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MOLECULAR ETHYLENE ADSORPTION ON RH(III) AND RH(100): ESTIMATION OF THE C-C STRETCHING FORCE CONSTANT FROM THE SURFACE VIBRATIONAL FREQUENCIES

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### Publication Date

1987

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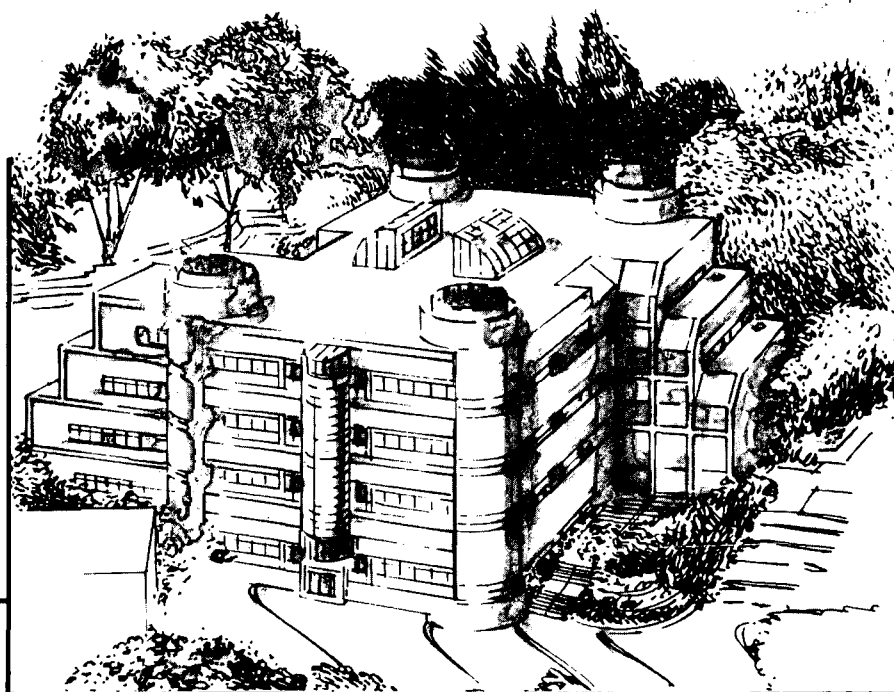
DOCUMENTS SECTION

Submitted to Journal of Physical Chemistry

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January 1987



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LBL-24240

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**Molecular Ethylene Adsorption on Rh(111) and Rh(100):  
Estimation of the C-C Stretching Force Constant  
From the Surface Vibrational Frequencies**

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## Abstract

Molecular ethylene adsorption on Rh(111) and Rh(100) between 90 and 200 K has been studied by thermal desorption spectroscopy (TDS), low-energy electron diffraction (LEED), and high-resolution electron energy loss spectroscopy (HREELS). The HREEL vibrational spectra for molecularly adsorbed ethylene on these surfaces are interpreted using the Dewar-Chat-Duncanson model for ethylene coordination to metal atom(s); gas phase ethylene and gauche 1,2- dibromoethane are used to model the coordination extremes. It is shown that the traditional  $\text{CH}_2$  functional group modes are coupled in adsorbed ethylene and do not adequately describe the normal modes of vibration. However, the C-C stretching force constant in adsorbed ethylene can be estimated from the deuterated ethylene vibrational frequencies, and a general correlation between deuterated vibrational frequency and adsorbed C-C force constant is proposed. Using this correlation together with empirical correlations between force constant and bond length derived for gas phase molecules, we estimate C-C bond orders of 1.5 and 1.2 for ethylene adsorbed on Rh(111) and Rh(100) respectively. These results indicate that on both surfaces chemisorbed ethylene is strongly distorted from its gas phase geometry.

## 1. Introduction

The low temperature bonding and chemistry of hydrocarbons on single crystal transition metal surfaces in ultra-high vacuum (UHV) may be particularly relevant for heterogeneous catalysis. At low temperatures, the possibility exists of isolating adsorbed reactants and catalytic intermediates that are unstable on clean metal surfaces in UHV at the actual catalytic reaction temperature. For example, on group 8-10 metal surfaces, alkenes and alkynes begin to decompose between 150 and 300K, while catalytic transformations of these molecules by these metals are typically carried out at 400 to 500K. It may also be possible to mimic, in UHV, catalytic hydrocarbon chemistry that is performed with high hydrogen pressures by studying the surface chemistry of hydrocarbons below the temperature at which surface hydrogen desorbs (usually about 300K).

In this paper we present low-energy electron diffraction (LEED), thermal desorption spectroscopy (TDS), and high-resolution electron energy loss spectroscopy (HREELS) results for molecular ethylene adsorption on Rh(111) and Rh(100). The thermal fragmentation of ethylene on Rh(111) has been discussed in several previous papers [1-7], and future papers will compare these results to recent studies on Rh(100) [8].

The low temperature bonding of ethylene has been previously studied on a number of different metals and different crystal faces. The molecular bonding of ethylene on surfaces is found (primarily by HREELS) to be highly sensitive to the type of metal, the surface geometry, and the presence of coadsorbates [9,10]. In all cases, the main interaction with the metal is through the electrons in C-C bond, causing the carbon atoms to rehybridize from  $sp^2$  towards  $sp^3$ . Sheppard has recently noted that the vibrational spectra for chemisorbed ethylene can be divided into three basic categories - type I, type I', and type II [9]. Type I spectra are typified by ethylene on Pt(111), where the spectra indicate strong distortion from gas phase bonding towards di- $\sigma$  bonding [11]. Type II spectra are typified by ethylene on Pd(110) where

$\pi$ -bonding and little distortion have been inferred from the small shift in the surface vibrational frequencies from their gas phase values [12]. The third type of spectra, type I', generally have vibrational frequencies between those for type I and type II and relative intensities different from both types I and II; no satisfactory structural model has been proposed for type I'. Surface crystallography is needed to substantiate and extend this correlation.

In the absence of surface crystallography, the surface vibrational spectra can provide information about the C-C bond in adsorbed ethylene. We show here, based on a detailed interpretation of HREEL spectra, that a general correlation may exist between the vibrational frequencies in the deuterated ethylene spectra and the C-C stretching force constant in adsorbed ethylene. Using this correlation and our HREELS results for Rh(111) and Rh(100), we estimate C-C stretching force constants of 7.7 and 5.3 mdyne/Å for ethylene adsorbed on Rh(111) and Rh(100) respectively. These carbon-carbon stretching force constants correspond to C-C bond orders of about 1.5 and 1.2 on Rh(111) and Rh(100) respectively.

## 2. Experimental

Experiments were performed in two UHV chambers with base pressures of  $1 \times 10^{-10}$  Torr. Each chamber is equipped with LEED, Auger electron spectroscopy (AES), a mass spectrometer for TDS, and a HREEL spectrometer. Both chambers have been previously described [13-15]. One Rh(100) and three Rh(111) single crystal samples were used. All four were  $0.5\text{-}1 \text{ cm}^2$  disks  $\sim 2$  mm thick, cut from a single crystal rod of  $>99.996\%$  purity obtained from the Materials Research Corporation. After polishing by standard methods [5], the crystals were mounted in UHV by spotwelding 0.5 mm Ta wire between the crystal edges and the manipulator. The crystals were heated to  $>1200\text{K}$  resistively and cooled to 77K by flowing liquid nitrogen through the manipulator [16]. The single crystal surfaces were cleaned by a combination of heating in oxygen, argon ion sputtering, and annealing in UHV until free of C, S, O, and B [17] as detected by AES, LEED, and HREELS.

Gases were adsorbed on the surfaces using microcapillary array dosers. 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 (the dosers are  $\sim 4$  and  $\sim 2$  cm from the crystal surfaces in the two chambers), but is uncorrected for differing ion gauge sensitivities of the gases. The term saturation coverage is used to mean the highest attainable surface coverage of ethylene at the adsorption temperature. Typically,  $>5$  L exposures gave saturation coverages of about one hydrocarbon per four surface Rh atoms. Gases were checked for purity by mass spectrometry and used as received from the following sources:  $C_2H_4$  (Matheson Cp, 99.5%),  $C_2D_4$  (MSD Isotopes, 99 atom %).

For TDS, both sides of the single crystal disk were cleaned and exposed to gases using the nozzle dosers. The crystal was heated at 10-30 K/sec with one side facing a UTI mass spectrometer with ionizer  $\sim 5$  cm from the surface. Multiple masses were recorded as a function of time and temperature using a Commodore PET 2001 computer interfaced to the mass spectrometer.

The HREEL spectrometers are similar to designs commonly used and consist of  $127^\circ$  cylindrical monochromator and analyzer sectors. In one of the spectrometers [14] the total scattering angle is fixed at  $120^\circ$ , so for specular HREELS,  $\Theta_{in} = \Theta_{out} = 60^\circ$  from the surface normal. The other HREEL spectrometer [15] has a rotatable analyzer and was 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 ( $40-60\text{ cm}^{-1}$ ,  $1\text{ meV} = 8.0655\text{ cm}^{-1}$ ) and with incident beam energies of 2-5 eV. HREEL spectra were recorded in the specular direction at temperatures between 77 and 90K.

### 3. Results and Discussion

The results are presented and discussed in three parts: LEED, TDS, and HREELS. In each section the Rh(111) data are presented first, followed by the Rh(100) data and a comparison to other surfaces. An appendix is included which discusses in more detail the assignment of the HREEL spectra for molecularly adsorbed ethylene.



### 3.1 Low-Energy Electron Diffraction (LEED)

Two LEED patterns can be formed by adsorption of ethylene at 90K on a clean Rh(111) surface. A 1.5 L exposure of ethylene produces a (2x2) LEED pattern, while a 4L exposure produces a  $(\sqrt{3}\times\sqrt{3})R30^\circ$  pattern. Intermediate exposures result in a superposition of these patterns. Both of these ordered overlayers are sensitive to electron bombardment, and they rapidly disorder under the microamp crystal currents above 100 eV used in the LEED experiments.

These ordered LEED structures are thermally stable from 90 to 200K. In this temperature range, TDS and HREELS indicate that adsorbed ethylene is molecularly intact on Rh(111). From packing arguments using van der Waals radii, it appears that the  $(\sqrt{3}\times\sqrt{3})R30^\circ$  structure has 1 ethylene molecule per unit cell, corresponding to a surface coverage of 1 ethylene molecule for every three surface Rh atoms ( $\Theta_{\text{ethylene}} = 0.33$ ). Since the (2x2) LEED structure forms for lower ethylene exposures, this structure must also have one ethylene per unit cell or a coverage of 0.25.

On Rh(100) no sharp LEED patterns were observed for ethylene adsorption between 90 and 200K. A diffuse (2x2) LEED pattern was obtained near saturation coverage, but small islands of some contaminant like water could not be ruled out as the cause of this pattern. Adsorption of residual water on clean Rh(100) at 90K was particularly a problem. Since adsorption was much slower on top of an ethylene monolayer, high surface coverages of ethylene were used to avoid contamination.

The other transition metal surfaces on which ethylene has been found to form ordered monolayers below 150K are Pt(111), where a (2x2) pattern has been reported [11], and Ni(110), where a complex pattern was reported [18]. No surface crystallography by LEED has been reported for these ordered overlayers, but an analysis of the LEED spot intensities for the (2x2) structure on Rh(111) below 100 eV is in progress.

### 3.2 Thermal Desorption Spectroscopy (TDS)

On Rh(111) the strongest evidence that ethylene adsorbs molecularly at 90K is that some ethylene molecularly desorbs above 100K. Molecular ethylene desorption spectra for several exposures of ethylene at 90K on Rh(111) are shown in Fig. 1. Two peaks are evident below 220K (the adsorption temperature in previous studies [1]), but the previously reported small peak at 375K is not observed (the broad, high temperature feature is due to desorption from the manipulator as it slowly warms up during the desorption experiment). For a 1.5 L exposure, which produces a sharp (2x2) LEED pattern, the peak at 215K is quite small, as indicated by the x10 expansion on this spectrum. This peak grows relative to that at 135K as the ethylene exposure is increased to form the saturation ( $\sqrt{3} \times \sqrt{3}$ )R30° LEED structure. The 135K peak can be attributed to ethylene desorption from the thin support wires and the 215K peak to desorption of the ethylene in excess of the (2x2) LEED structure from Rh(111). This means that 25% of the ethylene adsorbed at saturation coverage desorbs molecularly, while the remaining 75% decomposes.

On Rh(100), like Rh(111), most of the ethylene is irreversibly adsorbed and decomposes rather than desorbing molecularly. A small amount of molecular desorption is observed in a broad peak centered at 155K for high (10 L) exposures of ethylene. The broadness of this peak, however, suggests that it may be due to desorption from the manipulator or the Ta support wires rather than from the crystal.

Besides Rh(111), some molecular ethylene desorption has definitely been observed from Pt(111) [11, 19-21], Pd(111) [22], Pd(100) [23], Ru(001) [24], Ni(110) [18], Ni(100) [25], Cu(100) [26], Cu(111) [27], and Ag(100) [26] surfaces below room temperature. In general, the percentage of adsorbed ethylene that molecularly desorbs from transition metal surfaces increases as one moves to the right in the periodic table. Only 20% molecularly desorbs from Ru(001) [24], while 60% desorbs molecularly from Pt(111) [19-21], and 100% desorbs from Cu(111) [27]. On Pt(111), some ethane also desorbs from adsorbed ethylene monolayers at about 290K, slightly above the temperature at which molecular ethylene desorbs and at which the remaining

adsorbed ethylene begins to decompose [11,20]. Coadsorption of hydrogen with ethylene on Pt(111) increases the amount of ethane produced and lowers the desorption temperature to 250K [20]. While no ethane desorption is observed for ethylene adsorption on Rh(111), when 10 L of hydrogen are coadsorbed with 0.2 L of ethylene, a small fraction of the adsorbed ethylene can be hydrogenated and desorbed as ethane with a peak maximum at 230K.

### 3.3 High Resolution Electron Energy Loss Spectroscopy (HREELS)

In Fig. 2 the HREEL spectra of  $C_2H_4$  and  $C_2D_4$  ordered on Rh(111) at 90K in  $(\sqrt{3} \times \sqrt{3})R30^\circ$  LEED patterns are compared. These spectra are nearly identical to the spectra for the lower coverage (2x2) monolayers and are unchanged by annealing to just below the molecular ethylene desorption peak at 215K. This indicates that the 25% of the ethylene that desorbs molecularly has the same bonding as the 75% that decomposes. The relative intensities of the HREELS peaks appear most similar to those in spectra for molecularly adsorbed ethylene on Pd(100) [23], Ru(001) [24], and Fe(111) [28]. These spectra fit into Sheppard's type I' category.

HREEL spectra of ethylene at low temperature on Rh(100) were taken only at saturation coverage to avoid contamination. At less than saturation coverage, contaminant HREELS peaks were observed at 275, 455, 665, 940, and 1630  $cm^{-1}$ . While this (these) contaminant(s) was (were) not definitively identified, these peaks correspond closely to the vibrational frequencies for water adsorbed on Pt(111) [29]. The contaminant-free HREEL spectra for 4 L exposures of  $C_2H_4$  and  $C_2D_4$  on Rh(100) below 200K are shown in Fig. 3. Presumably ethylene is molecularly adsorbed at these temperatures.

The HREEL peaks in Fig. 3 for ethylene on Rh(100) are not nearly as sharp as those in Fig. 2 for molecular ethylene on Rh(111). The peak positions at 1420, 1475, 2905, and 3015  $cm^{-1}$  are approximate because of peak overlap, but the peak widths (3 times the instrumental resolution) justify the assignment as two peaks. In the deuterated ethylene spectrum of Fig. 3b, the feature at 1275  $cm^{-1}$  is quite weak, but reproducible.

It's relative intensity is larger in some spectra and appears to scale with the intensity of the  $2275\text{ cm}^{-1}$  peak. It is possible that this weak feature may result from some H,D-exchange by residual hydrogen atoms or from a small fraction of adsorbed  $\text{C}_2\text{D}_4$  bound near surface defects or contaminants.

The vibrational frequencies for ethylene adsorbed on Rh(111) and Rh(100) are very different from those of gas phase ethylene, indicating at least that the chemical bonding has changed substantially within the chemisorbed molecules. In the absence of ethylene complexes having similar vibrational frequencies, interpretation of the vibrational frequencies is facilitated by considering the general characteristics of ethylene coordination that have been determined by vibrational spectroscopy. The vibrational frequencies observed by HREELS for molecularly adsorbed  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$  are given in Tables 1 and 2. For all surfaces except Ni(100), the "carbon-carbon stretching" mode [ $1623(1515)\text{ cm}^{-1}$  for gas phase  $\text{C}_2\text{H}_4$  ( $\text{C}_2\text{D}_4$ )] is either not observed or is shifted to lower frequency after adsorption, suggesting that ethylene bonds to the metal surface through the electrons originally involved in the carbon-carbon double bond. This type of bonding can be described by the Dewar-Chat-Duncanson (DCD) [37] model originally proposed to explain ethylene coordination in organometallic complexes. In this model, as shown in Figs. 4a and 4b, the filled, ethylene  $\pi$  orbital donates electron density to an empty metal orbital, and the empty ethylene  $\pi^*$  orbital accepts electron density from filled metal orbitals. Both interactions increase the heat of adsorption of ethylene on the surface but weaken the carbon-carbon bond in ethylene. In valence bond terms, these donor and acceptor interactions between electrons in the surface and within ethylene rehybridize the ethylene carbon atoms to somewhere between  $\text{sp}^2$  (Fig. 4c) and  $\text{sp}^3$  (Fig. 4d).

This DCD coordination model for ethylene adsorption on transition metal surfaces has been implicitly assumed in previous interpretations of adsorbed molecular ethylene vibrational spectra. Based on this model, molecularly adsorbed ethylene vibrational spectra have been assigned using gas phase  $\text{C}_2\text{H}_4$  [30] and  $\text{C}_2\text{H}_4\text{Br}_2$  [36] as models for the  $\text{sp}^2$  and  $\text{sp}^3$  hybridization extremes in DCD coordination and interpolating between the vibrational frequencies of these model compounds. The interpolated

vibrational peaks have then been attributed to traditional  $\text{CH}_2$  functional group modes ( $\text{CH}_2$  scissor,  $\text{CH}_2$  wag, etc.). However, for rehybridizations midway between  $\text{sp}^2$  and  $\text{sp}^3$ , these functional group modes are inadequate descriptions of the actual normal modes of vibration which involve substantial motion of several functional group modes at once. This point is explicitly made in the appendix.

Assigning the vibrational spectra in terms of these functional group modes does not substantially increase our understanding of how ethylene bonds to transition metal surfaces. Such assignments can in fact lead to confusion. For example, the molecular ethylene vibrational spectra on Ru(001) [24] and Fe(111) [28] which are similar to the Rh(111) spectra have been given different assignments in terms of functional group modes, disguising the spectral similarities. In particular, the strong mode at 880-900  $\text{cm}^{-1}$  on these surfaces has been assigned to a  $\text{CH}_2$  twist on Ru(001) and to a  $\text{CH}_2$  wag on Fe(111). The different assignments merely reflect the inadequacy of functional group modes to describe the actual normal modes.

Useful information can, however, be extracted from the surface vibrational spectra about the bonding of molecular ethylene by explicitly considering how the normal modes of vibration should shift with rehybridization of the carbon-carbon bond. This issue has been previously discussed for organometallic complexes by Powell, et al. [39] and for surfaces by Stuve and Madix [10]; their discussions are elaborated upon and extended in the appendix. Our conclusion is that the  $\text{C}_2\text{D}_4$  vibrational spectra, where the coupling between the C-C stretching and  $\text{CD}_2$  bending motions is minimal, can be used to estimate the C-C stretching force constant,  $k_{\text{C-C}}$ , for adsorbed ethylene. The resulting correlation derived in the appendix is shown in Fig. 5. The correlation predicts that the observed vibrational frequency between 1100 and 1550  $\text{cm}^{-1}$  in the  $\text{C}_2\text{D}_4$  vibrational spectrum (there should be only one peak per type of adsorbed ethylene in this region) continuously decreases in frequency with rehybridization from  $\text{sp}^2$  to  $\text{sp}^3$ . This trend should be independent of adsorbed ethylene geometry as long as the C-C bond is approximately parallel to the surface, the C-H bonds point away from the surface, and both ends of the ethylene molecule are nearly equivalent. Under these conditions, carbon atom hybridization will be the major factor in determining the vibrational frequencies.

Since the observed vibrational frequency between 1100 and 1550  $\text{cm}^{-1}$  in the  $\text{C}_2\text{D}_4$  vibrational spectrum is proposed to decrease continuously with decreasing C-C force constant, this peak can be used as a measure of rehybridization. The closer the peak frequency to 1100  $\text{cm}^{-1}$ , the more rehybridized the C-C bond. Further, by estimating the C-C force constant for adsorbed ethylene using the correlation in Fig. 5, it may be possible to estimate C-C bond lengths and bond orders using empirical relations determined for gas phase molecules. The points for Zeise's salt, Pt(111), and Cu(100) in Fig. 5 were determined using such a correlation between C-C force constant and bond length known as Badger's rule [41]. In this case, the bond lengths measured by x-ray diffraction for Zeise's salt [46] and by NEXAFS for ethylene on Pt(111) [43] and Cu(100) [26] were used together with Badger's rule to predict the C-C force constant which was then plotted in Fig. 5 using the measured vibrational frequencies. The agreement of the Zeise's salt and Pt(111) points to the proposed correlation is good, suggesting that both the correlation in Fig. 5 and the application of Badger's rule to C-C bonds coordinated to metal atoms have some validity. The large discrepancy in the Cu(100) point, however, indicates either that these correlations are not generally applicable, or that the Cu(100) data are suspect.

Surface crystallography is needed to determine how reliably surface vibrational frequencies can be used to estimate adsorbed C-C bond lengths. Presuming that such gas phase correlations are applicable to surfaces, the vibrational frequency of 1300  $\text{cm}^{-1}$  in the deuterated ethylene spectrum on Rh(111) (Fig. 2) corresponds to a C-C force constant of 7.7  $\text{mdynes}/\text{\AA}$  (from Fig. 5) and to a C-C bond length of 1.39  $\text{\AA}$  (from Badger's rule). On Rh(100) there are two peaks in the 1100 - 1550  $\text{cm}^{-1}$  region suggesting two different types of ethylene bonding on the surface. The predominate peak at 1155  $\text{cm}^{-1}$  corresponds to a C-C force constant of 5.3  $\text{mdynes}/\text{\AA}$  and to a C-C bond length of 1.5  $\text{\AA}$ . While the bonding geometry of ethylene on Rh(111) and Rh(100) has not been determined, these results indicate that ethylene is substantially more rehybridized on Rh(100) than Rh(111) and that the bonding geometry on both surfaces is significantly distorted from that for gas phase ethylene.

In Table 3 we compare the Rh(111) and Rh(100) vibrational frequencies and estimated C-C force constants and bond orders to other surfaces where deuterated ethylene vibrational spectra have been reported. Results for Pd(111) and Ni(100) are not included, since the DCD coordination model for ethylene may not apply on these surfaces [47]. Also included in Table 3 are the  $\pi\sigma$  parameters previously proposed as measures of rehybridization in adsorbed ethylene. The relation between these parameters and the deuterated "C-C stretching" frequency used here to quantify rehybridization is discussed in the appendix. We note that based on the existing data in Table 3, there is no obvious correlation in the C-C stretching frequency determined by HEELS and (1) the position of the metal in the periodic table, (2) the lattice constant, (3) the types of high symmetry bonding sites on the surface, (4) the work function of the surface, (5) the metal-molecule stretching frequency, (6) the amount of molecular desorption, or (7) the subsequent thermal decomposition fragments. There may be a correlation with the molecular desorption temperature [26] or a correlation with some of the above parameters for a given row of the periodic table or as a function of crystal surface geometry for a given metal, but more data are needed to substantiate these trends. We recommend that the parameters mentioned above, along with the work function change after ethylene adsorption, be measured whenever possible and reported. Clearly, the molecular bonding of ethylene is a sensitive probe of the steric and electronic differences between transition metal surfaces.

#### 4. Conclusions

We find that ethylene is molecularly adsorbed on Rh(111) and Rh(100) between 90 and 200K. Two ordered LEED patterns, (2x2) and  $(\sqrt{3}\times\sqrt{3})R30^\circ$ , can be formed on Rh(111), while no sharp patterns were found on Rh(100). The HREEL vibrational spectra on Rh(111) and Rh(100) show that ethylene is strongly distorted from its gas phase geometry when molecularly chemisorbed on these surfaces. While these spectra cannot be definitively assigned, we have derived a correlation between the vibrational frequencies in the 1100 to 1550  $\text{cm}^{-1}$  of the  $\text{C}_2\text{D}_4$  spectra and C-C force constant

for ethylene coordinated in Dewar-Chat-Duncanson fashion. Using this correlation, we estimate C-C force constants of 7.7 and 5.3 mdynes/Å for adsorbed ethylene on Rh(111) and Rh(100) respectively. By empirical correlations, these force constants correspond to C-C bond orders of about 1.5 and 1.2 on Rh(111) and Rh(100).

## 5. Appendix

If the DCD coordination model is valid for ethylene adsorption on metal surfaces, then the surface vibrational frequencies should be determined mainly by the carbon atom hybridization. The vibrational frequencies cannot, however, be assigned by linearly interpolating between the functional group frequencies in  $C_2H_4$  and  $C_2H_4Br_2$  because the functional group modes do not accurately describe the actual normal modes of vibration for hybridizations midway between these extremes. The coupling of functional group modes that occurs for carbon atom hybridizations between  $sp^2$  and  $sp^3$  is illustrated in Fig. 6. Here an interpolation is made between the vibrational frequencies in gas phase ethylene and in gauche 1,2-dibromoethane as a function of C-C stretching force constant, a measure of rehybridization. The solid lines are approximations for the square root dependence of the vibrational frequencies on force constant. The dashed lines illustrate the kinds of couplings that can occur between modes having the same symmetry when ethylene is adsorbed on the surface [45]. In this case, the C-C stretch,  $CH_2$  scissor, and  $CH_2$  wag modes were coupled, since these modes are of the same symmetry type for  $C_{2v}$  adsorption symmetry. ( $C_{2v}$  adsorption symmetry is the highest possible symmetry for adsorbed ethylene; for lower adsorption symmetries, additional modes will be coupled.) The degree of coupling shown by the dashed curves has been arbitrarily chosen to avoid curve crossings. These mode couplings mean that the observed vibrational frequencies do not continuously increase or decrease as the carbon atoms rehybridize from  $sp^2$  to  $sp^3$ . Further, different functional group modes will couple depending on the adsorption symmetry. Thus, ethylene could bond with an identical C-C force constant but with different symmetry on two different surfaces, and the vibrational modes and frequencies would be different. It is not surprising, then, that the vibrational frequencies observed for ethylene adsorbed on transition metal surfaces (Table 1) show no uniform trends.



More information about ethylene bonding can be extracted from the deuterated spectra. Here, because of the isotope shift, the  $\text{CD}_2$  bending motions are substantially less coupled to the C-C stretching motion. This is evident in the vibrational correlation between  $\text{C}_2\text{D}_4$  and  $\text{C}_2\text{D}_4\text{Br}_2$  given in Fig. 7. The only substantial coupling with the C-C stretch is due to the  $\text{CD}_2$  scissors vibration. The approximated coupling between these modes given by the dashed line in Fig. 7 shows that, even with coupling, the observed normal mode frequency between 1100 and 1550  $\text{cm}^{-1}$  in the deuterated spectrum will probably continuously decrease in frequency with rehybridization towards  $\text{sp}^3$ . Further, this trend should be essentially independent of adsorption symmetry, since the symmetric  $\text{CD}_2$  scissor and C-C stretch modes will always have the same symmetry and other modes of similar symmetry are too low in frequency to couple significantly. Consequently, the type of correlation shown in Fig. 5 should hold for ethylene on all surfaces where the DCD coordination model is applicable. The accuracy of the correlation in Fig. 5 for surface-bound ethylene depends on (1) how well the symmetric  $\text{CD}_2$  scissor frequency in  $\text{C}_2\text{D}_4\text{Br}_2$  approximates the surface frequency for  $\text{sp}^3$  carbons in surface-bound ethylene and (2) how well the coupling between the scissors and stretch modes was chosen.

Extracting the degree of rehybridization in adsorbed ethylene from surface vibrational spectra has previously been discussed by Stuve and Madix [10]. They considered couplings between the C-C stretch and the  $\text{CH}_2$  ( $\text{CD}_2$ ) scissor vibrations and proposed a parameter called  $\pi\sigma$  as a measure of rehybridization. This parameter combines the percentage shift to lower frequency upon adsorption of both the gas phase C-C stretch and  $\text{CH}_2$ ( $\text{CD}_2$ ) scissor vibrations; the parameter is normalized to 0 for gas phase ethylene and 1 for 1,2-dibromoethane. One problem with this parameter is that the deuterated and hydrogenated versions do not always predict the same degrees of rehybridizations. These discrepancies probably occur because (1) in the hydrogenated case, couplings with other  $\text{CH}_2$  bending modes which may have a substantial effect as shown in Fig. 6 were not considered and (2) it is not always clear which peaks to use in calculating these parameters. We feel that the deuterated  $\pi\sigma$  parameter is the

more reliable of the two parameters and is comparable with our use here of the deuterated "C-C stretching" frequency. The advantage of using just the "C-C stretching" frequency along with the correlation in Fig. 5 is that choice of which spectral peaks to use is trivial, since this mode should be the only one with a vibrational frequency between 1100 and 1550  $\text{cm}^{-1}$  (Fig. 7).

More than one peak in the 1100 to 1550  $\text{cm}^{-1}$  region of the deuterated vibrational spectra suggests there is more than one bonding geometry for molecularly adsorbed ethylene, unless one or more of the peaks are overtone or combination bands. Indeed,  $\text{C}_2\text{D}_4$  adsorbed on most transition metal surfaces gives only one vibrational peak between 1100 and 1550  $\text{cm}^{-1}$  as can be seen from Table 2. Cu(100) [31], Pd(110) [12], and Rh(100) are the three exceptions. For Cu(100), the 1347  $\text{cm}^{-1}$  peak is almost certainly an overtone of the very intense 672  $\text{cm}^{-1}$  peak. On Pd(110), however, the two peaks at 1246 and 1371  $\text{cm}^{-1}$  have been interpreted as C-C stretches for two different types of molecular ethylene on the surface analogous to our interpretation of the Rh(100) results here. We should add that while multiple peaks in the 1100-1550  $\text{cm}^{-1}$  region are a good indicator for multiple ethylene bonding geometries on the surface, there may be cases where the C-C stretching vibration may be of sufficiently weak intensity as to be undetected.

### Acknowledgements

The experimental work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DEAC03-76F00098. We thank Profs. J.M. White, B.E. Koel, and E.M. Stuve for insightful comments on this work, and Dr. J. Stohr for a preprint of the Cu(100) NEXAFS results prior to publication. B.E. Bent gratefully acknowledges a National Science Foundation Fellowship, C.M. Mate gratefully acknowledges a scholarship from the American Vacuum Society, and A.J. Slavin gratefully acknowledges support from the Natural Sciences and Engineering Research Council of Canada.

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TABLE 1: VIBRATIONAL FREQUENCIES FOR C<sub>2</sub>H<sub>4</sub> MOLECULARLY ADSORBED ON TRANSITION METAL SURFACES

SURFACE	OBSERVED VIBRATIONAL FREQUENCIES (cm <sup>-1</sup> )											REF.			
Cu(100)					903				1290		1557		2992	31	
Pd(110)	270	350	530		906		1151	1243	1413	1520		3003	3074	12	
Pd(111)	256	341	533		911	1078	1145	1229	1418	1502	2780	2996		22	
Zeise's Salt	219	405	493		975					1234		1515	3031	3094	32
Pt(111)	355		530	645	905			1200		1485		3000	3080	This Work	
Ni(110)	420				850			1145		1435		2970		18	
Ni(100)	380		600	830	880		1100		1395	1560		2995		25,34	
Pd(100)	390				920			1135		1455		2980		23	
Ru(001)	460			775	900	1040		1145		1450		2985		24,38	
Fe(111)	385		580		886			1130		1410	2740	2950		28	
Ni(111)	440		610	740	880		1100	1200		1440		2970		33	
Fe(110)	410	480		720	915		1105	1250		1410		2960		35	
Rh(100)	325	395			905		1095	1195	1420	1475		2905	3015	This Work	
Pt(111)	470		660	790	980			1060		1430		2930	3000	11	

TABLE 2: VIBRATIONAL FREQUENCIES FOR C<sub>2</sub>D<sub>4</sub> MOLECULARLY ADSORBED ON TRANSITION METAL SURFACES

SURFACE	OBSERVED VIBRATIONAL FREQUENCIES (cm <sup>-1</sup> )										REF			
Cu(100)				672			952		1347	1420		2234	31	
Pd(110)	272	322	536	665			937	1035	1246	1371		2233	2319	12
Pd(111)	270	365		673		840	953	1058		1355		2246		22
Zeise's Salt	200	385	451	757			962	1059		1353		2224	2349	32
Rh(111)	365		590	675			950	1055		1300		2185	2280	This Work
Ni(110)		390		615			925			1235		2170	2290	18
Ni(100)		420	600	640			920			1230	1550		2260	25
Pd(100)		385		660			920			1220		2215		23
Ru(001)		420		700			900	1040		1210		2210	2295	24
Ni(111)		420	590	650			810			1200		2170	2280	33
Fe(110)		440	540	635	700		850			1160		2175		35
Rh(100)	325			660			945	990	1155	1275		2160	2275	This Work
Pt(111)		450		600	740		900			1150		2150	2250	11

Table 3: Estimated C-C force constants, bond lengths, and bond orders for ethylene molecularly adsorbed on transition metal surfaces. Estimations are based on the "C=C stretching" frequency in adsorbed  $C_2D_4$ , the correlation in Fig. 5, and empirical relationships. The  $\pi\sigma$  parameters previously proposed as a measure of rehybridization [10] are included for comparison.

Surface	$\nu_{CC}(C_2D_4)$ ( $cm^{-1}$ )	C-C Force Constant <sup>a</sup> (mdynes/Å)	C-C Bond Length <sup>b</sup> (Å)	C-C Bond Order <sup>c</sup>	$\pi\sigma$ Parameter <sup>d</sup> $C_2H_4(C_2D_4)$
$C_2H_4(g)$	1515	9.7	1.33	2.0	0(0)
Cu(100)	1420	8.7	1.35(1.44) <sup>f</sup>	1.66	0.21(0.27)
Pd(110) <sup>e</sup>	1371	8.3	1.37	1.61	0.38(0.38)
Zeise's Salt	1353	8.1	1.37(1.375) <sup>h</sup>	1.57	0.38(0.35)
Rh(111)	1300	7.7	1.39	1.52	0.50(0.47)
Ni(110)	1235	6.9	1.41	1.41	0.72(0.66)
Pd(100)	1220	6.7	1.42	1.38	0.78(0.70)
Ru(001)	1210	6.5	1.43	1.35	0.85(0.78)
Ni(111)	1200	6.3	1.44(1.39) <sup>g</sup>	1.33	0.80(1.04)
Fe(110)	1160	5.4	1.48	1.20	0.55(1.00)
Rh(100) <sup>e</sup>	1155	5.2	1.50	1.16	0.55(0.62)
Pt(111)	1150	5.0	1.51(1.49) <sup>g,i</sup>	1.13	0.92(0.88)
$C_2D_4Br_2(g)$	1141	4.5	1.54	1.0	1.00(0.78)

- a) Estimated using the correlation proposed in Fig. 5  
b) Estimated using the force constant and the empirical relation [40-42]:  $d_{cc} = 1.56(k_{cc})^{-.33} + 0.594$ .  
c) Estimated using the force constant and the empirical relation [40]:  $(k_{cc}/4.2)^{0.69}$ .  
d) Parameter defined in ref. 10; ranges from 0 for gas phase ethylene to 1 for 1,2-dibromoethane.  
e) Of the two types of adsorbed ethylene, only the majority species is tabulated here.  
f) Bond length from NEXAFS, ref. 26.  
g) Bond length estimated from UPS data, ref. 27.  
h) Bond length from x-ray crystallography.  
i) Bond length from NEXAFS, ref. 43.

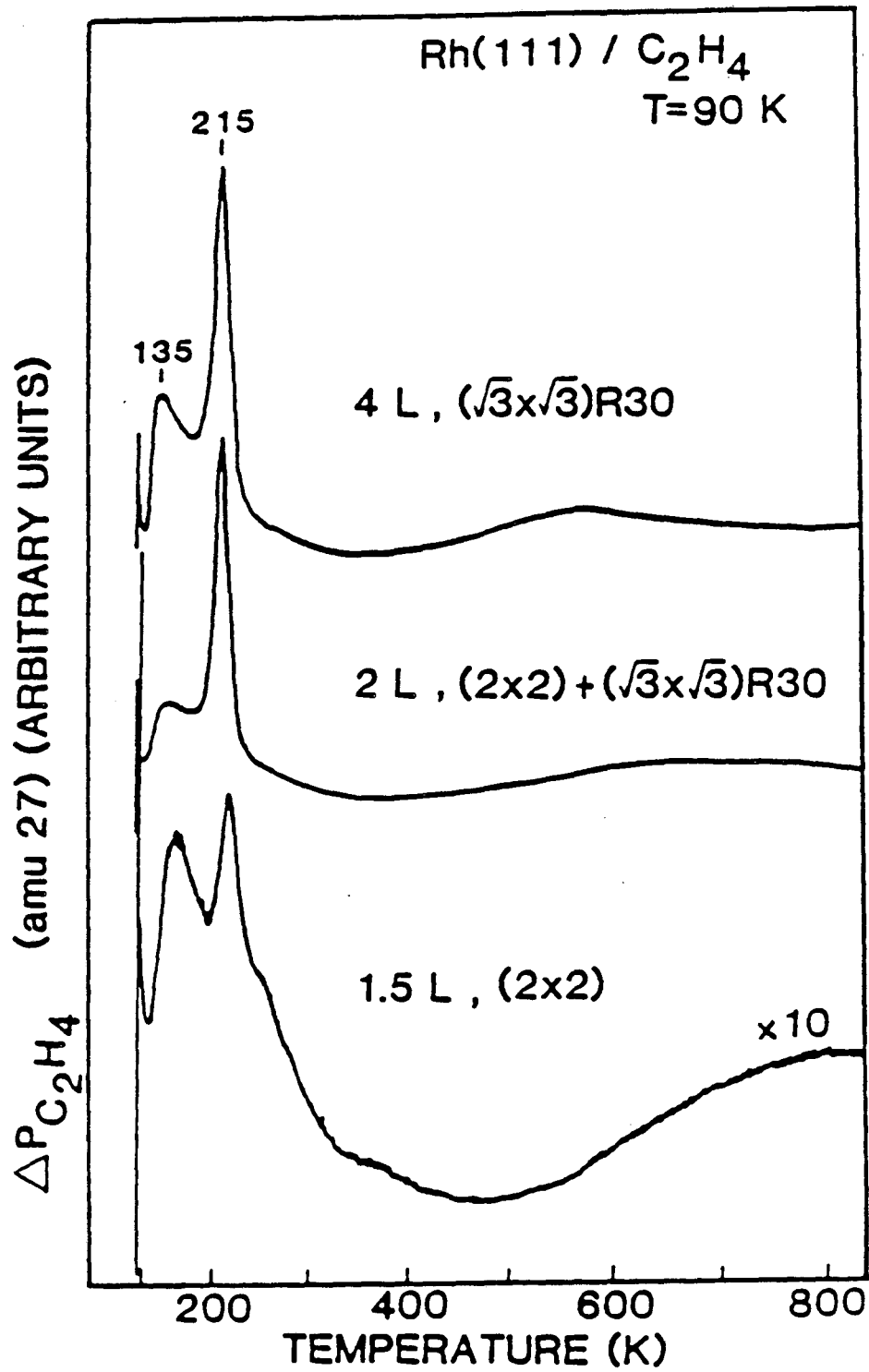


## Figure Captions

- Figure 1: Thermal desorption of molecular ethylene from Rh(111) after the indicated exposures at 90K. The heating rate was 25 K/sec. Molecular desorption at 215K is correlated with the formation of the  $(\sqrt{3}\times\sqrt{3})R30^\circ$  LEED pattern. Note that the 1.5 L spectrum is multiplied by a factor of 10.
- Figure 2: Specular HREEL vibrational spectra for saturation coverages of  $C_2H_4$  and  $C_2D_4$  on Rh(111) at 90K. Both overlayers were ordered in  $(\sqrt{3}\times\sqrt{3})R30^\circ$  LEED patterns.
- Figure 3: Specular HREEL vibrational spectra for saturation coverages of ethylene and deuterated ethylene adsorbed on Rh(100) at the indicated temperatures.
- Figure 4: The Dewar-Chat-Duncanson model of ethylene coordination to transition metal surfaces. Diagrams A and B show the interaction of the ethylene highest occupied ( $\pi$ ) and lowest unoccupied ( $\pi^*$ ) molecular orbitals with empty and filled metal surface orbitals respectively. Diagrams C and D depict, using valence bond formalism, the resulting extremes in bonding to the surface.
- Figure 5: Proposed correlation between the vibrational frequency between 1100 and 1550  $cm^{-1}$  for adsorbed  $C_2D_4$  and the C-C stretching force constant. The correlation is based on an interpolation between the C-C stretching frequency for gas phase deuterated ethylene and the  $CD_2$  scissors frequency for gauche 1,2-dibromoethane- $d_4$  as discussed in the appendix. The correlation is predicted to hold for surfaces where the Dewar-Chat-Duncanson model for ethylene coordination is applicable. The points for Zeise's salt, Pt(111), and Cu(100) were determined using measured vibrational frequencies and C-C bond lengths together with an empirical correlation between bond length and force constant as discussed in the text.

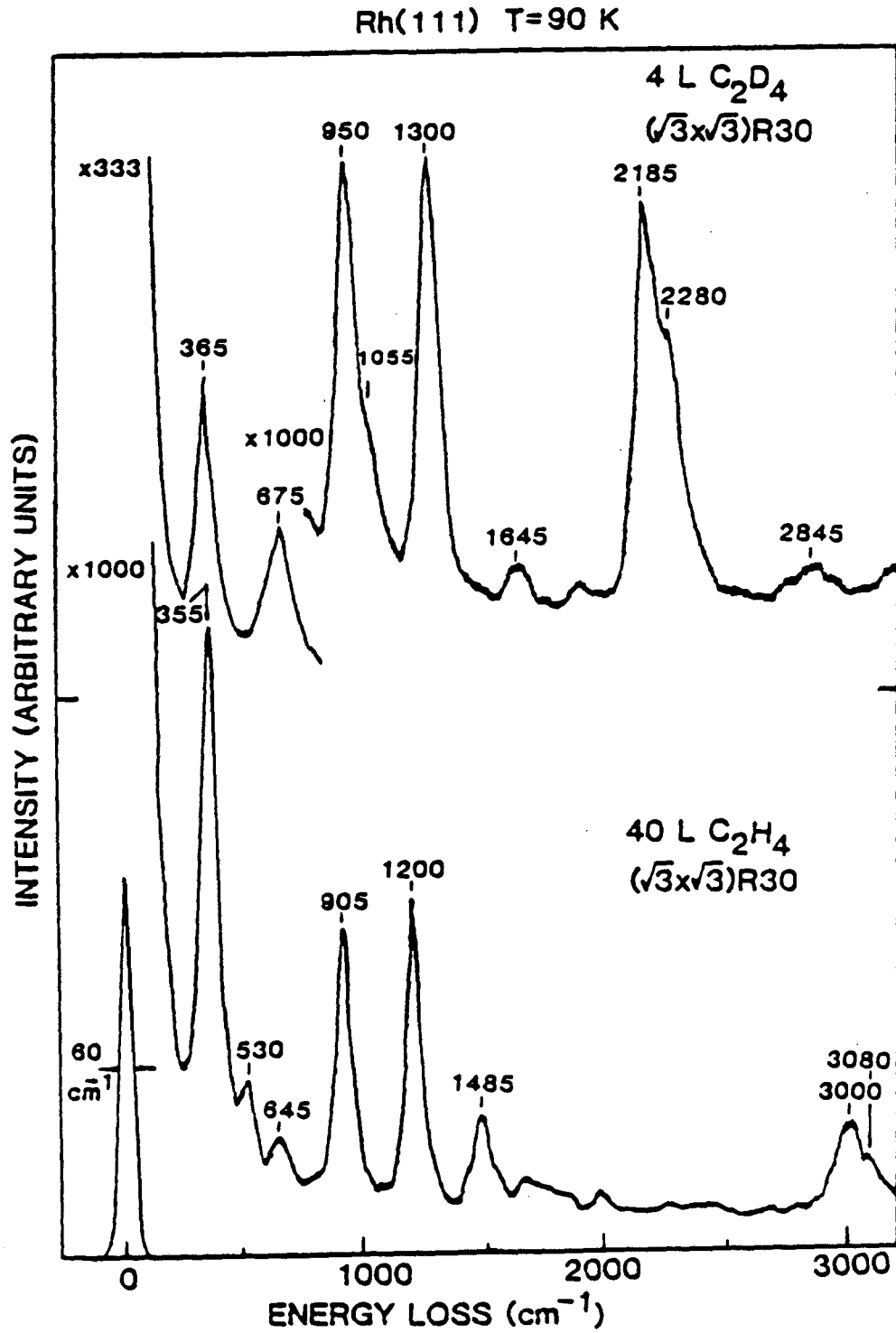
Figure 6: Correlation of the vibrational frequencies in ethylene [30] and gauche 1,2-dibromoethane [36] as a function of the C-C stretching force constant. The solid lines connect similar functional group modes in the two compounds. The dashed lines indicate the couplings that can occur between the various functional group modes.

Figure 7: Correlation (analogous to Fig. 6) of the vibrational frequencies in perdeuteroethylene and deuterated 1,2-dibromoethane. The dashed lines indicate coupling between the  $\nu_{CC}$ ,  $CD_2$  scissors, and  $CD_2$  wag modes, which is much less than in the hydrogenated case.



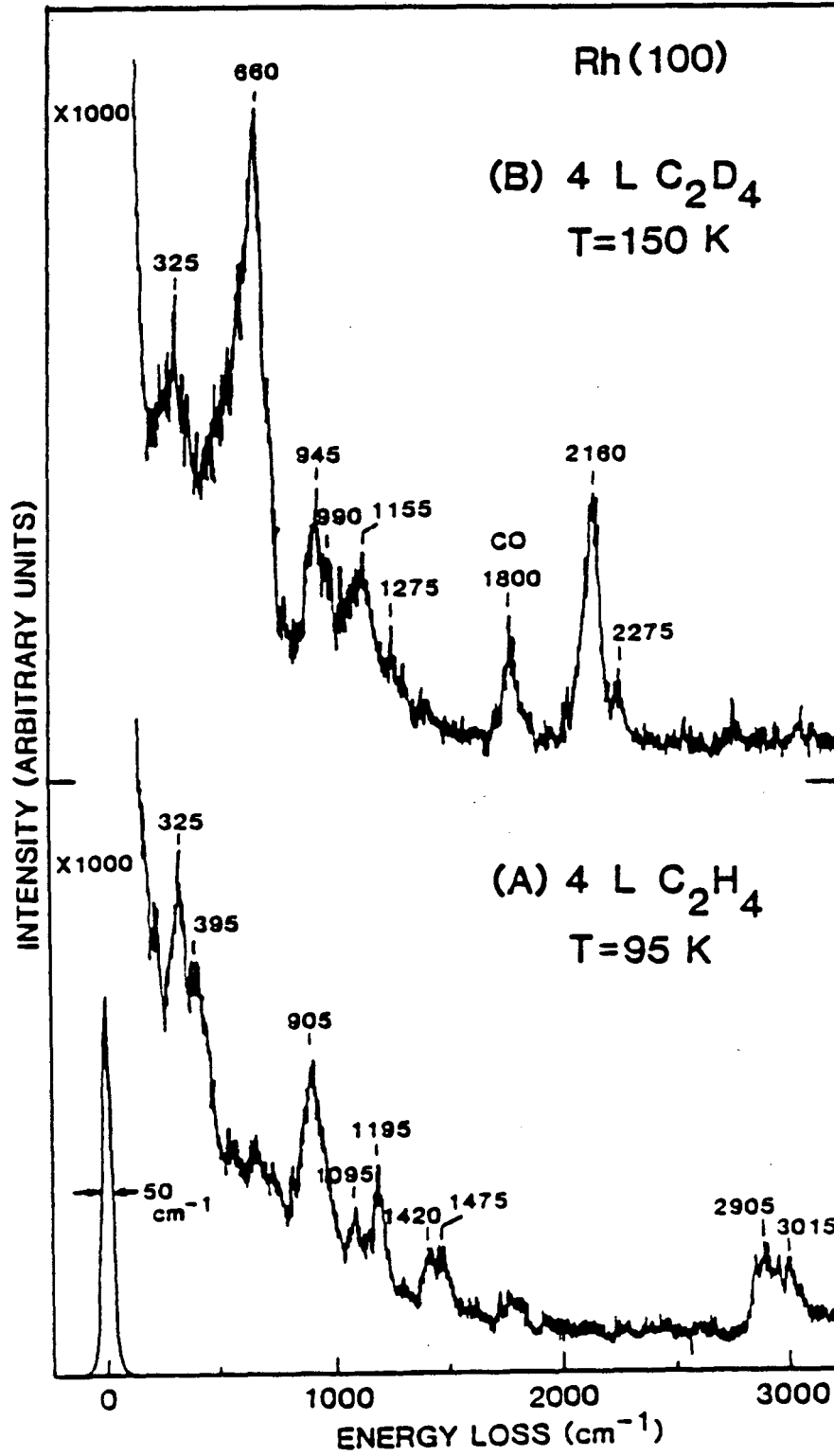
XBL 866-2425

Fig. 1



XBL 866-2422

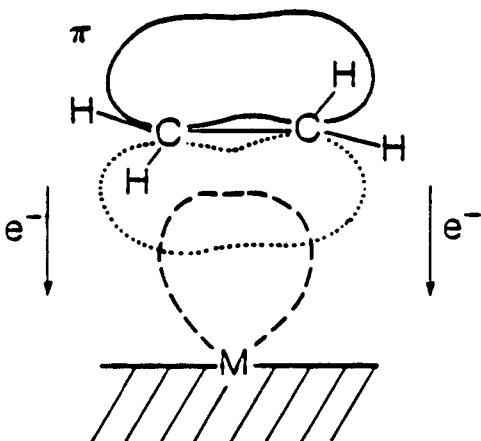
Fig. 2



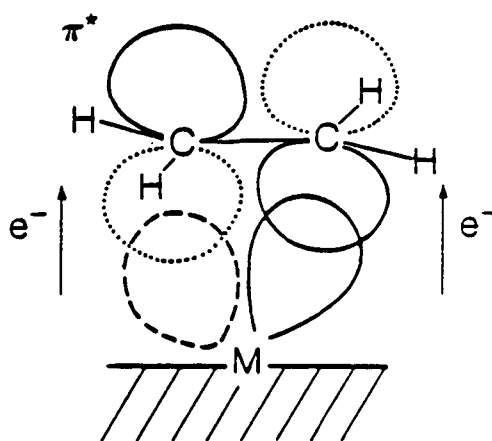
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Fig. 3

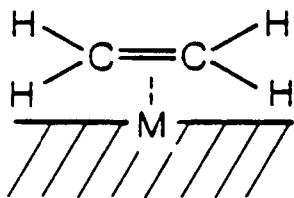
(A)



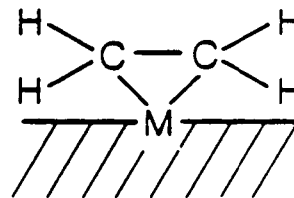
(B)



(C)



(D)

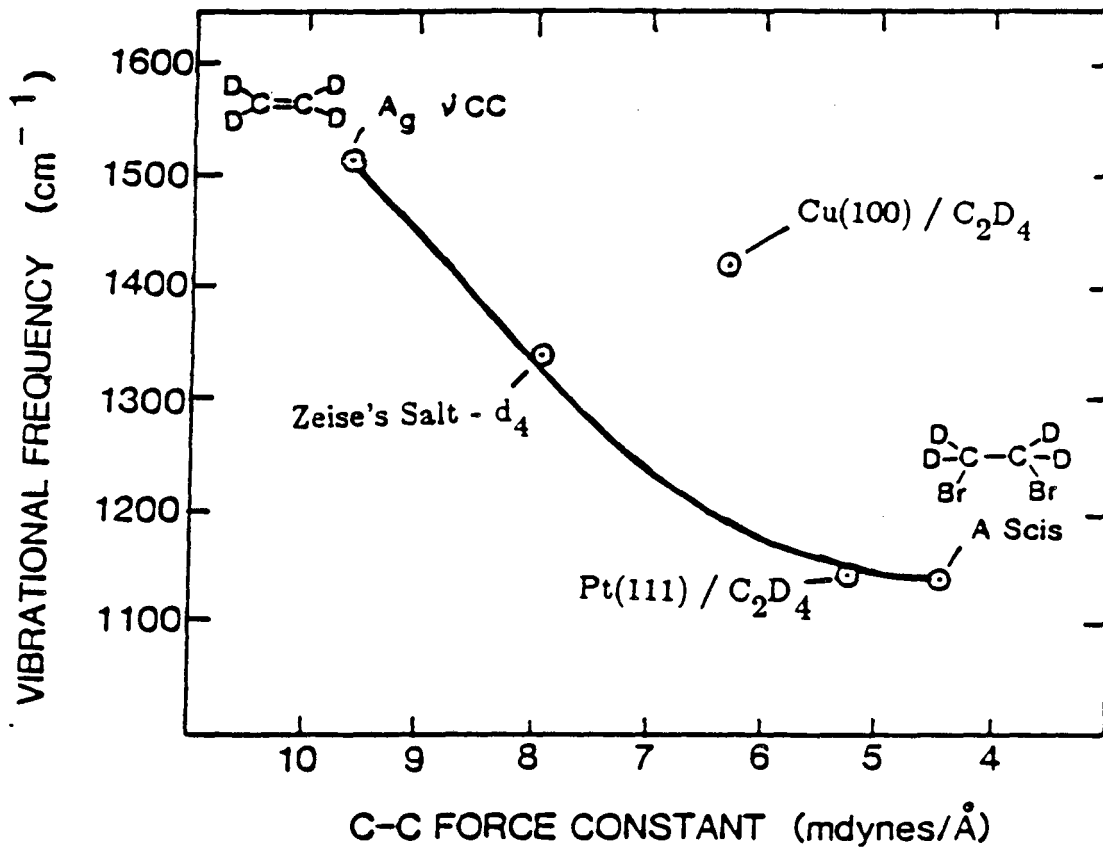


XBL 866-11177

Fig. 4

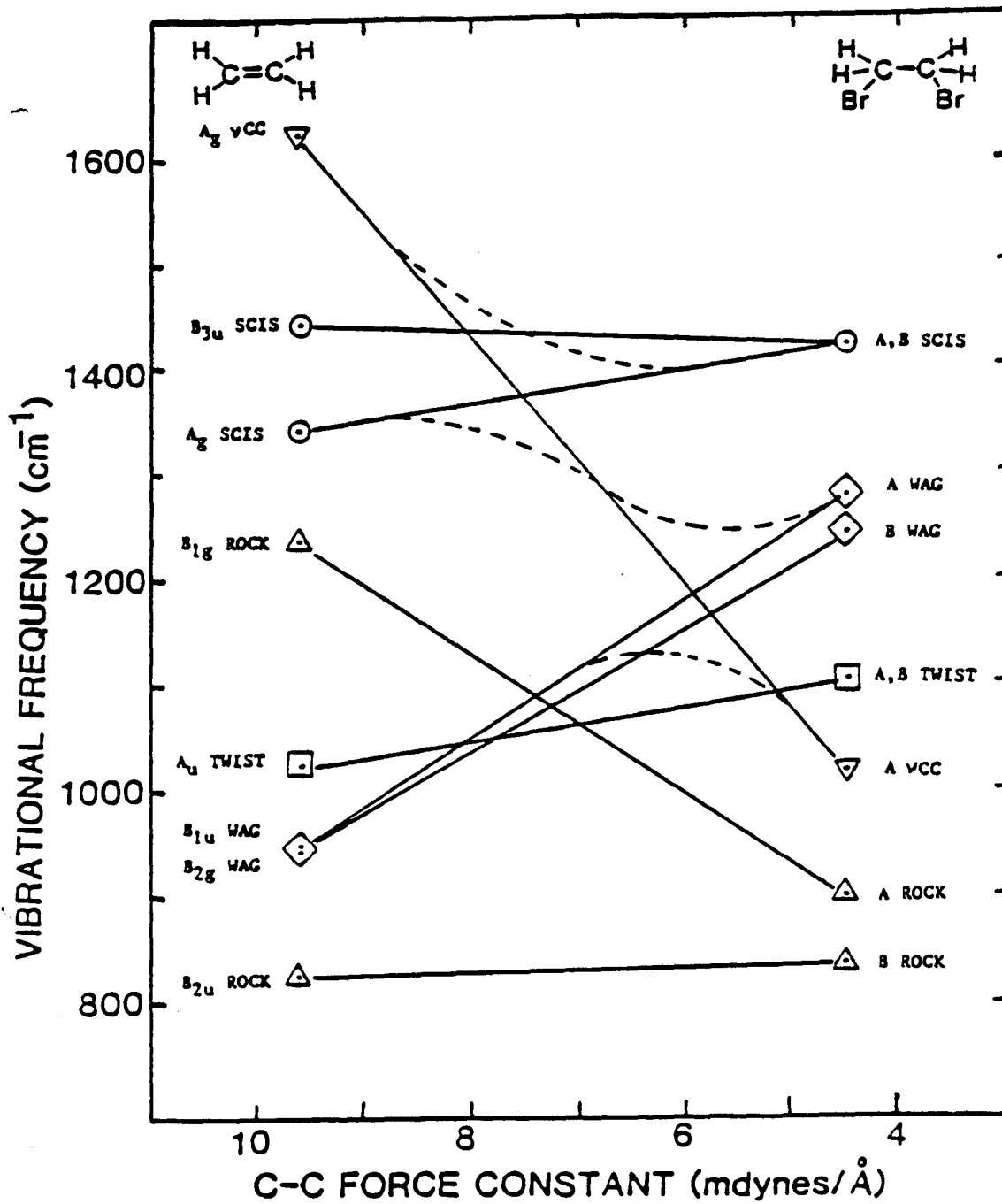
### Correlation of Adsorbed Ethylene-d<sub>4</sub>

#### Vibrational Frequencies with C-C Stretching Force Constant



XBL 868-3188 A

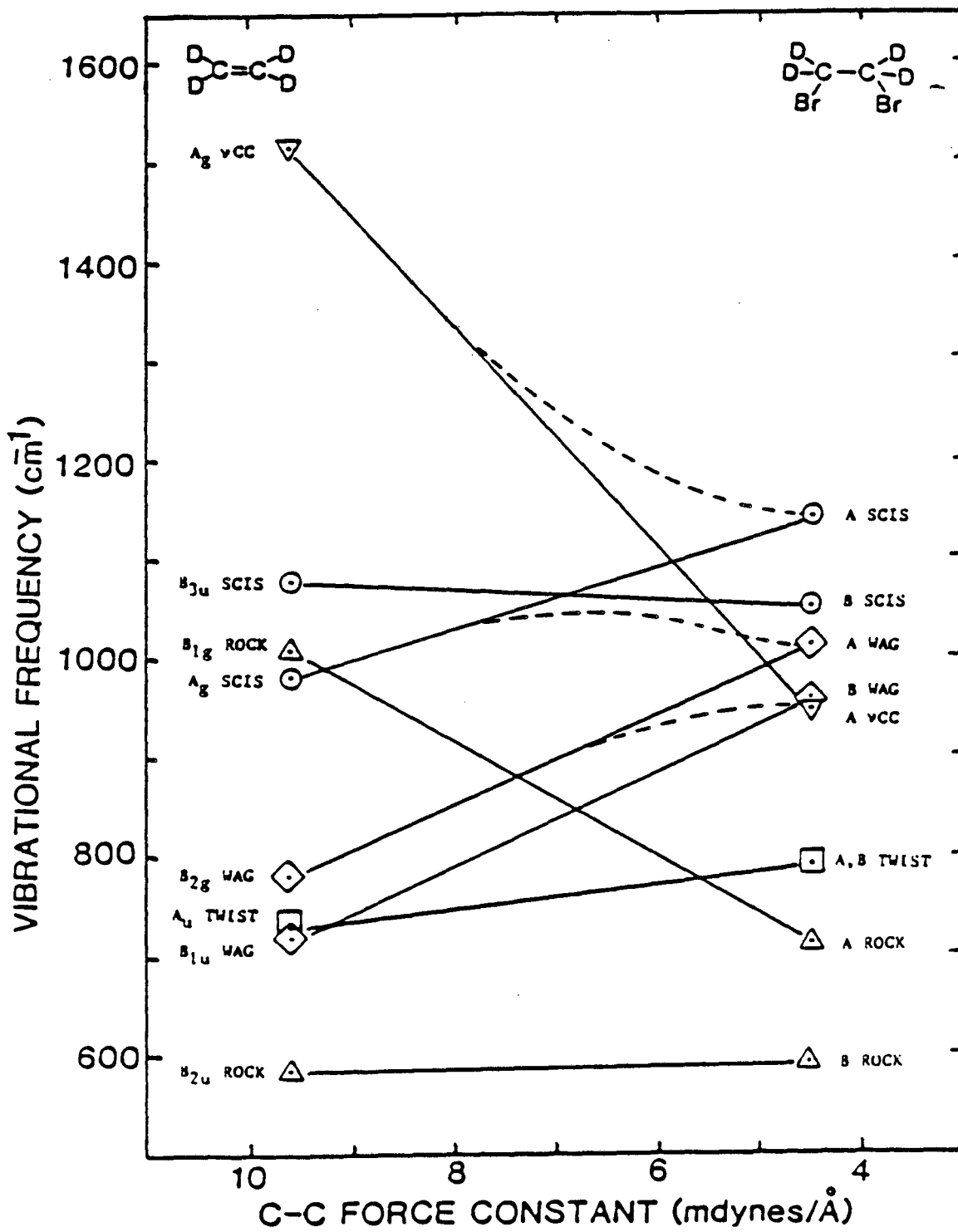
Fig. 5



XBL 866-2420

Fig. 6





XBL 866-2419 A

Fig. 7

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