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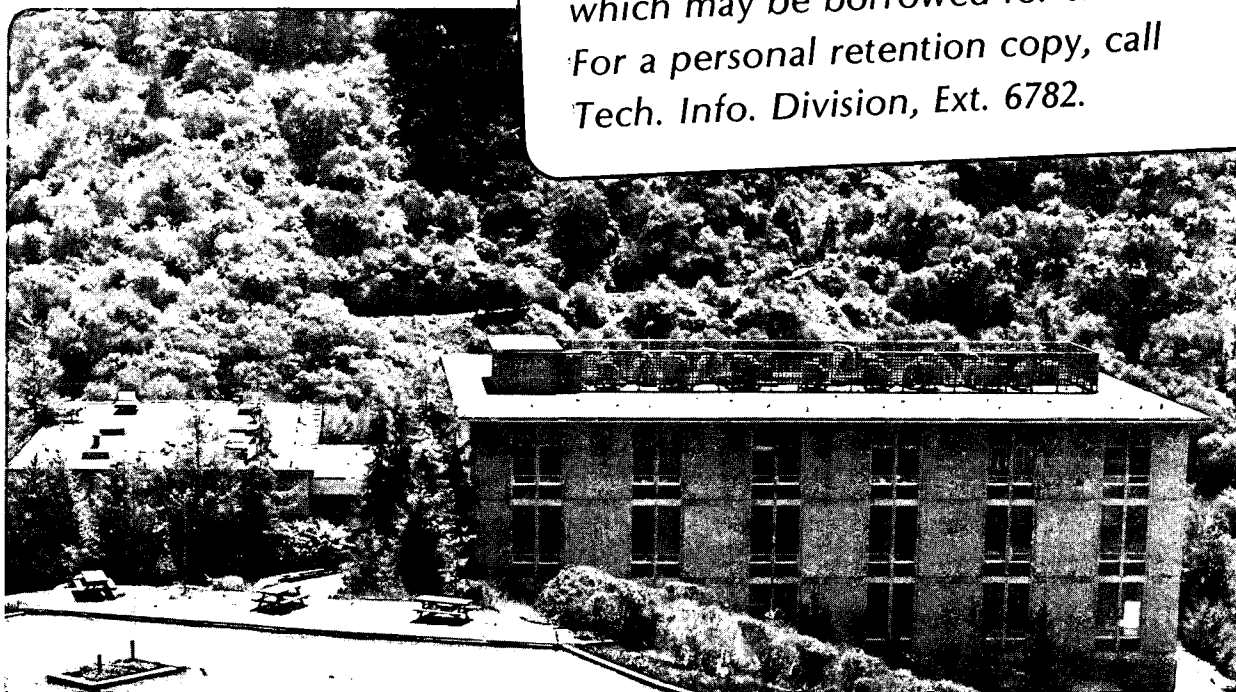
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W.T. Tysoe, F. Zaera, S.M. Davis, and
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ON THE ABSOLUTE COVERAGE OF ETHYLENE ON Pt(111) SINGLE
CRYSTAL SURFACES

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ABSTRACT

The absolute saturation coverage of ethylene on Pt(111) surfaces have been determined by using four independent techniques. XPS, AES, H₂ TDS, and a ¹⁴C radiotracer technique, all suggest a value of $\theta_{\text{sat}} = 0.25$.

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Introduction.

Although the absolute coverage of adsorbed layers on surfaces is an important parameter for catalytic studies, very few techniques are available for its measurement. If single crystals are used as substrates, and the adsorbate orders on the surface, perhaps the most common way of estimating these coverages is the use of low energy electron diffraction (LEED). In this regard, the (2x2) LEED pattern arising from ethylene adsorption on Pt(111) surfaces at room temperature suggests that the saturation coverage in this case is a quarter of a monolayer [1-3]. However, Bonzel et. al. [4,5] have recently measured the amount of carbon on the surface using X-ray photoelectron spectroscopy (XPS), and, by comparing with a CO saturated surface, reported a ethylene saturation coverage of $\theta_{\text{sat}}=0.5$. They then explained the LEED results as a superposition of three (2x1) domains with different orientations, rather than just one (2x2) superstructure.

In the present work we use XPS in a similar way as reported by Bonzel's group to estimate the saturation ethylene coverage on a platinum foil at room temperature. We find, in contrast, that the initial saturation coverage is closer to $\theta_{\text{sat}}=0.25$ than to $\theta_{\text{sat}}=0.5$, but due to the long data acquisition, additional carbon is deposited on the surface. We present additional information corroborating these results, viz., Auger electron spectroscopy (AES), temperature programmed desorption (TPD) and ^{14}C decay data.

XPS measurements.

The XPS experiments were performed in an ultra-high vacuum (UHV) chamber described in detail elsewhere [6], equipped with a X-ray gun and double pass cylindrical mirror analyzer for AES and XPS. The base pressure was

always better than 1×10^{-9} torr., but increased slightly after exposing the platinum foil to ethylene. XPS spectra for both ethylene and CO saturated surfaces were recorded. The C 1s peak for each adsorbate were obtained at two resolutions: 0.3 and 1.1 V (pass energies of 40 and 160 V, respectively). These are shown in fig. 1. The high resolution spectra required long data acquisition times (a couple of hours), and we found that additional carbon deposited on the surface. Low resolution spectra (10 minutes acquisition time) were obtained and corroborated this; they were used to estimate the amount of carbon on the surface in both cases. The results gave area ratios (normalized to the same ordinates) of $A_{\text{ethylene}}/A_{\text{CO}}=0.93$ for the low resolution spectra, and $A_{\text{ethylene}}/A_{\text{CO}}=1.24$ for the high resolution ones. Further confirmation of the increase in amount of carbon on the surface with time for ethylene adsorption was obtained using AES. Fig. 2 shows typical Auger spectra for saturation CO and ethylene. It is worth noticing the different shapes of the carbon 273 eV peak for the two cases. The $C(273\text{eV})/Pt(237\text{eV})$ peak height ratio (R_{AES}) were used to monitor surface carbon. The results are as follow: for saturation CO, $R_{\text{AES}}=0.54$, and saturation ethylene $R_{\text{AES}}=0.63$. However, after obtaining the high resolution ethylene XPS spectrum, $R_{\text{AES}}=2.48$. This shows that, using both the C 1s XPS peak area ratios and the Auger carbon signal, the amount of carbon on the foil surface after CO and ethylene saturation at room temperature are identical to within 10%, before the surface becomes further contaminated. If it is assumed for CO $\theta_{\text{sat}}=0.5$, this implies that ethylene saturates at a coverage of 0.25.

Other experiments.

To corroborate the value for ethylene saturation at 1/4 monolayer on

Pt(111), a series of independent experiments were carried out in a second UHV chamber, also described in detail elsewhere [7]. An absolute measurement of surface carbon was carried out using a ^{14}C radiotracer technique. The carbon auger signal from ethylene was also compared with saturation CO in this chamber. Finally, the H_2 TDS yield was identical when decomposing chemisorbed ethylene and when desorbing preadsorbed molecular H_2 .

a) Radiotracer technique.

Radiotracer experiments were carried out using a solid state detector for measuring the β decay of ^{14}C labeled compounds. The experimental set up and the calibration procedure have been extensively described previously [8,9]. Isotherms obtained for ^{14}C -ethylene chemisorption on Pt(111) at 330-570 K are shown in fig. 3. At temperatures below 450 K, the initial sticking coefficient was $s_0 = 0.9 \pm 0.2$, saturating at $C_s = 4 \times 10^{14}$ molec/cm² [9]. This corresponds to $\theta_{\text{sat}} = 0.27$, consistent with the proposed coverage by LEED.

b) AES measurements.

Carbon Auger signals were monitored with a retarding field analyzer, using a 10 V peak to peak modulation. The shape of the peaks were similar to those obtained using a cylindrical mirror analyzer and a foil, as shown in fig. 2, limiting the accuracy of the following measurements. For CO saturation at 150 K, $R_{\text{AES}} = 0.48 \pm 0.04$. This ratio was 0.50 ± 0.07 for ethylene adsorbed at 150 K, and did not vary significantly as the surface was warmed to 1000 K. The electron beam was defocussed to a spot size of about 1 mm to minimize electron stimulated desorption (esd). To further confirm that there was no esd, CO TDS were obtained before and after ta-

king AES spectra. These yielded identical desorption peak areas.

Since different LEED patterns were obtained for CO adsorption, there is some uncertainty in its absolute coverage, but it certainly lies between 0.5 and 0.6 [10,11]. This then corresponds to an ethylene saturation coverage of between 0.26 and 0.31 of a monolayer, in agreement with a value of $\theta_{\text{sat}}=1/4$.

c) Hydrogen thermal desorption.

Hydrogen thermal desorption spectra were obtained after either ethylene or molecular hydrogen adsorption at 130 K, and are shown in fig. 4. The desorptions were recorded as partial pressure of hydrogen against time, which eliminates errors due to variations in the heating rate. The H₂ desorption peak areas obtained were $(7.0 \pm 0.1) \times 10^{-9}$ torr·sec for ethylene, and $(8.2 \pm 0.3) \times 10^{-9}$ torr·sec for molecular hydrogen. Also from the ethylene TDS we can see that the first peak, corresponding to the transformation into ethynylidyne, corresponds to 25±2% of the total area, an improvement over the previously reported value of 33% [12]. Then, using the reported hydrogen saturation coverage on Pt(111) of unity [13,14], a value of $\theta_{\text{sat}}=0.21$ is obtained for ethylene, again in agreement with results from the other techniques.

Thus, in conclusion, we believe that there is overwhelming evidence to confirm that the saturation coverage of ethylene on a Pt(111) single crystal surface is a quarter of a monolayer, as originally proposed based on LEED data [1-3].

References

- 1) P.C. Stair and G.A. Somorjai, J. Chem. Phys. 66 (1977) 2036.
- 2) L.L. Kesmodel, P.C. Stair, R.C. Baetzold and G.A. Somorjai, Phys. Rev. Letters 36 (1976) 1316.
- 3) L.L. Kesmodel, R.C. Baetzold and G.A. Somorjai, Surface Sci. 66 (1977) 299.
- 4) N. Freyer, G. Pirug and H.P. Bonzel, Surface Sci. 125 (1983) 327.
- 5) N. Freyer, G. Pirug and H.P. Bonzel, Surface Sci. 126 (1983) 487.
- 6) A. Cabrera, H. Heinemann and G.A. Somorjai, J. Catal. 75 (1982) 7.
- 7) W.D. Gillespie, R.K. Herz, E.E. Petersen and G.A. Somorjai, J. Catal. 70 (1981) 147.
- 8) S.M. Davis, B.E. Gordon, M. Press and G.A. Somorjai, J. Vac. Sci. & Technol. 19 (1981) 231.
- 9) S.M. Davis, F. Zaera, M. Salmeron, B.E. Gordon and G.A. Somorjai, submitted to J. Am. Chem. Soc.
- 10) P.R. Norton, J.W. Goodale and E.B. Selkirk, Surface Sci. 83 (1979) 189.
- 11) G. Ertl, M. Neumann and K.M. Streit, Surface Sci. 64 (1977) 393.
- 12) M. Salmeron and G.A. Somorjai, J. Phys. Chem. 86 (1982) 341.
- 13) K. Christmann, G. Ertl and T. Pignet, Surface Sci. 54 (1976) 365.
- 14) J. Lee, J.P. Cowin and L. Wharton, Surface Sci. 130 (1983) 1.

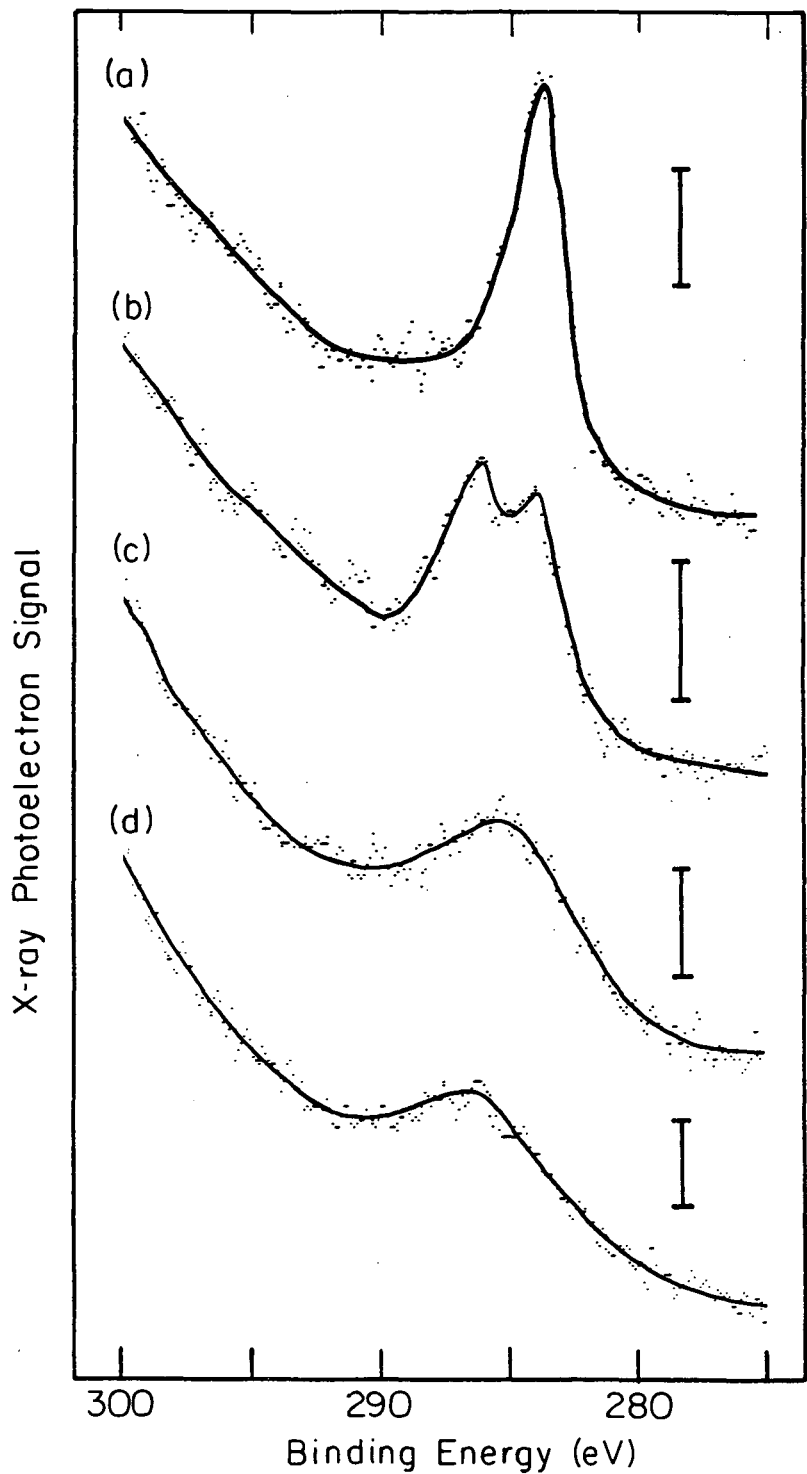
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Fig. 1 Carbon C 1s XPS spectra after room temperature saturation on a platinum foil: a) ethylene, 40 V pass energy, b) CO, 40 V pass energy, c) ethylene, 160 V pass energy, d) CO, 160 V pass energy. Vertical bars represent 1000 counts.

Fig. 2 Auger spectra of a Pt(111) single crystal surface after saturation at 150 K with ethylene (a) and CO (b). The spectra were obtained with a retarding field analyzer and 10 V modulation.

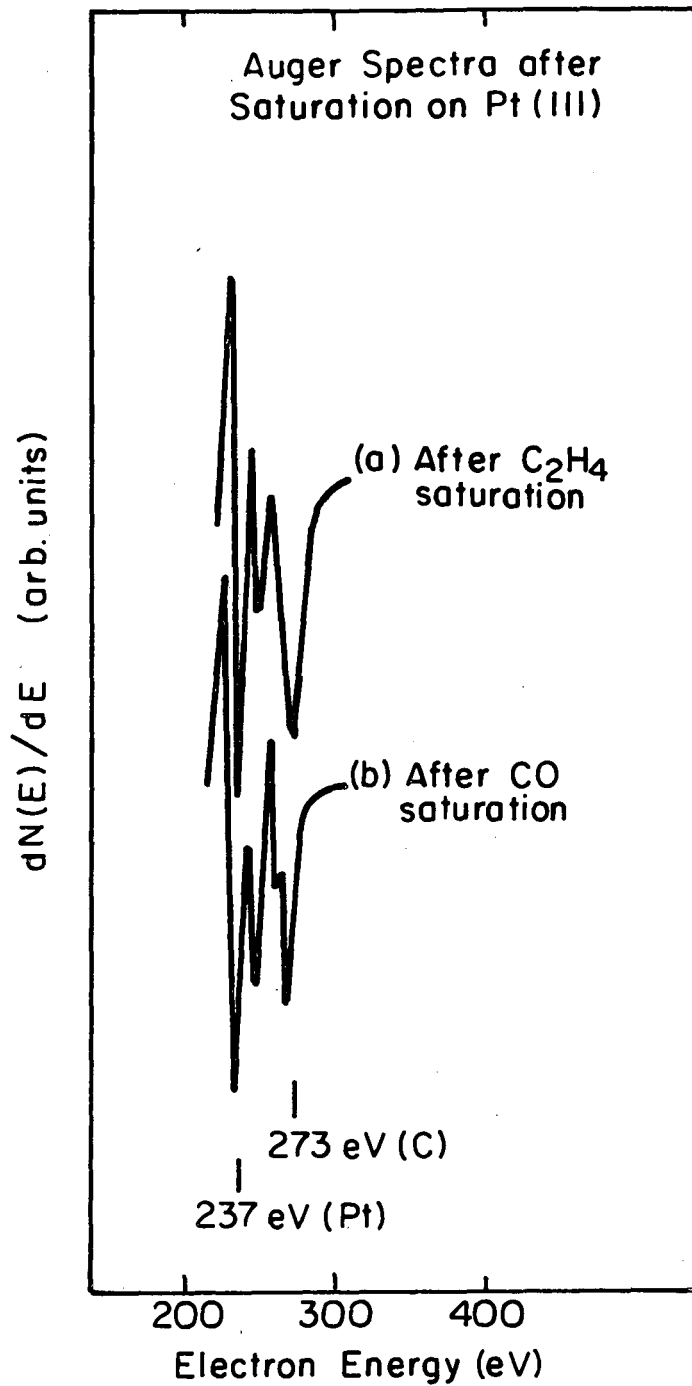
Fig. 3 Adsorption isotherms (left frame) for $^{14}\text{C-C}_2\text{H}_4$ chemisorption on Pt(111) at 330-570 K. The adsorption behavior below 420 K is well described by a first order langmuir model (right frame).

Fig. 4 Hydrogen thermal desorption spectra ($\text{amu}=2$) after H_2 (a) and C_2H_4 (b) saturation of a Pt(111) surface at 130 K. The heating rate is about 35 K/sec.



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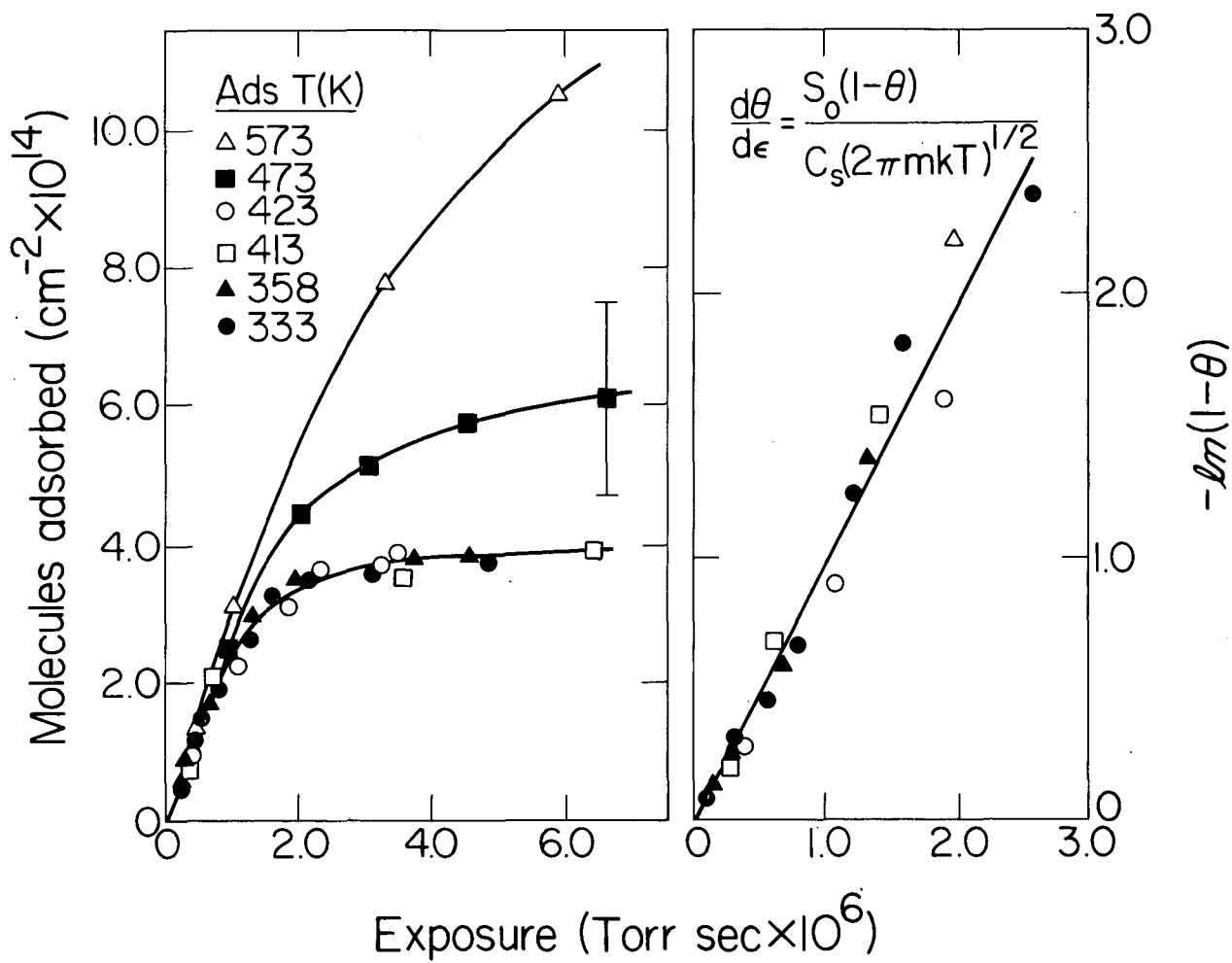
Fig. 1



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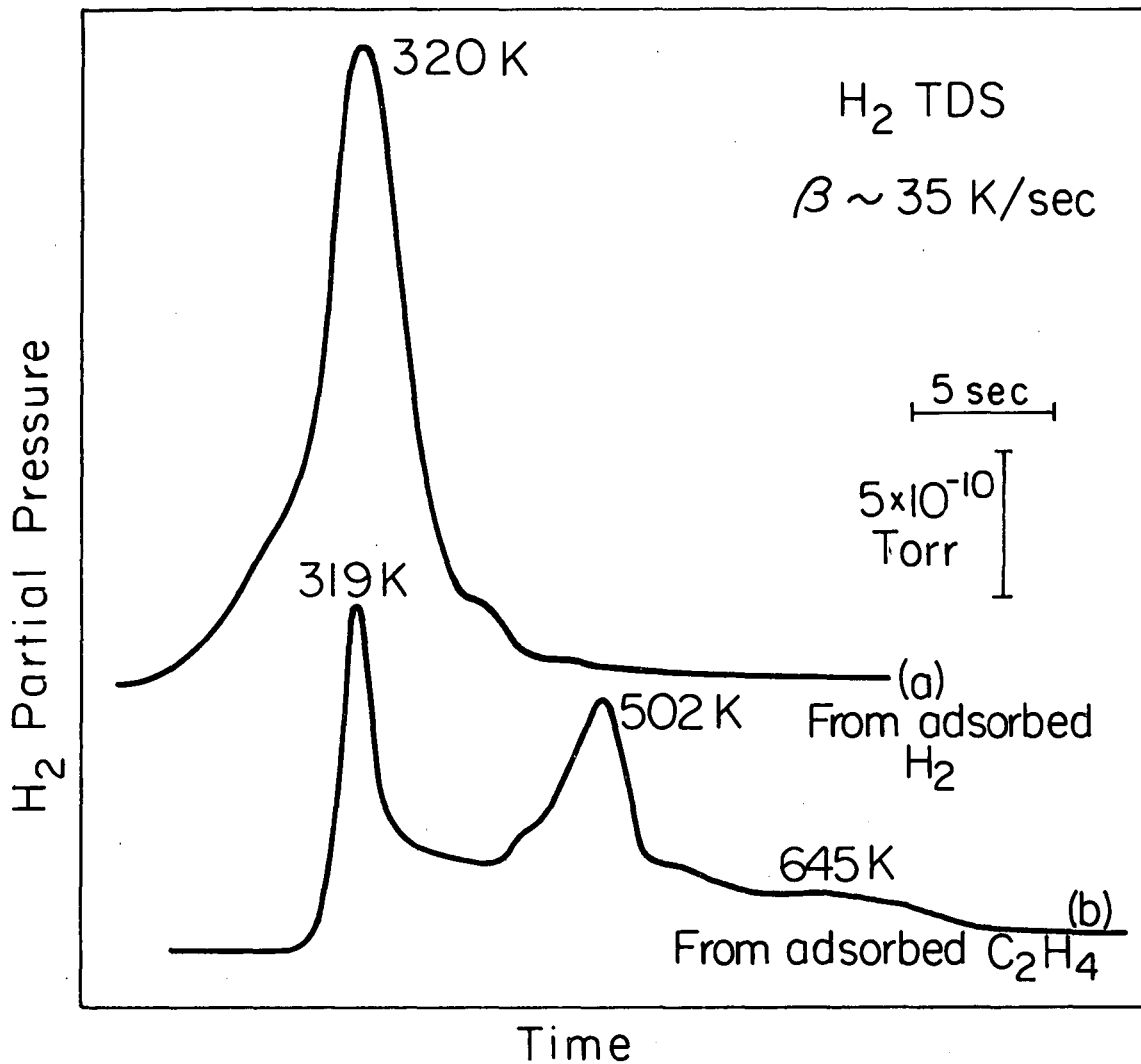
Fig. 2

$^{14}\text{C}_2\text{H}_4$ adsorption Pt(III)



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Fig. 3



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Fig. 4

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