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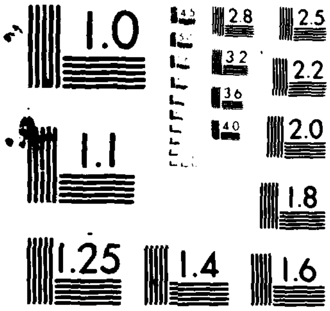

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Ethylene; chemisorption; palladium (111) surface; surface reaction; ethylidyne; vibrational spectroscopy; electron energy loss spectroscopy at high resolution.

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> The chemisorption and surface reactivity of ethylene on a palladium (111) surface near room temperature has been studied by high-resolution electron energy loss spectroscopy (EELS). The C_2H_4 molecule reacts with the Pd(111) surface to form a rather stable surface species which is identified as ethylidyne ($\geqslant$C-CH_3) by analysis of the EELS vibrational spectra. This molecule is also formed on Pt(111) and Rh(111) and is believed to be symmetrically bonded at threefold surface sites. Angle-dependent EELS spectra are reported and show the relative importance of impact and dipole excitation mechanisms.

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Block 20 (continued)

Off-specular data is found to be of critical importance in drawing conclusions about surface bonding symmetry from EELS spectra.

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TECHNICAL REPORT No. 2

ETHYLENE ADSORPTION AND REACTION ON Pd(111): AN ANGLE-DEPENDENT EELS ANALYSIS

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Submitted to Surface Science Letters

High-resolution electron energy loss spectroscopy (EELS) has proven in recent years to be a valuable method in surface science for identifying the nature of chemisorbed species by means of their vibrational spectra.[1] In this letter we report an EELS analysis of ethylene (C_2H_4) adsorption on a Pd(111) surface at room temperature. We find that the C_2H_4 molecule reacts with the Pd(111) surface to form a rather stable species which we identify as ethylidyne ($\geqslant$C-CH_3). The vibrational spectrum on Pd(111) closely resembles those reported earlier on Pt(111),[2] Pt(100)[3] and Rh(111),[4] indicating that the same hydrocarbon species is formed. However, several models have been proposed for the species on Pt(111) including ethylidene[2] ($>$CH-CH_3), ethylidyne[5] ($\geqslant$C-CH_3) and a multiply-bonded CH-CH_2 species.[6] This system has thus been controversial, although we believe most evidence supports the ethylidyne model, as was also concluded in a recent review.[7]

Our motivation for examining the adsorption of C_2H_4 on Pd(111) was first to explore possible similarities in the chemisorption to Pt, Rh, or Ni. Secondly, we wished to investigate the angular dependence of the EELS intensities as a method of identifying the character of the vibrational modes. As discussed below we find that this angular data lends further support to the ethylidyne model.

The experiments were carried out in an ion-pumped stainless-steel vacuum system (base pressure $\sim 10^{-10}$ Torr) equipped for EELS, low-energy electron diffraction (LEED), Auger spectroscopy, ion-sputtering and quadrupole mass spectrometry. The high-resolution EELS spectrometer has been described previously[8] and in these experiments was operated at a resolution (FWHM) of 80-100 cm^{-1}. The spectra were obtained by digital scanning and data acquisition with an LSI-11 microcomputer. The incident beam energy was 1.5 eV which gave an elastic beam count rate of $\sim 10^5$ Hz at the channeltron detector for specular reflection. Off-specular studies were performed by sample rotation. The Pd(111) sample was cut by spark erosion from a single crystal rod, polished down to 0.25 micron and oriented to within 0.5° by standard x-ray techniques. Surface cleanliness in vacuum was checked with Auger spectroscopy after removal of surface impurities (mainly carbon and sulfur) by 500 eV Ar^+ bombardment at elevated temperatures (~800K). Dosage of the sample to C_2H_4 was controlled with a precision leak valve, and gas exposures were corrected for ion-gauge sensitivity.

The energy loss spectrum for 10L exposure of Pd(111) to C_2H_4 at 300K is shown in Fig. 1 for specular reflection. Reproducible features attributed to the hydrocarbon phase occur at 409, 914, 1080, 1334 and 2900 cm^{-1} whereas the loss at 1808 cm^{-1} is due to residual CO adsorption. The CO coverage here is less than ~0.1 monolayer but the peak appears relatively large due to the large dynamic dipole moment of CO. We note both the high magnification and low spectral background which are necessary to study the rather weak hydrocarbon losses even though the hydrocarbon coverage is estimated to be ~0.25 monolayer. The background is quite low here except for a small, broad peak which underlies the 914 and 1080 cm^{-1} losses in Fig. 1. This background peak has no serious consequences here and has recently been eliminated by spectrometer adjustments.

The spectrum shown in Fig. 1 for specular reflection is very similar to those obtained for C_2H_4 adsorption on Pt(111), Pt(100) and Rh(111) near room temperature, both in terms of peak positions and relative intensities. Table 1 compares the reported peak positions for the (111) surfaces of these metals. Although there can be little doubt that the same hydrocarbon species is formed, its correct identification with EELS involves detailed vibrational mode assignments and comparison to vibrational spectra of model compounds.

In order to aid in this assignment for Pd(111) we investigated the angular dependence of the loss features. Those modes which are principallly excited by a long-range dipole mechanism should scatter predominantly in the specular direction. This mechanism leads to the well-known "dipole selection rule".[9] Modes which are excited by short range "impact" scattering are expected to exhibit much broader angular behavior.[10] In Figs. 2-3 we show non-specular data for 10° and 20° off specular. The same loss peaks are observed, but marked changes in relative intensities occur. The most striking feature is that the peak near 2900 cm^{-1} in the CH stretching region in the most prominent loss feature in the 20° data although this peak is relatively weak in the specular data. We note that this peak is always very broad (~200 cm^{-1}), indicating two overlapping vibrational modes. The center of this loss feature also shifts from 2900 to 2946 cm^{-1} as the angle increases, whereas no significant shifts were detected for the other loss peaks within experimental error (~10 cm^{-1}). This suggests that the higher energy component of the broad 2900 cm^{-1} peak is increasing in intensity relative to the lower energy component.

A summary of the overall angular dependence of the modes is given in Fig. 4. Fine structure for small angular changes has not been examined. We note that the 2900 cm^{-1} peak has essentially no angular variation within experimental error. We, therefore, attribute the excitation mechanism to impact scattering. The modes at 1080 cm^{-1} and 1334 cm^{-1}, however, decay with angle from specular in a manner similar to the elastic beam although not quite as rapidly. We identify these modes as predominantly dipole excited. The situation for the 914 cm^{-1} peak is less conclusive. It appears, however, to derive much of its intensity from an impact mechanism. Angular analysis of the CO loss at 1808 cm^{-1} also shows dipole behavior very similar to the losses at 1080 cm^{-1} and 1334 cm^{-1} as would be anticipated for the CO stretching vibration. However, residual impact contributions to the CO loss are also apparent.

The angular data discussed in connection with Fig. 4 is further described in Table 2. This table shows the percentage variation in intensity of the primary hydrocarbon modes with angle from specular. Under the present experimental conditions of a relatively broad elastic beam ($\simeq 10^\circ$ FWHM), theory predicts the dipole-enhanced modes to closely mimick the angular behavior of the elastic beam for small angles from specular. As shown in Table 2 this behavior is borne out for the 1080 cm^{-1} and 1334 cm^{-1} modes at 10° from specular. Very different angular behavior is seen for the 914 cm^{-1} and 2900 cm^{-1} losses, indicative of an impact scattering mechanism.

On the basis of the above data one may best assign the vibrational spectrum to a $\geqslant C{-}CH_3$ species bonded in a threefold surface site and oriented perpendicular to the surface. This species (shown in Fig. 5) was first proposed by Kesmodel, Dubois and Somorjai[5] for the Pt(111) system on the basis of LEED intensity analysis. These authors also suggested an analogy between the metal surface system and the bonding of $\geqslant C{-}CH_3$ in the trinuclear metal clusters $CH_3CCo_3(CO)_9$ and $CH_3CRu_3(CO)_9H_3$. This analogy was supported by the bonding geometry and the close similarities of the vibrational spectra.[5] Recently, an important refinement of the infrared data for the cobalt cluster has been made by Sheppard and co-workers,[11] who present both infrared measurements as well as a complete normal-coordinate analysis. We compare in Table 3 the present EELS data to their infrared assignments. For the C_{3v} symmetry of the $\geqslant C{-}CH_3$ model only the A_1 symmetry modes should be dipole enhanced. Therefore, according to the angular EELS analysis the 409, 1080 and 1334 cm^{-1} modes would be of A_1 symmetry. The broad 2900 cm^{-1} peak which is impact excited consists of both an A_1 and E symmetry ν-CH_3 modes. A weak shoulder (cf. Fig. 1) near 1400 cm^{-1} which is repeatedly seen on the 1334 cm^{-1} peak (also observed for Pt and Rh) is attributed to the E-symmetry assymmetric methyl deformation. We do not observe the assymmetric C-Pd stretch for the surface species. This completes the vibrational assignments except for the 914 cm^{-1} loss. As noted by Skinner et al.[11] this loss frequency seems too low to assign to the ρ-CH_3 mode which occurs at 1004 cm^{-1} in the Co compound. There is also recent evidence from work on Pt(111)[7] that the 900 cm^{-1} mode is not an essential feature of the surface species but may rather be due to partial decomposition. Indeed, Skinner et al. suggest that this mode is associated with chemisorbed atomic hydrogen whose bonding geometry is directly correlated with the parent ethylidyne group. Such surface hydrogen is, of course, a natural product in the conversion of ethylene to ethylidyne. This explanation is difficult to test directly but it does explain the presence of the corresponding 880 cm^{-1} loss for the species in well-ordered overlayers (as confirmed by LEED) on Rh(111).[4] Preservation of long-range order with decomposition to significant amounts of other surface species (which could cause the 880 cm^{-1} loss) seems unlikely.

Baró and Ibach[12] have recently reported an off-specular analysis of the surface species on Pt(111). They find several aspects in agreement with those reported here. Namely, they observe that the two most prominent losses (1130 cm^{-1}, 1360 cm^{-1}) are dipole enhanced and that the center of the ν-CH_3 loss shifts from 2900 cm^{-1} (0°) to 2940 cm^{-1} (14°) with angle from specular. However, they also report a loss at 1010 cm^{-1}, attributable to ρ-CH_3, which we have not observed on Pd(111). These authors also have not described both ν-CH_3 modes in the 2900 cm^{-1} region in terms of impact scattering. These differences, however, may be due to the different beam energies of 1.5 eV and 6.0 eV used for Pd and Pt, respectively.

In summary, we conclude that C_2H_4 adsorption on Pd(111) near room temperature leads to the formation of the same ethylidyne species observed on Pt(111), Rh(111) and Pt(100). However, we modify the earlier vibrational assignments of Kesmodel <u>et al</u>.[5] to the extent that the loss at 1130 cm^{-1} (on Pt) is now attributed to the ν-CC mode rather than the ρ-CH_3 mode. This change is necessary to agree with the angular dependence of our EELS data as well as the new infrared assignments of Skinner <u>et al</u>. for the $CH_3CCo_3(CO)_9$ compound.

We also emphasize the importance of non-specular EELS data. In particular we find that some modes observed on specular may be largely impact excited.[13] Thus, extreme caution should be exercised in the application of the "dipole selection rule" which has been used freely by some researchers to extract structural information on adsorbate systems.

This work was supported by the Office of Naval Research.

Table 1. Vibrational frequencies (cm^{-1}) for the stable hydrocarbon species formed from C_2H_4 adsorption on the (111) surfaces of Pd, Pt and Rh (T~300K).

Pd(111)[a]	Pt(111)[b]	Rh(111)[c]
2900[d]	3025-3105 2900-2940	3000 2900
~1400[e]	1420[e]	shoulder
1334	1350-1360	1350
1080	1130	1130
914	900	880
409	435	450

[a] Data of present work.

[b] EELS data of Ref. 2.

[c] EELS data of Ref. 4.

[d] Broad peak (~200 cm^{-1} FWHM)

[e] Weak shoulder.

Table 2. Comparison of measured relative intensities in percent of the specular intensity for each of the primary energy loss peaks at $\theta = 10°$ and $20°$. Values in parentheses are estimated errors.

Energy Loss (cm^{-1})	Angle from Specular	
	10°	20°
Elastic+(0)	13 (1) %	3 (1) %
914	45 (8)	37 (10)
1080	14 (3)	7 (3)
1334	16 (2)	9 (2)
2900	84 (17)	120 (20)

+Angular width of the elastic beam in these measurements was approximately 10°(FWHM).

Table 3. Comparision of frequencies (cm^{-1}) for the surface species on Pd(111) with those of the ethylidyne cluster compound.

Surface Species[a]	Assignment	$CH_3CCo_3(CO)_9$[b]
2900 (broad, I)	$\left\{\begin{array}{l}\nu_{as}\ CH_3\\ \nu_s\ CH_3\end{array}\right.$	2930 E 2888 A_1
~1400 (shoulder)	$\delta_{as}CH_3$	1420 E
1334 (DE)	$\delta_s CH_3$	1356 A_1
1080 (DE)	ν_{cc}	1163 A_1
--------	ρCH_3	1004 E
914 (I?)	(see text)	--------
--------	$\nu_{as}MC$	555 E
409 (DE)	ν_s MC	401 A_1

[a] EELS data of present work: I=impact excited, DE=dipole enhanced.

[b] Infrared analysis of Ref. 11.

References

1. See, e.g., R.F. Willis, A.A. Lucas and G.D. Mahan in The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, ed. D.A. King and D.P. Woodruff. (Elsevier, Holland).

2. H. Ibach and S. Lehwald, J. Vac. Sci. Technol. 15, 407 (1978).

3. H. Ibach, Proceedings Conference on Vibrations in Adsorbed Layers (Jülich, Germany, June, 1978).

4. L.H. Dubois, D.G. Castner and G.A. Somorjai, J. Chem. Phys. 72, 5234 (1980).

5. L.L. Kesmodel, L.H. Dubois and G.A. Somorjai, Chem. Phys. Lett. 56, 267 (1978); J. Chem. Phys. 70, 2180 (1979).

6. J.E. Demuth, Surface Sci. 80, 367 (1979); 93, L82 (1980).

7. H. Ibach (to be published).

8. L.L. Kesmodel, J.A. Gates and Y.W. Chung, Phys. Rev. B 23, 489 (1981).

9. See, for example, Ref. 1 and references therein.

10. Such close range impact excitations of adsorbates may be analogous to those in the gas phase. Such excitations have been reviewed by G.J. Schulz in Principles of Laser Plasmas, ed. G. Bekefi (Wiley, New York, 1976).

11. P. Skinner, M.W. Howard, I.A. Oxton, S.F.A. Kettle, D.B. Powell and N. Sheppard (to be published).

12. A.M. Baró and H. Ibach (to be published).

13. On-specular impact excitations have also been reported for NH_3 on Pt(111) by B.A. Sexton and G.E. Mitchell, Surface Sci. 99, 539 (1980).

Figure Captions

Fig. 1 Energy loss spectrum for the hydrocarbon surface species on Pd(111) for specular scattering. The incident beam energy is 1.5 eV at an angle of 60° from the surface normal.

Fig. 2 Off-specular energy loss spectrum obtained by rotating the sample by 5° about an axis perpendicular to the plane of electron beam incidence.

Fig. 3 Same as in Fig. 2 except the sample is rotated by 10°.

Fig. 4 Semi-log plot of the angular dependence of the elastic beam and energy loss peaks for the hydrocarbon surface species. The angle $\Delta\theta$ is the angle from specular and is twice the angular rotation given in Figs. 2-3. The elastic beam is scaled by 0.01, the 914 cm^{-1} loss by 0.33 and the 2900 cm^{-1} loss by 0.10 for clarity.

Fig. 5 Bonding structure for the ethylidyne species (Ref. 5) originally proposed for Pt(111) surface.

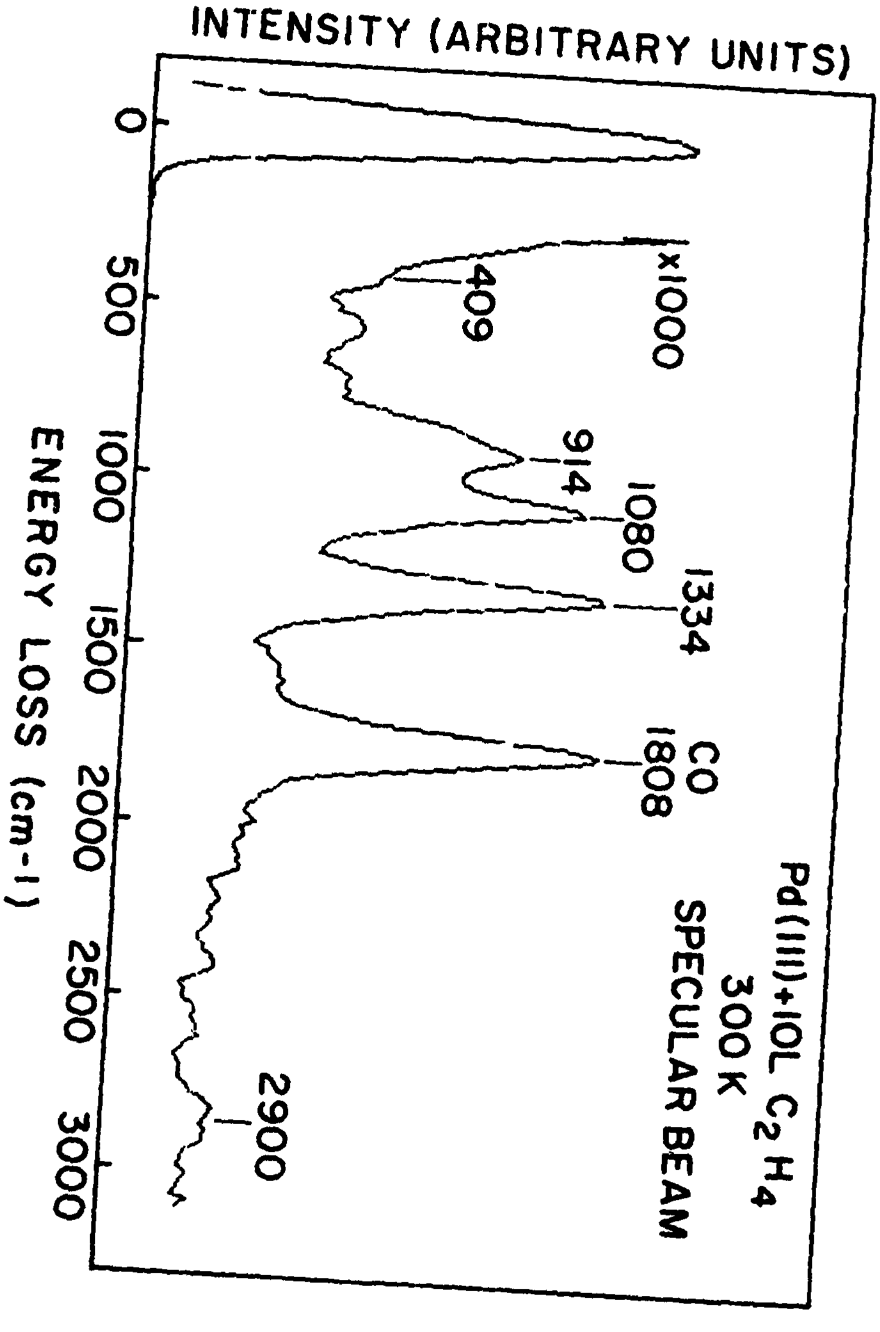
INTENSITY (ARBITRARY UNITS)
ENERGY LOSS (cm-1)
0
500
1000
1500
2000
2500
3000
x1000
409
914
1080
1334
CO
1808
2900
Pd(111)+10L C_2H_4
300 K
SPECULAR BEAM

FIG. 1

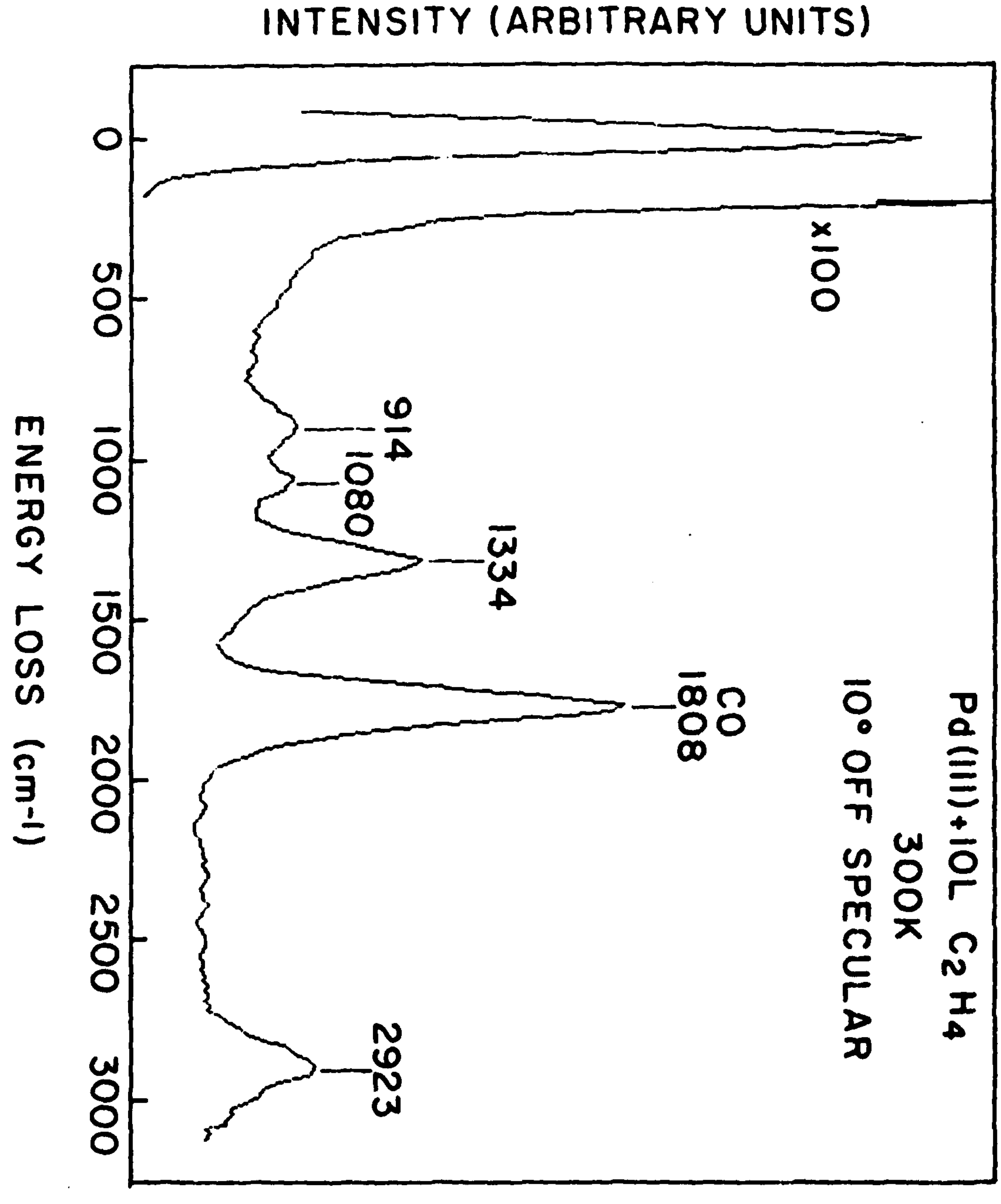
INTENSITY (ARBITRARY UNITS)
Pd(111)+10L C_2H_4
300K
10° OFF SPECULAR
x100
914
1080
1334
CO
1808
2923
0
500
1000
1500
2000
2500
3000
ENERGY LOSS (cm-1)

FIG. 2

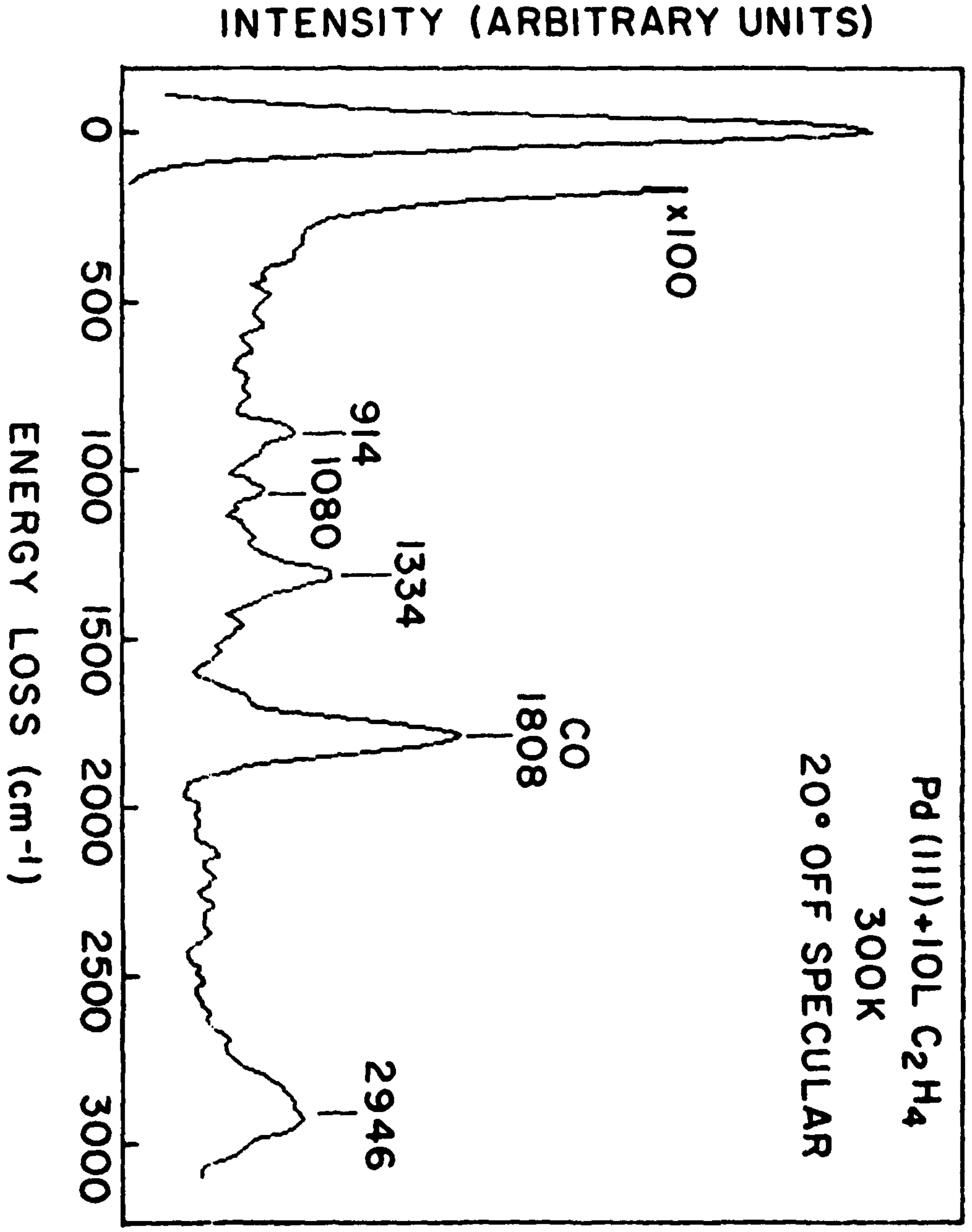
INTENSITY (ARBITRARY UNITS)
Pd(111)+10L C_2H_4
300K
20° OFF SPECULAR
×100
914
1080
1334
CO
1808
2946
0
500
1000
1500
2000
2500
3000
ENERGY LOSS (cm^{-1})

FIG. 3

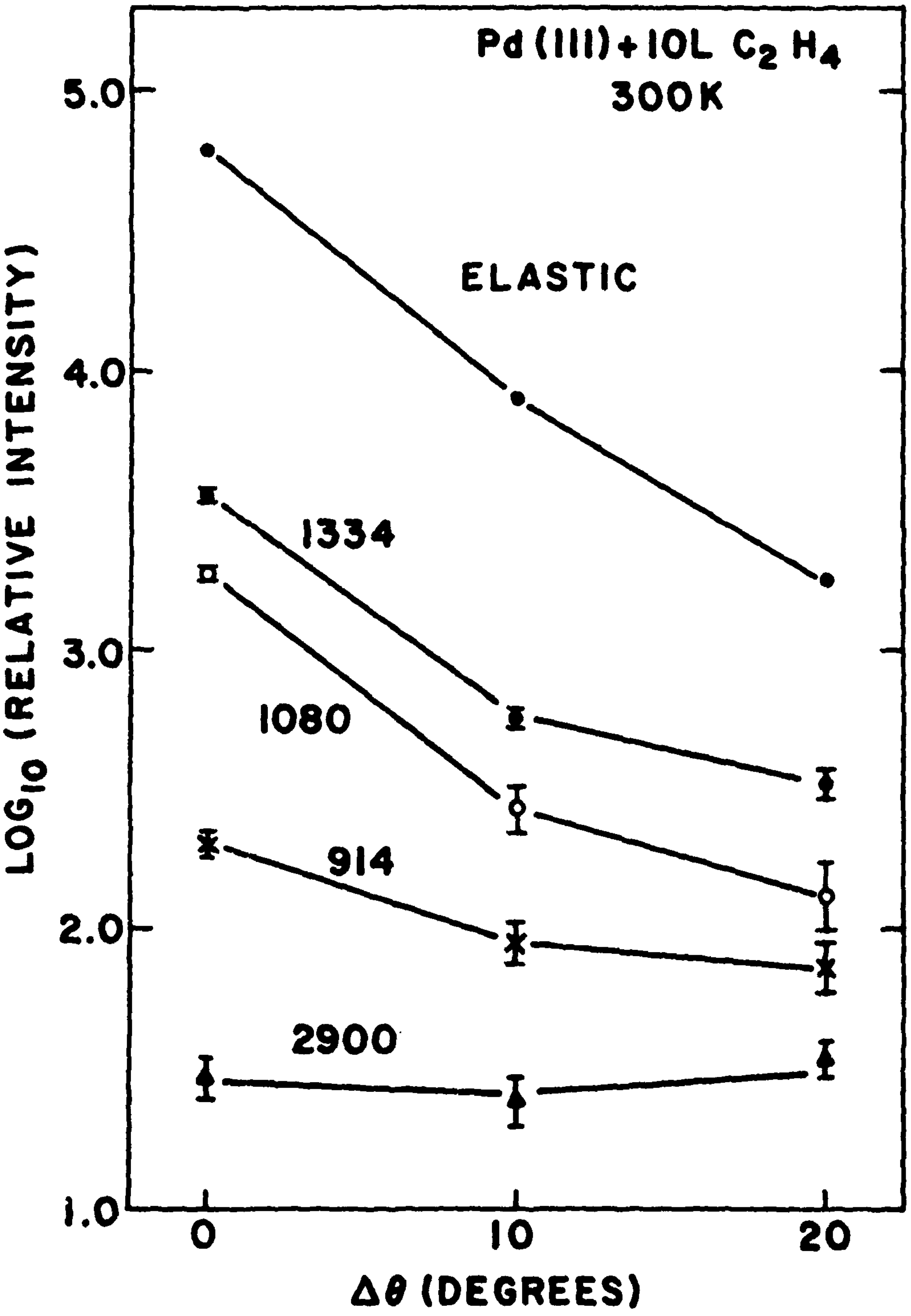
Pd (111) + 10L C_2H_4
300K
ELASTIC
1334
1080
914
2900
5.0
4.0
3.0
2.0
1.0
$\log_{10}$ (RELATIVE INTENSITY)
0
10
20
Δθ (DEGREES)

FIG. 4

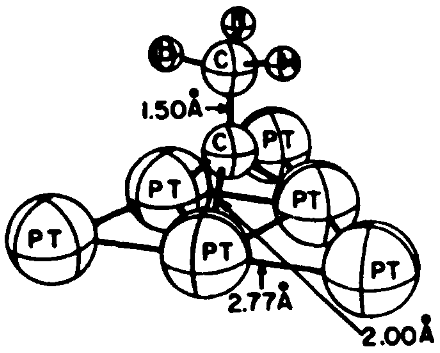

FIG. 5