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AND THE EFFECT OF COADSORBED CARBON MONOXIDE

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ABSTRACT

The surface structure and thermal chemistry of acetylene on the Rh(111) crystal surface have been studied from 30 to 800 K using high resolution electron energy loss spectroscopy (HREELS), low energy electron diffraction (LEED), and thermal desorption spectroscopy (TDS). Adsorbed acetylene on the Rh(111) is disordered at 30 K, but orders into a (2 x 2) LEED structure at 60 K; this is the lowest ordering temperature that has been reported for chemisorbed acetylene on a metal surface. HREEL spectra of C_2H_2 and C_2D_2 ordered in the (2 x 2) structure at 77 K on Rh(111) indicate that the carbon-carbon bond of chemisorbed acetylene rehybridizes between sp^2 and sp^3 . At 270 K, chemisorbed molecular acetylene decomposes predominantly to CCH_2 species. Above 400 K, further decomposition to a mixture of CCH and CH species is observed. When CO and molecular acetylene are coadsorbed at 220 K, we observe a $c(4 \times 2)$ LEED structure rather than the (2 x 2) LEED structures observed for acetylene or CO adsorbed alone on Rh(111). Also, chemisorbed acetylene, when coadsorbed with CO, decomposes at 270 K to a mixture of CCH_3 (ethylidyne) and CCH (acetylidyne) species rather than the CCH_2 species.

1. INTRODUCTION

Studies of the bonding and reactivity of unsaturated hydrocarbon molecules adsorbed on transition metal single crystal surfaces are important for a molecular-level understanding of heterogeneous hydrocarbon catalysis. With the development over the last 20 years of ultra-high vacuum (UHV) technology and of surface sensitive spectroscopies, a data base of adsorption geometries and fragmentation pathways for prototype hydrocarbons adsorbed on well-defined

single crystal metal surfaces is now accumulating.

High resolution electron energy loss spectroscopy (HREELS) [1], in providing surface vibrational spectra, has been a particularly powerful technique for determining the identity of hydrocarbon adsorbates. In combination with other techniques like low energy electron diffraction (LEED) [2], it has also been possible to determine the adsorption geometry, the bond lengths and the bond angles for several hydrocarbon adsorbates.[3] These structural results have been well-complemented by the desorption products and kinetics measured in thermal desorption spectroscopy (TDS) studies.

These techniques have been extensively applied to study the adsorption of acetylene, the prototype alkyne. To date, HREELS has been used to study the bonding and reactivity of acetylene adsorbed on Ni(111) [4-7], Ni(100) [8,9], Ni(110) [10,11], Pd(111) [12,13], Pd(100) [14], Pd(110) [10], Pt(111) [15,16], Cu(111) [10], Cu(110) [17], Ag(110) [18], Fe(110) [19], Fe(111) [20], Ru(0001) [21], Re(0001) [22], Rh(111) [23], W(110) [24], W(111) [25], W(100) [26], and Si(111) [27] surfaces. One of the major observations of these studies (except for the Ag(110) surface) was a large shift of the carbon-carbon stretching frequency from its value of 1974 cm^{-1} in gas phase acetylene to $1100-1400 \text{ cm}^{-1}$ for chemisorbed molecular acetylene. Such a frequency shift implies rehybridization of the C-C triple bond in adsorbed acetylene due to the chemisorption bond between acetylene and the metal surfaces. In this paper, we extend the previous study from our laboratory of acetylene chemisorption on the Rh(111) surface [23] to a wider temperature range in order to determine the fragmentation pathway both with and without coadsorbed CO. Further studies on the Rh(100) surface will be published in a separate paper [28].

In this work, we discuss first the results from TDS, then the low energy electron diffraction observations, and finally the HREELS results for chemisorbed acetylene and for acetylene coadsorbed with CO on Rh(111) as a function of temperature and coverage. We find that, for $T < 270 \text{ K}$, acetylene is adsorbed intact on Rh(111) in an ordered (2×2) overlayer, with a C-C bond hybridization between sp^2 and sp^3 . At $T > 270 \text{ K}$, acetylene decomposes predominately to CCH_2 (vinylidene), with further decomposition occurring at 400 K to CCH and CH species. Between 500 and 800 K , the complete dehydrogenation of these fragments is accompanied by carbon polymerization to

yield a graphite overlayer. Studies of the effect of coadsorbed CO on the bonding and decomposition of chemisorbed acetylene indicate that coadsorbed CO (1) induces the formation of a new $c(4 \times 2)$ LEED pattern for molecular acetylene at 220 K, and (2) alters the decomposition pathways at 270 K so that predominant fragments are ethynidyne (CCH_3) and acetylide (CCH) rather than vinylidene (CCH_2).

2. EXPERIMENTAL

Our experiments were carried out in three different ultra-high vacuum chambers with base pressures of 2×10^{-10} torr. Each chamber is equipped with LEED, Auger Electron Spectroscopy (AES), and a mass spectrometer for TDS. Two of the chambers, which have HREEL spectrometers, have been described previously [29,30]. The third chamber is designed for low temperature LEED studies. Here, we use a single stage Displex Closed Cycle Refrigeration System (Air Products, Displex OSP) to cool down our sample by copper braid connections (10 cm long x 0.8 cm wide) between the expander module cold head of the refrigerator and our crystal sample. Using electron bombardment to heat the sample, we can flash the crystal to $T > 1200$ K in 60 sec and recool back down to 30 K in another 90 sec.

Three different Rh(111) single crystals were used during the course of the experiments; all three were $0.5-1.0 \text{ cm}^2$ disks, 2 mm thick and cut from a single crystal rod of $> 99.996\%$ purity obtained from the Materials Research Cooperation. After polishing by standard methods [31], the crystals were mounted in the two HREELS chambers by spotwelding 0.020 inch Ta wire between the crystal edge and the manipulator and could be resistively heated to temperatures > 1200 K and cooled to 77 K by flowing liquid nitrogen through the manipulator. The crystal in the low temperature-LEED chamber was mounted by spotwelding the back side of the crystal onto two stainless steel plates, which were attached to the copper stand at the bottom of the manipulator and connected to the cold head through the copper braid. The single crystal surfaces were cleaned by a combination of heating in O_2 , Ar ion sputtering and annealing in UHV until free of C, S, O, and B as detected by AES, LEED, and HREELS [32].

Gases were adsorbed on the Rh(111) surfaces using microcapillary array doser in the HREELS chambers. Dosages are reported in Langmuirs [1

Langmuir(L) = 10^{-6} torr-sec] where the measured dose pressure has been corrected for x5 or x20 enhancements of the molecular flux at the crystal surface as a result of the array dosers in the two chambers. In the low temperature LEED chamber, the gases were adsorbed by back filling the chamber. Because the ion gauge in this chamber is positioned outside the μ -metal shielding surrounding the sample, LEED optics, and gas flux tube, the measured dosages in the multilayer TDS studies are multiplied by a factor of 3.5 to bring them in line with the dosages in the HREELS chambers. The term saturation coverage is used here to mean the highest attainable surface coverage of the hydrocarbons at temperatures above that where acetylene multilayers desorb (100 K). The sample gases were checked for purity by gas chromatography (GC) or mass spectrometry and were used as obtained from the following sources: C_2H_2 (Matheson, > 99.5% purity), C_2D_2 (MSD Isotope, 99% purity), and carbon monoxide (Matheson, > 99.5% purity). A dry ice-acetone trap was used to trap the acetone impurity in the C_2H_2 gas.

For the H_2 TDS, both sides of the single crystal were cleaned and exposed to gases using the array dosers. The crystal was heated at 10-30 K/sec with one side facing UTI mass spectrometer with the ionizer ~5 cm from the crystal surface. For multilayer desorption of molecular acetylene, the TDS experiments were done in the low temperature LEED chamber with only one side of the crystal cleaned and exposed to the acetylene gas by backfilling the chamber with acetylene.

The HREEL spectrometers are similar to designs commonly used and consist of 127° cylindrical monochromator and analyzer sectors. In one of the spectrometers the total scattering angle is fixed at 120°, so for specular HREELS, $\theta_{in} = \theta_{out} = 60^\circ$ from the surface normal. The other HREEL spectrometer has a rotatable analyzer and is operated with $\theta_{in} = 65^\circ$ from the surface normal. Both spectrometers were operated at an overall system resolution (FWHM) of 5-7.5 meV (40-60 cm^{-1} , 1 meV = 8.0655 cm^{-1}) and with incident beam energy of 2-5 eV. HREEL spectra were recorded at 77 K after briefly annealing the adsorbed monolayer to the temperature indicated on the spectra. All transformations with heating were irreversible.

3. RESULTS AND INTERPRETATION

3.1 Thermal Desorption Spectroscopy

Acetylene (Amu = 26) and hydrogen (Amu = 2) were the only thermal desorption products observed after acetylene adsorption at 30 K. Molecular

acetylene desorption spectra as a function of exposure at 30 K are shown in Figure 1a. We observed only one desorption peak at 100 K for acetylene exposures above 1.0 L (The broad higher temperature feature is due to the desorption from the crystal support as it slowly warms up). The 100 K desorption peak grows with increasing acetylene exposure; we attribute this peak to the desorption of physisorbed acetylene multilayers, consistent with the desorption temperature of 95 K observed recently for acetylene multilayers on a Ru(0001) surface by Parmeter et al. [21].

Figure 1b shows the hydrogen desorption spectra as a function of surface temperature for different acetylene exposures. Consistent with the observed multilayer desorption peak for exposures above 0.7 L, the H₂ TD spectra are unchanged above 0.7 L. The main features of the saturation coverage spectrum are the major peak at 440 K and a long hydrogen desorption tail between 500 and 800 K, consistent with previously published TDS results for acetylene adsorbed on Rh(111) at 240 K [23]. The first desorption peak temperature of 440 K is significantly higher than that observed for desorption of hydrogen atoms bonded to Rh(111). The desorption temperature of H₂, both adsorbed alone on Rh(111) [33] and when coadsorbed with various hydrocarbon fragments (CCH₃ [23,34] and CCH₃ + CH [51]), ranges from 275 to 390 K. Consequently, the hydrogen atoms most likely remain bonded to the carbon up to 400 K in the case of acetylene adsorption. This is a significant point, since the HREELS results presented below in Section 3.3 show that acetylene begins to decompose at 270 K on Rh(111). The long hydrogen desorption tail in the temperature range of 500-800 K for acetylene decomposition has also been observed in TDS studies of C₂H₄ and C₆H₆ on Rh(111) surfaces [34,35], as well as for C₂H₂ on Pt(111) surfaces [36]. This feature has been attributed to the final stages of hydrocarbon dehydrogenation accompanied by carbon polymerization to form a graphitic overlayer for T > 800 K [35].

3.2 Low Energy Electron Diffraction

We have studied by LEED the ordered overlayers that form after acetylene is adsorbed on Rh(111) from 30 to 800 K. At 30 K no ordered structures are observed. With increasing temperature, a sharp (2 x 2) LEED pattern is

observed in the temperature range of 60–270 K following 0.5 L acetylene dosages at 30 K. At lower and higher exposures only a diffuse (1 x 1) LEED pattern is observed. Above 270 K, a (1 x 1) disordered overlayer with high LEED background intensity occurs. It is interesting that the ordering temperature of the molecular acetylene is as low as 60 K, which has not been previously observed, probably because most studies of adsorbed acetylene have been limited to temperatures above 77 K.

Coadsorption of carbon monoxide with acetylene on Rh(111) produces a new ordered LEED pattern. To form this ordered structure, the surface was predosed with about a quarter monolayer of CO at 77 K with the observation of a (2 x 2) LEED pattern [Note, acetylene and CO both form (2 x 2) patterns when adsorbed separately], followed by a saturation exposure (1 L at 77 K) of C₂H₂. The resulting overlayer was disordered. However, when the surface was heated above 220 K, a new c(4 x 2) pattern was observed. This structure, which can also be formed by reversing the order of CO and acetylene addition, is stable up to 270 K where a (1 x 1) disordered pattern forms. The formation of new LEED patterns when adsorbates are coadsorbed with CO has been described recently in several publications by Mate et al. [37,38].

3.3 High Resolution Electron Energy Loss Spectroscopy

The HREEL vibrational spectra observed for acetylene adsorption and decomposition on Rh(111) are of three basic types, corresponding to three temperature regimes: below 270 K, 270–400 K, and above 400 K. These three categories of HREEL are presented and assigned in Sections 3.3.1–3.3.3. The spectra were recorded at 77 K after adsorbing acetylene at 77 K and annealing to the temperatures indicated on the spectra. The effects of coadsorbed carbon monoxide on the acetylene adsorption and decomposition HREEL spectra are presented and discussed in Section 3.3.4.

3.3.1 Spectra of molecular acetylene at 77 K to 270 K

Figure 2 shows HREEL spectra for quarter monolayers of C₂H₂ and C₂D₂ ordered on Rh(111) at 77 K with (2 x 2) LEED patterns. The spectra obtained here are similar to the previously published results at 240 K by Dubois et al. [23], except the spectra offer improved resolution and signal to noise. In particular, the carbon-carbon stretching frequency (1260 cm⁻¹) is well-resolved in this study, which allows us to determine the rehybridization

of C-C bond due to the interaction between the acetylene and Rh surface. A tacit assumption in this analysis is that acetylene is molecularly adsorbed at this low temperature of 77 K. There are no reports of acetylene decomposition below 150 K on any other transition metal surface. We conclude from the similarity of the HREEL spectra at 77 and 240 K on Rh(111), and based on the observation of a stable LEED pattern up to 270 K, that adsorbed molecular acetylene is stable in the whole temperature range from 77 K to 270 K.

Several features in the 77 K HREEL spectra in Figure 2 can be readily assigned. The peak at 2960 (2200) cm^{-1} for C_2H_2 (C_2D_2) is due to a CH(CD) stretching mode, presumably the symmetric stretch. The additional loss feature at 3050 cm^{-1} for C_2H_2 reported by Dubois et al. [23] and assigned as the asymmetric CH stretching mode is not observed in our spectra. We assign the loss peaks at 1260 cm^{-1} for C_2H_2 and 1230 cm^{-1} for C_2D_2 to CC stretching modes based on the small isotope shift, while the low frequency peak at 320 cm^{-1} in the C_2D_2 spectrum is assigned to the metal-acetylene stretching frequency. (The corresponding mode for C_2H_2 is obscured by the background intensity.) The remaining peaks in the 500-1200 cm^{-1} region are due to CH(CD) bending modes.

The nature of the EELS scattering mechanism of the vibrational losses for molecular acetylene on Rh(111) has been investigated by off-specular HREELS studies. Figure 3 shows the angular distributions of the inelastically scattered electrons for most of the acetylene HREELS peaks. Only a partial data set was recorded for the C-H stretching mode (2960 cm^{-1}), so these results are not plotted. From Figure 3, we conclude that the 720 and 950 cm^{-1} C-H bending modes of C_2H_2 adsorbed on Rh(111) are dipole active, since the scattering intensity of these modes decreases dramatically for angles away from the specular direction as expected for the dipole scattering process [1]. The scattering intensities of the 1120 cm^{-1} C-H bending mode and of the 1260 cm^{-1} C-C stretching mode have a much more constant angular distribution, indicating that impact rather than dipole scattering is the predominant scattering mechanism for these modes. The lack of dipolar scattering by the C-C stretching mode, which is necessarily dipole active for all adsorption geometries, implies that the dynamic dipole moment normal to the surface for this mode is small, presumably because the C-C bond lies

parallel to the surface. The implications of these results for acetylene adsorption symmetry on Rh(111) and a full assignment of the surface vibrational spectrum will be given in the discussion section.

3.3.2 Spectra from 270 K to 400 K

As the temperature of the Rh(111) surface is raised above 270 K, the vibrational spectrum changes dramatically, corresponding to the disordering of the (2 x 2) LEED pattern at this temperature. Figure 4 shows the HREEL spectra for 0.5L C₂H₂ and C₂D₂ adsorbed on Rh(111) at 77 K and briefly annealed to 320 K. The 320 K HREEL spectrum remains essentially unchanged throughout the temperature range of 270-400 K. The lack of correspondence between any of the peaks in the 320 K and 77 K spectra and the appearance of the 1405 cm⁻¹ peak in the CH₂ scissor/CH₃ deformation region of the vibrational spectrum at 320 K are compelling evidence that the 320 K HREEL spectrum is due to acetylene decomposition rather than to a reorientation of chemisorbed molecular acetylene. However, as determined from the TDS results discussed in Section 3.1, all hydrogen atoms remain bonded to carbon atoms in the 320 K decomposition fragment(s) and the surface stoichiometry remains C:H = 1:1. Also C-C bonds are probably still intact, since in Figure 4a peaks at 1160 and 1305 cm⁻¹ are observed in the deuterated spectra, which can only be explained as C-C stretching modes [39]. Consequently, we conclude that the C-H bonds break first when adsorbed acetylene decomposes on Rh(111). Previously reported results for the decomposition of C₂H₄ [34], and C₂H₂ + H₂ [23] on Rh(111) also indicate that the C-H bonds begin to break 100-200 K lower temperatures than C-C bonds.

If polymerization does not occur [40], there are only five combinations of fragments which have the correct stoichiometry and intact C-C bonds as observed for decomposed acetylene on Rh(111): CCH + CCH₃, CCH₂, CHCH₂ + CCH, C₂ + C₂H₄, C₂ + CHCH₃. C₂ species, which has been observed on nickel surface previously [41], are unlikely to be a major fragment as the HREEL spectra are dominated by hydrogenated species. For the combination of CCH₃ (ethylidyne) and CCH (acetylide) species, the characteristic modes for ethylidyne are a strong CH₃ group deformation mode around 1350 cm⁻¹, a less intense C-C stretching mode at 1120 cm⁻¹, and a weak C-H stretching mode at 2900 cm⁻¹ [34], while CCH species have a distinct C-H bending mode at ~800 cm⁻¹ and a C-H stretching mode around

3030 cm^{-1} [35]. These peaks cannot completely account for the spectra we observe, particularly the strong vibrational modes at 2950 (2195) and 1405 (1025) cm^{-1} . However, the presence of some CCH_3 and CCH species cannot be ruled out, and as we show later, when CO is coadsorbed with acetylene, the predominant decomposition fragments at 270 K are indeed CCH_3 and CCH . By process of elimination, the predominant fragment at 320 K in the absence of CO is either CCH_2 or $\text{HCCH}_2 + \text{CCH}$. Both CCH_2 and HCCH_2 have been previously proposed for transition metal surfaces and isolated in organometallic cluster complexes. The vibrational frequencies measured by HREELS or IR for the CCH_2 and HCCH_2 surface and cluster species have been reported in several studies [13,16,42-47] [45,48-50]. The most distinguishing feature between these vibrationally similar ligands is the δ CH mode for HCCH_2 at about 1250 cm^{-1} which is absent in CCH_2 . Since this mode should be dipole active for all adsorption geometries, we conclude from its absence in our spectra that CCH_2 is the predominant species on $\text{Rh}(111)$ at 320 K.

Accordingly, we assign the HREEL spectrum as given in Table I. There are several noteworthy points about the assignment: (1) the C-C stretching mode is lower on $\text{Rh}(111)$ by 180 cm^{-1} in comparison with the cluster compound; we attribute the difference to be due to a stronger interaction of CCH_2 with the $\text{Rh}(111)$ surface (and also $\text{Pt}(111)$, $\text{Fe}(110)$ surfaces) that distorts the C-C bond more toward a single bond C-C rehybridization. (2) The CH_2 rocking mode at 1051 cm^{-1} observed in the cluster compound was not detected on the $\text{Rh}(111)$, $\text{Pt}(111)$, and $\text{Pd}(111)$ surfaces, which may be due to a different bonding symmetry on the surface. (3) The peak at 765 cm^{-1} in Figure 4b is left unassigned. It is close to the CH_2 twisting frequency reported for CCH_2 in the triosmium cluster, but it is difficult to explain why this mode would be observed with strong intensity in HREELS when the CH_2 rock is not observed at all. Ibach et al. assigned a similar peak at 760 cm^{-1} in the $\text{Pt}(111)$ vinylidene spectrum to a C-H bending mode of some coexisting molecular acetylene [16]. However, it is unlikely that there is any acetylene left on $\text{Rh}(111)$ at 320 K as judged by the complete disappearance of characteristic acetylene vibrations like the C-C stretch at 1260 cm^{-1} . A more likely possibility is that the 765 cm^{-1} peak on $\text{Rh}(111)$ is a C-H bending mode of some coexistent CCH . The observed weak mode at 1305 cm^{-1} in Figure 4a for

the deuterated acetylene can be assigned to C-C stretching frequency of such a CCH species. (4) The peaks at 1780 cm^{-1} and 2000 cm^{-1} in Figure 4 are due to small percentages of CO contamination from the background ambient.

3.3.3 Spectra above 400 K

Figure 5 shows the hydrogenated and deuterated spectra for the surface species formed above 400 K. The surface overlayer left at this temperature can be assigned to a combination of CCH + CH [CCD + CD] fragments on the Rh surface; very similar spectra have been obtained in a previous study of benzene decomposition on the Rh(111) surface [35]. Based on that work, the spectral features attributable to the CCH (CCD) fragment are a weak $\nu\text{C-C}$ mode at 1405 (1365) cm^{-1} , a δCH (CD) bending mode at 800 (550) cm^{-1} , a νCH (CD) mode at 3025 (2250) cm^{-1} , and a $\nu\text{M-C}$ at 480 (445) cm^{-1} , as well as a combination band at 1150 (not observed) cm^{-1} . The vibrational features observed for the CH fragment are mostly obscured by the modes from the CCH fragment. The strongest evidence for the CH fragment is a mode at 720 cm^{-1} of the deuterated spectrum which can be assigned as the νMC mode (the corresponding mode in the undeuterated spectrum overlaps with the 800 cm^{-1} peak). We cannot rule out the possibility of some polymerized C_xH ($x > 2$) species on the surface, since the observable modes of such species are likely to be rather similar to those for the CCH fragment. In fact, the broad C-C stretching peak may indicate that some polymerization occurs during the dehydrogenation of CCH_2 at 470 K. Further dehydrogenation above 470 K, is almost certainly accompanied by polymerization until all the hydrogen desorbs leaving a graphitic overlayer at 800 K. Again, this graphitic overlayer is similar to that formed during benzene decomposition on Rh(111) [35], as well as for several C_3 hydrocarbons on Rh(111) [51].

3.3.4 Coadsorption of Carbon Monoxide with Acetylene

Recently, Mate et al. have reported that the coadsorption of CO with various adsorbates - acetylene, benzene, fluorobenzene, ethylidyne, propylidyne, and sodium - on the Rh(111) and Pt(111) surfaces can induce these adsorbates to form ordered overlayers that might not otherwise form [37,38]. In the present work we have found that CO effects both the ordering and the thermal fragmentation chemistry of acetylene on Rh(111).

First, when CO is coadsorbed with acetylene on Rh(111), it is possible to form a new $c(4 \times 2)$ LEED structure as detailed in Section 3.2; however, we

found this CO-induced LEED structure to be more difficult to form than those for other coadsorbates [52]. Figure 6 shows the HREEL spectra for C_2H_2 [(2 x 2)] and CO + C_2H_2 [c(4 x 2)] on Rh(111). To form the c(4 x 2) structure, the surface, at 77 K, was exposed first to CO then to C_2H_2 , and we found it necessary to anneal the sample above 220 K. The HREEL spectra for coadsorbed acetylene and CO still exhibit the vibrational peaks of chemisorbed acetylene, indicating that acetylene maintains its molecular integrity when coadsorbed with CO. However, the vibrational frequencies for coadsorbed acetylene are shifted slightly from those observed for the (2 x 2) acetylene structure, indicating that some interaction occurs between coadsorbed acetylene and CO. Two CO stretching frequencies are at 1780 cm^{-1} and 2025 cm^{-1} , but when the c(4 x 2) structure was formed by reversing the order of CO and acetylene addition, only the 1780 cm^{-1} was observed. Since CO can order in small islands on Rh(111) surface at low coverages [53], we conclude that the peak at 2025 cm^{-1} observed by predosing the surface with CO is due to the small CO islands on the surface outside the coadsorbed c(4 x 2) domains.

The effect of CO on acetylene decomposition at 320 K is shown in Figure 7. Figure 7a is the same spectrum as Figure 4b, which was formed by warming acetylene to 320 K in the absence of CO. This spectrum was attributed to predominantly CCH_2 species. Figure 7b shows the much different spectrum, particularly in the distribution of intensities among the loss peaks, that results when the c(4 x 2) coadsorbed CO + C_2H_2 structure is warmed to 320 K. In comparison with the CO-free spectrum, there is a dramatic decrease in the vibrational features at 2950 cm^{-1} and 1405 cm^{-1} for the CCH_2 fragment along with the appearance of a new weak peak at 2935 cm^{-1} and an intense peak at 1365 cm^{-1} . These new peaks along with those at 970 cm^{-1} and 1120 cm^{-1} are in excellent agreement with both frequencies and intensities of the vibrational fingerprint of an CCH_3 (ethylidyne) species, which has previously been formed on the Rh(111) surface both by the thermal decomposition of ethylene [34] and by the reaction of acetylene coadsorbed with hydrogen atoms above 270 K [23]. The complete assignment for the ethylidyne fragment has been published [54]. The vibrational modes at 1805 and 2010 cm^{-1} can be attributed to carbon-oxygen stretching frequency of the

coadsorbed CO which remains on the surface at this temperature. These are approximately the same frequencies observed for CO coadsorbed with molecular acetylene and attributed to top and hollow site bonding. The weak and broad feature centered at 780 cm^{-1} along with a weak mode at 3050 cm^{-1} in Figure 7b can be assigned to the C-H bending and C-H stretching modes of CCH species coadsorbed with ethynidyne on the surface; the carbon-carbon stretching mode for this species would be obscured by the coadsorbed ethynidyne vibrational modes. Based on the above assignment, we conclude that the coadsorbed CO at 1/4 monolayer coverage changes the fragments of acetylene decomposition from predominantly CCH_2 to a combination of mainly CCH_3 and CCH on the Rh(111) surface.

4. DISCUSSION

We discuss our results for acetylene adsorption and thermal decomposition on Rh(111) in two parts: molecular adsorption below 270 K and thermal fragmentation above 270 K. In each section we note the changes that were observed when CO was coadsorbed, and we compare our Rh(111) results to those reported for acetylene adsorption on other metal surfaces.

4.1 Molecular Acetylene Adsorption

Our results show that acetylene is strongly chemisorbed on Rh(111) and remains molecularly intact up to 270 K. No molecular acetylene thermally desorbs except for multilayers condensed on top of the monolayer below 100 K. Compared with gas phase acetylene ($\nu_{\text{CC}} = 1974\text{ cm}^{-1}$, $\nu_{\text{CH}} = 3374\text{ cm}^{-1}$) both the CC (1260 cm^{-1}) and CH (2960 cm^{-1}) stretching frequencies for chemisorbed acetylene are dramatically shifted to lower frequency. These frequency shifts indicate strong bonding of acetylene to Rh(111); they are also consistent with rehybridization of the C-C triple bond from sp towards sp^2 and sp^3 in chemisorbed acetylene. A large degree of C-C bond rehybridization is characteristic of acetylene bonding to transition metal surfaces. In fact, on all metal surfaces studied to date except for Ag(110) [18], the acetylene C-C stretching frequency is shifted to below 1450 cm^{-1} , indicative of rehybridizations between sp^2 and sp^3 . Such rehybridization of the carbon-carbon bond is generally explained by the Dewar-Chatto-Duncanson model for coordination of unsaturated CC bonds to metal centers [55]. In this model, weakening and rehybridization of the CC bond occurs because the filled

acetylene π orbital overlaps an empty metal d orbital, while the empty π^* orbital overlaps a filled metal d orbital. However, this explanation does not predict the binding site or adsorption symmetry for chemisorbed acetylene.

Information concerning the adsorption geometry of acetylene on Rh(111) can be obtained from intensities of the peaks in the vibrational spectra. Sheppard [56] has noted that the HREEL spectra for chemisorbed acetylene appear to be of three basic types, which he labels A, A' and B. The classification is based mainly on the HREELS intensity profiles, since, in essence, the HREELS intensity profiles may be more indicative of the acetylene bonding configuration on the surface than are the vibrational frequencies. This proposal seems reasonable, since, as a consequence of the dipole selection rule, the specular HREELS peak intensities are determined largely by the adsorbate symmetry and orientation. The vibrational frequencies, on the other hand, depend mainly on the C-C bond rehybridization which is likely to be determined more by the nature of the metal and by the degree of charge transfer than by the particular adsorption geometry. The spectra in Fig. 2 for acetylene chemisorbed on Rh(111) are best classified as type B spectra in Sheppard's classification, which are thought to correspond an acetylene molecule σ -bonded to two metal atoms and π -bonded to a third [56]. We depict the geometry for this complex for a 3-fold hollow site on Rh(111) in Fig. 8a. This type of di- σ + π coordination can also explain the observed relative intensities of the dipole active C-H bends in our HREEL spectra; i.e., since the HCCH molecular plane is tilted from the surface normal, both the in-plane (δ) and out-of plane (γ) C-H bends, which are dipole active can be expected to have comparable dynamic dipole moments normal to the surfaces consistent with their similar HREELS peak intensities. The HREEL spectra are consistent with an adsorption geometry such as the one on Fig. 8a which as C_s symmetry, since in C_s symmetry there would be two totally symmetric (dipole active) CH bending modes and one C-H bending mode of lower symmetry (dipole inactive) consistent with the off-specular HREELS studies in Fig. 3.

On the basis of these considerations, we assign our Rh(111)/molecular acetylene HREEL spectra in Table II to a di- σ + π coordinated species having C_s symmetry. We include in Table II the vibrational frequencies for the

analogous triosmium acetylene cluster as well as the vibrational frequencies for chemisorbed acetylene on other face-centered cubic metal surfaces where $di-\sigma+\pi$ coordination (i.e., type B) has been proposed. The surface bonding geometry for molecularly adsorbed acetylene which best accounts for our HREEL spectra and (2 x 2) LEED pattern is shown in Figure 8b.

Despite the strong interaction between acetylene and Rh(111), chemisorbed molecular acetylene is still kinetically able to form an ordered (2 x 2) structure on Rh(111) at 60 K. The low disorder-order transition temperature on this face centered cubic (fcc) (111) surface implies a small barrier to the surface diffusion for chemisorbed acetylene at a quarter monolayer coverage. Indeed, a previous theoretical study of acetylene chemisorption on Rh(111) surface using the Extended Hückel method did predict such a small surface diffusion barrier for acetylene [58]; similar low-temperature ordering behavior for other small adsorbates (CO, NO, Na, and ethylene) on Rh(111) will be discussed in a separate paper [59].

4.1.1 Effects of Coadsorbed Carbon Monoxide

Coadsorption of carbon monoxide with molecular acetylene has several effects as noted in the results. First, a new c(4 x 2) LEED structure can be formed when acetylene is coadsorbed with CO rather than the (2 x 2) structure acetylene forms when adsorbed alone on Rh(111). Second, the molecular acetylene vibrational frequencies shift an average of about 20 cm^{-1} when CO is coadsorbed, which is larger than the $\pm 10\text{ cm}^{-1}$ uncertainty in the determination of the HREELS peak positions. Thirdly, the relative intensities of the molecular acetylene HREELS peaks are altered by coadsorbed CO. In particular, the 750 cm^{-1} symmetric out-of-plane C-H bend loses intensity relative to the 975 cm^{-1} symmetric in-plane bend. And finally, the CO stretching frequency of 1780 cm^{-1} is substantially lower than that observed for top site CO (2015 cm^{-1}) or bridge site CO (1855 cm^{-1}) in the absence of acetylene.

All these observations are evidence for an interaction between coadsorbed acetylene and carbon monoxide which affects the bonding of both adsorbates to Rh(111). The change in the CO stretching frequency can be attributed to an acetylene-induced shift to a 3-fold hollow binding site. Similar low CO stretching frequencies of 1655-1700 and 1790 cm^{-1} have been reported for CO

coadsorbed with benzene and ethylidyne [37,38] on Rh(111) and in both cases the CO bonding site was determined by dynamical LEED calculations to be the 3-fold hollow.

The shift up in frequency of the acetylene CC and CH stretch modes is indicative of less rehybridization and of weaker bonding to Rh(111). This weaker bonding is probably the result of decreased π -bonding in the di- $\sigma+\pi$ coordination. Less π -bonding would mean that acetylene bonds with its molecular plane more nearly along the surface normal, which would account for the change in the relative intensities of the in-plane and out-of-plane CH bending modes. Less π -bonding and a more vertical orientation for acetylene also leaves more space for coadsorbed carbon monoxide, and from the interactions evident between acetylene and CO, it appears that the c(4 x 2) coadsorbed structure is quite densely packed, having one CO and one acetylene per unit cell.

4.2 Thermal Fragmentation of Acetylene above 270 K

As discussed in section 3.3.2, our HREEL spectra show that, in the absence of carbon monoxide, acetylene on Rh(111) converts predominantly to CCH₂ above 270 K. Based on the known bonding geometry of CCH₂ in trimetallic clusters, we have suggested that CCH₂ bonds in a 3-fold hollow site on Rh(111) as shown in Figure 9. We attribute the lower C-C stretching frequency on Rh(111) as compared to the triosmium cluster to increased π -bonding with the surface. Indirect evidence for the bonding geometry of CCH₂ on Rh(111) comes from studies of CCH₂ on Pt. On Pt(111), CCH₂ has a similar HREEL spectrum [16] and presumably similar bonding to Rh(111), while nuclear magnetic resonance studies of acetylene adsorption on small Pt particles have identified the adsorbed species as CCH₂ [60]. A recent molecular orbital calculation by Kang et. al. also predicted a tilted μ/π vinylidene species on Pt(111) [61].

On Rh(111) these CCH₂ species are stable up to 400 K where they decompose to C_xH species. The predominant species is probably C₂H, but there is also evidence for CH and polymerized C_xH(x>2) species. Further dehydrogenation and polymerization of these species occur up to 800 K [35].

4.2.1 Effect of Coadsorbed Carbon Monoxide

In the presence of carbon monoxide, the predominant fragments from

acetylene decomposition at 270 K are CCH and CCH₃ rather than CCH₂. The bonding of these fragments and their thermal chemistry above 400 K are not detectably affected by the presence of CO. The CO-induced change in the chemistry at 270 K is interesting, since previous studies of CO coadsorption with ethylene [34], propylene [50] and benzene [35] on Rh(111) showed no significant effects on the thermal fragmentation chemistry. However CO has been reported to have a dramatic effect on hydrogen desorption from transition metals [62] and has recently been found to alter the relative amounts of several species that are formed in ethylene decomposition on Ru(0001) [63], Ni(100) [64], and Rh(100) [65]. This CO-induced chemistry deserves further investigation.

4.2.2 Trends in Acetylene Fragmentation on Metal Surfaces

The acetylene thermal chemistry on metal surfaces that has been determined by HREELS is summarized in Figure 10. The various classes (A, A', B) of molecular acetylene adsorption are noted; however, there is not enough data to determine whether types of molecular adsorption can be correlated with thermal fragmentation pathways. There do appear to be significant differences between the 3d and 4d/5d metals, with the former showing increased dehydrogenation and C-C bond breaking at any given temperature. The differences in the amount of dehydrogenation on the 3d and 4d/5d metals may be amplified by the hydrogenations which can occur on the 4d/5d metals, e.g., acetylene is hydrogenated and converted to ethylidyne on Rh(111) [23], Pt(111) [16], and Pd(111) [13] when hydrogen is added.

5. CONCLUSION

There are three main results we would like to stress:

1) Ordering of molecular acetylene at 60 K with the formation of a (2 x 2) ordered monolayer has been observed on Rh(111). The corresponding HREEL spectra of molecular acetylene at 77 K are consistent with previously published spectra for adsorption at 240 K and are very similar to those observed for acetylene on both Pt(111) and Pd(111). We attribute these spectra to di- σ bonding of acetylene in a 3-fold hollow site as shown in Figure 8.

2) Acetylene thermally decomposes at 270 K on Rh(111) to predominant CCH₂ (vinylidene) species which in turn dehydrogenate and polymerize to C_xH species above 400 K. These results are summarized and compared to other metal surfaces in Figure 10.

3) The coadsorption of CO with C_2H_2 can induce the formation of a new $c(4 \times 2)$ LEED structure between 220 K and 270 K. The bonding of both acetylene and CO are affected by this coadsorption. While the desorption temperature for CO is not significantly affected by this interaction, the thermal decomposition pathway of acetylene on the Rh(111) surface changes with CCH_3 and CCH being the predominant fragments at 270 K instead of CCH_2 .

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Table I. Assignment of vibrational modes observed for the acetylene decomposition fragment stable on Rh(111) in the temperature range of 270 -400 K to adsorbed vinylidene (CCH_2). The corresponding frequencies assigned to similar species on other metal surfaces and the IR frequencies for the triosmium vinylidene compound $[Os_3(CO)_9(\mu-H)_2 (\mu_3-n^2-C=CH_2)]$ and 1,1-dichloroethylene ($C_2H_2Cl_2$) are listed for comparison.

Mode ^h	Rh(111)/C ₂ H ₂ T=320 K ^a	Pt(111)/C ₂ H ₂ T=350 K ^b	Pd(111)/C ₂ H ₂ T=250 K ^c
$\nu_s CH_2$	2950(2195,1.34) [s,br]	2970 [m,br]	2986 [s,br]
$\nu_a CH_2$	----	----	----
δCH_2	1405(1025,1.37) [m,br]	1420 [m,br]	----
ν_{CC}	1145(1160,0.99) [m]	1130 [w]	1437 [m]
ρ_r	----	----	----
ρ_w	990(775,1.28) [w]	900 [m]	----
ρ_t	----	----	----
ν_{MC}	470(445,1.06) [w]	420 [w]	----

	Fe(110)/CH ₂ CO T=410 K ^d	Ru(0001)/O+C ₂ H ₄ T=350 K ^e	$Os_3(CO)_9(\mu-H)_2 (\mu_3-n^2-C=CH_2)$ ^f	C ₂ H ₂ Cl ₂ ^g
	3050 [m]	2985(2180,1.37) [w]	2986(----) [w]	3035(2262,1.34) [w]
	----	3050(2290,1.33) [sh]	----	3130(2380,1.32) [w]
	----	1435(1010,1.42) [s]	1470(1040,1.41) [m]	1400(1039,1.35) [m]
	1230 [m]	1435(1350,1.06) [s]	1331(1363,0.98) [m]	1627(1565,1.04) [ν_s]
	----	965(----) [sh]	1051(877,1.20) [s]	1095(998,1.10) [ν_s]
	850 [w]	895(700,1.28) [m]	963(752,1.28) [s]	875(697,1.26) [s]
	----	----	811(----) [m]	
	----	455(435,1.05) [m]	311(----) [s]	

Frequencies are in cm^{-1} ; Numbers in parenthesis are (frequencies for deuterated analogue, $\nu CH/\nu CD$)

s-strong, m-medium, w-weak, br-broad, sh-shoulder

^aThis work. ^bRef. 16. ^cRef. 13. ^dRef. 42,43. ^eRef. 44. ^fRef. 45,46.

^gRef. 47. ^h_s = symmetric; a = asymmetric.

Table II. Vibrational mode assignment for molecular acetylene adsorbed on Rh(111) in the temperature range 77 -270 K. The corresponding frequencies for C₂H₂ adsorbed on metal surfaces classified as Type B by Sheppard [56] and the IR frequencies of the triosmium-acetylene cluster compound Os₃(CO)₁₀(C₂H₂)₂ [57] are also listed for comparison. All frequencies are reported in cm⁻¹.

Modes ^g	Rh(111) ^a	Pd(111) ^b	Pd(110) ^c	Ni(110) ^d	Pt(111) ^e	Os ₃ (CO) ₁₀ (C ₂ H ₂) ₂ ^f
ν_s CH stretch	2960	2992	2990	2950	3010	2996
ν_a CH stretch	----	----	----	----	----	2945
ν CC stretch	1260	1402	1400	1350	1310	1301
δ_a CH bend	1120	1034	----	----	----	1035
δ_s CH bend	950	872	915	910	985	978
γ_s CH bend	720	673	690	675	770	848
ν_a MC stretch	----	----	----	----	570	521
ν_s MC stretch	----	500	----	473	340	----

^a This work. ^b Ref. 12. ^c Ref. 10. ^d Ref. 10,11. ^e Ref. 15,16. ^f Ref. 57.

^g s = symmetric; a = asymmetric; δ = in-plane bend; γ = out-of-plane bend.

FIGURE CAPTIONS

Figure 1: Thermal desorption spectra for C_2H_2 adsorbed on Rh(111) at 30 K. (A) molecular acetylene desorption at different exposures; note that for exposures above 0.7 L, a sharp desorption occurs at 100 K which increases with dosage; this peak is attributed to multilayer desorption, while the long desorption tail at higher temperatures comes from the support wires. (B) hydrogen desorption as a function of acetylene exposure; at 0.50 L a sharp (2 x 2) LEED pattern was observed at 60 K. The heating rate was 19 K/sec for both cases.

Figure 2: Vibrational spectra obtained by HREELS in the specular direction for the (2 x 2) structure of C_2H_2 and C_2D_2 on Rh(111) at 77 K.

Figure 3: The intensities of the indicated vibrational modes for (2 x 2)- C_2H_2 adsorbed on Rh(111) at 77 K as a function of off-specular detection angle. The plus and minus signs indicate the two different directions of analyzer rotation. The angle of the incident electron beam relative to surface normal direction was held constant at 65°, and the incident beam energy was 1.5 eV.

Figure 4: Vibrational spectra of 0.5 L C_2H_2 and C_2D_2 ($\theta_{C_2H_2} = 0.5$) adsorbed on Rh(111) at the sample annealing temperature of 320 K, (A) C_2D_2 . (B) C_2H_2 . Both spectra were taken at 77 K in the specular direction. The observed peaks at both 1780 and 2000 cm^{-1} are due to a small amount ($\theta_{CO} \sim 0.05$) of coadsorbed CO contamination from background gas.

- Figure 5: Vibrational spectra of 0.5 L C_2H_2 and C_2D_2 adsorbed on Rh(111) at the sample annealing temperature of 470 K. (A) C_2H_2 . (B) C_2D_2 . Both spectra were taken at 77 K in the specular direction. The observed peak at 2000 cm^{-1} is due to CO contamination from background gas.
- Figure 6: Specular HREEL spectra of C_2H_2 and of CO plus C_2H_2 on Rh(111). (A) C_2H_2 at 77 K ((2 x 2) LEED structure; same HREEL spectrum as in Figure 3). (B) C_2H_2 + CO-(4 x 2) LEED structure formed by first exposing to CO and then C_2H_2 at 77 K, followed by annealing to 220 K). Both spectra were taken at a sample temperature of 77 K.
- Figure 7: Specular HREEL spectra of C_2H_2 and of CO plus C_2H_2 at 320 K following adsorption on Rh(111) by the procedure described in Figure 6. (A) is the same spectrum as in Figure 4b which was assigned to surface vinylidene (CCH_2) species. (B) shows the effect of CO. This spectrum is attributed to CCH_3 and CCH species.
- Figure 8: The proposed surface structure for molecularly adsorbed acetylene on Rh(111). This structure is thermally stable up to 270 K. For (A) the $d\pi-\sigma + \pi$ bonding geometry was represented. The top view of the (2 x 2) structure is shown in (B) with an indicated unit cell mesh. For the symbol used in both figures - large, open circles represent the rhodium surface atoms, smaller open circles represent carbon atoms, and the small, black circles represent hydrogen atoms.
- Figure 9: The proposed surface bonding geometry for the vinylidene (CCH_2) species observed from acetylene decomposition on Rh(111) in the temperature range of 270-400 K.

Figure 10: Acetylene thermal fragmentation pathways on metal surfaces based on our results and on published data. The three classes of molecular acetylene HREEL spectra (A,A',B) which are discussed in the text are also listed for comparison.

^a The letters A, B, A' inside the brackets represent the three types of low temperature molecular acetylene structure that have been observed on metal surfaces based on Sheppard's classification [56]

^b The temperatures listed indicate the range of temperature for which a certain scheme of decomposition process has been observed.

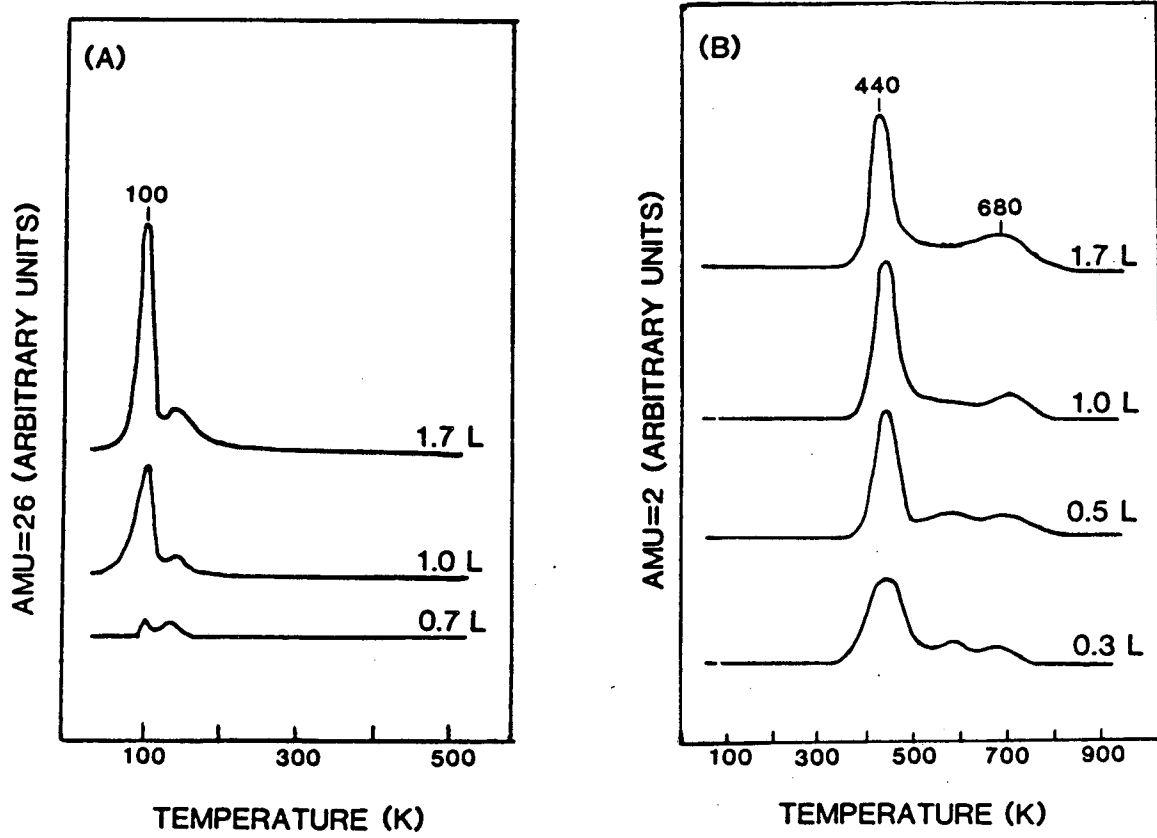
^c Surface vinylidene (CCH_2) species is the predominant fragment from acetylene decomposition on Rh(111) at 270 K, although small amounts of coadsorbed CCH and CCH_3 species cannot be completely ruled out.

^d The low temperature molecular acetylene on Ru(0001) has not been classified by Sheppard, but the spectra look quite similar to type B.

^e The intermediate species $\text{CCH}_{2(a)}$ has been observed at 250K on Pd(111) during the disproportionation reaction from acetylene to CCH (acetylide) plus CCH_3 (ethylidyne).

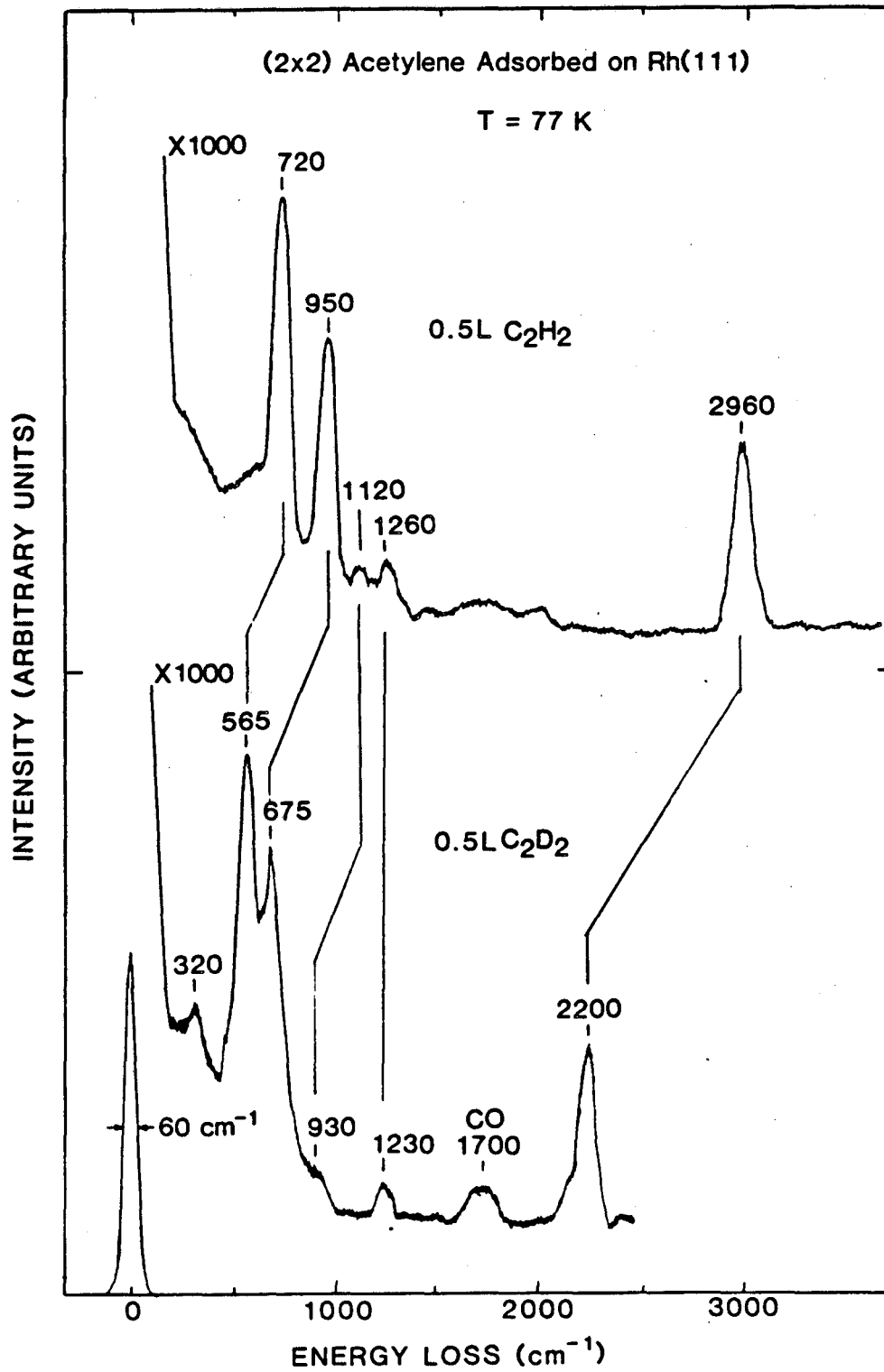
^f The Ni(111)/acetylene fragments originally assigned as CH have been reinterpreted as C_2H [35]. It is difficult to distinguish by HREELS between CH, C_2H , and C_xH ($x > 2$)

Thermal Desorption Spectra for C₂H₂ Adsorption at 30 K on Rh(111)



XBL 873-1394

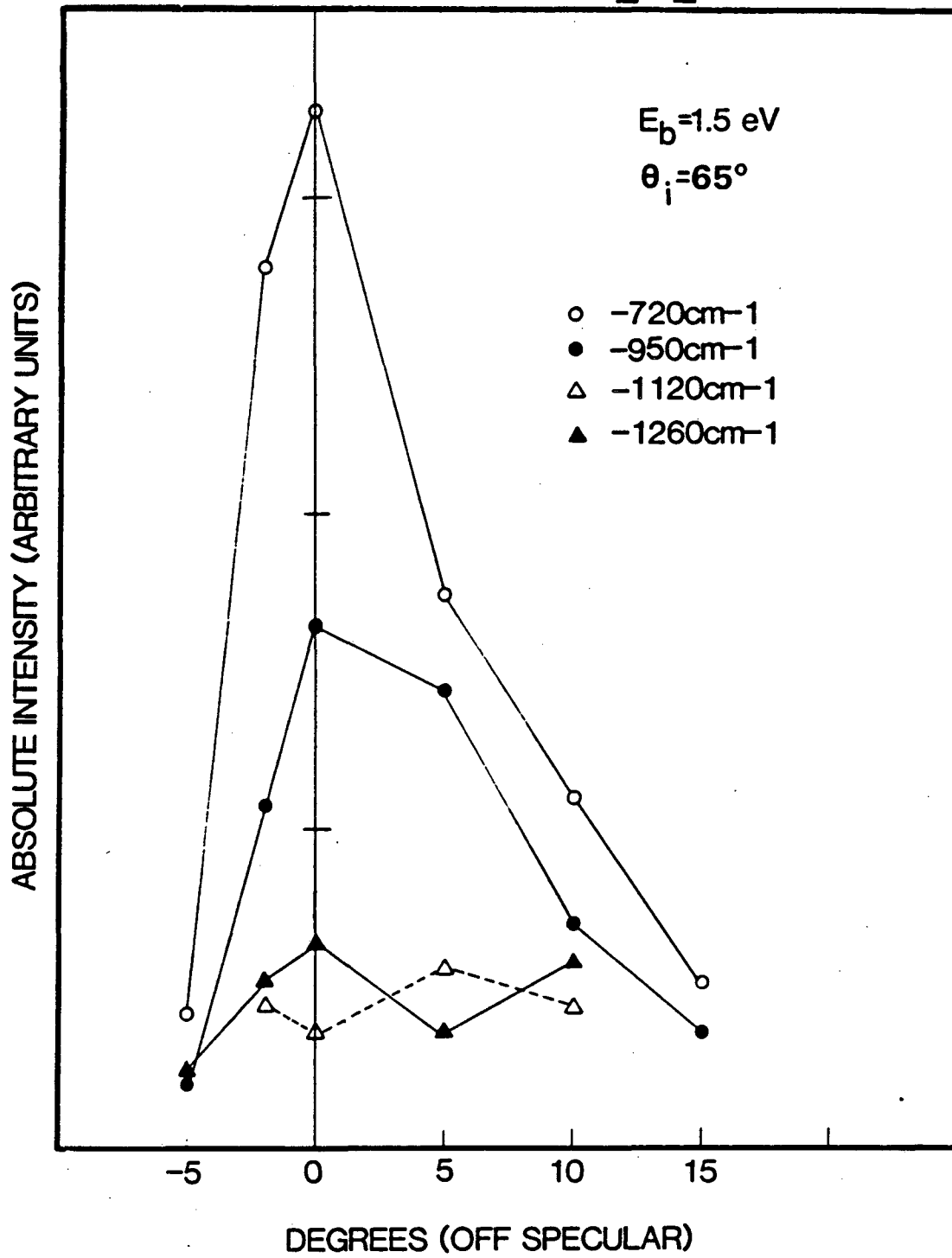
Fig. 1



XBL 872-474

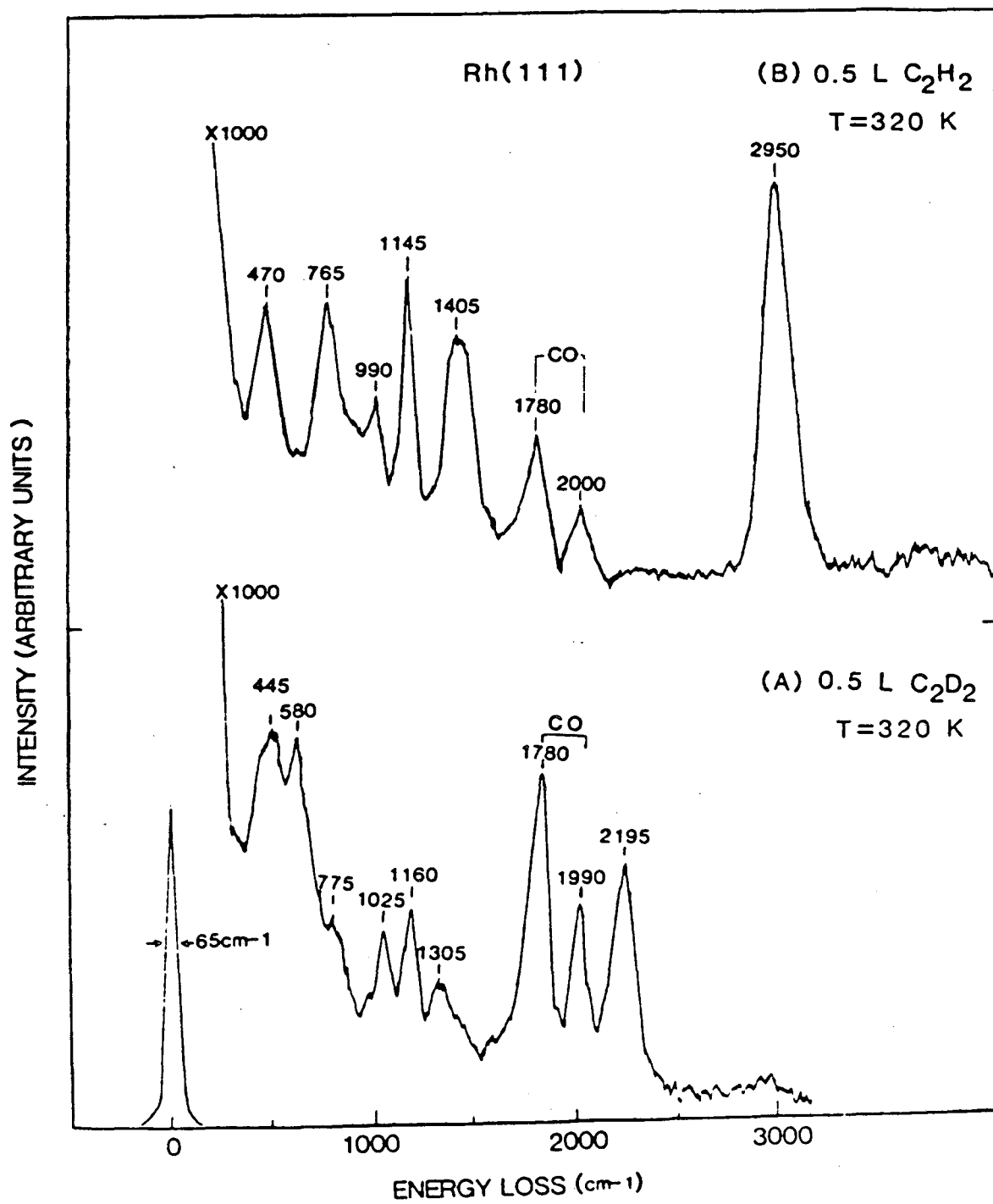
Fig. 2

Rh(111)-(2X2) C₂H₂



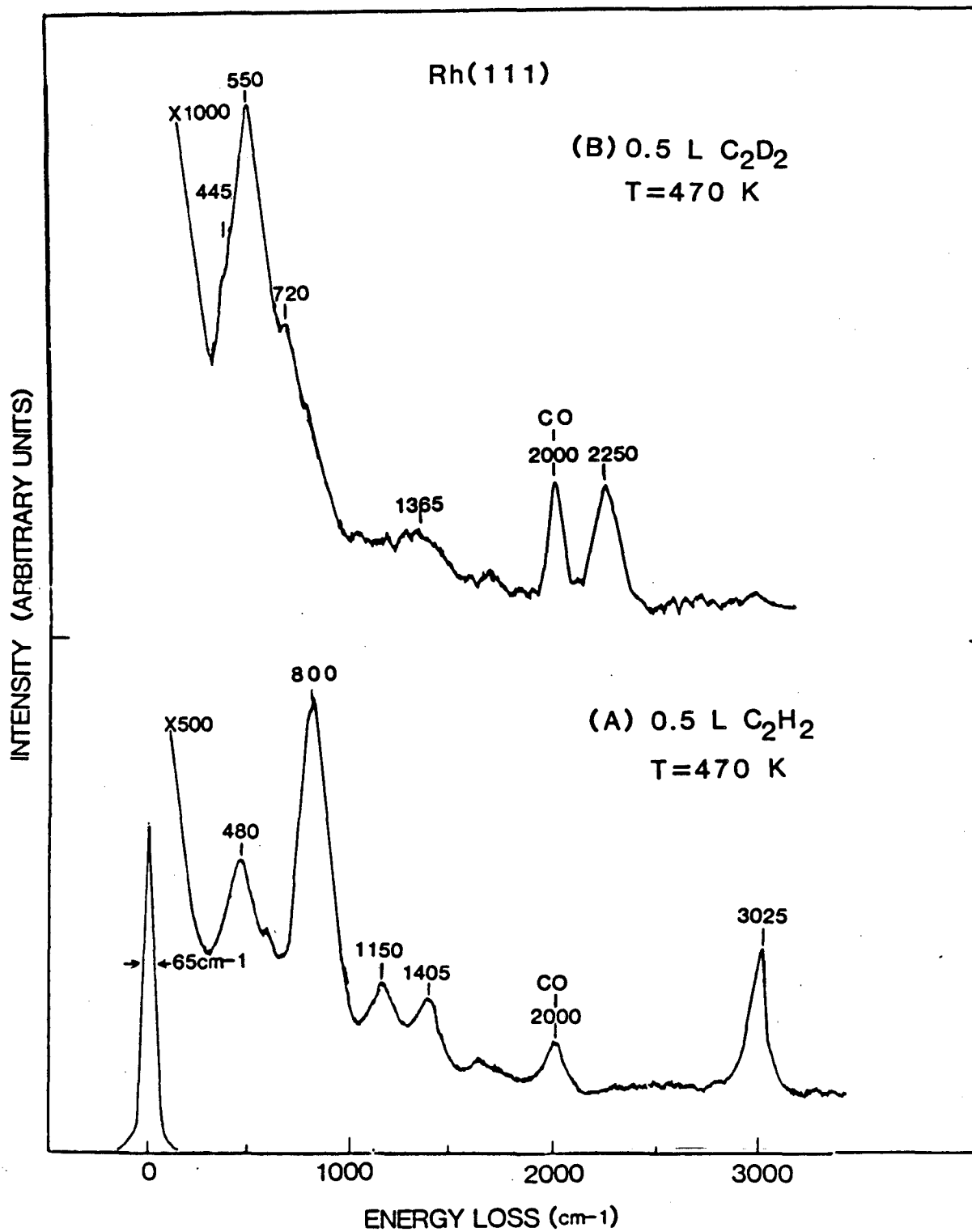
XBL 872-473

Fig. 3



XBL 876-2793

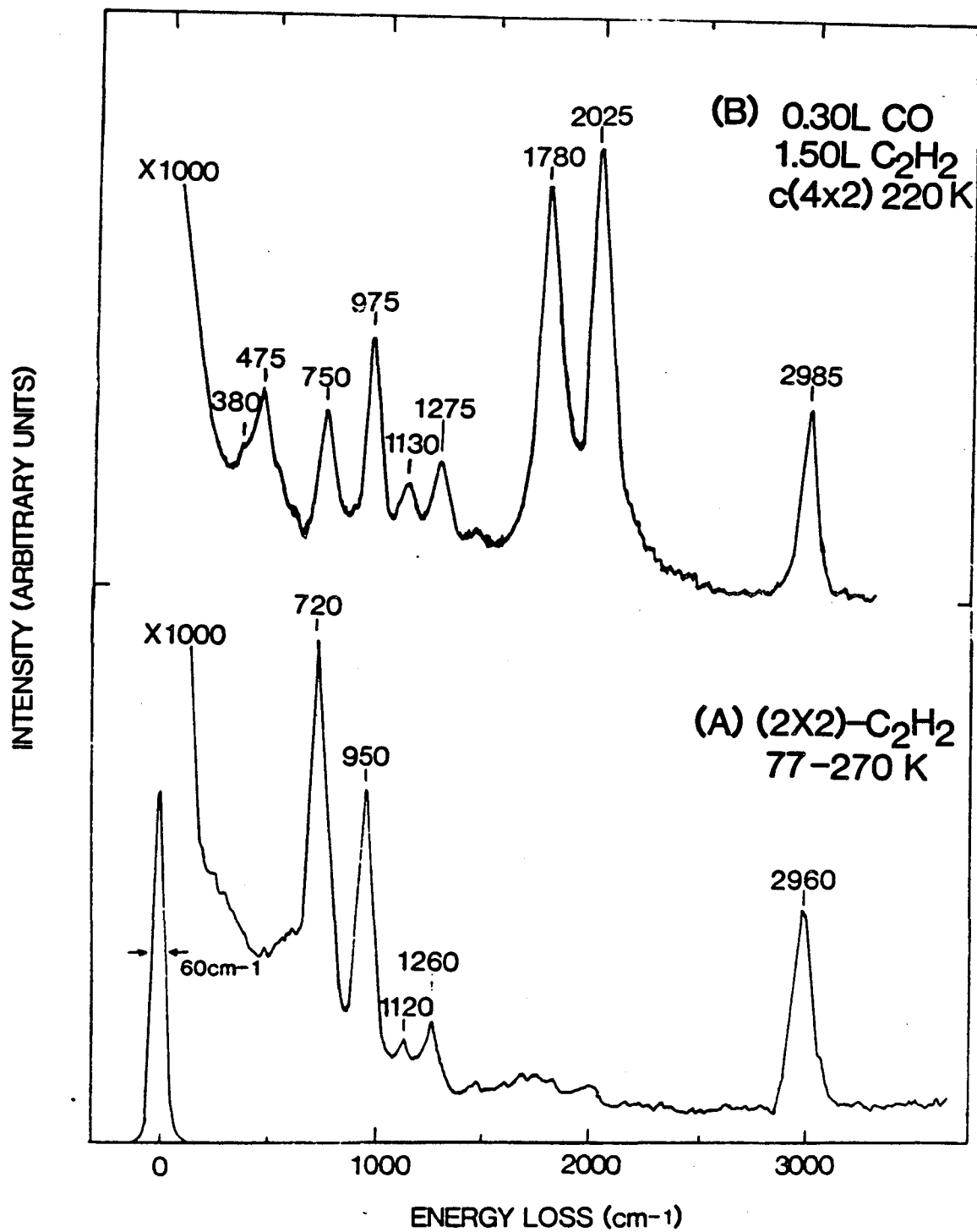
Fig. 4



XBL 872-471

Fig. 5

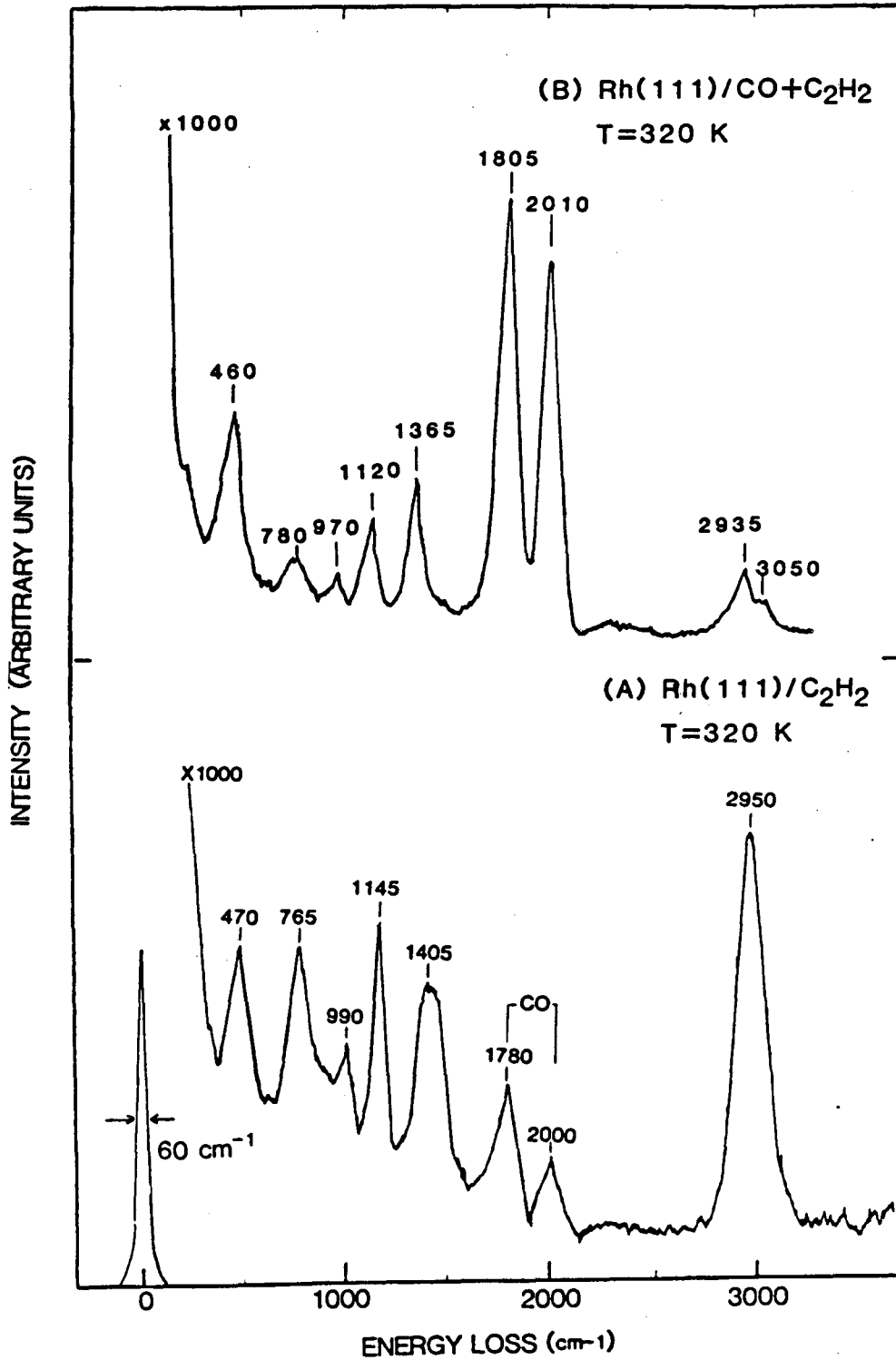
Coadsorption of CO and C₂H₂ on Rh(111)



XBL 872-470

Fig. 6

The Effect of Coadsorbed CO to Acetylene Decomposition



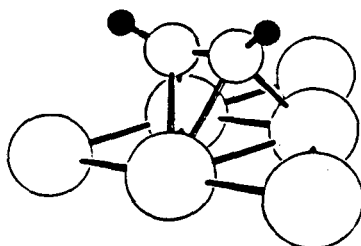
XBL 872-469

Fig. 7

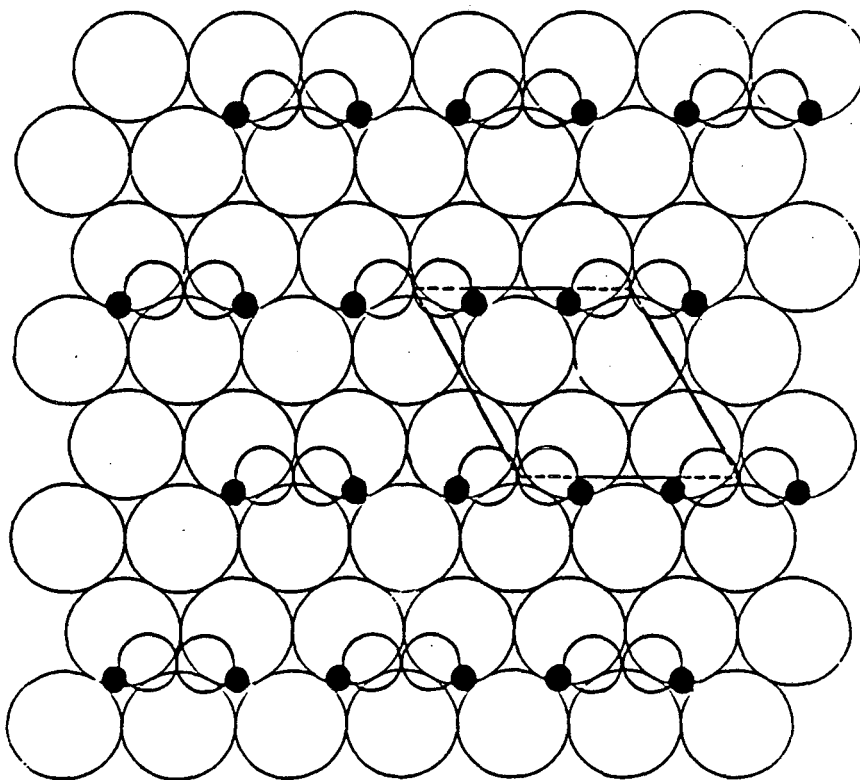
Proposed Structure:

(2x2)-C₂H₂ on Rh(111)

(A)

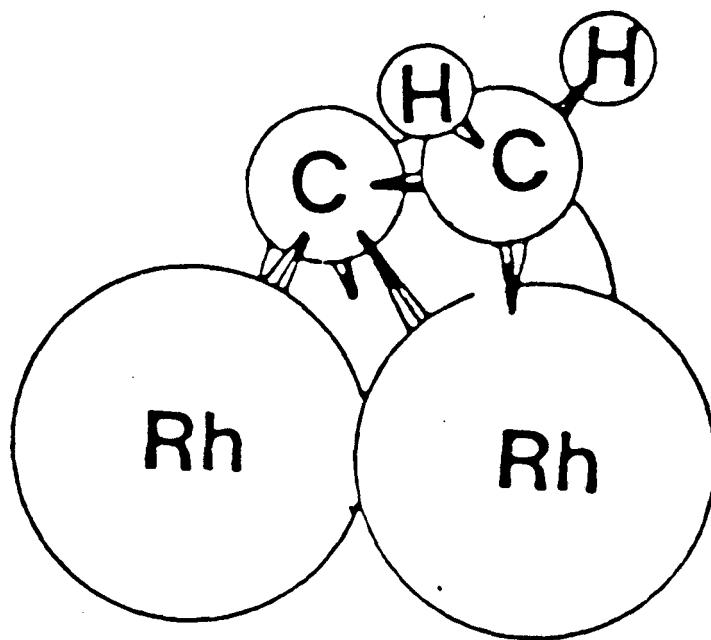


(B)



XBL 872-464

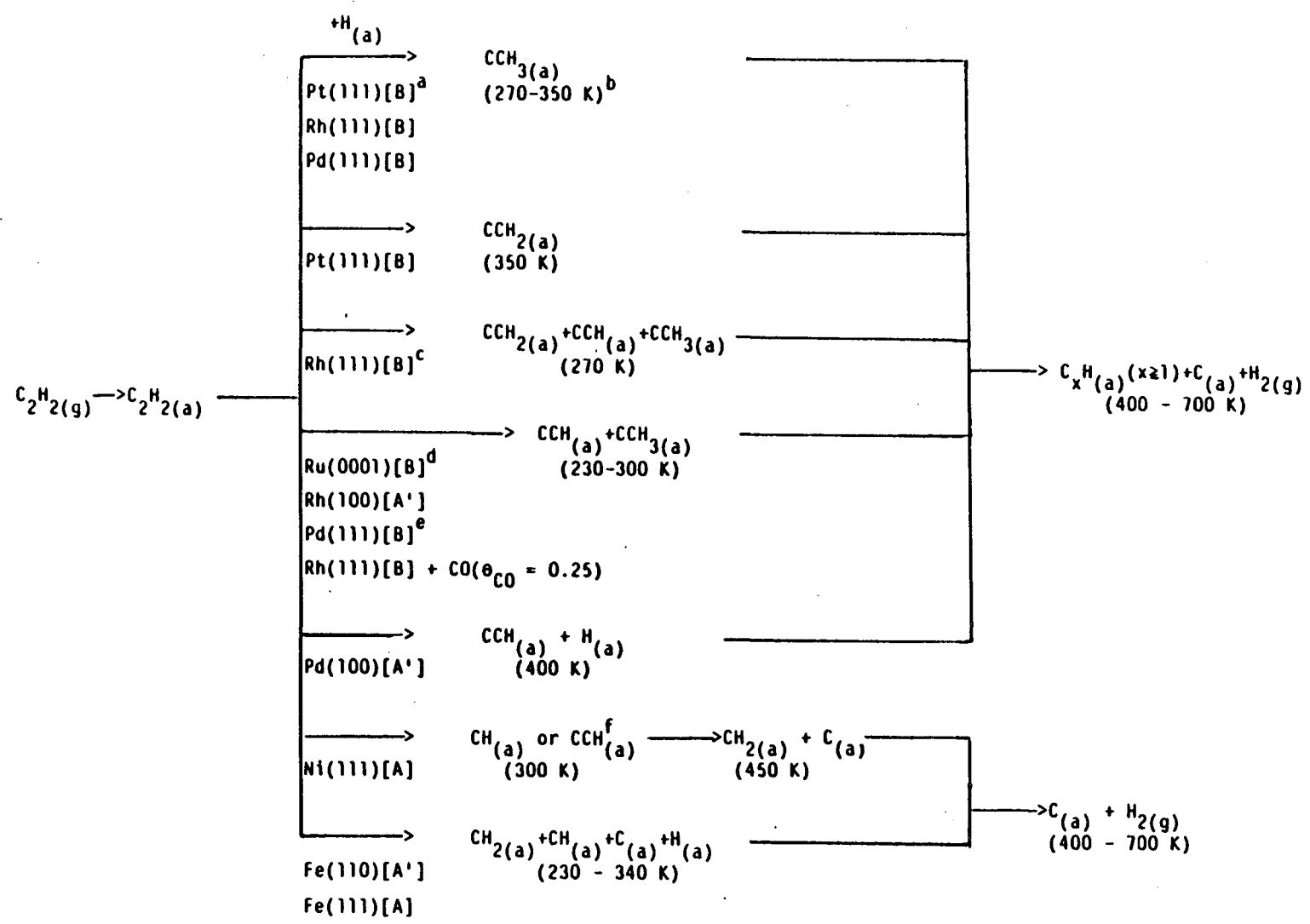
Fig. 8



XBL 876-3013

Fig. 9

Thermal Decomposition Pathways for Acetylene on Transition Metal Surfaces



XBL 876-2792 A

Fig. 10

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