Specular and off-specular high resolution electron energy loss spectroscopy of acetylene and ethylene on tungsten (100)

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High resolution electron energy loss spectroscopy (EELS) in both specular and off-specular directions has been used to identify the vibrational modes of acetylene and ethylene on tungsten (100). The off-specular data were essential to this study since, at low coverages, some of the vibrational modes were detectable only for off-specular scattering. In addition, analysis of the relative intensities of the specular and off-specular loss peaks allows us to infer orientations of molecular dipole derivatives and bond directions for the adsorbed species. We find at 135 K that ethylene on tungsten (100) dissociates to acetylene and hydrogen for exposures less than 1 L. At saturation coverage molecular ethylene is also adsorbed. Warming of this adsorbed ethylene to 300 K causes dissociation to acetylene. Analysis of specular and off-specular loss intensities suggests a geometry with the C–H bonds lying parallel to the surface. Previous UPS data for this adsorption system can be reinterpreted giving a C–C bond length of 1.35 Å and a C–C–H bond angle of 180°: This reinterpretation is consistent with the geometry suggested by our EELS measurements. We also present data for acetylene adsorption at room temperature and for ethylene physisorption at 82 K. Physisorbed ethylene shows vibrational losses identical to those seen in gas phase IR.

I. INTRODUCTION

Studies of hydrocarbon adsorption on transition metal surfaces have made a continuing contribution in the search to understand catalytic reactions on surfaces. The chemical composition and molecular geometries of these adsorbates have been studied intensively using a variety of surface sensitive techniques including flash desorption, ultraviolet photoemission spectroscopy (UPS), Auger line shape analysis, and high resolution electron energy loss spectroscopy (EELS). Electron stimulated desorption ion angular distribution (ESDIAD) studies also hold promise in determining bond orientations of chemisorbed molecules.[1] In this paper we report an investigation of the adsorption of acetylene and ethylene on the tungsten (100) surface using high resolution electron energy loss spectroscopy (EELS). This chemisorption system has been studied previously using flash desorption,[2–4] UPS,[5] Auger spectroscopy,[6,7] and work function measurements.[8] EELS studies of acetylene adsorption on W(111) and W(110) have also been published.[9,10] In our study of ethylene and acetylene adsorption, a wide range of coverages and temperatures was utilized in order to resolve apparent discrepancies between UPS[5] and Auger measurements.[6,7]

In addition, we have measured both specular and off-specular loss intensities. The collection of both types of data is important for a complete understanding of the adsorption process for two reasons. First, in some cases, certain vibrational modes are not seen in specular scattering, but may be observed in off-specular scattering. The ability to detect these vibrational modes can be crucial to a correct identification of adsorbed molecules. Second, the use of selection rules for specular scattering to obtain information about bond directions has been suggested.

A number of theoretical treatments have been proposed to date,[11–19] and selection rules derived for inelastic scattering. For scattering in the specular direction, the momentum transfer in scattering from the adsorbate is very small, and the dominant mechanism is dipole scattering. A consideration of a dipole and its image at a surface, leads to the conclusion that if a vibrational loss is not seen, then either the dipole derivative is oriented parallel to the surface or, more unlikely, it is identically zero. For off-specular scattering a variety of explanations for inelastic scattering by modes with dipole derivatives parallel to the surface have been proposed. For off-specular scattering the momentum transfer is large and the expansion into dipole and higher terms is less useful. Exchange scattering may make an important contribution for small impact parameters and low energies. Negative-ion resonances may also contribute to the scattering process. The experimental observation is that in off-specular scattering, vibrational modes with dipole derivatives parallel to the surface may be readily observed. This is a very useful result since it allows detection of these modes resulting in a more accurate determination of molecular structure.

This paper is arranged as follows: The experimental procedures are discussed in Sec. II. In Sec. III, results for acetylene adsorption on W(100) at room temperature are presented. Section IV discusses ethylene adsorption at 135 K and also ethylene condensation at 82 K. In Sec. V, we present data on the effect of higher temperatures on adsorbed ethylene. Section VI contains a discussion of previous experimental results for this chemisorption system; in particular, we present a reinterpretation of the previous UPS data[5] which is consistent with these new EELS results. Section VII is a summary.

II. EXPERIMENTAL

Our measurements were performed using a Simpson–Kuyatt hemispherical monochromator and analyzer.[20]

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The incident electron beam energy was 5 eV. The monochromator could be rotated in the scattering plane allowing the angle Θ between the incident and the detected electrons to vary from 90° to 180°. The single crystal tungsten surface, oriented within 1/2° of the (100) plane, was mounted on a precision manipulator allowing rotation of the surface normal in the scattering plane. Provision was also made for cooling with liquid nitrogen and for heating using electron bombardment or radiative heating. In this series of experiments Θ was fixed at 120° and the crystal was rotated to study both specular and off-specular scattering. We studied the scattering for $\Theta_i - \Theta_r$ equal to 0° (specular), 10° and 20° (see Fig. 1). Two features of the spectrometer were crucial in allowing a study of the off-specular scattering as distinguished from the specular scattering. The angular resolution of the spectrometer was better than 1° as measured by rocking the crystal about specular while observing the elastically scattered intensity. Since all of the beam defining apertures in the spectrometer are circular, it may be assumed that the angular resolution in the vertical direction would also be better than 1°. This angular resolution allowed a clear separation of specular from off-specular scattering. In addition, the count rate of the monochromator-analyzer combination was extremely high. Under favorable conditions 10^7 cps were obtained in the elastically scattered beam at better than 20 meV instrumental resolution. This high count rate facilitated data collection for the relatively weak off-specular scattering.

Initial cleaning of the tungsten crystal was accomplished by repeated cycling between 1600 and 2500 K in about 2×10^{-6} Torr of oxygen. Before each adsorption measurement the crystal was exposed to oxygen and then flashed to 2500 K. The absence of any detectable loss peaks was used as a criterion of sample cleanliness. This criterion was checked by doing preliminary studies of hydrogen adsorption which were in agreement with previously published results.[21] The ultra high vacuum system was pumped with a cryopump and had a base pressure of 2×10^{-10} Torr.

III. ACETYLENE ON W(100)

We have studied acetylene adsorption on W(100) at 300 K. The acetylene used was purified by repeated freeze-thaw cycling. Figures 2 and 3 show the loss spectra for specular scattering and for scattering at 20° off the specular direction. At low coverages (< 1.0 L exposure) only two loss peaks are detectable in either specular or off-specular scattering. For 0.25 L exposure these peaks are at 69 and 150 meV. We identify these as a carbon–tungsten stretch and a hydrogen–tungsten stretch, respectively, in agreement with previously reported studies of carbon contaminated W(100)[22] and hydrogen adsorption on W(100).[21] The appearance of these two modes and the complete absence of any molecular vibrations in either the specular or off-specular directions leads to the conclusion that initial adsorption of acetylene at this temperature is dissociative as shown schematically in Fig. 4(a). Initially the HW stretch is seen at 150 meV; as the exposure is increased to 0.5 and 1.0 L the HW stretch moves to lower frequency.

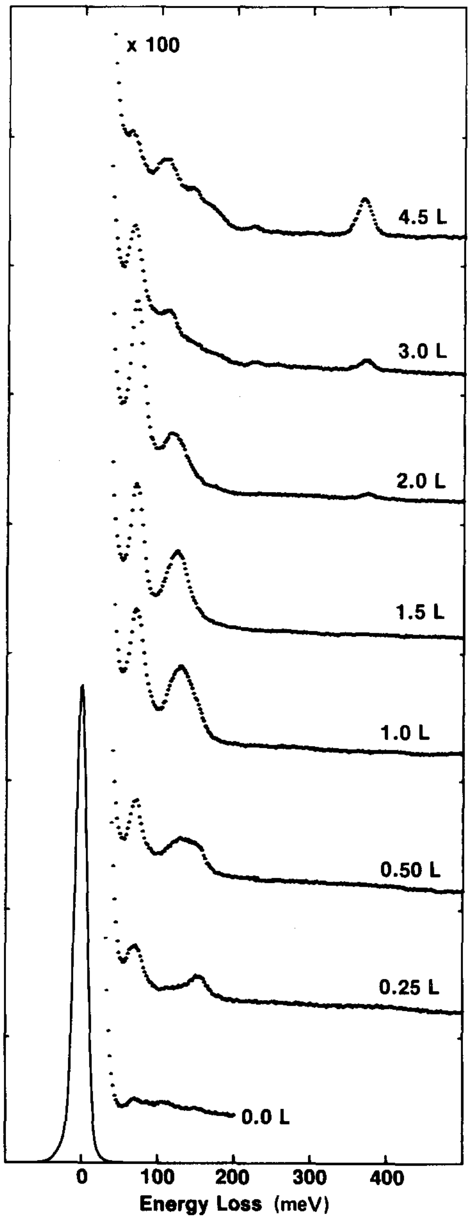

FIG. 2. Loss spectra for acetylene adsorption on W (100) at room temperature. Loss spectra were taken in the specular direction. The curves are labeled with acetylene exposures in L. Incident beam energy was 5 eV.

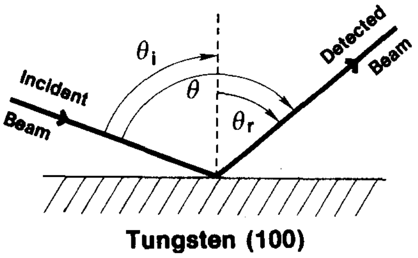

FIG. 1. Scattering geometry. θ, the angle between the incident and detected beams was fixed at 120°. θ_i, the angle of incidence was varied from 60° to 70° to give values of $\theta_i - \theta_r$ varying from 0° to 20°.

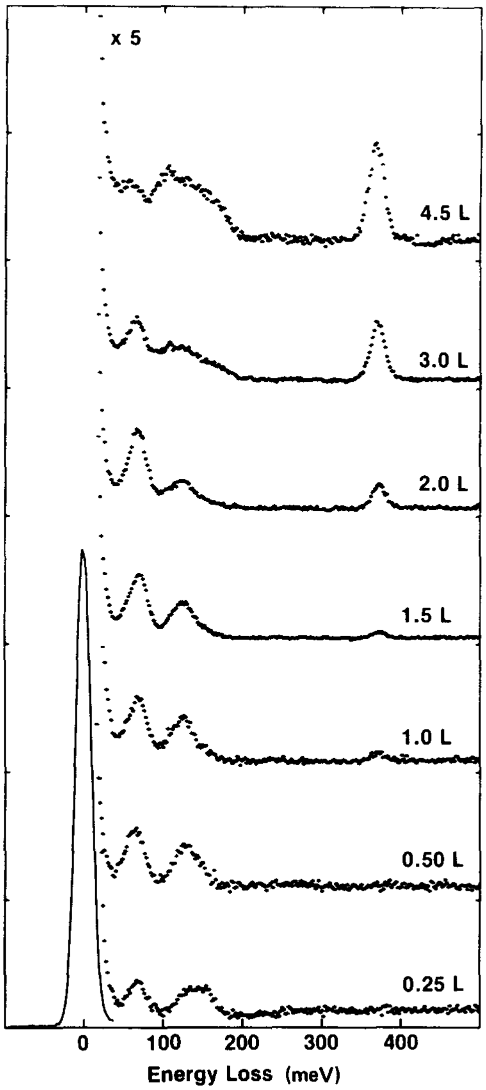

FIG. 3. Loss spectra for acetylene adsorption on W (100) at room temperature. Loss spectra were taken in a direction 20° removed from specular. The curves are labeled with acetylene exposures in L.

This is precisely what is seen for hydrogen adsorption on W(100).[21] We conclude that at exposures less than 1 L, acetylene adsorption on tungsten (100) at room temperature is dissociative. At higher exposures any additional adsorption will occur on the carbon and hydrogen covered surface.

At exposures of 1 L, a new loss appears in the off-specular scattering at 372 meV, not detectable for specular scattering. We identify this peak as a carbon–hydrogen stretch. It provides clear evidence that at this exposure hydrocarbons are beginning to adsorb. Based upon the observed C–H stretching frequency and on previous UPS results[5] we believe that the C–C bond of acetylene is not broken upon adsorption. The C–H stretching vibrational loss is detectable only for off-specular scattering suggesting that the dipole moment associated with this mode lies nearly parallel to the surface. Probably molecular acetylene is being adsorbed with a C–H bond direction nearly parallel to the surface as shown in Fig. 4b.

At exposures of 2.0 L and above, the C–H stretching mode at 372 meV is also detectable in the specularly scattered loss spectra. We infer that the dipole moment associated with this mode has a component perpendicular to the surface for these exposures. The suggested geometry is shown in Fig. 4c. We are unable to conclusively identify the small peak at 225 meV in Fig. 2 for 3.0 and 4.5 L exposures; it is conceivable that it is a carbon–carbon stretching vibration of acetylene.

In order to confirm that the relative intensities of the CH stretch peak for specular and off-specular scattering vary in a manner consistent with the geometries shown in Fig. 4, we have plotted the ratio of the CH stretch peak intensity to the elastic peak intensity as a function of exposure as shown in Fig. 5. The *Y* scales are chosen so this ratio will appear comparable at saturation coverage. For exposures of 1 to 2.5 L this ratio increases more rapidly for off-specular than for specular scattering, consistent with a dipole moment more nearly parallel to the surface at these exposures than at saturation.

IV. ETHYLENE ON W(100): LOW TEMPERATURE ADSORPTION

We have studied ethylene on tungsten (100) in a chemisorbed and a condensed form. In order to condense ethylene the crystal was cooled to 82 K and an ethylene pressure of 2×10^{-5} Torr (uncorrected gauge reading) was maintained in the chamber. Any decrease in the ethylene pressure caused rapid vaporization of the condensed ethylene which was detected by a change to a loss spectrum characteristic of saturation chemisorption. In Fig. 6 the loss spectrum for condensed ethylene is shown. Loss peaks are observed at 118, 176, and 376 meV, identical to those seen for gas phase infrared spectroscopy of ethylene,[23] and identified as the CH_2 wag, CH_2 scissors, and CH stretch modes, respectively. The exact correspondence between gas phase and con-

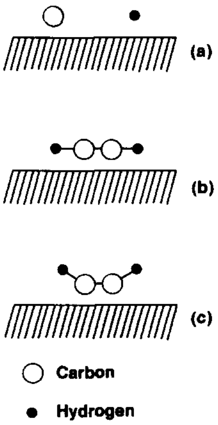

FIG. 4. Schematic representation of acetylene adsorption on W (100) at room temperature. Figure 4(a) shows dissociation to carbon and hydrogen at exposures less than 1 L. At exposures between 1 and 1.5 L the acetylene starts to adsorb molecularly with C–H bonds parallel to the surface as shown in Fig. 4(b). For exposures of 2 L and above, the C–H bonds start to move out of the surface plane as shown in Fig. 4(c).

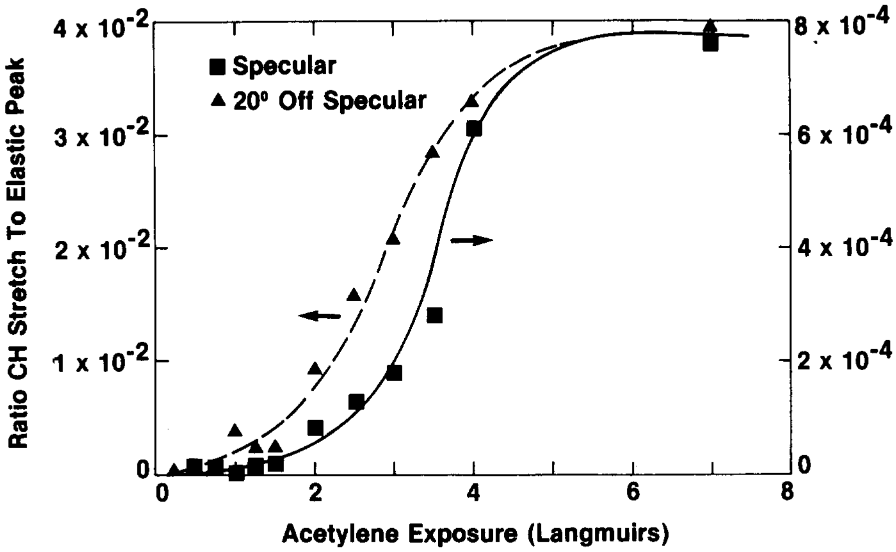

FIG. 5. Ratio of CH stretch peak intensity to elastic peak intensity for acetylene adsorption on W (100), at room temperature. The *Y* scales for specular and off-specular scattering were chosen so that the ratios would appear comparable at saturation.

densed spectra indicates that intermolecular bonds have a negligible effect on the vibrational modes of condensed ethylene.

In Figs. 7 and 8 the loss spectra for ethylene chemisorbed on tungsten (100) at 135 K are shown. The differences between specular and off-specular scattering are particularly striking for this chemisorption system. At 0.5 L exposure both specular and off-specular loss spectra show a vibrational loss at 150 meV, characteristic of the HW stretch for low hydrogen exposures on W(100).[21] We conclude that initial ethylene adsorption at 135 K is at least partially dissociative. The off-specular scattering for this exposure shows a CH stretch at 370 meV, but there is no evidence of a CH_2 scissors mode. The absence of the scissors mode is consistent with partial dissociation of initially adsorbed ethylene. The CH stretching vibration indicates the presence of intact carbon hydrogen bonds. Based upon the observed CH stretching frequency and on previous UPS results[5] we believe that the C–C bond is not broken upon adsorption. We suggest that the adsorbed species at this temperature are acetylene and hydrogen. The appearance of the CH stretching mode only for off-specular scattering suggests that the associated dipole moment and the C–H bond are nearly parallel to the surface. The probable geometry for initial adsorption of ethylene is shown in Fig. 9a.

At 1.0 L ethylene exposure the HW stretch has moved to a lower frequency. At this exposure the CH stretch is barely visible in the specular scattering at 374 meV,

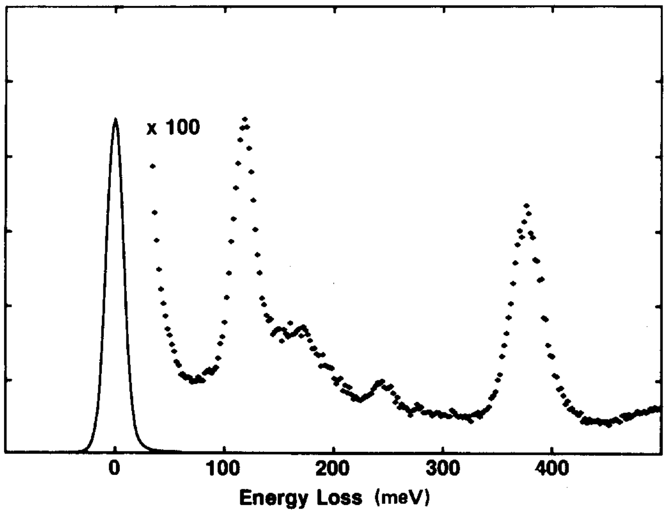

FIG. 6. Loss spectrum for ethylene condensed on W (100) at 82 K and 2×10^{-5} Torr. Spectrum was taken in specular direction.

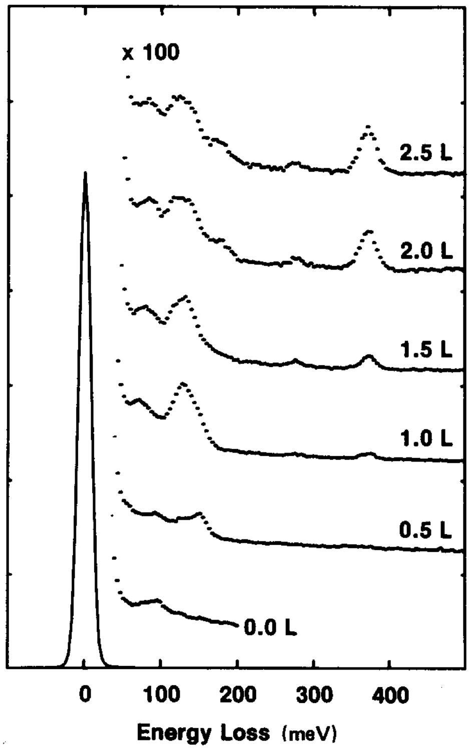

FIG. 7. Loss spectra for ethylene adsorption on W (100) at 135 K. Loss spectra were taken in specular direction. The curves are labeled with ethylene exposures in L.

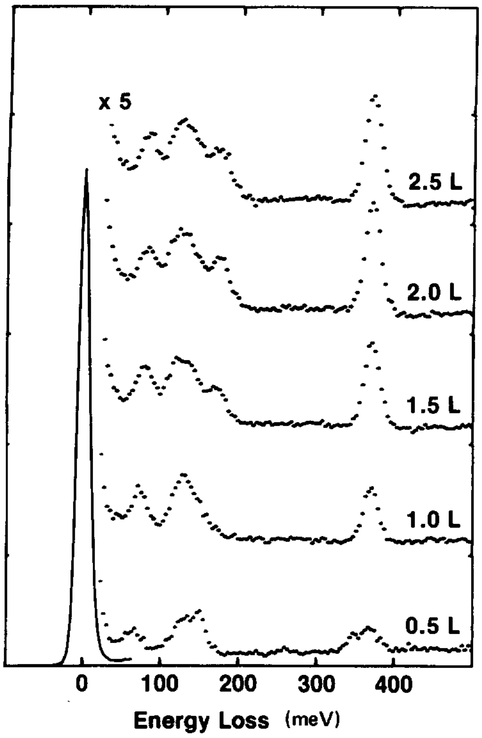

FIG. 8. Loss spectra for ethylene adsorption on W (100) at 135 K. Loss spectra were taken in a direction 20° removed from specular. The curves are labeled with ethylene exposures in L.

but is much larger in the off-specular scattering. We infer that the ethylene is still dissociated to acetylene lying nearly parallel to the surface and atomic hydrogen.

At exposures of 1.5 L the CH_2 scissors vibration is detectable in the off-specular loss spectra at 170 meV. This indicates that molecular ethylene is being adsorbed at this exposure. At higher exposures (2.0 and 2.5 L) both the CH_2 scissors and the CH stretch vibration are detectable in the specular direction. We conclude that additional molecular ethylene is being adsorbed and suggest that the C–H bonds of this additional ethylene are no longer parallel to the surface plane. Figure 9b shows the proposed out-of-plane geometry for these higher exposures.

To confirm the qualitative trends discussed above, we have used two different normalization procedures to quantify the relative intensities of specular and off-specular loss peaks. In Fig. 10 the ratio of the CH stretch peak intensity to the elastic peak intensity is plotted as a function of exposure for specular and for off-specular scattering at two different angles. There is a much more abrupt increase in the specular scattering between 1.5 and 2.0 L exposures, suggesting that ethylene is starting to adsorb with the C–H bonds out of plane. In Fig. 11 the ratio of the CH stretch intensity to the loss intensity at about 130 meV is plotted. Since the peak at 130 meV is due to HW stretching vibrations with a possible unresolved CH_2 wagging vibration of ethylene, we expect it to be dipole active. By plotting the ratio, we can distinguish whether the CH stretching vibration is dipole active or not. For a dipole active mode this ratio should be comparable in both specular and nonspecular directions. For nondipole scattering this ratio should be much larger for off-specular scattering than for specular scattering. For exposures less than 1.5 L it is clear that the vibrational loss associated with the CH stretch is nondipole.

V. DISSOCIATION OF ETHYLENE ON TUNGSTEN (100) ABOVE 300 K

Previous UPS and Auger studies have indicated that ethylene chemisorbed at low temperatures and then warmed dissociates to form acetylene.[5,7] In order to confirm these results and obtain additional geometrical information we have studied thermal dissociation of adsorbed ethylene using EELS. Initially the surface was saturated by a 2.5 L ethylene exposure at 135 K. The loss features shown at 135 K in Figs. 12 and 13 are the carbon tungsten stretch at about 75 meV, the CH_2 scissors at about 175 meV and the CH stretch at 372 meV. Upon warming to 400 K a dramatic decrease in the CH stretching intensity is seen for specular scattering only. In addition, the CH_2 scissors vibration is virtually undetectable after warming to 400 K. The disappearance of the CH_2 scissors vibration indicates partial dissociation of the chemisorbed ethylene. The large decrease in the CH stretching vibration intensity in the specular direction suggests that the dissociation product has C–H bonds nearly parallel to the surface. This is consistent with dissociation to form acetylene in agreement with the previous studies.[5,7] The acetylene produced appears to be parallel to the surface as shown in Fig. 4b.

In order to study the final stages of thermally induced dissociation, ethylene was adsorbed at 323 K. The loss spectra for 2 L ethylene exposure at 323 K shown in Figs. 14 and 15 are essentially identical to those obtained by adsorbing at 135 K and then warming. Figures 14 and 15 also show the effect of warming above 400 K. At temperatures between 400 and 500 K all the C–H bonds are broken yielding only carbon on the surface.

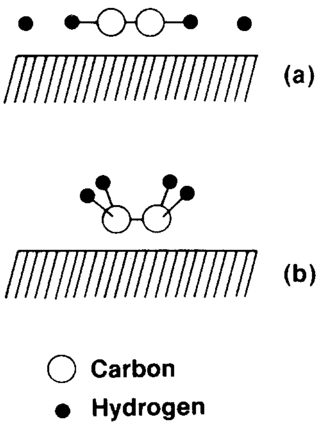

FIG. 9. Schematic representation of ethylene adsorption on W (100) at 135 K. Figure 9(a) shows dissociation to acetylene and hydrogen at exposures less than 1.5 L. At exposures above 1.5 L molecular ethylene is also adsorbed. For the lower exposure the C–H bonds of the acetylene produced lie parallel to the surface. For higher exposures the C–H bonds of ethylene are out of plane.

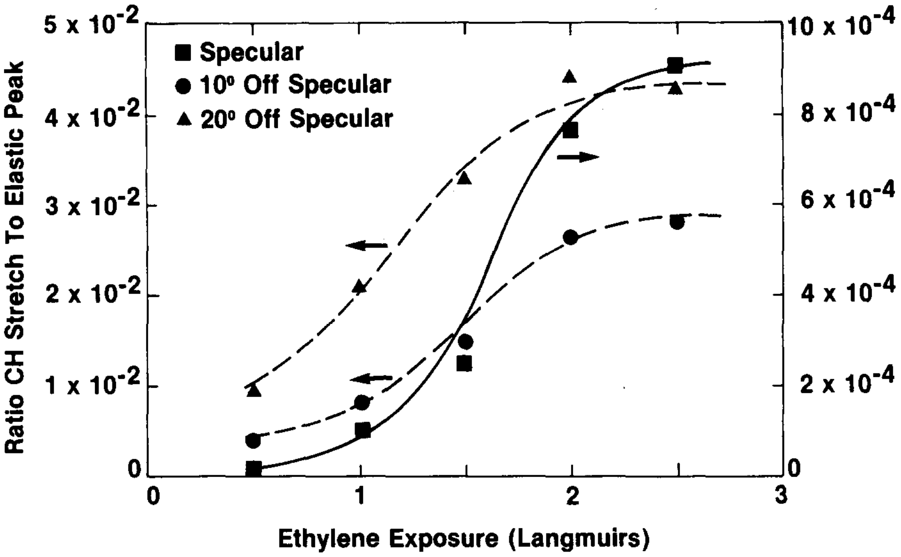

FIG. 10. Ratio of C–H stretch peak intensity to elastic peak intensity for ethylene adsorption on W (100) at 135 K.

VI. COMPARISON WITH PREVIOUS UPS WORK

In a UPS study of ethylene and acetylene on W(100),[5] ethylene was chemisorbed at a saturation exposure and the photoelectron energy distribution was interpreted by comparison with LCAO calculations[24] for rehybridized free molecules. The conclusion was that at saturation the C–C bond length of adsorbed ethylene was 1.5 Å and that the angle between the C–H bond and the surface was 28°. For saturation ethylene exposure, we also see evidence for out of plane C–H bonds using EELS.

In the UPS study acetylene was produced by dehydrogenation of ethylene at 295 K. By measuring the energy difference between the $3\sigma g$ and $2\sigma u$ molecular orbitals of chemisorbed acetylene and comparing with LCAO calculation[24] for rehydridized acetylene, a C–C bond distance of 1.3 Å and a C–C–H bond angle of 60° was calculated for acetylene on W(100). This latter conclusion does not agree with our EELS study which shows that acetylene on W(100) has a more linear configuration with the C–H bonds essentially parallel to the surface.

In order to resolve this question we propose the following reinterpretation of the UPS data based on more recent LCAO calculations.[25,26] In these calculations the effect of molecular distortions on the molecular orbital energy differences have been investigated for free ethylene and acetylene. In particular, the effect of varying the C–C bond length and varying the C–C–H bond angle were investigated separately. The essential feature of the UPS experiments[5] which must be fit by the calculation is the $3\sigma g$ to $2\sigma u$ energy difference of 3.8 eV. The LCAO calculations show that a range of geometries will yield this level splitting for acetylene. Of these geometries we prefer the ones with a C–C–H bond angle near 180° which would agree with our EELS data. In particular, a C–C–H bond angle of 180° and a C–C distance of 1.35 Å gives the $3\sigma g$–$2\sigma u$ energy splitting observed in photoemission. This geometry is consistent with both the EELS and the UPS observations for acetylene adsorbed on W(100).

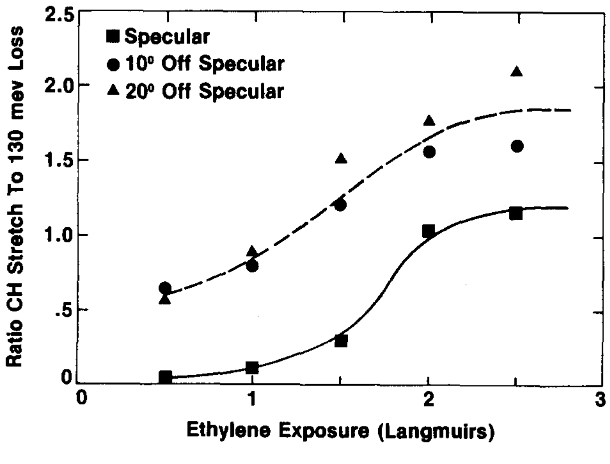

FIG. 11. Ratio of C–H stretch peak intensity to loss peak intensity in vicinity of 130 MeV for ethylene adsorption on W (100) at 135 K.

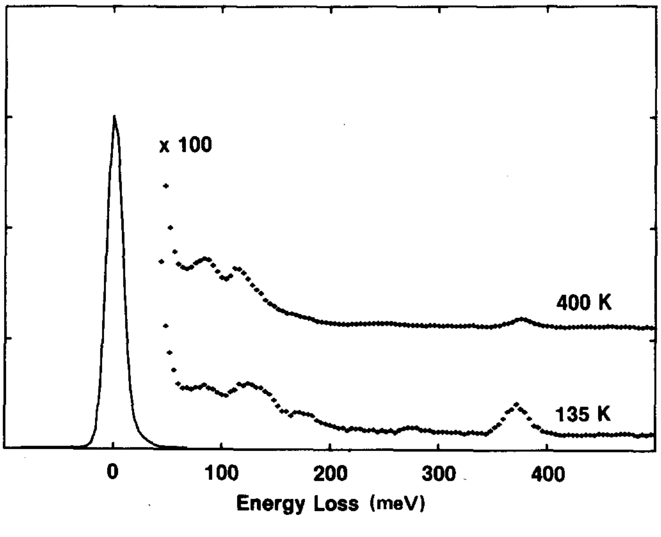

FIG. 12. Loss spectra for 2.5 L ethylene adsorption on W (100) at 135 K before and after warming to 400 K. Loss spectra were taken in the specular direction.

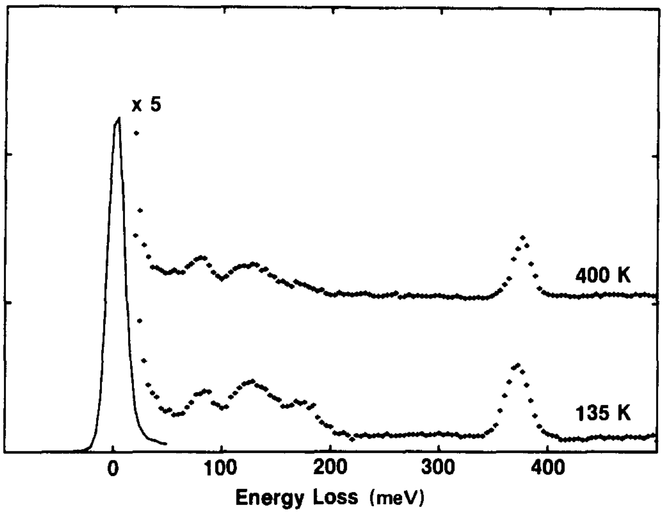

FIG. 13. Loss spectra for 2.5 L ethylene adsorption on W (100) at 135 K before and after warming to 400 K. Loss spectra were taken in a direction 20° removed from specular.

VII. SUMMARY AND CONCLUSIONS

We have used high resolution EELS in both specular and nonspecular directions in order to identify the vibrational modes of acetylene and ethylene on W(100). The nonspecular data were essential for a correct analysis of the adsorption process since, at low coverages, several of the vibrational modes were detectable only in the nonspecular direction. In addition, analysis of the relative intensities of the specular and nonspecular losses allows us to infer the orientation of molecular dipole moments and thus the bond directions in the adsorbed species.

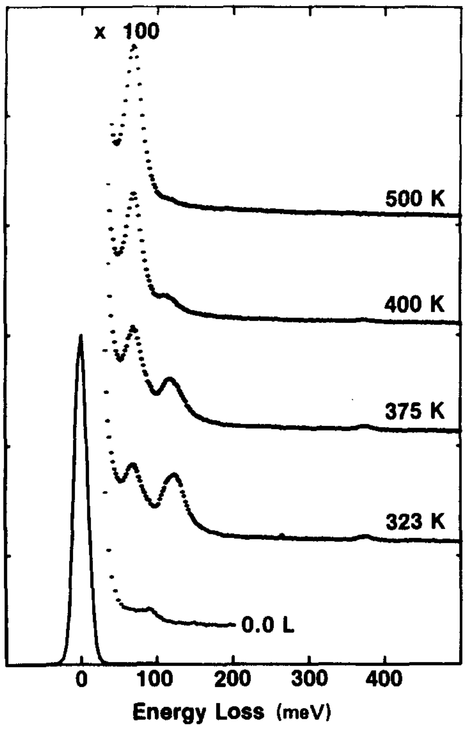

FIG. 14. Loss spectra for 2.0 L ethylene adsorbed on W (100) at 323 K and then warmed to higher temperatures. Loss spectra were taken in the specular direction.

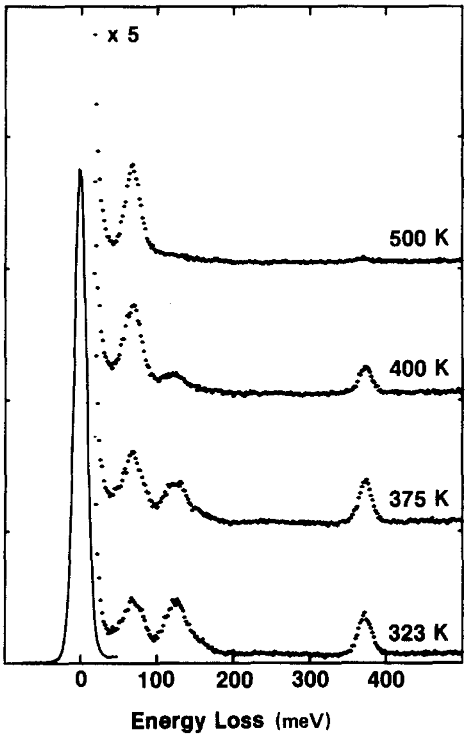

FIG. 15. Loss spectra for 2.0 L ethylene adsorbed on W (100) at 323 K and then warmed to higher temperatures. Loss spectra were taken in a direction 20° removed from specular.

Previous studies of ethylene and acetylene adsorption on W(100) have been in only partial agreement regarding the extent of dissociation of the adsorbed species. UPS measurements[5] indicate that ethylene chemisorption is nondissociative at 80 K, whereas Auger line shape analysis[7] indicates initial dissociative adsorption to form acetylene. Our EELS measurements indicate initial (ethylene exposure less than 1 L) dehydrogenation forming acetylene probably in a linear configuration parallel to the surface at 135 K. For higher exposures molecular ethylene is also adsorbed at 135 K. Warming of adsorbed molecular ethylene to 300 K causes dissociation to acetylene in which the C–H bonds probably lie *parallel* to the surface. This disagrees with the rehybridization interpretation of the previous UPS data[5] for which the C–H bonds were bent away from the surface. Using a more recent LCAO calculation[25,26] to reinterpret the original UPS data[5] we find it to be consistent with a C–C bond length of 1.35 Å and a C–C–H bond angle of 180°: This reinterpretation is consistent with our EELS measurements.

For acetylene adsorption at room temperature we see initial (< 1 L) dissociation to carbon and hydrogen. For higher exposures molecular acetylene was also adsorbed.

In conclusion we emphasize the crucial importance of making measurements in the off-specular as well as specular direction in order to correctly describe the adsorption of these hydrocarbons on W(100).

ACKNOWLEDGMENTS

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