is not obvious why re-conversion of strongly adsorbed benzene

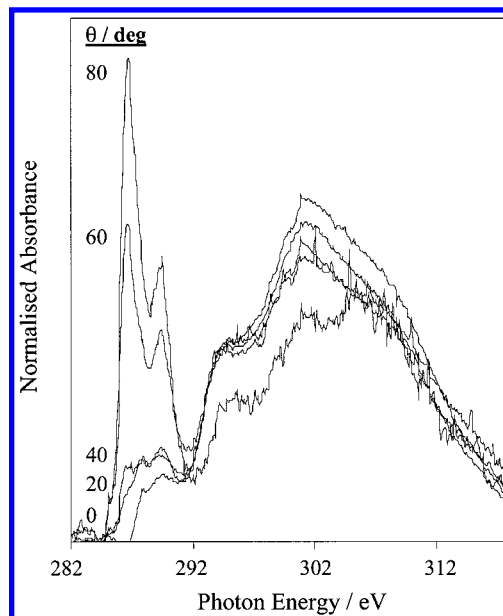


Figure 8. C 1s NEXAFS of a C_6H_6 -saturated Pd{111} surface subsequently annealed to 323 K as a function of incident photon angle.

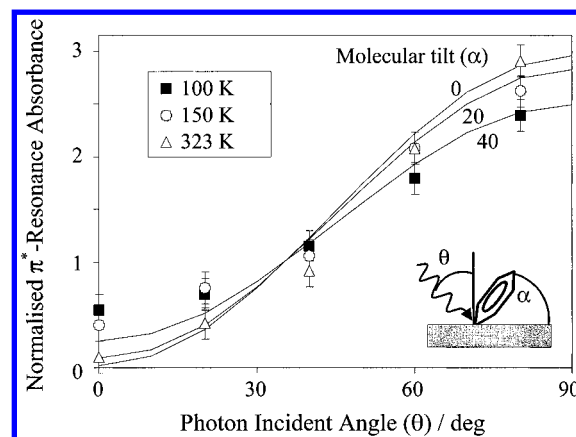


Figure 9. Angular dependence of C 1s π^* resonance intensities from a saturation C_6H_6 overlayer on Pd{111} as a function of surface temperature.

back to weakly adsorbed benzene should occur at the lowest coverages. However, at these high temperatures and low coverages, a new process becomes possible for flat benzene, namely C–H bond scission.²³ This could lead to the formation of a metastable tilted phenyl species which gives rise to the high-temperature high BE C 1s signal, and which subsequently desorbs as benzene by phenyl + H recombination.¹² Carbon atoms in the tilted phenyl moiety and in η^1 - C_6H_6 are in very similar environments and the associated C 1s emission might therefore be expected to be indistinguishable in our experiments. We may note in passing that entirely analogous behavior involving N–H cleavage, formation of a metastable tilted pyrrolyl species, and subsequent desorption of pyrrole has been reported for pyrrole adsorbed on Pd{111}.²⁴

These changes in adsorption geometry as a function of temperature and coverage deduced on the basis of fast XPS are consistent with the temperature dependence of the C 1s NEXAFS spectra observed when a benzene saturated adlayer was progressively annealed from 100 K (Figure 3b) to 150 K and then 323 K. The 323 K spectra are shown as a function of photon incidence angle θ in Figure 8, from which a much weaker angular dependence of the π^* resonance intensity is apparent at higher temperatures (Figure 9), thus confirming

evolution of the adlayer toward a flat-lying geometry as coverage decreases.

Conclusions

1. At low coverages benzene initially adopts a flat-lying geometry on Pd{111}, bonding via the aromatic π -electron system. This strongly bound species desorbs in the range 250–600 K.

2. At coverages above 0.16 ML a different type of benzene is also present, distinguishable by its higher C 1s BE. This species is more weakly adsorbed, desorbing at \sim 150 K, and NEXAFS shows that it is strongly tilted with respect to the metal surface.

3. The coverage-dependent adsorption of benzene into flat and tilted geometries, originally suggested in order to account for the kinetics of acetylene trimerization of Pd{111}, has been unequivocally demonstrated.

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References and Notes

- (1) Thomas, F.; Chen, N.; Lee, I.; Ford, L.; Blowers, P.; Masel, R. I. *J. Vac. Sci. Technol. A* **1999**, *17*, 2339.
- (2) Zebisch, P.; Stichler, M.; Trischberger, P.; Weinelt, M.; Steinruck, H. P. *Surf. Sci.* **1998**, *396*, 61.
- (3) Eng, J.; Bent, B. E.; Fruhberger, B.; Chen, J. G.; *J. Phys. Chem. B* **1997**, *101*, 4044.
- (4) Treboux, G.; Aono, M. *J. Phys. Chem. B* **1997**, *101*, 4620.
- (5) Yoon, H. A.; Salmeron, M.; Somorjai, G. A. *Surf. Sci.* **1997**, *373*, 300.
- (6) Kang, J. H.; Toomes, R. L.; Robinson, J.; Woodruff, D. P.; Schaff, O.; Terborg, R.; Lindsay, R.; Baumgartel, P.; Bradshaw, A. M. *Surf. Sci.* **2000**, *448*, 23.
- (7) Koschel, H.; Held, G.; Trischberger, P.; Widdra, W.; Steinruck, H. P. *Surf. Sci.* **1999**, *437*, 125.
- (8) Doering, M.; Rust, H. P.; Briner, B. G.; Bradshaw, A. M. *Surf. Sci.* **1998**, *410*, L736.
- (9) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *J. Chem. Soc., Chem. Commun.* **1983**, 623.
- (10) Ormerod, R. M.; Lambert, R. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1421.
- (11) Ormerod, R. M.; Lambert, R. M. In *Springer Series in Surface Science, Vol. 34, Surface Reactions*; Madix, R. J., Eds.; Springer-Verlag: Berlin, 1994; p 89.
- (12) Lee, A. F.; Wilson, K.; Middleton, R. L.; Baraldi, A.; Goldoni, A.; Paolucci, G.; Lambert, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 7969.
- (13) Patterson, C. H.; Lambert, R. M. *J. Phys. Chem.* **1988**, *92*, 1266.
- (14) Lomas, J. R.; Baddeley, C. J.; Tikhov, M. S.; Lambert, R. M. *Langmuir* **1995**, *11*, 3048.
- (15) Hoffmann, H.; Zaera, F.; Ormerod, R. M.; Wang, L. P.; Tysoe, W. T.; Lambert, R. M. *Surf. Sci.* **1990**, *232*, 259.
- (16) Lee, A. F.; Baddeley, C. J.; Hardacre, C.; Ormerod, R. M.; Lambert, R. M.; Schmid, G.; West, H. *J. Phys. Chem.* **1995**, *99*, 6096.
- (17) Weiss, K.; Gebert, S.; Wuhn, M.; Wadepohl, H.; Woll, C. *J. Vac. Sci. Technol. A* **1998**, *16*, 1017.
- (18) Solomon, J. L.; Madix, R. J.; Stohr, J. *Surf. Sci.* **1991**, *255*, 12.
- (19) Stohr, J.; Jaeger, R. *Phys. Rev. B* **1982**, *26*, 4111.
- (20) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *Surf. Sci.* **1983**, *135*, 128.
- (21) Patterson, C. H.; Lambert, R. M. *J. Am. Chem. Soc.* **1988**, *110*, 6871.
- (22) Tysoe, W. T.; Ormerod, R. M.; Zgrablich, G.; Ramirezcuesta, A.; Lambert, R. M. *J. Phys. Chem.* **1993**, *97*, 3365.
- (23) Moyes, R. B.; Baron, K.; Squire, R. C. *J. Catal.* **1971**, *22*, 333.
- (24) Baddeley, C. J.; Hardacre, C.; Ormerod, R. M.; Lambert, R. M. *Surf. Sci.* **1996**, *369*, 1.