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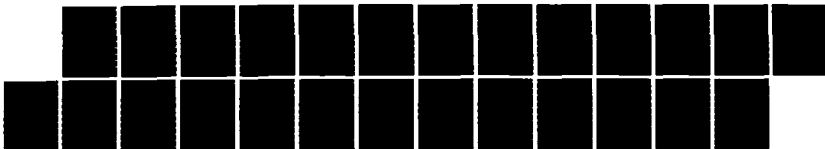
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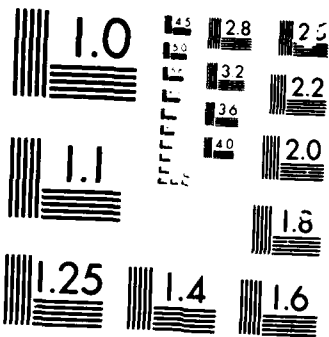
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potassium sulfate. The absorption intensity of the CO on platinum electrode is ca. 4-5% while that of the  $\text{CN}^-$  on silver and gold is 0.2-0.5%. The potential dependence of the vibrational spectra was observed for both systems. Oxidation of the linearly adsorbed CO layer proceeds by different mechanisms depending on whether CO was adsorbed at a potential in the double layer region or in the hydrogen region, i.e., at the edges of the CO islands in the former case and randomly in the latter case, in which the bridged CO species plays an important role. The vibrational frequency of the linearly adsorbed CO changes linearly with potential at a rate of  $30 \text{ cm}^{-1}/\text{volt}$ , which is independent of anion specific adsorption. The origin of the shift is most reasonably explained by the first order Stark effect. For Ag, Au/ $\text{CN}^-$  systems, the surface cyanide species is the linearly adsorbed  $\text{CN}^-$ . The anodic reaction products in the solution from cyanide ions and the electrode metals are also observed in the vibrational spectra. The bands due to surface species and those due to solution species are distinguished by measuring the spectra with s and p-polarized lights.



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## ELECTRODE/ELECTROLYTE INTERPHASE STUDY USING POLARIZATION MODULATED FT-IR REFLECTION ABSORPTION SPECTROSCOPY

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**ABSTRACT:** The polarization modulated Fourier transform infrared reflection-absorption spectroscopy (FT-IRRAS) is applied to the studies of adsorption and oxidation of  $^{13}\text{CO}$  on a platinum electrode in 0.5M sulfuric acid and of adsorption of cyanide on gold and silver electrodes in 0.5M potassium sulfate. The absorption intensity of the CO on platinum electrode is ca. 4-5% while that of the  $\text{CN}^-$  on silver and gold is 0.2-0.5%. The potential dependence of the vibrational spectra was observed for both systems. Oxidation of the linearly adsorbed CO layer proceeds by different mechanisms depending on whether CO was adsorbed at a potential in the double layer region or in the hydrogen region, i.e., at the edges of the CO islands in the former case and randomly in the latter case, in which the bridged CO species plays an important role. The vibrational frequency of the linearly adsorbed CO changes linearly with potential at a rate of  $30 \text{ cm}^{-1}/\text{volt}$ , which is independent of anion specific adsorption. The origin of the shift is most reasonably explained by the first order Stark effect. For Ag, Au/ $\text{CN}^-$  systems, the surface cyanide species is the linearly adsorbed  $\text{CN}^-$ . The anodic reaction products in the solution from cyanide ions and the electrode are also observed in the vibrational spectra. The bands due to surface species and those due to solution species are distinguished by measuring the spectra with s and p-polarized lights.

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## INTRODUCTION

The feasibility of infrared reflection absorption spectroscopy (IRRAS) as an in-situ probe of the electrode/electrolyte interphase was demonstrated initially by Bewick and coworkers<sup>1</sup> utilizing electrochemically modulated infrared spectroscopy (EMIRS). An EMIRS spectrum is a difference spectrum between two potentials and being a differential method has high sensitivity in detecting the vibrational spectra of adsorbed species at the electrode/electrolyte interphase.

Russell et al<sup>2,3</sup>, applied the polarization modulation method using a grating spectrometer to obtain vibrational spectra of CO adsorbed on a platinum electrode at fixed potentials. A similar attempt was made by Kunimatsu<sup>4-7</sup> by utilizing the linear potential sweep method at fixed wave numbers: the vibrational spectra of CO species produced upon chemisorption of methanol molecules onto a platinum electrode (4-6) and of CO adsorbed on a palladium electrode<sup>7</sup> were measured as a function of the electrode potential. The shift of the C-O stretching frequency of adsorbed CO with electrode potential, which was first observed by the EMIRS measurements of Beden et al.<sup>8</sup>, was verified quantitatively by these studies.

The FTIR spectrometer was introduced for in-situ spectroscopic study of the electrode/electrolyte interphase by Neugebauer et al.<sup>9-11</sup>, Pons et al.<sup>12-16</sup> and Aurian-Blajeni et al.<sup>17</sup> The measurements were done using p-polarized IR radiation and taking the spectral difference between two potentials.

Here, we present some of the main results from our recent studies of adsorption and oxidation of CO on a platinum electrode and adsorption of  $\text{CN}^-$  on silver and gold electrodes. These results were obtained by combining the technique of rapid

polarization modulation in IRRAS<sup>18,19</sup> with a FTIR spectrometer for the in-situ study of electrode/electrolyte interphases. In addition to the established advantages of FTIR spectroscopy, this combination results in the reduction of the background IR intensity and a complete compensation of the atmospheric IR absorption without having to modulate the electrode potential. Recently we have used this technique and demonstrated that a full spectra can be obtained from a submonolayer of species adsorbed on the electrode<sup>20-22</sup>.

Adsorption and oxidation of carbon monoxide on a platinum electrode has been the subject of many investigations over the last two decades because of its importance in fuel cells<sup>23-27</sup>. It is generally agreed since Gilman<sup>23</sup> that the so-called linearly adsorbed carbon monoxide is produced, in most cases, as the predominant surface species when CO adsorbs onto a platinum electrode. It has also been reported by Breiter<sup>28,29</sup>, Grambow and Bruckenstein<sup>30</sup> and Cerwinski and Sobkowski<sup>31</sup> that the electrochemical behaviour of the adsorbed CO layer depends on whether CO adsorbed at a potential in the double layer region or in the hydrogen region.

Adsorption of cyanide ions and its electrochemical behaviour on silver and gold electrodes are of great interest for two reasons: first, to understand the role of cyanide as an important ingredient in plating baths of these metals and second, because of the recent surface enhanced Raman scattering (SERS) measurements of their vibrational spectra<sup>32-47</sup>

## EXPERIMENTAL

The rapid polarization modulated FT-IRRAS was carried out using an IBM Instruments Inc., IR/98 FTIR spectrometer with a gold wire grid polarizer and a Hinds International Inc., ZnSe photoelastic modulator. The frequency of the polarization modulation was 78 kHz. The details of the technique and the arrangement in the sample chamber of the FTIR spectrometer are described elsewhere<sup>19-22</sup>. The angle of incidence at the window/electrolyte interface was 60°. All FT-IRRAS spectra were taken with 4 cm<sup>-1</sup> resolution using either a MCT (Infrared Associates) or an InSb (Santa Barbara Research Center) detector cooled to Liquid N<sub>2</sub> temperature. Three hundred interferograms were usually collected and coadded at each potential to improve the S/N ratio taking about 10 minutes. All experiments were carried out in ambient. The reference electrode was Ag/AgCl(3M KCl saturated by AgCl) but the potentials are reported here in terms of the NHE scale.

For studies of the CO/Pt system a spectro-electrochemical cell made from pyrex glass was used with a CaF<sub>2</sub> prism window. Adsorption of carbon monoxide was carried out by bubbling CO gas through the solution. The potential of the platinum electrode during this process, either at 0.05V or 0.4V, determined whether CO was adsorbed in the hydrogen region or in the double layer region, respectively. Adsorption of cyanide on silver and gold electrodes were studied in 0.5M potassium sulfate solution containing either 10<sup>-2</sup> or 10<sup>-1</sup>M KCN. The spectro-electrochemical cell used in this case was made from Kel-F.

## RESULTS AND DISCUSSION



## 1. Adsorption and oxidation of CO on a Platinum electrode in 0.5M H<sub>2</sub>SO<sub>4</sub>

### 1.1 Potential dependence of the adsorbed CO spectra

In Figure 1 the FT-IRRAS spectra of the adsorbed CO layers are shown between 2000 and 2150 cm<sup>-1</sup> at various electrode potentials for the two different adsorption cases: Figure 1a is the case of CO adsorption in the double layer region (0.4V) and Figure 1b is the case of adsorption in the hydrogen region (0.05V). All the spectra are referred to 0.8V at which voltage the electrode surface is free from adsorbed CO. The spectra are assigned to the linearly adsorbed CO species by their spectral position. The shift of the C-O stretching frequency with potential and the sharp decrease of the band intensity at higher potentials, due to the onset of electro-oxidation of the adsorbed CO layer, are commonly observed although the shift takes place in different ways in the two cases. In Figure 2a,b,c the integrated band intensity, CO stretching frequency and the line width are plotted as a function of potential. In Figure 2a the integrated absorption intensity of the carbon dioxide evolved at each potential is also plotted. The absorption intensity of CO<sub>2</sub> is referred to 0V at which no oxidation of the adsorbed CO takes place. The ability of detecting the minute amount of CO<sub>2</sub> evolved in on the electrode owes to the thin layer structure of the cell the cancellation of the atmospheric CO<sub>2</sub> absorption by polarization modulation and the difference of the intensities of the of the p and s-polarized lights in the thin layer region, the thickness of which is ca. a quarter of the wave length for the CO<sub>2</sub> absorption<sup>22</sup>.

For CO adsorbed at 0.4V, the intensity is constant throughout the potential range until the onset of electro-oxidation of the CO layer, and the evolution of carbon dioxide takes place simultaneously with the oxidation of the adsorbed CO layer. The C-O stretching frequency shifts linearly with potential at a rate of 30 cm<sup>-1</sup>/volt, upon

which the sharp coverage decrease due to the electro-oxidation has little effect, and the line width is almost constant, ca.  $8\text{-}9\text{ cm}^{-1}$ , but increases slightly, by ca.  $2\text{ cm}^{-1}$ , in the process of the oxidation.<sup>48</sup>

For CO adsorbed at 0.05V, the intensity of the adsorbed CO is constant up to 0.40V and then decreases sharply. However the evolution of  $\text{CO}_2$  starts after ca. 0.2V, while the intensity of the linearly adsorbed CO remains constant. This implies that there is another surface species which is oxidized first giving rise to the early evolution of  $\text{CO}_2$ . Furthermore, the C-O stretching frequency starts deviating from linearity at ca. 0.2 V showing a plateau before 0.40V and then decreases sharply. The line width increases slightly, ca.  $2\text{ cm}^{-1}$ , between 0.2V and 0.40V and then increases sharply after 0.40V.<sup>49</sup>

## 1.2 Mechanism of oxidation of the adsorbed CO layers on the electrode

We have seen that the IR spectroscopic behaviour of the linearly adsorbed CO layers produced at 0.05V and 0.4V is quite different during their electro-oxidation process. In summary, oxidation of the CO layer produced at 0.4V proceeds without the C-O stretching frequency and line width being affected to an appreciable extent by the decrease in the surface coverage of the CO layer, while these vibrational parameters are greatly affected during the oxidation of the linearly adsorbed CO layer produced at 0.05V. The sharp contrast between the behaviour of the two types of CO layers implies a different oxidation mechanism in the two cases. The former case is very similar to the heterogeneous oxidation of the linearly adsorbed CO layer on Pt(111) in the gas phase with oxygen, observed by Shigeishi and King<sup>50</sup>. They observed no shift of the C-O stretching frequency with the decrease of the surface coverage during the oxidation and that led them to conclude an oxidation mechanism in

which it proceeds at the edges of the CO islands between the adsorbed CO molecules and oxygen atoms. It is reasonable to conclude that the process is the same for the electro-oxidation of the CO layer produced at 0.4V.

For the linearly adsorbed CO layer produced at 0.05V, its oxidation mechanism would be an alternative to that of the CO layer adsorbed at 0.4V. It is in fact almost straightforward to conclude a mechanism in which the oxidation proceeds randomly or uniformly in the linearly adsorbed CO layer. The reason why this case is different is closely related to the existence of another surface species which is oxidized first from ca. 0.2V giving rise to the evolution of CO<sub>2</sub> before the predominant linearly adsorbed CO layer is oxidized as shown in Figure 2a. Based on electrochemical determination of the charge to oxidize this surface species, it was shown that the surface species contributes ca. 10% to the total oxidation charge of the adsorbed layer on the platinum electrode.<sup>49</sup> Therefore, after oxidation of the surface species there would be vacant sites accessible for water molecules to adsorb and react with the linearly adsorbed CO molecules at higher potentials. The decrease of the C-O stretching frequency and the increase of the line width between 0.2V and 0.4V as shown in Figure 2b and c can be explained as a result of the oxidation of the minor surface species which would give rise to the decrease of the interaction between the species and the linearly adsorbed CO molecules. This minor surface species has turned out in fact to be bridge bonded CO species which gives rise to a very weak and broad band around 1860 cm<sup>-1</sup>.<sup>49</sup>

1.3 Origin of the C-O stretching frequency shift with potential under constant coverage

In Figure 2b, curve 1, it was seen that the C-O stretching frequency shifts with the electrode potential at a rate of  $30 \text{ cm}^{-1}/\text{volt}$  under a constant surface coverage. Ray and Anderson<sup>51</sup> tried to explain the shift by a theoretical calculation for a  $\text{Pt}_4(\text{CO})_2$  system in which they simulated the increase of the positive potential by increasing the valence state ionization potential of the Pt atoms. The treatment led to a decreased occupancy of the  $2\pi^*$  antibonding level of the adsorbed CO molecules in going to more anodic potentials, resulting in vibrational frequency increase. The rate of increase, however, was too high for the treatment to be satisfactory.

Recently, Holloway and Norskov<sup>52</sup> estimated the shift using empirically determined values of the resonance position and width for the  $2\pi^*$  orbital of the adsorbed CO and assuming that the antibonding level shifts with the applied potential linearly with a slope of 0.4, i.e., the adsorbed CO molecules experience approximately 40% of the applied potential. Their results led to a decreased occupancy of the antibonding orbital by the metal electrons as the potential was made more positive and the linearity as well as the slope of the frequency shift versus potential difference (from arbitrarily chosen points) were in agreement with the experimental results of Kunimatsu<sup>5</sup> and Beden et al.<sup>53</sup>

On the other hand, Lambert<sup>54</sup> reported recently that the applied electric field across the metal/gas interface could give rise to a shift of the vibrational frequency of the adsorbed CO molecules on Ni(111) in vacuum due to a first order Stark effect. He estimated the vibrational Stark tuning rates using empirical molecular parameters and obtained reasonable values of about  $9.5 \times 10^{-7} \text{ cm}^{-1}/(\text{V}/\text{cm})$  for CO on Ni which agree with the observed linear frequency shift.

Most recently *ab initio* calculations for a cluster model of CO chemisorbed on Cu(100) have been carried out, both without and with an applied electric field, which indicate that up to fields of the order of  $10^7$  V/cm there is very little change in the occupancy of the  $2\pi^*$  orbital. The molecular parameters required to obtain the Stark tuning rates were computed and gave essentially the same results reported by Lambert. These parameters also did not vary appreciably with the field.<sup>56</sup> Based on these results we are inclined to favor Lambert's proposal that the potential dependent linear frequency shift of the C-O stretching mode is primarily due to the first order Stark shift.

## 2. Adsorption of cyanide on silver and gold electrodes

Figure 4 shows the change of the FT-IRRAS spectrum of the silver/0.5M  $K_2SO_4$  interface with  $10^{-1}$ M KCN with potential. All the spectra are referred to the cyanide free solution. There are essentially four bands. The band centers of three of them, i.e., 2080, 2136 and 2167  $cm^{-1}$ , do not change with potential, while the band between the 2080 and 2136 bands shows shift of its band center with potential, which is a good indication that the band is due to surface species.

In the assignment of these bands, it is essential to know whether these bands are due to surface or solution species. Application of the surface selection rules can often provide clues to this question as will be described in the following experiments. Figure 5a and b are the spectra taken by using either p or s-polarized light. They are the spectral ratio between two potentials. In Figure 5a, the 2167 band is the one at 0.4V while the band at 2109 and 2080  $cm^{-1}$  are those at -0.6V. The 2080 band is seen by both s and p-polarized lights while 2109 and 2167 bands are seen only by p-polarized light. This proves that the band at 2080  $cm^{-1}$  is a solution band while the other two

are surface bands. From Figure 5b, it turns out that the band at  $2136\text{ cm}^{-1}$  is a solution band. The sharp peaks between  $2000$  and  $2050\text{ cm}^{-1}$  are the noise due to the water rotational bands in the air which are not readily compensated without the polarization modulation. Based on these results, we can refer to the vibrational frequencies of known cyano-silver complexes or the cyanide ion itself<sup>55</sup> for the assignment of the solution bands. Thus, the  $2080$  band is assigned to the cyanide ions in the solution while the  $2136$  band is to the  $\text{Ag}(\text{CN})_2^-$  complex ion which is the product of anodic reaction from ca.  $-0.4\text{V}$  between the cyanide ions and the silver electrode. The band at  $2167\text{ cm}^{-1}$  is an interesting example of a surface band which does not change its band position with potential. From its vibrational frequency it is most likely a band of AgCN solid deposited on the silver electrode.

The band which shifts with potential is certainly assigned to a surface cyanide species, which has often been assigned to cyano-silver complexes with different coordination numbers in the SERS studies.<sup>38,43,46</sup> However, both  $\text{Ag}(\text{CN})_2^-$  and AgCN bands disappear if the potential is reversed to the negative side due to the electrochemical reduction of these anodic reaction products. Therefore, it is unlikely that any cyano-silver complexes exist on the electrode surface as an adsorbate without being reduced at more negative potentials than ca.  $-0.5\text{V}$ . The most reasonable assignment of the surface cyanide band is to the linearly adsorbed cyanide ions itself.<sup>22,57</sup> The decrease of the band intensity at negative potentials is simply due to partial desorption of this anionic adsorbate at negative potentials. The shift of the C-N stretching frequency with electrode potential before the anodic reaction takes place, which was also seen by SERS<sup>42,43</sup>, is very similar to that of CO on platinum,

i.e., ca.  $30 \text{ cm}^{-1}/\text{volt}$ . Further discussions comparing the SERS and FT-IRRAS are presented elsewhere.<sup>57</sup>

The situation is very similar for the Au/CN<sup>-</sup> system as shown in Figure 6 which shows the change with potential of the FT-IRRAS spectrum of the system with  $10^{-2}\text{N}$  KCN. As the concentration of the cyanide is lower, the 2080 band due to the cyanide ions in the solution is hardly seen. The band at  $2146 \text{ cm}^{-1}$  which appears from ca.  $-0.7\text{V}$  is seen by both s and p-polarized lights as demonstrated in Figure 7 and readily assigned to the  $\text{Au}(\text{CN})_2^-$  complex ions in solution, a product of anodic reaction between the cyanide ions and the gold electrode. The band around  $2100 \text{ cm}^{-1}$  which shifts its position with potential is seen only by p-polarized light and assigned to the surface cyanide species. Because  $\text{Au}(\text{CN})_2^-$  is the only known complex between cyanide ions and gold and because the  $\text{Au}(\text{CN})_2^-$  band disappears when the potential is reversed more negative than  $-0.6 \text{ V}$  due to electrochemical reduction, it is most likely that the surface cyanide species is not a cyano-gold complex but the linearly adsorbed cyanide ions, contrary to the conclusion from SERS measurements alone.<sup>47</sup>

## CONCLUSION

It is clear from the preceding parts that the polarization modulation method combined with a FTIR can be applied to the in-situ studies of the electrode/electrolyte interphase successfully to give a quantitative as well as a qualitative spectroscopic information of the species involved in the electrochemical processes. The IR absorption intensity of the monolayer of CO on platinum electrode is ca. 4-5% while it is 0.2-0.5% for the adsorbed CN<sup>-</sup> on silver and gold electrodes, respectively. It should

be feasible to look at an adsorbed species with less IR absorption intensity than CO and  $\text{CN}^-$  on electrodes.

#### ACKNOWLEDGEMENT

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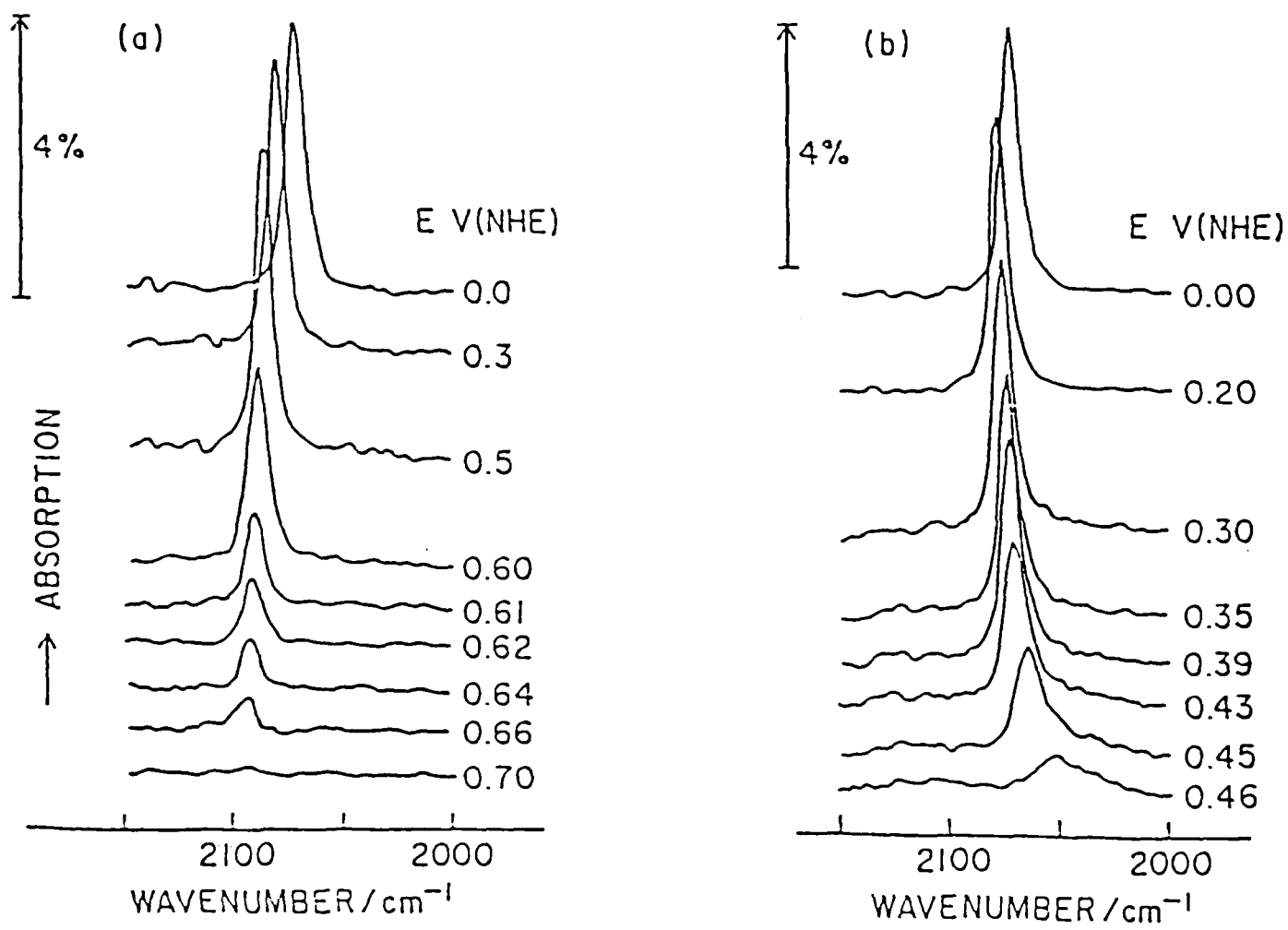


Figure 1. Change in the FT-IRRAS spectrum with potential of CO adsorbed at 0.4 V (a) and 0.05 V (b) on a platinum electrode in 0.1 M  $\text{H}_2\text{SO}_4$ .

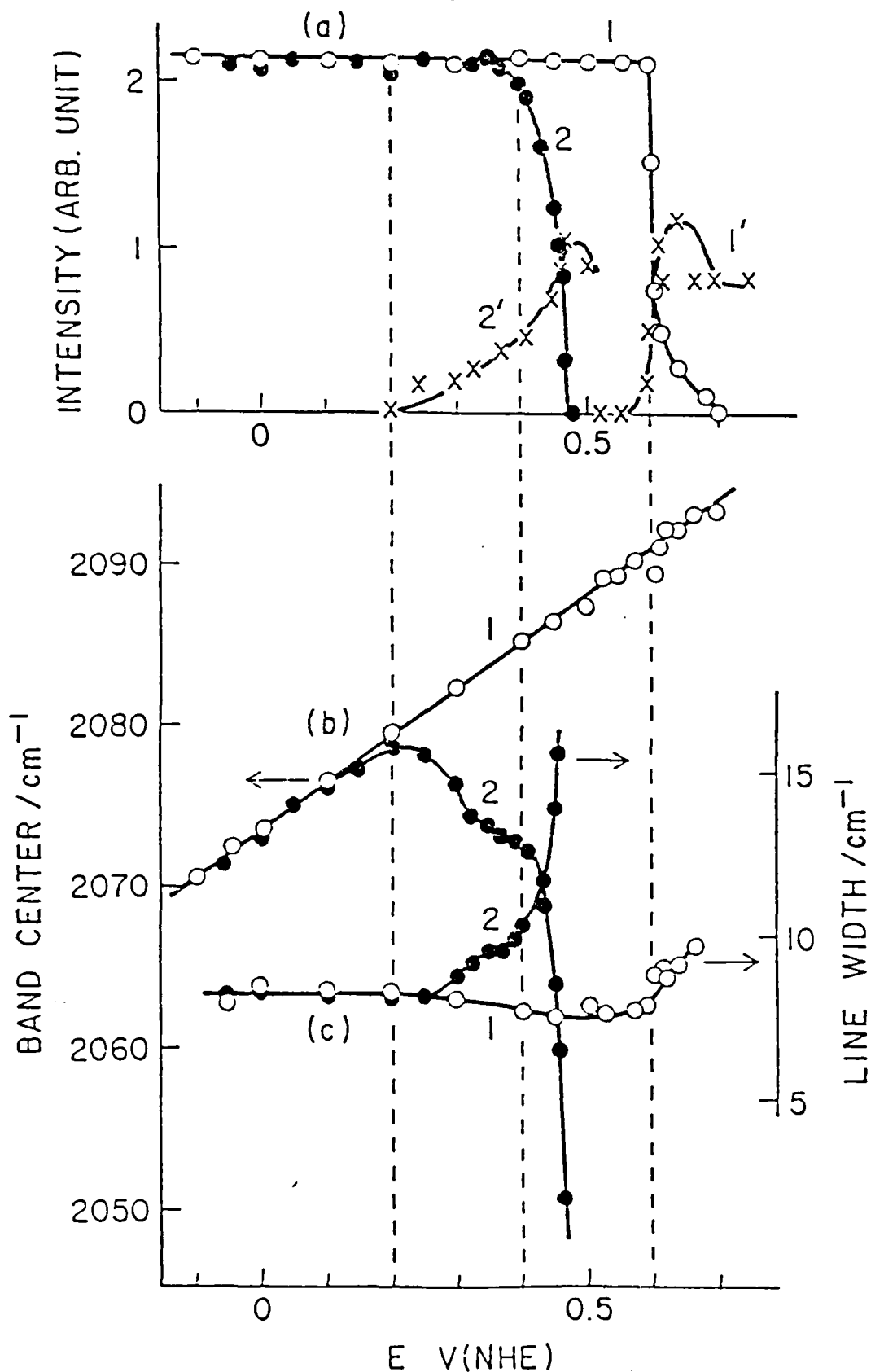


Figure 2. Potential dependence of the integrated IR absorption intensity (a), C-O stretching frequency (b) and line width (c) of the CO adsorbed at 0.4 V (curves 1) and 0.05 V (curves 2). The curves 1' and 2' in (a) are the IR absorption intensity of  $\text{CO}_2$  evolved at each potential.

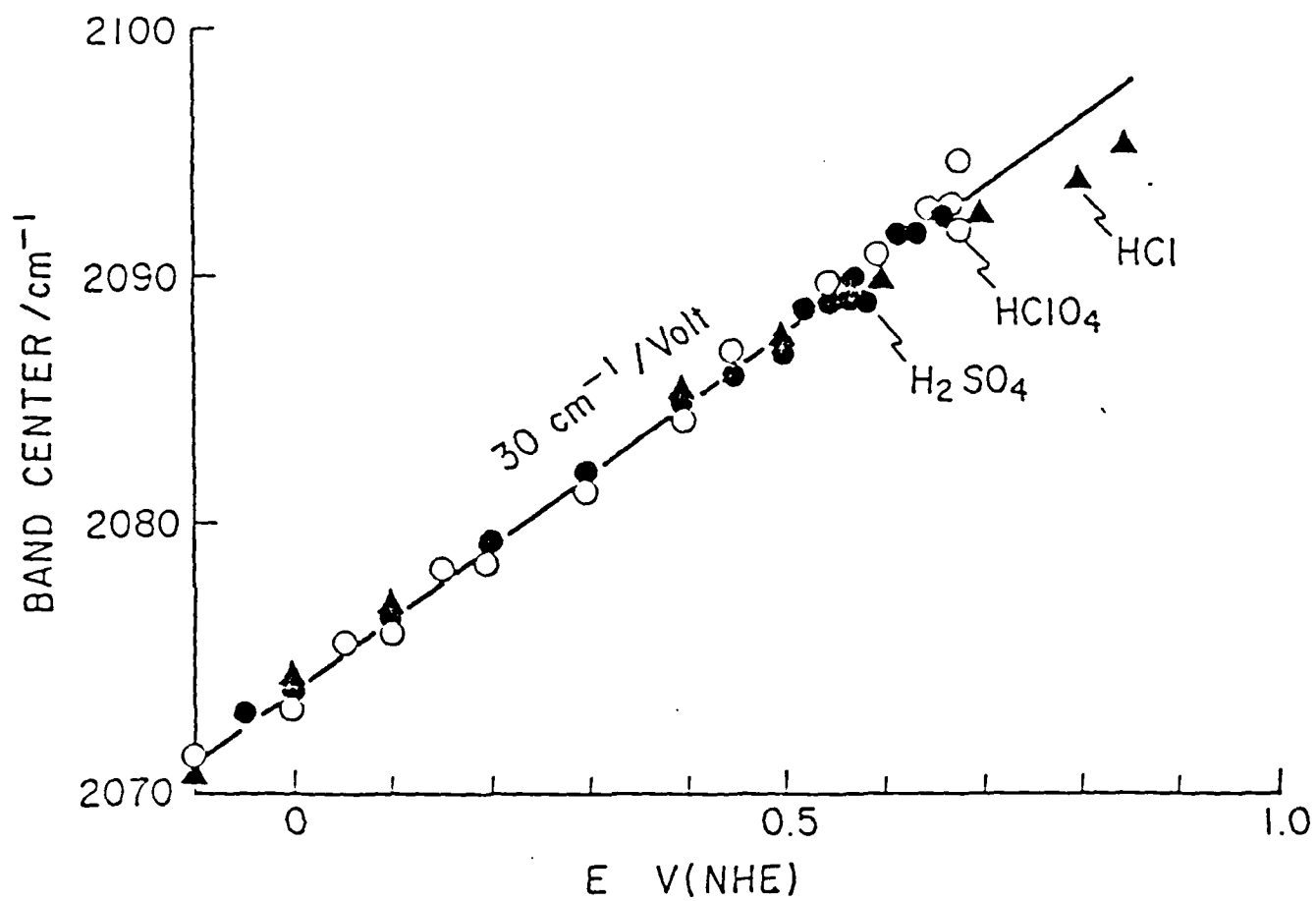


Figure 3. Effect of anions on the potential dependence of the vibrational frequency of the CO adsorbed on a platinum electrode at 0.4 V.

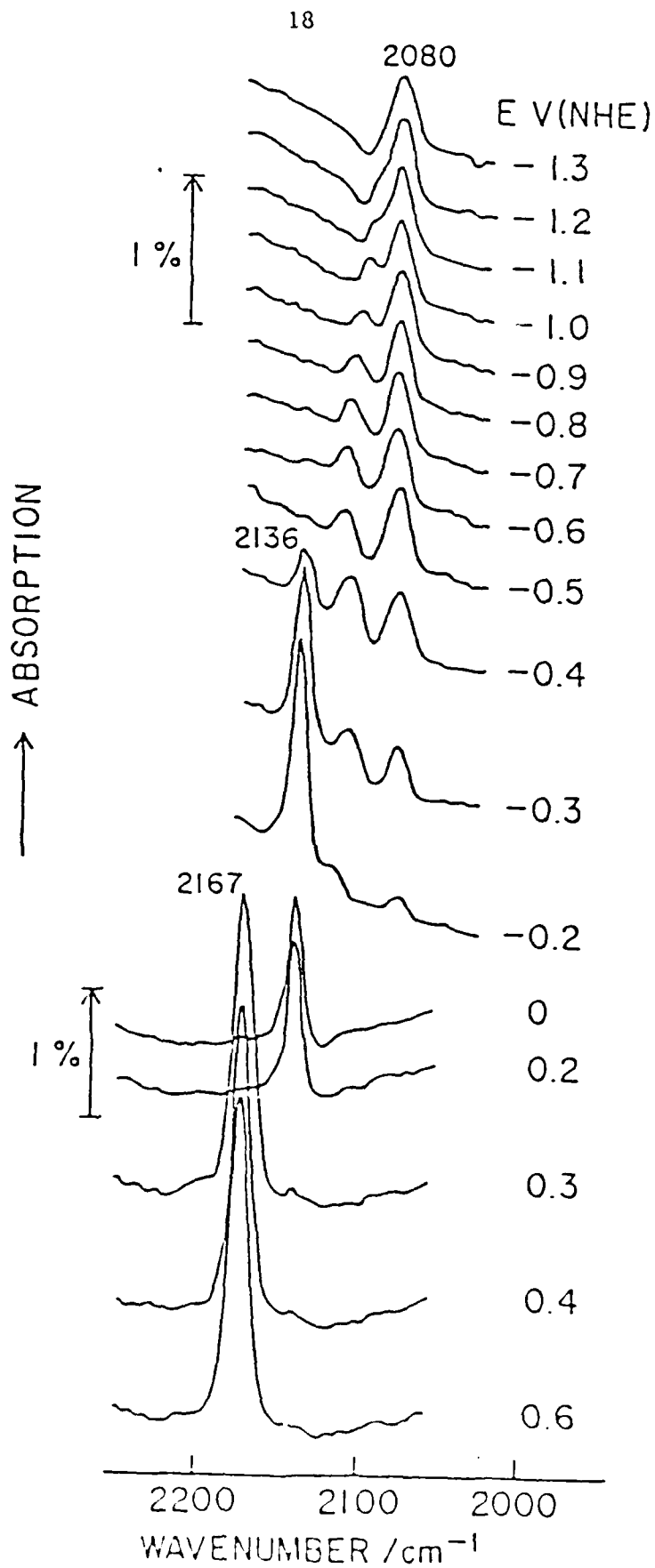


Figure 4. Change of the FT-IRRAS spectrum with potential of the Ag/10<sup>-1</sup> N KCN solution interphase. All the spectra are referred to to CN<sup>-</sup> free 0.5 M K<sub>2</sub>SO<sub>4</sub> solution.

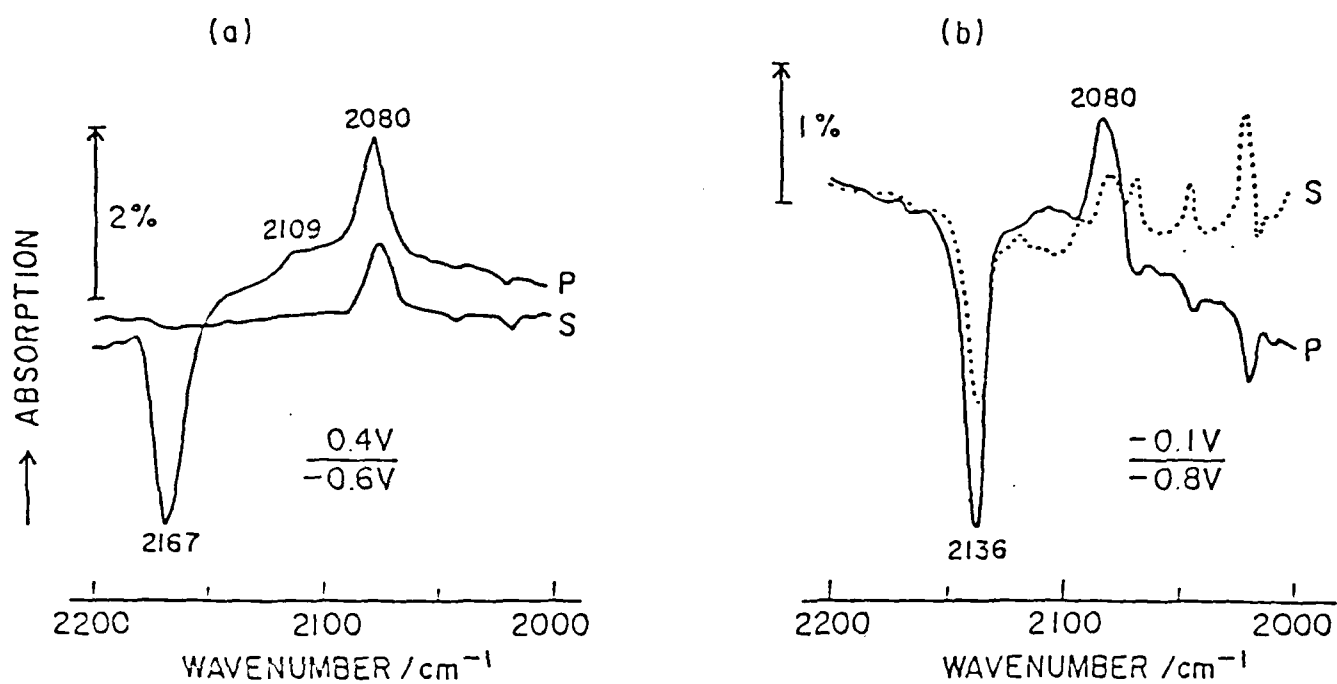


Figure 5. Spectral ratio between 0.4 V and -0.6 V (a) and -0.8 V (b) by s and p-polarized lights for the  $\text{Ag}/10^{-1}\text{N}$  silver.



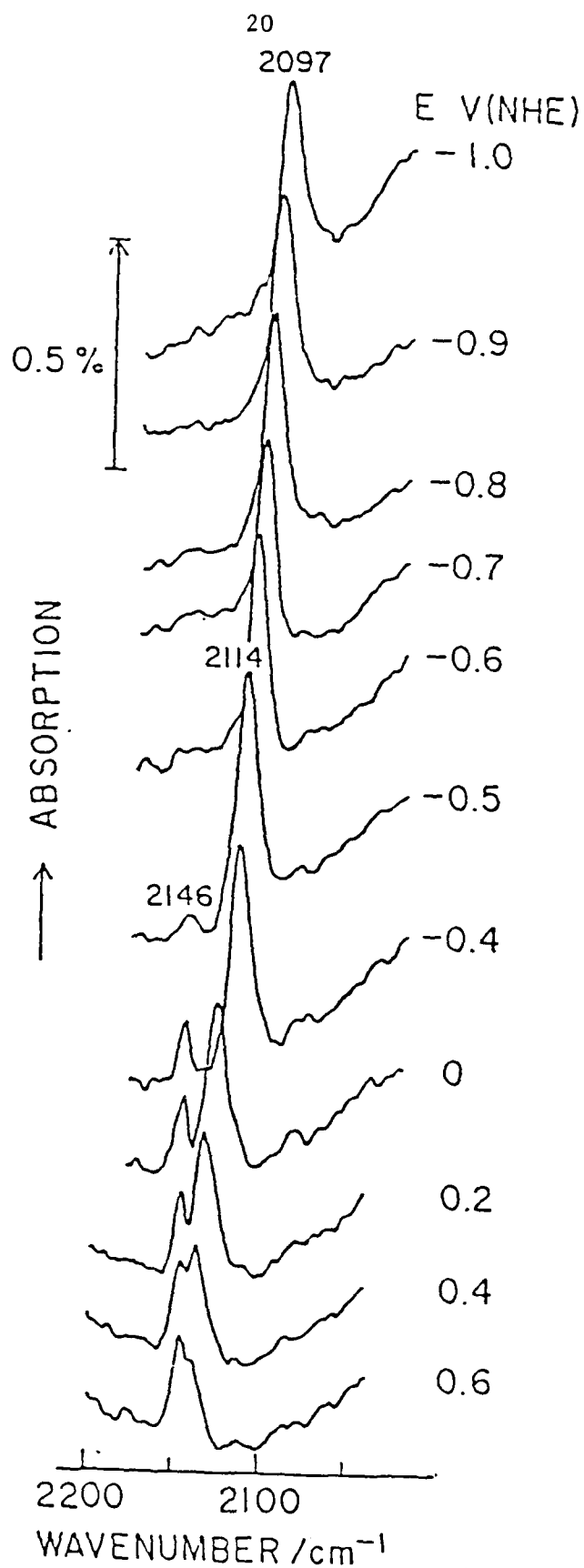


Figure 6. Change of the FT-IRRAS spectrum with potential of the Au/10/-2/ N KCN solution interphase. Spectra are referred to the  $\text{CN}^-$  free 0.5 M  $\text{K}_2\text{SO}_4$  solution.

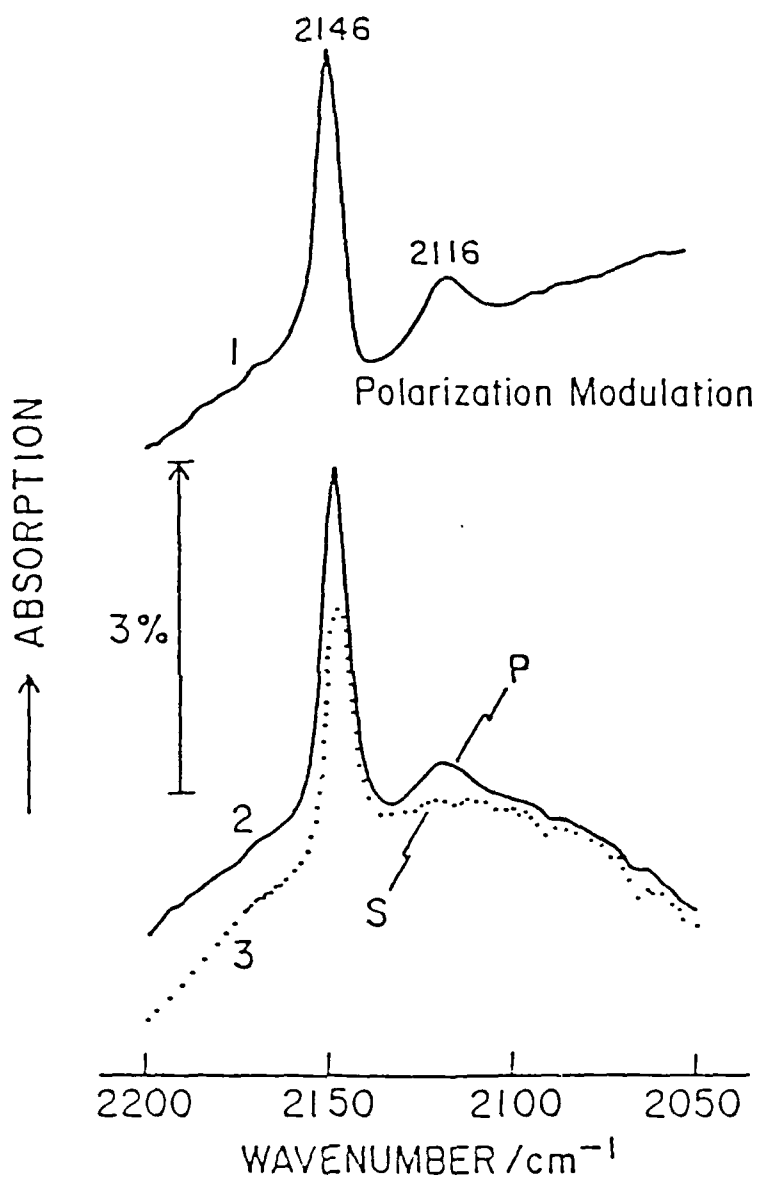


Figure 7. The polarization modulated FT-IRRAS spectrum at  $-0.4$  V (1), the spectrum by p-polarized (2) and s-polarized (3) light ratioed against the  $\text{CN}^-$  free solution.

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