

Vibrational Study of the Interaction of Acetylene and Benzene on Clean and Carbide-Modified W(211) Surfaces

J. Eng, Jr. and J. G. Chen^{*,†}

Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801

I. M. Abdelrehim[‡] and T. E. Madey^{*}

Department of Physics and Astronomy and the Laboratory for Surface Modification Rutgers, The State University of New Jersey Piscataway, New Jersey 08854-8019

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As a part of a continuing investigation of acetylene reactions on tungsten surfaces covered by ultrathin metal films, the chemistry of acetylene on clean and carbide-modified W(211) surfaces has been investigated using high-resolution electron energy-loss spectroscopy (HREELS) and temperature-programmed desorption (TPD) measurements. Acetylene decomposes between 100 and 450 K on the clean W(211) surface, ultimately forming carbidic carbon and gaseous hydrogen. During this decomposition process, a mixture of different hydrocarbon fragments are formed, most likely vinylidene (CCH₂) or vinyl (HCCH₂) and acetylide (CCH). On the carbide-modified W(211) surface, acetylene also decomposes to produce carbon and gaseous hydrogen. However, compared to clean W(211), the CH bond activation is suppressed on the carbide-modified W surface, as evidenced by the broadening and significant shifting of the H₂ TPD features toward higher temperatures as well as by the HREEL spectra monitoring the thermal decomposition of acetylene on the carbide-modified W(211) surface.

1. Introduction

Recently, there has been considerable interest in the structure and catalytic properties of W(111) surfaces which are covered by thin metal films.^{1–5} This interest stems from the novel properties of certain metal films (e.g., Pd, Pt, Rh, Ir, Au) on the W(111) surface that grow pseudomorphically at room temperature but induce a significant reconstruction of the W(111) substrate upon heating above ~750 K. For example, using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED),⁵ it has been shown that for Pd coverages of one monolayer or greater, this reconstruction results in the formation of three-sided pyramids which have Pd-covered W(211) faces. Such behavior makes the Pd/W(111) system particularly significant in the area of catalysis, since it is one of the few systems in which one can tailor the morphology of the metal overlayer and substrate in a well-defined, controlled manner.

In this series of articles,^{1,4} we investigate the catalytic properties of ultrathin Pd layers on W(211). These studies are useful for understanding the reactivity of reconstructed Pd/W(111) surfaces because the faces of the pyramids that form during the W(111) surface reconstruction are W(211) surfaces covered by a monolayer of Pd. To study the reactivity of the Pd/W(211) surface, we have chosen acetylene as a probing molecule. As discussed in the companion paper,¹ acetylene has a rich surface chemistry on Pd/W(211) surfaces. For example, although the predominant reaction of acetylene on Pd/W(211) surfaces is hydrogenation to produce ethylene, other reaction

channels, such as cyclotrimerization to form benzene, are also possible.

To provide deeper insight into the different reaction pathways of acetylene on clean W(211) and Pd-covered W(211) surfaces, in this paper we discuss the reactivity of acetylene on clean W(211) surfaces. To place our work in context, it is useful to mention briefly previous studies of acetylene on W surfaces. For acetylene on W(111), early HREELS studies showed that acetylene dissociates completely at low coverages but adsorbs molecularly at higher coverages.⁶ HREELS studies also showed that acetylene behaves similarly on W(110) surfaces, but at intermediate coverages, disproportionation reactions could occur to produce hydrocarbon fragments which have CH₂ groups.⁷

In addition to studying the chemistry of acetylene on the clean W(211) surface, we have also investigated the behavior of acetylene on carbide-modified W(211) surfaces. Our interest in the reactivity of the carbide-modified W(211) surfaces arises from previous work which demonstrated that the reactivities of carbide overlayers on close-packed early transition metal surfaces, such as Mo(110) and V(110) surfaces, are similar to those of the Pt-group metals.⁸ Our goal in the current study is to understand how the formation of a carbide overlayer changes the reactivity of an early transition metal surface which intrinsically has a corrugated structure, such as the W(211) surface.

The remainder of this paper is organized as follows. After briefly describing the experimental procedures, we present vibrational spectra which monitor the decomposition of acetylene on clean W(211). Next, vibrational spectra of benzene on the clean W(211) surface are presented to confirm that acetylene does not cyclotrimerize to form benzene on the clean W surface. For comparison, spectra of benzene on the carbide-modified

* To whom correspondence should be addressed.

[†] Present address: Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716.

[‡] Present address: Evans East, Plainsboro, NJ 08536.

W surface are also shown. Finally, TPD and HREEL spectra which monitor the reaction and thermal decomposition of acetylene on the carbide-modified W(211) surface will be shown. In the Discussion section, the intermediates formed from the decomposition of acetylene will be identified when possible and the similarities and differences between the reactivities of the clean and carbide-modified W(211) surfaces will be emphasized.

2. Experimental Section

2.1. Techniques. The ultrahigh vacuum chamber used in these studies, which has been described in detail in a previous publication,⁹ features an LK-3000 high-resolution electron energy-loss spectrometer that was operated at an electron energy of 6.0 eV. The elastic peak, as recorded from a W(211) surface saturated by acetylene, typically had a full-width at half-maximum (fwhm) of ~ 35 cm^{-1} and an intensity of approximately 1×10^5 cps. The spectra were recorded in the on-specular and -15° off-specular direction, where -15° refers to $\theta(\text{detector}) - \theta(\text{monochromator}) = -15^\circ$. For the spectra reported below, all of the elastic peaks have been normalized to unity and the expansion factors that are shown refer to the expansion relative to the on-specular elastic peak. Also, for the HREEL studies monitoring the thermal decomposition of acetylene, the W(211) crystal was flashed to each specified temperature and then cooled immediately. All HREEL spectra were obtained with the crystal temperature at 100 K.

The W(211) single-crystal (Aesar) surface was cleaned by neon sputtering (3 mA sample current, 5 kV electron energy, $P_{\text{Ne}} = 7 \times 10^{-5}$ Torr) with the crystal held at 1000 K, followed by annealing at 1150 K. Typically, this sputtering/annealing procedure generated a clean, well-ordered W(211) surface, as verified by Auger electron spectroscopy (AES) and LEED. However, occasionally the sputtering procedure was supplemented with an oxygen titration step to remove surface carbon, particularly after the carbide studies. This titration was performed by dosing small amounts of molecular oxygen (~ 0.25 – 1.0 L, where $1 \text{ L} = 1 \times 10^{-6}$ Torr s) into the vacuum chamber while the W crystal was held at 1000 K and then flashing the crystal to 1150 K to remove carbon as CO.

The C_2H_2 (spectral grade, 99.96% purity) was purified by passing it through a dry ice/acetone-cooled trap in order to remove the acetone stabilizer. The purified acetylene was collected in an evacuated vessel. The acetylene- d_2 (Cambridge Isotope Labs, 99% purity) was purchased in a glass break-seal flask which was subsequently connected to a precision leak valve for direct dosing into the chamber. The C_6H_6 (Aldrich, 99.99% pure) was stored in a stainless steel cylinder and purified by several freeze–pump–thaw cycles prior to use. The purity of all hydrocarbons was verified in situ by mass spectrometry prior to use. Oxygen (99.99% purity) was purchased from Matheson and used without further purification. All exposures reported are uncorrected for differences in ion gauge sensitivity.

2.2. Formation of the Carbide-Modified W(211) Surface. The carbide-modified W(211) surfaces used in these studies were formed by successive dosing/flashing cycles in which the crystal was held at 100 K, exposed to 3 L of acetylene, and then subsequently flashed to $T \geq 1000$ K (typically to 1150 K). These dosing/flashing cycles were repeated until the ratio of the C(KLL 272 eV)/W(169 eV) Auger features was ~ 0.6 , which corresponds to a C/W atomic ratio of approximately 0.36, after taking into account the differences in the Auger sensitivity factors the W(169 eV) feature as compared to the W(MNN 1736 eV) feature.¹⁰ Usually, two or three dosing/flashing cycles were

needed to achieve such a C/W Auger ratio. (In the following, a 1-cycle carbide refers to 1 dosing/flashing cycle, a 2-cycle carbide refers to 2 dosing/flashing cycles, etc.) At all times, the C(KLL 272 eV) Auger feature displayed a line shape characteristic of carbidic carbon, rather than graphitic carbon. Additionally, preliminary LEED studies indicate that this carbide-modified W(211) surface is disordered, since no LEED pattern was observable at the end of the dosing/flashing cycles.

3. Results

3.1. Acetylene on Clean W(211). Figure 1 shows HREEL spectra obtained by exposing a clean W(211) surface at 100 K to increasing amounts of C_2H_2 and C_2D_2 . These spectra clearly show that different intermediates can be formed on the surface, depending on the coverage. For example, following a 1.0 L exposure of acetylene, the dominant spectral features are consistent with the presence of a strongly chemisorbed acetylene species (Figures 1b and 1f). This chemisorbed acetylene species is characterized by $\nu(\text{CH})$ and $\nu(\text{CC})$ features which are substantially shifted relative to the gas-phase values;¹¹ the assignments of these features are summarized in Table 1. In particular, the $\nu(\text{CC})$ feature is shifted toward lower frequencies by almost 600 cm^{-1} .¹¹

The large shift in the frequency of the $\nu(\text{CC})$ feature is typically observed for acetylene adsorbed on single-crystal transition-metal surfaces and indicates that the $\text{C}\equiv\text{C}$ bond of acetylene has rehybridized upon adsorption. There are three possible bonding configurations which result from such a rehybridization:^{12,13} (1) a di- σ -bonded species, where the two carbon atoms are only σ -bonded to the surface; (2) a di- σ/π -bonded species, where the two carbon atoms are σ -bonded to the surface but also π -bonded to a third metal atom, and (3) a di- $\sigma/\text{di-}\pi$ -bonded species, where the carbon atoms are bonded by two σ bonds and two π bonds to four metal atoms. Since case 1 would result in a double bond between the two carbon atoms and since no $\nu(\text{C}=\text{C})$ features are observed between 1500 and 1650 cm^{-1} in Figures 1b and 1f, we can exclude the possibility that acetylene is simply di- σ bonded to the clean W(211) surface. In case 2, the additional π bond to the surface typically lowers the bond order of the $\text{C}\equiv\text{C}$ bond from 3 to ~ 1.7 , causing the $\nu(\text{CC})$ feature to be relatively weak and occur between 1210 and 1410 cm^{-1} . For example, di- σ/π bonding has been reported for C_2H_2 and C_2D_2 on Pt(111), and correspondingly a weak $\nu(\text{CC})$ mode has been observed at 1310 cm^{-1} for C_2H_2 and at 1260 cm^{-1} for C_2D_2 on Pt(111).¹⁴ Finally, in case 3, the bond order of the $\text{C}\equiv\text{C}$ bond is typically lowered from 3 to 1.3 – 1.7 , causing the $\nu(\text{CC})$ feature to appear between 1100 and 1310 cm^{-1} . However, unlike case 2, the $\nu(\text{CC})$ feature which results from di- $\sigma/\text{di-}\pi$ bonding is typically dominant relative to the other spectral features.¹² In the present case, we observe a relatively weak feature at 1366 cm^{-1} which appears to have no gas-phase analogue (cf. Table 1). On the basis of the foregoing arguments, we conclude that this feature results from the CC stretch of a di- σ/π -bonded acetylene species.

Although vibrational features in the spectra obtained following a 1.0 L exposure of acetylene are completely consistent with the presence of a di- σ/π -bonded acetylene species, the spectra recorded at lower exposures of acetylene (i.e., 0.5 L) show additional features which are not attributable to molecular acetylene but rather to intermediates which result from the decomposition of a fraction of adsorbed acetylene. In particular, the feature at 1448 cm^{-1} in Figure 1a is not characteristic of strongly chemisorbed acetylene (cf. Table 1) but instead can be attributed to the C–H deformation modes of CH_2 or CH_3

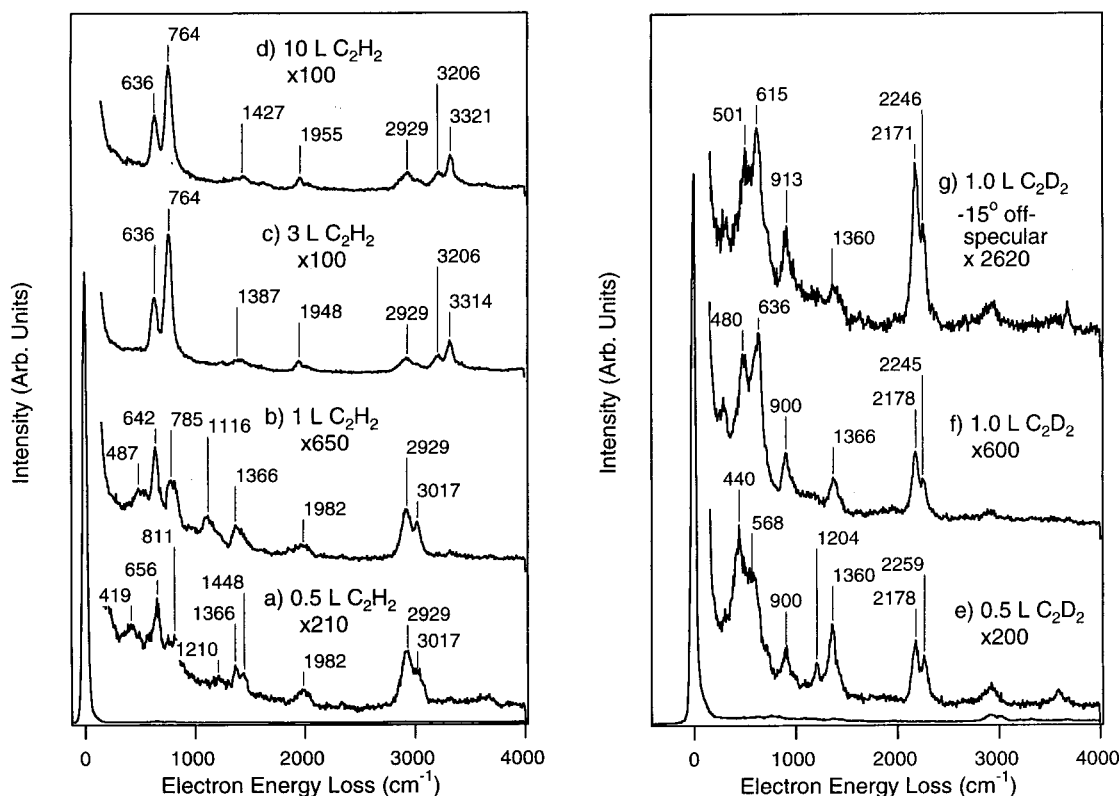


Figure 1. HREEL spectra of C_2H_2 and C_2D_2 on clean W(211) at 100 K, recorded as a function of exposure.

TABLE 1: Vibrational Mode Assignments (cm^{-1}) for C_2H_2 and C_2D_2 on Clean W(211) and C_2H_2 on C/W(211)^a

mode description	gas phase ¹¹			clean W(211) (this work)			C/W(211) (this work)		
	C_2H_2	C_2D_2	ω_H/ω_D	C_2H_2	C_2D_2	ω_H/ω_D	C_2H_2	C_2D_2	ω_H/ω_D
$\nu(M-C)$					291				
$\nu(M-C)$				487					
$\rho(CH)_s$	729	539	1.35	756	616	1.24	764	616	1.24
$\rho(CH)_{as}$	612	505	1.21	629	494	1.27	622	527	1.18
$\delta(CH)_s$	729	539	1.35	1116	913	1.22	1211		
$\delta(CH)_{as}$	612	505	1.21				967	705	1.35
$\nu(CC)$	1974	1752	1.13	1366	1366	1.00	1353	1440	1.04
$\nu(CH)_{as}$	3287	2427	1.35	2929 (3206)	2178	1.34	2956	2218	1.33
$\nu(CH)_s$	3374	2701	1.25	3017 (3321)	2246	1.34	3017	2340	1.28

^a The numbers in parentheses refer to weakly bonded acetylene present at high exposures, as shown in Figure 1.

groups.¹⁵ Additionally, a $\nu(CC)$ feature is observed at $\sim 1200\text{ cm}^{-1}$ in the spectra obtained after a 0.5 L exposure of C_2H_2 and C_2D_2 (Figures 1a and 1e). The presence of these features clearly demonstrates that the surface has reacted strongly with a fraction of the adsorbed acetylene to form new intermediates, which will be identified in the Discussion section. The remaining features in the 0.5 L spectra (Figures 1a and 1e) are similar to those in the 1.0 L spectra (Figures 1b and 1f) and indicate that strongly chemisorbed acetylene is also present on the surface at these exposures (cf. Table 1).

In direct contrast to the behavior observed after low (i.e., 0.5 L) exposures of acetylene, a weakly bonded surface acetylene species is present after high (≥ 3 L) exposures of acetylene (Figures 1c and 1d). This acetylene species is characterized by symmetric and asymmetric C–H rocking (i.e., $\rho(CH)_s$ and $\rho(CH)_{as}$) features which are shifted slightly to lower frequency and reversed in their intensities as compared to those in the spectrum following the 1 L exposure of acetylene (Figure 1b). Additionally, the $\nu(CH)$ features of this acetylene species appear at 3206 and 3314 cm^{-1} , unlike the $\nu(CH)$ features observed following a 1.0 L exposure of acetylene (cf. Figures 1b and 1c,d). Since the $\rho(CH)_s$, $\rho(CH)_{as}$, and $\nu(CH)$ features of this

acetylene species are quite close in frequency to the corresponding C–H vibrational modes of acetylene in the gas phase (cf. Table 1), we conclude that this acetylene species is only weakly bonded to the surface. Finally, a comparison of the spectrum taken after a 3 L exposure of acetylene (Figure 1c) with the one taken after a 10 L exposure (Figure 1d) reveals that the spectra are nearly identical, indicating that the W(211) surface is saturated by a 3 L exposure of acetylene and that no multilayer adsorption occurs, as expected.

Another interesting aspect of Figure 1 is the lack of any angular-dependent variation in the intensities of the vibrational features, as seen by the comparison of the on- and off-specular spectra obtained after exposing a clean W(211) crystal to 1 L of C_2D_2 (Figures 1f and 1g). Aside from changes in the $\nu(CD)$ stretching features, the relative intensities of all other features remain similar in the on- and off-specular spectra. This behavior is addressed in the Discussion section.

Figure 2 shows the on-specular HREEL spectra of 1 L of acetylene on clean W(211), recorded as a function of temperature. Molecularly chemisorbed acetylene decomposes between 100 and 250 K to form a mixture of surface intermediates, as reflected by significant changes in the spectra in this temperature

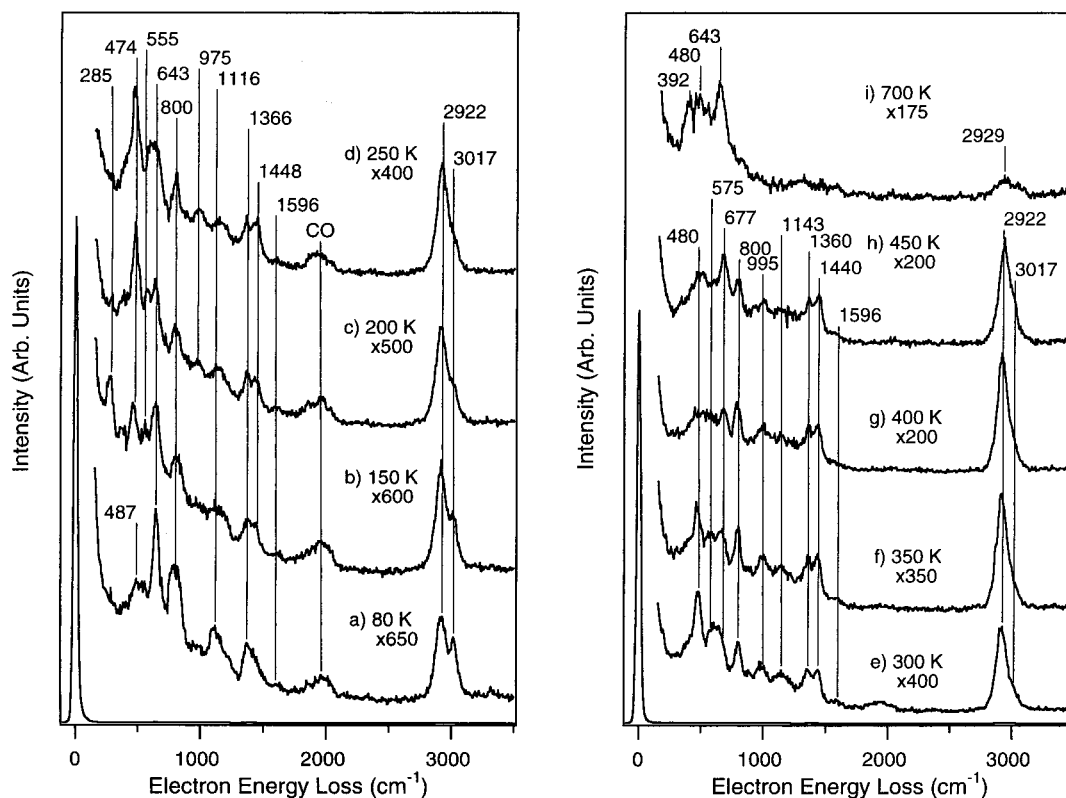


Figure 2. On-specular HREEL spectra monitoring the thermal decomposition of 3 L of C_2H_2 on clean W(211).

range (Figures 2a–d). For example, the $\nu_s(CH)$ and $\nu_a(CH)$ modes of molecularly adsorbed acetylene are replaced by a single broad feature at 2922 cm^{-1} at 250 K, suggesting that a significant fraction of the molecularly adsorbed acetylene has decomposed. Additionally, following the flash to 150 K (Figure 2b), a new feature appears at 1448 cm^{-1} , similar to the case observed in Figure 1a. The appearance of this feature, along with the sharp reduction in the intensity of the $\nu_s(CH)$ feature of molecularly adsorbed acetylene, suggests that a fraction of the acetylene has decomposed and new surface intermediates containing CH_2 or CH_3 groups are produced.¹⁵ We also note that a feature at 474 cm^{-1} , which occurs in the frequency range typical for metal–carbon bonds, as shown below, grows significantly in intensity upon heating to 250 K. Such behavior indicates either the formation of new metal–carbon bonds or the reorientation of some surface intermediate(s). The HREEL spectra recorded between 350 and 450 K (Figures 2f–h) show only minor changes. In particular, aside from changes in the relative intensity of the metal–carbon stretching feature at $\sim 480\text{ cm}^{-1}$, the spectra recorded between 350 and 450 K are remarkably similar to the one recorded at 300 K (cf. Figures 2e–g). Upon heating to 700 K, the surface intermediates experience further decomposition, as seen by the disappearance of the C–H deformation features between 1300 and 1450 cm^{-1} . As will be discussed below, the remaining features in the frequency range below 650 cm^{-1} are characteristic of metal–carbon vibrations of atomic carbon bonded to W(211).

As a reference point for the companion article,¹ we have also examined the chemistry of a saturation layer of acetylene on clean W(211) to determine if acetylene cyclotrimerizes at high coverages. Figure 3 compares HREEL spectra obtained after flashing a saturation coverage (10 L) and a submonolayer coverage (1 L) of acetylene to 300 K. In both cases, the W(211) surface was held at 100 K during dosing. The spectra in Figure 3 are remarkably similar, suggesting that the same surface intermediates are produced, regardless of the initial acetylene

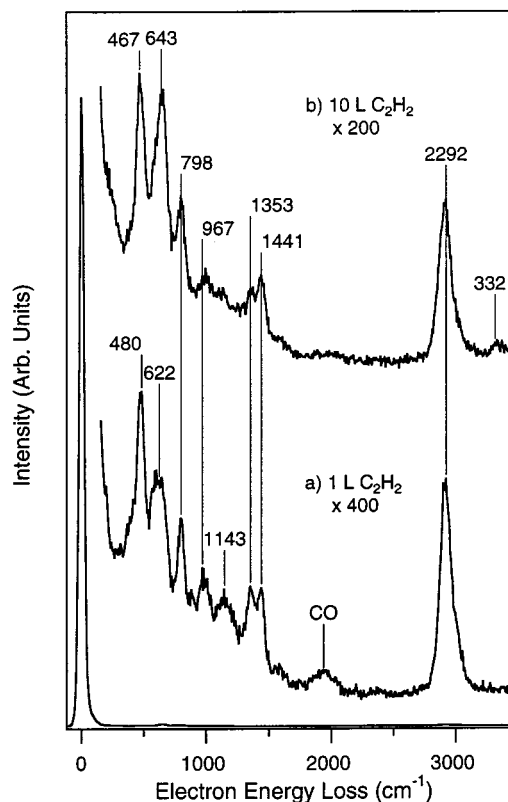


Figure 3. On-specular HREEL spectra characterizing the surface intermediates formed at 300 K on clean W(211) after a 3 and 10 L exposure. The similarities between the spectra indicate that the same surface intermediates are present.

coverage. Importantly, Figure 3 also implies that no benzene is present on the W(211) surface at 300 K, even after a saturation exposure of acetylene. This conclusion is based on the absence

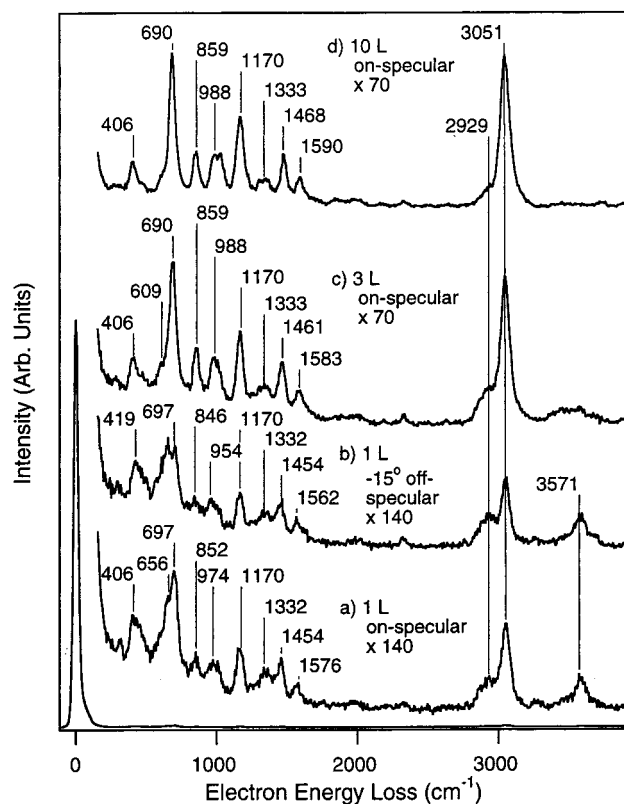


Figure 4. HREEL spectra of benzene (C_6H_6) on clean W(211) obtained as a function of increasing exposure

TABLE 2: Vibrational Mode Assignments (cm^{-1}) for C_6H_6 on Clean W(211) on C/W(211)

mode description		$\text{C}_6\text{H}_6^{11}$ (gas phase)	C_6H_6 on W(211)	C_6H_6 on C/W(211)
$\gamma(\text{C-H})$	ν_4	673	697	697
$\gamma(\text{C-H})$	ν_{11}	845	852	
$\nu(\text{C-C})$	ν_2	993	974	961
$\delta(\text{C-H})$	ν_{14}	1038		
$\delta(\text{C-H})$	ν_{10}	1150	1170	1157
$\delta(\text{C-C})$	ν_9	1309	1332	1339
$\nu(\text{C-C}) + \delta(\text{C-C})$	ν_{13}	1486	1454	1454
$\nu(\text{C-C})$	ν_{16}	1596	1576	1542
$\nu(\text{C-H})$	ν_1	2929	2936	
		3074	3051	3051

of vibrational features characteristic of chemisorbed benzene, as discussed below.

3.2. Benzene on Clean W(211) and C/W(211). To confirm that acetylene does not cyclotrimerize to form benzene on the clean W(211) surface, we have recorded HREEL spectra of benzene directly dosed onto the surface. There are two noteworthy aspects of these spectra, which are shown in Figure 4. First, the excellent agreement of all the vibrational features between 600 and 1600 cm^{-1} in Figures 4a and 4b with those of benzene in the gas phase¹⁵ (cf. Table 2) and in multilayers (Figure 5d) indicates that benzene is molecularly bonded to the surface at submonolayer coverages. However, the presence of a softened $\nu(\text{C-H})$ mode at 2929 cm^{-1} suggests that the interaction between benzene and the W(211) surface is quite strong. Second, a comparison of the on- and off-specular spectra shown in Figures 4a and 4b reveals that the intensities of all of the features exhibit a very weak angular dependence. Such behavior suggests, on the basis of the surface dipole selection rule, that most of the benzene molecules are bonded with their molecular planes not parallel to the macroscopic surface plane (i.e., the plane that passes through all of the W atom rows on

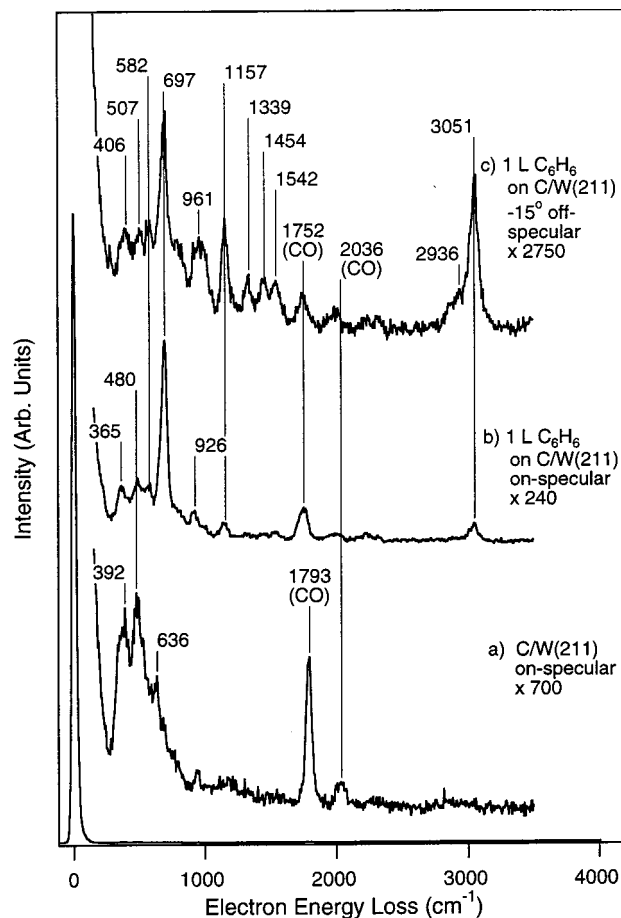


Figure 5. (a) HREEL spectrum of the clean carbide-modified W(211) surface. Also shown are spectra obtained following a 1 L exposure of benzene on C/W(211), recorded in the (b) on-specular and (c) -15° off-specular directions.

the corrugated W(211) surface). Although a tilted adsorption geometry is not surprising, given the row-and-trough structure of the clean W(211), we note that a parallel adsorption geometry for benzene has been observed on the corrugated surface of Ni(110).¹⁶ The different adsorption geometry for benzene on W(211) is addressed in the Discussion section.

For the sake of comparison with the results for acetylene on the carbide-modified W(211) surface, we also present here the HREEL spectra of benzene on the carbide-modified W(211) surface. For reference, we first show the HREEL spectrum of a clean carbide-modified W(211) surface in Figure 5a. Particularly interesting is the presence of multiple metal-carbon stretching features at 392, 582, and 636 cm^{-1} , indicating that the surface carbon atoms are located in a variety of different sites. This result, along with the absence of any overlayer pattern in our preliminary LEED studies, suggests that the carbide-modified W(211) surface is not well-ordered. Figures 5b and 5c show the on- and off-specular spectra obtained after a carbide-modified W(211) surface is exposed to 1 L of benzene at 100 K. There are some important similarities between the behavior of benzene on clean W(211) and on C/W(211). For example, as in the case for benzene on the clean W(211) surface, benzene molecules adsorb molecularly on C/W(211), as illustrated by the good agreement between the vibrational features in Figure 5c with those of benzene in the gas phase (cf. Table 2).¹⁵ Another important similarity is that benzene also interacts strongly with the carbide-modified W(211) surface, as manifested by the presence of a softened $\nu(\text{C-H})$ mode at 2936 cm^{-1} in the off-specular spectrum in Figure 5c. However, a key

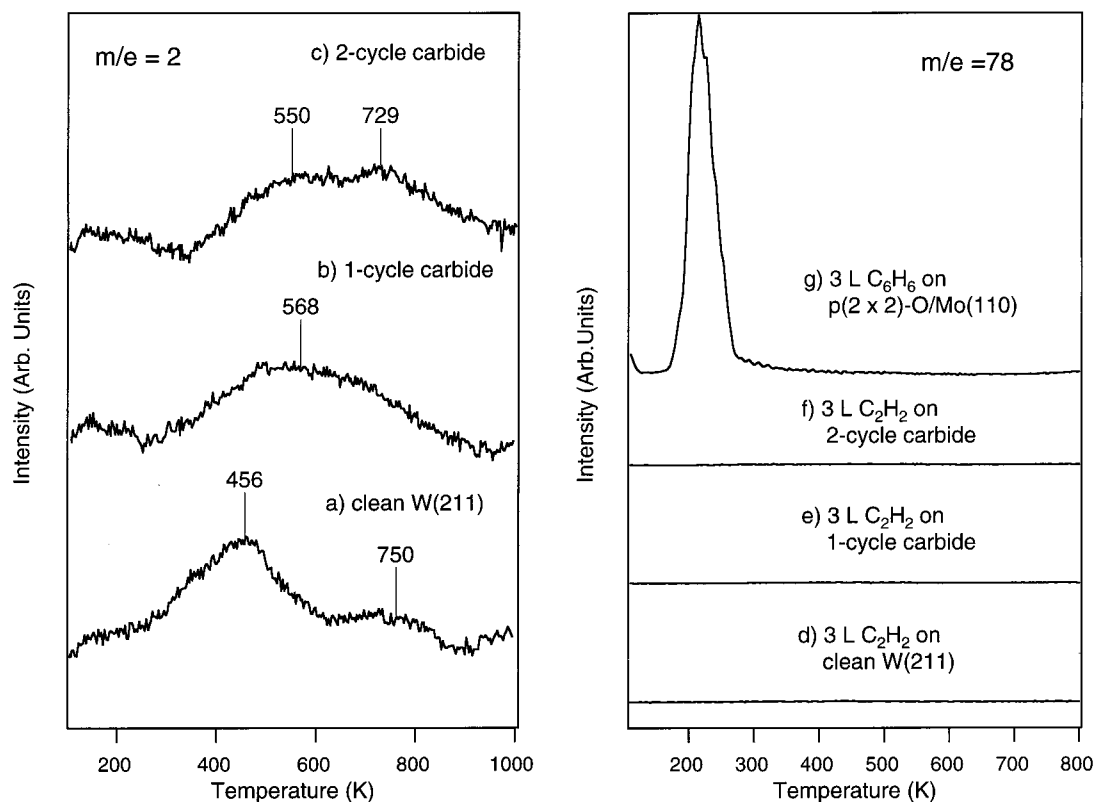


Figure 6. TPD spectra monitoring the evolution of H₂ and benzene from clean W(211) and C/W(211) following a 3 L exposure of C₂H₂ at 100 K. For the sake of comparison, we show that a strong benzene desorption feature is observed after dosing 3 L of benzene onto an inert p(2 × 2)-O/Mo(110) surface. The oxygen-modified Mo(110) surface was formed by exposing a clean Mo(110) surface at 1000 K to 10 L of O₂ and then flashing to 1150 K. The dosing/flashing cycles are repeated until a p(2 × 2) LEED pattern is observed, as discussed in ref 30.

difference between the behavior of benzene on clean W(211) versus on C/W(211) can be found in the molecular adsorption geometry. More specifically, whereas benzene bonds on clean W(211) in a tilted configuration with respect to the surface plane, as described above, a strong angular dependence of the relative intensities of the vibrational features for benzene on C/W(211) is observed in the on- and off-specular HREELS measurements (Figures 5b and 5c). In particular, the ν_4 feature at 697 cm⁻¹ is strongly attenuated in the off-specular spectrum (Figure 5c). Since the ν_4 mode has a dynamic dipole perpendicular to the benzene ring, its angle-dependent variation in intensity indicates that benzene bonds with the molecular plane parallel to the carbide-modified W(211) surface plane. This behavior is addressed in the Discussion section.

3.3. Acetylene on C/W(211). To investigate how the reactivity of the W(211) surface is modified upon the formation of a carbide overlayer, TPD experiments monitoring the evolution of H₂ and benzene from the surface after successive C₂H₂ dosing/flashing cycles (i.e., dosing 3 L of C₂H₂ at 100 K, then flashing the crystal ≥ 1000 K, to form the carbide) were performed. The H₂ TPD spectra (Figures 6a–c) show that though the formation of a carbide overlayer alters the H₂ desorption profile, indicating a modification in the reactivity of the surface toward acetylene, the surface remains active toward the decomposition of acetylene, as judged by the similar overall H₂ peak area. Particularly interesting is the shift of the hydrogen desorption features toward higher temperature as the number of dosing/flashing cycles is increased. For example, the H₂ TPD spectrum from the clean W(211) surface clearly exhibits two features: a relatively intense feature at 456 K and a rather weak one at ~ 775 K. However, after the formation of a 1-cycle carbide, only one broad H₂ desorption feature at ~ 568 K is observed, and for $T_s \geq 600$ K, the integrated area of this

desorption profile is clearly greater than that for the clean surface (cf. Figures 6a and 6b). A similar trend is seen in the H₂ desorption profile following a 2-cycle carbide.

Despite the changes in surface reactivity caused by carbide formation, acetylene does not cyclotrimerize to evolve benzene on the C/W(211) surface. This behavior is illustrated by the right panel in Figure 6 which shows TPD spectra of benzene from the reaction of acetylene on carbide-modified W(211) and clean W(211) surfaces. Figure 6d shows that a negligible amount of benzene is produced by the reaction of 3 L of acetylene on clean W(211), which is consistent with the findings in the companion paper.¹ Similarly, very little benzene is produced by the reaction of 3 L of acetylene on a 1-cycle and a 2-cycle carbide surface (Figures 6e and 6f). To contrast, we show that a strong benzene desorption feature is observed after dosing 3 L of benzene onto a p(2 × 2)-O/Mo(110) surface. Previous studies have demonstrated that the adsorption and desorption of benzene is completely reversible from this surface and that the TPD area corresponds to a benzene coverage of approximately 0.3 monolayers.³⁰

To determine whether acetylene cyclotrimerizes to form a chemisorbed benzene species on C/W(211), we have used HREELS to study how chemisorbed acetylene thermally decomposes on C/W(211). Figure 7 shows that a 3 L exposure at 100 K produces vibrational features at 825, 697, 2942, and 3051 cm⁻¹, which can be assigned to the $\rho_a(\text{CH})$, $\rho_s(\text{CH})$, $\nu_a(\text{CH})$, and $\nu_s(\text{CH})$ features of molecular acetylene. However, the interaction with the surface is strong enough to rehybridize the carbon atoms of acetylene from sp to sp², as evidenced by the $\nu(\text{C}=\text{C})$ feature at 1515 cm⁻¹ which is characteristic of a di- σ -bonded acetylene species,¹² as discussed earlier. Upon heating to 200 K, the $\nu_s(\text{CH})$ and $\nu_a(\text{CH})$ features in Figures 7a,b are replaced by a single, broad, intense feature at 2956

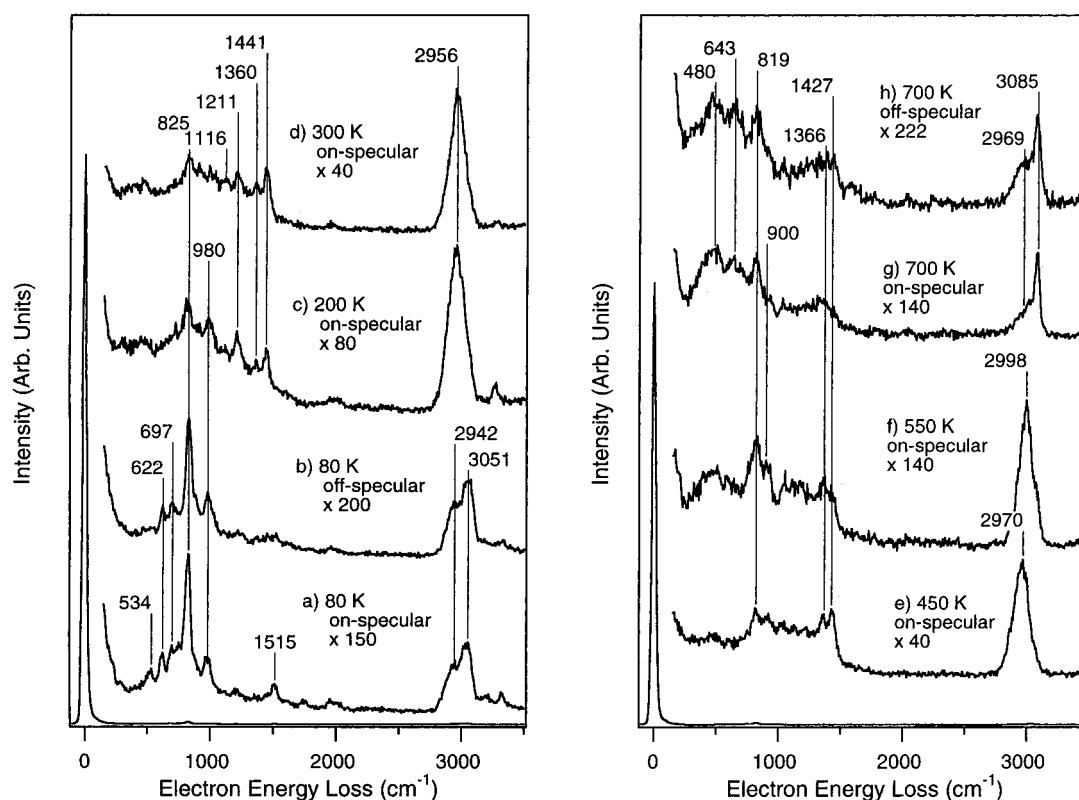


Figure 7. HREEL spectra monitoring the decomposition of 3 L of C_2H_2 on carbide-modified W(211).

cm^{-1} . In addition, the $\nu(C=C)$ feature at 1515 cm^{-1} disappears and concomitantly distinct features belonging to new surface intermediates appear at 1211 , 1360 , and 1441 cm^{-1} . These intermediates are stable between $300\text{--}450\text{ K}$ (cf. Figures 7d and 7e), but the loss of the well-resolved doublet between 1350 and 1450 cm^{-1} by 550 K , along with the appearance of a shoulder at 3085 cm^{-1} , indicates that the intermediates decompose further. Interestingly, upon heating to 700 K , the line shape of the feature in the $\nu(CH)$ region (i.e. between 2900 and 3100 cm^{-1}) changes drastically (Figures 8g,h), as most of the intensity below 3000 cm^{-1} disappears, leaving a relatively sharp $\nu(CH)$ feature at 3085 cm^{-1} and a broader shoulder centered at $\sim 2969\text{ cm}^{-1}$. The C–H stretching feature at 3085 cm^{-1} occurs at a frequency characteristic of a C–H group in which the carbon atom is sp - or sp^2 -hybridized. This behavior is examined in more detail in the Discussion section.

4. Discussion

4.1. Reactions of Acetylene on Clean W(211) and C/W(211). Identifying the surface intermediates formed on W(211) as a result of acetylene decomposition is particularly difficult for several reasons. First, since the surface of this early transition metal is extremely reactive, the initial fraction of acetylene inevitably decomposes to form a mixture of different surface intermediates. Unfortunately, many of the possible intermediates are expected to possess overlapping vibrational features, making an unambiguous assignment impossible.¹⁷ A second, more subtle difficulty in identifying the decomposition intermediates on clean W(211) results from the corrugation of this surface. As mentioned above in the discussion of Figures 5a,b, such corrugation can lead to adsorbate geometries that are substantially different from those typically observed on flat transition-metal surfaces. Consequently, though the same intermediates may be present on both the corrugated W(211)

surface and other flat transition-metal surfaces, the HREEL spectra which characterize the intermediates on these two types of surfaces could be quite different. Thus, comparisons of the current vibrational results with previously reported data in the literature must be made carefully.

Bearing these caveats in mind, we now consider the intermediates which can be formed as a result of acetylene decomposition on clean W(211). The plausible surface intermediates can be classified as C_1 intermediates (i.e., CH, CH_2 , or CH_3) or C_2 intermediates (i.e., CCH, CCH_2 , $HCCH_2$, or CCH_3). We consider first the low coverage limit, which is represented by the HREEL spectrum obtained after exposing a clean W(211) surface to 0.5 L of acetylene (Figure 1a). The presence of features at 1366 and 1448 cm^{-1} , attributable to $\delta(CH_2)$ or $\delta(CH_3)$ modes, clearly indicates that CH_2 or CH_3 groups are present and argues against the possibility that acetylene decomposes completely on this surface via CC bond scission to yield methylidyne (CH). Additional evidence against the possibility of complete CC bond scission is given by the presence of the C–C stretching mode at $\sim 1200\text{ cm}^{-1}$ (Figures 1a and 1e). Thus, the $\delta(CH_2)$ or $\delta(CH_3)$ features between 1300 and 1450 cm^{-1} in Figure 2a must result from C_2 intermediates containing CH_2 or CH_3 moieties, such as vinyl ($HCCH_2$), vinylidene (CCH_2), or ethylidyne (CCH_3). However, given that the C–C stretching mode of ethylidyne typically occurs at $\sim 1100\text{ cm}^{-1}$,^{18–20} we can exclude ethylidyne as a possibility. Therefore, the features between 1300 and 1450 cm^{-1} likely result from adsorbed vinyl or vinylidene. Distinguishing between these two remaining cases is difficult, since vinyl is expected to be spectroscopically similar to vinylidene. However, in either case, both carbon atoms in the CC bond of the C_2 intermediate must interact strongly with the W(211) surface, since the C–C stretching frequency occurs at $\sim 1200\text{ cm}^{-1}$ rather than between 1500 and 1600 cm^{-1} , which would be typical for a CC bond in which both atoms are sp^2 -hybridized.¹²

TABLE 3: Vibrational Assignments (cm⁻¹) for Vinylidene on W(211) and Other Single-Crystal Transition-Metal Surfaces

mode description	from C ₂ H ₂ /W(211) (this work)	from CCH ₃ /Ru(001) p(2×2)O ²¹	from C ₂ H ₂ /Pd(111) ²²	from C ₂ H ₄ /Pt(100) ²³
τ(CH ₂)				
ω(CH ₂)	975	895		1000
ρ(CH ₂)		965		
δ(CH ₂)	1448			
ν(CC)	1596			1581
ν(CC) + δ(CH ₂)		1435	1437	
ν _s (CH ₂)	2922	2985	2986	2950
ν _a (CH ₂)		3050		

TABLE 4: Vibrational Assignments (cm⁻¹) for Acetylide on W(211) and Various Other Single-Crystal Transition-Metal Surfaces

mode description	from C ₂ H ₂ /W(211) (this work)	from C ₆ H ₆ /Rh(111) ²⁴	from C ₂ H ₂ /Rh(100) ²⁵	from C ₂ H ₂ /Pd(111) ²⁶	from C ₂ H ₄ /Ni(110) ²⁷
ν _a (MC)		325	~370		380
ν _s (MC)		475	~430		465
ν(MC) + δ(CH)	1150	1155			
δ(CH)	800	850	805	750	790
ν(CC)	1360	1365	1305	1340	1290
ν(CH)	~3000	3008	3025	3000	2990

Vinyl or vinylidene intermediates are also produced upon the thermal decomposition of chemisorbed acetylene (Figure 2). However, the vibrational features in Figures 2d,e are more consistent with the presence of an sp²-hybridized vinylidene or vinyl species. In particular, the weak ν(C=C) feature at 1596 cm⁻¹ suggests the presence of a C=C bond and a ω(CH₂) feature now appears at 975 cm⁻¹ (Figures 2c–h), which is in the characteristic frequency range for a wagging mode of a CH₂ group which has an sp²-hybridized carbon atom.¹⁵ A summary of the vibrational assignments for the C₂ intermediate (vinylidene or vinyl) is given in Table 3. For the sake of comparison, a summary of the vibrational assignments for vinylidene on other single-crystal transition-metal surfaces, such as Ru(001)–p(2 × 2)O,²¹ Pd(111),²² and Pt(100),²³ is also given in Table 3.

In many of the previously reported vibrational studies in which acetylene forms a vinylidene intermediate, acetylide (CCH) was also observed.²¹ It has been argued that the formation of the CH₂ groups in vinyl or vinylidene most likely occurs through the C–H bond cleavage of a fraction of the adsorbed acetylene, subsequently followed by C–H bond formation.²¹ This behavior also occurs for acetylene on clean W(211), as seen by the spectroscopic changes in Figure 2. For example, although the disappearance of the ν_s(CH) and ν_a(CH) modes of molecularly adsorbed acetylene clearly establishes that a significant fraction of the acetylene has decomposed by 250 K, we observe a moderately intense δ(C–H) feature at 800 cm⁻¹, not attributable to vinylidene, even after heating to 450 K (Figure 2h). Additional evidence for the presence of acetylide is given by the persistence of the ν(CC) feature at 1360 cm⁻¹, even at temperatures above 300 K, when most of the acetylene has decomposed. The vibrational assignments for acetylide are summarized in Table 4, along with the assignments for acetylide on Rh(111),²⁴ Rh(100),²⁵ Pd(111),²⁶ and Ni(110).²⁷

Compared to the case for acetylene on clean W(211), it is more difficult to identify the surface intermediates that are formed on the carbide-modified W(211) surface, primarily because the features between 800 and 1500 cm⁻¹ are not as well resolved. Nevertheless, the spectra shown in Figure 7 do provide some information about the decomposition reactions that are occurring on the surface. For example, since the fwhm

of the elastic beam was less than 40 cm⁻¹, the poor resolution between 800 and 1500 cm⁻¹ suggests that there are several overlapping features in this frequency range. Most likely, such behavior results from the presence of more than one type of surface intermediate. Furthermore, the doublet feature between 1350 and 1450 cm⁻¹ clearly indicates that CH₂ or CH₃ groups are present, though we cannot determine if these groups occur in C₁ or C₂ intermediates based solely on these data. However, the similarities between Figures 7d and 7e indicate that the decomposition intermediates present on the carbide-modified W(211) surface are stable between 300–450 K. Such thermal stability is unlike that of the intermediates on the clean surface, which experience further decomposition in this temperature range, as demonstrated by the gradual changes in Figures 2e–h.

One important observation is that although the vibrational features below 1600 cm⁻¹ are consistent with the formation of sp²-hybridized vinylidene/vinyl and acetylide at temperatures ≥ 200 K (Figures 2c–h), the ν(CH) feature occurs at 2922 cm⁻¹, which is in a frequency range typical for sp³-hybridized hydrocarbon fragments on flat metal surfaces.¹² Such behavior also has been observed for sp²-hybridized vinylidene on Pt(100).²³ In the present case, the unusually low C–H stretching frequency also might be attributed to the interaction of the CH₂ and CH groups with the corrugated W(211) surface; detailed studies on less corrugated surfaces, such as W(110), would be useful in addressing this question.

The increased stability of the intermediates on the carbide-modified W(211) surface, as compared to the clean surface, suggests that there is a difference in the abilities of clean W(211) and C/W(211) to activate C–H bonds. This difference is evident in Figure 6, which shows that the H₂ desorption features shift to higher temperatures when a W(211) surface is modified by a carbide overlayer. This behavior is also supported by a comparison of the HREEL spectra of the surface decomposition intermediates on the clean and carbide-modified W(211) surfaces after heating to 700 K (cf. Figure 2i and Figures 7g,h). These spectra reveal that although only one weak C–H stretching feature is observed after flashing the clean surface to 700 K, several moderately intense CH-related features can be observed in the corresponding spectrum obtained from the carbide-modified W(211) surface. In particular, the features between 1350 and 1450 cm⁻¹, though unresolved, suggest that even some CH₂ or CH₃ groups remain intact at this temperature. Furthermore, the sharp, intense ν(CH) feature at 3085 cm⁻¹ in Figure 7h and the moderately intense feature at 819 cm⁻¹, which have no analogues in the corresponding spectrum of the decomposition intermediates on clean W(211) (Figure 2i), respectively, occur in frequency ranges typical for the ν_s(CH) and δ(CH) modes of surface methylidyne (CH) species.^{28,29} Thus, although we are unable to identify the chemical nature of all of the surface intermediates completely, based on these data, the presence of vibrational features characteristic of CH, CH₂, and CH₃ groups at 700 K clearly indicates that the C/W(211) surface is less active toward C–H bond scission as compared to the clean W(211) surface.

4.2. Adsorption Geometry of Benzene on Clean W(211) and C/W(211): Comparison to Benzene on Other Single-Crystal Surfaces. One of the more interesting aspects about benzene on clean W(211) is that the on- and off-specular HREEL spectra are nearly identical at low coverages (Figures 4a and 4b). This result is substantially different from the majority of the previously reported HREELS studies of benzene on low-index single-crystal surfaces, where instead the intensity

of the $\nu(\text{CH})$ feature (i.e., the ν_4 mode, in Herzberg notation¹¹) varies sharply at different detection angles relative to the other spectral features, as a result of the surface dipole selection rule.¹² Since it has been established that a strong angular dependence for the ν_4 feature is characteristic for benzene bonded parallel to the surface,¹² the clearly different behavior for benzene on W(211) suggests that benzene may not be bonded parallel to the W(211) surface.

To establish whether such a bonding geometry is plausible, one can survey the previously reported literature. While the vast majority of the studies in the literature shows that benzene bonds parallel to the surfaces of single-crystal transition-metal surfaces,^{12,13,30} we focus on comparisons with studies of benzene on the (110) surfaces of face-centered cubic (fcc) metals, since these surfaces have a row-and-trough structure similar to that of the W(211) surface. This comparison reveals an interesting trend: although benzene is adsorbed in an essentially flat-lying geometry on Ni(110),³¹ it has been found to be slightly tilted on the Pd(110) surface.^{32,33} Although the origin of this difference in adsorption geometries for benzene on the two surfaces is not fully understood at this time, one possible explanation is that the atomic rows on the Pd(110) surface are spaced sufficiently apart to allow the benzene molecule to interact slightly with the second layer of metal atoms (i.e., the "troughs"), causing a tilted geometry to be preferred. For reference, the rows on the Ni(110) and Pd(110) surfaces are separated by 3.5 and 3.8 Å, respectively. Thus, since the distance between the atomic rows of the W(211) surface is 4.2 Å (10% larger than the atomic row spacing for Pd(110)), it is perhaps not surprising that benzene is adsorbed in a tilted configuration on the clean W(211) surface. However, note that, in principle, the lack of angular dependence in the HREEL spectra in Figures 4a and 4b could be caused by two different benzene adsorption configurations: (1) if all benzene molecules are tilted by the same angle with respect to the surface or (2) if there is a distribution of tilt angles. More structurally sensitive tools, such as polarization-dependent near-edge X-ray absorption fine structure (NEXAFS) measurements, would give a more definitive answer regarding the adsorption geometry of benzene on clean W(211).

Finally, for the carbide-modified W(211) surface, the possible presence of carbon adatoms in the troughs may reduce the interaction of benzene with the second layer of metal atoms. Thus, benzene is adsorbed on the carbide-modified W(211) surface in a parallel geometry, as seen by the strong angular dependence of the intensity of the ν_4 mode in Figures 5b,c.

Interestingly, unlike the case for benzene, the intensities of the vibrational features of chemisorbed acetylene on either clean W(211) (Figures 1f and 1g) or C/W(211) (Figures 7a and 7b) do not show a strong angular dependence, especially for the low-frequency modes $<1500\text{ cm}^{-1}$. Because some of these modes possess dynamic dipole moments that are either perpendicular or parallel to the carbon-carbon bond of acetylene,^{11,12,34,35} one would expect to observe an angle-dependent variation in intensities if the chemisorbed acetylene molecules are parallel to the surface (see Table 1). Thus, the absence of such a variation suggests that acetylene is tilted on both W(211) and C/W(211). Particularly intriguing is that the formation of the carbide on W(211) converts the benzene orientation from a tilted geometry to one which is nearly parallel but does not cause a similar effect for acetylene. More studies are needed to understand the origins of such differences.

5. Conclusions

The TPD and HREEL spectra clearly show that acetylene does not cyclotrimerize to form benzene on either clean W(211) or C/W(211). Instead, in both cases acetylene decomposes, forming carbidic carbon and gaseous hydrogen, though these products are obtained by different pathways on the two surfaces. On clean W(211), acetylene reacts strongly with the clean W(211) surface, even at 100 K, producing a mixture of vinylidene (or vinyl), acetylide, and strongly chemisorbed (di- σ/π bonded) acetylene, which reacts further between 300 and 450 K. On the carbide-modified W(211) surface, the acetylene adsorbs to form a di- σ -bonded species at 100 K, but subsequent decomposition forms surface intermediates which have either CH_2 or CH_3 groups. Though the strongly overlapping vibrational features between 800 and 1500 cm^{-1} preclude an unambiguous identification of these intermediates, the spectra indicate that these intermediates are stable in the temperature range between 300 and 450 K, unlike the intermediates on the clean W(211) surface. This different behavior for the two surfaces clearly indicates that the reactivity of the clean W(211) surface has been altered by the formation of a carbide overlayer. Furthermore, TPD results, as well as vibrational data taken at 700 K, reveal that the activation of CH bonds is suppressed on the carbide-modified W(211) surface, as compared to the clean surface.

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