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by

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ABSTRACT: In-situ FT-IR vibrational spectra of thiocyanate ions adsorbed on polycrystalline Ag electrodes as a function of electrode potential and electrolyte concentration are reported. Interpretation of the results are performed with the help of ab initio SCF calculations of the electronic structure and bonding of thiocyanate to small silver clusters. It was concluded that thiocyanate ion adsorbs with S- and N-end down in the double layer region for potentials greater than −0.3V (versus Ag/AgCl). At potentials close to the potential of zero charge thiocyanate ion is adsorbed flat and cannot be detected by IR.

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I. Introduction

The adsorption of the pseudohalide ion thiocyanate SCN^{-} from aqueous electrolyte solutions on to metals is of interest because it contact adsorbs either N- or S- end down.[1-8] Thiocyanates' ability to bind in this fashion in metal complexes is well known[9-13] and it is also known to act as a bridging ligand in the configuration M-SCN-M or M-S(CN)-M.[10,13,14] The primary issues concerning the contact adsorption of thiocyanate on metal electrodes are: nature of the bonding (ionic or covalent), orientation N-down or S-down, and the polar angle between the normal to a given crystal surface and the configuration axis of the ligand. Secondary issues are the degree of surface coverage and how all the above mentioned properties depend on electrolyte concentration and electrode potential.

In this paper we describe in-situ FT-IR reflection absorption spectroscopy (FT-IRRAS) measurements of the C-N stretching vibration of thiocyanate adsorbed from 0.1M $NaClO_4$ solutions onto polycrystalline silver electrodes. These measurements were performed at varying thiocyanate concentrations for all electrode potentials throughout the double layer range (ca. -1.0V to 0.0V versus Ag/AgCl). Interpretation of these spectra required extensive ab initio calculations of the electronic structure and associated vibrational frequencies of one thiocyanate ion, either in isolation or bonded to single atoms or small clusters of silver atoms including clusters carrying a positive charge. For our purposes it was sufficient to consider adsorption to an on-top site, and we did not consider adsorption to hollow sites as on Ag(111) or grooves as on Ag(110). Calculations more specific to individual surfaces await experiments on single crystal studies.

It is well established from IR and vibrational Raman spectroscopy of metal coordination complexes containing SCN ligands that M-SCN has ν_{CN} stretching frequencies in the range 2090 to 2130 cm^{-1}, whereas M-NCS coordination has ν_{CN} stretching modes in the range 2050 to 2100 cm^{-1}.[9] Note that although these two ranges overlap S-coordination occurs in the high range whilst N-coordination has ν_{CN} in the lower range.

II. Experiments

Vibrational IR spectra of adsorbed thiocyanate on a silver electrode were obtained in reflection geometry on an IBM IR/98 Fourier transform spectrometer using polarization modulation IRRAS[15]. The polarization modulation IRRAS involved modulation of incident IR beam with a photoelastic modulator (Hinds International) and use of a lock-in amplifier (PAR) to obtain the difference in intensity between the s- and p-polarized light, (I_s - I_p). All the spectra shown here represent the ratio (I_s - I_p)/(I_s + I_p) and typically are average of 1000 scans each of two seconds duration. The detector used was liquid nitrogen cooled InSb (Infrared Associates) which had a lower detection limit of 1800 cm^{-1}. The infrared cell was constructed from Kel-f^{TM} and a bevelled CaF_2 prism was used as IR transmitting window[15]. The IR beam was incident on the electrode at approximately 65°.

The electrolyte with various concentration of thiocyanate ions (0.1, 0.4, 1, 5, 10, 100, and 1000 mM) in 0.1 M perchlorate as supporting electrolyte were prepared from reagent grade NaSCN and $NaClO_4$. The deionized water was obtained from Barnstead "Nanopure" system. A smooth silver electrode was prepared by sequential mechanical polishing with 5, 1, and 0.3 μ alumina on a pad using water as a lubricant. The electrode was then ultrasonically cleaned and repeatedly electrochemically cycled in the double layer region. Spectra representative of equilibrium surface coverage were obtained by exposing the electrode to the bulk solution at each potential before returning the cell into a thin layer geometry essential for obtaining acceptable signal to noise ratio[16]. All the potentials here are referenced to a Ag/AgCl (3M KCl) electrode.

Figure 1 shows the range $-0.3V$ to $+0.075V$ for 1 mM SCN^- and Fig. 2 for potentials in the 0.075V to 0.1V where oxidation sets in. These spectra show a band growing in intensity and shifting to higher frequencies from ca. 2100 cm^{-1} at $-0.3V$ to 2139 cm^{-1} at $+0.1V$. The frequency range suggests this band is likely to be due to S-bound thiocyanate and the intense band at 2139 cm^{-1} in Fig. 2 at $+0.1V$ is due to a thin film of Ag SCN solid. In solid AgSCN the ν_{CN} stretch occurs at 2145 cm^{-1}, close to the value of the very intense band at 2139 cm^{-1} in Fig. 2. Figure 3 shows spectra for solutions with 5 mM of thiocyanate ions and these resemble the spectra in Fig. 1 except that the higher solution concentration enables the observation of surface species at more cathodic conditions ($-0.4V$ versus $-0.3V$). The spectra shown in Fig. 4 are for 10 mM thiocyanate. At positive potentials, for example 0.05 V, two peaks appear clearly at 2118 and 2098 cm^{-1}. Note also that the integrated intensity grows rapidly as the potential is shifted positive of 0.0 V. The low frequency peak is possibly N-bound thiocyanate, that may well be responsible for the shoulders seen near 2100 cm^{-1} in Fig. 1. As mentioned previously N bound thiocyanate has ν_{CN} in a range 30-40 cm^{-1} down shifted from S bound thiocyanate. The 100 mM SCN spectra displayed in Fig. 5 show no clear sign of the minor 2100 cm^{-1} peak which is likely present as the weak shoulder on the low frequency side of the 2095 (-0.6V) to 2118 cm^{-1} ($+0.0$V) peak in Fig. 5. In 1 M SCN^{-} solutions (see Fig. 6) there is only one visible potential dependent peak moving from 2071 cm^{-1} at -1.0V (solution peak) to 2075 cm^{-1} at 0.2V. At higher potentials this peak weakens and is replaced by a doublet split around 2150 cm^{-1}. This is most likely an oxidized Ag consisting of a thick layer of solid AgSCN. Asymmetry on the low frequency side may indicate the presence of the N-down species. Figure 7 shows the concentration dependence at 0.0V. The band assigned as N-down species appears clearly only in one of these spectra, namely at 10 mM thiocyanate.

III. Theoretical calculations of thiocyanate adsorbed on silver clusters

In this section we summarize the results of calculations designed to aid the interpretation of the FTIR spectra. Our goal is to provide a framework for a logical explanation of the double layer in terms of N- and S-bound thiocyanate species. To this end we consider a simple model. The thiocyanate ion is assumed to bind N- or S-down at an on-top Ag site. Apart from the Ag atom of the on-top site all other metal atoms will be ignored except in one case to check the importance of the second layer on the geometry. In this last case four Ag atoms are added to represent a second layer of metal atoms.

Ab initio self-consistent field (SCF) calculations have been performed for small systems chosen to model the consequences of the silver-thiocyanate interaction in the limiting case of zero coverage, i.e., isolated adsorbed thiocyanate ions. The simplest systems considered are $[Ag\text{-}NCS]^{-,0}$ and $[Ag\text{-}SCN]^{-,0}$; the total charge of the clusters has been changed to obtain a very simple representation of the silver atoms of the electrode. Thus $Ag^0\text{-}L^-$, can be thought to model adsorbed thiocyanate near the potential of zero charge (pzc) and Ag^+L^-, to model the change in electrode charging as the potential is made positive. Additionally, the interaction of the SCN^- on the top site of an $Ag_5(1,4)$ cluster containing one Ag atom in the first and four Ag atoms in the second layer has been considered (see Fig. 8). The metal atoms are fixed at their positions for bulk Ag. The metal-ligand geometry has been fully optimized for both N-down and S-down coordination modes as well as for charged and neutral systems. The effect of an external uniform electric field on the chemisorption geometry has been investigated for the mono metal atom Ag-SCN and Ag-NCS systems. Calculations have been performed on Ag-NCS and Ag-SCN to determine the low-frequency C-S stretch, ν_{CS}, and the high-frequency C-N stretch, ν_{CN}, as well as the frequency shifts as a function of the charge on the silver atom.

A. Computational details

In the study of the Ag-NCS and Ag-SCN systems, the Ag atom has been treated with an Effective Core Potential (ECP)[17] in which the 28 electrons from the deep core 1s to 3d shells are represented by the ECP while the 19 electrons arising from the 4s, 4p, 4d, and 5s shells are explicitly included in the wavefunction. The valence basis set for Ag has been contracted to 4s4p3d (see Ref. 17 for the GTO exponents and the ECP parameters). In $Ag_5(1,4)$ the first layer Ag atom directly interacting with the SCN adsorbate has been treated in the same way; the ECP operator which explicitly includes in the valence only the outermost 5s electron (1 electron ECP)[18] has been used for the description of the four Ag atoms in the second layer. The C, N, and S atoms have been treated at the all electron level. The basis set for C and N is a 4s3p contracted GTO basis.[19] The basis set for S contracted to 5s4p, has been taken from Ref. 20.

Calculations have been performed in the absence of an applied electric field, $F=0$ case, and in a static uniform electric field of $F = \pm\ 0.01$ a.u. = $\pm 5.2 \times 10^7$ V/cm normal to the surface. This field is typical of those existing inside the compact part of the Helmoltz double layer. More details of the calculations are described elsewhere.[21,22]

B. Geometry and bonding of SCN on silver

In the calculation of the molecular geometry a two-dimensional potential energy surface has been determined by varying simultaneously the metal-ligand (M-L) distance, r, and the M-S-C and M-N-C internal angles, α. The equilibrium geometry values r_e and α_e have been determined from a two-dimensional polynomial fit. The results of the geometry optimization for both Ag-L and Ag_5-L show that when the thiocyanate molecule is bound at the N-side a perpendicular orientation is preferred (see Tables 1 and 2 and Fig. 8); on the other hand, when a Ag-SCN bond is formed the molecule assumes a bent conformation forming an Ag-S-C internal angle of approximately 105 degrees (see Tables 1 and 2 and Fig. 8). The nature of the potential surface for the bending is very different for the negatively charged with respect to the neutral clusters; for Ag-L^- case, the potential surface for the bending is very shallow for both N-down and S-down cases; when the total charge of the molecule is 0, corresponding to the interaction between Ag_n^+ (n = 1,5) and a SCN^- ligand, the potential surface exhibits a more pronounced minimum.[23]

The nature of the metal ligand interaction in the charged and neutral complexes is basically different; in the first case the bonding originates mainly from the polarization of the metal which respond to the presence of the negative SCN ligand; of course, the Ag_5 cluster is much more polarizable than the single Ag atom and the bonding in Ag_5-L, approximately 1.2-1.4 eV (see Table 2), is stronger than in Ag-L, approximately 0.5-0.6 eV (see Table 1). In the neutral systems, the electrostatic attraction between the positive metal and the negative thiocyanate ligand dominates and yields a net bonding around 4-5 eV (Tables 1 and 2). Other bonding contributions originate from the ligand polarization and, in particular for the neutral M-L system, from the thiocyanate to Ag donation. In both neutral and charged systems the SCN ligand behaves as a pseudohalogen and its ionicity is essentially ~ 1.[23]

The different nature of the bonding in the neutral and charged molecules is reflected also in the changes in the equilibrium geometry caused by an external electric field. These have been investigated for the single metal atom system only. For Ag-NCS, with the ligand normal to the surface the only effect of a field parallel to the molecular axis is to move the SCN^- ion up and down, depending on the sign of the field (see Table 3) without changing the linear shape of the molecule; the change in bond distance is much smaller for the more strongly bound neutral system than for the charged one. This is true, however, assuming that the molecule does not oscillate around the perpendicular orientation. In a real system, because of the thermal motion of the thiocyanate ligand, an attractive field can interact with the adsorbate when it deviates from the perpendicular orientation and bring it closer to the surface. This possibility, which has not been explicitly investigated here, depends on the energy required to reorientate the molecule, or, in other words, on how deep is the minimum on the potential energy surface for the bending motion. For the model of thiocyanate adsorbed near the potential of zero charge, Ag^0-NCS^-, the barrier for the bending is low[23] and the electrostatic interaction between the external field and the adsorbed ion is likely to rotate the SCN^- molecule to form an angle with the surface smaller than 180°; for the Ag^+-NCS^- system, representing adsorption on an electrode at positive potential, the barrier for bending is considerably higher due to stronger electrostatic interaction. Further calculations are needed to clarify this point. Let us now consider the effect of an external electric field on the geometry of the S-bound thiocyanate. As suggested by simple electrostatic arguments, an attractive field $F = -0.01$ *a.u.* (-5.2×10^7 V/cm), where the electrons are attracted toward the metal, further bends the molecule to form an Ag-S-C angle of 82 degrees; on a real metal surface this bending motion is limited by the presence of other Ag atoms and the SCN molecule will probably assume an orientation parallel to the Ag surface ($\alpha = 90°$). On the other hand, a repulsive field $F = +0.01$ *a.u.*, where the electrons are repelled away from the surface towards the ligand, first orients the SCN^- ion parallel to the field making the Ag-SCN^- molecule linear ($\alpha = 180°$), and then pushes the ligand away from the metal to such an extent that no minimum is found. Since this result could be an artifact of using a single metal atom (the Ag-SCN^- bonding is in fact rather weak) we applied the same field to the Ag_5-SCN^- system which is bound by approximately 1.2 eV, but the effect was essentially the same as observed already for a single metal atom. In fact, the analysis of the potential energy surface shows that in the presence of the field the SCN^- ion is oriented along the field direction and pushed away from the surface, the linear conformation induced by the field implies a weakening of the bonding mechanism since the ligand, in the case of zero coverage, prefers the bent orientation (for the $F = 0$ case, the linear form of Ag_5-SCN^- is destabilized by about 0.5 eV with respect to the bent one). Hence, making the electrode more negative corresponds to destabilize the S-bonded orientation more than the N-bonded one because in the first case an additional molecular strain is introduced.

Also for more strongly bound neutral Ag-SCN system, a field $F = -0.01$ *a.u.* further bends the molecule and brings the SCN$^-$ ion closer to the metal, while an opposite field opens the Ag-S-C angle to 114 degrees. It is worth noting, however, that in this case the applied field is not large enough to make the molecule linear, indicating a strong directionality of the Ag-SCN bond.

C. CN and CS vibrations in free and coordinated SCN

The vibrational frequencies for the C-N and C-S stretching modes have been determined for the $[\text{Ag-NCS}]^{0,-}$ and $[\text{Ag-SCN}]^{0,-}$ systems (see Table 1). The distance of the Ag atom from the ligand has been fixed at the M-L equilibrium bond distance; for the ligand vibrations, internal coordinates which fixed the SCN center of mass have been used. The coupling of the C-N and C-S stretching modes has been taken into account by determining a full two-dimensional potential energy surface. The equilibrium values r_e and the ν_e are determined from a two-dimensional polynomial fit (see Table 1). Significant shifts with respect to the free SCN^- frequencies values are found. When the thiocyanate ligand is bound at the N-site, the larger shifts are observed in ν(C-S); for Ag-NCS$^-$ the frequency ν(C-S) increases by $55\,cm^{-1}$ while for the neutral molecule the shift is about $100\,cm^{-1}$ (see Table 1). The result of the N-coordination on ν(C-N) is much smaller and of opposite sign for Ag^0 and Ag^+ substrates (see Table 1). When the thiocyanate molecule is bound at the sulphur, the C-S stretching frequency barely changes in both neutral and charged systems; on the other hand, there is a significant shift to higher frequencies of the ν(CN); again this is much more pronounced for the case of Ag^+SCN^- interaction (see Table 1). Figure 9 summarizes these shifts.

Experimentally, when the SCN ligand is N-bounded to transition metal atoms in inorganic complexes large positive shifts are found for the ν(C-S) vibration while the C-N stretching exhibits small positive shifts. The coordination on sulphur usually significantly increases the vibrational frequency of the C-N stretching while lowers that of the C-S stretching. Our present calculated vibrational frequency shifts are consistent with these experimental data.

IV. Interpreting IR Spectra

A. Comparison with SERS Spectra

There have been several surface-enhanced Raman studies of thiocyanate adsorbed on polycrystalline silver electrodes[24-26], and overall the reversible Raman spectral intensity for the C-N stretching mode parallels that described here for the IR spectra. There are, however, some noteworthy differences in band shape, peak position, and potential dependence. In particular, peak positions of ν_{CN} are smaller at the same potential (ignoring differences in electrolyte composition which may be the physical source of this displacement) and FWHMs are much narrower 25 cm^{-1} for IR compared to 35 cm^{-1} for SERS. Raman and IR exist over the same range, though IR are reproduced after polarizing the electrode beyond -700 mV for several seconds, whereas SERS are not. This difference is due to the metastable nature of SERS active sites as discussed previously.[3] The main difference is the structure resolved in Fig. 4 indicating the existence of two characteristically different populations, one with a strong potential dependence and one with minimal dependence. For easy reference Table 4 summarized experimental stretching mode frequencies ν_{CN} and ν_{CS} for thiocyanate ions adsorbed on electrodes and in the solid or in solution.

B. State of the Electrode Surface

Polycrystalline silver electrode surfaces can be envisioned as a jumble of exposed (111), (100) and (110) surface offering a manifold of coordination sites for the thiocyanate anions and water molecules. For polycrystalline silver the pzc is around -900 mV (versus Ag/AgCl) in the absence of specific ion adsorption. The ideally polarizable potential range from cyclic voltammograms is ca. 50 mV to -1200 mV. Capacitance measurements shows that the electrode adsorbs approximately a monolayer in this range. It is only for potentials more negative than -800 mV that the coverage drops below saturation values. This is shown in Fig. 10 adapted from Ref. 3. The extrapolation in this figure is done to bring out some qualitative points and is by no means a quantitative or an accurate representation of what actually happens.

The picture which emerges then is of a mosaic of low index faces with coverage in the range $\theta \gtrsim 0.5$ where $\Gamma_z = 0.98 \times 10^{15}$ *molecules/cm*^{2} and $\Gamma_x - 0.48 \times 10^{15}$ *molecules/cm*^{2} for geometric saturation with ligand axis perpendicular (z) or parallel to the surface. The range of potentials and concentrations over which the IR data is obtained the electrode surface coverage is greater than saturation coverage for parallel configuration The averaged oxidation state of the surface atom has been estimated[3] to lie between 0.1 (-1000 mV) and

0.2 (0 mV). It is conceivable that this mosaic surface undergoes considerable reconstruction driven by electrode potential and specific ion adsorption.

C. Interpretation of IR Spectra

Figure 11 shows the position of the surface thiocyanate vibrational frequency (cm^{-1}) plotted against electrode potential for all concentrations of thiocyanate ions in solution. The vibrational frequency of adsorbed thiocyanate (with S- end down) is independent of the thiocyanate ion concentration in solution but shows a variation with electrode potential of about 50 cm^{-1}/V. This would be consistent with either weak lateral interactions or saturation coverage and lateral interactions of any strength. In contrast the intensity of the band has an interesting and significant dependence on thiocyanate ion concentration in solution (see Figure 12). Three regimes are observed in intensity variation with potential based on the solution concentration. At potentials more negative than -0.6 V there is an almost total absence of IR intensity, yet experimental measurement of double layer capacitance implies the presence of high fractional monolayer coverage of thiocyanate ions.

The theoretical calculations pertain to isolated ligands and therefore offer no new insight regarding lateral interactions. For isolated ligands the theory calculations show N down adsorption to be perpendicular to the surface ($\alpha = 180°$) and S down to be almost parallel ($\alpha = 90°$). Furthermore the binding energy is qualitatively the same when equilibrium geometries are compared (see Tables 1 and 2). However for $\alpha = 180°$, N is preferred over S bonding. The following interpretation attempts to judiciously interpret the observed spectra using our SCF calculations and what is already known about thiocyanate ion adsorption on metal electrode.

First we note from Table 1 that the SCF calculations predict that ν_{CN} for S-bound will be greater than ν_{CN} for N-bound to the silver atom or ion. This is consistent with experiment where relative to the solution value of the acqueous ion (ν_{CN} = 2053 cm^{-1}) the corresponding value for M-SCN is ν_{CN} = 2120 cm^{-1} (70 cm^{-1} shift) and for M-NCS is ν_{CN} = 2080 cm^{-1} (30 cm^{-1} shift). Note that the calculated SCF are several hundred wavenumbers larger overall. This is a well known effect due to lack of correlation in the SCF wavefunction. It is unimportant for our deliberations.

We next assert that at large negative potentials, negative of 0.60 V, the adsorbed thiocyanate ion is adsorbed approximately parallel to the surface, and consequently by the surface selection rule shows no IR adsorption intensity. The absence of IR intensity from ν_{CN} due to N bound thiocyanate ion at large negative potentials is interesting since it will be allowed by the surface selection rule. Given the approximately equal electrostatic binding energies D_e in Tables 1 and 2 we conclude a greater gain in free energy from entropic forces for S down at high dilution. Recall that for contact adsorbing ligands like halides, thiocyanate, etc, the electrostatic interactions between metal and ion, though large are relatively constant, and adsorption characteristics are controlled more by entropic effects. As the electrode is made more positive (0 to $+0.20$ is the effective range in the double layer region) more thiocyanate is attracted to the electrode and to accommodate higher surface packing the ligands are assumed to orient more perpendicular. At this point the surface selection rule permits experimental detection of ν_{CN}. This reorientation might also be the result of surface morphological changes, such as a change in the relative areas of exposed (110), (100), and (111) facets. Indeed it is not inconceivable that thiocyanate ion adsorption at negative potentials occurs on terraces of width small enough to accommodate both S and N down adsorption.

We further note that relative to the SCF calculation of the free ion, adsorption on silver increases ν_{CN} and ν_{CS} stretching frequencies for all except one case for which the ν_{CN} of Ag-NCS is smaller by less than two percent. Figure 9 plots how these frequencies might change with valence state between Ag^0 and Ag^+. The ν_{CS} mode is less sensitive to oxidation state of the metal for S-coordination than N-coordination. This supports the interpretation of SERS of thiocyanate on Ag that the ν_{CS} mode arises from S-coordination. For ν_{CN} there is greater overall positive shift for S adsorption compared to ν_{CN} for N end adsorption. This is consistent with empirical observations of the IR spectra of coordination compounds.[9] We can, therefore, interpret the high frequency bands in the IR spectra as due to S-down adsorption. However, for N-bonding there is an overall negative shift in frequency with increasing oxidation state of the metal. Experimentally, N-bonding generally leads to little change or even a decrease below the free ion value in coordination compounds.[9] In our IR we see a shift from 2070 cm^{-1} to 2095 cm^{-1} with no dependence on electrode potential.

The theoretical calculations show N-bonding energetically slightly more favorable than S, certainly for perpendicular orientation of S- end down. However, for the optimized geometry, 180° for N-down and approximately 100° for S-down the differences are small enough to be within the accuracy of the calculation. Hence the energetics favoring S-bonding over N-bonding may not be so distinct and so it becomes energetically possible to adsorb N-down. This would explain the occurrence of the doublet in the spectra of Fig. 4 and the shoulders apparent in Figs. 1 and 3. The high frequency mode (at 2120 cm^{-1}) is assigned to S-bonded and the lower frequency component to N-bonded (at 2098 cm^{-1}). However it is worth noting that at potentials negative of -0.3 V because vibrational frequency of S-end down thiocyanate should be around

2100 cm^{-1} which is quite close to that for N-end down thiocyanate it is not possible to unequivocally assign the observed IR band to either S- or N- end down species.

These results allow us to hypothesize that the N down thiocyanate adsorbs on a particular low index plane. The preferential orientation for N-end down thiocyanate species is perpendicular to the surface and hence these species reach saturation coverage at fairly high negative potential which is dependent on the thiocyanate concentration in solution. The surface coverage of these N- end down thiocyanate depends on the abundance of this particular low index plane and it represents only a small fraction of the total thiocyanate coverage. This results in a weak band which shows almost no dependence on thiocyanate ion concentration in solution. Furthermore, in agreement with the computation the vibrational frequency of this band shows only a weak dependence on electrode potential. The thiocyanate concentration of 10 mM is optimum in regards that there is proper balance between the adsorbed thiocyanate both S- and N- end down which allows for resolution of their corresponding bands. The S- end down thiocyanate adsorbs mainly on all other lower index facets (not the ones with N end down). The surface coverage and the orientation angle α of these S- end down species increases as the potential becomes more positive. This results in observation of increased band intensity and field dependence.

Another point of interest is the motion of the ion against the metal in the presence of a static electric field (see Table 3). The movement is larger the closer the oxidation state of the metal is to zero. Clearly, the adsorption of ions near the pzc region should be sensitive to changes in the electrolyte composition even though the changes in the electric field at the silver surface are small.

V. Summary

In-situ FT-IR spectroscopy of adsorbed thiocyanate and ab initio calculations of the ion adsorbed to simple metal clusters has been used to build a picture of the electric double layer. At potentials close to but positive of the pzc thiocyanate adsorbed flat bound through the S atom to a top site of the surface lattice. The support for this conclusion comes from diminished IR intensity under conditions known to have considerable surface coverage and the theoretical calculation of preferred S bound with ligand almost parallel to the surface ($\alpha = 90°$). As the electrode is made more positive increased coverage forces the S bound ligands to reorientate with configuration axis more perpendicular ($\alpha = 180°$). This is a result of steric contributions to free energy of adsorption winning out over bonding interactions of the isolated ligand. The vibrational frequency of the S bound thiocyanate is independent of the thiocyanate ion concentration in solution but shows a variation with electrode potential of about 50 cm^{-1}/V. A band at about 2098 cm^{-1} is assigned to N-down binding which occurs possibly on facets distinct from those covered by S-bonded ligands or at grain boundaries. The stretching mode frequency ν_{CN} for N-down sites is lower in frequency than for S-down and is independent of the electrode potential.

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Table 1

Geometry and Vibrational Frequency
For Free and Coordinated SCN^- and SCN Ligands

	D_e eV	r(M-L) bohr	α degrees	r(S-C) bohr	r(C-N) bohr	ν(C-N) cm^{-1}	ν(C-S) cm^{-1}
				Theory			
SCN^-(SCF)				3.268	2.179	2334/...	681/...
SCN^-(CAS)				3.294	2.220	2183/...	662/...
Ag-NCS^-	0.64	4.47	180.	3.221	2.175	2356/+22	736/+55
Ag-NCS	5.27	4.04	180.	3.177	2.188	2299/−35	778/+97
Ag-SCN^-	0.49	5.39	107.	3.272	2.172	2369/+35	687/+6
	0.25	5.81[a]	180.[b]	3.254	2.175	2355/+21	703/+22
Ag-SCN	5.17	4.82	98.	3.276	2.163	2421/+87	698/+17
	4.35	4.78[a]	180.[b]	...	...	...	...

a) Minimum geometry for a linear conformation
b) Not optimized

Note $[Ag\text{-}NCS]^{0,-}(\alpha = 180°)$
NCS^- more strongly bound than
$[Ag\text{-}SCN]^{0,-}(\alpha = 180°)$

Table 2

Geometry of SCN^- Ligand
Chemisorbed on the Top Site of a Ag_5 Cluster

	D_e eV	r(M-L)[a] bohr	α[a] degrees
$\lvert Ag_5\text{-}NCS \rvert^-$	1.41	4.25	180.
$\lvert Ag_5\text{-}NCS \rvert$	4.12	4.11	180
$\lvert Ag_5\text{-}SCN \rvert^-$	1.17	5.09	105.
	0.69	5.28[b]	180.[c]
$\lvert Ag_5\text{-}SCN \rvert$	3.99	4.91	97.

a) r(M-L) and α(M-L) were obtained from a two-dimensional fitting of the potential energy surface; the S-C and C-N distances were fixed at the values 3.2 a.u. and 2.2 a.u., respectively.

b) Minimum geometry for a linear conformation

c) Not optimized

Note S down less strongly bound than N down.

Table 3

Geometry of $|\text{Ag-NCS}|^{0,-}$ and $|\text{Ag-SCN}|^{0,-}$
In the Presence of an Electric Field

System	Field a.u.	r(M-L)[a] bohr	α(M-L)[a] degrees	r(S-C) bohr	r(C-N) bohr
SCN^-	−0.01			3.24	2.19
	0			3.27	2.18
	+0.01			3.30	2.17
Ag-NCS^-	−0.01	4.29	180.[c]	3.21	2.19
	0	4.47	180.	3.22	2.18
	+0.01	4.92	180.[c]	3.27	2.19
Ag-NCS	−0.01	3.92	180.[c]	...	...
	0	4.04	180.	3.18	2.19
	+0.01	4.22	180.[c]	...	...
Ag-SCN^-	−0.01	5.34	82.	...	...
	0	5.39	107.	3.27	2.17
	+0.01[b]	...	...	...	...
Ag-SCN	−0.01	4.72	84.	...	...
	0	4.82	98.	3.28	2.16
	+0.01	5.01	114.	...	...

a) r(M-L) and α(M-L) were obtained from a two-dimensional fitting of the potential energy surface; the S-C and C-N distances were fixed at the values 3.2 a.u. and 2.2 a.u., respectively.

b) This geometry is not stable in a repulsive electric field of $F = +0.01$ a.u.; the molecule becomes linear and then dissociates.

c) Not optimized.

Table 4

Vibrational Frequencies (cm^{-1}) of Thiocyanate

SCN^-/Ag			ν_{CN}		ν_{CS}
Potential	SERS		IR		SERS
mV vs. Ag/AgCl	10 mM	1 mM	10 mM	100 mM	
75		2121			
50		2122	2118,2098		
0		–	2114,2098	2118	
−50		2111	2112,~2091	2114	
−100	2116	2108	–	2111	735
−200	2114	2102	2108	2100	
−300	2111	2100	–	2098	735
−400	2108		2094	–	
−500	2106		2095	2095	735
−600	2103			2095	
−700	2100				
−800	2097				
SCN^- aqueous	2067				750
KSCN solid	2053				746
AgSCN solid	2140				–
$NH_4Ag(SCN)_2$	2101,2086				718
M-SCN	ca. 2100-2130				~700
M-NCS	ca. 2040-2070				ca. 800-820
M-NCS-M	ca. 2120-2100				–
M-S(CN)-M	ca. 2150-2185				

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Legends for Figures.

Figure 1. FT-IRRAS spectra of adsorbed thiocyanate ions on a Ag electrode as a function of the electrode potential. Electrolyte 1mM NaSCN in 0.1 M $NaClO_4$. All potentials measured relative to the Ag/AgCl (3M KCl) reference electrode.

Figure 2a & b. FT-IRRAS spectra of adsorbed thiocyanate ions on a Ag electrode as a function of the electrode potential. Electrolyte 1mM NaSCN in 0.1 M $NaClO_4$. All potentials measured relative to

Figure 3. FT-IRRAS spectra of adsorbed thiocyanate ions on a Ag electrode as a function of the electrode potential. Electrolyte 5mM NaSCN in 0.1 M $NaClO_4$. All potentials measured relative to the Ag/AgCl (3M KCl) reference electrode.

Figure 4. FT-IRRAS spectra of adsorbed thiocyanate ions on a Ag electrode as a function of the electrode potential. Electrolyte 10mM NaSCN in 0.1 M $NaClO_4$. All potentials measured relative to the Ag/AgCl (3M KCl) reference electrode.

Figure 5. FT-IRRAS spectra of adsorbed thiocyanate ions on a Ag electrode as a function of the electrode potential. Electrolyte 100mM NaSCN in 0.1 M $NaClO_4$. All potentials measured relative to the Ag/AgCl (3M KCl) reference electrode.

Figure 6. FT-IRRAS spectra of adsorbed thiocyanate ions on a Ag electrode as a function of the electrode potential. Electrolyte 1000mM NaSCN in 0.1 M $NaClO_4$. All potentials measured relative to the Ag AgCl (3M KCl) reference electrode.

Figure 7 FT-IRRAS spectra of adsorbed thiocyanate ions on a Ag electrode at electrode potential of 0.0 V (versus Ag/AgCl reference electrode) for various concentrations of thiocyanate ions in solution

Figure 8 The minimum energy configurations of SCN^- adsorbed on a Ag_5(1,4) cluster with S- and N-end down.

Figure 9. The vibrational frequencies for CN and CS stretches in $[Ag\text{-}NCS]^{0,-}$ and $[Ag\text{-}SCN]^{0,-}$.

Figure 10. The dependence of Surface concentration of thiocyanate ions on the Ag electrode with potential measured versus Ag/AgCl (3M KCl) reference electrode. The solid curve is data from Ref. 3. The dashed curve is extrapolation of the data from Ref. 3 to cover the potential range used in this IR study.

Figure 11. Dependence of the surface S- end down thiocyanate peak vibrational frequency (cm^{-1}) on electrode potential. All potentials measured relative to Ag/AgCl (3M KCl) reference electrode.

Figure 12. Variation of intensity of the surface S- end down thiocyanate peak with electrode potential for different concentration of thiocyanate ions in solution. All potentials measured relative to Ag/AgCl (3M KCl) reference electrode.

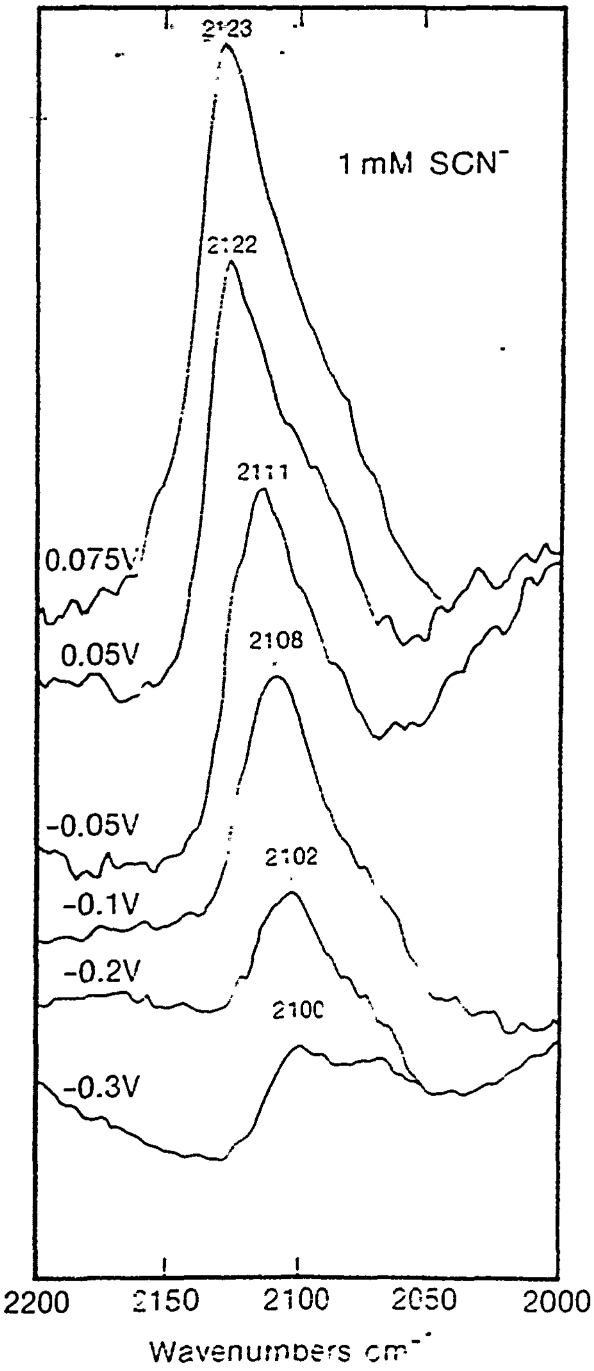
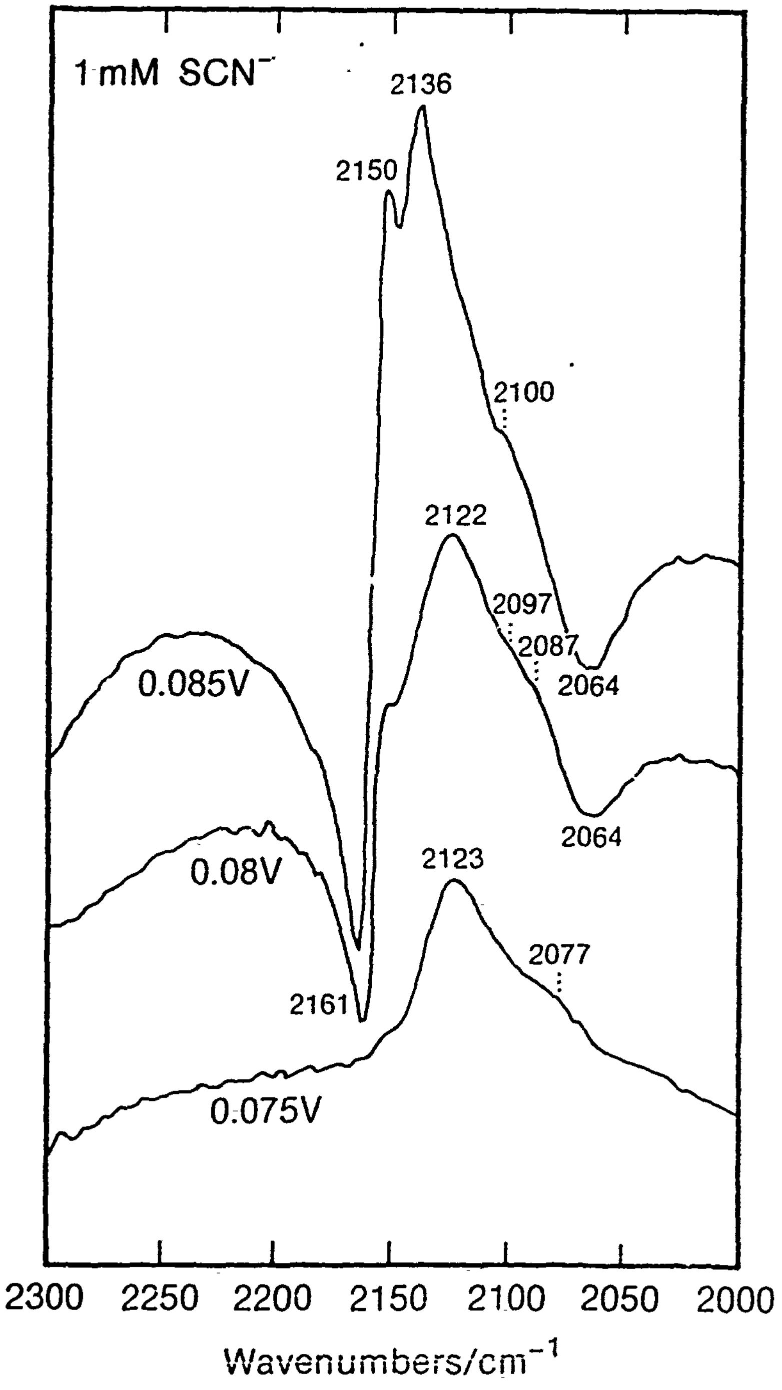

2123
1 mM SCN⁻
2122
2111
2108
2102
2100
0.075V
0.05V
-0.05V
-0.1V
-0.2V
-0.3V
2200
2150
2100
2050
2000
Wavenumbers cm⁻¹

Figure 1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2150
2100
2122
2097
2087
2064
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2064
0.08V
2123
2077
2161
0.075V
2300
2250
2200
2150
2100
2050
2000
Wavenumbers/cm⁻¹

Figure 2a

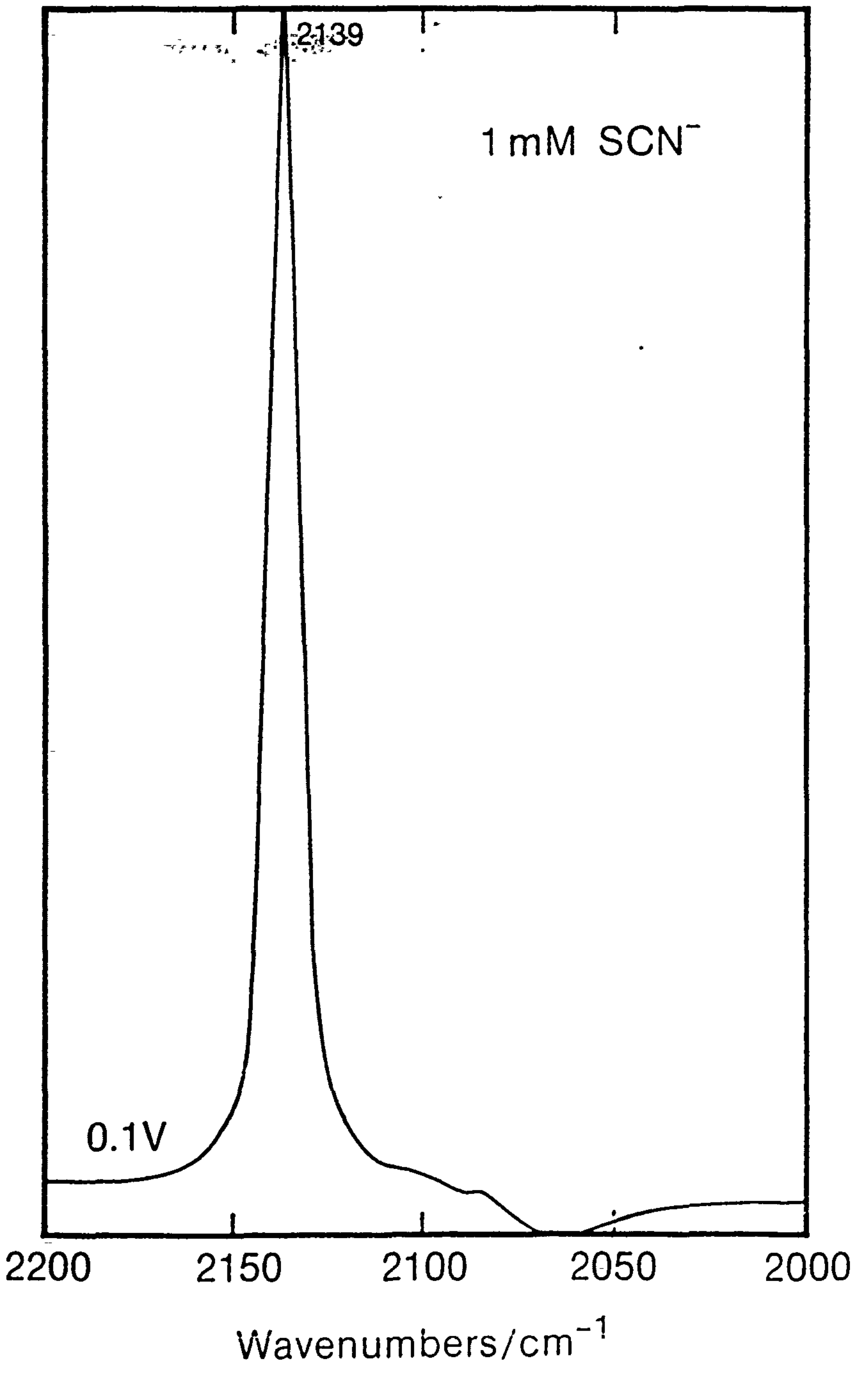


Figure 2b

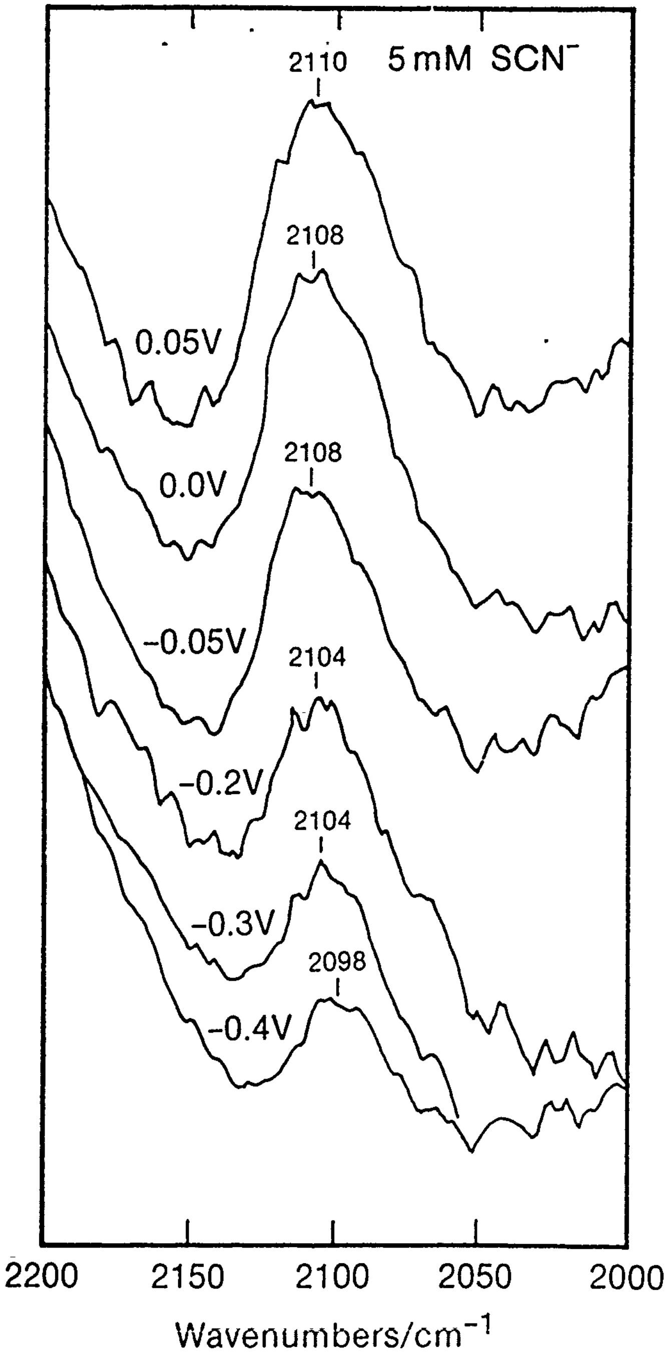
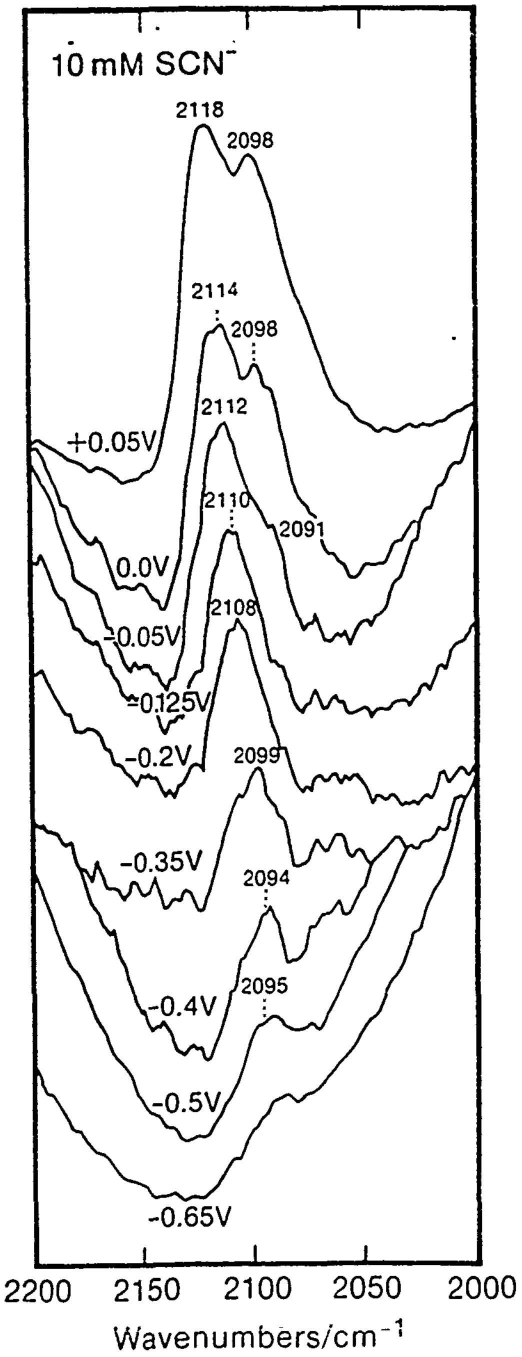

5 mM SCN⁻
2110
2108
2108
2104
2104
2098
0.05V
0.0V
−0.05V
−0.2V
−0.3V
−0.4V
2200
2150
2100
2050
2000
Wavenumbers/cm⁻¹

Figure 3


10 mM SCN$^-$
2118
2098
2114
2098
2112
2091
2110
2108
2099
2094
2095
+0.05V
0.0V
-0.05V
-0.125V
-0.2V
-0.35V
-0.4V
-0.5V
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2200
2150
2100
2050
2000
Wavenumbers/cm^{-1}

Figure 4

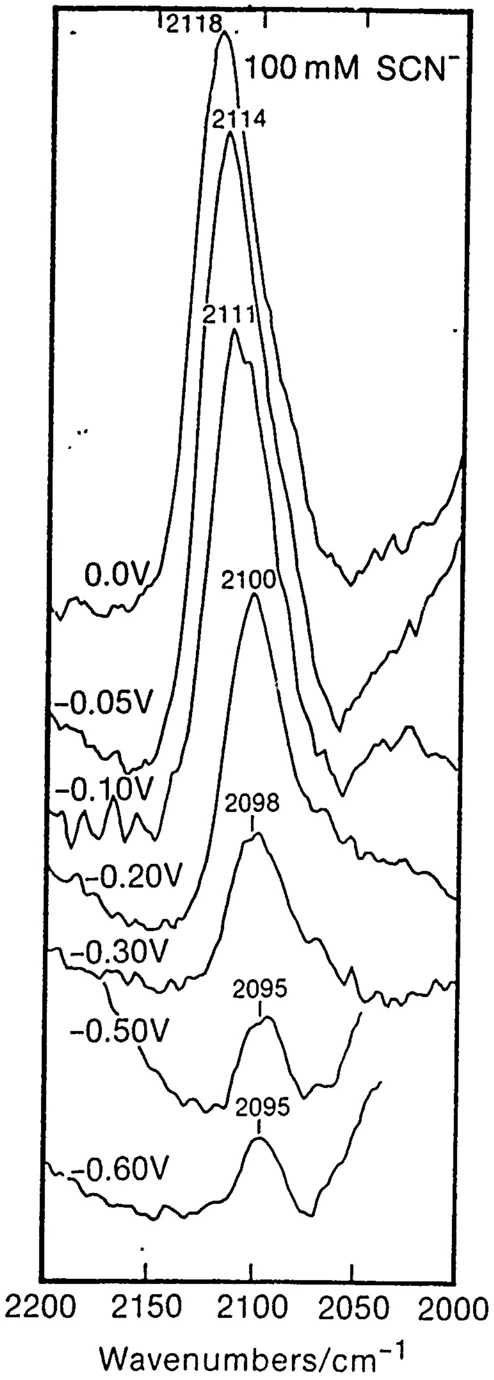
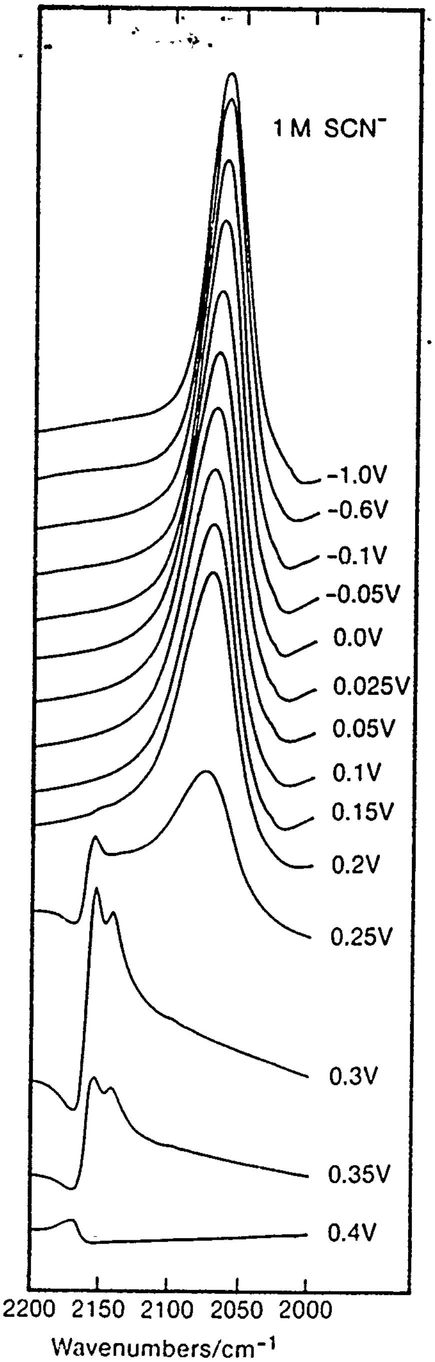

2118
100 mM SCN⁻
2114
2111
2100
2098
2095
2095
0.0V
-0.05V
-0.10V
-0.20V
-0.30V
-0.50V
-0.60V
2200
2150
2100
2050
2000
Wavenumbers/cm⁻¹

Figure 5


1 M SCN⁻
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-0.6V
-0.1V
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0.0V
0.025V
0.05V
0.1V
0.15V
0.2V
0.25V
0.3V
0.35V
0.4V
2200
2150
2100
2050
2000
Wavenumbers/cm⁻¹

Figure 6

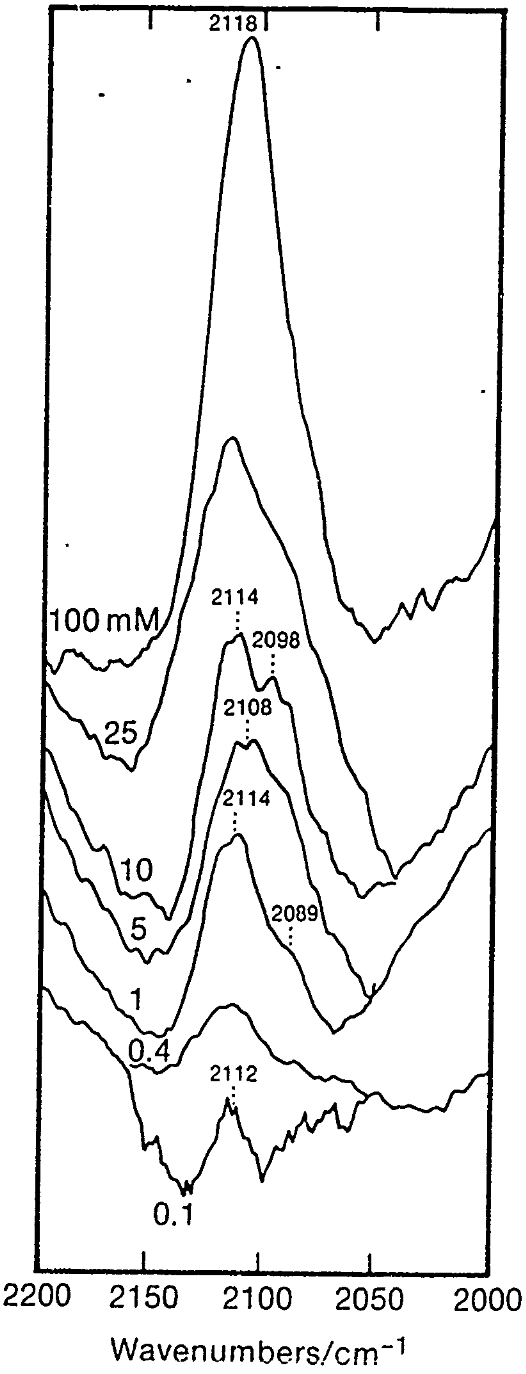
2118
100 mM
25
2114
2098
10
2108
5
2114
2089
1
0.4
2112
0.1
2200
2150
2100
2050
2000
Wavenumbers/cm-1

Figure 7

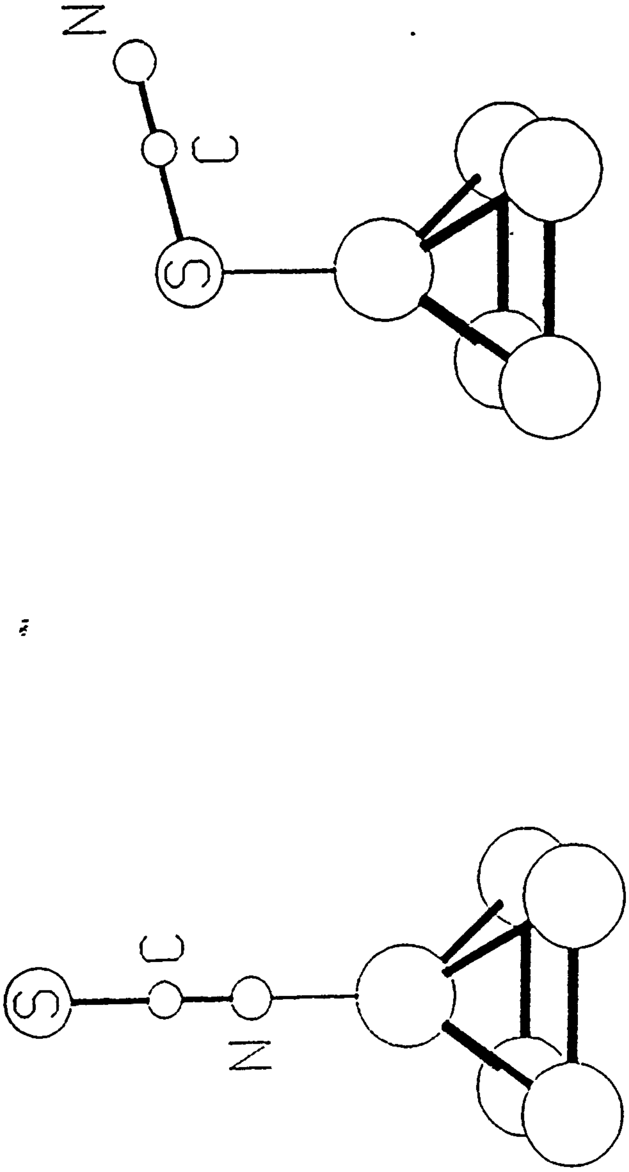

Figure 5

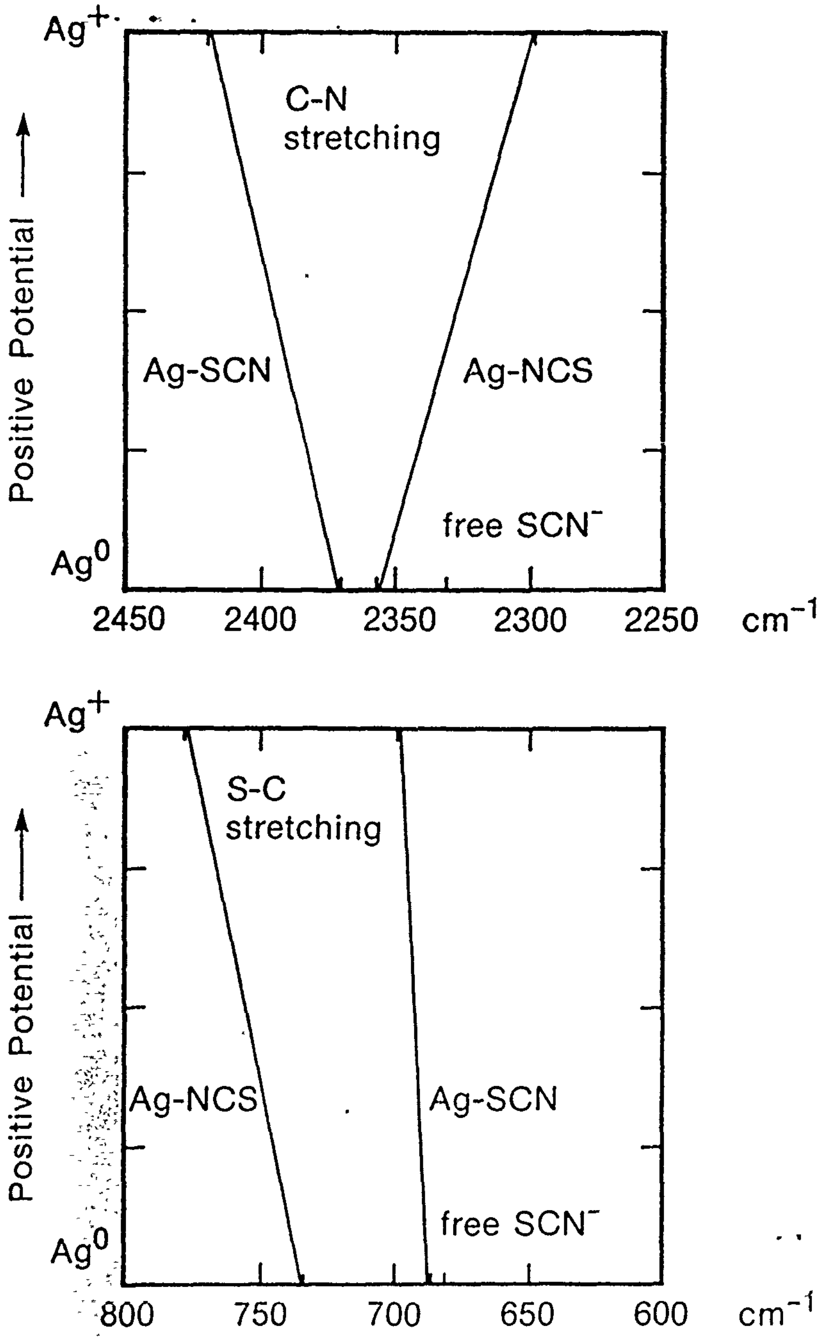
Ag+
Ag0
Positive Potential
C-N stretching
Ag-SCN
Ag-NCS
free SCN-
2450
2400
2350
2300
2250
cm-1
Ag+
Ag0
Positive Potential
S-C stretching
Ag-NCS
Ag-SCN
free SCN-
800
750
700
650
600
cm-1

Figure 9

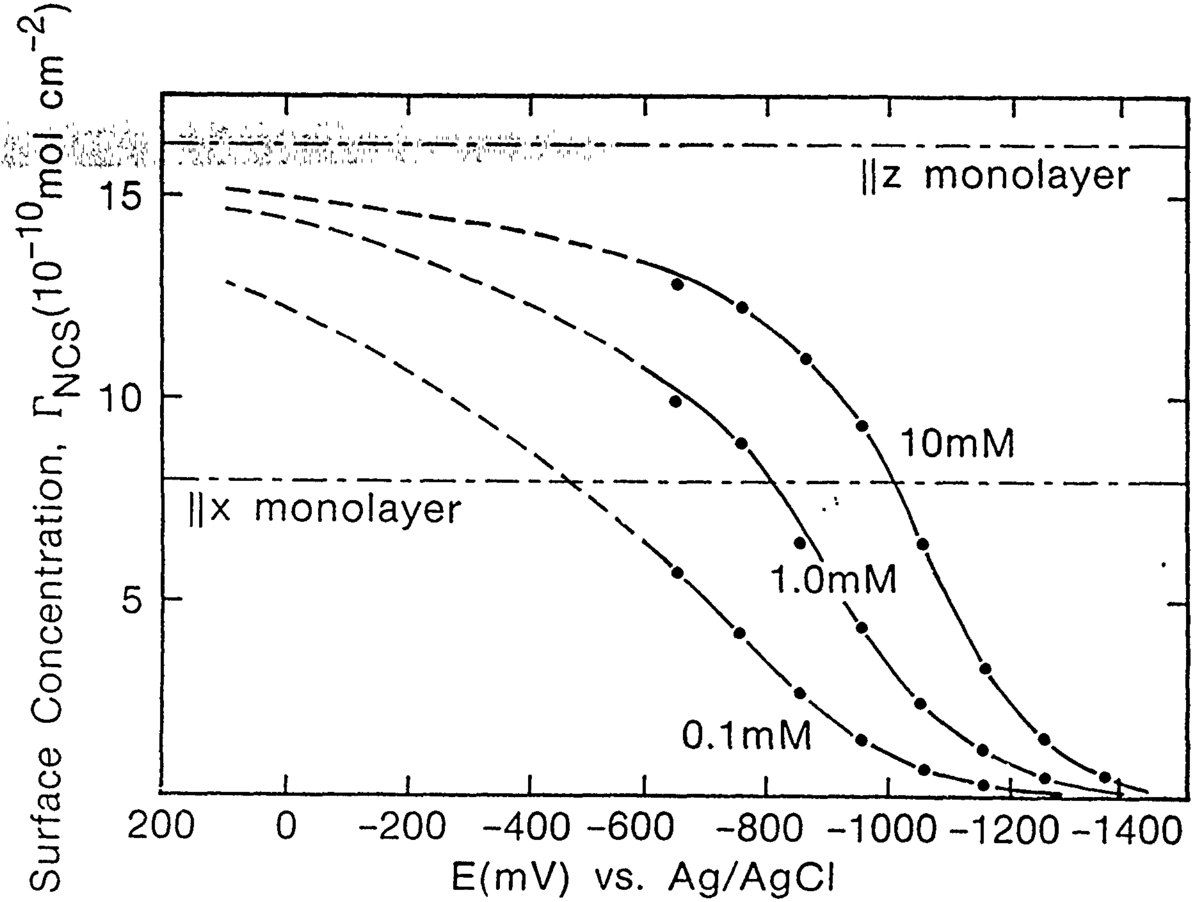
||z monolayer
||x monolayer
10mM
1.0mM
0.1mM
15
10
5
200
0
-200
-400
-600
-800
-1000
-1200
-1400
Surface Concentration, $\Gamma_{NCS}(10^{-10}\text{mol cm}^{-2})$
E(mV) vs. Ag/AgCl

Figure 10

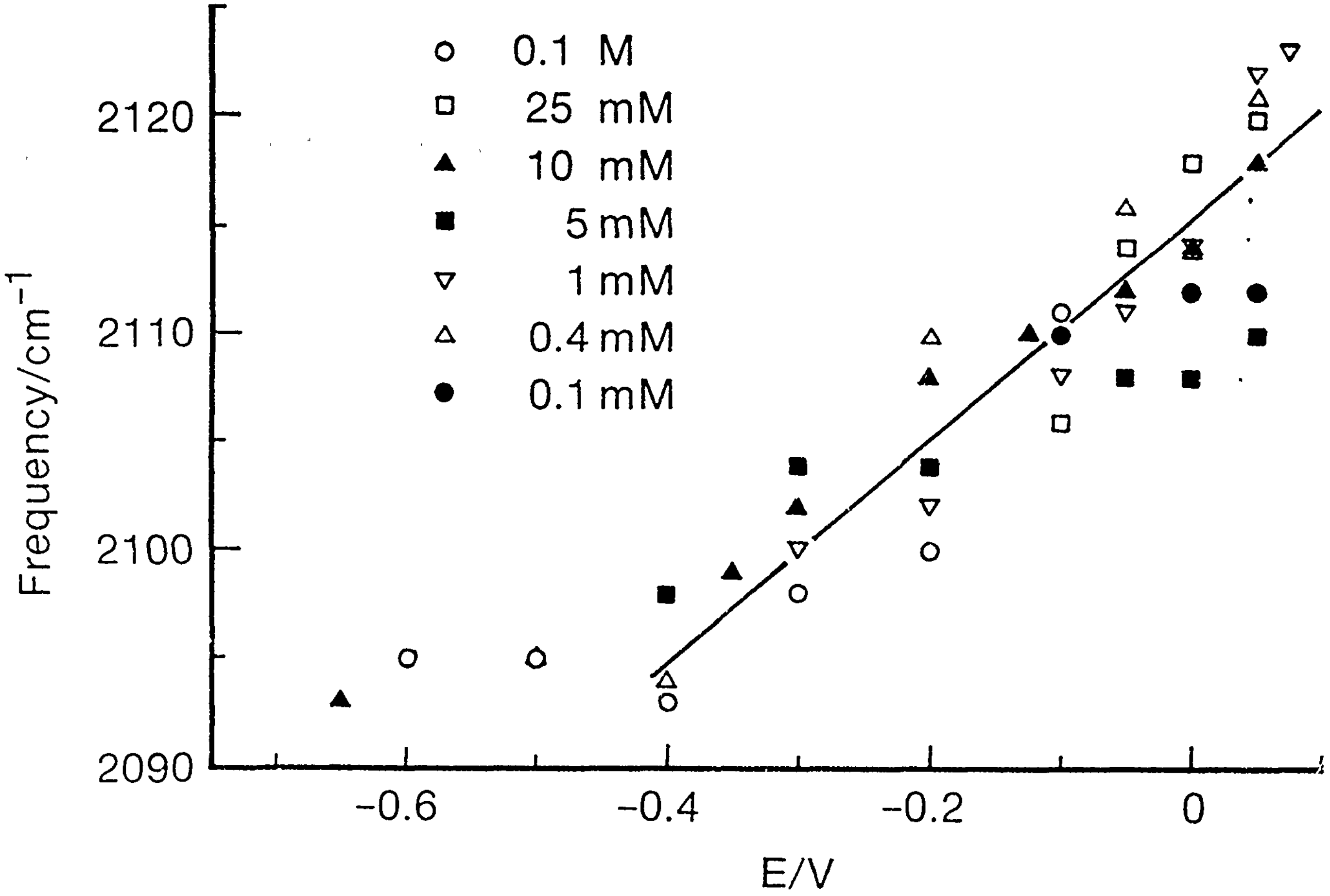
○ 0.1 M
□ 25 mM
▲ 10 mM
■ 5 mM
▽ 1 mM
△ 0.4 mM
● 0.1 mM
Frequency/cm⁻¹
2090
2100
2110
2120
−0.6
−0.4
−0.2
0
E/V

Figure 11

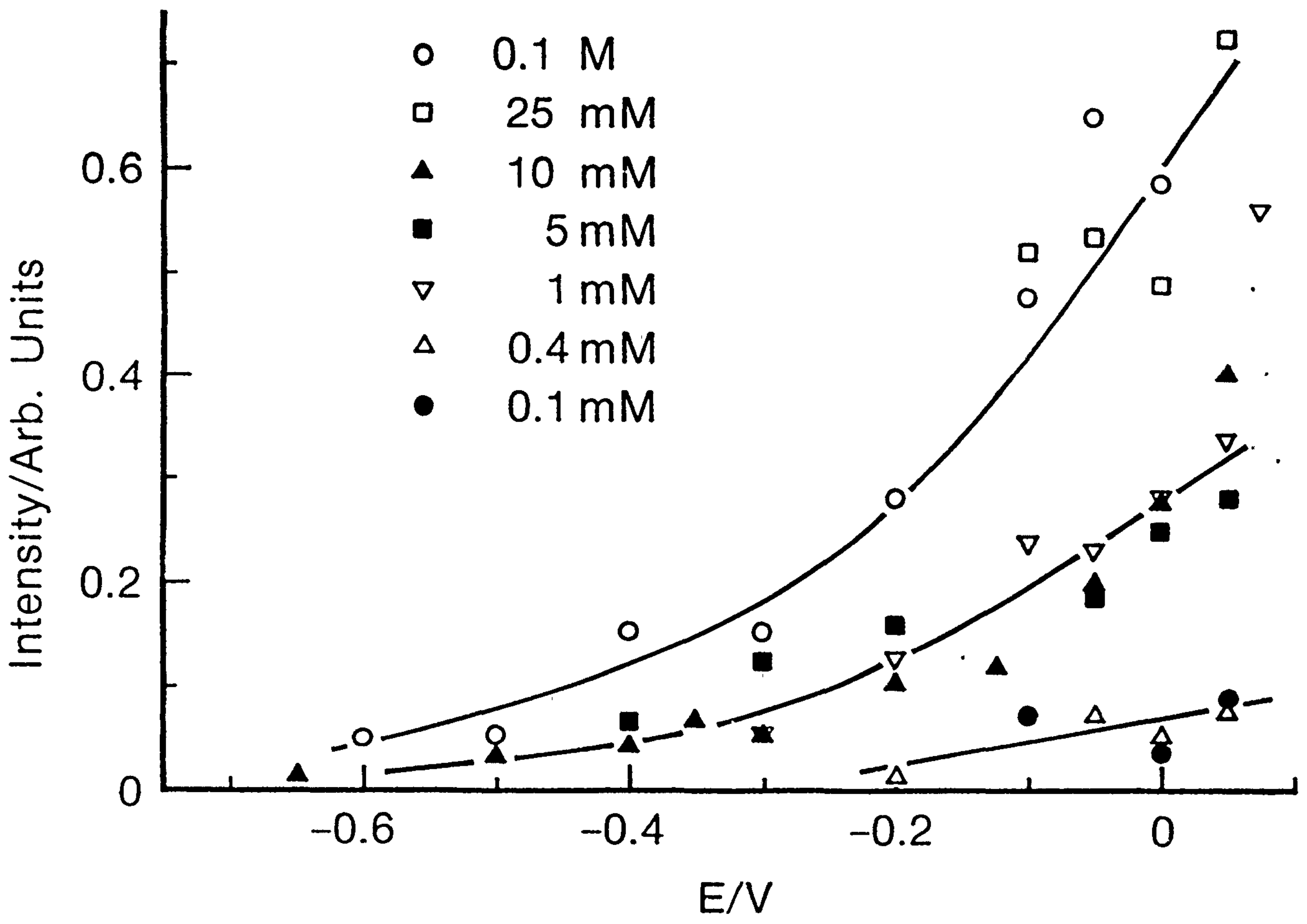
○ 0.1 M
□ 25 mM
▲ 10 mM
■ 5 mM
▽ 1 mM
△ 0.4 mM
● 0.1 mM
Intensity/Arb. Units
0
0.2
0.4
0.6
E/V
−0.6
−0.4
−0.2
0

Figure 12