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INFRARED SPECTROELECTROCHEMICAL STUDY OF CYANIDE ADSORPTION AND REACTIONS AT PLATINUM ELECTRODES IN AQUEOUS PERCHLORATE ELECTROLYTE

by

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INFRARED SPECTROELECTROCHEMICAL STUDY OF CYANIDE ADSORPTION AND REACTIONS AT PLATINUM ELECTRODES IN AQUEOUS PERCHLORATE ELECTROLYTE

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ABSTRACT

In situ infrared (IR) spectroelectrochemistry is used to investigate the behavior of cyanide (CN^-) at polycrystalline platinum surfaces in aqueous perchlorate (ClO_4^-) electrolyte. IR spectroelectrochemical data reveal the existence of a number of surface, as well as solution, cyanide species in the interfacial region. Within the double-layer potential region, there is IR evidence for several forms of adsorbed cyanide, CN^-_{ads} ($\nu_{max} \approx 2070$ cm^{-1}, $\nu'_{max} \approx 2145$ cm^{-1}, and $\upsilon''_{max} \approx 2170$ cm^{-1}). When the potential is made sufficiently positive, cyanide is oxidized to form cyanate (OCN^-; $\nu_{max} = 2171$ cm^{-1}). Other solution cyanide species which may be formed at the platinum-cyanide solution interface include hydrogen cyanide (HCN; $\nu_{max} \approx 2095$ cm^{-1}) and square planar platinum cyanide complex ($Pt[CN]_4^{2-}$; $\nu_{max} = 2133$ cm^{-1} (IR-active E_u mode)). The interfacial electrochemistry of the $Pt/CN^-/ClO_4^-$ system was found to be influenced not only by the applied electrode potential, but is also driven by in part changes in the interfacial pH, which is potential-dependent. In situ IR spectroelectrochemistry reveals details of the potential-dependent surface chemistry of the Pt/CN^- system, the complexities of which cannot be easily studied by other techniques.

INTRODUCTION

In recent years, the combination of infrared (IR) spectroscopy and electrochemistry, i.e., IR spectroelectrochemistry, has been shown to be a powerful tool for investigations of the electrode/solution interface (1, 2). The technology has long been employed for investigations of electrode surfaces, and has also seen use in solution studies (3, 4). As a surface-sensitive in situ vibrational spectroscopic tool, IR spectroelectrochemistry is extremely useful for studies of the structural, bonding, and dynamical properties of adsorbate species on electrode surfaces where the system is under potentiostatic control (1, 2). Furthermore, the methodology has been shown to provide highly detailed information on the potential-dependent behavior of supporting electrolyte and solvent molecules at electrochemical interfaces (5, 6). In this study, in situ IR spectroelectrochemistry is used to probe the behavior of cyanide at the interface between a platinum electrode and an aqueous perchlorate electrolyte.

The vibrational spectroscopy of cyanide species on various polycrystalline metal electrode surfaces (e.g., Ag, Au, Cu, Pt, Pd) has been investigated by surface-enhanced Raman scattering (SERS) (7-14) and/or IR spectroelectrochemistry (15-26). Since platinum is not a SERS-active surface, surface vibrational spectroscopic studies of adsorbate species on this metal are limited to other techniques besides SERS. In situ IR spectroscopic studies of cyanide species on platinum in electrochemical systems have been relatively few (19, 20, 22, 26), owing to the difficulties in obtaining useful information from the spectral data, which tend to be rather complex. Other methods which have been used to investigate the surface vibrational spectroscopy of cyanide species on platinum electrodes include the in situ laser spectroscopic technique of sum-frequency generation (SFG) (27, 28), and the ex situ techniques of low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) (29, 30). In situ spectroscopic techniques are generally preferred for studies of electrochemical systems, for the spectra are taken while the electrode remains under potential control. This ensures that any observed changes in spectral features result from changes in the applied potential, and not from changes in the surface environment that may arise from removal of the electrode from solution or from potential control. Nevertheless, ex situ spectroscopic methods can provide data which may be crucial for interpreting spectra which are obtained by in situ techniques.

IR spectroscopic features of surface cyanide species on platinum tend to be obscured by solution species such as cyanide, cyanate, and platinum/cyanide complexes (19, 22, 26). For this reason, alternative techniques have been employed in efforts to eliminate spectral interferences from solution cyanide species which are formed when the system remains under potential control (19, 26-28). In previous IR spectroscopic studies of cyanide on platinum, potential modulation experiments were not attempted since the oxidation reaction was found to be irreversible (19). Also, IR experiments have been conducted in which the electrode is first exposed to cyanide in an electrolyte solution, and then solution cyanide is removed and replaced with cyanide-free electrolyte (26). In the work presented here, we employ in situ IR spectroelectrochemistry to investigate the platinum/cyanide system in perchlorate electrolyte by potential modulation techniques. In this study, results of previous spectroscopic investigations provide for an interpretation of IR spectroelectrochemical data which are obtained (from a cyanidecontaining electrolyte solution) by modulating the electrode potential. This is successfully accomplished, even though the system under study demonstrates complex interfacial processes.

EXPERIMENTAL

The IR spectroelectrochemical technique employed was a potential modulation method, subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) (31).. The surface sensitivity of this potential difference infrared (PDIR) (32) spectroscopic technique was enhanced by using p-polarized radiation. Spectroscopic information on solution species was obtained by using s-polarized IR radiation. Typically 500 to 1000 spectra were recorded at each potential, and difference IR spectra were obtained at 4 cm^{-1} resolution. Reference spectra were recorded at the more negative potential, while sample spectra were obtained at a more positive applied voltage. The voltage was switched after every 32 scans (approximately 1 sec/scan) at each (reference or sample) potential.

A custom-made external reflection spectroelectrochemical cell, fabricated from borosilicate glass, was placed in the sample chamber of a Fourier transform infrared (FTIR) spectrometer (IBM IR/98). The spectrometer contained a globar IR source and a liquid nitrogen-cooled indium antimonide detector (Infrared Associates). The spectroelectrochemical cell employed a calcium fluoride prism IR window (Frank Cooke, Inc.) and a bulk polycrystalline platinum mirror electrode (Johnson-Matthey). The platinum surface was polished mechanically with successively smaller grades of polishing alumina (Buehler; 1.0, 0.3, and 0.05 μm). A KRS-5 wire grid polarizer (Harrick) was used to polarize the incident IR radiation, which was approximately 65° with respect to the electrode surface normal. Potential control was achieved with a potentiostat/waveform generator system (Princeton Applied Research 175/179 system), and voltages were recorded vs. the Ag/AgCl (3 M KCl) reference electrode (Microelectrodes, Inc.). Voltammograms were recorded on an IBM model 7424 MT x-y plotter.

For some spectra, the polarization modulation technique, Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS) (16), was combined with potential modulation in an effort to obtain confirmatory surface-specific information. Polarization modulation was accomplished with a zinc selenide photoelastic modulator (Hinds International), operated at 78 kHz, and a two-phase lock-in amplifier (Princeton Applied Research model 5206). Difference spectra were obtained as described above for SNIFTIRS in the absence of polarization modulation.

Reagent grade sodium cyanide and sodium perchlorate (Aldrich) were used as received. Deionized (Barnsted Nanopure, 18 MΩ), organic-free (Barnsted Organopure) water was used for the preparation of all solutions, and electrolyte solutions were purged with ultrapure nitrogen (99.99%) prior to each experiment. Experiments were conducted at room temperature (23° ± 1°C).

RESULTS AND DISCUSSION

The cyclic voltammetry of 0.1 M $NaClO_4$ electrolyte in water (no cyanide present) at a polycrystalline platinum electrode is shown in Figure 1. The characteristic voltammetry of this system has been published previously (5, 26, 28), but is shown again here for illustrative purposes. The broad, featureless wave which is observed at more positive potentials (> ~-0.2 V) is due to the formation of a surface oxide layer. This oxide layer is stripped off as the potential is swept to more negative voltages, giving rise to a cathodic current peak at approximately -0.2 V. At further negative applied potentials (about -0.4 to -0.8 V), peaks due to hydrogen adsorption/desorption are observed, while evolution of hydrogen occurs at potentials more negative than -0.85 V. The voltammogram illustrates the high potential-dependent reactivity of the solvent (water) at a clean platinum surface.

Figure 2 shows the cyclic voltammogram, obtained at a platinum electrode, of aqueous 0.1 M $NaClO_4$ in which cyanide is present. The voltammogram is similar to previously published electrochemical data for this system (26, 28). The voltammetry shows that the presence of cyanide prevents hydrogen adsorption in the negative potential regime, and also suppresses the formation of surface oxide until more positive potentials when compared to the system in which no cyanide is present (Figure 1). Above about +0.4 V, evidence for oxide formation is observed (Figure 2), with a corresponding reduction peak appearing at approximately -0.3 V. Irreversible oxidation of cyanide occurs above +0.9 V. A "double layer" region, due to the existence of surface-bound cyanide species, is observed to exist between ~-0.9 V and ~+0.4 V (Figure 2, dashed line). Radiotracer experiments indicate that the cyanide surface coverage is nearly constant within the double layer and oxide regions, and that the CN^- coverage decreases significantly at the positive potential extreme (33), where it becomes oxidized. Unfortunately, few additional details regarding the electrochemical behavior of cyanide at platinum can be discerned from the cyclic voltammogram. Hence, in order to extract more information about the cyanide/platinum electrochemical system in perchlorate electrolyte, IR spectroelectrochemical data were obtained within the potential region shown in Figure 2.

IR spectroelectrochemical data (from applied potentials between -0.8 and +0.5 V) of the platinum/cyanide system in sodium perchlorate are shown in Figures 3 and 4. SNIFTIRS spectra arising from both p- and s-polarized IR radiation are shown in Figure 3, while a potential-difference FT-IRRAS spectrum is shown in Figure 4. FT-IRRAS difference spectra and p-polarized SNIFTIRS spectra are sensitive to surface species, while s-polarized SNIFTIRS spectra are sensitive only to species in solution (1, 2). However, it has been observed that FT-IRRAS and p-polarized SNIFTIRS techniques are not always entirely surface-specific. In fact, these two IR spectroelectrochemical techniques will sometimes be sensitive to dissolved species that are present within the diffusion layer near the electrode surface (23). Thus, it is important to obtain SNIFTIRS spectra with s-polarized radiation so that solution species, if they give rise to features in the "surface-sensitive" potential-dependent IR spectra, can be identified.

The IR spectroelectrochemical data of Figures 3 and 4 show a series of bands in the ~2050 to ~2200 cm^{-1} range. The SNIFTIRS spectrum that was taken between -0.8 and +0.5 V with s-polarized IR radiation yields negative bands at 2095 and 2133 cm^{-1} (Figure 3). The s-polarized SNIFTIRS spectrum from applied potentials between -0.8 and +0.2 V gave rise to a small positive peak at 2179 cm^{-1}, and a strong negative peak at 2094 cm^{-1}. SNIFTIRS spectra that were obtained with p-polarized radiation (Figure 3) show strong positive bands in the 2050 to 2150 cm^{-1} region, and a strong negative band centered at about

2170 cm^{-1}. By comparing s- and p-polarized SNIFTIRS spectra, it can be seen that negative contributions from peaks at 2095 and 2133 cm^{-1} are superimposed upon the broad positive feature which is prevalent between 2050 and 2150 cm^{-1}. Also, if the s-polarized spectrum is subtracted from the p-polarized spectrum (Figure 3), the result is essentially identical to the surface-sensitive FT-IRRAS difference spectrum (Figure 4). The FT-IRRAS difference spectrum (Figure 4) gives rise to a strong positive peak at 2145 cm^{-1} with a shoulder at ~2100 cm^{-1}, and a negative peak at ca. 2160 cm^{-1}. By comparison with the SNIFTIRS p-polarized spectrum (Figure 3), these features (which appear in both spectra) can be attributed to surface species.

Potential-dependent SNIFTIRS spectra of the $CN^-/Pt/ClO_4^-$ system (Figure 5) which were obtained with p-polarized radiation yielded a broad positive peak in the 2050 to 2100 cm^{-1} region, a strong positive peak near 2145 cm^{-1}, and a negative peak at frequencies >2155 cm^{-1}. SNIFTIRS spectra that were obtained within the double layer potential region are plotted in Figure 5, while spectral data from higher sample potentials are presented in Figure 6. These data demonstrate some similarities as well as differences from previous IR spectral studies of cyanide on platinum, which were conducted under different experimental conditions (19, 26). Comparisons of our data with results from previous _in situ_ studies of the Pt/CN^- system are discussed below.

Based on the IR spectroelectrochemical data (Figures 3-6), band assignments for various cyanide species in the platinum/perchlorate system were made, and are summarized in Table I. We note that definitive assignments of peak frequencies from IR difference spectra such as those obtained here are often difficult to make (34), but estimation of peak positions to within a few wavenumbers is sufficient for the study which was undertaken. A number of solution species were observed in the SNIFTIRS spectra of the Pt/CN^-/ClO_4^- system. As mentioned above, potential-dependent SNIFTIRS spectra which were taken with s-polarized radiation gave rise to solution bands at 2133, 2095, and 2079 cm^{-1}. The peak at 2079 cm^{-1} is assigned as free solution cyanide ion, CN^-_{soln}, based on the literature value of 2080 cm^{-1} for this ion in aqueous solution (19, 35). The 2095 cm^{-1} band can be assigned as solution HCN; a similar frequency band which was attributed to solution HCN has been observed in earlier IR spectroscopic studies of cyanide on silver (15) and platinum (19, 26). This assignment was originally based on the reported literature value for gas phase HCN of 2097 cm^{-1} (36). The 2133 cm^{-1} peak was also observed in a previous IR study of cyanide on a platinum electrode in which CN^- has been removed from solution (26), and was attributed to the infrared-active E_u mode of square-planar platinum/cyanide complex, $Pt(CN)_4^{2-}$ (36, 38). In other IR spectroscopic studies of the Pt/CN^- system (19, 26), peaks in the frequency region near 2170 cm^{-1} have been attributed to solution cyanate ion (OCN^-_{soln}) (37). At potentials of +0.8 V and greater, a peak at 2171 cm^{-1} was observed (Figure 6). This peak is assigned as OCN^-_{soln} (Table I), based on previous _in situ_ IR studies of CN^- and OCN^- on platinum (19, 26, 37).

Several peaks in the C-N stretching region, which may be attributed to surface species, were observed in the IR spectroelectrochemical results (Figures 3-6). Features that were seen in FT-IRRAS spectra (Figure 4) and p-polarized SNIFTIRS spectra (Figures 3, 5, and 6) which were not observed in the s-polarized SNIFTIRS spectra are assigned as surface bands. The most prominent surface bands appear in the ≈ 2150 (±20) cm^{-1} region, and they are observed in both p-polarized SNIFTIRS (Figure 3) and potential-difference FT-

IRRAS (Figure 4) spectra. The strong positive peak at ~2145 cm^{-1} (Figures 3, 5) has been observed in previous IR studies of the Pt/CN^- system (22, 26), and has been attributed to various forms of adsorbed cyanide in which the cyanide species is bound to the platinum surface through the carbon atom. In the preliminary in situ SNIFTIRS investigation (22), this peak was attributed to C-down CN^-_{ads}. In the study in which solution cyanide was removed prior to accumulation of spectra (26), a peak at ~2150 cm^{-1} was assigned as an adsorbed CNH species in which carbon is toward the Pt surface. This assignment was based on ex situ spectroscopic studies of cyanide on platinum surfaces (29). Another plausible assignment of this peak is as adsorbed cyanide ion, CN^-_{ads}, which is bound to the electrode surface via the nitrogen atom (Table I). Spectral features in the ~2150 cm^{-1} frequency region were not observed in separate in situ IR spectroelectrochemical studies in which CN^- was present in solution (19, 26), presumably because these peaks were obscured by solution species.

A strong negative peak at ~2160 cm^{-1} is observed in the FT-IRRAS spectrum (Figure 4), and bands near this frequency are seen in p-polarized SNIFTIRS spectra as well (Figure 5). Since no solution feature at this frequency appears when the potential is pulsed from -0.8 to +0.5 V (Figure 3), we attribute this peak to a surface species. Cyanogen, $(CN)_2$, has an IR frequency of 2157 cm^{-1} (40). However, since cyanogen is an oxidation product of CN^-, and the ~2160 cm^{-1} peak appears at far negative potentials (Figure 5), it is unlikely that this spectral feature is due to cyanogen. The frequency of this band appears to be potential-dependent; we note that there is an apparent shift in the peak frequency from ~2155 to nearly 2180 cm^{-1} (Figure 5). However, difficulties which are inherent in the interpretation of difference spectra (34) make it impossible to quantitate the frequency potential dependence of the surface species giving rise to this negative band.

We emphasize that the spectral feature observed between approximately 2130 and 2180 cm^{-1} is probably not a bipolar band arising from a potential-dependent frequency shift in the C-N stretch of CN^{-}_{ads}. If it were, we would expect a shift from lower to higher frequencies as the applied potential is increased. Our data show just the opposite trend (Figures 3-5): as the potential is stepped to higher voltages, the frequency shifts from a negative peak at higher frequency (~2155 to ~2180 cm^{-1}) to a positive peak at lower frequency (~2145 cm^{-1}). These data are consistent with a potential-dependent reorientation of CN^{-}_{ads} from C-down at more negative potentials to N-down at more positive voltages. Evidence for a similar potential-dependent reorientation of surface thiocyanate (SCN^{-}_{ads}) has been observed in previous IR spectroelectrochemical studies of this ion on platinum (5) and gold (41) surfaces. An alternative explanation is that as the potential is made more positive, an adsorbed CNH species is favored (26). Thus, we attribute the negative band near 2170 cm^{-1} ($\pm$10 cm^{-1}) to an adsorbed cyanide ion in which the carbon atom is bound to the electrode surface (Table I).

There is IR spectroelectrochemical evidence for additional surface features in the 2050 to 2100 cm^{-1} range (Figures 3-5). At more negative applied potentials, a broad positive peak in this frequency region, attributed to CN^{-}_{surf}, is observed (Figure 5). As the potential is made more positive, this feature grows in intensity and shifts to higher frequency (Figure 5). Since the intensity of this 2050 to 2100 cm^{-1} band is far greater than that obtained for the CN^{-}_{soln} peak in s-polarized SNIFTIRS spectra, it is ascribed to a surface species. Further evidence for a surface feature in the ~2050-

2100 cm^{-1} range exists in the FT-IRRAS spectrum (Figure 4). Also, the observation that the ~2050 to ~2100 cm^{-1} feature in the SNIFTIRS spectra (Figure 5) shifts from lower to higher frequency as the potential is increased offers additional evidence for the existence of a surface species in this wavenumber region, since IR bands of solution species do not typically undergo potential-dependent frequency shifts. Hence, we attribute this ~2050 to ~2100 cm^{-1} feature to a surface cyanide species, CN^-_{surf} (Table I), based on experiments in the previous IR investigation which were conducted in basic cyanide-free solution (26). Additionally, a surface cyanide band near this frequency (2070 cm^{-1}) has been observed in IR spectroelectrochemical studies of the Pt/CN^- system in sulfate media (2).

Thus, there is IR spectroscopic evidence for at least two forms of adsorbed cyanide on platinum: one at lower frequency (~2050-2100 cm^{-1}) and one at higher frequency (~2150 cm^{-1}). Our observations are consistent not only with previous IR spectroscopic investigations of the CN^-/Pt/ClO_4^{2-} system on polycrystalline surfaces (26), but are also consistent with results from IR experiments on single-crystal platinum electrodes (42). The studies on single-crystal platinum show two different frequencies (~2070 and ~2150 cm^{-1}) of adsorbed cyanide, and the site occupancy is dependent upon the nature of the Pt crystal face which is probed (42). The low-frequency band appears at a similar wavenumber region to linear-bound CN^- on palladium (23), but no bridge-bound surface cyanide is observed on Pt. Based on the experimental data, the implication is that this (lower frequency) surface cyanide species has a higher binding energy than the high-frequency CN^-_{ads} species (24), which is more ionic in character. The greater ionic character of the high-frequency CN^-_{ads} species would lead to an increased likelihood of a potential-dependent reorientation of this ion, which we have suggested above.

A potential-dependent reorientation of surface cyanide was suggested in a sum-frequency generation (SFG) study of CN^-_{ads} on platinum (28). In the SFG work, both low- and high-frequency bands due to surface cyanide species were observed. The lower wavenumber peak frequency was highly potential-dependent, and the higher wavenumber peak frequency was largely potential-independent (27, 28); these results were similar to those of the IR spectroscopic study in cyanide-free solution (26). In the SFG studies, the high-frequency peak was prevalent at higher applied potentials, while the low-frequency band was prominent at more negative voltages (27, 28). The low-frequency peak was assigned to CN^-_{ads} bound to the Pt surface via the nitrogen atom, while the high-frequency feature was attributed to C-down surface cyanide (28). However, this explanation would imply that the more electron-rich portion of the cyanide ion (i.e., the nitrogen end) would be toward the electrode surface at more negative potentials. For electrostatic reasons, the proposed modal in which the negatively charged portion of the ion is toward the electrode surface at more negative voltages (27, 28) is not feasible. Undoubtedly the features observed in the SFG experiments (27, 28) are due to the same species which give rise to peaks at similar frequencies in the IR spectroelectrochemical studies. A nitrogen-down cyanide species, if it indeed exists, would more likely be present at more positive applied potentials.

The assignment of the higher-frequency surface cyanide band (~2150) to a cyanide species with more ionic character than the low-frequency surface species (~2050-2100 cm^{-1}) would not only result in a greater likelihood of a potential-dependent reorientation of the ion, but could also lead to protonation or hydrogen bonding (with H^+) of this surface cyanide species. An alternative scenario to a potential-dependent reorientation of CN^-_{ads} may be the assignment of two different forms of (high-frequency) adsorbed cyanide: one which is associated with H^+ (~2145 cm^{-1}) and one that is not (~2170 cm^{-1}). This rationalization is consistent with previous assignments of the higher-frequency surface cyanide band (26, 29). Alternatively, a potential-dependent reorientation of CN^-_{ads} could also be accompanied by increased likelihood of H-bonding in either the C-down or N-down species. This may be responsible for the observation of one peak (~2170 cm^{-1}) having a higher frequency potential dependence than the other (~2145 cm^{-1}).

The potential dependencies of the intensities of several major bands that were observed in the SNIFTIRS experiments with p-polarized radiation (Figures 5, 6) are illustrated in Figure 7. The band at ~2070 cm^{-1} continually increases in intensity as the potential is increased, suggesting increasing surface coverage at more positive voltages. The intensity potential dependence of the ~2050 to 2100 cm^{-1} is difficult to quantitate, due to possible interference from the solution CN^- peak. As the applied voltage is made more positive, more CN^-_{soln} can migrate into the thin layer between the Pt electrode and the IR window of the spectroelectrochemical cell. At potentials within the double layer region, the intensity of the ~2145 cm^{-1} peak remains more or less constant (Figures 5, 7). The negative ~2170 peak appears at rather negative applied potentials (Figures 5, 7), lending further support of the assignment of this peak to a carbon-down CN^-_{ads} species. The intensity (and presumably the coverage) of the species giving rise to the peak at ca. 2170 cm^{-1} is largely invariant with applied potential (Figure 7). However, we reiterate that this band frequency is highly potential-dependent.

Above the potential of zero charge (PZC) of polycrystalline platinum, which is at approximately +0.2 V in perchlorate electrolyte (43), the intensity of the ~2145 cm^{-1} peak increases dramatically. This rise in intensity (Figures 5, 6) is also concurrent with the formation of a surface oxide layer which is indicated in the voltammetry (Figure 2). Nearly concomitant with the increase in the ~2145 peak is a substantial decrease in the intensity of the peak due to HCN_{soln} at ~2095 cm^{-1}. The implication is that the coverage of surface cyanide increases at the same time that the solution concentration of HCN decreases. This is consistent with deprotonation of HCN in solution to form a surface cyanide species. We note that this effect is pH-dependent, for as the potential is made more positive, the pH of the interface is increased since H^+ is expelled from the interface (44). The surface cyanide species which is prevalent in the oxide region (peak frequency ~2145 cm^{-1}) is a precursor to cyanate, which is formed when the surface cyanide layer is oxidized at higher applied potentials.

At the positive potential extreme where cyanide oxidation occurs (Figure 6, +0.8 V), a positive peak attributed to solution cyanate at 2171 cm^{-1} appears due to the following reaction (19, 39):

$$CN^- + 2OH^- \rightarrow OCN^- + H_2O + 2e^- .$$

The mechanistic details of this reaction remain unclear, but the formation of a surface oxide layer prior to oxidation of cyanide ion which is immobilized on the surface appears to be a necessary step (19). Also at higher applied potentials (+0.9 V or greater), surface bands near 2200 cm^{-1}, attributed to the formation of surface-bound cyanate species, OCN^-_{surf} (37), were observed. This surface species may be a precursor to the ultimate oxidation product,

OCN^-_{soln}. Since the 2133 cm^{-1} peak, ascribed to $Pt(CN)_4^{2-}$ (Table I), was observed at lower applied potentials (Figure 5), it appears that the reaction of cyanide with the metal surface (to form square-planar Pt/CN^- complex) does not require the application of extreme voltages.

CONCLUSION

In situ IR spectroelectrochemical studies of the Pt/CN^-/ClO_4^{2-} system show that the behavior of cyanide species at a polycrystalline platinum surface are rather complex. SNIFTIRS data give evidence for at least two forms of adsorbed cyanide species, one at lower frequencies (~2050-2100 cm^{-1}) and (at least) one at higher frequencies (~2145 cm^{-1}). Evidence for a third type of CN^-_{ads} (peak maxima 2155 to 2180 cm^{-1}) was also obtained for the first time. Unfortunately, possible interference from the solution peak due to solution CN^-, as well as band broadening due to the polycrystalline nature of the electrode surface, make it difficult to attribute definitive band assignments for surface cyanide species that give rise to bands in the 2050 to 2100 cm^{-1} region. Square-planar platinum cyanide complex, $Pt(CN)_4^{2-}$, appears to be formed at applied potentials within the double layer region, as suggested by a peak at 2133 cm^{-1} (E_u mode). SNIFTIRS data indicate that cyanide oxidation to cyanate (peak frequency 2171 cm^{-1}) occurs at the positive potential extreme, above the double-layer and oxide formation potential regimes. Depletion of solution HCN (2095 cm^{-1}) at more positive potentials is accompanied by an increase in the CN^-_{ads} peak at ~2145 cm^{-1}, suggesting that a potential-induced surface pH effect is responsible for this conversion. This study has shown a number of spectroscopic similarities to, but also some significant differences from, previous in situ spectroscopic investigations of the Pt/CN^- electrochemical system. This investigation illustrates the utility of complementary surface-sensitive spectroscopic techniques in probing interfacial electrochemical processes.

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Table I. Assignments for various cyanide bands observed in infrared spectroelectrochemical data from the $CN^-/Pt/ClO_4^-$ system; (+/-) indicates whether the observed peaks are positive or negative in sign.

Peak frequency, cm^{-1}; (+/-)	Assignment	Reference(s)
~2050 to ~2100 (+)	CN^-_{surf}	1, 2, 26, 28
2080 (+)	CN^-_{soln}	22, 35
2095 (-)	HCN_{soln}	15, 19, 26
2133 (-)	$Pt(CN)_4^{2-}$ (E_u mode)	26, 36, 38
~2145 (+)	CNH_{ads} or CN^-_{ads} (N-down)	22, 24, 26
~2160 to ~2180 (-)	CN^-_{ads} (C-down)	this work
2171 (+)	OCN^-_{soln}	19, 26, 37
~2200 (-)	OCN^-_{surf}	37

FIGURE LEGENDS

Figure 1. Cyclic voltammetry of aqueous 0.10 M $NaClO_4$ at a polished platinum disc electrode; sweep rate = 50 mV/sec.

Figure 2. Cyclic voltammetry of 25 mM NaCN in aqueous 0.10 M $NaClO_4$ at a polished platinum disc electrode; sweep rate = 50 mV/sec.

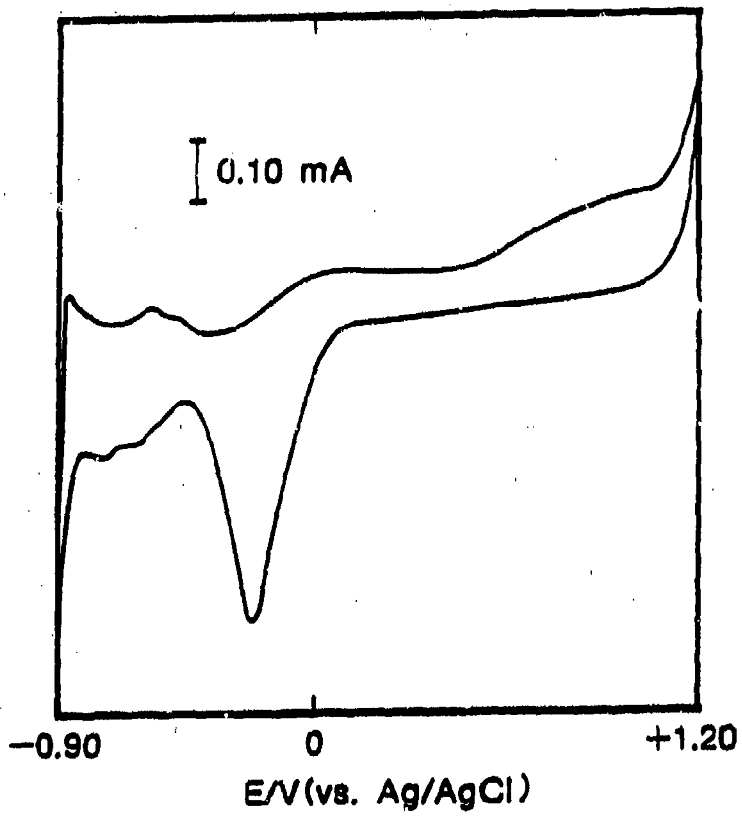
Figure 3. SNIFTIRS spectra recorded in 25 mM NaCN in aqueous 0.10 M $NaClO_4$ at a platinum mirror disc electrode as a function of the polarization of the incident infrared beam. Reference and sample potentials were -0.80 V and +0.50 V (vs. Ag/AgCl), respectively. Spectra were averaged over 1000 scans (500 at each potential).

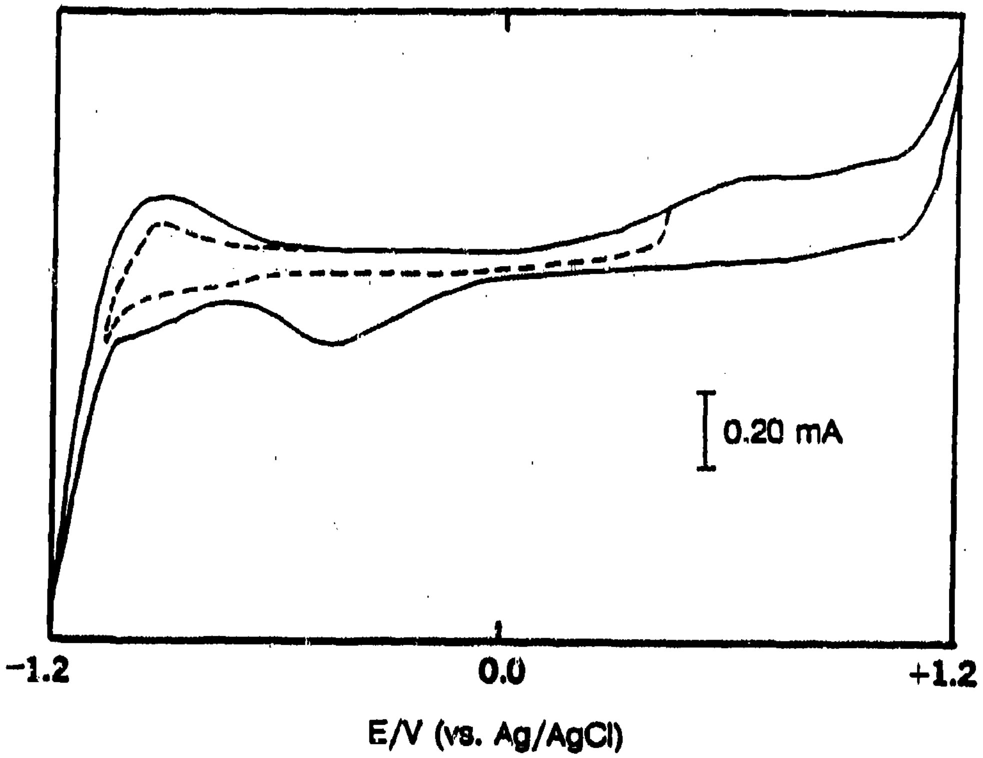
Figure 4. FT-IRRAS difference spectrum recorded in the aqueous 25 mM NaCN + 0.10 M $NaClO_4$ system at a platinum mirror electrode. Reference and sample potentials were -0.80 V and +0.50 V (vs. Ag/AgCl), respectively. Spectra were averaged over 1000 scans (500 at each potential).

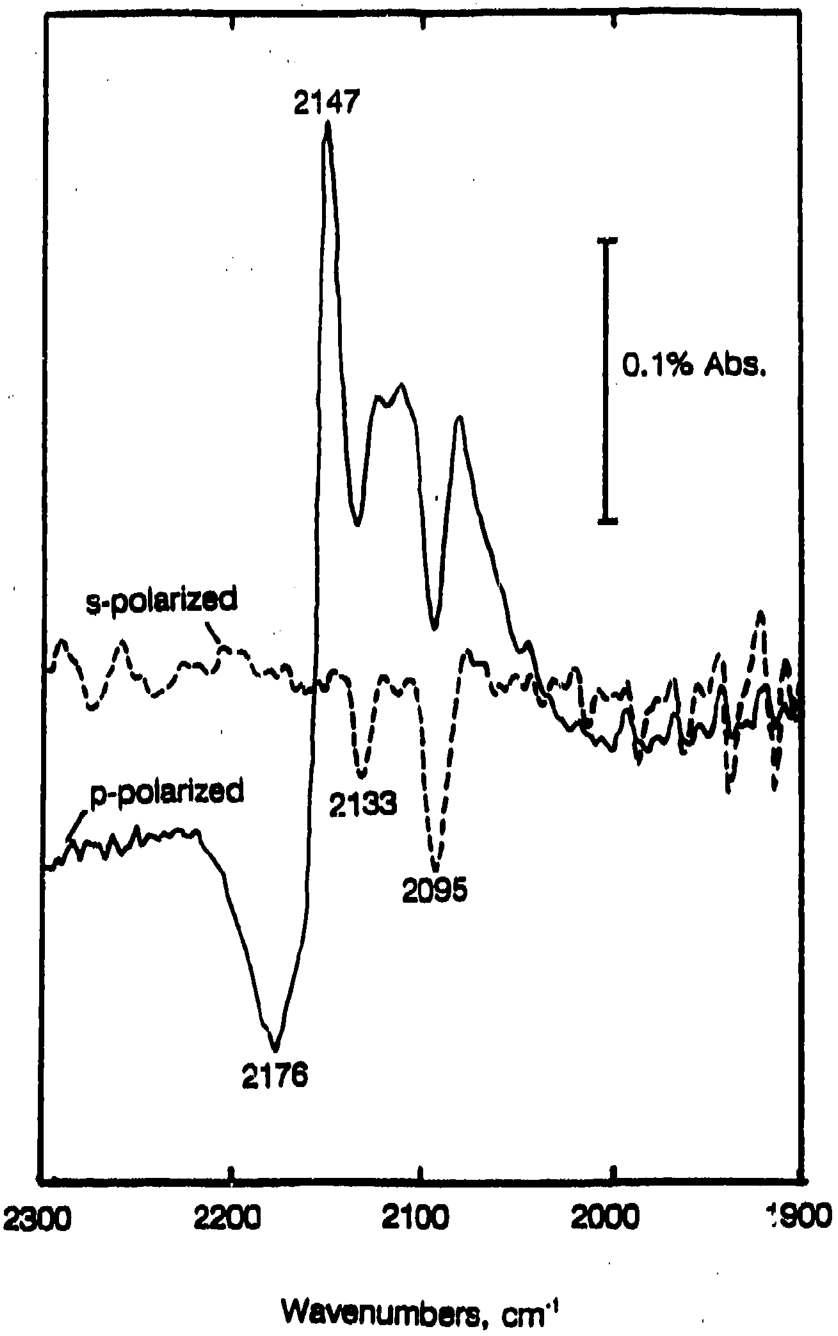
Figure 5. Potential-dependent SNIFTIRS spectra of aqueous 25 mM NaCN + 0.10 M $NaClO_4$ at a polished platinum electrode. The incident radiation was p-polarized with respect to the electrode surface plane. Applied voltages are within the double-layer potential regime. The reference voltage was -0.80 V vs. Ag/AgCl, and sample potentials are as shown in the figure.

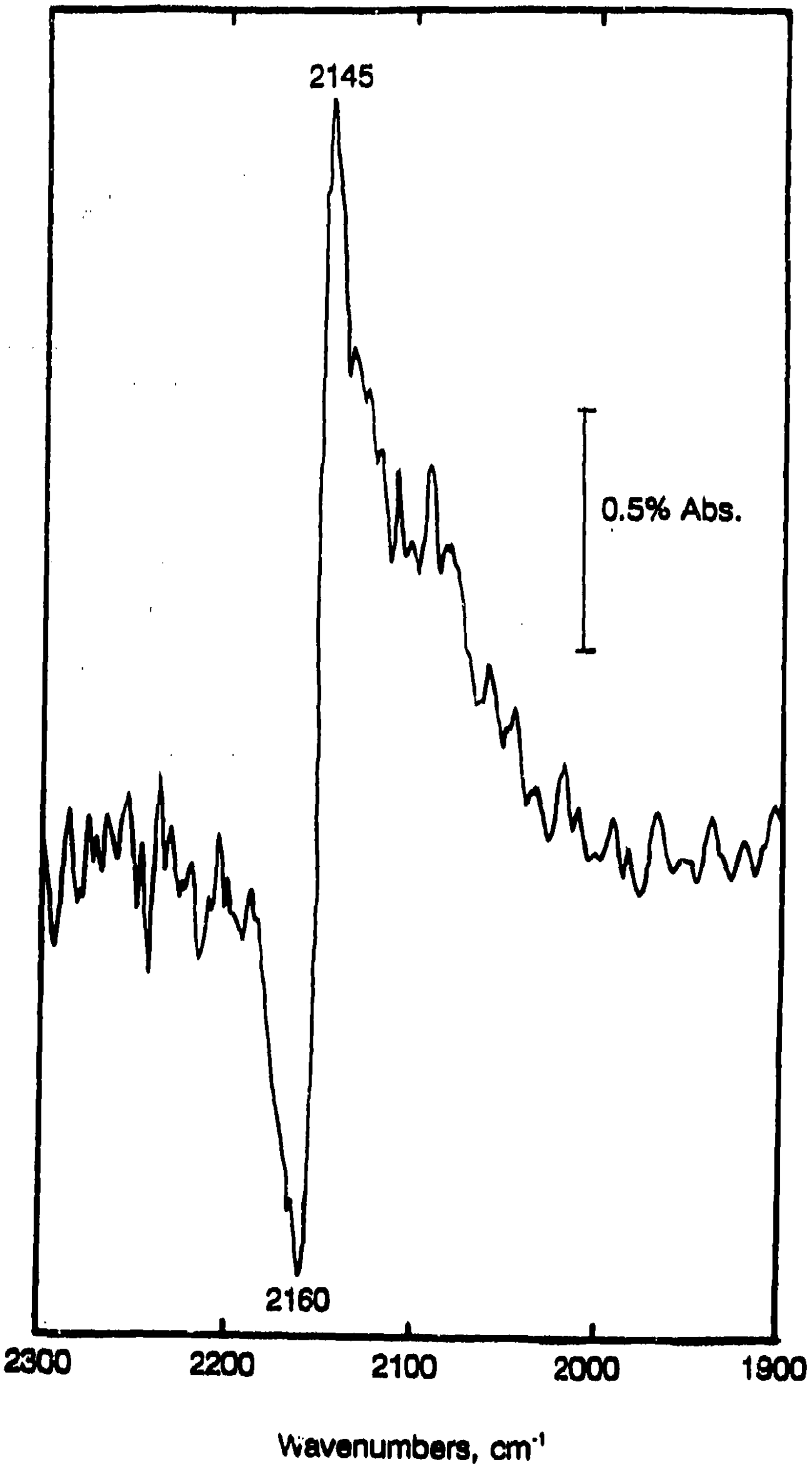
Figure 6. Same as Figure 5, except that sample voltages are within the cyanide oxidation region.

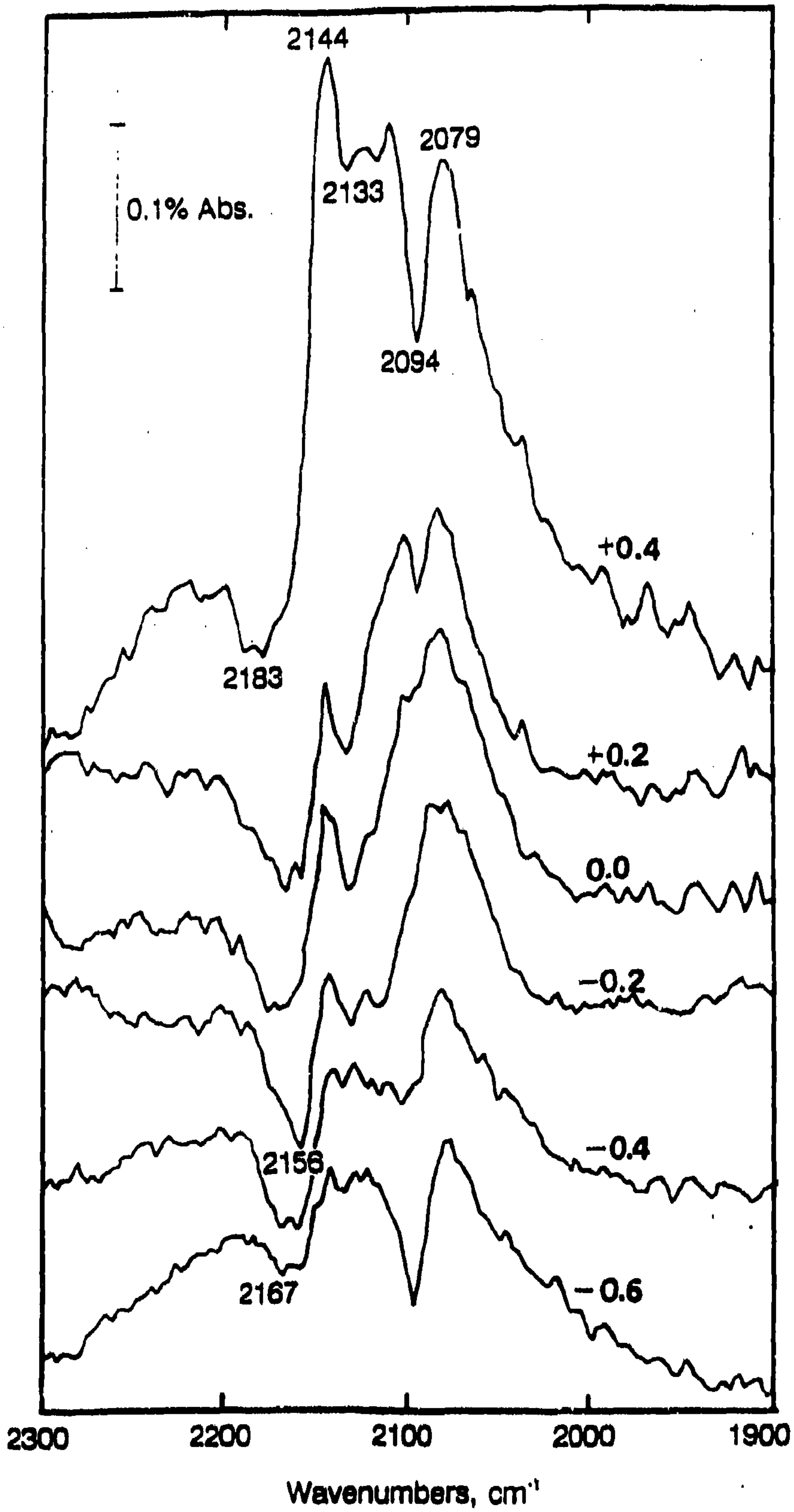
Figure 7. Plots of peak intensity vs. applied potential for major bands observed in the 25 mM NaCN + 0.1 M NaClO$_4$ on Pt system. Band frequencies: ·-·- ~2070 cm^{-1}; ---- 2094 cm^{-1}; —— 2145 cm^{-1}; ··-··- ~2170 cm^{-1}.

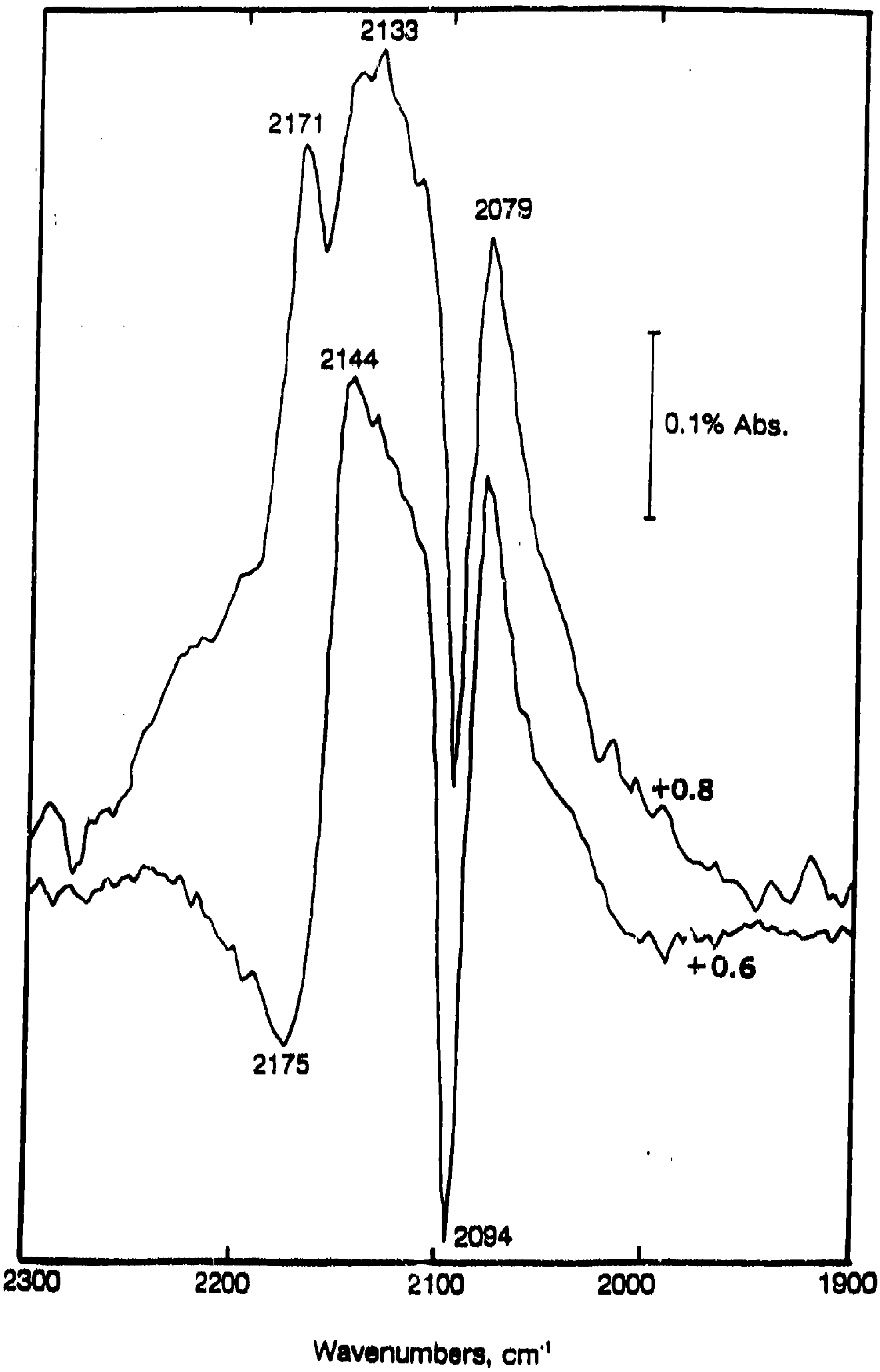

0.10 mA
−0.90
0
+1.20
E/V(vs. Ag/AgCl)

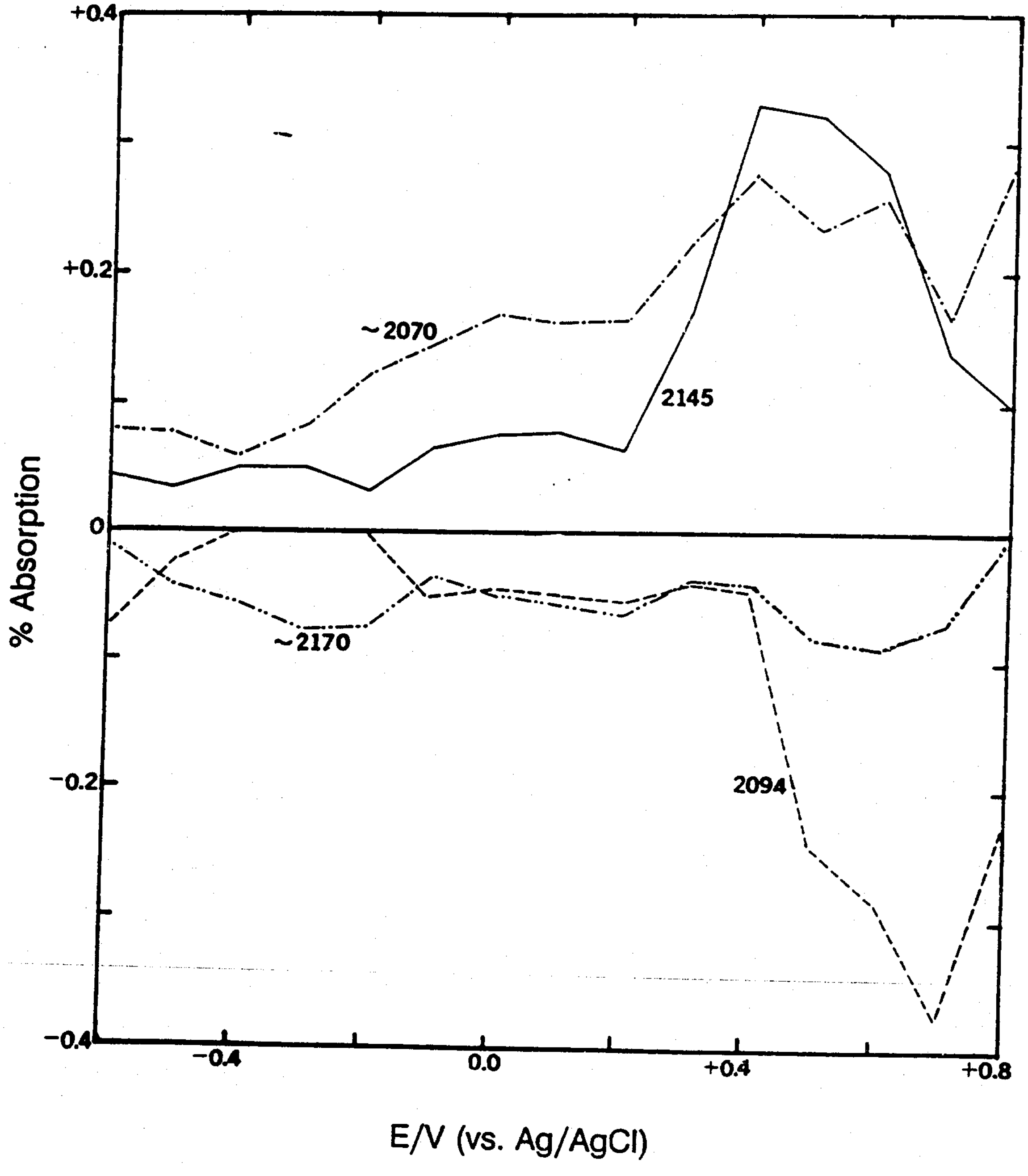

0.20 mA
−1.2
0.0
+1.2
E/V (vs. Ag/AgCl)


2147
0.1% Abs.
s-polarized
p-polarized
2133
2095
2176
2300
2200
2100
2000
1900
Wavenumbers, cm⁻¹


2145
0.5% Abs.
2160
2300
2200
2100
2000
1900
Wavenumbers, cm⁻¹


2144
2133
2079
2094
0.1% Abs.
2183
+0.4
+0.2
0.0
−0.2
2156
−0.4
2167
− 0.6
2300
2200
2100
2000
1900
Wavenumbers, cm⁻¹


2133
2171
2079
2144
0.1% Abs.
+0.8
+0.6
2175
2094
2300
2200
2100
2000
1900
Wavenumbers, cm⁻¹


+0.4
+0.2
0
−0.2
−0.4
% Absorption
~2070
2145
~2170
2094
−0.4
0.0
+0.4
+0.8
E/V (vs. Ag/AgCl)