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A STUDY OF THE GOLD/CYANIDE SOLUTION INTERPHASE BY
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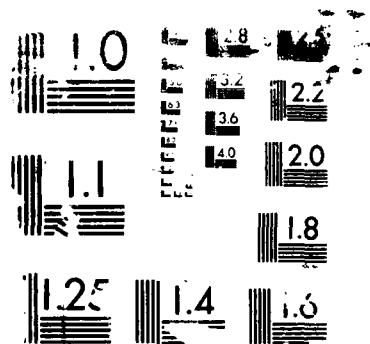
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AD-A189 140

A Study of the Gold/Cyanide Solution Interphase by
In-Situ Polarization Modulated FT IRRAS

by

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Prepared for Publication

in

Langmuir
(1987)

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 15	2. GOVT ACCESSION NO. <i>12-1</i>	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) A Study of the Gold/Cyanide Solution Interphase by In-Situ Polarization Modulated FT IRRAS		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) K. Kunimatsu, H. Seki, W. G. Golden, J. G. Gordon II, M. R. Philpott		8. CONTRACT OR GRANT NUMBER(s) N00014-82-C-0583
9. PERFORMING ORGANIZATION NAME AND ADDRESS IBM Research Division, Almaden Research Center 650 Harry Road, San Jose, California 95120-6099		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE November, 1987
		13. NUMBER OF PAGES 19
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.		
18. SUPPLEMENTARY NOTES Prepared for publication in <i>Langmuir</i>		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) infrared, vibrational spectroscopy, electrochemistry, gold, cyanide ←		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Polarization modulated Fourier transform infrared reflection absorption spectroscopy (FT-IR-RAS) is used to study the interphase between polycrystalline gold electrodes and 0.5 M K_2SO_4 solution as a function of potential and CN^- concentration. Surface cyanide species, adsorbed on the gold electrode, give rise to a C-N stretching band at $2105/cm^{-1}$ at -1.0V (Ag/AgCl) which undergoes a shift of approximately $30/cm^{-1}/V$ to higher wavenumber		

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IN-SITU POLARIZATION MODULATED FT IRRAS

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ABSTRACT: Polarization modulated Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS) is used to study the interphase between polycrystalline gold electrodes and 0.5 M K_2SO_4 solution as a function of potential and CN^- concentration. Surface cyanide species, adsorbed on the gold electrode, give rise to a C-N stretching band at 2105 cm^{-1} at -1.0V (Ag/AgCl) which undergoes a shift of approximately $30\text{ cm}^{-1}/V$ to higher wavenumber at more positive potentials. The species is identified as linearly adsorbed CN^- ions. The $Au(CN)_2^-$ complex, which gives rise to a C-N stretching vibration at 2146 cm^{-1} , is produced in the solution phase by anodic reaction at approximately -0.7 V(Ag/AgCl) and more positive potentials. The shift with coverage of the C-N stretching mode at -1.0 V(Ag/AgCl) is less than ca. 10 cm^{-1} from low coverage to saturation coverage. Experiments using isotopic mixtures of ^{12}CN and ^{13}CN show that this shift is due to direct lateral interactions between adsorbed cyanide ions.

INTRODUCTION

The adsorption of cyanide ions on metal electrodes has been studied extensively by surface enhanced Raman Spectroscopy (SERS). Silver electrodes have been the most frequently studied¹⁻⁴. However, the nature of the surface cyanide species giving rise to SERS is still not yet known with certainty. Recently Baltruschat and Heitbaum⁵ conducted a comparative study regarding the adsorption of cyanide on gold and silver electrodes by SERS. Their conclusion that the surface species was a gold dicyanide complex, $\text{Au}(\text{CN})_2^-$, was based mainly on the difference between the frequencies of the band seen by SERS near 2100 cm^{-1} and the Raman active mode of the gold dicyanide complex in solution. The difference was similar to what was observed at a silver electrode. For the latter, silver electrode, it was argued that the coordination number of 2 for the surface complex best explained their analysis of the dissolution and deposition of the silver, involving partial charge transfer to the electrode in the formation of the adsorbed complex⁴. In SERS experiments Gao and Weaver⁶ have assigned several low frequency ca. $300\text{--}400\text{ cm}^{-1}$ modes to SERS active cyanide on gold and noted a potential dependence of $12\text{ cm}^{-1}/\text{V}$ for the C-N stretching mode near 2100 cm^{-1} .

To avoid interpretational difficulties associated with roughened surfaces in SERS we have investigated cyanide adsorbed on flat polycrystalline copper⁷, silver^{8,9} and gold⁹ electrodes using polarization modulated FT-IRRAS¹⁰⁻¹². In these studies, potential dependent C-N stretching modes were detected and assigned to CN^- adsorbed linearly on the electrode surface. The different conclusions obtained by Raman and infrared spectroscopy suggest that these two spectroscopic methods may be detecting different surface species on the electrode surface. There is no doubt that infrared spectroscopy detects the majority species on the surface while Raman spectroscopy (SERS) may only detect a very small number of surface species adsorbed on the SERS active sites. Most

recently Corrigan et al. have published results comparing SERS and potential difference IR spectroscopy (PDIR)¹³ which includes a section for cyanide on gold and silver electrodes.

We report here further results on the gold/cyanide system obtained by polarization modulated FT-IRRAS in support of our conclusion⁷⁻⁹ regarding the nature of the surface cyanide species.

EXPERIMENTAL

Experimental details of the polarization modulated FT-IRRAS¹⁰⁻¹² and a full description of the optical arrangement and the electrochemical cell for the infrared measurements have been described elsewhere¹⁴. The gold working electrode was made by sealing a spectroscopically pure gold disk (Johnson & Matthey) of 1 inch diameter into a kel-F rod. The electrode was polished mechanically to a mirror finish, successively using alumina powder of 1, 0.3 and 0.05 μ size, and then cleaned in an ultrasonic bath. The electrode was subjected to the usual anodic/cathodic cleaning cycle in 0.5 M K_2SO_4 after which an FT-IRRAS spectrum was taken, to be used as a reference spectrum for subtraction from the spectra observed in the solution containing CN^- ions. Then an appropriate amount of KCN solution was added to the cell to achieve the desired concentration of CN^- ions. All spectra were taken using a liquid nitrogen cooled InSb detector (Infrared Associates) with the spectrometer set at 4 cm^{-1} resolution. Usually 300 scans was averaged to improve the signal to noise ratio. The counter electrode was a platinum wire wrapped loosely around the kel-F rod into which the gold electrode had been sealed. All potentials were referred to an Ag/AgCl(3M KCl) reference electrode.

RESULTS AND DISCUSSION

Figure 1 shows a series of spectra in the C-N stretch region taken at various potentials in the solution containing 10^{-2} M CN^- . Starting at -1.2V a band clearly seen around 2100 cm^{-1} (band A) shifts to higher wavenumber with increasingly positive potentials. It does not lose intensity in the potential region more negative than -0.7V. As the electrode is made more positive, a new band at 2146 cm^{-1} (band B) appears, first at -0.7 V. The position of the new band B is independent of the applied potential and appears to develop its intensity at the expense of the potential dependent band A, which continues a gradual shift to higher frequency as it loses intensity. Eventually, at 0.4 V the 2146 cm^{-1} band B becomes the dominating feature with considerable overlap with the potential dependent band A. These results strongly suggest that the band which undergoes the shift with potential originates from species on the electrode surface while the 2146 cm^{-1} band comes from species in the solution trapped between the electrode and the infrared window. The polarization modulation method detects solution species as well as surface species because of inhomogeneities in the electromagnetic field across the electrode prism gap. This has been explained fully elsewhere¹³.

Further experiments using p and s polarized radiation, respectively, were conducted in order to confirm what is suggested from the results in Figure 1. A solution containing a much higher cyanide concentration, 0.1 M CN^- , was employed for this purpose, the results of which are shown in Figure 2. The spectra were observed at -0.6 V. In contrast to the data from the solution containing only 10^{-2} M CN^- , the intensity of the 2146 cm^{-1} band B is much higher than the 2117 cm^{-1} band A, as shown in the polarization modulated spectrum at the top of Figure 2. The spectra at the bottom clearly show that the 2146 cm^{-1} band B is seen by both p and s polarized radiation, although with different intensities due to the differing intensities of p and s polarized radiation in the solution phase between

the electrode and the window¹⁴. At the same time, the 2117 cm⁻¹ band A is seen only by p-polarized radiation. The result is a direct proof that, based on the surface selection rule¹⁵ in IRRAS, the 2117 cm⁻¹ band A originates from the gold electrode surface while the 2146 cm⁻¹ band B comes from the solution phase. This is consistent with the results in Figure 1 that band A shifts with potential while the 2146 cm⁻¹ band B does not.

The 2146 cm⁻¹ band B is assigned to the Au(CN)₂⁻ complex ions^{9,16} in the solution phase. This is in fact the anodic reaction product between the gold electrode and the cyanide ions in the solution. We assign band A to the linearly adsorbed CN⁻ ions, although one might argue that band A should be assigned to some adsorbed cyano gold complex and that the change shown in Figure 1 between -0.7 V and 0.4 V is simply the conversion of adsorbed complex to complex dissolved in the solution phase. The fact that Au(CN)₂⁻ is the only stable Au(I) species makes it unlikely that the adsorbed complex is of a higher species. Evidence that the development of the 2146 cm⁻¹ band B is not caused by the desorption of the surface Au(CN)₂⁻ complex is shown in Figure 3. The spectra were recorded as the potential was stepped positive from -1.0 V up to -0.7 V and then reversed. We can see that the 2146 cm⁻¹ band undergoes a reversible change, appearing and disappearing, when the potential is reversed at -0.7 V. It should be noted, however, that appearance of the 2146 cm⁻¹ band is accompanied by the disappearance of the band at 2080 cm⁻¹, which is assigned to the solution CN⁻, and vice versa. This cannot be explained by the desorption of the surface complex, which should not be accompanied by the disappearance of the solution CN⁻. The process seen here is undoubtedly the electrochemical production of the Au(CN)₂⁻ complex and its reduction around -0.7 V, as evidenced in the cyclic voltammogram in Figure 4, taken with the gold electrode pushed against the infrared window. The data obtained in Figures 3 and 4 also confirm that the Au(CN)₂⁻ complex produced by the anodic reaction between the gold electrode

and cyanide ions in the solution is reduced again when the potential is reversed. And when the potential reaches -0.9 V all the gold complex in the solution is reduced as indicated by the disappearance of the 2146 cm^{-1} band. It is therefore highly improbable that a $\text{Au}(\text{CN})_2^-$ complex could remain on the gold surface unreduced at potentials more negative than -0.9 V. Since the band around 2100 cm^{-1} persists into highly negative potential regions, it can not be assigned to the $\text{Au}(\text{CN})_2^-$ and therefore must be assigned to specifically adsorbed CN^- oriented primarily perpendicular to the surface.

The dicyano metal complexes in solution have two distinct modes of vibration, symmetric and asymmetric, which are Raman and IR active, respectively. Their frequencies differ by more than 10 cm^{-1} and, even though the adsorbed species are no longer likely to be linear, they are expected to have two distinct modes. However, the band seen by SERS and assigned to the adsorbed $\text{Au}(\text{CN})_2^-$ complex by Baltrushat and Heitbaum⁴, has essentially the same frequency at a given potential and potential dependence as the IR band observed here. The fact that the same one band is seen by IR and SERS is also a strong indication that the observed surface species is linearly adsorbed cyanide rather than $\text{Au}(\text{CN})_2^-$.

Figure 5 shows the potential dependence of the C-N stretching frequency of the linearly adsorbed CN^- ions, its integrated infrared absorption intensity and the intensity of the $\text{Au}(\text{CN})_2^-$ complex, which were determined from the spectra in Figure 1. The gradual decrease in the intensity for potentials more positive than -1.0V is due to the loss of CN^- to the oxidation of gold to form $\text{Au}(\text{CN})_2^-$. The slope of the potential dependence of the C-N stretching frequency is almost $33\text{ cm}^{-1}/\text{V}$ in the potential region (-1.2V to -0.5V) where the absorption intensity of the surface CN^- is almost constant. This value is considerably higher than the $12\text{ cm}^{-1}/\text{V}$ reported by Gao and Weaver⁶ from SERS but

is in reasonable agreement with the measurements for 10mM KCN by PDIR and SERS reported more recently by Corrigan et al¹³. The sharp decrease of the intensity of the adsorbed CN^- and the change in slope of the C-N stretching frequency (see Figure 5) at about -1.25V are most likely due to the desorption of the CN^- ions at more negative potentials.

It is also interesting to consider the relative extinction coefficient of the C-N stretching mode depending on its configuration. The total amount of CN^- in the layer between the electrode and the window can be assumed to remain constant over the period of an experiment when the layer is very thin. In Figure 1 the cyanide concentration is 10^{-2} M of the solution meaning that only about a monolayer equivalent of cyanide is present in a cell of $2\ \mu$ thickness. Note that at 0.4 V the intensity of the band A is a small fraction of its maximum value at -1.1 V while the $2146\ \text{cm}^{-1}$ band peak is at about 1/3 the intensity of the maximum value of band A. If it is assumed that most of the CN in the thin layer is linearly adsorbed on the electrode at -1.0 V (see Figure 6) and that most of it is used to oxidize the Au to form $\text{Au}(\text{CN})_2^-$ at ca. 0.4 V, then based on the integrated intensity, it can be estimated that the extinction coefficient of the surface CN is at least 3 times that of the C-N stretching mode in the $\text{Au}(\text{CN})_2^-$ complex in solution. The extinction coefficient per single C-N of the stretching mode in the $\text{Au}(\text{CN})_2^-$ complex is usually much higher than that of the free CN^- ions, which can also be seen in Figure 3 by comparing the band intensity of the CN^- ions in the solution phase observed at -0.9 V or -1.0 V to that of the $\text{Au}(\text{CN})_2^-$ complex produced at -0.7 V. This ratio is about 8 based on the reported the extinction coefficients¹⁶. Therefore the ratio of the extinction coefficient of the C-N stretching mode of the surface CN^- to that of the CN^- in solution is at least 24. The much higher scattering cross-section of the adsorbed CN^- compared to the CN^- ions in solution is not explained simply by image charges. This could be the

result of a field dependent dynamic dipole moment of the C-N bond of CN^- being larger on the gold surface than in the free ion. Possibly this could be due to the coupling of the low frequency metal-ligand mode with the high frequency C-N stretch induced by the double layer field with consequential infrared intensity transfer.

Another interesting aspect of the gold/cyanide system is the concentration dependence of the C-N stretching frequency at a constant potential, which is shown in Figure 6. The C-N stretching frequency shifts to higher wavenumbers by ca. 10 cm^{-1} from very low infrared absorption intensity, low coverage, to the the saturation value of the intensity, saturation coverage at -1.0 V . The C-N stretching frequency and the integrated absorption intensity are plotted as a function of concentration in Figure 7.

In the case of CO adsorption on single crystal metals in ultra high vacuum, a shift in the vibrational frequency due to coverage was seen which was attributed to lateral adsorbate-adsorbate interactions, the simplest component of which is dipole coupling^{17,18}. To explore this aspect further, we carried out an experiment using isotopic mixtures of $^{13}\text{CN}^-$ and $^{14}\text{CN}^-$ ions, keeping the total concentration of the CN^- ions constant at 10^{-2} M/l . Thus, the total coverage of CN^- ions on the gold surface was kept constant but the concentration of the isotopic cyanide and hence their interaction was changed. The potential for which the surface species, band A, had maximum intensity was chosen (see Figure 5). The result using $0.5\text{ M K}_2\text{SO}_4$ for spectra taken at -1.0 V is shown in Figure 8. As the $^{12}\text{CN}^-$ concentration is diluted by $^{13}\text{CN}^-$, its band gradually shifts to lower wavenumbers, losing intensity, while the $^{13}\text{CN}^-$ band gradually shifts to higher wavenumbers developing its intensity. Figure 9 shows the C-N stretching frequency of the two isotopic CN^- ions adsorbed on the gold surface as a function of the percent concentration of the $^{13}\text{CN}^-$ ions in the adsorbed layer. This result shows clearly

that the lateral interaction, most likely dipole coupling, shifts the C-N stretching frequency with coverage by ca. $4\text{-}5\text{ cm}^{-1}$. This is almost equal to the total shift observed by changing the surface coverage in the pure $^{12}\text{CN}^-$ solutions. These are important results because they clearly point to insignificant lateral interactions between adsorbed CN^- ions, compared to the potential driven shift of $30\text{ cm}^{-1}/\text{V}$.

The shift seen here should be compared to the much larger shifts observed from the CO/Pt system¹⁷ or the CO/Cu system¹⁸ in ultra high vacuum. The small frequency shift as a function of coverage for the gold/cyanide system may be explained by assuming that the maximum coverage of CN^- on gold at -1.0 V is smaller than a full monolayer, although the IR absorption intensity is a maximum at this potential. This is frequently true for the anions specifically adsorbed on negatively charged electrode surfaces, which is the case here. -1.0 V is much more negative than the PZC of polycrystalline gold, 0.005V ¹⁹.

ACKNOWLEDGMENT

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

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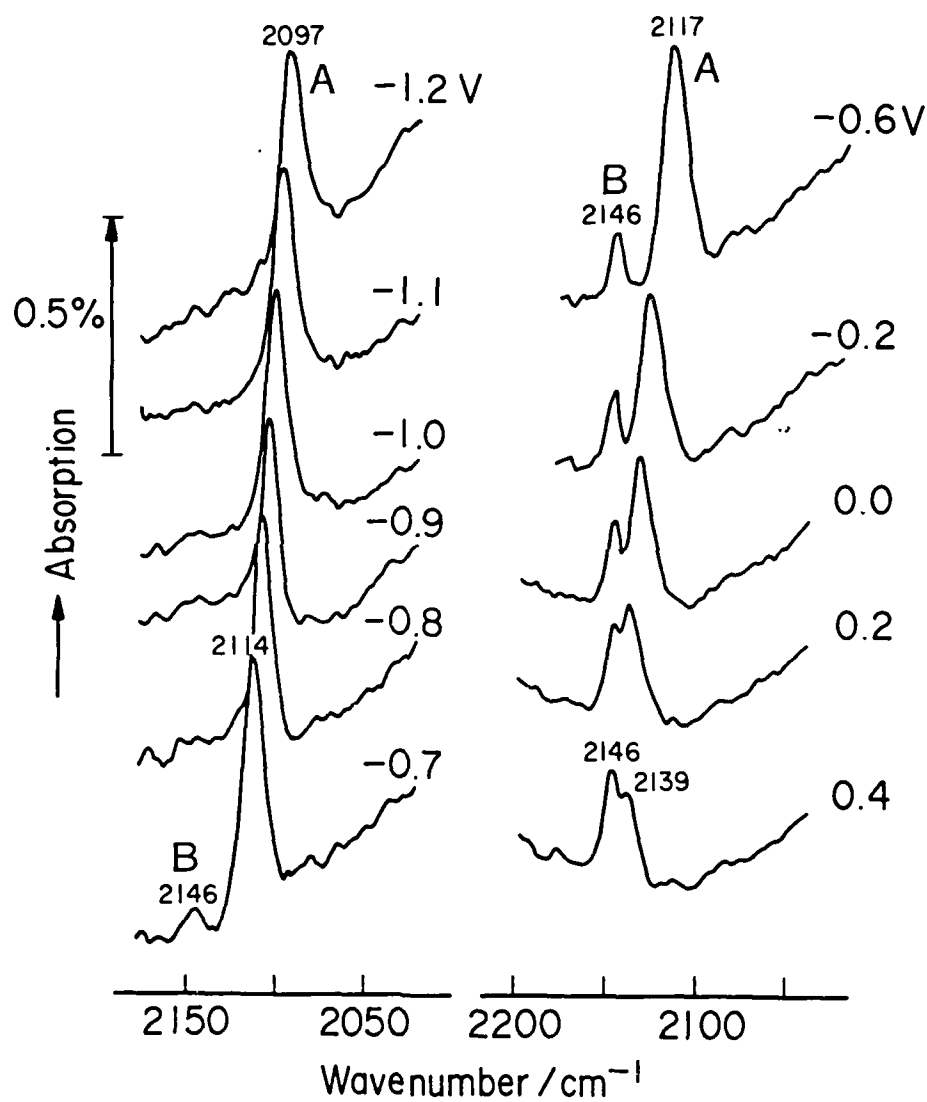


Figure 1. Potential dependence of polarization modulated FT-IRRAS spectra of the Au/10⁻² M CN⁻ interphase.

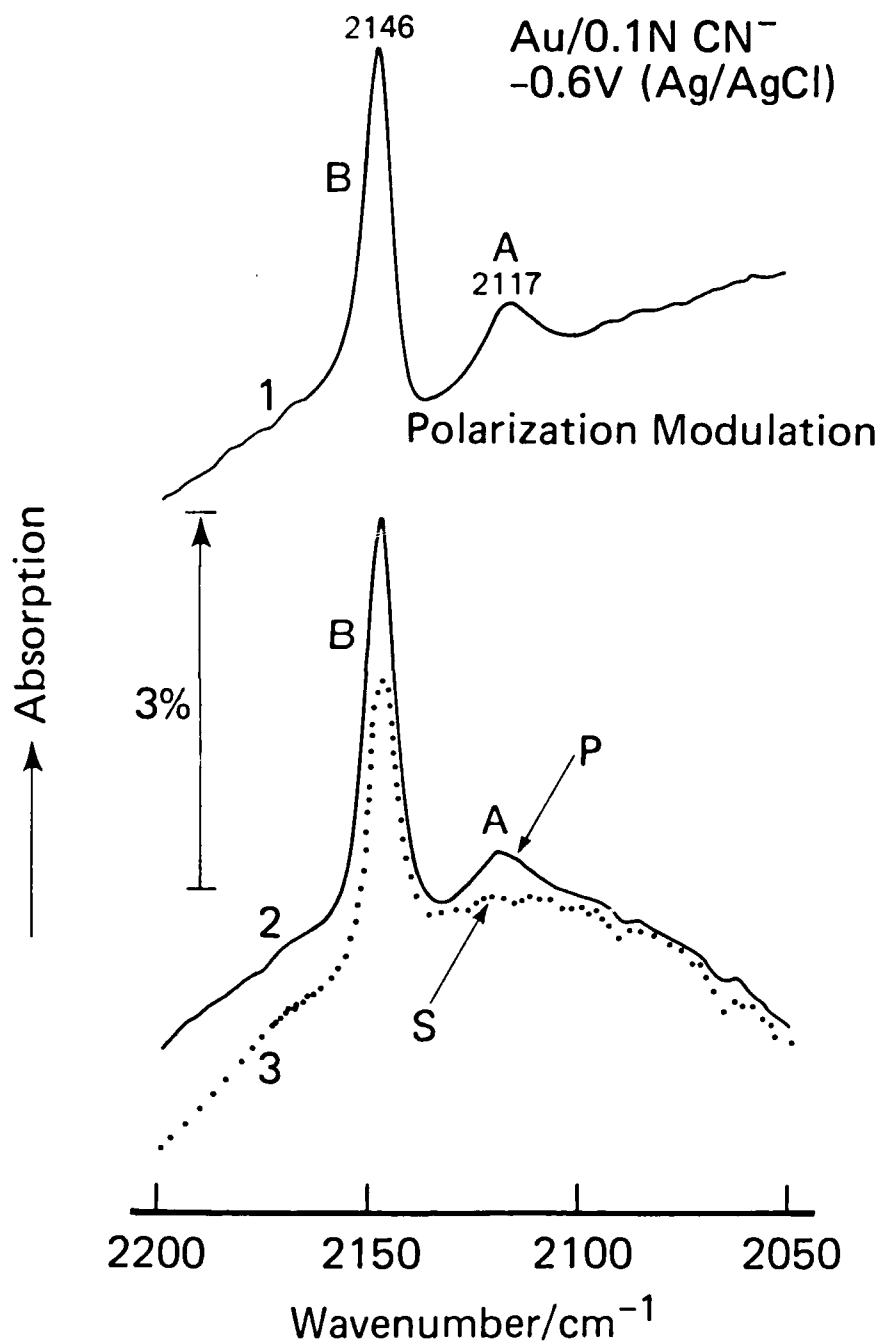


Figure 2. (top) Polarization modulated spectrum and (bottom) spectra observed using p and s polarized radiation at -0.6 V from the Au/10⁻¹ M CN⁻ interphase.

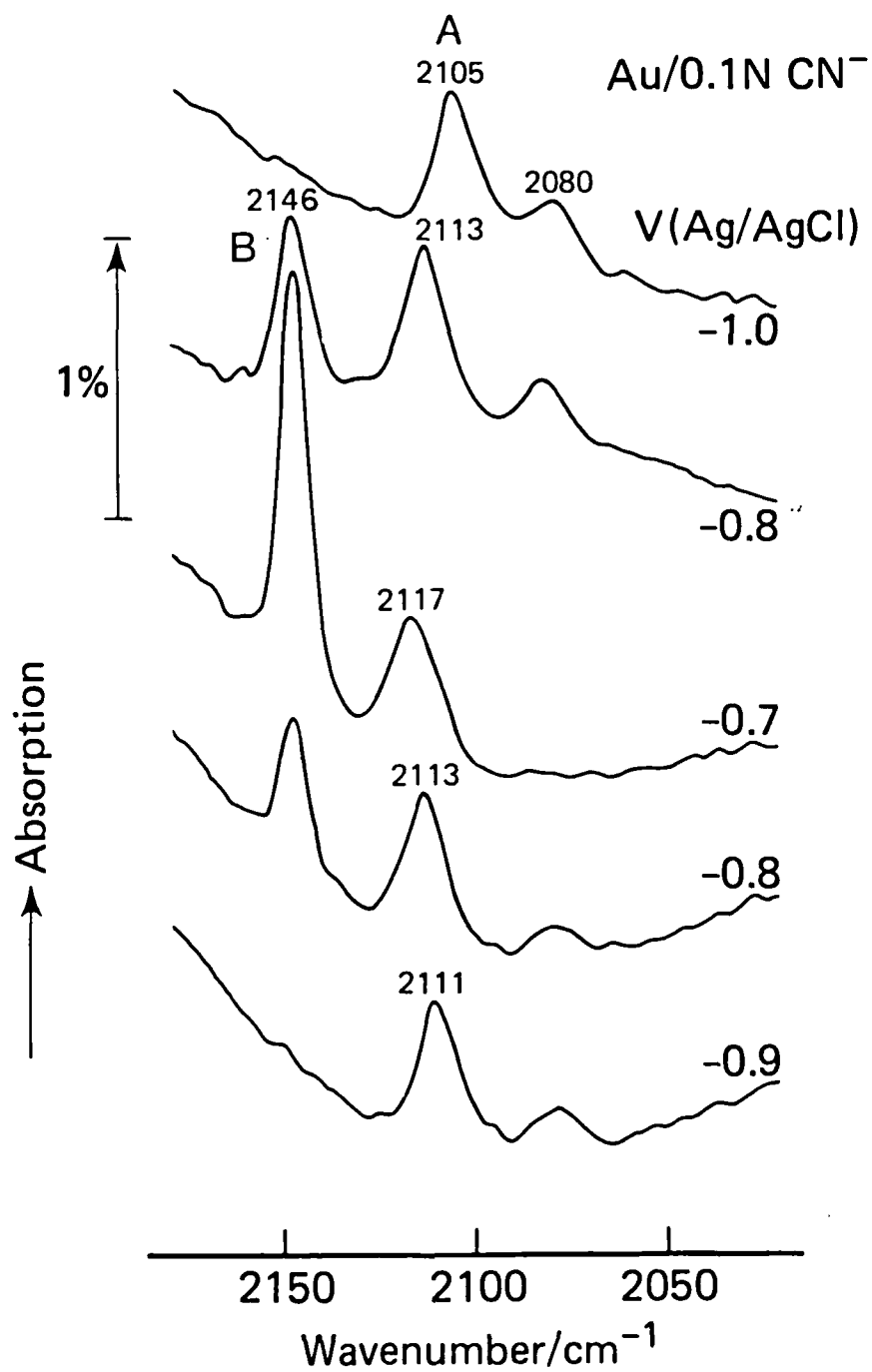


Figure 3. Reversible change of the FT-IRRAS spectra observed at the Au/10⁻¹ M CN⁻ interphase when the direction of the potential change was reversed at -0.7 V.

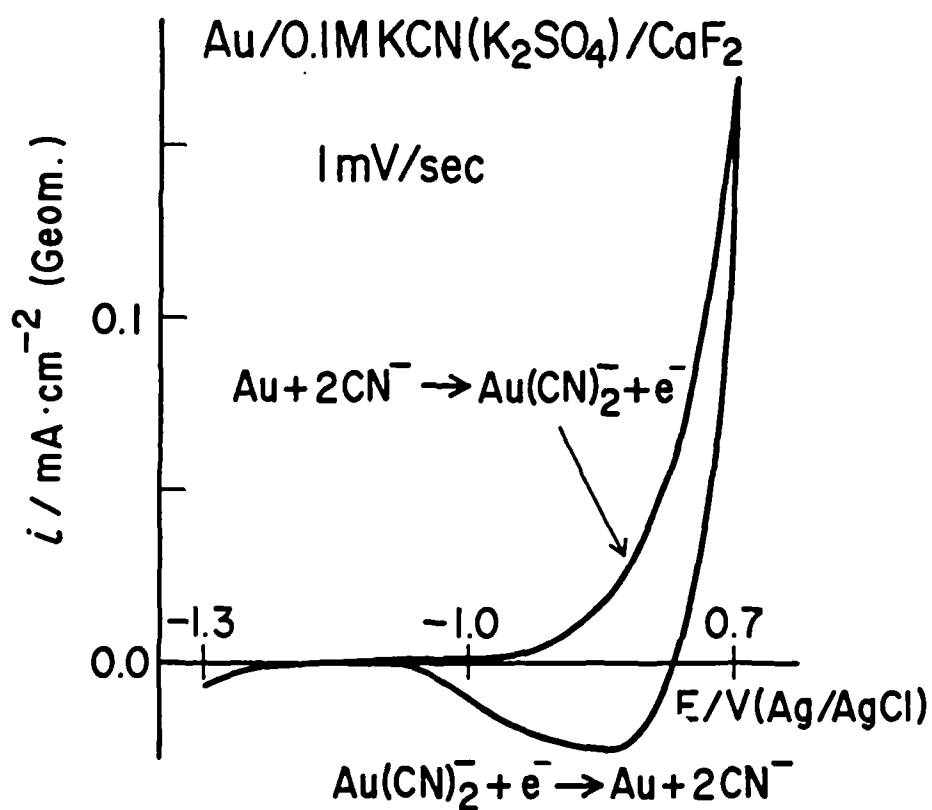


Figure 4. Cyclic voltammogram of the Au/ 10^{-1} M CN^- interphase observed at 1 mV/sec with the gold electrode pushed to the infrared window.

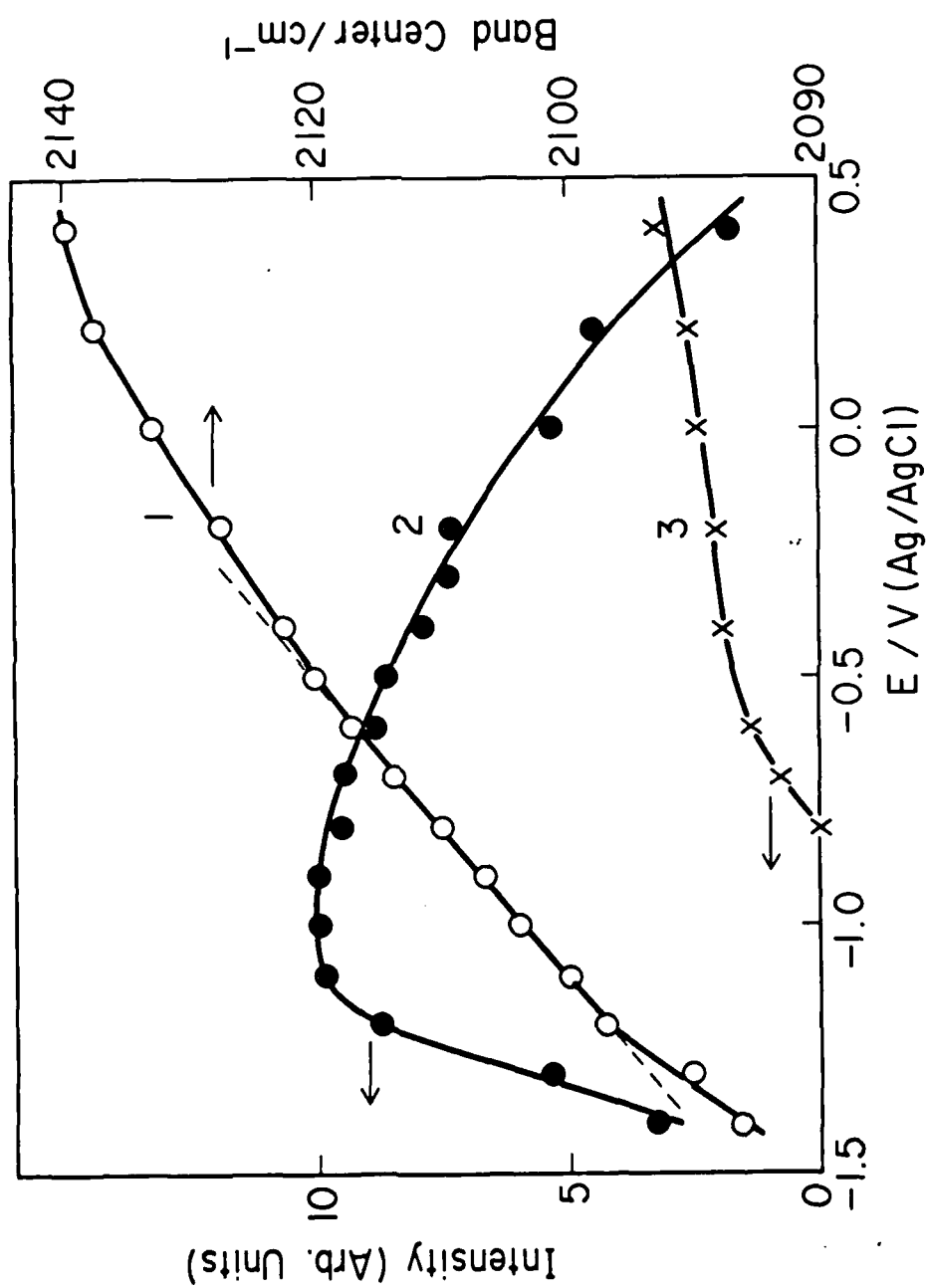


Figure 5. Potential dependence of (1) the band center position, (2) the integrated band intensity of the C-N stretching band of the CN^- ions and (3) integrated band intensity of the C-N stretching band of the $\text{Au}(\text{CN})_2^-$ complex.

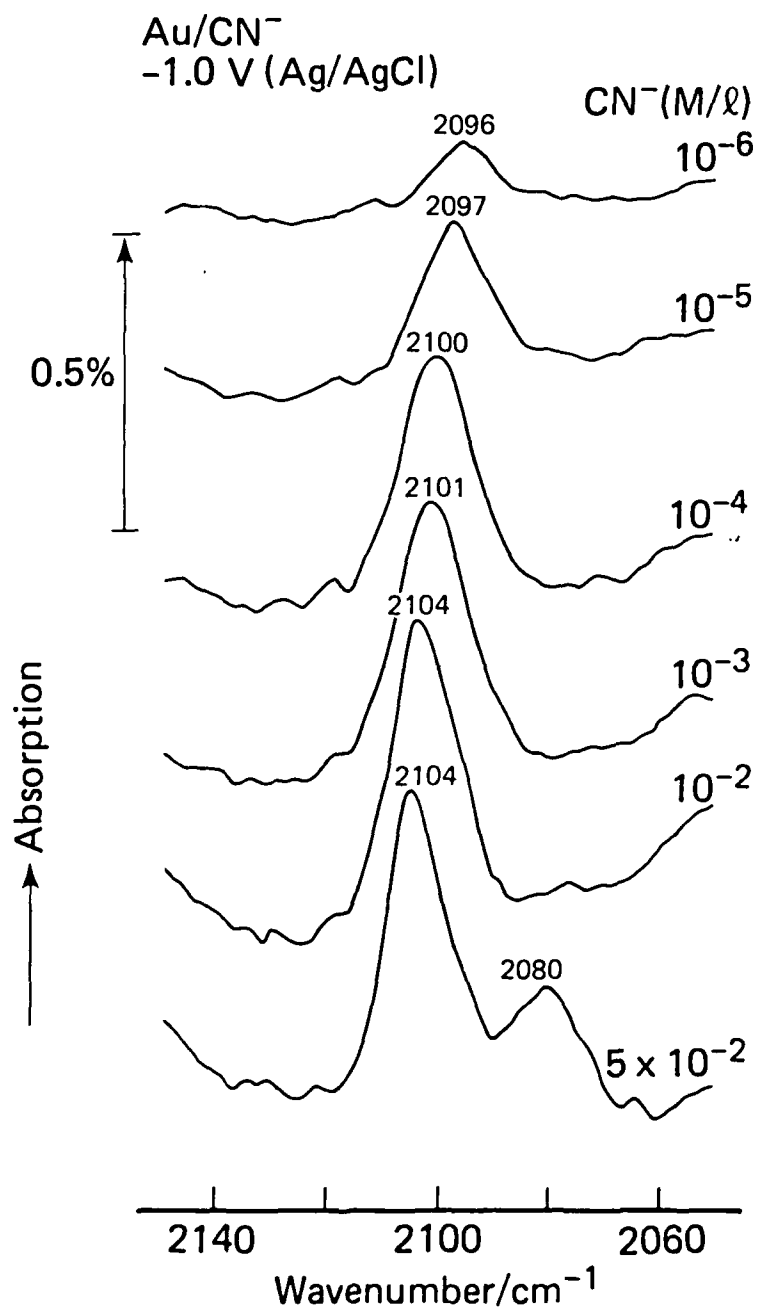


Figure 6. Concentration dependence of the C-N stretching band of the adsorbed CN⁻ ions on gold electrode.

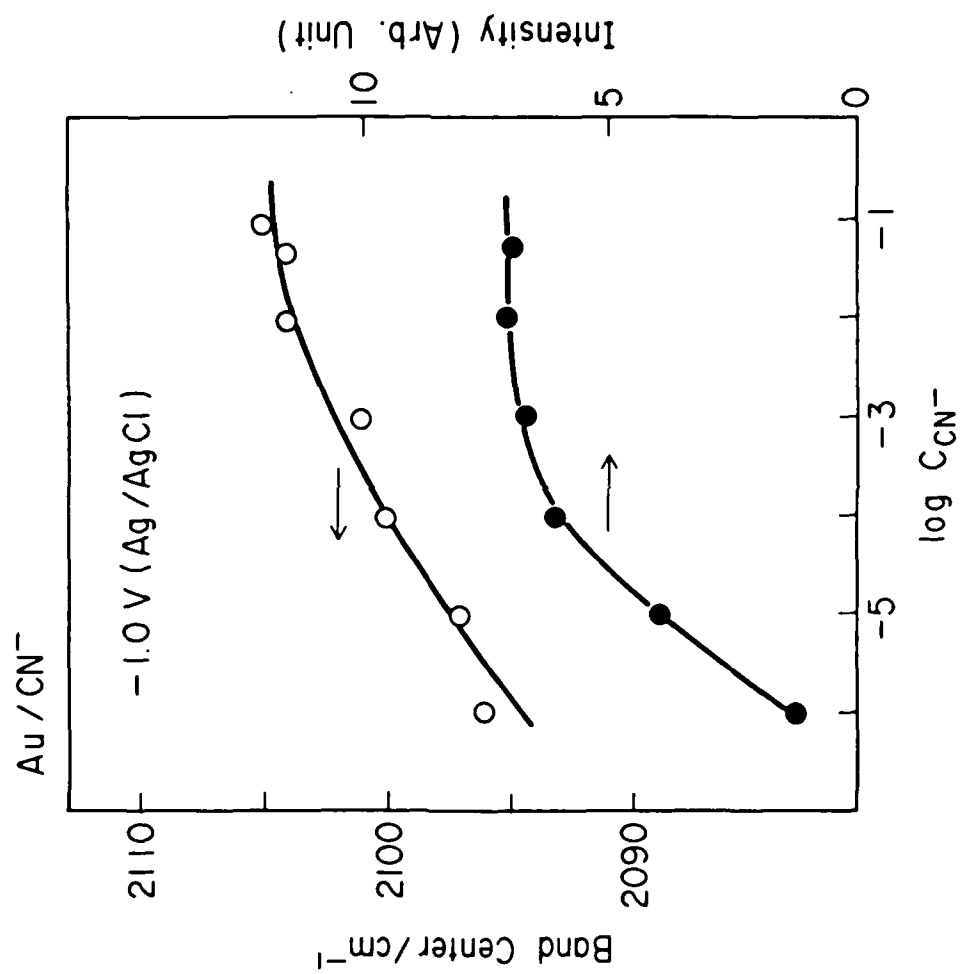


Figure 7. Dependence on the concentration of CN^- ions of (a) band center position and (b) integrated band intensity of the C-N stretching band of the adsorbed CN^- ions on gold.

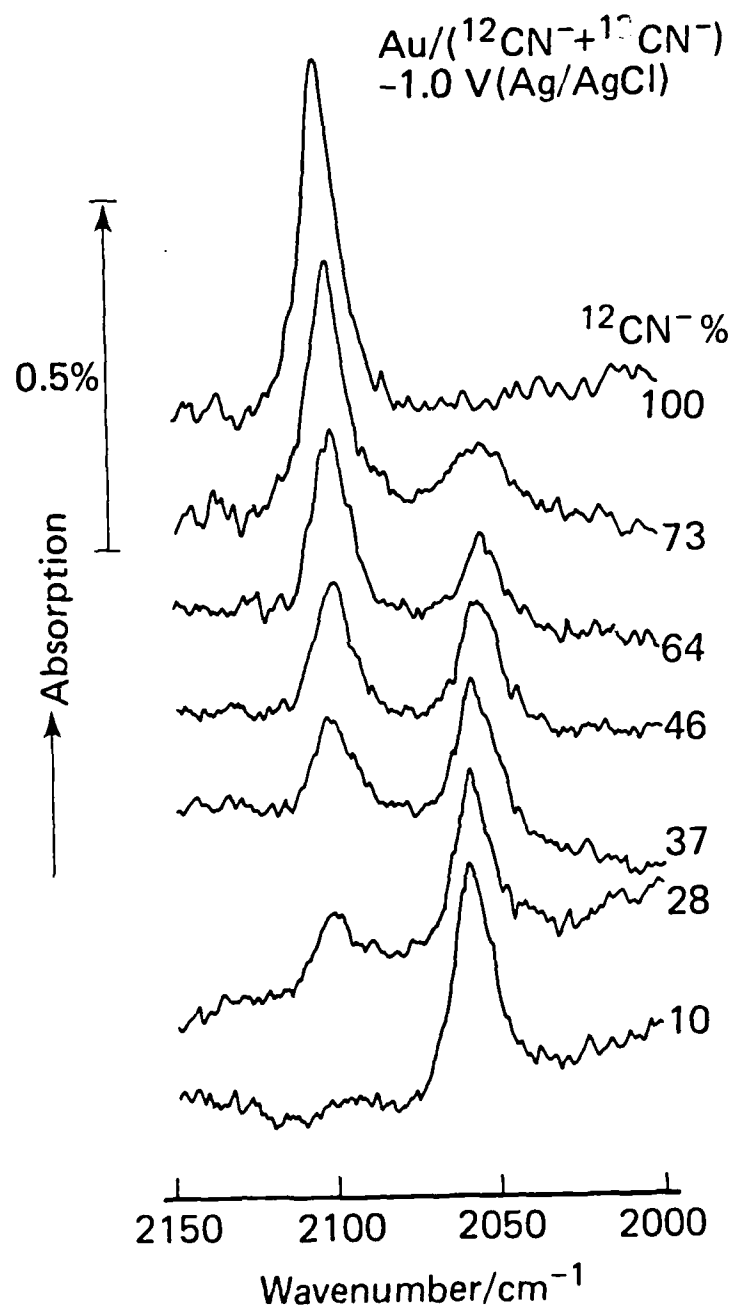


Figure 8. Change of the C-N stretching band spectra of the adsorbed CN⁻ ions at -1.0 V with the isotopic composition of ¹²CN⁻ and ¹³CN⁻ in the adsorbed layer. The total concentration of the CN⁻ ions in solution phase was kept at 10⁻² M/l.

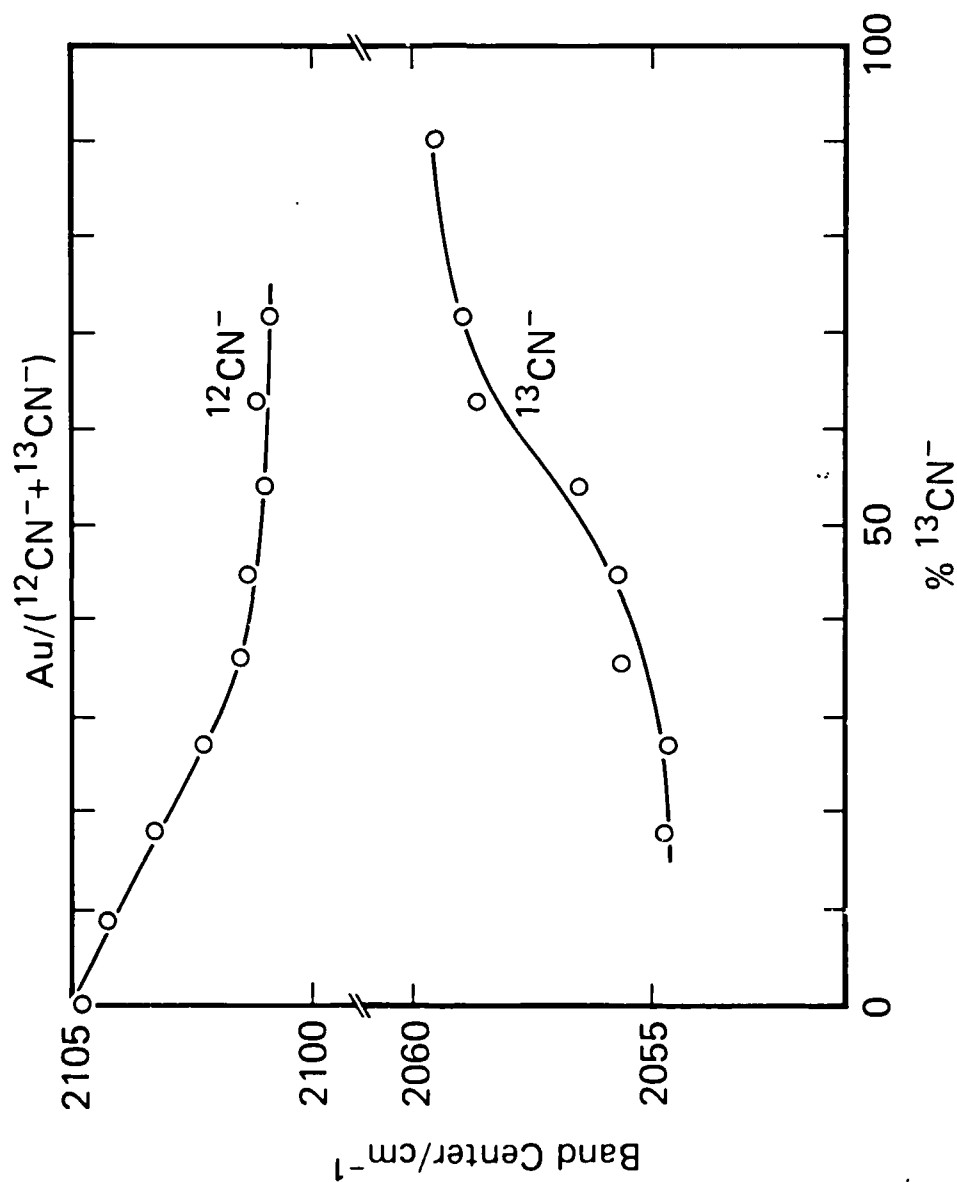


Figure 9. Dependence on the C-N stretching frequency of the adsorbed $^{12}\text{CN}^-$ and $^{13}\text{CN}^-$ ions on the isotopic composition of the adsorbed layer. The data were obtained from Figure 8.

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