VIBRATIONAL SPECTROSCOPY OF ACETYLENE DECOMPOSITION ON PALLADIUM (111) AND (100) SURFACES (U) INDIANA UNIV AT BLOOMINGTON DEPT OF PHYSICS L L KESMODEL ET AL.

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**Vibrational Spectroscopy of Acetylene Interim Decomposition on Palladium (111) and (100) Surfaces**

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**ABSTRACT**

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Vibrational spectra for thermal decomposition of acetylene (C<sub>2</sub>H<sub>2</sub>) on (111) and (100) surfaces of palladium obtained with high-resolution electron energy loss spectroscopy (HREELS) are described. Of particular interest is the formation of C<sub>2</sub>H species on both surfaces, which are identified spectroscopically in this context for the first time. On Pd(100) C<sub>2</sub>H forms with thermal processing of chemisorbed acetylene to -400K but on Pd(111) is co-adsorbed with a C<sub>2</sub> species following 300K C<sub>2</sub>H<sub>2</sub> adsorption.
further annealing to 450K CCH is the dominant species on both surfaces. The EELS spectra indicate that both carbon atoms are involved in the CCH interaction with the surface as implied by a C-C bond order between 1 and 2. In view of recent reports of acetylene trimerization to benzene (C₆H₆) on Pd surfaces the EELS spectra of C₆H₆ and isotopic mixtures were also analyzed but no evidence for this reaction was found.
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ON PALLADIUM (111) AND (100) SURFACES

by

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Abstract
Vibrational spectra for thermal decomposition of acetylene (C$_2$H$_2$) on (111) and (100) surfaces of palladium obtained with high-resolution electron energy loss spectroscopy (EELS) are described. Of particular interest is the formation of CCH species on both surfaces, which are identified spectroscopically in this context for the first time. On Pd(100) CCH forms with thermal processing of chemisorbed acetylene to 400K but on Pd(111) is co-adsorbed with a C-CH$_3$ species following 300K C$_2$H$_2$ adsorption. With further annealing to 450K CCH is the dominant species on both surfaces. The EELS spectra indicate that both carbon atoms are involved in the CCH interaction with the surface as implied by a C-C bond order between 1 and 2. In view of recent reports of acetylene trimerization to benzene (C$_6$H$_6$) on Pd surfaces the EELS spectra of C$_6$H$_6$ and isotopic mixtures were also analyzed but no evidence for this reaction was found.
1. Introduction

Recent spectroscopic studies of acetylene (C$_2$H$_2$) chemistry on palladium surfaces by several research groups [1-5] have raised many questions concerning the thermal evolution of this species. In high-resolution electron energy loss (EELS) studies on Pd(111) the formation of CCH$_2$, CCH$_3$, and CH species were detected as thermal evolution products of initially chemisorbed C$_2$H$_2$ in the temperature range 150-500K [1,2]. However, in subsequent studies with thermal desorption spectroscopy (TDS) [3-5] and ultraviolet photoemission spectroscopy (UPS) [3,4] the formation of benzene (C$_6$H$_6$) has been emphasized. Ethylene formation was also reported [4,5]. Several questions remain concerning possible C$_6$H$_6$ formation: UPS evidence [3,4] for this species is not definitive, and aspects of the TDS results are inconsistent. For example, in the study by Sesselmann et al. [3] C$_6$H$_6$ was reportedly formed only under low temperature and high exposure (> 100L) conditions whereas Tysoe et al. [4] and Gentle and Muetterties [5] detected reactively-formed C$_6$H$_6$ at both low (230K) and high (500K) temperatures. We note that the studies in Refs. 1-4 were restricted to the (111) surface whereas (111), (100), and (110) surfaces were considered in Ref. 5.

The central issue addressed in the present work concerns the nature of acetylene-derived species present on both Pd(111) and Pd(100) surfaces in the temperature range 300-500K. In this regard the work expands on our earlier EELS studies on Pd(111) [2] and focuses on the question of C$_6$H$_6$ formation. Detailed EELS
analysis of $\text{C}_2\text{H}_2$, $\text{C}_6\text{H}_6$ and their deuterated counterparts were carried out, including various isotope mixing experiments. Although a 450K acetylene-derived surface species observed on both Pd(111) and Pd(100) exhibits vibrational features similar to benzene we find that this species is, in fact, CCH. On Pd(100) the CCH species is formed near 400K from $-\text{sp}^3$ hybridized acetylene. On Pd(111) both CCH and ethylidyne ($\equiv\text{C-CH}_3$) [2] are formed upon adsorption of $\text{C}_2\text{H}_2$ at 300K, the ethylidyne species decomposing by 450K. The Pd(100) vibrational data suggests that the CCH stereochemistry involves bonding of both carbon atoms to the surface with a bond order between 1 and 2.

Our lack of EELS vibrational evidence for benzene formation does not directly conflict with the recent studies [3-5] but rather suggests that benzene may be (i) formed in relatively small amounts on the surface or (ii) largely formed in a process leading to rapid desorption.
2. Experimental Procedures

The high-resolution electron energy loss measurements were carried out with two 127° cylindrical deflection electron spectrometers at Indiana University. The Pd(111) experiments were performed with a single-pass instrument [6] which is housed in an ion-pumped ultrahigh vacuum system (base pressure \(-1 \times 10^{-10}\) Torr), also equipped for ion-sputtering, low-energy electron diffraction and Auger spectroscopy. This instrument was operated at 10 meV (80 cm\(^{-1}\)) system resolution at typical elastic beam signal levels of 0.3-1.0 \(\times 10^5\) cps for hydrocarbon adsorption. The Pd(100) experiments employed a new double-pass spectrometer which achieves high signal levels at 2.5-10 meV system resolution [7]. This instrument is incorporated in a diffusion/sublimation-pumped system (base pressure \(-5 \times 10^{-11}\) Torr) equipped for ion-sputtering and mass spectrometry. Due to the generally low intensity of the hydrocarbon modes the spectrometer was operated at 8-9 meV (64-72 cm\(^{-1}\)) system resolution providing specular elastic beam count rates of \(-2 \times 10^6\) cps at beam energies of 4-6 eV. The high sensitivity afforded under these conditions proved valuable for detection of weak losses and facilitated off-specular measurements.

Sample preparation and cleaning for the EELS experiments has been described elsewhere [2]. High purity \(\text{C}_2\text{H}_2\), \(\text{C}_2\text{D}_2\), \(\text{C}_6\text{H}_6\), \(\text{C}_6\text{D}_6\), \(\text{H}_2\), and \(\text{D}_2\) gases were used and were examined with a mass spectrometer for impurities. Hydrocarbon exposures quoted in Langmuirs (1L = \(10^{-6}\) Torr-s) were corrected for reported
ion-gauge sensitivity [8].

3. Results

Extensive high-resolution EELS spectra for \( \text{C}_2\text{H}_2, \text{C}_2\text{D}_2, \)
\( \text{C}_6\text{H}_6, \text{and C}_6\text{D}_6 \) on \( \text{Pd(111)} \) and \( \text{Pd(100)} \) have been obtained under
various temperature and coverage conditions; isotope mixing
experiments (\( \text{C}_2\text{H}_2 + \text{C}_2\text{D}_2, \text{C}_6\text{H}_6 + \text{D}_2, \text{etc.} \)) have been performed as
well. In this section the salient results of this study are
discussed with emphasis on (i) the possible detection of \( \text{C}_2\text{H}_2 \)
trimerization to \( \text{C}_6\text{H}_6 \) and (ii) the nature of acetylene
decomposition product(s) in the temperature range 300-500K.

3.1. \( \text{Pd(100)} \) vibrational spectra

The EELS spectrum for 300K adsorption of \( \text{C}_2\text{H}_2 \) on \( \text{Pd(100)} \) is
shown in Fig. 1a. As discussed elsewhere [9] this spectrum is
due to acetylene in a near \( \text{sp}^3 \) hybridization state as evidenced
by \( \nu_{\text{CC}} = 1210 \text{ cm}^{-1} \) and \( \nu_{\text{CH}} = 2920 \text{ cm}^{-1} \). This spectrum transforms
upon warming to 450K (Fig. 1b) to one resembling those reported
for CH species on (111) surfaces of Ni, Pd, Pt, and Rh [10];
characteristic is the strong CH bending loss at 750 cm\(^{-1}\) and the
CH stretch at 3000 cm\(^{-1}\). However, a broad band ca. 1340 cm\(^{-1}\) is
also found which does not appreciably shift with deuteration and
is, therefore, assigned to a CC stretching mode. Importantly, we
find that the 750 cm\(^{-1}\), 1340 cm\(^{-1}\), and 3000 cm\(^{-1}\) loss intensities
decay at the same rate (within experimental error of 10%) upon
thermal processing from 475K to 650K. This is strong evidence
that a single surface species is responsible for these modes. A
likely interpretation of Fig. 1b is thus in terms of a
multiply-bonded CCH species.

Figure 1c indicates that C₆H₆ formation might also provide an explanation of the 450K acetylene-derived species. Benzene adsorbed at 300K is fairly stable until ~500K with an EELS spectrum characterized by a very intense loss at 730 cm⁻¹ with much weaker losses at 1130, 1440, and 3020 cm⁻¹. Quite similar spectra have been reported for C₆H₆ adsorption on Ni(111) [11,12], Ni(100) [12], Pt(111) [11], and Rh(111) [13] and consistently interpreted in terms of predominant π-bonding with the benzene ring parallel to the surface. The exceptionally strong loss at 730 cm⁻¹ is assigned to the ν₄ out-of-plane CH bending mode of A₂u symmetry and 673 cm⁻¹ frequency in the gas phase [14,15]. This mode has strong infrared activity in the gas phase and will be dipole active on the surface for parallel adsorption. The resemblance of major features of Figs. 1b,c leaves C₆H₆ formation a possibility we discuss further below.

3.2 Pd(111) vibrational spectra

EELS vibrational spectra for 150K C₂H₂ adsorption and thermal evolution were reported earlier [2]. It was found that C₂H₂ chemisorbed at 150K in an sp².5 hybridization state (Fig. 2a, νCC = 1400 cm⁻¹, νCH = 2990 cm⁻¹) and underwent hydrogenation to ethylidyne (≡C-CH₃) near 300K via a probable vinylidene (≡C=CH₂) intermediate. Here we consider room temperature C₂H₂ adsorption at relatively low (1.5L) and higher (12L) exposures. Under these conditions a mixture of ethylidyne and CCH species form as shown in Fig. 2b,c. Ethylidyne has been
characterized [2] in terms of strong modes near 1330 cm⁻¹ (methyl deform.) and 1100 cm⁻¹ (CC stretch). These modes are present for 300K adsorption along with the strong CH bending vibration indicative of CCH (or possibly C₆H₆). Upon warming to 500K decomposition of ethylidyne has occurred but the 750 cm⁻¹ loss remains (Fig. 2d). As noted for the (100) surface this spectrum is quite similar to the EELS spectrum for associatively adsorbed C₆H₆ (Fig. 2e). Signal-to-noise levels in the Pd(111) study were not sufficient to permit conclusive identification of νCH loss features in the 1000-1500 cm⁻¹ region for Fig. 2d,e. However, comparison of the Pd(100) and (111) spectra strongly suggests that the same acetylene-derived species is present on both surfaces at 450K. Finally, we note a 300K exposure-dependent ratio of this product and ethylidyne evident in Fig. 2b,c. This aspect will be discussed in a subsequent paper in connection with hydrogen thermal desorption results.

3.3. Off-specular analysis

In order to further explore possible detection of C₆H₆ formation selected off-specular analyses comparing C₆H₆ and the 475K acetylene-derived species were undertaken on Pd(100). As shown in Fig. 3b,c marked differences between C₆H₆ and the C₂H₂-derived species occur in the 1000-1600 cm⁻¹ region. The νCH loss is also much stronger for the latter species. As shown in Fig. 3a the broad 1360 cm⁻¹ band is hardly shifted upon deuteration.

These spectra indicate that the species is not benzene but
rather CCH. In Fig. 3a the presence of a small amount of CCH in the CCD spectrum is evident from weak features near 750 cm\(^{-1}\) (shoulder) and 3000 cm\(^{-1}\). Other features of note are the presence of shoulders at 850 (640) cm\(^{-1}\) in the CCH (CCD) spectra. These weaker modes may be due to the other CH bending mode (parallel to the surface plane) or to CCH species in another surface bonding configuration. The latter interpretation is consistent with the broad nature of the \(\nu_{CC}\) band centered at 1360 cm\(^{-1}\). We rule out CCH\(_2\) or CH\(_2\) species due to the absence of characteristic scissor vibrations (ca.1400 cm\(^{-1}\)) and on the basis of isotope mixing experiments discussed below.

3.4. Isotope mixing experiments

If the acetylene-derived species formed at 450K is C\(_6\)H\(_6\) it is clear that mixtures of C\(_2\)H\(_2\) and C\(_2\)D\(_2\) will give rise to C\(_6\)H\(_x\)D\(_{6-x}\) molecules with even \(x\); the other isotopes will occur if H-D exchange occurs. Furthermore, by scaling to known gas phase frequencies for the strong \(\nu_4\) bending mode \([15]\) reasonable predictions for the surface isotopes can be made. This mode should be dipole active in each case for parallel-bonded benzene. The various bands (\(\nu_4\)) are found to occur in separated groupings \([15]\) and the predicted surface frequencies are, for example: C\(_6\)D\(_6\) (545 cm\(^{-1}\)); sym-C\(_6\)H\(_3\)D\(_3\) (588 cm\(^{-1}\)); para-C\(_6\)H\(_4\)D\(_2\) (658 cm\(^{-1}\)); C\(_6\)H\(_6\) (740 cm\(^{-1}\)). Benzene mixtures should, therefore, be characterized by a very broad band between 545-740 cm\(^{-1}\). Such a band was consistently produced by mixing C\(_6\)H\(_6\) with D\(_2\) at 150K on Pd(111) and warming to 450K. Figure 4 provides clear evidence
for statistically probable C$_6$H$_3$D$_3$ or C$_6$H$_2$D$_4$ isotopes whereas C$_6$D$_6$ is largely absent as expected. Another loss appearing as a shoulder near 825 cm$^{-1}$ is quite probably due to another strong mode for one of the isotopes [16]. These results (and similar ones for C$_6$D$_6$ + H$_2$) are qualitatively different than predictions for the CCH model which would, of course, simply give rise to the same two bands when C$_2$H$_2$ and C$_2$D$_2$ are mixed.

Isotope mixing of C$_2$H$_2$ and C$_2$D$_2$ are illustrated in Fig. 5 for Pd(100). Panel (a) shows the unreacted mixture at 300K which gives rise to two strong modes at 545 cm$^{-1}$ and -770 cm$^{-1}$ upon warming to 450K. Analogous results were obtained on the (111) surface. This result clearly favors the CCH model and rules out C$_6$H$_6$ formation. In the benzene model, for example, the 770 cm$^{-1}$ mode associated with pure C$_6$H$_6$ would have very low statistical weight for the 1:2 mixture, contrary to the EELS spectra (Fig. 5). Furthermore, we find that calibration to relative loss intensities for the separate C$_2$H$_2$ and C$_2$D$_2$ heating experiments allows fairly accurate prediction (5-20% error) of relative intensities of the two loss peaks for various isotope mixing ratios. This result again strongly supports the CCH model but cannot be reconciled with the benzene model or other polymerization products.
4. Conclusions

The high-resolution EEL data discussed in Sec. 3 provides rather clear spectral evidence for CCH formation from $C_2H_2$ on both (111) and (100) palladium surfaces. Although this species was interpreted as CH in earlier work on Pd(111) [2] the present investigation strongly favors the CCH model since the band attributable to $v_{CC}$ is consistently found on the (100) surface. Furthermore, an appealing aspect of room-temperature CCH formation on Pd(111) is the release of hydrogen necessary to also form the $=C-CH_3$ species from acetylene. This is the first clear evidence for such a species on (100) and (111) surfaces of Pd or related metals although a CCH species was proposed on Ni(110) in UPS studies [17]. In this regard it may be important to reconsider the earlier assignments made to CH species on Ni, Pt, and Rh [10] in terms of CCH formation due to the close resemblance of the various spectra.

Evidently CCH stereochemistry on palladium involves bonding of both carbon atoms to the metal surface leading to a C-C bond order between 1 and 2 judging from the present EELS results. We postulate that a likely bonding geometry involves the C-C axis parallel or slightly skewed to the surface, consistent with a strong CH bending loss and a weak loss due to the CC stretch. These general features would not be sensitive to structural details on the (100) and (111) surfaces.

We also note the high stability of the CCH species. Thermal processing measurements on Pd(100) indicate that decomposition
begins only after -550K and -30% of the original species remains at 650K. In this regard, ab initio calculations on CCH bonding geometry and relative stability compared to \( \text{C}_2\text{H}_2 \), \( \text{CH} \), etc., would be of considerable interest.

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References

[8] Varian ionization gauge sensitivity factors: acetylene, 2.0; benzene, 6.0.
[10] A tabulation of data and further references are given in Ref. 2.
p. 324.

[16] We find a mode of medium intensity ca. 830 cm$^{-1}$ for C$_6$D$_6$ on Pd(111); a similar mode was reported on Rh(111) [13].

Figure Captions
Fig. 1: High-resolution EELS spectra for hydrocarbon adsorption on Pd(100).
(a) 10L C₂H₂ exposure at 300K
(b) Thermal processing of (a) to 450K
(c) 2L C₆H₆ exposure at 300K
Scale changes refer to the elastic beam for each panel in this and subsequent figures.
Fig. 2: High-resolution EELS spectra for hydrocarbon adsorption on Pd(111).
acetylene: (a) 3 L exposure at 150K,
(b) 1.5 L exposure at 300K,
(c) 12 L exposure at 300K,
(d) Thermal processing of (c) to 500K
benzene: (e) 1 L exposure at 300K, warmed to 450K.
Fig. 3: Comparison of high-resolution EELS spectra for the 475K acetylene-derived surface phase and benzene for off-specular scattering on Pd(100).
Fig. 4: High-resolution EELS spectra due to mixing of C₆H₆ and D₂ on Pd(111). Lines labeled A-D show the predicted positions for various benzene isotopes due to the v₄ modes (see text). Positions of sym-C₆H₃D₃, para-C₆H₄D₂, and para-C₆H₂D₄ are shown. The additional ortho-, meta-C₆H₄D₂, 1,2,3-C₆H₃D₃, etc., isotopes
are slightly shifted from the respective groupings shown [15]. Information on the C$_6$HD$_5$ isotope was not found for this mode.

Fig. 5: High-resolution EELS spectra due to isotope mixing of C$_2$H$_2$ and C$_2$D$_2$ on Pd(100).
(a) 300K spectrum due to co-adsorbed C$_2$H$_2$ and C$_2$D$_2$.
(b) Thermal processing of (a) to 450K leads to CCH, CCD spectrum. Dashed lines indicate predicted isotope vibrational losses in the event of benzene formation (cf. Fig. 4).
Fig. 1

Pd (100)

(c) 2 L C₆H₆ 300K

(b) 10 L C₂H₂ 450K

(a) 10 L C₂H₂ 300K

ENERGY LOSS (cm⁻¹)
Fig. 2
Fig. 3
Pd (111)

$\nu_4$ MODES

A: $C_6D_6$
B: $C_6H_2D_4$
C: $C_6H_4D_2$
D: $C_6H_6$

$C_6H_6 + D_2$ 150K
HEATED TO 450K

Fig. 4
Pd (100)

$C_2H_2 + C_2D_2$

1:2 MIXTURE

Fig. 5