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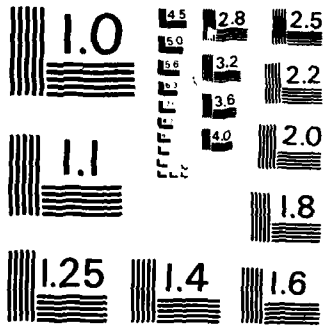
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Surface-Enhanced Raman Spectroscopy of Electrochemically  
Characterized Interfaces. Transition-Metal Isothiocyanate  
Adsorbates at Silver Adsorbates

by

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SURFACE-ENHANCED RAMAN SPECTROSCOPY OF  
ELECTROCHEMICALLY CHARACTERIZED INTERFACES.  
TRANSITION-METAL ISOTHIOCYANATE ADSORBATES AT SILVER ~~ELECTRODES~~ **ADSORBATES**

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Abstract

Surface-enhanced Raman (SER) spectra have been obtained at the silver-aqueous interface for nine  $\text{Cr}^{\text{III}}$ ,  $\text{Co}^{\text{III}}$ ,  $\text{Ru}^{\text{II}}$ , and  $\text{Rh}^{\text{III}}$  ammine or ethylenediamine complexes containing one or more thiocyanates as surface bridging groups. These complexes provide stereochemically well-defined adsorbates having at least one sulfur surface binding site but with electronic properties that differ substantially from thiocyanate itself. The dependence of the SER spectra were examined in each case over a potential range where the complexes are stable with respect to reduction or oxidation, and where the adsorbate coverage remained close to a monolayer. The adsorbate coverage could be evaluated in several cases from the faradaic charge required for one-electron reduction. SER spectra were obtained using a spectrograph-optical multichannel analyzer (OMA) as well as a conventional scanning spectrometer. This enabled the rapid reversible component of the SERS potential dependence to be separated from the irreversible signal decay associated with surface rearrangement. SERS bands due to metal ammine and internal ammine vibrations were observed in addition to those associated with internal thiocyanate and ligand-surface vibrations. The intensities and frequencies of most of these SERS bands were only mildly dependent upon the electrode potential. However, the peak frequency and bandshape of the thiocyanate C-N stretching mode ( $\nu_{\text{CN}}$ ) was found to be sensitive both to the electrode potential and the nature of the coordinated transition metal. These differences can be understood in terms of electron withdrawal by the silver surface.

We have recently been examining surface-enhanced Raman scattering (SERS) for a variety of adsorbates at the silver-aqueous interface for which quantitative information on the surface concentration can be obtained by electrochemical means.<sup>1-6</sup> These adsorbates include those that engage in reversible one-electron transfer reactions within the available potential range at silver electrodes. This enables quantitative assessments to be made of the response of the SERS signals to variations in the surface concentration of the Raman scatterer brought about by alterations in redox<sup>5</sup> as well as adsorption-desorption equilibria.<sup>1-4</sup> Another virtue of employing electroactive adsorbates is that their surface concentrations can often be readily obtained by using faradaic perturbation techniques. Although we have found that chronocoulometry often yields unreliable adsorption data at solid electrodes,<sup>7</sup> rapid scan cyclic voltammetry has proved to be a valuable means of obtaining such data at silver surfaces.<sup>5b,7,8</sup> For electroinactive adsorbates at silver, accurate surface concentration data can be obtained in favorable cases from measurements of the differential double-layer capacitance as a function of electrode potential and bulk adsorbate concentration in constant ionic strength media.<sup>2,9</sup>

These results demonstrate that there are approximate correlations between the SERS intensity and the potential-dependent adsorbate coverage, at least when the SERS data are gathered sufficiently rapidly to avoid the irreversible signal decay associated with loss of Raman-active sites.<sup>1,4</sup> An interesting exception is adsorbed thiocyanate in that substantial decreases in intensity of the SERS modes occur as the electrode potential is made more negative, even under conditions where the coverage of this adsorbate remains

close to a monolayer. We have suggested that these intensity decreases are most likely due to field-induced structural changes, such as reorientation, in the adsorbate layer.<sup>1,2,4</sup>

More recently, we have been examining SERS of a number of transition-metal N-bound thiocyanate complexes ("isothiocyanates"). These have the general formula  $M^{III}(NH_3)_{6-x}(NCS)_x$  or  $M^{III}(en)_2(NCS)_2$ , where en = ethylenediamine and  $M^{III} = Cr^{III}, Ru^{III}, Co^{III}, Os^{III},$  or  $Rh^{III}$ . These adsorbates were selected for detailed study for several reasons. Firstly, in contrast to uncoordinated thiocyanate the complexes can only bind to the surface via the sulfur atom since the nitrogen is rigidly bound to the transition-metal cation. They are also stable with respect to photochemical dissociation by the 647 nm light used for Raman excitation. Such substitution inert complexes therefore offer important advantages over labile complexes such as cadmium thiocyanates that have also been studied recently using SERS.<sup>10</sup> Secondly, they provide a means of exploring the influence of alterations in the electronic structure upon the vibrational modes brought about by variations in the transition-metal cation. Such electronic factors have previously been suggested to influence adsorbate-surface binding involving thiocyanate and related bridging ligands.<sup>11</sup> Thirdly, such adsorbates, especially those containing two or more thiocyanates in the cis-configuration, provide unusually rigid and stereochemically well-defined adsorbates.<sup>12</sup> They exhibit a number of clearly identifiable vibrational modes associated with the nonbridging ammine as well as the bridging thiocyanate ligands.

In addition, we have recently examined the electroreduction kinetics of adsorbed Cr(III) and Co(III) complexes bound to silver, platinum, and gold surfaces via thiocyanate, azide, and halide bridging ligands.<sup>7,8,13</sup> These complexes provide valuable model adsorbates with which to examine the fundamental influences of the adsorbate-surface interactions upon electrochemical reactivity. The evaluation of the vibrational properties of such electroactive adsorbates and the comparison with corresponding data for the bulk-phase complexes is therefore of considerable interest.

Surface-enhanced Raman (SER) spectra obtained for these thiocyanate-bridged adsorbates at the silver-aqueous interface are reported here, along with corresponding data for these and related systems as bulk solids obtained using normal Raman (NR) and infrared (IR) spectroscopy. Taken together, the results shed light both on the nature of the adsorbate-surface interactions and some of the major factors that influence SERS in these and related systems.

### Experimental

The various thiocyanate complexes were prepared as solid perchlorate, hexafluorophosphate, or chloride salts using literature procedures as follows:  $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$ <sup>14</sup>,  $\text{c-Cr}(\text{NH}_3)_4(\text{NCS})_2^+$ <sup>15</sup>,  $\text{c-Cr}(\text{en})_2(\text{NCS})_2^+$ <sup>16</sup>,  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$ <sup>17</sup>,  $\text{c-Co}(\text{en})_2(\text{NCS})_2^+$ <sup>18</sup>,  $\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+}$ <sup>19</sup>,  $\text{Rh}(\text{NH}_3)_5\text{NCS}^{2+}$ <sup>20</sup>.  $\text{t-Cr}^{\text{III}}(\text{NH}_3)_2(\text{NCS})_4 \cdot \text{Ag}^{\text{I}}$  was prepared from  $\text{K} \cdot \text{Cr}(\text{NH}_3)_2(\text{NCS})_4$  (Alfa Chemicals) by precipitation with  $\text{AgNO}_3$  (cf. ref. 21).  $\text{K}_3 \cdot \text{Cr}(\text{NCS})_6$  (Alfa Chemicals) was recrystallized before use. Ammine or ethylenediamine deuteration of these complexes in solution was achieved by dissolving them in a small volume of neutral  $\text{D}_2\text{O}$ , and acidifying before dilution with water.<sup>24</sup> The potassium chloride and sodium perchlorate used as supporting electrolytes

were reagent grade, and were recrystallized prior to use. Water was purified by means of a "Milli Q" system (Millipore Inc.).

Both electrochemical and SERS measurements utilized a silver electrode of rotating disk construction having a disk radius of 0.2 cm surrounded by a teflon sheath. The electrode was mechanically polished on a wheel successively with 5, 1, and 0.3  $\mu\text{m}$  alumina immediately prior to immersion in the solution. The cell used for SERS measurements was of conventional electrochemical design, being constructed of glass and having a working compartment (ca 10 mL volume) containing the silver and platinum counter electrodes separated from another compartment containing a saturated calomel electrode (s.c.e.) by means of a fine glass frit. The bottom of the working compartment consisted of a 1/16" thick glass flat through which the laser beam was illuminated vertically onto the silver electrode surface. The cell was tilted at a suitable angle so that the scattered light could be collected at 90° to the incident beam and about 60° to the electrode surface.

The Raman spectra were gathered using either a conventional scanning spectrometer or using a spectrograph-optical multichannel analyzer (OMA) arrangement. The former consisted of a SPEX 1403 double monochromator equipped with holographic gratings (1800 gr/mm), a RCA C31034 photomultiplier tube, a SPEX DPC-2 photon counter, a SPEX CD2 Compudrive and a Kipp and Zonen BD40 strip chart recorder. The Raman scattered light was focussed into the entrance slit using a Olympus F1-2 55 mm focal length camera lens. The latter arrangement consisted of a SPEX 1877 triple spectrograph with a 600 gr/mm grating in the filter stage and either 1200 or 1800 gr/mm in the dispersion stage, a PAR 1420-3 photodiode array detector, a PAR 1218 detector controller, and a PAR 1215 control console.

The Raman scattered light was collected by means of a SPEX 1459 illuminator. Laser irradiation was either a Spectra-Physics 165 Kr<sup>+</sup> laser operated at 647.1 nm or Ar<sup>+</sup> laser at 514.5 nm. The laser beam was spot focussed on the electrode surface, typically using 100-200 mW power at the sample. The scanning spectrometer system was primarily employed for initial studies or for detailed measurements where the SERS signals were stable over the time period (ca 20-60 mins) necessary when making a series of measurements using this approach. This system could also be utilized for Raman frequencies down to ca 100 cm<sup>-1</sup>, whereas stray light from the spectrograph effectively limited the OMA system to recording frequencies above ca 200 cm<sup>-1</sup>. However, the OMA was preferred for most measurements where extensive potential-dependent data were obtained since good-quality spectra could be obtained in only 1-2 secs. The OMA also enabled SER spectra to be obtained for a number of these complexes using 514.5 nm as well as 647.1 nm light, even though relatively rapid photolysis commonly occurs at the former wavelength.<sup>22</sup>

The silver electrode was mildly roughened in order to optimize the SER signal intensity by means of one to five oxidation-reduction cycles (ORC). This generally entailed stepping the potential from ca -150 mV to +350 mV versus s.c.e., returning after the accumulation of ca 20-40 mC cm<sup>-2</sup> anodic charge. Stronger SER signals for the thiocyanate complexes were generally obtained in the absence of laser irradiation during the ORC (contrast the behavior of thiocyanate in ref. 23); this procedure was therefore usually followed. The ORC's were performed either in a separate 0.1 M KCl solution and rapidly transferred to the solution of interest, or directly in the latter if this contained chloride ions, with essentially identical results. Normal Raman spectra of the bulk-phase solid complexes were obtained with 647.1 nm irradiation,

mostly using solid pellets mounted on the tip of a spinning rod to minimize photodecomposition. The bulk-phase Raman spectra utilized to estimate surface enhancement factors (vide infra) were obtained either in a Nujol mull or in dimethylsulfoxide solution. Infrared spectra were obtained from 600-3000  $\text{cm}^{-1}$  on a Perkin-Elmer Model 267 spectrometer using KBr pellets or Nujol mulls, and from 50-500  $\text{cm}^{-1}$  on a Digilab FTS 20 spectrometer using polyethylene disks.

Potential control during the electrochemical SERS measurements was achieved using a PAR 173/179 potentiostat. Rapid linear sweep voltammetry additionally employed a PAR 175 potential programmer, the voltammograms being recorded with a Nicolet 2090-1 digital oscilloscope coupled with a Houston 2000 X-Y recorder. Differential capacitance measurements were made using a phase-sensitive detection method.<sup>9</sup> This utilized a PAR 173/179 potentiostat and a PAR 5204 lock-in amplifier with internal oscillator, interfaced to an LSI 11-23 microcomputer in order to provide a direct readout of both the capacitance and resistive components of the cell impedance.

All solutions were degassed with nitrogen or argon prior to the electrochemical measurements. All electrode potentials are quoted versus the s.c.e., and all measurements were made at room temperature,  $23 \pm 1^\circ\text{C}$ .

### Results

Table I contains a summary of peak frequencies for the various thiocyanate vibrational modes for each complex bound to the silver electrode at four electrode potentials. For comparison, it also contains corresponding data for the bulk-phase complexes. The SERS data were generally obtained using 1-2  $\text{mM}$  of the thiocyanate complex in either 0.01 or 0.1  $\text{M}$   $\text{HCl}$ , or 0.1  $\text{M}$   $\text{NaClO}_4$ , acidified in each case with 2  $\text{mM}$   $\text{HClO}_4$  to avoid any base-catalyzed hydrolysis. As for adsorbed thiocyanate<sup>1</sup> all three internal thiocyanate modes, the C-N

stretch ( $\nu_{\text{CN}}$ , ca  $2100 \text{ cm}^{-1}$ ), and C-S stretch ( $\nu_{\text{CS}}$ , ca  $730\text{-}800 \text{ cm}^{-1}$ ), and the N-C-S bend ( $\delta_{\text{NCS}}$ , ca  $450 \text{ cm}^{-1}$ ), were observed for most complexes, although the  $\nu_{\text{CS}}$  band was very weak. These assignments were made by means of their characteristic frequencies (vide infra). In addition, a band around  $210\text{-}220 \text{ cm}^{-1}$  appeared for most complexes (Table I), attributed to a surface-sulfur stretching mode ( $\nu_{\text{Ag-S}}$ ) by comparison with SERS for adsorbed thiocyanate.<sup>1</sup>

The least negative potential in Table I,  $-150 \text{ mV}$ , was chosen since it is significantly negative of the potential, ca  $0 \text{ mV}$ , where anodic oxidation of the silver surface commences in these media. However, some reduction of  $\text{c-Co(en)}_2(\text{NCS})_2^+$  occurs even at  $-150 \text{ mV}$ . Indeed, spectra obtained for this adsorbate at more negative potentials are indistinguishable from those for free thiocyanate. This is expected since these ligands are released upon the one-electron reduction of Co(III). The Cr(III) thiocyanate adsorbates can be examined over a wider potential range; although their one-electron electroreductions are also chemically irreversible they do not occur at a significant rate until around  $-600 \text{ mV}$ <sup>7,8</sup> (vide infra). The SERS of  $\text{Rh}(\text{NH}_3)_5\text{NCS}^{2+}$  was also examined since Rh(III) reduction does not commence until ca  $-800 \text{ mV}$ . Unfortunately, the spectra for this adsorbate were sufficiently weak that the  $\nu_{\text{CN}}$  mode appeared at only the most positive potentials. However, uniformly intense SER spectra were obtained for  $\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+}$  from  $-150$  to  $-900 \text{ mV}$ . Although this complex is reduced at  $-140 \text{ mV}$ ,<sup>25</sup> the resulting Ru(II) species,  $\text{Ru}(\text{NH}_3)_5\text{NCS}^+$ , is also substitutionally inert and does not undergo further reduction within this potential range.

Representative SER spectra for a typical complex,  $\text{c-Cr}(\text{NH}_3)_4(\text{NCS})_2^+$ , in the frequency regions  $160\text{-}500 \text{ cm}^{-1}$  and  $2050\text{-}2200 \text{ cm}^{-1}$  are shown as a function of potential in Fig. 1, along with bulk-phase Raman spectrum. Besides the bridging thiocyanate modes already noted, several other bands appear in the frequency region  $200\text{-}500 \text{ cm}^{-1}$  for this and the other thiocyanate-bound adsorbates. The band around  $460 \text{ cm}^{-1}$ , ascribed in part to  $\delta_{\text{NCS}}$ , also

appears to be due to a metal-amine stretching mode  $\nu_{M-NH_3}$ . This accidental degeneracy can be removed by deuterating the ammine ligand, whereupon the  $\nu_{M-ND_3}$  mode shifted to about  $420\text{ cm}^{-1}$ , (shown as a dashed curve in Figures 1A and D). This frequency decrease is consistent with that expected ( $35\text{ cm}^{-1}$ ) on the basis of the greater mass of the  $ND_3$  versus the  $NH_3$  ligand. In addition, bands around 240, 270, and  $330\text{ cm}^{-1}$  were often obtained for this and most other complexes. Since the  $240\text{ cm}^{-1}$  band only appeared in the presence of chloride and occurs at the same frequency as in pure chloride electrolytes,<sup>26</sup> it is assigned to a surface-chloride stretching mode. This band was often obscured by the surface-sulfur stretch at  $210\text{-}220\text{ cm}^{-1}$ .

The other two bands are less straightforward to assign. Barely discernable peaks were seen around these frequencies in the bulk-phase Raman spectra (eg. Fig. 1A). However, much stronger bands were seen in the IR spectra for the Cr(III) thiocyanato ammine complexes. (For example, these bands occurred at 260 and  $325\text{ cm}^{-1}$  in the IR spectra of  $c\text{-Cr}(NH_3)_4(NCS)_2^+$ ). Since only a band at  $270\text{ cm}^{-1}$  was seen in the IR spectrum of  $Cr(NH_3)_6^{3+}$ , we tentatively attribute the corresponding SERS band to the asymmetric MNM bending mode,  $\delta_{NMN}$ , on the basis of the assignments detailed in ref. 27. This mode is expected to shift to significantly (ca  $10\text{-}20\text{ cm}^{-1}$ ) smaller frequencies upon ammine deuteration;<sup>27</sup> although some shift was indeed observed in the SER spectra under these conditions, the band was insufficiently well defined to enable a quantitative conclusion to be made on this point. Attempts were made to detect internal ammine stretching and bending modes; for example  $\nu_{NH}$  bands should occur around  $3200\text{ cm}^{-1}$ .<sup>27</sup> However, these were apparently too weak to be observed in the SER spectra.

For the ethylenediamine complexes, a number of other bands were observed in both the SER and bulk-phase Raman spectra which are clearly due to internal

ethylenediamine modes. A prominent band at  $485 \text{ cm}^{-1}$  was generally observed, somewhat (2-3 fold) more intense than  $\nu_{\text{M-NH}_3}$  for the ammine complexes. This is assigned to a metal-ethylenediamine stretching mode,  $\nu_{\text{M-en}}$ ; as expected this shifted to about  $460 \text{ cm}^{-1}$  upon ethylenediamine deuteration. Several other bands were seen in the range  $500\text{-}2000 \text{ cm}^{-1}$  which can be identified as arising from internal ethylenediamine modes by comparison with NR and IR spectra for these and related ethylenediamine complexes.<sup>28</sup> For example, peaks were seen for  $\text{t-Cr(en)}_2(\text{NCS})_2^+$  at 800, 880, 1050, 1285, 1400, 1595, and  $1895 \text{ cm}^{-1}$ .

The SERS metal-ammine, metal-ethylenediamine, and internal ethylenediamine bands are relatively narrow (full width at half maximum,  $\text{FWHM} \approx 15\text{-}25 \text{ cm}^{-1}$ ), similarly to that seen in the bulk-phase Raman and IR spectra. However, the SERS  $\nu_{\text{CN}}$  bands ( $\text{FWHM} \sim 40\text{-}65 \text{ cm}^{-1}$ ) are markedly broader than those in the NR and IR bands ( $\text{FWHM} \sim 20\text{-}30 \text{ cm}^{-1}$ ) and significantly dependent upon the nature of the transition-metal cation. This is exemplified by Fig. 2, which contains SERS  $\nu_{\text{CN}}$  bands for  $\text{NCS}^-$ ,  $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$ , and  $\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+}$  at  $-300 \text{ mV}$  plotted on a common frequency axis with the peak intensities normalized to a single value. The  $\nu_{\text{Ag-S}}$  bands were also typically broad,  $\text{FWHM} \sim 30\text{-}40 \text{ cm}^{-1}$  (Fig. 1).

Particular attention was paid to the dependence of the SERS band intensities and peak frequencies upon the electrode potential. Whenever convenient the OMA system was used for these measurements in order to minimize the time dependence of the Raman intensities associated with the irreversible loss of Raman-active sites.<sup>1,4</sup> This procedure enables the rapid "reversible" portion of the potential dependence to be determined separately from the irreversible component.<sup>1,4</sup> We have noted previously that the intensity of

$\nu_{\text{CN}}$  and  $\nu_{\text{Ag-S}}$  for adsorbed  $\text{NCS}^-$  decreases markedly as the potential is made more negative. In contrast, the peak intensity and bandshape (and hence the integrated band intensity) for all four Cr(III) thiocyanate complexes (Table I) remained approximately constant (within ca 20-30%) between -150 and ca -550 mV, although the intensity typically increased by 20-30% between -150 and -300 mV. By comparison, the reversible intensity of the SERS  $\nu_{\text{CN}}$  mode for  $\text{NCS}^-$  decreases by ca 2-3 fold from -150 to -600 mV.<sup>1</sup>

Essentially the same results were obtained for the  $\nu_{\text{CN}}$ ,  $\nu_{\text{M-NH}_3}$ , and  $\nu_{\text{Ag-S}}$  modes by using the scanning spectrometer system, although marked intensity decreases were seen around -500 to -600 mV. These were traced to an increasingly rapid temporal decay of the SERS signals as the potential is made more negative in this region. Such potential dependence could be largely eliminated by gathering potential-dependent data within 10 sec or so using the OMA. Altering the potential more negative of ca -600 mV yielded a rapid and almost complete loss of the  $\nu_{\text{CN}}$  band. This is undoubtedly due to irreversible reduction of the Cr(III) adsorbates since the voltammetric reduction waves occur in this potential region.<sup>8,29</sup>

The potential-dependent SERS of  $\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+}$  is of particular interest in this regard; as noted above the Ru(III)/(II) couple is chemically reversible so that the Ru(II) product should stay intact at the electrode surface over an especially large potential range. Indeed, the intensity and bandshape of the  $\nu_{\text{CN}}$  mode for this adsorbate remains virtually constant (10%) throughout the potential region -150 to -900 mV. The  $\nu_{\text{M-NH}_3}$  mode at

455  $\text{cm}^{-1}$  behaved similarly, although the  $\nu_{\text{Ag-S}}$  mode was too weak to enable its reversible intensity-potential dependence to be determined. The frequency of  $\nu_{\text{M-NH}_3}$ , 450  $\text{cm}^{-1}$ , was also essentially independent of potential in the region -50 to -750 mV. This value is consistent with the presence of Ru(II) rather than Ru(III); we therefore designate this adsorbate as  $\text{Ru}(\text{NH}_3)_5\text{NCS}^+$  rather than  $\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+}$ . The peak frequency of the  $\nu_{\text{CN}}$  mode for adsorbed  $\text{Ru}(\text{NH}_3)_5\text{NCS}^+$  decreased progressively with increasing negative potential (Fig. 3); this potential dependence was smaller than those seen for the Cr(III) adsorbates (Table I).

That these complexes are adsorbed in amounts close to a monolayer under the conditions employed for the SERS measurements were deduced from three lines of evidence. Firstly, the Cr(III) complexes and  $\text{c-Co(en)}_2(\text{NCS})_2^+$  can be reduced by an irreversible one-electron transfer at potentials prior to the negative limit of silver in mildly acidic media (ca -800 to -900 mV). By employing linear sweep voltammetry with small bulk reactant concentrations ( $\leq 0.1 \text{ mM}$ ) and rapid sweep rates ( $\geq 10 \text{ V sec}^{-1}$ ) the initially adsorbed species provides the major contribution to the faradaic reduction wave, enabling the extent of adsorption at the initial potential to be obtained.<sup>7,8</sup> Details of the experimental results at polished silver electrodes are given in refs. 7 and 8. Surface reactant concentrations close to that expected for a monolayer ( $1.5 \text{ to } 2 \times 10^{-11} \text{ mol cm}^{-2}$ ) were typically obtained. No electroactivity could be detected for adsorbed  $\text{Ru}(\text{NH}_3)_5\text{NCS}^+$  or  $\text{Rh}(\text{NH}_3)_5\text{NCS}^{2+}$  at silver from -100 to -800 mV. Similar results were obtained at electrochemically roughened silver, the extent of adsorption (in moles per apparent  $\text{cm}^{-2}$ ) simply being increased in proportion to the roughness factor RF (ratio of actual to apparent area) as determined by the corresponding increase in the background capacitance.<sup>2</sup> (Values of RF around 1.5-2.5 were typically found by using the above ORC roughening procedure.<sup>2</sup>)

A second line of evidence indicating monolayer adsorption was obtained from differential capacitance-potential ( $C_d$ -E) data. Addition of ca 0.1 mM or more of the thiocyanate complex to 0.1 M KCl yielded marked decreases in the capacitance in the potential region -50 to -500 mV, indicating that the complex was replacing the initially adsorbed chloride ions<sup>2</sup> (cf Fig. 1 of ref. 1). Thirdly, the electroreduction kinetics of the Cr(III) complexes display apparent electrochemical reaction orders substantially below unity; this is again indicative of adsorbate coverages approaching saturation at the reactant concentrations (0.5 - 2 mM) employed.<sup>8</sup>

Some measurements of the SERS  $\nu_{CN}$  region were made using 514.5 nm as well as 647.1 nm laser excitation. Although relatively rapid photo-decomposition occurred, especially for the Cr(III) complexes,<sup>22</sup> a satisfactory set of potential-dependent data could be obtained without significant signal decay using the OMA. Essentially similar SERS results were obtained using 514.5 and 647.1 nm irradiation. However, the  $\nu_{CN}$  bandshapes were slightly different, 5-10  $\text{cm}^{-1}$  higher frequencies being typically obtained with the former laser line. This result was obtained irrespective of laser illumination conditions during the ORC.

The intensities of the thiocyanate SERS modes for the various complexes (excepting  $\text{Rh}(\text{NH}_3)_5\text{NCS}^{2+}$ ) are closely similar to one another as well to those for free thiocyanate at the least negative potentials (-100 to -200 mV). Similar results were obtained for the  $\nu_{CN}$  band using 541.5 nm as well as 647.1 nm irradiation. We have made extensive comparisons of the integrated SERS and bulk-phase Raman intensities for these and a variety of other adsorbates. These measurements when coupled with the surface concentration

data enable estimates of the "surface enhancement factor", SEF, (i.e. the increase in Raman scattering intensity per molecular upon adsorption) to be obtained. Details are given elsewhere.<sup>31</sup> Broadly speaking, the SEF values for the thiocyanate adsorbates are insensitive to their electronic structure and indeed are similar (within 2-5 fold) to those for related inorganic adsorbates. Representative values of SEF for the  $\nu_{\text{CN}}$  mode of  $\text{NCS}^-$ ,  $\text{Cr}(\text{NCS})_6^{3-}$ , and  $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$  are at -300 mV;  $2.5 \times 10^6$ ,  $3.5 \times 10^6$ , and  $6 \times 10^6$ , respectively (cf SEF for pyridine<sup>33</sup>). An examination was also made of the relative SEF values for the  $\nu_{\text{CN}}$  and  $\nu_{\text{M-N}}$  bands for adsorbed  $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$  and  $\text{c-Cr}(\text{NH}_3)_4(\text{NCS})_2^+$ . Although somewhat dependent upon the experimental conditions, the SEF values for the  $\nu_{\text{CN}}$  bands tend to be ca 2-5 fold larger than the corresponding  $\nu_{\text{M-N}}$  bands.

### Discussion

The marked ( $\geq 30 \text{ cm}^{-1}$ ) increases in  $\nu_{\text{CN}}$  upon adsorption of the various thiocyanate complexes (Table I) are similar to that seen when binding the

sulfur atom of metal isothiocyanate complexes to another metal cation.<sup>34</sup> Similar frequency shifts also occur for binding  $\text{NCS}^-$  to a silver electrode (Table I)<sup>1</sup> and to metal cations via the sulfur atoms.<sup>34</sup> These shifts can be understood in part through an increase of the C-N force constant via withdrawal of electron density from the sulfur.<sup>34</sup> This result for  $\text{NCS}^-$  provides strong evidence that adsorption at silver involves the sulfur rather than the nitrogen atom.<sup>1,10</sup> The similar behavior seen for the present thiocyanate complexes supports this conclusion since the sulfur atom clearly provides the only means of surface binding. The significantly ( $10\text{-}30\text{ cm}^{-1}$ ) higher values of  $\nu_{\text{CN}}$  for the adsorbed complexes versus that for adsorbed  $\text{NCS}^-$  at the same electrode potential (Table I) recalls the especially high values of  $\nu_{\text{CN}}$  seen for a number of metal complexes where thiocyanate is acting as a bridge between a pair of metal ions.<sup>34</sup> Comparison of the corresponding values of  $\nu_{\text{CN}}$  for each complex with that for  $\text{NCS}^-$  shows that comparable increases ( $10\text{-}40\text{ cm}^{-1}$ ) in  $\nu_{\text{CN}}$  are brought about by nitrogen coordination of  $\text{NCS}^-$  to Cr(III), Co(III), Ru(II), and Rh(III) in both bulk-phase and adsorbed environments (Table I). This suggests that the perturbation of the C-N bond due to sulfur surface coordination is roughly additive with that resulting from transition metal-nitrogen binding. However, it is interesting to note that the increase in  $\nu_{\text{CN}}$  associated with the latter tends to be largest for the low-spin  $d^6$  metals Co(III) and Rh(III); these metals are expected to yield the largest increase in the C-N force constant via metal-thiocyanate  $\pi$  bonding.<sup>11</sup>

The frequency of the  $\nu_{\text{CS}}$  band for adsorbed  $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$  ( $790\text{ cm}^{-1}$ ) is also similar to that seen for several bridging thiocyanate complexes,<sup>34</sup> and noticeably larger than for adsorbed thiocyanate ( $735\text{ cm}^{-1}$ , Table I) as

well as in other terminal S-bound environments.<sup>34</sup> The latter frequency shift is consistent with vibrational coupling with the metal-nitrogen bond.<sup>34</sup>

The comparison between  $\nu_{\text{CN}}$  for the complexes when bound to the silver surface and when bound to bulk-phase Ag(I) is anticipated to provide valuable insight into the nature of surface bonding for these systems. Comparison of the relevant data in Table I shows that the values of  $\nu_{\text{CN}}$  for the adsorbed Cr(III) complexes at the most positive potential, -150 mV, approach that for the binuclear complex  $t\text{-Cr}^{\text{III}}(\text{NH}_3)_2(\text{NCS})_4\text{Ag}^{\text{I}}$  ( $2140\text{ cm}^{-1}$ ). The potential region in Table I is considerably positive of the potential of zero charge (p.z.c.), so that the silver surface carries a large positive electronic charge density.<sup>1</sup> However, the average "formal oxidation state",  $x$ , of the surface silver atoms under these conditions is considerably less than unity.<sup>1</sup> For example,  $x \approx 0.2$  for a monolayer of  $\text{NCS}^-$  anions at -150 mV, the p.z.c. (i.e. where  $x = 0$ ) being around -1800 mV under these conditions.<sup>1,35</sup> Such estimations of  $x$  are precluded for the metal thiocyanate complexes since the required differential capacitance data cannot be obtained over a sufficiently wide potential range. However, similar results are expected on the basis of the demonstrated similarities in the adsorption thermodynamics of thiocyanate and Cr(III) thiocyanates at mercury electrodes.<sup>12</sup>

We have previously pointed out that the potential dependence of  $\nu_{\text{CN}}$  and  $\nu_{\text{Ag-S}}$  for adsorbed thiocyanate is rather larger than might be expected on the basis of changes in bond polarization effects alone.<sup>1</sup> It was noted that this might arise in part from the reorientation and/or adsorption site redistributions that apparently yield the corresponding changes in intensity and FWHM of these bands. The noticeably smaller reversible potential dependence

of  $\nu_{\text{CN}}$  for adsorbed  $\text{Ru}(\text{NH}_3)_5\text{NCS}^+$  ( $18 \text{ cm}^{-1} \text{ V}^{-1}$ , Fig. 3) than for  $\text{NCS}^-$  (up to  $40 \text{ cm}^{-1} \text{ V}^{-1}$ )<sup>1</sup> is particularly pertinent. Given that the intensity and bandshape of the former is essentially independent of potential, this smaller potential dependence of  $\nu_{\text{CN}}$  might then be taken as the "true" value associated with bond polarization effects alone. However,  $x$  is only mildly dependent upon the electrode potential  $E$  (roughly  $dx/dE \sim 0.1 \text{ V}^{-1}$ ).<sup>1</sup> The perturbations in  $\nu_{\text{CN}}$  induced by surface binding are therefore more pronounced than would be expected on the basis of the effective ionic charge of the surface silver atoms.<sup>1</sup>

Nevertheless, an array of charged metal surface atoms might be anticipated to have distinctly different bonding properties to those of an isolated metal ion. In addition, it is likely that the surface sites primarily responsible for SERS of these and related adsorbates are associated with adatoms or, more likely, metal clusters.<sup>1</sup> These sites are expected to have distinctly different electronic and stereochemical properties to those of a plane array of surface atoms.<sup>36</sup> In particular, the electronic charge of such sites should be significantly more positive than the plane lattice sites. Consequently SERS may arise from surface sites that are more electron deficient (i.e. have larger  $x$ ) than for the "ensemble average" as monitored by the differential capacitance. Such metal clusters would also be expected to provide a variety of subtly different coordination environments since their electronic properties will be sensitive to their size and structure. This provides an explanation for the unusual breadth and asymmetry of the SERS  $\nu_{\text{CN}}$  and  $\nu_{\text{Ag-S}}$  bands in relation to the nonbridging  $\nu_{\text{M-NH}_3}$  modes (Figs. 1, 2) since the former should be much more sensitive to the coordination environment of the adsorbed sulfur atom.

The observed insensitivity of the thiocyanate SERS intensities to the nature of, or even the presence, of a transition metal coordinated to the

thiocyanate nitrogen suggests that the electronic structure of the adsorbate exerts little influence upon SERS of these systems. The similar SERS intensities and SEF values seen for the  $\nu_{\text{CN}}$  band for the metal complexes and free thiocyanate using 514.5 nm irradiation is especially interesting in that this wavelength is situated amidst a relatively intense d-d adsorption band for most of the transition-metal adsorbates.<sup>22</sup> This band is absent for free thiocyanate and silver thiocyanate. This suggests that a "resonance Raman" effect associated with electronic excitation within the adsorbate is not providing a major contribution to SERS for these systems.<sup>31</sup>

It remains to consider the possible dependence of the surface Raman intensities upon the electrode potential. Given that the coverage of adsorbed thiocyanate remains close to a monolayer, at least in the potential range -100 to -600 mV, the observation that the intensity of the  $\nu_{\text{CN}}$  and  $\nu_{\text{Ag-S}}$  bands decreases sharply with increasing negative potential in this region indicates that the surface enhancement factor (SEF) is also diminished in roughly the same proportion.<sup>1</sup> This result has been interpreted as indicating that the polarizability of the SERS-active adsorbate is a strong function of the electrode potential, associated with a mechanism arising from surface optical resonance.<sup>37</sup> However, as noted above the potential-induced decreases in SEF may well arise at least partly from a change in adsorbate orientation.<sup>1,2,4</sup> The latter is supported by the "peaked" structure of the differential capacitance-potential ( $C_d$ -E) curves for adsorbed thiocyanate within this potential region, signaling potential-induced changes in the dielectric properties of the adsorbed thiocyanate layer.<sup>2</sup> Interestingly, capacitance data

gathered for adsorbed monolayers of  $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$  and  $\text{c-Cr}(\text{NH}_3)_4(\text{NCS})_2^+$  in the potential region -100 to -600 mV prior to their electroreduction yield relatively flat featureless  $C_d$ -E curves similar to those found for bromide or iodide monolayers.<sup>38</sup> This suggests that the transition-metal thiocyanate adsorbates do not undergo any noticeable structural alterations within this potential region. The roughly potential-independent SEF observed for these adsorbates, particularly  $\text{Ru}(\text{NH}_3)_5\text{NCS}^+$ , under these conditions is in harmony with this finding, and suggests that the potential dependence of SEF for thiocyanate arises primarily from changes in adsorbate structure rather than in the effective polarizability.

#### Conclusions

We believe that the foregoing provides a demonstration of the considerable virtues of employing structurally simple transition-metal complexes as model adsorbates for exploring the SERS effect in electrochemical environments. The use of substitution-inert complexes containing one or more strongly adsorbing ligands enable systematic changes to be made in the electronic and stereochemical properties of the adsorbate while the nature of the surface binding remains unchanged. While the SERS frequencies are noticeably dependent upon the electrode potential as well as the electronic structure of the coordinated transition metal, the SERS intensities are relatively insensitive to these factors. Vibrational bands associated with nonbridging as well as bridging ligand modes appear in the SER spectra, albeit with diminished intensity.

It is hoped that these results will spawn further efforts to apply SERS to structurally well-defined adsorbates at interfaces that can be characterized independently by electrochemical means. Unfortunately, much of the recent experimental work focussing on the elucidation of the surface enhancement mechanisms has employed electrochemical interfaces of unknown surface composition and structure so that the conclusions are often of questionable validity. However, the judicious selection of structurally well-defined adsorbates along with the utilization of surface electroanalytical techniques should aid such mechanism diagnoses, and perhaps more importantly, lay the groundwork for further applications of SERS to surface electrochemistry.

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Table I. Vibrational frequencies ( $\text{cm}^{-1}$ ) for thiocyanate modes in transition-metal ammine and ethylenediamine complexes at silver electrodes and in bulk-phase environments.

Complex	Mode <sup>a</sup>	Silver Electrode, mV vs. s.c.e. <sup>b</sup>				Bulk Phase	
		-150	-300	-450	-600	Uncord. <sup>c</sup>	Ag(1) <sup>f</sup>
$\text{NCS}^-$	$\nu_{\text{Ag-S}}$	215	210	205			
	$\delta_{\text{NCS}}$	450	450	450			
	$\nu_{\text{CS}}$	735	735	735		750	720
	$\nu_{\text{CN}}$	2115	2110	2102	2095	2055	2140 <sup>e</sup>
$\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$	$\nu_{\text{Ag-S}}$	220	220	215			
	$\delta_{\text{NCS}}$	460	460	460		460	
	$\nu_{\text{CS}}$	790	790	790		960	
	$\nu_{\text{CN}}$	2135	2130	2125	2118	2090(sh) 2080	
$\text{c-Cr}(\text{NH}_3)_4(\text{NCS})_2^+$	$\nu_{\text{Ag-S}}$	225	225	215			
	$\delta_{\text{NCS}}$	460	460	455		460	
	$\nu_{\text{CN}}$	2165 2130	2155 2125	2120	2114	2100(sh) 2082 <sup>e</sup>	
$\text{t-Cr}(\text{NH}_3)_2(\text{NCS})_4^-$	$\nu_{\text{Ag-S}}$	215	210				~200 <sup>g</sup>
	$\delta_{\text{NCS}}$	460	460			450	450
	$\nu_{\text{CN}}$	2150(sh) 2120	2150(sh) 2120			2110 2060	2140 2120
$\text{c-Cr}(\text{en})_2(\text{NCS})_2^+$	$\nu_{\text{Ag-S}}$	232	225	215			
	$\delta_{\text{NCS}}$	460	460	460		460	
	$\nu_{\text{CN}}$	2125	2119	2114	2107	2098 <sup>e</sup> 2080	
$\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$	$\nu_{\text{Ag-S}}$	207	205				
	$\delta_{\text{NCS}}$	460	460	460		465	
	$\nu_{\text{CN}}$	2125	2119	2113	2108	2100 2085	
$\text{Cr}(\text{NCS})_6^{3-}$	$\nu_{\text{Ag-S}}$	205	205				
	$\delta_{\text{NCS}}$	460	460			475	465
	$\nu_{\text{CN}}$	2140	2140			2090	2150 2120(sh)

Complex	Mode <sup>a</sup>	-150	-300	-450	-600	Uncord. <sup>c</sup>	Ag(I) <sup>f</sup>
c-Co(en) <sub>2</sub> (NCS) <sub>2</sub> <sup>+</sup>	$\nu_{\text{Ag-S}}$	210					
	$\delta_{\text{NCS}}$	450				460	
	$\nu_{\text{CN}}$	2162 2121				2110 <sup>e</sup> 2075	
Ru(NH <sub>3</sub> ) <sub>5</sub> NCS <sup>+</sup>	$\nu_{\text{Ag-S}}$	215					
	$\delta_{\text{NCS}}$	465		460			
	$\nu_{\text{CN}}$	2132	2130	2127	2124	2050 <sup>d</sup> 2040	
Rh(NH <sub>3</sub> ) <sub>5</sub> NCS <sup>2+</sup>	$\nu_{\text{CN}}$	2140				2115 <sup>d</sup> 2070	

<sup>a</sup>  $\nu_{\text{Ag-S}}$  = silver-sulfur stretch;  $\delta_{\text{NCS}}$  = N-C-S bend;  $\nu_{\text{CS}}$  = C-S stretch;  $\nu_{\text{CN}}$  = C-N stretch.

<sup>b</sup> SERS band frequencies obtained for ca 1-5 mM complex in 0.01-0.1 M KCl + 3 mM HClO<sub>4</sub> at silver-aqueous interface at electrode potential indicated. Values listed are peak frequencies; for relative intensities, bandshapes see text and Figure 2. Obtained using 647.1 nm excitation; slightly different values of  $\nu_{\text{CN}}$  obtained using 514.5 nm radiation (see text).

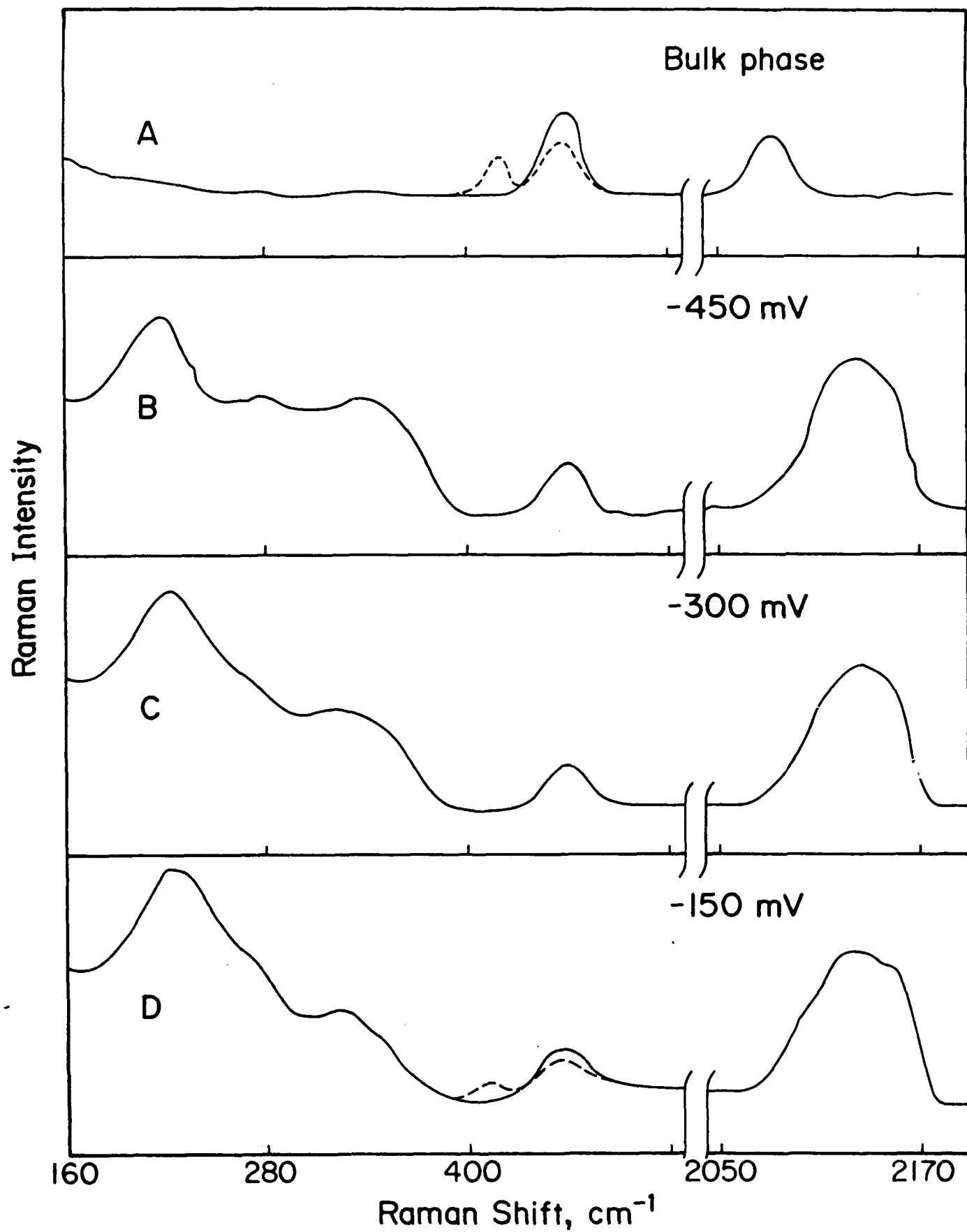
<sup>c</sup> Normal Raman and/or infrared peak frequencies obtained for bulk solid complex. Raman data given except where indicated.

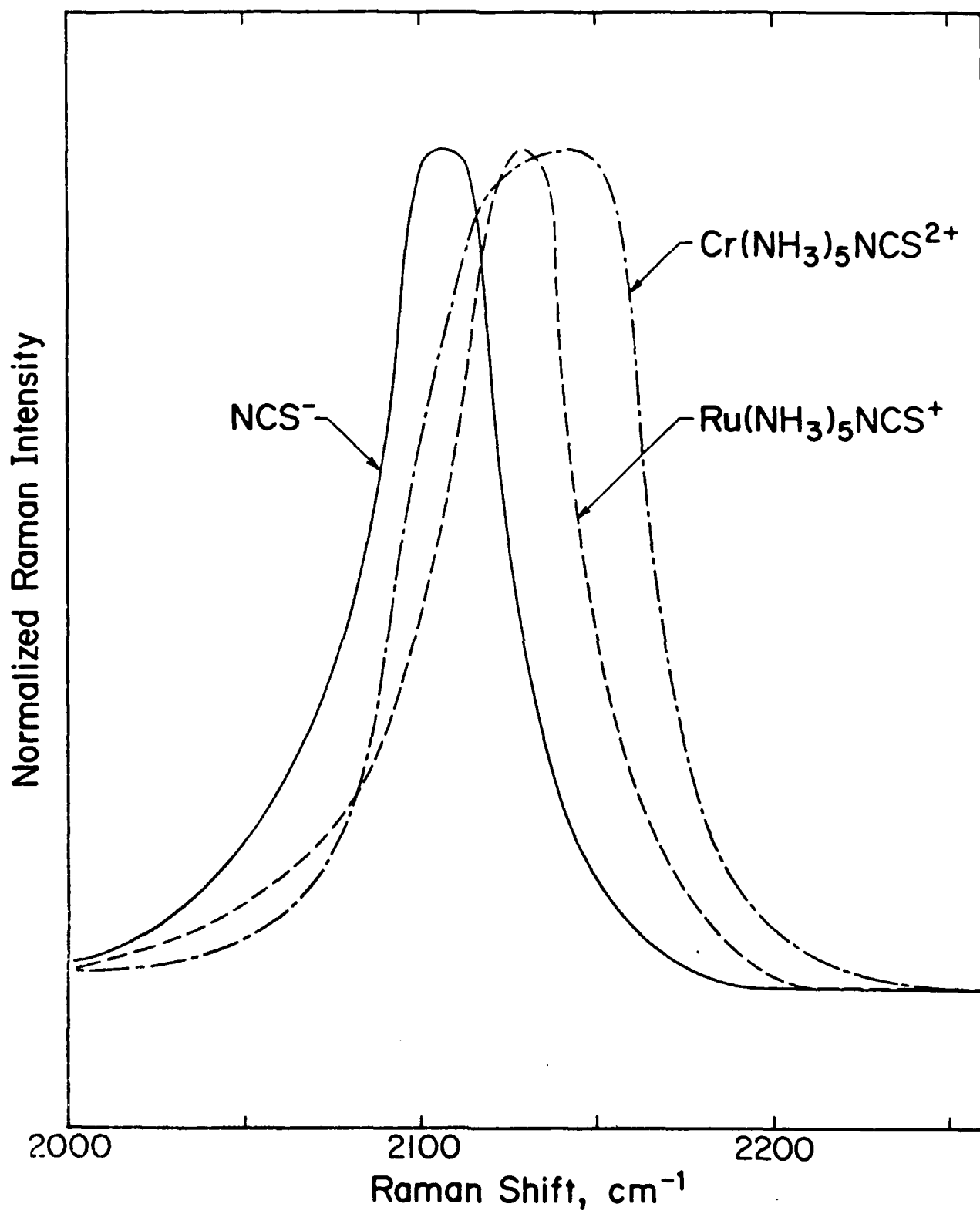
<sup>d</sup> Infrared data.

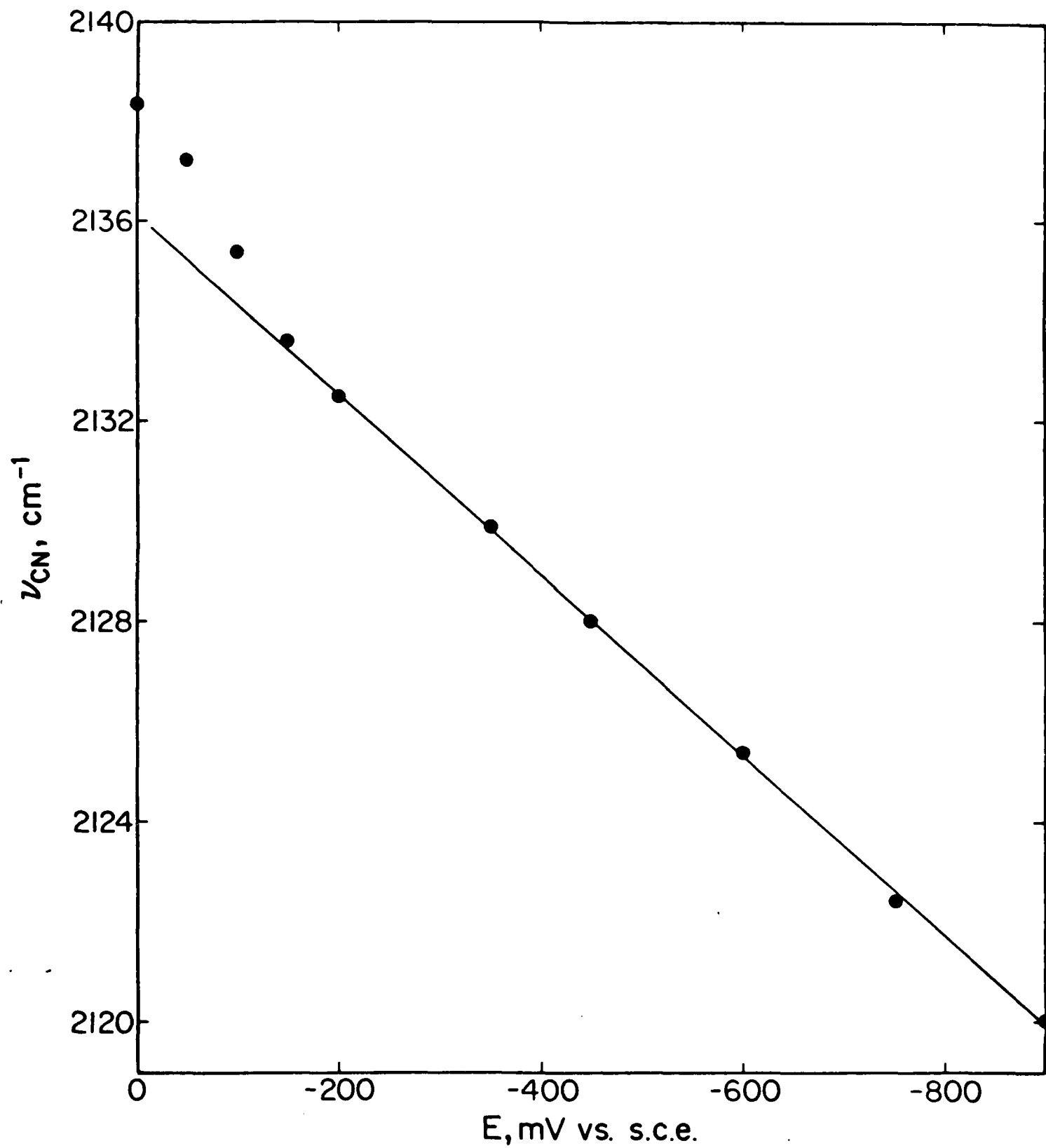
<sup>e</sup> Both Raman and Infrared data.

<sup>f</sup> Infrared peak frequencies obtained for solid binuclear complex with S coordinated to Ag(I).

<sup>g</sup> Tentative assignment - IR band is broad and ill defined.







### Figure Captions

Figure 1. Bulk-phase (A) and surface-enhanced Raman spectra (B-I) at silver electrode for  $c\text{-Cr}(\text{NH}_3)_4(\text{NCS})_2^+$  obtained using scanning Raman spectrometer with 647.1 nm laser excitation. Dashed lines refer to spectral segments determined for deuterated complex. SER spectra are for 1 mM complex in 0.01 M KCl + 2 mM HClO<sub>4</sub>. For other conditions, see text.

Figure 2. Surface-enhanced Raman C-N stretch bands for adsorbed  $\text{NCS}^-$ ,  $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$ , and  $\text{Ru}(\text{NH}_3)_5\text{NCS}^+$  at silver at -300 mV vs s.c.e., obtained using 647.1 nm laser excitation. Peak intensities are normalized to a common value; however, actual intensities were within ca twofold of each other.

Figure 3. Peak frequency of SER  $\nu_{\text{CN}}$  band for adsorbed  $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{NCS}^+$  as a function of electrode potential. Solution contained 1 mM  $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{NCS}^{2+}$  in 0.1 M KCl; 647.1 nm laser excitation. Slope of straight line is  $18.0 \text{ cm}^{-1} \text{ V}^{-1}$ .

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