J. Am. Chem. Soc. 1981, 103, 7497-7501

# Molecular Generality of Surface-Enhanced Raman Spectroscopy (SERS). A Detailed Investigation of the Hexacyanoruthenate Ion Adsorbed on Silver and Copper Electrodes

**Craig S. Allen* and Richard P. Van Duyne**

*Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received November 14, 1980*

**Abstract:** SERS scattering from adsorbed hexacyanoruthenate ion provides a wealth of information about adsorbate structure. It is clearly demonstrated that the molecule interacts with the metal via a CN bridge, the strength of which is dependent upon the metal surface (Ag or Cu) and the applied potential. The spectra from both metals show vibrational modes which are only IR active in bulk phase, indicating a symmetry lowering on adsorption. The potential dependence of SER scattering on copper clearly shows an inherent potential dependence of the enhancement process on that metal.

The demonstration of enhanced Raman scattering from heterocycles and amines adsorbed on silver electrodes[1] has sparked an explosion of experimental[2] and theoretical[3] activity aimed at elucidation of the enhancement mechanism. We have reported a study of a series of inorganic anions[4] adsorbed on silver and copper electrodes and now wish to extend that work to a detailed study of the surface-enhanced Raman (SER) scattering from adsorbed $Ru(CN)_6^{4-}$ ($HCR^{4-}$). In the earlier anion study,[4] we showed that the SER effect was essentially molecule independent and gave rise to large enhancements for molecules with widely varying electronic and molecular structure. By examining the surface spectra, we clearly showed that the interaction of the adsorbate with the metal surface caused a symmetry lowering which resulted in the appearance of bands in the SER spectrum which were not Raman active in bulk phase.

For many of the organic SER systems studied to date, the observed SER spectra are not strongly perturbed from that observed for scattering from the same species in bulk phase. In contrast, the spectra obtained from the relatively small ($\leq 9$ atoms), symmetric ($T_d$ or $D_{4h}$) anions were markedly different in both band frequencies and relative intensities comparing surface with bulk phase. The results presented here for hexacyanoruthenate ion ($HCR^{4-}$) show clear evidence for relatively strong surface interaction. Three separate observables demonstrate this interaction. (1) SER intensities are potential modulated. (2) SER vibrational frequencies for $HCR^{4-}$ are perturbed in a manner which is consistent with the formation of a chemisorption bond between the complex and the surface (a $C\equiv N$ bridge in this case). (3) The site symmetry of adsorbed $HCR^{4-}$ is lowered, resulting in the activation of vibrational modes which are not Raman active in the bulk phase.

By means of a detailed comparison between the Ag and Cu SER spectra with the bulk phase normal Raman (NR) and IR spectra, it is possible to determine what spectral changes are induced by symmetry lowering and which ones reflect surface chemical interaction. By comparing the voltage dependence of the SER spectra on Cu and Ag, it is possible to separate out intensity changes caused by changes in surface number density from those caused by an inherent voltage dependence of the enhancement process. This information has important bearing on the enhancement mechanism or mechanisms and also provides a basis for understanding the wavelength dependence of the potential dependence of pyridine on silver[5] as well as the similarity between the potential dependence of pyridine/Ag and pyridine/Cu.[6]

When the potential dependence of the SER scattering from $HCR^{4-}$/Cu was measured, a monatonic increase with increasing negative potential was observed. Spectral frequencies and relative intensities indicated that the strength of interaction was decreasing over this potential range, and hence surface concentrations would remain at best constant but most probably decrease. Therefore, the observed intensity increase is most likely representative of the voltage dependence of the surface electronic process(es) giving rise to the enhancement. Some possible sources of such an effect are proposed.

## Experimental Section

$K_4Ru(CN)_6{\cdot}3H_2O$ was obtained from Alfa Chemical Co., Danvers, MA, and was used without further purification. Solutions were prepared in distilled, deionized water and were $1.0 \times 10^{-2}$ M in ruthenium complex and 0.1 M in $Na_2SO_4$. NaCl was also used as supporting electrolyte with comparable results.

The electrochemical cell used has been described in detail elsewhere[5]. The electrochemical and spectroscopic instrumentation has been previously described.[2] The bulk metal Cu and Ag electrodes were prepared by mechanical polishing (0.3-$\mu$m alumina) and anodization in the presence of the adsorbate. For silver, the anodization was accomplished with a single, double potential step from −0.6 to +0.2 V and back with 25.0 mC cm$^{-2}$ passed in the forward step. For copper, the anodization was carried out with a single voltage sweep from −0.6 to 0.0 V and back at 20 mV s$^{-1}$. (All potentials are vs. the saturated calomel electrode.) Later studies[7] have shown that double step anodizations on copper work just as well.

Laser excitation was with the 514.5-nm line of an $Ar^+$ laser or with an $Ar^+$-pumped, Rhodamine B dye laser ($\lambda$ = 640 nm). Laser powers and monochromator band-pass are given in the figure captions.

## Results and Discussion

Strong SER spectra were observed on both Ag and Cu electrodes in NaCl and $Na_2SO_4$ electrolytes. In accordance with our previous results on pyridine[1,8] and $MoO_4^{2-}$,[4] $HCR^{4-}$ adsorbed on Ag gave SER scattering with either 514.5-nm or 635-nm excitation; whereas, when adsorbed on Cu, it gave observable Raman scattering only when excited with wavelengths longer than 600 nm. No detailed excitation frequency dependence was made for $Ru(CN)_6^{4-}$. In contrast to pyridine/Cu SER spectra,[8] the intensities observed for $HCR^{4-}$/Cu were stable over a period of hours

---

*To whom correspondence should be addressed at the Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

(1) Jeanmaire, D. L.; Van Duyne, R. P. *J. Electroanal. Chem.* **1977**, *84*, 1-20.

(2) Van Duyne, R. P. In "Chemical and Biochemical Applications of Laser"; Moore, C. B., Ed.; Academic Press: New York, 1979; Vol. IV, pp 101-185.

(3) Furtak, T. E.; Reyes J. *Surf. Sci.* **1980**, 351-382.

(4) Allen, C. S.; Van Duyne, R. P., submitted for publication in *Surf. Sci.*

(5) Allen, C. S. Ph.D. Thesis, Northwestern University, 1980.

(6) Wenning, U.; Pettinger, B.; Wetzel, H. *Chem. Phys. Lett.*, **1980**, *70*, 49-54.

(7) Allen, C. S., unpublished results.

(8) Allen C. S.; Schatz, G. C.; Van Duyne, R. P. *Chem. Phys. Lett.*, in press.

0002-7863/81/1503-7497$01.25/0 © 1981 American Chemical Society

Table I. Vibrational Frequencies of $Ru(CN)_6^{4-}$ in Various Environments[b]

| mode no. | $\nu$(bulk phase) | $\nu$(solution Raman) | $\nu$(Ag SERS) |  | $\nu$(Cu SERS) |  |
|---|---|---|---|---|---|---|
|  |  |  | −0.2 V | −0.8 V | −0.75 V | −1.1 V |
|  |  |  | 214 |  | 220 sh | 220 sh |
| $\nu_5$ | (340) |  | 337 w, br |  | 340 m, br |  |
| $\nu_{12}$ | $365_{IR}$ |  | *a* |  | *a* |  |
| $\nu_8$ | (376) |  | *a* |  | *a* | 392 vw |
| $\nu_4$ | 416 |  | *a* |  | *a* |  |
| $\nu_2$ | 427 | 427 m |  |  | 435 | 435 |
| $\nu_{10}$ | 465 | 464 m | 476 s, br |  | 453 | 465 sh, br |
|  |  |  |  |  | 500 br, w | 500 s |
| $\nu_7$ | $550_{IR}$ |  | 546 s |  | 548 s | 548 w, sh |
| $\nu_6$ | $2048_{IR}$ |  | 2051 s | 2057 m, sh | $2042^a$ s |  |
| $\nu_3$ | 2071 | 2069 vs |  |  |  | $2071^a$ |
|  |  |  | 2097 vs | 2099 vs | $2097^a$ s |  |
| $\nu_1$ | 2111 | 2109 vs |  |  |  | $2110^a$ vs |
|  |  |  | $2122^a$ sh |  | $2120^a$ vs |  |

[a] Unresolved feature. [b] Bulk phase frequencies and assignments are from ref 9. All frequencies are in $cm^{-1}$.

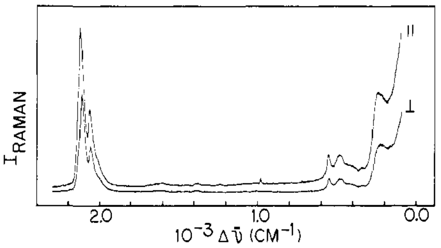

**Figure 1.** Surface-enhanced Raman spectra from $Ru(CN)_6^{4-}$ (0.01 M) in 0.1 M $Na_2SO_4$ aqueous solution, adsorbed on an anodized Ag electrode (applied potential = −0.2 V; Laser power was 150 mW at 514.5 nm; 2-$cm^{-1}$ band-pass).

and were not measurably degraded by the 150-mW laser powers employed.

Figure 1 shows SER spectra detecting polarized light parallel (||) and perpendicular (⊥) to the incident laser light for $HCR^{4-}$ adsorbed on Ag. The applied potential was −0.2 V (SCE). The intense features near 2100 $cm^{-1}$ are due to vibrational modes comprised mainly of CN stretching vibrations. The lower frequency modes arise from Ru–C stretching and Ru–C–N bending vibrations. Depolarization ratios ($\rho$) are about the same for all bands ($\rho$ = 0.60) which is very close to the value measured in pyridine/Ag SERS.[1] When normal Raman (NR) depolarization ratios are measured in aqueous solution, the two totally symmetric modes (2109 and 427 $cm^{-1}$) are completely polarized ($\rho$ = 0). For Raman scattering in bulk phases, $\rho$ values of less than 0.75 are only expected for totally symmetric modes, but SER depolarization ratios always seem to fall between 0.5 and 0.6 for all bands and are useful for distinguishing between SER and bulk phase scattering. The scattering features in the CN region are somewhat perturbed; Figure 2 shows an expanded comparison of the CN bands in solution (c), adsorbed on Ag (b), and adsorbed on copper (a). Two new features appear in the SER spectrum. On Ag, a band at 2051 $cm^{-1}$ is clearly seen along with a high-frequency shoulder on the 2097-$cm^{-1}$ band. On copper, the 2097- and 2051-$cm^{-1}$ bands are not resolved and the high-frequency feature is very intense.

The same series of spectra of the low frequency region is shown in Figure 3 and is characterized by the appearance of several new bands. As in the cases of $MoO_4^{2-}$ and $Pt(CN)_4^{2-}$[4] the appearance of most of the new bands in $HCR^{4-}$ can be directly correlated with symmetry lowering on adsorption, but the appearance of the high-frequency peak on copper and a shoulder on Ag is not correlated with an IR-active or -inactive mode in bulk phase $HCR^{4-}$. We assign this new vibration to the CN stretch of the CN group forming the bridge between ruthenium and the surface.

Table I lists the observed vibrational frequencies for $HCR^{4-}$ in various environments. The assignments and wavenumber shifts for bulk phase are taken from the work of Griffith and Turner.[9]

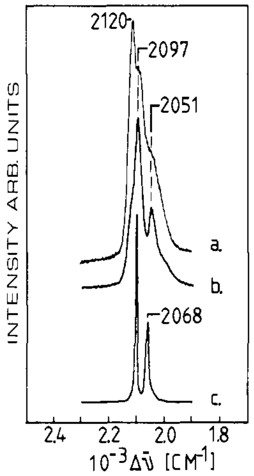

**Figure 2.** Comparison of Raman spectra for $Ru(CN)_6^{4-}$ in various environments. a. SER spectrum of 0.01 M $Na_2SO_4/H_2O$ (applied potential = −0.7 V; laser power was 150 mW at 640 nm; monochromator band-pass = 4 $cm^{-1}$). b. SER spectrum of 0.01 M $Ru(CN)_6^{4-}$ adsorbed on an anodized silver electrode in 0.1 M $Na_2SO_4/H_2O$ (applied potential = −0.2 V; laser power was 75 mW at 514.5 nm; band-pass = 2 $cm^{-1}$). c. Normal Raman spectrum of 0.50 M $Ru(CN)_6^{4-}$ in water (laser power was 500 mW at 514.5 nm; 2-$cm^{-1}$ band-pass).

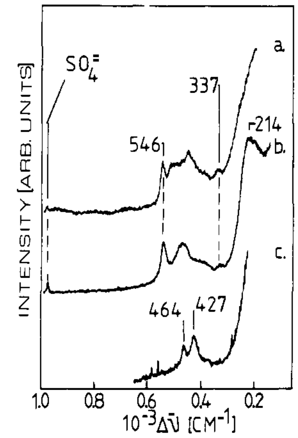

**Figure 3.** Comparison of the low wavenumber regions of Raman spectra of $Ru(CN)_6^{4-}$ in various environments: a, copper; b, silver; c, solutions are the same as in Figure 2.

All values for aqueous solution NR and SER scattering were obtained in this laboratory.

As was observed for $Pt(CN)_4^{2-}$ ion,[4] there is a low-frequency mode (214 $cm^{-1}$) associated with adsorbed $Ru(CN)_6^{4-}$. The band is clearly resolved on silver but appears only as a shoulder in the copper spectrum. The latter was excited with a dye laser, and

---

(9) Griffith, W. T.; Turner, G. T. *J. Chem. Soc. A* **1970**, 858–862.

Table II. Symmetry Lowering in $Ru(CN)_6^{4-}$[a]

| mode | $O_h$ | $D_{4h}$ | $C_{4v}$ |
|---|---|---|---|
| $\nu_1, \nu_2$ | $A_{1g}$ (R) | $A_{1g}$ (R) | $A_1$ (R) |
| $\nu_3, \nu_4$ | $E_g$ (R) | $A_{1g}$ (R)<br>$B_{1g}$ (R) | $A_1$ (R)<br>$B_1$ (R) |
| $\nu_5$ | $T_{1g}$ | $A_{2g}$<br>$E_g$ (R) | $A_2$<br>E (R) |
| $\nu_{10}, \nu_{11}$ | $T_{2g}$ | $B_{2g}$ (R)<br>$E_g$ (R) | $B_2$ (R)<br>E (R) |
| $\nu_6, \nu_7, \nu_8$ | $T_{1u}$ | $A_{2u}$<br>$E_u$ | $A_1$ (R)<br>E (R) |
| $\nu_{12}, \nu_{13}$ | $T_{2u}$ | $B_{2u}$<br>$E_u$ | $B_1$ (R)<br>E (R) |

[a] R denotes Raman activity.

although a tunable grating filter was used, fluorescence from the dye jet is not completely removed when it is close in wavelength to the laser line. This fluorescent light is then transmitted into the monochromator by the highly reflective electrode surface causing low-frequency bands to be obscured. The low-frequency feature is assigned to an adsorbate/surface vibration. The frequency of this mode is very close to the low-frequency mode observed for pyridine in chloride-containing media.[1,10] In this case, the supporting electrolyte is $SO_4^{2-}$ and hence no contribution from adsorbed $Cl^-$ could be responsible for this feature.

Weak bands in the SER spectra are observed at 337 $cm^{-1}$ on both copper and silver. These are very close to the frequency calculated for $\nu_5$, an inactive mode composed of Ru—C≡N bending motions. From measurements of IR combination bands, Griffith and Turner[9] calculated a value of 340 $cm^{-1}$ for $\nu_5$ which is of $T_{1g}$ symmetry in the free molecule. This mode is expected to become Raman active when the symmetry is lowered from octahedral. Table II lists vibrational modes according to symmetry species along with the appropriate correlations as the molecule is subjected to a tetragonal distortion. This would correspond to the formation of a single bridging cyanide bond with the metal surface. Other types of surface interaction are possible which would also lead to symmetry lowering, but the strength of the bridging CN bond as evidenced by the perturbations of the CN frequencies (vide infra) tends to argue for a linear Ru—C≡N—M bridge. This is by no means conclusive evidence, however, and it can be readily verified that interaction of two or three CN groups with the surface would yield symmetries low enough to activate this and the other new bands discussed below.

The spectral region between 337 and 435 $cm^{-1}$ is characterized by a broad, weak scattering feature which probably contains contributions from modes $\nu_2$, $\nu_4$, $\nu_8$, and $\nu_{12}$ all of which are Raman active in lowered symmetry. These modes correspond to stretching and bending vibrations which may be perturbed by adsorption. Symmetry lowering would also allow extensive mode mixing between $\nu_2$ and $\nu_4$ as well as between $\nu_8$ and $\nu_{12}$.

Moving to higher wavenumber shift, the next resolved features are at 476 $cm^{-1}$ on silver and 453 $cm^{-1}$ on copper. These broad bands are most likely Ru–C stretches that have been perturbed by the formation of the CN bridge (or bridges). There is an additional feature on copper at about 500 $cm^{-1}$. As discussed below, the copper–complex interaction is stronger than the corresponding silver–complex interaction and CN bridge formation is expected to cause an upshift in Ru–C frequency for the bridge bond[11] but the high density of vibrational modes in this region precludes a definitive assignment without a detailed mode analysis of bridge-bonded $Ru(CN)_6^{4-}$.

In both spectra (Cu and Ag), there are sharp bands near 550 $cm^{-1}$ (546 $cm^{-1}$ on Ag, 548 $cm^{-1}$ on Cu). This is probably $\nu_7$, an IR-active mode in solution that becomes Raman active upon adsorption. It is a Ru—C≡N bending vibration in which four CN groups move out of plane, in phase. The fact that the frequency of this mode is not strongly perturbed lends credence to the single CN bridge adsorption geometry. This bending vibration is also perpendicular to the plane of the metal surface and, therefore, is expected to be strongly enhanced if image field forces play a significant role in the enhancement process.[4,12]

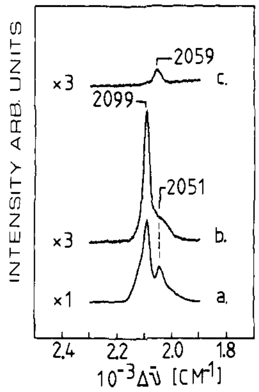

**Figure 4.** Surface-enhanced Raman spectra of $Ru(CN)_6^{4-}$ (0.01 M) adsorbed on an anodized Ag electrode at (a) −0.2 V and (b) −0.8 V and (c) after addition of 19 mM $K^{13}CN$ (laser excitation was at 514.5 nm; power = 75 mW; monochromator band-pass = 2.4 $cm^{-1}$).

There are no vibrational frequencies observed for $HCR^{4-}$ between 550 and 2000 $cm^{-1}$. Between 2000 and 2200 $cm^{-1}$ are the three modes assigned (Table I) to CN stretching vibrations in the free molecule. $\nu_1$ is a totally symmetric stretch (Raman active, 2109 $cm^{-1}$ in solution), $\nu_3$ is of $E_g$ symmetry (Raman active, 2069 $cm^{-1}$), and $\nu_6$ is an IR-active mode ($T_{1u}$, 2048 $cm^{-1}$ in the solid phase IR). Upon symmetry lowering to $C_{4v}$, $\nu_7$ splits into E and $A_1$ modes which are both Raman active.

When $HCR^{4-}$ is adsorbed, one observes the CN region spectra shown in Figure 2. On silver at −0.2 V, Figure 2b, two distinct peaks are observed (2097 and 2051 $cm^{-1}$) along with unresolved shoulders at higher and lower frequency. The spectrum on copper is also complex. Here there are three features readily discerned; the highest frequency feature at 2120 $cm^{-1}$ is the most intense. Strong scattering is seen also at 2097 and 2042 $cm^{-1}$, but all three are severely overlapped.

The lower frequency bands 2051 $cm^{-1}$ on Ag and 2042 $cm^{-1}$ on copper can be correlated with the IR-active mode $\nu_6$ at 2048 $cm^{-1}$ in bulk; again symmetry lowering allows this mode to become Raman active.

The bands at 2097 $cm^{-1}$ on copper and silver may have complex origins. When the symmetry is lowered, the CN vibrations may mix extensively. It is safe to assume that it is a CN stretch but impossible to identify it with any single vibrational mode in the free molecule.

The high-frequency shoulder on Ag and the peak on copper at 2120 $cm^{-1}$ are more easily assigned as originating from the stretching vibration of the CN bond forming the bridge to the metal surface. It has been reported that the formation of bridge bonded cyano compounds results in an increase in the CN stretching frequency.[11,13] The bonding interaction of the nitrogen via its lone pair ($\sigma^*$) to another metal atom (M′) causes an increase in the CN force constant.[11] In the analogous iron complex $Fe(CN)_6^{4-}$, the formation of a bridging CN bond with cobalt(III) results in a frequency upshift of 35 $cm^{-1}$.[13] Free $Co(CN)_6^{3-}$ shows a single CN stretch in the infrared at 2130 $cm^{-1}$, but when the silver complex $Ag_3Co(CN)_6$ is formed, a strong feature of 2187 $cm^{-1}$ is seen in addition to the 2130-$cm^{-1}$ vibration ($\Delta\nu$ = 57 $cm^{-1}$).

The bridging cyanide system has been modeled by Kharitonov and Evstaeva.[13] Their calculations show that increasing the force constant of the N–M′ bond (M′ = surface in our case) causes a slight increase in the $\nu_{CN}$ and $\nu_{MC}$ if $K_{CN}$ and $K_{MC}$ are kept constant. This is purely due to a change in the mechanics of the vibrating system. They also found that the frequency shifts were relatively independent on the mass of M′ so their calculations

---

(10) Dornhaus, R.; Chang, R. submitted for publication in *Surf. Sci.*

(11) Kharitonov, Y.; Evstafeva, O. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1969**, *14*, 403–406.

(12) Allen, C. S.; Van Duyne, R. P. *Chem. Phys. Lett.* **1979**, *63*, 455–459.

(13) Dows, D. A.; Haim, A.; Wilmarth, W. K. *J. Inorg. Nucl. Chem.* **1961**, *21*, 33–37.

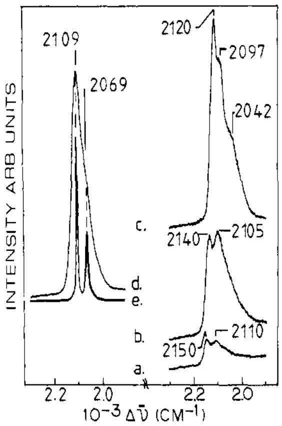

**Figure 5.** Potential dependence of SER scattering from $Ru(CN)_6^{4-}$ adsorbed on an anozided copper electrode at (a) −0.2 V, (b) −0.4 V, (c) −0.7 V, and (d) −1.1 V (reduced in size by 0.50) and (e) solution spectrum (0.50 M in water) (laser excitation was at 640 nm; power = 150 mW; monochromator band-pass = 4.0 cm$^{-1}$).

should be applicable to an adsorbate/metal system. The large shifts observed in the discrete bridged complexes and in the SER are undoubtedly due to a combination of electronic and mechanical effects.

Examination of the potential dependence of the SER spectra lends support to the bridge bonded interpretation of the high-frequency modes. Figure 4 shows a comparison between SER scattering from HCR$^{4-}$ on Ag at −0.2 V (a) and −0.8 V (b). Since the potential of zero charge (pzc) on silver is usually very close to −0.7 V vs. SCE,[14] as the potential is moved from −0.2 to −0.8 V, we change from a positively charged surface to a slightly negative or neutral surface. It can be clearly seen that both the bands at 2120 and 2050 cm$^{-1}$ weaken compared to the 2099-cm$^{-1}$ band. (The overall intensity of the spectrum is also slightly reduced.) If the 2120-cm$^{-1}$ band is really due to bridge bonding of an anionic complex with an electrode surface, then one would expect it to shift to lower frequency as the interaction strength with the surface ($K_{M'N}$) is weakened. Making the electrode surface more negative has precisely this effect. One would also expect that as the strength of the N–M′ surface bond is decreased, the symmetry will approach that of the free molecule and the IR-active modes will disappear. The 2051-cm$^{-1}$ band does lose intensity as a result of the potential change.

In reality we are dealing with a surface which is no doubt quite heterogeneous in its structure. Therefore, the fact that we see a gradual decrease in the intensity of the 2051-cm$^{-1}$ band should not be interpreted as a gradual return to $O_h$ symmetry so much as a changing in the population of surface species which are bound strongly enough to lower symmetry.

The potential dependence of HCR$^{4-}$/Cu SER scattering is even more dramatic. Figure 5 shows the potential dependence along with the solution NR spectrum for reference. At −0.2 V, spectrum a is obtained which shows two broad peaks in the CN region at 2150 and 2110 cm$^{-1}$. The asymmetry of the lower frequency peak suggests the presence of yet another peak at about 2050 cm$^{-1}$. The high-frequency feature is not doubt due to the vibration of a CN group participating in strong bridge bonding with the surface. At −0.7 V (b) this band has shifted in frequency to 2120 cm$^{-1}$, demonstrating a weaker surface interaction, and at −1.1 V (d), the spectrum is virtually identical with the solution spectrum (e) if line broadening is taken into account. One notices in comparing the spectra in this series that the relative intensity of the unresolved low-frequency shoulder ~2042 cm$^{-1}$ remains almost constant as a function of potential until −1.1 V where it is barely discerible. As in the case of HCR$^{4-}$/Ag this is indicative of an adsorbed molecule which is almost undistorted and hence $\nu_6$ is not Raman active. When the lower frequency SER scattering was recorded at −1.1 V, the band at 548 cm$^{-1}$ ($\nu_7$) was also dramatically decreased in intensity and was seen as a weak shoulder on a single, very broad band centered about 500 cm$^{-1}$. Table I lists the observed frequencies for HCR$^{4-}$/Cu at −1.1 V.

It is interesting to note that even at this very negative potential the low-frequency region spectrum is still strongly perturbed whereas the CN region spectrum looks very much like the free molecule. Obviously more detailed investigations are necessary to determine the origin of the low-frequency scattering features and the importance of mode mixing.

It can be seen, however, that by using an electrode surface as the second metal in a bridging cyanide allows changing the strength of the N→M′ interaction by merely adjusting the potential. A comparison of the spectra for Cu and Ag shows that the surface interaction is much stronger on the former metal. On the other hand, IR-active modes (in $O_h$ symmetry) are seen in the SER spectra of both metals at comparable intensities; therefore the symmetry lowering is common to both systems and can occur over a wide range of applied potentials (interaction strengths). In all cases of potential dependence measurements, the changes obseved in the spectra were reversible.

The proximity at the 2099-cm$^{-1}$ feature in the SER spectrum of $Ru(CN)_6^{4-}$ on Ag at −0.8 V to that observed for SER scattering from free $CN^-$[4-8] (2105 cm$^{-1}$) raised the question of whether or not the interaction with the surface had displaced $CN^-$ from the complex. To test this, after acquisition of the spectrum shown in Figure 4b, isotopically labled cyanide ($^{13}C$) was added to a concentration of 0.02 M. The result was the spectrum shown in Figure 4c. The frequency of the single band observed is identical with that found for pure $^{13}CN$ on silver.

Evidently, the bonding of the HCR$^{4-}$ on Ag is quite weak at this potential, and all of it is displaced by $^{13}CN^-$. This is in agreement with our earlier assertion based on frequency shifts and symmetry correlations that $Ru(CN)_6^{4-}$ is weakly bound at these potentials. Returning to −0.2 V, no SER spectrum could be obtained due to the dissolution at the surface to form soluble $Ag(CN)_x^{(x-1)-}$ complexes.[15]

The intensities observed in the potential dependence studies on copper deserve some comment. As one moves the potential more and more negatively, the SER scattering intensity for HCR$^{4-}$ is seen to increase monotonically. Although there is clear evidence cited above that the interaction of the complex with the surface is becoming progressively weaker, the SER intensity rises. Pettinger and co-workers,[6] in their investigation of pyridine on copper, found a maximum intensity at −0.6 to −0.7 V which is very close to the maximum potential seen for silver with excitation at 514.5 nm.[1] The latter was interpreted as resulting from the potential dependent modulation of the surface concentration of adsorbed pyridine; the maximum adsorption for a neutral organic molecule is expected at the pzc[14] which is −0.7 V for Ag. The result on copper was, therefore, surprising since one would expect the maximum SER intensity to occur near the pzc for that metal, −0.1 V.[16]

One would expect an even more dramatic effect for HCR$^{4-}$ since at all potentials studied, the electrode was negatively charged. It is well-known from electrochemical studies that the standard potential for the oxidation of the analogous iron complex $Fe(CN)_6^{4-}$ is strongly affected by solution cations.[17] This effect has been interpreted as arising from ion-pair formation between the ferrocyanide (HCF$^{4-}$) and alkali-metal cations. The formation constant for HCF$^{4-}$K$^+$ is ~220 at room temperature.[18] The analogous value for HCR$^{4-}$K$^+$ is 320.[19] No measurements have

---

(14) Argard, S. D.; Gileadi, E. In "Electrosorption"; Gileadi, E., Ed.; 1967; pp 87–115.

(15) Billman, J.; Kovacs, G.; Otto, A. *Surf. Sci.* **1980**, *92*, 153.

(16) Bertocci, U.; Turner, D. R. In "Encylopedia of Electrochemistry of the Elements"; Bard, A. J., Ed.; Vol. II, pp 383–497.

(17) Kolthoff, I. M.; Tomsicek, W. J. *J. Phys. Chem.* **1935**, *39*, 945–954.

(18) Eaton, W. A.; George, P.; Hanania, G. I. H. *J. Phys. Chem.* **1967**, *71*, 2016–2022.

(19) Fidler, A.; Kralik, F. *Collect. Czech. Chem. Commun.* **1970**, *35*, 1913–1916.

(20) Nichugovskii, G. F.; Shvendov, V. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1969**, *14*, 156–157.

been made of $HCR^{4-}Na^+$, but on the basis of the $HCF^{4-}Na^+$ result ($K$ = 135), it is probably substantial. Any microscopic model of the adsorbate then should include closely associated cations. In the experiments described here, there was 0.2 M $Na^+$ and 0.04 M $K^+$ present in solution and one can envision the stabilization of the negatively charged $HCR^{4-}$ by one or several alkali-metal cations in the electrical double layer. Based on cation interactions, then, we can rationalize the fact that $HCR^{4-}$ can be adsorbed at potentials quite negative of the pzc. This still does not explain why the SER intensity *increases* as the potential is moved negatively. This can only be the result of an inherent potential dependence of the Raman enhancing ability of copper metal.

Due to the very large number of theoretical models for the surface-enhanced Raman effect, it is not practical to discuss here the potential dependence of all of them. Indeed, very few make specific predictions about this so the discussion will center on potential dependence changes in the optical properties of copper. McIntyre[21] has measured electroreflectance curves for copper in Ar-saturated 1 M $HClO_4$. The measured curves show a pronounced maximum near 590 nm (2.1 eV) at the plasma resonance peak. At 640 nm (1.83 eV) the electroreflectance parameter ($R^{-1}\Delta R/\Delta q_m$) is $-1 \times 10^{-4}$ cm$^{-2}$ $\mu$C$^{-1}$. While this value would obviously change in the presence of an adsorbate, it does show clearly that the reflectivity of copper changes substantially with potential in this range, increasing as the potential is movved negatively. According to image field models[22] of SERS, the increase in Raman enhancing ability would be correlated to this reflectance increase and would explain the observed potential dependence of the $HCR^{4-}$ on copper. If the Raman measurements were carried out far from the plasma edge, 830 nm (1.5 eV) one would expect the SER enhancement to be governed by surface concentrations alone. It should be noted, however, that these are not independent; the adsorption of molecules at the metal surface will have a large effect on the surface optical properties due to changes in the electrical double layer.[21]

Similar effects might cause the potential dependence seen for py/Cu.[6] Due to a weaker interaction of py with the surface (spectral perturbations are considerably smaller than with $HCR^{4-}$), its surface concentration may decrease substantially as the potential is moved negatively from the pzc. This may, however, be compensated by the increased enhancing ability of Cu at more negative potentials resulting in a slight peak in the SER intensity vs. potential at −0.6 V. When the potential dependence of py/Ag was measured at 635 nm,[5] the maximum intensity was found about 200 mV more negative than at 514.5 nm (1008-cm$^{-1}$ band).[1] This stands as further evidence for the potential dependent enhancement mechanism which requires investigation over a large wavelength range.

## Conclusions

We have presented a detailed study of the SER spectroscopy of $Ru(CN)_6^{4-}$ on Ag and Cu. As we observed for other inorganic anions,[4] the surface interactions are stronger on copper than on silver and adsorption onto either metal can induce symmetry lowering and thus cause activation of bands which are not Raman active in bulk phase. The observed frequencies are interpretable in terms of vibrational modes of the free molecule and perturbations caused by the formation of a CN-bridging bond to the surface. Due to the complexity of the 300–500-cm$^{-1}$ region, theoretical modeling is required in order to sort out the bending and stretching vibrations of the $HCR^{4-}$ framework.

When the intensities were measured as a function of potential, it was discovered that the interaction strength of the complex and metal could be varied over a substantial range and that the enhancement mechanism for SER scattering from copper is inherently potential dependent.

**Acknowledgment.** We acknowledge financial support from the National Science Foundation (Grant CHE-7824866) and from the Office of Naval Research (Contract N00014-79-C-0794). C.S.A. gratefully acknowledges fellowship support for the academic year 1979–1980 from the Eastman Kodak Co.

---

[21] McIntyre, J. D. E. *Surf. Sci.* **1973**, *37*, 658–682.

[22] King, F. W.; Van Duyne, R. P.; Schatz, G. C. *J. Chem. Phys.* **1978**, *69*, 4472–4481.

[23] Efrima, S.; Metiu, H. *Chem. Phys. Lett.* **1978**, *60*, 59–64.

[24] Efrima, S.; Metiu, H. *J. Chem. Phys.* **1979**, *70*, 1602–1613.

[25] Efrima, S.; Metiu, H. *J. Chem. Phys.* **1979**, *70*, 2297–2309.

[26] Schatz, G. C.; Van Duyne, R. P. *Surf. Sci.* **1980**, *101*, 425–438.