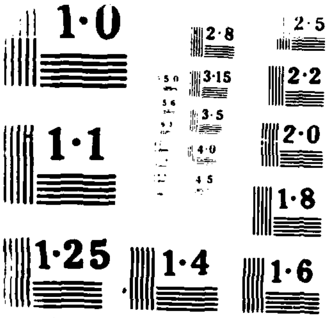
AD-A169 082 CARBON MONOXIDE ADSORPTION ON A PLATINUM ELECTRODE 1/1
STUDIED BY POLARIZATIO..(U) IBM ALMADEN RESEARCH CENTER
SAN JOSE CA K KUNIMATSU ET AL. 16 MAY 86 TR-10
UNCLASSIFIED N00014-82-C-0583 F/G 7/4 NL


1·0
2·8
2·5
3·15
2·2
3·5
2·0
4·0
1·1
1·8
1·25
1·4
1·6

(12)

AD-A169 082

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
Technical Report No. 10

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE *(and Subtitle)*
Carbon Monoxide Adsorption on a Platinum Electrode Studied by Polarization Modulated FT-IR Reflection-Absorption Spectroscopy: II CO Adsorbed at a Potential in the Hydrogen Region and Its Oxidation in Acids

5. TYPE OF REPORT & PERIOD COVERED
Technical Report

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)

8. CONTRACT OR GRANT NUMBER(s)
N00014-82-C-0583

9. PERFORMING ORGANIZATION NAME AND ADDRESS
IBM Almaden Research Center, K33/801
650 Harry Road
San Jose, CA 95120-6099

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

12. REPORT DATE
16 May 86

13. NUMBER OF PAGES
11 + 9 figures

14. MONITORING AGENCY NAME & ADDRESS *(If different from Controlling Office)*

15. SECURITY CLASS *(of this report)*
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*
Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*
Approved for public release; distribution unlimited.

DTIC
ELECTE
JUN 2 7 1986
S D
B

18. SUPPLEMENTARY NOTES
Prepared for publication in *Langmuir*

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*
Electrode, FTIR, carbon monoxide

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The carbon monoxide layer on a platinum electrode, which is adsorbed at 0.05 V relative to a normal hydrogen electrode (NHE) in 0.5 M surfuric acid, and its oxidation to carbon dioxide at higher electrode potentials has been studied by both electrochemical and *in-situ*

DTIC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

Fourier transform infrared reflection-absorption spectroscopy (FT-IRRAS). Polarization modulated FT-IRRAS was used to measure the vibrational spectra of adsorbed carbon monoxide as well as the evolved CO_2 as a function of electrode potential. It is shown that the dominant surface species is linearly adsorbed CO, but that the bridge bonded species is oxidized first at about 0.20 V, giving rise to a decrease in the linear C-O stretching frequency along with a broadening of the band. Oxidation of the linearly adsorbed CO begins at 0.35 V, producing a further, sharp decrease in the C-O stretching frequency as well as a considerable broadening of the band. It is concluded that the oxidation of the CO adlayer produced at 0.05 V occurs randomly throughout the adlayer, in contrast to oxidation at island edges, which is characteristic of CO adsorbed at 0.4 V. It is proposed that the difference in behavior of these two kinds of adsorbed CO is due to crystallographic modification of the platinum surface when the CO is adsorbed at 0.05 V in the hydrogen region which results in a higher density of bridge bonded CO.

✓

A-1

CARBON MONOXIDE ADSORPTION ON A PLATINUM ELECTRODE STUDIED BY POLARIZATION MODULATED FT-IR REFLECTION-ABSORPTION SPECTROSCOPY: II CO ADSORBED AT A POTENTIAL IN THE HYDROGEN REGION AND ITS OXIDATION IN ACIDS

K. Kunimatsu*
H. Seki
W. G. Golden
J. G. Gordon,II
M. R. Philpott

IBM Almaden Research Center
San Jose, California 95120-6099

ABSTRACT: The carbon monoxide layer on a platinum electrode, which is adsorbed at 0.05 V relative to a normal hydrogen electrode (NHE) in 0.5 M sulfuric acid, and its oxidation to carbon dioxide at higher electrode potentials has be studied by both electrochemical and *in-situ* Fourier transform infrared reflection-absorption spectroscopy (FT-IRRAS). Polarization modulated FT-IRRAS was used to measured the vibrational spectra of adsorbed carbon monoxide as well as the evolved CO_2 as a function of electrode potential. It is shown that the dominant surface species is linearly adsorbed CO, but that the bridge bonded species is oxidized first at about 0.20 V, giving rise to a decrease in the linear C-O stretching frequency of along with a broadening of the band. Oxidation of the linearly adsorbed CO begins at 0.35 V, producing a further, sharp decrease in the C-O stretching frequency as well as a considerable broadening of the band. It is concluded that the oxidation of the CO adlayer produced at 0.05 V occurs randomly throughout the adlayer, in contrast to oxidation at island edges, which is characteristic of CO adsorbed at 0.4 V. It is proposed that the difference in behavior of these two kinds of adsorbed CO is due to crystallographic modification of the platinum surface when the CO is adsorbed at 0.05 V in the hydrogen region which results in a higher density of bridge bonded CO.

---

*IBM Visiting scientist (1983-1984): On leave from the Research Institute for Catalysis, Hokkaido University, Sapporo 060 Japan

INTRODUCTION

In a previous paper we reported an *in-situ* IR spectroscopic study of CO adsorbed on a smooth platinum electrode in acids, the adsorption being initiated at a potential of 0.4 V (NHE) in the double layer region.[1,2] The band center position, intensity and linewidth for the C-O stretch were measured as a function of electrode potential. The potential was varied from ca. 0.05 V (NHE) well into the oxidation region. The evolution of CO_2 during oxidation was also monitored spectroscopically. It was concluded that the linearly adsorbed CO (linear CO(a)) was the predominant surface species, the quantity of bridge bonded CO species (bridged CO(a)) being very low, consistent with other electrochemical studies of CO on both polycrystalline[3-6] and single crystal[7,8] platinum electrodes. On the basis of the spectroscopic data obtained it was concluded that the electrooxidation of the adsorbed CO layer occurred primarily at the edges of CO islands and involved water molecules adsorbed adjacent to the CO sites.

The present study focuses on the adsorption and oxidation of CO on the platinum electrode when initial CO adsorption occurs in the hydrogen potential region. There have been some differences in the literature[9-14] concerning the nature of the surface species produced when CO is adsorbed at a potential in the hydrogen region. Additional information regarding the structure of this adlayer can now be obtained using the polarization modulated FT-IRRAS.[1]

EXPERIMENTAL

The technique of polarization modulated FT-IRRAS as employed in this work and the experimental details in relation to the electrochemical cell have been described in previous reports.[1,2,15,16] The electrolyte is 0.5 M sulfuric acid prepared from the organic free water (Barnstead) and sulfuric acid (double distilled from Vycor, GFS Chemicals).

The platinum electrode was prepared by sealing a 99.95% pure Pt electrode disk (20 mm × 1 mm) into a soda glass piston, leaving one side exposed as the electrode surface. The surface of the electrode was polished successively with 1.0, 0.3 and 0.05 micron alumina on a polishing cloth. In order to study the adsorption of CO in the hydrogen region, the Pt electrode was first cleaned by cycling the potential between 0 V and 1.5 V. All electrode potentials in this paper are relative to the normal hydrogen electrode (NHE). The electrode was then held at the appropriate potential with several mm of solution between the window and the electrode while carbon monoxide was bubbled through the solution for ten minutes. FT-IRRAS spectra of the Pt/solution interphase were taken, with the electrode pressed against the CaF IR window, as a function of the electrode potential. The first spectrum was usually taken immediately after the CO bubbling was halted, although the CO layer is adsorbed so strongly that a stable spectra could be observed in the double layer potential region for very long periods even after the CO in the solution had been purged. The potential was changed stepwise towards positive potentials and an FT-IRRAS spectrum (4 cm^{-1} resolution) was taken at each of these potentials. Each spectrum usually involved 300 scans taking about ten minutes; hence the spectra are for an interphase system under steady state conditions. The infrared detectors used were either InSb or HgCdTe cooled by liquid N_2.

RESULTS AND DISCUSSION

1. Comparison between the Electrochemical Behavior of the CO Adsorbed on Pt at 0.05 V and 0.4 V.

First, the electrochemical behavior of the adsorbed CO layer produced at the two potentials was examined CO was adsorbed on the platinum surface at 0.05 V and 0.4 V, respectively. After the solution had been purged by nitrogen gas for twenty minutes to remove dissolved CO, cyclic voltammograms for each case were taken at

1 mV/sec up to 0.8 V. The results, given in Figure 1, show that the surface CO species produced in the hydrogen region exhibits a small prewave around 0.35 V followed by a main oxidation peak at 0.57 V. This main peak is ca. 50 mV below the first oxidation peak for the CO adlayer adsorbed at 0.4 V. Integration of the curves in Figure 1 indicates that the total charge to oxidize the CO is similar in each case, when the charge under the small prewave in the 0.05 V case is included (this prewave contributes ca. 10% to the total oxidation charge). These observations agree with previous electrochemical studies by Breiter[9-11] who employed a galvanostatic charging curve technique and by Grambow and Bruckenstein[12] who performed cyclic voltammetry on a platinum sponge electrode.

2. Potential Dependence of the FT-IRRAS Spectra of the Linearly Adsorbed CO and Evolved CO_2

After adsorbing CO at 0.05 V, the FT-IRRAS spectra were taken as function of the electrode potential in a stepwise fashion and in smaller increments through the oxidation region. These spectra seen in Figure 2 show that the center for the linear CO(a) band first shifts to higher frequencies with electrode potential, up to 0.2 V, but then begins to shift to lower frequencies as the oxidation reaction begins. At 0.4 V this shift to lower frequency accelerates with concomitant loss in band intensity as the linear species is removed. The band center and the integrated area of these spectra are plotted in Figure 3 as a function of electrode potential.

From 0V to 0.2 V there is a voltage dependent shift of the linear CO(a) band center of ca. 30cm^{-1} volt, as in the case of CO adsorbed at 0.4 V. As described previously[2] this is due, not to increased back donation into the $2\pi^*$ orbital of the CO but rather to Stark tuning of the C-O stretching frequency.[17-19] However, as the potential is made more positive, we see in Figures 3 and 4 the following significant developments:

a) At 0.2 V the frequency shift of the linear CO(a) deviates from the linear potential dependence and the linewidth of this band starts to increase.

b) The integrated band intensity of the linear CO(a) band remains constant up to 0.35 V.

c) A band at ca. 2344 cm^{-1} which corresponds to that of CO_2 appears at 0.2 V and increases.

Items a) and b) indicate that, although the total number of linear CO(a) molecules is constant from 0.2 V to 0.35 V, some change is taking place in the distribution of the linear CO(a) layer which is decreasing the average dipole-dipole interaction.

One of the characteristics of PM FT-IRRAS is its ability to detect dissolved species near the electrode surface.[1,15] There is no potential induced frequency shift for the band at 2344 cm^{-1} and the appearance of the CO_2 band coincides with the beginning of the oxidation band which peaks at 0.34 V (Figure 1b). This indicates that this band is due to CO_2 in solution, an oxidation product trapped in the thin layer cell, of some as yet unknown surface species. This oxidation results in the above mentioned redistribution of linear CO(a).

In an effort to explore the possible presence of coadsorbed species other than linear CO(a) the FT-IRRAS spectra was examined for features due to C-H and carbonyl stretches. Figure 5 is the difference between spectra taken at 0.05 V and 0.55 V. Apart from the expected intense bands due to CO(a) at 0.05 V and CO_2 (aq) at 0.55 V there is no evidence for the presence of a C-H stretching band, but there is a band at 1860 cm^{-1} assigned, in the usual fashion, to bridged CO(a). Experiments were performed in D_2O/0.5 M D_2SO_4 solution in order to eliminate strong water absorptions in the infrared spectral region characteristic of carbonyl containing species. Behavior of the linear CO(a) in this system is qualitatively similar to that observed in the H_2O/H_2SO_4 system with the notable exception that the oxidation occurs at ca. 100 mV more positive potentials; compare Figures 3 and 6. The spectra, shown in Figure 7, taken at several electrode potentials show no evidence of a carbonyl stretch.

We conclude from these data that either there is no significant amount of hydrocarbon or carbonyl type impurities on the surface, or that the species have their appropriate dipoles lying in the plane of the surface. The latter conclusion is unlikely, however, since molecules lying flat on the surface of the platinum electrode would radically affect the coverage of CO. What is significant is that the band of bridged CO(a) at 1860 cm^{-1}, which was seen very weakly in the case of CO adsorbed at 0.4 V, is clearly visible as seen in Figure 7 for CO adsorbed at 0.05 V. Furthermore this band disappears at potentials more anodic than 0.2 V. The most straightforward interpretation is that the unknown coadsorbed species which is oxidized between ca. 0.2 V and 0.4 V is the bridged CO(a).

3. The Effect of CO Adsorption in the Hydrogen Region on the Platinum Surface

The higher population density of bridged CO and the consequent shift of the oxidation peak of the linear CO(a) to lower potentials (0.62V to 0.57 V) when CO is adsorbed in the hydrogen potential region suggests the development of electrocatalytic activity for oxidation of linear CO(a). The following experiment was carried out in order to further understand the apparent increase of electrocatalytic activity. CO was adsorbed at 0.05 V on a freshly prepared Pt electrode surface as before. Then the electrode was pressed against the IR window and all surface species oxidized at 0.55 V. Curves 1 in Figure 8 are the spectra obtained at this point confirming the complete oxidation of linear CO(a) into CO_2 in solution. Subsequently, with the solution still saturated with

CO, the electrode was separated from the IR window and the potential was cycled from 0.55 V to a more positive potential and back after which the electrode was pressed against the window for spectral measurement. The remaining curves 2, 3 and 4 of Figure 8 were obtained by this potential excursion procedure in which the potential to which the excursion limit was 0.65 V, 0.8 V and 1.2 V, respectively.

It is seen that the amount of CO_2 evolved decreases while the amount of remaining CO(a) increases with the potential excursion limit. For the 1.2 V excursion, no evolution of CO_2 is observed whereas the intense band due to linear CO(a) is clearly present. These results indicate that the platinum electrode surface is becoming less electrocatalytically active for CO oxidation at 0.55 V as the potential is swept between 0.55 V and higher potentials. After cycling up to 1.2 V the platinum surface appears to be completely deactivated. Since one would expect a cleaner platinum electrode to be more electrocatalytically active, this suggests that a simple oxidation/reduction cleaning process is not responsible for the changes observed with the progressive potential excursions.

Cyclic voltammograms in the hydrogen region, known to be sensitive to the electrode surface crystallography[20], was used in the following experiment. Adsorption of CO was carried out at 0.05 V and then the solution was purged of CO by N_2 bubbling. The electrode potential was then set to 0.55 V to oxidize all surface species. The voltammogram taken immediately after this procedure is shown in Figure 9, curve 1. The potential was scanned at 50 mV/sec from 0.55 V to 0V and back to 0.55 V. The voltammogram obtained here is different from that which is usually observed for polycrystalline platinum electrode surfaces, *i.e.*, the hydrogen deposition and oxidation peaks at 0.23 V is much smaller than the peak found at lower potential. Sweeping the potential to values progressively higher than 0.55 V, however, eventually produces a cyclic voltammogram which is identical to that obtained for polycrystalline platinum electrode surfaces. This gradual progression is shown in curves 2 through 4 of Figure 9. The change in the relative intensities of the hydrogen deposition and oxidation waves reflects a modification of the initial polycrystalline platinum surface, due to the interaction of CO adsorbed in the hydrogen potential region, and a reconstruction of the original surface structures be excursions into the oxygen electrosorption region.

These data support the notion that the crystallographic and hence the electrocatalytic nature of the platinum surface can be strongly affected by the potential at which the CO is adsorbed. At 0.05 V the change in the morphology of the platinum electrode surface favors the formation of more bridged CO (a) than in the case of adsorption at 0.4 V.

CONCLUSION

It is clear from these observations that the oxidation of CO on platinum electrodes proceeds differently when CO is adsorbed at different electrode potentials in acid electrolytes. In the previous report,[2] when the CO was adsorbed at 0.4 V in the double layer region, it was determined that the oxidation occurs at the edges of adsorbed CO islands. This causes the CO stretching frequency shift to be due principally to a change in the electrode potential, *i.e.*, the first order Stark shift[17-19] rather than to coverage dependent dipole-dipole coupling.[21]

The processes which take place when the CO is adsorbed at 0.05 V in the hydrogen region are not completely clear. It is possible that there is some relation to what is observed in the cyclic voltammetry of well prepared single crystal Pt electrodes in aqueous HF.[22] It was found that the Pt(100) surface produced an unusual cathodic spike followed by an anodic peak after the electrode had been swept into the hydrogen region. The effect is removed by cycling into the oxygen electrosorption region. In this case it was thought that adsorption of some impurity, most likely CO which is a common component of the residual gas of UHV systems, was the cause of this behavior, becasue the adsorption in UHV of CO on the Pt electrode accentuated the cathodic spike.

In the case of CO adsorption in the hydrogen region, based on the results obtained here and discussed in the previous section, we are inclined to hypothesize that this process causes morphological changes on the initial polycrystalline platinum surface which favor a higher concentration of bridged CO(a) than when the CO is adsorbed in the double layer region. The fact that the oxidation of linear CO(a) occurs at potentials which differ by 100 mV (seen in Figures 3 and 6), depending on whether the solution is deuterated or not, strongly suggests the involvement of the hydrogen atom in the CO oxidation process. There are examples of CO adsorption or coadsorption with other species which seem to result in modification of the crytallographic structure of the substrate model. One is the case of catalytic CO oxidation on Pt(100) surface[23] in which the top most surface layer oscillates between the reconstructed (hex) phase and the nonreconstructed 1x1 phase of the Pt(100) surface. The other less clear example is the irreversible change in the SERS bands of pyridine on silver films when CO is coadsorbed in vacuum.[24] The observed changes can be attributed to some morphological change of the silver surface. The first example is observed at about 200°C, well above room temperature, while the second example takes place close to liquid N_2 temperatures.

The site for bridged CO(a) can be considered to be the active electrocatalytic site. The bridged CO(a) are oxidized more readily than linear CO(a) causing the prewave which peaks at 0.34 V. The removal of the oxidized bridged CO creates vacancies into which adjacent linear CO(a) diffuse. This leads to an immediate decrease in the average dipole-dipole interaction between the linear CO(a) which is reflected in the deviation of the frequency shift from linear potential dependence. As the bridged CO(a) is depleted there may be a momentary decrease in the overall oxidation rate but the resulting vacancies facilitate the oxidation of linear CO(a) which becomes increasingly rapid as the linear CO(a) density decreases.

We, of course, can not claim to know exactly how the oxidation takes place and the above is our best estimate, most likely oversimplified. The restoration of the original polycrystalline surface through excursions into the oxygen electrosorption region is undoubtedly similar to the case of Pt in HF described in Ref. 22. The mechanism by which the initial modification of the surface takes place during CO adsorption on platinum in the hydrogen region and the exact structure of the site for bridged CO bonding are remaining mysteries.

ACKNOWLEDGEMENTS

This work has been supported in part by the Office of Naval Research.

REFERENCES

1. Golden, W. G.; Kunimatsu, K.; Seki, H. *J. Phys. Chem.*, **1984**, *88*, 1275.
2. Kunimatsu, K.; Golden, W. G.; Seki, H.; Philpott, M. R. *Langmuir*, **1985**, *1*, 245.
3. Breiter, M. W. *J. Electroanal. Chem.*, **1979**, *101*, 329.
4. Gilman, S. *J. Phys. Chem.*, **1963**, *67*, 78.
5. Brummer, S. B.; Ford, J. I. *J. Phys. Chem.*, **1965**, *69*, 1355.
6. Beden, B.; Blimes, S.; Lamy, C.; Leger, J. M. *J. Electroanal. Chem.*, **1984**, *164*, 129.
7. Furuya, N.; Motoo, T. Proc. of the Fall Conf. of Japan Electrochemical Soc., **1982**, p. 16.
8. Czerwinskin, A.; Sobkowski, J. *J. Electroanal. Chem.*, **1978**, *91*, 47.
9. Breiter, M. W. *J. Phys. Chem.*, **1969**, *73*, 3283.
10. Breiter, M. W. *J. Phys. Chem.*, **1968**, *72*, 1305.
11. Breiter, M. W. *J. Electroanal. Chem.*, **1985**, *180*, 25.
12. Grambow, L.; Bruckenstein, S. *Electrochim. Acta*, **1977**, *22*, 377.
13. Stonehart, P. *Electrochim. Acta*, **1973**, *18*, 63.
14. Kazarinov, W. E.; Andreev, W. N.; Tysyachnaya, G. J. *Elektrokhimiya*, **1972**, *6*, 927.
15. Golden, W. G.; Saperstein, D. D. *J. Electron Spectrosc.*, **1983**, *30*, 43.
16. Seki, H.; Kunimatsu, K.; Golden, W. G. *Applied Spectrosc.*, **1985**, *39*, 437.
17. Lambert, D. K. *Solid State Commun.*, **1984**, *51*, 297.
18. Bagus, P. S.; Mueller, W. *Chem. Phys. Lett.*, **1985**, *115*, 540.
19. Bagus, P. S.; Mueller, W.; Seki, H. to be submitted.
20. Scortichini, G. L.; Reilly, C. N. *J. Electroanal. Chem.*, **1982**, *139*, 233, 247, 265, and the references therein.
21. Crossley, A.; King, D. A. *Surf. Sci.*, **1977**, *68*, 528.
22. Wagner, F. T.; Ross, Jr., P. N. *J. Electroanal. Chem.*, **1983**, *150*, 141.

23. Imbihl, R.; Cox, P. M.; Ertl, G.; Muller, H.; Brenig, W. *J. Chem. Phys.*, **1985**, *83*, 1578.

24. Seki, H. *J. Vac. Sci. Technol.*, **1982**, *20*, 584.

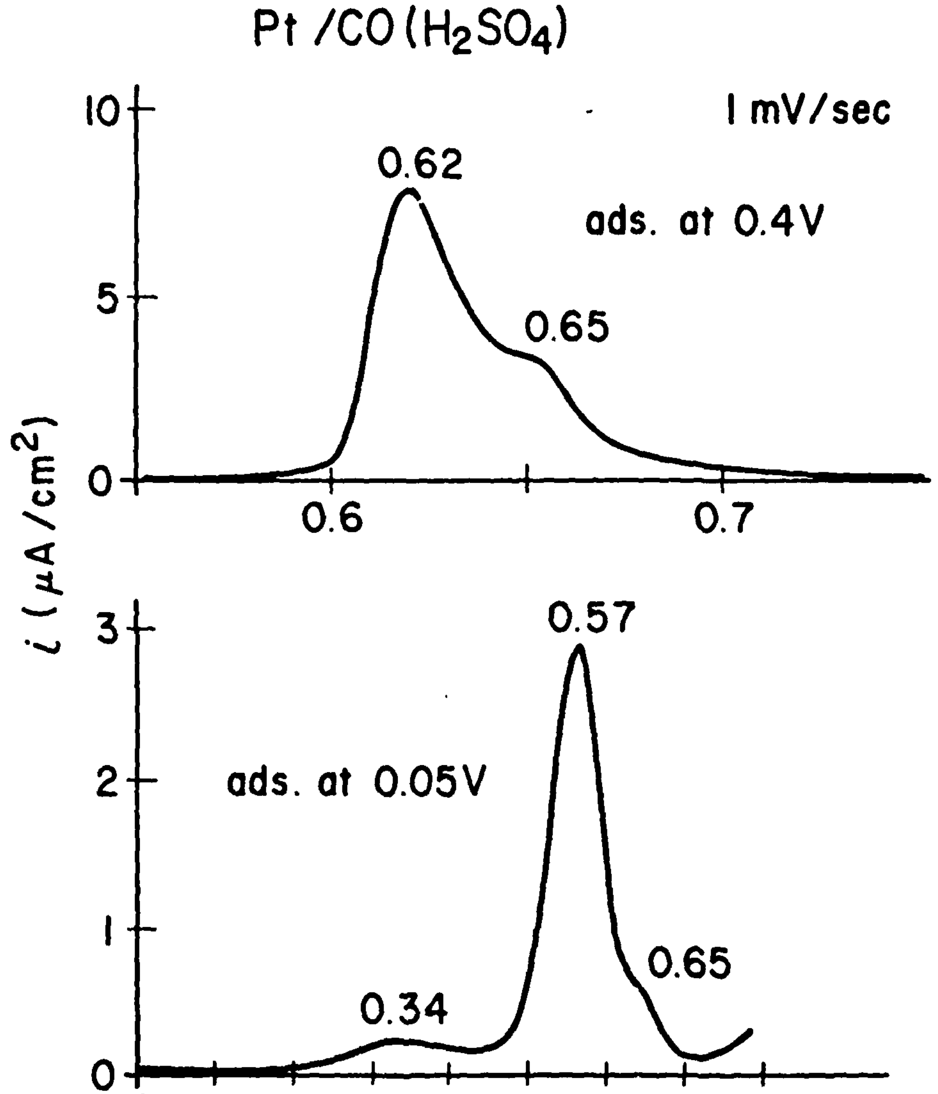


Figure 1. Linear sweep voltammograms for the oxidation of the adsorbed CO on a platinum electrode (1 mV/sec). Above) CO adsorbed at 0.4 V. Below) CO adsorbed at 0.05 V. Note the different electrode potential scales for the two graphs.

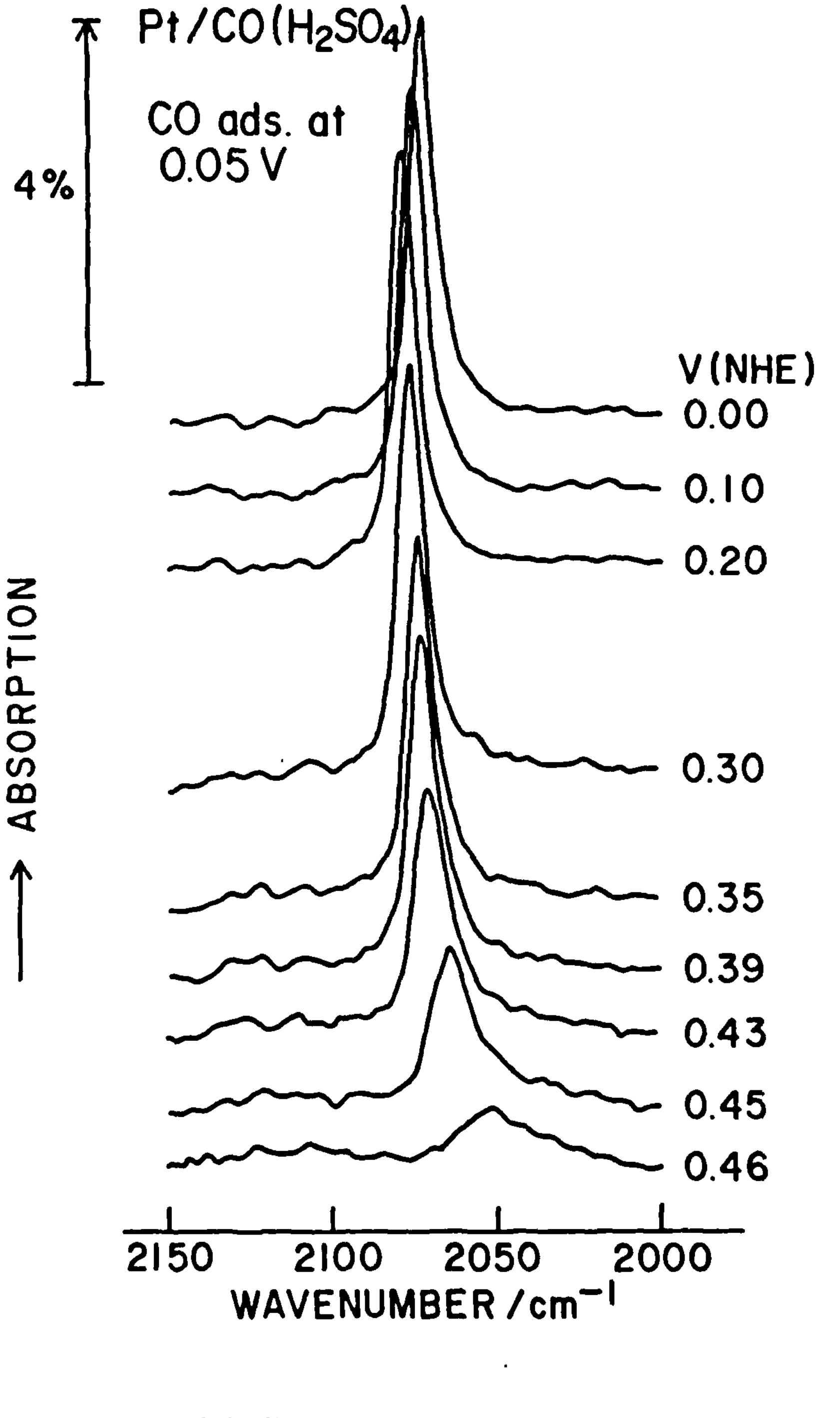


Figure 2. FT-IRRAS spectra of the linear CO(a) species adsorbed at 0.05 V on a platinum electrode in 0.5 M H_2SO_4 for various electrode potential.

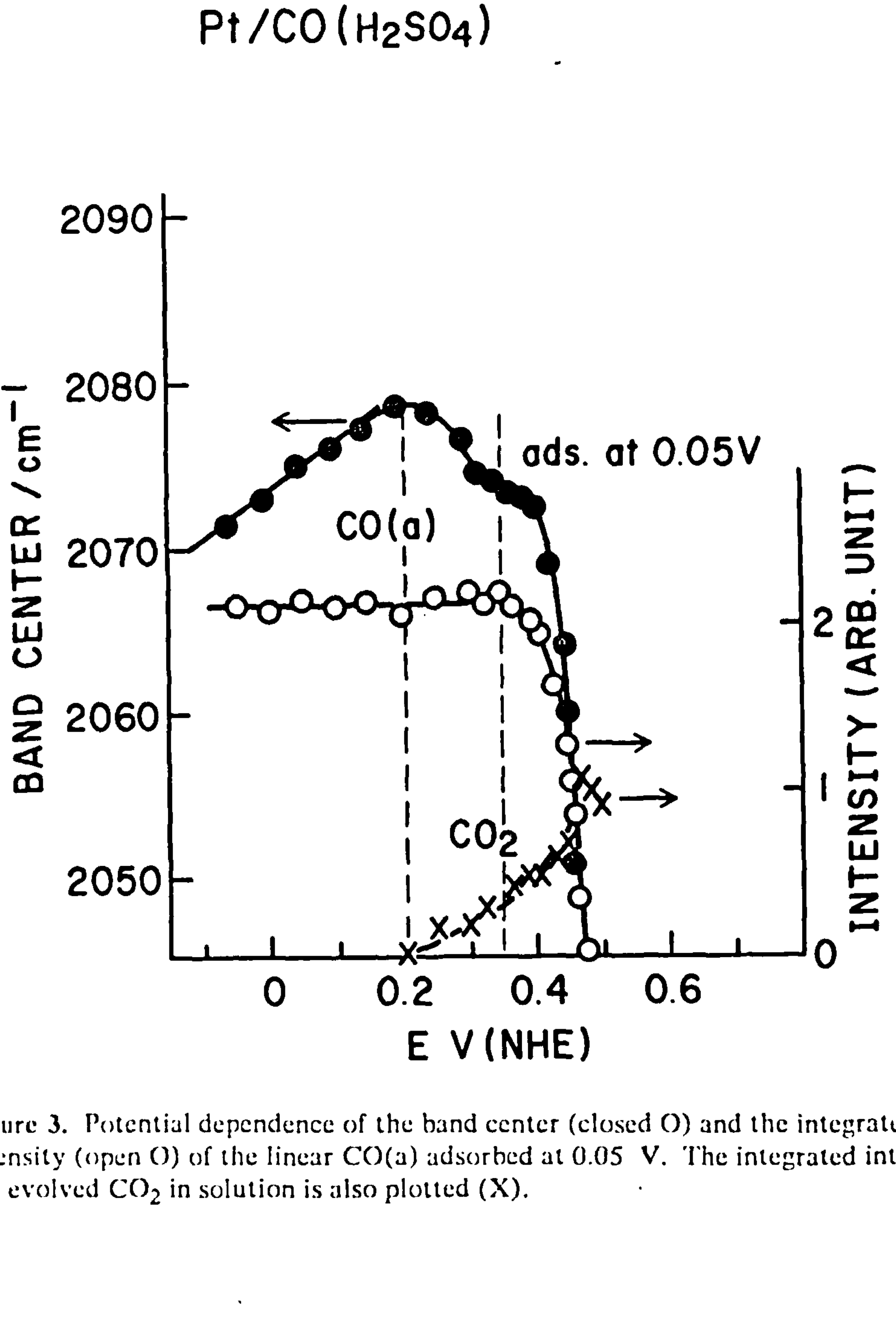


Figure 3. Potential dependence of the band center (closed O) and the integrated band intensity (open O) of the linear CO(a) adsorbed at 0.05 V. The integrated intensity of the evolved CO_2 in solution is also plotted (X).

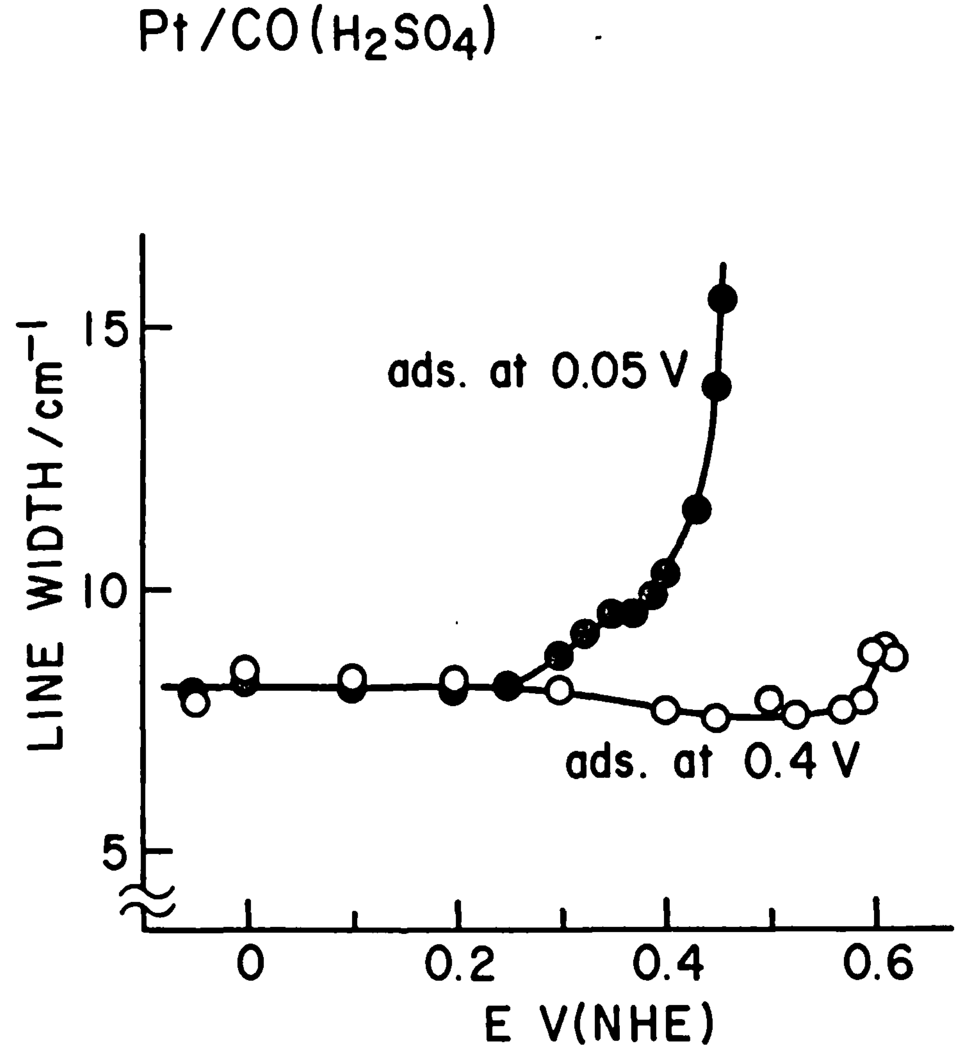


Figure 4. Potential dependence of the linewidth of the FT-IRRAS band due to linear CO(a) adlayer produced at 0.4 V and 0.05 V.

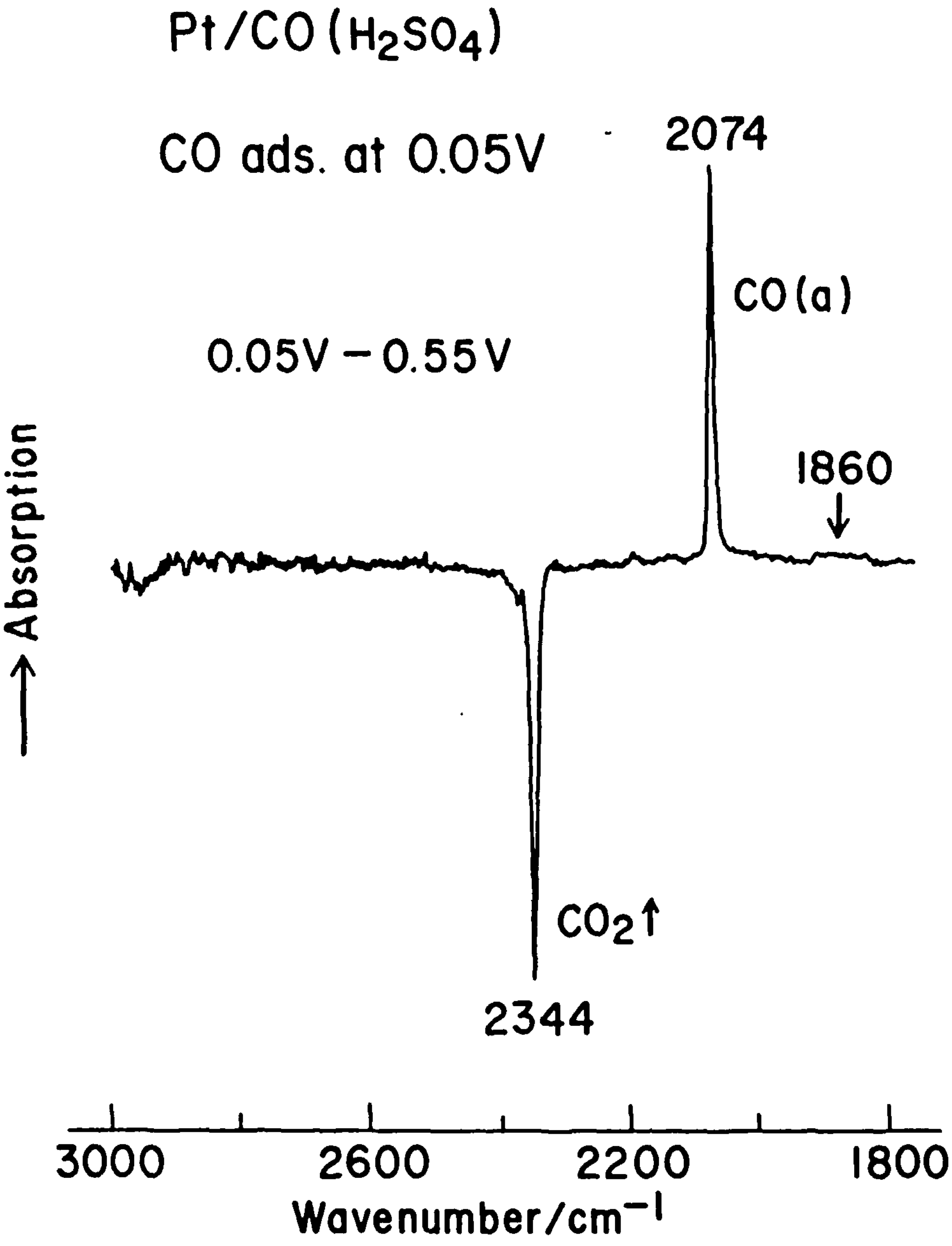


Figure 5. The FT-IRRAS spectrum of the platinum/solution interphase after CO had been adsorbed at 0.05 V. The spectrum is referred to 0.55 V, at which an intense CO_2 spectrum is seen.

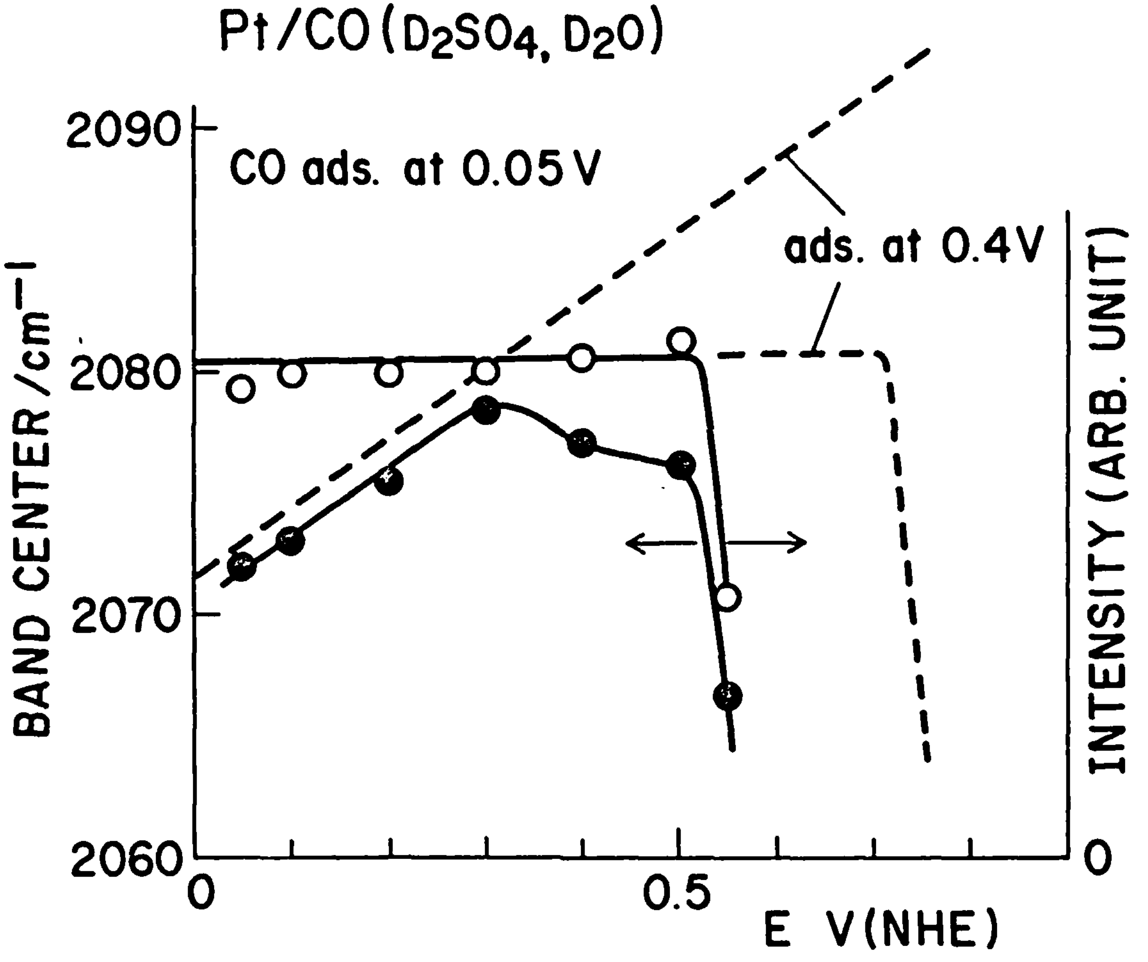


Figure 6. Potential dependence of the 1) band center and 2) integrated band intensity of the linearly adsorbed CO layer at 0.05 V on a platinum electrode in D_2O/D_2SO_4 system.

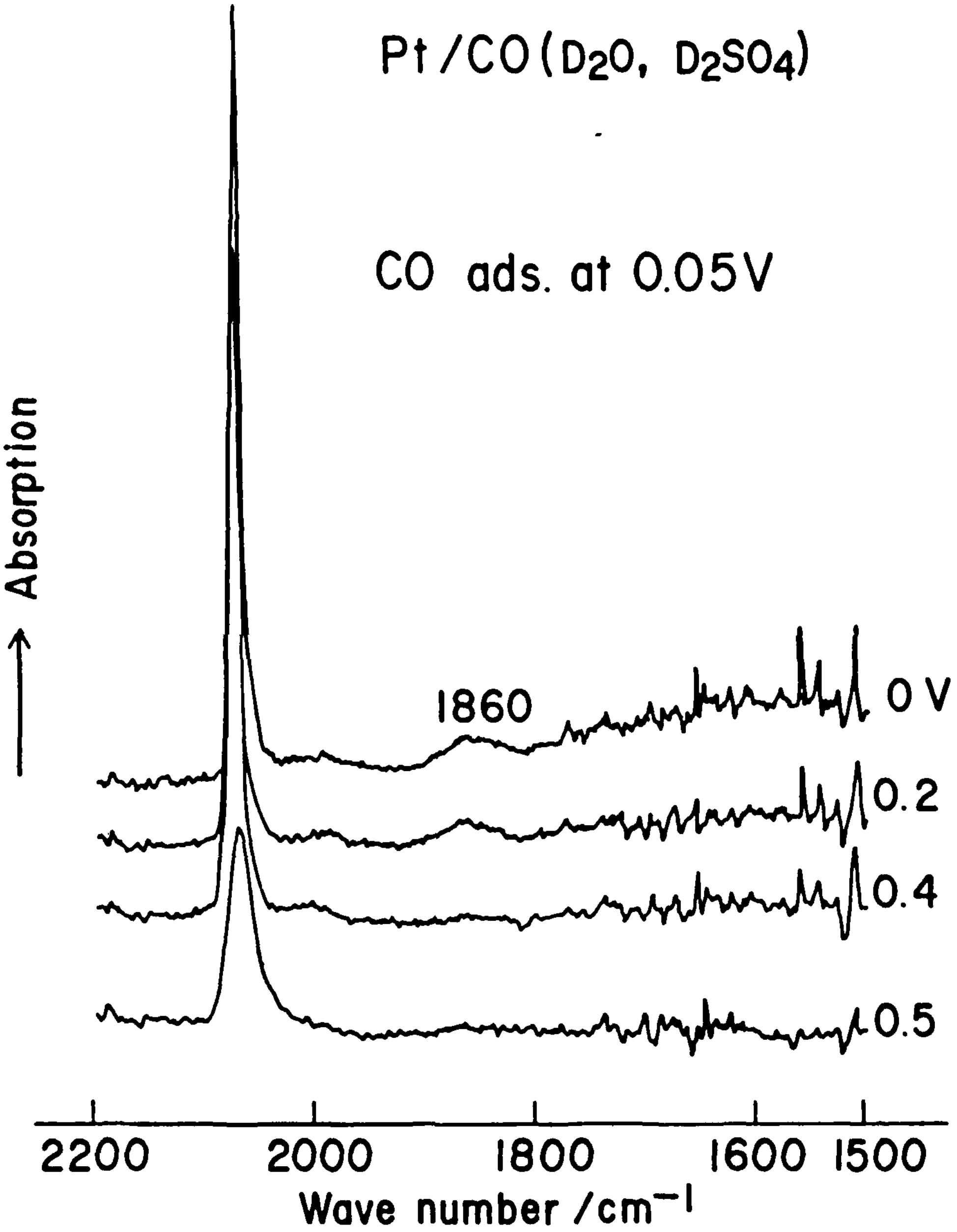


Figure 7. The FT-IRRAS spectra between 1500 and 2200 cm^{-1} for the D_2O/D_2SO_4 system for various potentials. CO was adsorbed at 0.05 V.

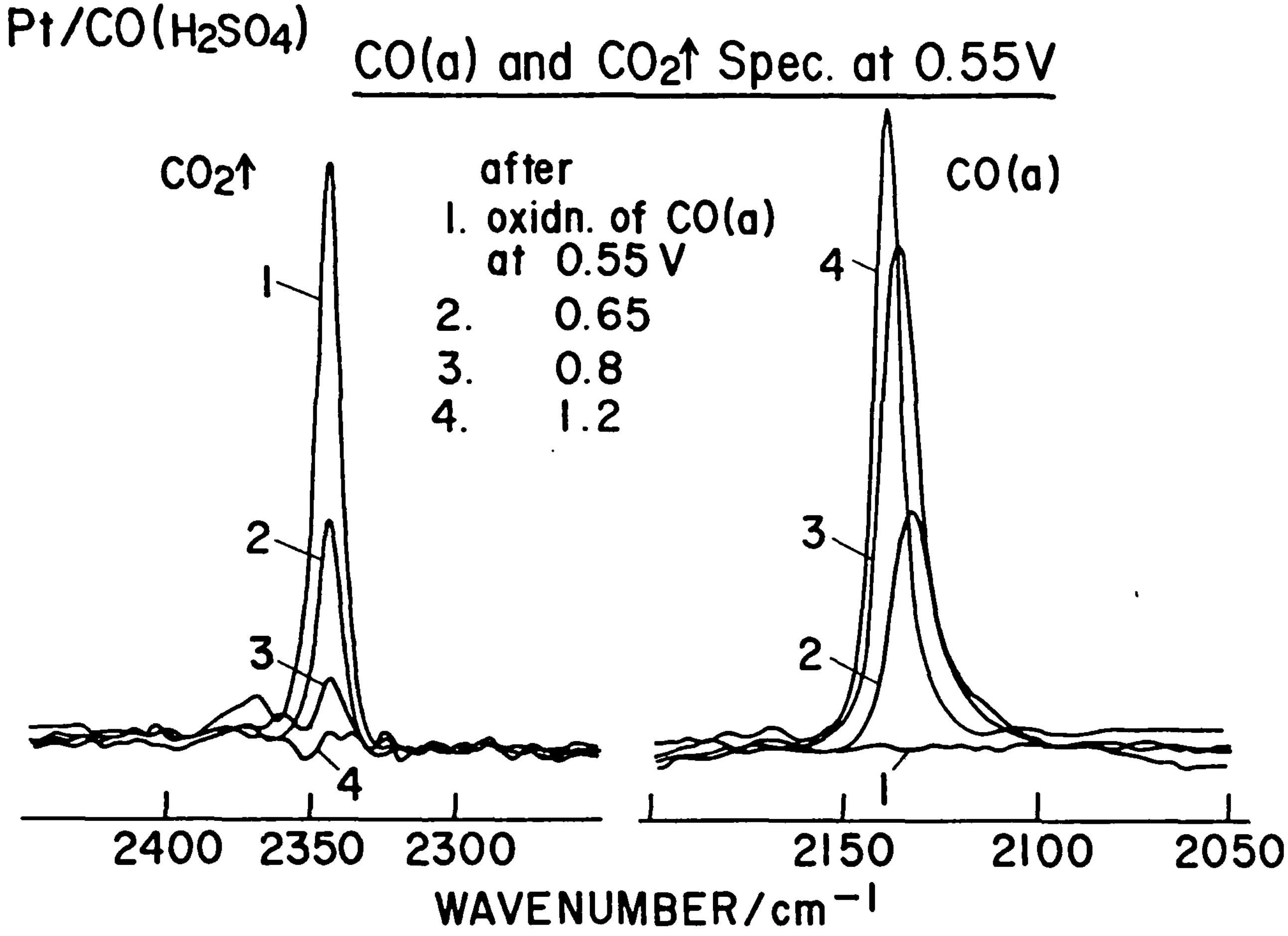


Figure 8. FT-IRRAS spectra of the linear CO(a) and of the CO_2(aq) at 0.55 V. The experimental conditions are the same as in Figure 5. The CO_2 spectra and CO(a) spectra are referenced to 0.0 V and 0.8 V, respectively.

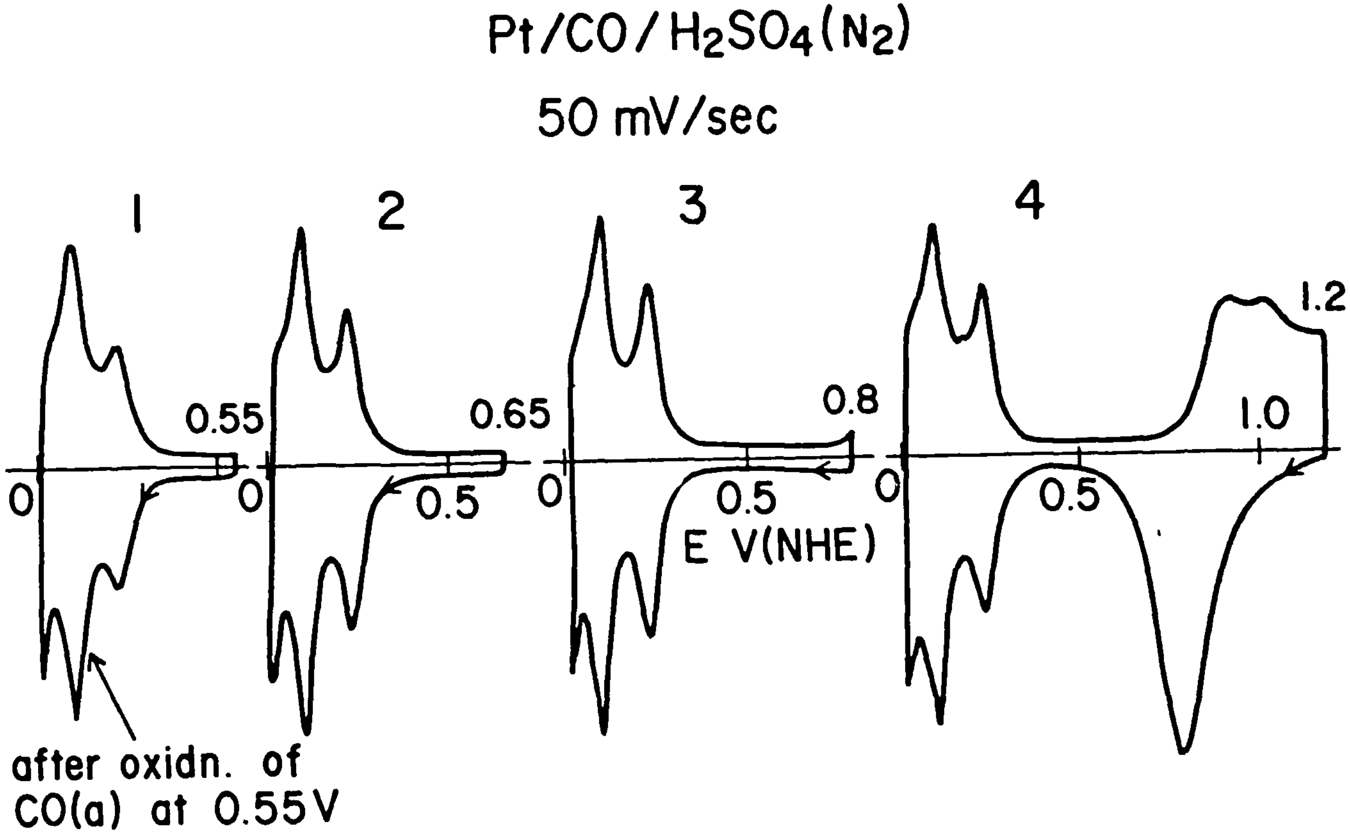


Figure 9. Cyclic voltammograms of the platinum electrode in the hydrogen potential region: 1) after oxidation of CO(a) at 0.55 V; after the potential was cycled between: 2) 0.55 V and 0.65V, 3) 0.55 V and 0.8 V, 4) 0.55 V and 1.2 V.

END

DTIC

8-86