Structure of ***CO*** on ***Pt(533)***

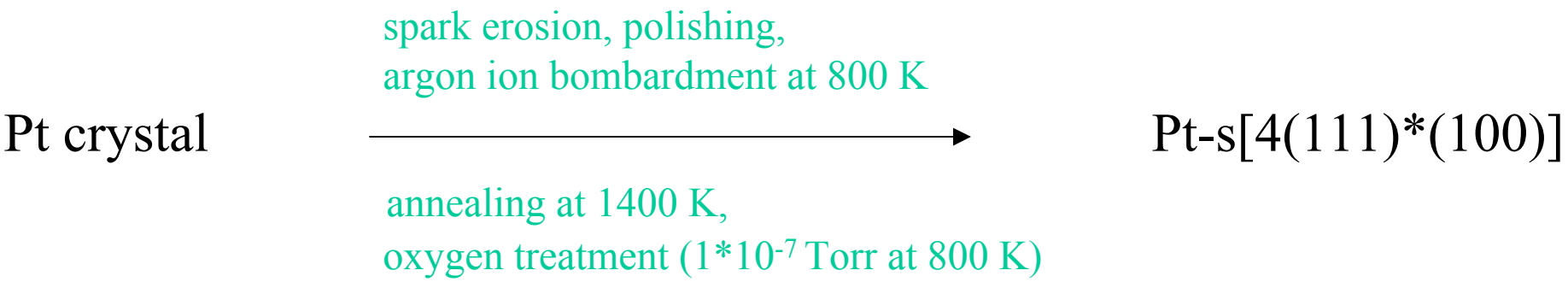
Presented by

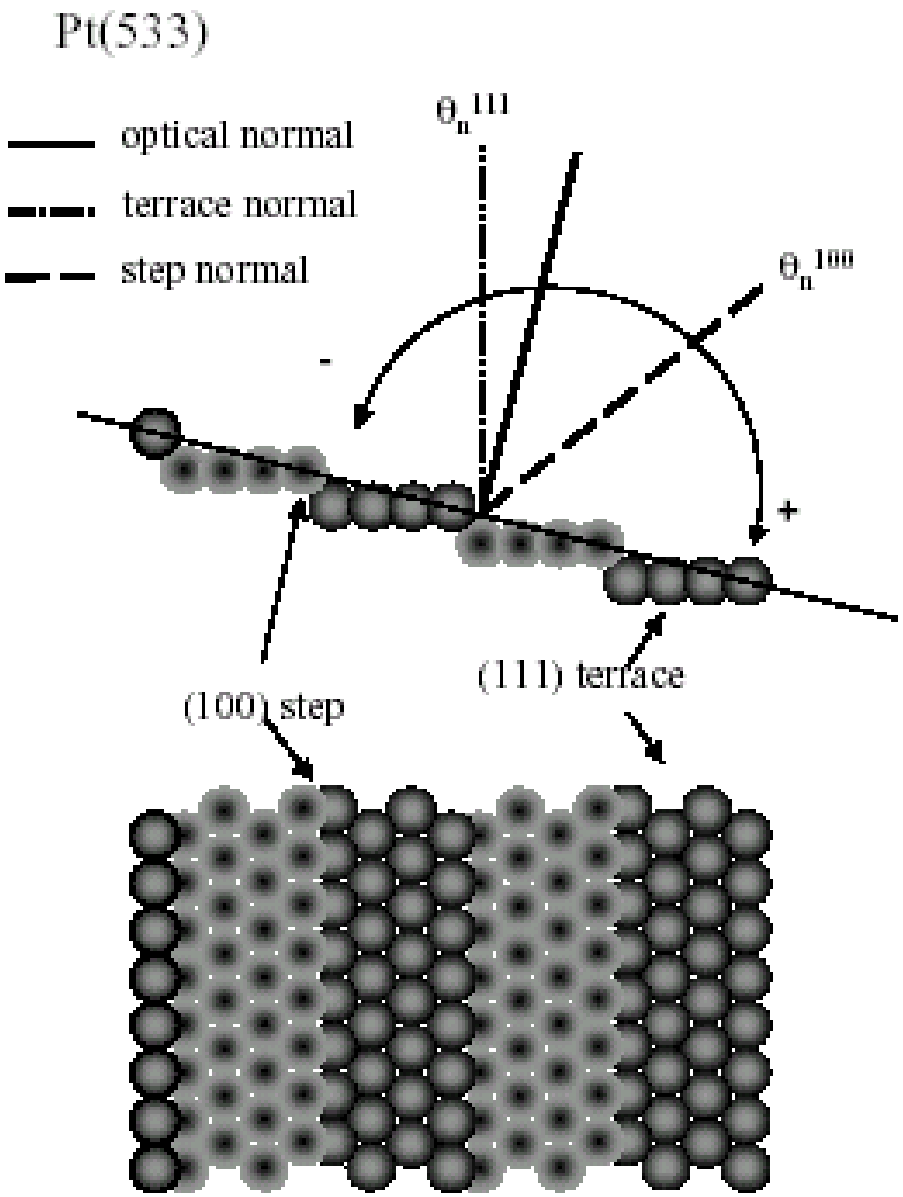
Kumar Suman
CY01C010

Contents

Introduction

The adsorption of CO on a stepped platinum surface was studied using a combination of infrared reflection absorption spectroscopy (IRAS), temperature programmed desorption (TPD), and low energy electron diffraction (LEED) in an attempt to gain more information on the CO species associated with the steps.




Pt(533)
optical normal
terrace normal
step normal
θ_n^{111}
θ_n^{100}
-
+
(100) step
(111) terrace

Techniques to determine the surface arrangement

Temperature Programmed Desorption (TPD)

relative binding energies of CO at different adsorption sites.

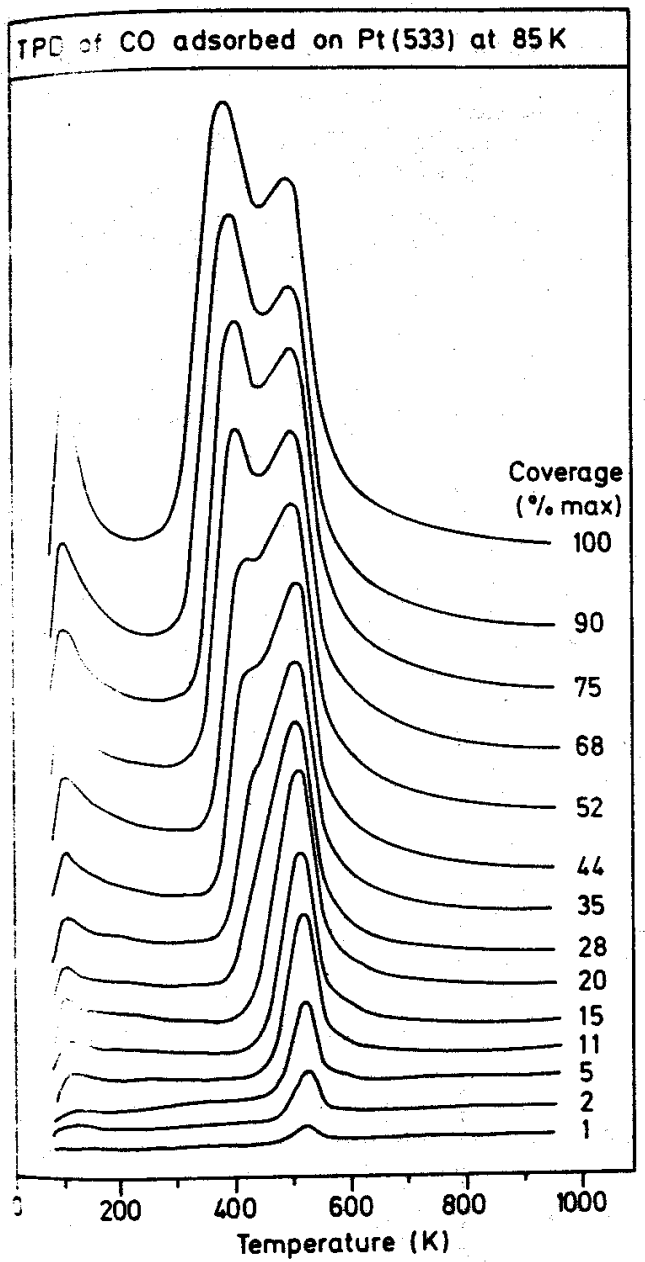
Reflection-Absorption Infrared Spectroscopy (RAIRS)

vibrational properties of adsorbed CO molecules.

Low Energy Electron Diffraction (LEED)

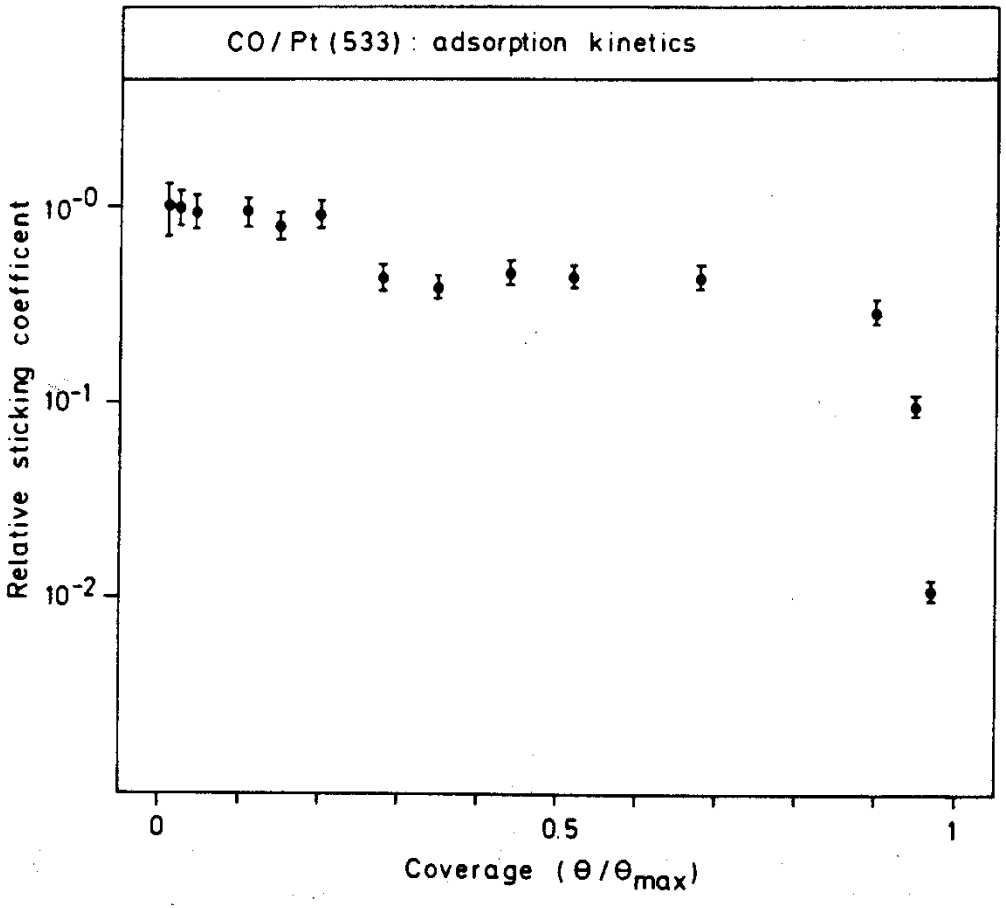
periodicity of the CO adsorbed layer.

Temperature Programmed Desorption (TPD)



@ high coverages, the spectrum shows two molecular desorption peaks at about 400 and 500 K .
@ low coverages, only the high temperature component is present.

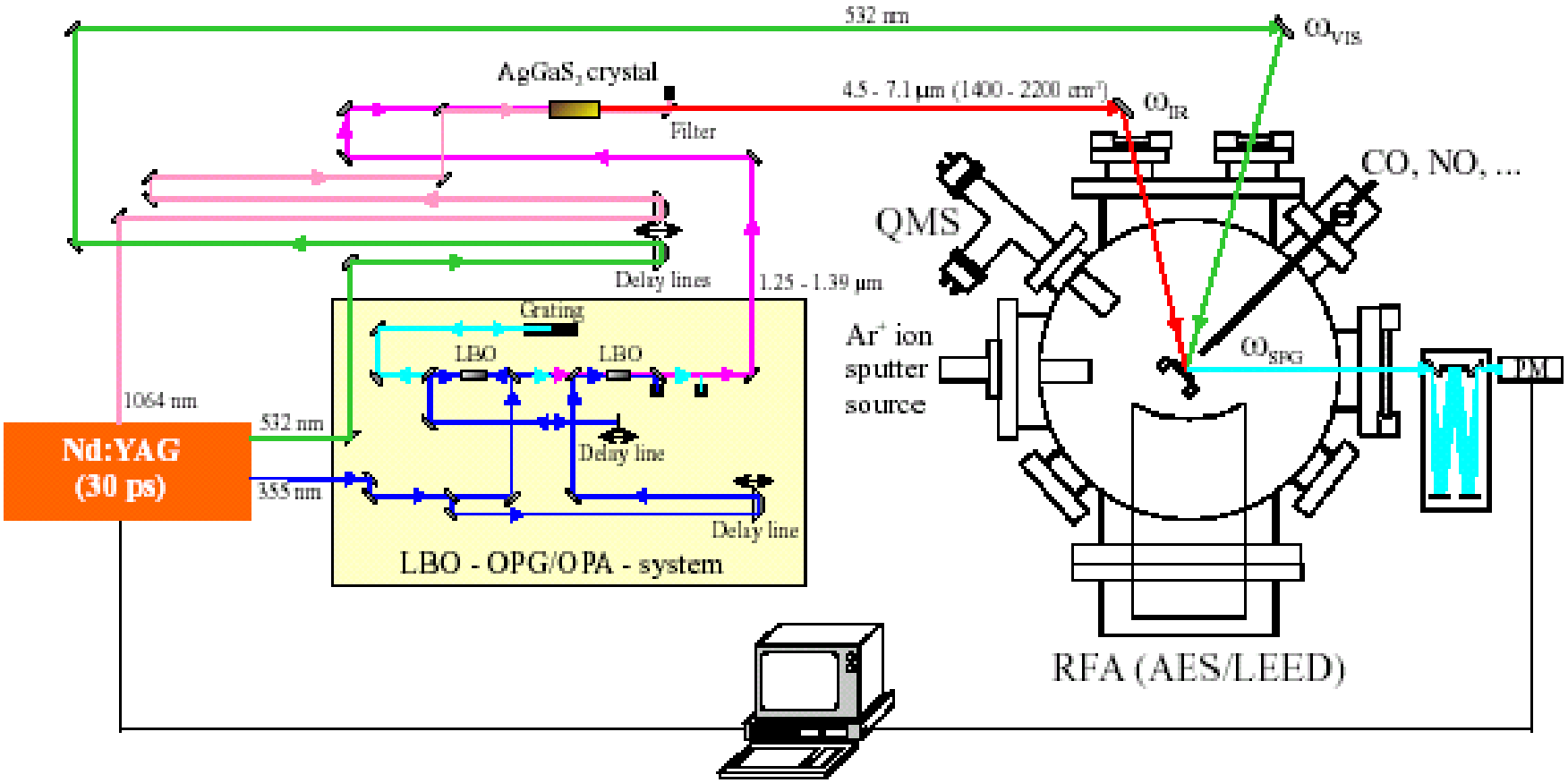
As the coverage increases, the position of high temperature peak remains constant and the low temperature peak shifts to lower temperatures.

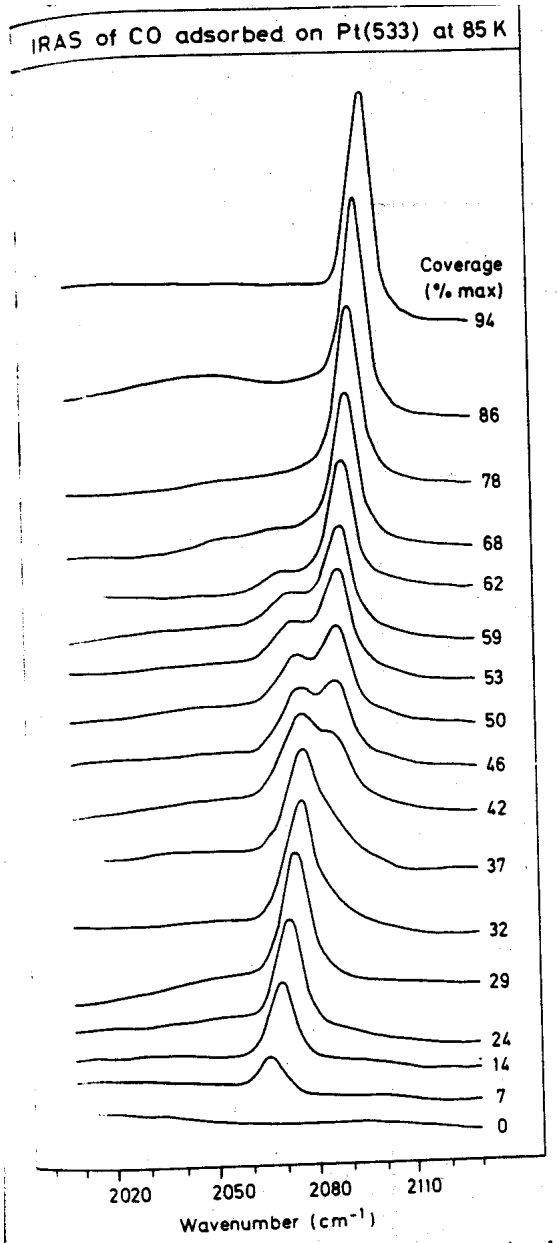


At low coverages, adsorption of CO on Pt (533) at 85 k takes place at the step sites, once the step sites are saturated, the sticking probability is reduced, then the low temperature TPD component appears. This peak corresponds to the adsorption on the terraces.

Reflection-Absorption Infrared Spectroscopy (RAIRS)

Experimental set up





- 1300-2000 cm^{-1} - no peak

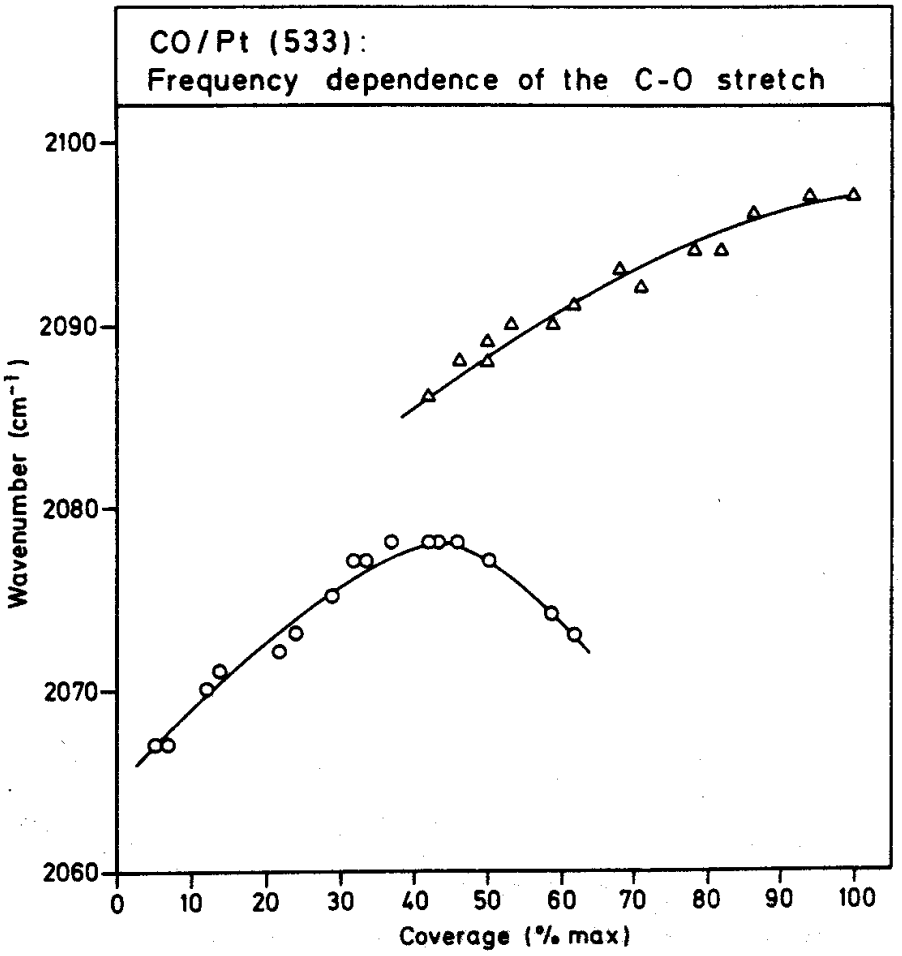
→ no CO adsorbed in bridging configuration.

- 2065 cm^{-1} - low frequency band

C-O stretch of the CO species adsorbed at a step site. This band increases in intensity as a function of coverage up to ~ 0.30 θ_{max} at 2076 cm^{-1}.

2086 cm^{-1} - high frequency band

C-O stretch of the CO species adsorbed at a terrace site. This band grows with increasing coverage, while the intensity of the first band diminishes. $\theta > 0.30\ \theta_{max}$

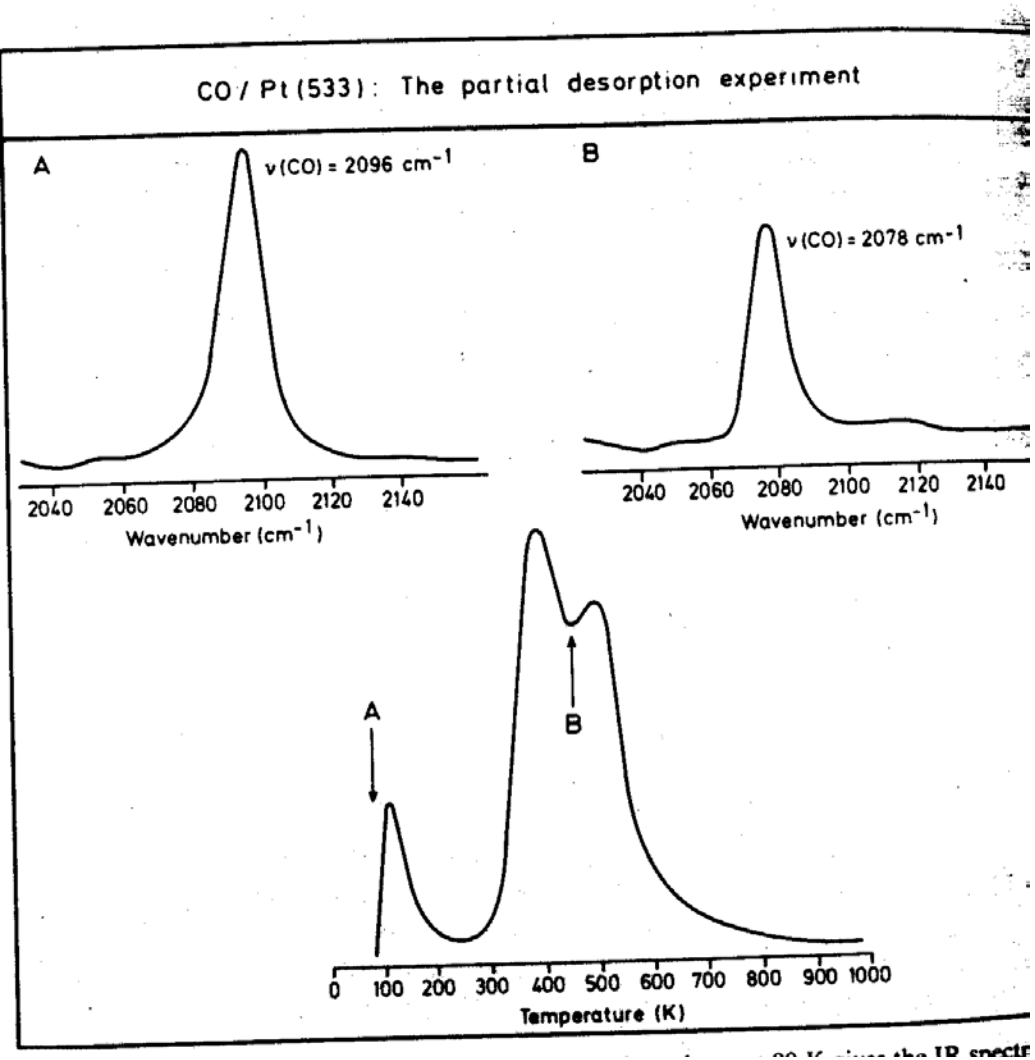


- $\theta < 0.30\ \theta_{max}$ band appears due to one-dimensional array of CO molecules adsorbed along the steps. As coverage increases, the band shifts to a higher frequency due to increased vibrational coupling.

- $\theta > 0.30\ \theta_{max}$ CO begins to adsorb on the terraces and two-dimensional islands including both steps and terrace molecule (vibrational coupling) forms, giving rise to the second, high frequency band.

- As the two-dimensional island grows, the remaining one-dimensional domains shrink, with a resulting decrease in frequency and intensity of the low-frequency band.

Partial Desorption Experiment

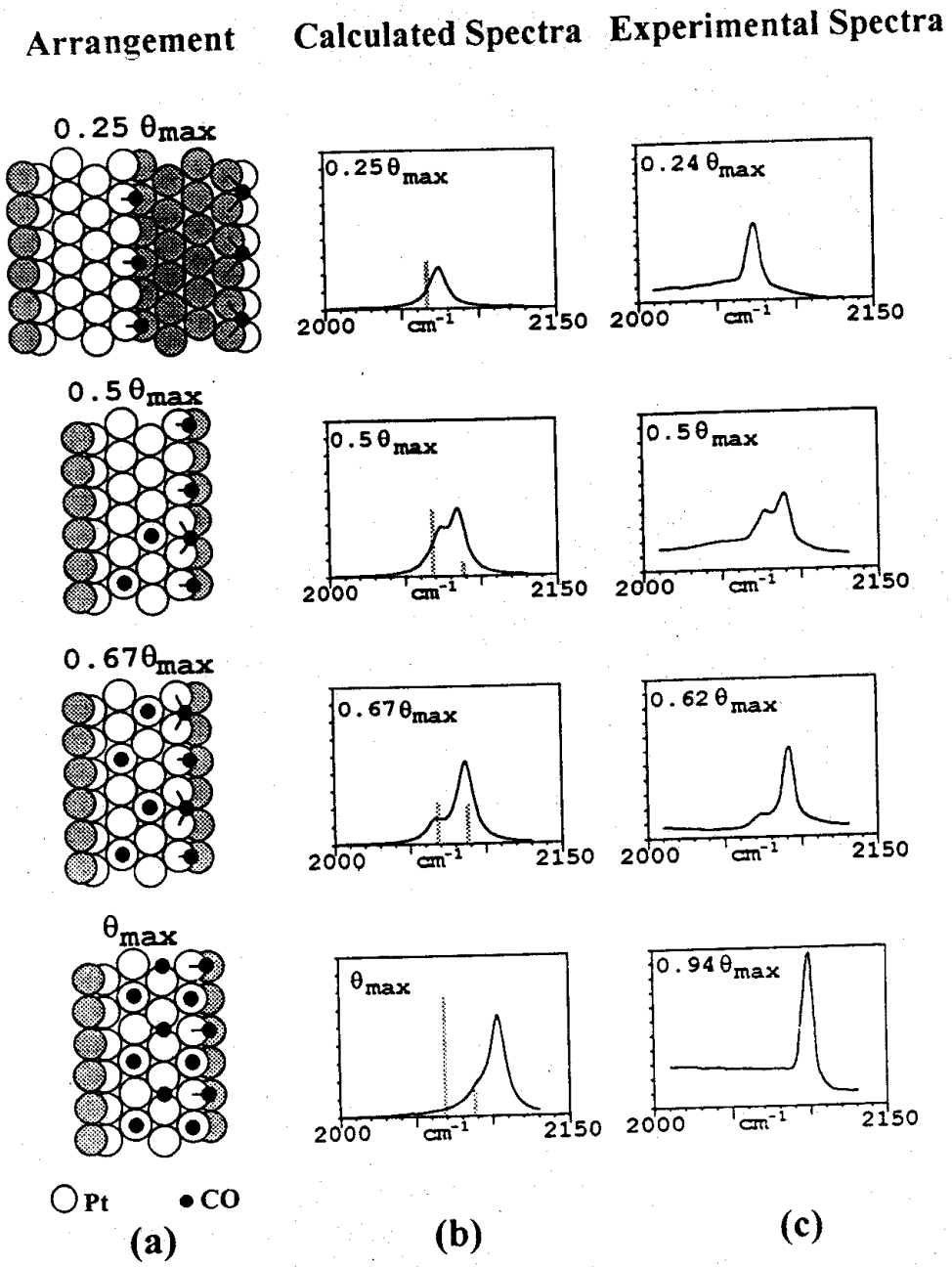


IRAS confirms the sequential filling of sites i.e assignment of low frequency IR peaks to the steps through partial desorption experiment.

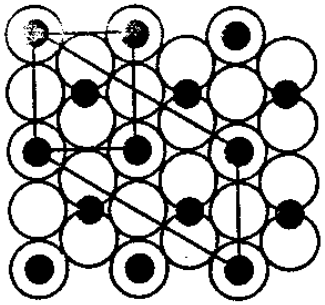
Spectrum A - Saturated CO layer at 90 K.

Spectrum B - Surface exposed to a coverage of 0.30 θ_{max} and at this coverage only a high temperature peak appears in the TPD.

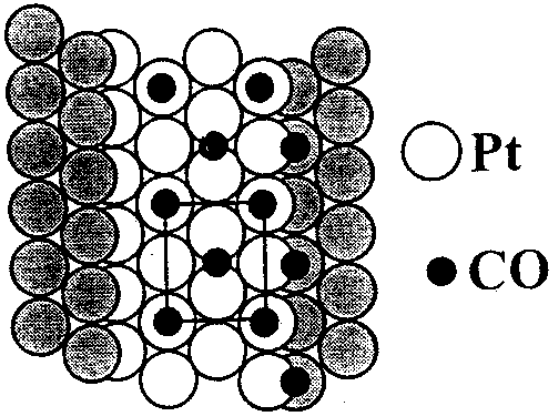
Proposed Arrangement



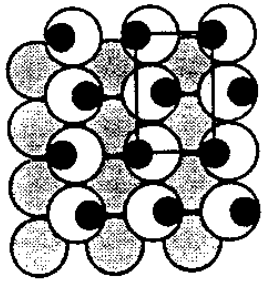
Conclusion



Pt(111)-CO c(4×2)



Pt(533)-CO



Pt(110)-CO (2×1) p1g1

The terrace is occupied by a localized √3 * √3 pattern consisting entirely of top bonded CO. The edge sites are two-thirds covered by CO; half top and half bridge bond. At θ_{max} all of the edge sites are occupied by the top CO that forms a structure in which CO adsorbed on adjacent edge sites are tilted away from each other. The terrace is occupied by a layer of CO molecules that forms a localized c(4*2) structure and contains an equal amount of top- and bridge-bonded CO molecules.

References

1) R.K. Brandt, R.G. Greenler, *Chemical Physics Letters* **221** (1994) 219-223.

2) B.E. Hayden, K. Kretzschmar, A. M. Bradshaw, *Surface Science* **149** (1985) 394-406.

3) Chapter 6 "**Dissociative adsorption of methane on Pt(533)**" from thesis "*Activation barriers in gas-surface reactions*", submitted by Bernd Riedmüller, University of Leiden, 22 March 2001.