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In Situ Infrared Spectroelectrochemical Studies of Cyanide Adsorbed on Platinum and Palladium

by

Kevin Ashley, Mark Lasaga, Mahesh G. Samant, H. Seki, M. R. Philpott

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IBM Research Division
Almaden Research Center
650 Harry Road
San Jose, California 95120-6099

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IN SITU INFRAFED SPECTROELECTROCHEMICAL STUDIES OF CYANIDE ADSORBED ON PLATINUM AND PALLADIUM

Kevin Ashley
Mark Lasaga

San Jose State University
Department of Chemistry
San Jose, CA 95129

Mahesh G. Samant
H. Seki
M. R. Philpott

IBM Research Division
Almaden Research Center
San Jose, California 95120

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Short Communication

IN SITU INFRARED SPECTROELECTROCHEMICAL STUDIES OF CYANIDE ADSORBED ON PLATINUM AND PALLADIUM

Kevin Ashley* and Mark Lazaga
Department of Chemistry, San Jose State University
San Jose, California 95192

Mahesh G. Samant, H. Seki, and M. R. Philpott*
IBM Research Division, Almaden Research Center
650 Harry Road, San Jose, California 95120

in situ FTIR difference spectra of adsorbed cyanide on polished platinum and palladium electrodes in perchlorate media are presented. A linear CN^-_{ads} moiety is observed on Pt, while on Pd four surface cyanide species are seen: linear and bridge-bound CN^-_{ads}, as well as two surface Pd-CN films.

This divergence

We wish to report the results of some preliminary in situ infrared spectroelectrochemical studies of cyanide specifically adsorbed on polished platinum and palladium electrode surfaces. Similar studies of this and several other pseudohalides on various metal surfaces have been conducted [1], but to date no work of this kind has been reported for CN^- (CN(-)) species adsorbed on the metals platinum and palladium. Also, most previous studies of this kind have been carried out in the presence of sulfate, which competes with the adsorbing anion of interest for surface sites, since sulfate may specifically adsorb to the electrode surface [2]. This work was done in the presence of perchlorate electrolyte anion, which does not specifically adsorb on the surface to an appreciable extent [3]. Surface-enhanced Raman (SERS) scattering has been used to examine cyanide adsorption on Cu [4] and Ag [5] in sulfate electrolyte media; the results were consistent with data from infrared experiments [~~1~~6]. [illegible]

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*To whom correspondence should be addressed

Studies of pseudohalide adsorption on metal surfaces are of interest for theoretical as well as experimental reasons, for these investigations will lead to a more thorough fundamental understanding of the nature of the electrode/solution interface. To this end, we have carried out surface-sensitive in situ infrared experiments in electrochemical systems on the aforementioned metal surfaces, the results of which are presented herein.

The electrode potential was controlled via a PAR 175/179 potentiostat system, and all potentials were recorded versus the Ag/AgCl (3M KCl) reference. in situ IR spectroelectrochemical data were obtained by combining a potential difference method (subtractively normalized interfacial Fourier transform infrared spectroscopy, or SNIFTIRS [6]), with a polarization modulation technique (Fourier transform infrared reflection absorption spectroscopy, or FT-IRRAS [7]). In this way the surface sensitivity of the optical technique was optimized. The spectrometer was an IBM IR/98 Fourier transform instrument, and the IR spectroelectrochemical cell contained a polished platinum or palladium mirror working electrode in reflection geometry, as described previously [8]. A cooled (77 K) InSb detector (Infrared Associates) was utilized for collection of the reflected IR radiation, and a globar infrared source was employed. Reagent grade NaCN and $NaClO_4$ were obtained from Aldrich and used as received. Deionized water (Nanopure, 18 Mohms) was used in the preparation of all solutions, and electrolytes were degassed with pure N_2 prior to each experiment.

Voltammetric studies on Pt and Pd in 25 mM NaCN (0.10 M $NaClO_4$) indicated wide double layer regions on both Pt and Pd metal surfaces (about +0.8V to -0.9V vs. Ag/AgCl). Surface-sensitive in situ FTIR spectra were then obtained for the NaCN system within these ideally polarized regions on both electrodes. Figure 1 shows the SNIFTIRS spectra of adsorbed cyanide at a Pt electrode surface (p-polarized light). The large bipolar band centered at about 2155 cm^{-1} is attributed to a cyanide species adsorbed perpendicularly to the surface through the carbon atom (linear CN^-_{ads}), while the band at 2080 cm^{-1} is assigned to solution species [1]. The SNIFTIRS spectrum for this system obtained with s-polarized incident radiation was mostly flat, with a small peak at about 2080 cm^{-1} due to cyanide dissolved in the solution thin layer. The band due to linear CN^-_{ads} on Pt (Figure 1) is shifted by about 50 cm^{-1} compared to the analogous band on Ag [9], Au [10], and Cu [11] in sulfate electrolytes. This large shift is probably due in part to the absence of coadsorbed electrolyte species in the case of perchlorate electrolytes. Sulfates are known to specifically adsorb on electrode surfaces, even in the presence of strong pseudohalide adsorbates [12], while in the case of perchlorates specific adsorption of the supporting electrolyte is disfavored. The shoulder appearing in the difference spectrum on Pt (Figure 1) is at present difficult to explain, but may arise from the polycrystalline nature of the electrode surface. The band frequency due to linear CN^-_{ads} was seen to shift with potential by approximately 30 cm^{-1}/V; this value of $d\nu/dE$ is similar to previously reported values for this system [1].

The combined FT-IRRAS/SNIFTIRS spectrum of the cyanide/perchlorate system on Pd is shown in Figure 2 (solid line). For comparison, a SNIFTIRS spectrum taken under conditions of s-polarized radiation is plotted (dashed line). In the former spectrum five bands are observed, with positive bands at about 1980, 2065, and 2135 cm^{-1}, and negative bands near 2155 and 2200 cm^{-1}. In the latter spectrum two positive-tending maxima appear at 2170 and 2135 cm^{-1}, and bands due to rotational modes of trace background gaseous H_2O are seen between 1900 and 2000 cm^{-1}. The results indicate that the bands observed at 2135 and 2170 cm^{-1} are due to species dissolved in solution, while the remaining bands appearing in the combined potential difference/polarization modulation results (Figure 2, solid line) are due to surface species.

The results from Pd differ markedly from spectra obtained on Pt; many more bands were seen in the Pd-CN^- system (Figure 2) than in the Pt-CN^- system (Figure 1). On Pd, the band near 2060 cm^{-1} was observed to shift with potential by approximately 15 cm^{-1}/V, and is assigned to linear CN^-_{ads}. What appears to be a bipolar band centered at about 2155 cm^{-1} (on Pd) is in fact due to a surface species (at 2154 cm^{-1}) and a solution species (at 2135 cm^{-1}), and the bands for each of these species are opposite in sign. The surface species near the same frequency on Pd (Figure 1) is most certainly not the analogous surface species that is seen on Pt (which gives rise to a bipolar band centered at about 2155 cm^{-1}, see Figure 2), for the position of the surface band on Pt was observed to shift appreciably with changes in potential, while dv/dE for the surface band on Pd was found to be essentially zero. Based on these experimental considerations, we contend that the surface bands arising from these two systems at similar frequencies are due to different species.

dv/dE for the band near 1980 cm^{-1} (on Pd) was found to be about 25 cm^{-1}/V, and the frequency maximum is shifted considerably downward in wavenumber with respect to solution cyanide, whose C-N stretching mode occurs at 2080 cm^{-1}, and is not observed in the spectra obtained on Pd (Figure 2). No bands in the 1950-2000 cm^{-1} frequency range have been observed previously for either surface cyanide species or cyanide-transition metal complexes. We tentatively attribute this band (on Pd) to bridge-bonded CN^-_{ads}, based on analagous assignments for bridge-bound CO_{ads} on Pt [13]. The negative bands near 2200 and 2155 cm^{-1} are assigned to surface films of PdCN and $Pd(CN)_4^-$, respectively [14], while the positive bands near 2170 and 2135 cm^{-1} are attributed to PdCN and $Pd(CN)_4^-$ dissolved in solution; analogous bands of this type have been observed on other metal surfaces [11, 15]. The maxima for the surface bands near 2200 and 2155 cm^{-1} do not shift appreciably with potential; such observations have been made previously in other systems [10b].

The linear CN^-_{ads} band appears at much lower wavenumber on Pd (Figure 2) than on Pt (Figure 1). This observation may be due to differences in the bonding mechanism of the adsorbate to the respective metal surface. The bonding of linear CN^-_{ads} to the metal surface is presumably ionic in the case of Pt. This contention is based on theoretical calculations for linear CN^-_{ads} species on Cu that predict the normal C-N stretching mode for the cyanide moiety to be shifted to higher wavenumber when compared to the solution free species [16]. It is possible that the bonding of this adsorbate on Pd may be less ionic in nature, resulting in a wavenumber shift to lower frequency instead of higher (with respect to the solution band). Theoretical calculations on the Pd-CN^- system are presently underway, and will be published elsewhere.

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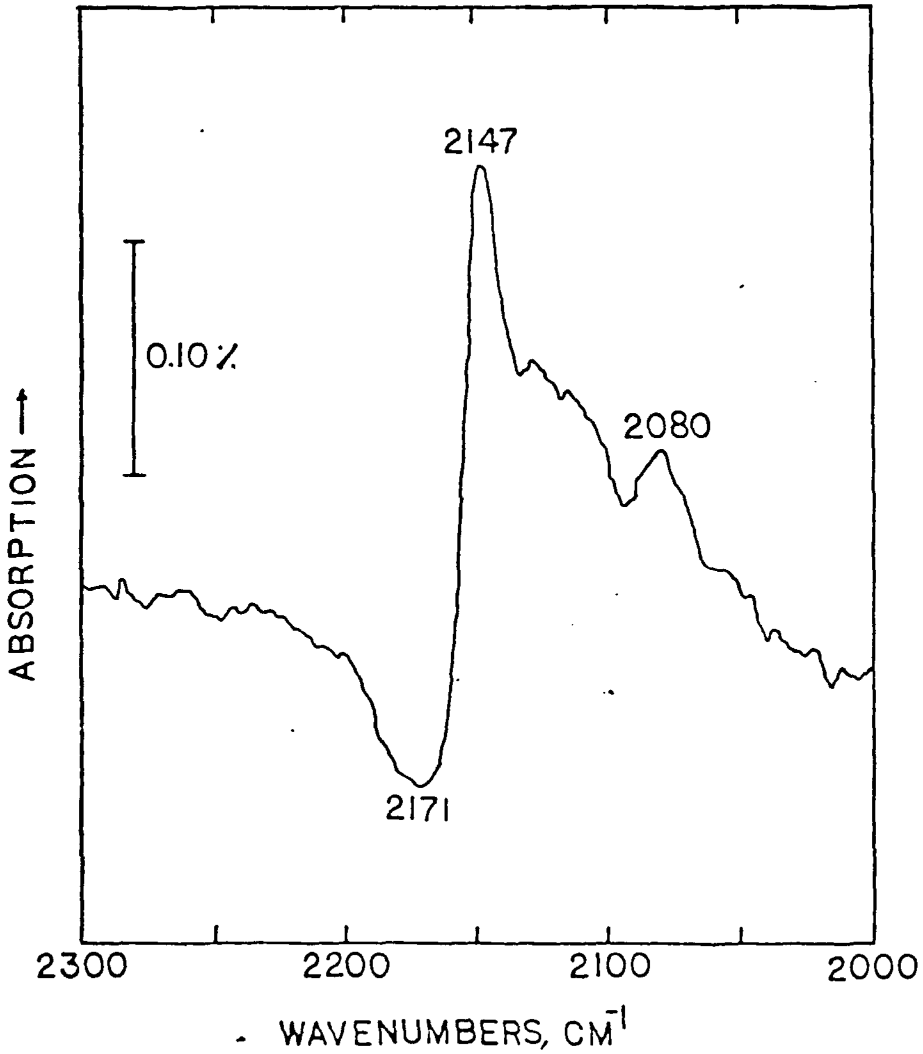

Figure 1. SNIFTIRS spectrum of NaCN (25 mM) in 0.10 M $NaClO_4$; potential limits were +0.50 V and -0.80 V vs. Ag/AgCl. The spectrum is a difference spectrum, and represents a ratio of spectra taken at the two applied potentials at a platinum surface. The spectra at both potentials were taken with p-polarized light, and the spectrum taken at the negative potential functioned as the reference.

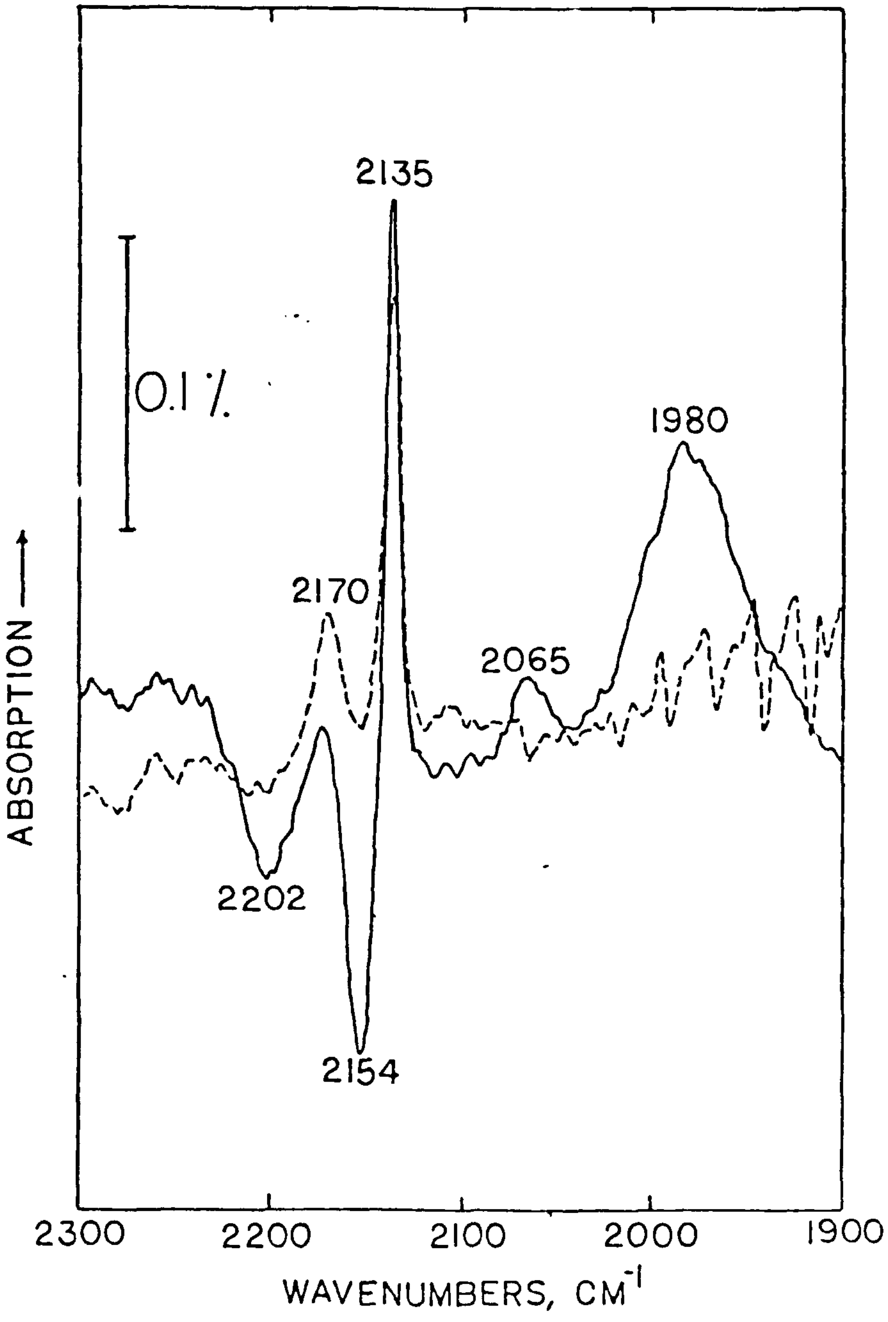

Figure 2. Solid line: Combined SNIFTIRS/FT-IRRAS spectra of $NaCN$ (25 mM) in 0.10 M $NaClO_4$ on polished palladium, p-polarized light. Dashed line: SNIFTIRS spectrum of the same solution obtained with s-polarized radiation. The positive potential limit was +0.7 V vs. Ag/AgCl; the negative (reference) potential limit was -0.90 V.