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Comparisons Between Surface-Enhanced Raman and Surface

Infrared Spectroscopies For Strongly Perturbed

Adsorbates: Thiocyanate At Gold Electrodes

by

Dennis S. Corrigan, John K. Foley, Ping Gao,

Stanley Pons and Michael J. Weaver
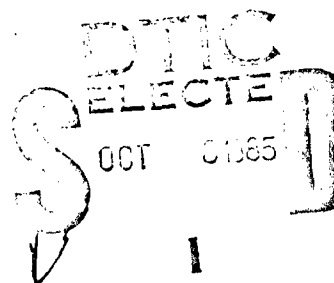
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The potential-dependent C-N stretching mode, ν_{CN}, for thiocyanate adsorbed at the gold-aqueous interface is examined by both surface-enhanced Raman spectroscopy (SERS) and subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS). Both SERS and SNIFTIRS exhibit a ν_{CN} band around 2120-2130 cm^{-1} over the potential range +500 to -500 mV vs. s.c.e., consistent with the presence of a predominantly S-bound adsorbate. The potential-dependent ν_{CN} frequencies were very similar (within ca. 5 cm^{-1}) for SNIFTIRS at smooth and electrochemically roughened gold, as well as for SNIFTIRS

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COMPARISONS BETWEEN SURFACE-ENHANCED RAMAN AND SURFACE INFRARED SPECTRO-
SCOPIES FOR STRONGLY PERTURBED ADSORBATES: THIOCYANATE AT GOLD ELECTRODES.

Dennis S. Corrigan,[1] John K. Foley,[2] Ping Gao,[1]

Stanley Pons[2*] and Michael J. Weaver[1*]

Department of Chemistry, Purdue University
West Lafayette, IN 47907
and
Department of Chemistry, University of Utah
Salt Lake City, UT 84112

Abstract

The potential-dependent C-N stretching mode, ν_{CN}, for thiocyanate

adsorbed at the gold-aqueous interface is examined by both surface-enhanced

Raman spectroscopy (SERS) and subtractively normalized interfacial Fourier

transform infrared spectroscopy (SNIFTIRS). Both SERS and SNIFTIRS exhibit

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adsorbate. The potential-dependent ν_{CN} frequencies were very similar

(within ca. 5/cm^{-1}) for SNIFTIRS at smooth and electrochemically

roughened gold, as well as for SNIFTIRS and SERS on the latter surface.

This suggests that the SERS-active sites do not differ substantially

from the preponderant sites sensed by SNIFTIRS. Some features of the SER

spectra suggest that N- as well as S-bound adsorbed thiocyanate exists at

far negative potentials.

There is currently rapid development occurring in the application of vibrational spectroscopic methods to the *in-situ* molecular characterization of electrochemical interfaces. Two such techniques are surface-enhanced Raman spectroscopy (SERS)[3] and subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS).[4,5] A virtue of the former approach is that the very large (ca. 10^5-10^7) surface enhancement of the Raman scattering, including unattached as well as surface-bound species,[6] enable absolute vibrational spectra to readily be obtained at SERS-active surfaces, even for solutions containing high (≤ 0.1 M) bulk adsorbate concentrations. On the other hand, it is possible that adsorbate molecules at the particular surface sites that are primarily responsible for SERS exhibit atypical chemical and vibrational properties compared to those for the preponderant adsorbate molecules. Surface infrared spectroscopy does not suffer from this disadvantage since detectable spectra for adsorbed species can readily be obtained at smooth metal interfaces using SNIFTIRS or related difference spectral techniques, for which little or no surface enhancement of the infrared absorption appears to occur.[4]

This suggests that a valuable way of checking the applicability of SERS as a quantitative probe of surface structure is to compare surface Raman and infrared spectra obtained under identical conditions for adsorbates whose vibrational frequencies are known to be sensitive to the nature and type of the surface bonding involved. No such quantitative comparisons appear to have been reported previously.

In this communication we compare corresponding potential-dependent SERS and SNIFTIRS data gathered for the C-N stretching mode of thiocyanate adsorbed at gold electrodes, and summarize other SER spectral features for this system. The SNIFTIR spectra were obtained at both mechanically polished and electrochemically roughened surfaces, the latter also being

employed to acquire the SER spectra. Gold surfaces prepared by prior potential sweep oxidation-reduction cycles in chloride have recently been shown to provide remarkably stable and intense SER spectra for a miscellany of adsorbates in aqueous media.[7] Thiocyanate is an interesting model adsorbate for several reasons, not the least of which are the large $(40-80 \text{ cm}^{-1})$ increases in the C-N stretching frequencies accompanying metal-sulfur bonding, and the several spectral features that enable a distinction to be made between N- and S-coordination.[8] Besides demonstrating close similarities in the potential-dependent C-N stretching frequencies for the corresponding surface Raman and infrared spectra, the present results provide an illustration of the merits of employing SERS and SNIFTIRS as complementary tools for gaining molecular structural information at electrode interfaces.

Experimental

Details of the SERS measurements are as given in ref. 9. Raman excitation was provided by a Spectra-Physics Model 165 Kr$^+$ laser operated at 647.1 nm, and the spectra gathered by using a SPEX Model 1403 double monochromator. SNIFTIRS measurements utilized an IBM Model 98-4A vacuum spectrometer, with the thin-layer electrochemical cell positioned in a small external compartment purged with nitrogen. Most details of the cell and the spectral measurements are given in ref. 5a. The electrode potential was switched between the two potentials required for the SNIFTIRS measurement every 15 sec so to minimise the deleterious effects of baseline drift.

The electrode used for the SERS measurements consisted of a 4 mm diameter gold disk sealed into a Teflon sheath of rotating disk construction (Pine Instruments). The SNIFTIRS electrode was a 7 mm gold disk sealed into Teflon. The electrodes were mechanically polished on a wheel with alumina down to 0.05 μm particle diameter and rinsed with water. The electrochemical roughening,

necessary for SERS, consisted of 20-30 potential sweeps between -300 mV and +1200 mV vs saturated calomel electrode (s.c.e.) in 0.1 $\underline{M}$ KCl. The surface remained shiny after this process, although gold electrodes displaying a pale brown hue . _ yielding even greater SERS intensities could be produced by holding the potential at the positive limit for 0.5-1 secs during each scan. Roughened as well as smooth electrodes having reflective properties were preferred for the SNIFTIRS measurements so to maximize the signal throughput. Differential capacitance measurements on these electrodes were undertaken as described in ref. 10. All electrode potentials are quoted versus the s.c.e., and all measurements were made at room temperature, 23 ± 1°C.

Results and Discussion

Aqueous solutions containing $\geq$ 0.01 m$\underline{M}$ thiocyanate in 0.1 to 0.5 $\underline{M}$ Na_2SO_4, $NaClO_4$, or KCl supporting electrolytes yielded several SER spectral features at gold electrodes that indicate that NCS^- is specifically adsorbed over the entire polarizable potential range, +700 to -900 mV vs s.c.e. Representative SER spectra for 1 m$\underline{M}$ NaNCS in 0.5 $\underline{M}$ Na_2SO_4 at four electrode potentials are shown in Fig. 1. At the two most positive potentials, 500 and 100 mV (Fig. 1A,B), the spectra are similar to those seen previously for thiocyanate adsorbed at silver electrodes.[11,12] Thus an intense and relatively broad (FWHM $\sim$ 30 cm^{-1}) C-N stretching band (ν_{CN}) is seen at 2110-2130 cm^{-1}, a weak band at about 700 cm^{-1} assigned to C-S stretching (ν_{CS}), a band around 450 cm^{-1} attributed to N-C-S bending (δ_{NCS}), and a broad feature around 240 cm^{-1}. The frequency of this last band is diagnostic of a metal surface-sulfur vibration (ν_{Au-S}), SERS bands at similar frequencies being found at silver[9] and gold[13] electrodes for several N-bound metal thiocyanate complexes for which surface

attachment must occur via the sulfur atom. The low-frequency bands associated with surface-adsorbate vibrations for the supporting electrolyte anion, which occur at 135, 178, and 265 cm^{-1} for SO_4^{2-}, ClO_4^-, and Cl^- respectively,[7] are completely removed upon addition of $\geq$ 0.1 mM thiocyanate.

At more negative potentials ($\leq$ -100 mV, Fig. 1C,D), a new feature at 295 cm^{-1} appears and the 240 cm^{-1} band is reduced in intensity. This suggests that the S-bound thiocyanate is progressively being replaced by the N-bound form since these relative frequencies are consistent with that expected from the relative masses of the surface binding atoms.[7]

The behavior of the other vibrational modes are less conclusive in this regard. Thus the δ_{NCS} band remains at about 450-460 cm^{-1} throughout the complete potential range even though slightly higher frequencies would be anticipated if N-bound adsorbed thiocyanate is being formed.[3] Although the ν_{CN} band decreases in intensity and shifts to progressively small frequencies in the range 2100-2130 cm^{-1} as the potential is made more negative, this frequency range is typical of that encountered for S- rather than N-bound thiocyanate, the latter most commonly being found around 2050-2080 cm^{-1}.[8] In addition, a weak band around 700 cm^{-1}, also indicative of S-coordination, is obtained at positive potentials that weakens and eventually disappears at the most negative potentials.

Measurements of the differential double-layer capacitance against electrode potential (C_{dl}-E) also indicate the presence of substantial thiocyanate adsorption over the entire potential range 600 to -900 mV. This can readily be discerned from the addition of $\geq$ 0.1 mM thiocyanate to 0.1 M KCl which results in loss of the broad C_{dl}-E peak centered at 300 mV due to potential-dependent chloride adsorption. Smaller, roughly potential-independent capacitances, around 25 $\mu F\ cm^{-2}$, are obtained, which are indicative of high adsorbate coverages.[10] The C_{dl}-E curve shapes were essentially unaffected

by electrode roughening, although somewhat surprisingly this resulted in significantly (ca. 20%) *smaller* capacitance values.

The SNIFTIRS spectra were obtained using -900 mV as the reference potential, where the extent of thiocyanate adsorption should be minimised. (Hydrogen evolution commences at more negative potentials.) Representative spectra obtained by stepping to several more positive potentials for 1 mM NCS⁻ in 0.5 $\underline{M}$ Na$_2$SO$_4$ at smooth gold are given in Fig. 2. Comparable results have also been obtained for similar conditions using electrochemically modulated infrared spectroscopy (EMIRS).[4a,14] At the most negative potentials, ca. < -200 mV (Fig. 1A), a bipolar band occurs with positive- and negative-going peaks (features I and II) around 2105 and 2120 cm^{-1}, respectively. At more positive potentials the negative-going band broadens and shifts to higher frequencies, and a large positive-going band appears at around 2065 cm^{-1} (feature III, Figs. 1B-D).

Figure 3 shows a corresponding series of SNIFTIRS spectra for gold that was electrochemically roughened in the same manner as that used to produce the SER spectra in Fig. 1. These two sets of SNIFTIRS spectra are very similar; however, the broad negative-going band (feature II) on roughened gold is resolved into a pair of peaks at more positive potentials and a low frequency shoulder around 2040-2050 cm^{-1} appears on feature III (Fig. 3B,C).

Feature II is entirely consistent with the formation of additional S-bound thiocyanate as the potential becomes more positive. Figure 4 contains a plot of the SNIFTIRS peak frequencies, v_{CN}^P, of this band for smooth and roughened gold (closed triangles and circles, respectively) as a function of potential. (For the latter surface, v_{CN}^P for the major, lower frequency, band is plotted.) Also included are the v_{CN} frequencies obtained from the potential-dependent SER spectra on roughened gold (open symbols). Two sets of points are shown; the squares are the SERS

peak frequencies, ν_{CN}^P, for the ν_{CN} band, whereas the circles are the "band center" (or average) frequencies, ν_{CN}^a, obtained by bisecting the band area. [Small yet significant differences between ν_{CN}^P and ν_{CN}^a occur because the SERS bands are slightly asymmetric, ν_{CN}^P shifting from the high- to the low-frequency side of the band center as the potential becomes more negative (Fig. 1).]

Inspection of Fig. 4 shows that the SERS and SNIFTIRS ν_{CN} values are mostly within ca. 5 cm^{-1} of each other throughout the potential range 500 to -500 mV. The small differences are indeed comparable to the uncertainties in evaluating ν_{CN}^P, especially for the infrared data. Admittedly, the high-frequency shoulder obtained on the SNIFTIRS spectra at more positive potentials at roughened gold (Fig. 3) is not seen in SERS (Fig. 1). A high-frequency shoulder is seen for the latter but only at more negative potentials (Fig. 1). This indicates that the distribution of adsorption sites sensed by SERS does differ in some respects from that observed using the infrared probe. The potential dependence of ν_{CN}^P at roughened gold is also significantly smaller for the SNIFTIRS than for the SERS data (Fig. 4). This apparent discrepancy is, however, probably due chiefly to the distortion of the negative SNIFTIRS ν_{CN} band (feature II) by its positive-going partner (feature I) since these two halves of the bipolar band overlap. Correction for this distortion will decrease ν_{CN}^P more at the negative potentails where features II and I are least resolved. Nevertheless, the potential dependence of ν_{CN} appears to be relatively small; after allowing for these corrections one finds for both SERS and SNIFTIRS $d\nu_{CN}^P/dE \sim 12$ cm^{-1} V^{-1} and for SERS $d\nu_{CN}^a/dE \sim 8$ cm^{-1} V^{-1}.

The values of $d\nu/dE$ are somewhat smaller than those found for
several other structurally related systems using surface infrared or
Raman measurements, such as NCS$^-$ at silver,[11] CN$^-$ at silver,[15] or CO at
Pt,[16] although similar to that obtained for CN$^-$ at Au using SERS,
15 cm^{-1} V^{-1}.[13] Some of the literature values may be influenced by
potential-dependent variations in adsorbate coverage or structure.
Given that an important component of these potential dependencies appears
to be from an electric field (Stark) effect,[17] the small $d\nu_{CN}/dE$ values for
NCS$^-$ at gold may reflect the separation of the C-N group from the surface such
that it experiences a smaller electrical field.

The large positive-going band at 2060 cm^{-1} (feature III) in the
SNIFTIRS spectra has also been seen under similar conditions using EMIRS,
and attributed chiefly to the presence of N-bound thiocyanate at negative
potentials which reorients to the S-bound form at more positive potentials.[4a,14]
While this interpretation is qualitatively consistent with the low-frequency
SERS data, as noted above there is an absence of SERS bands around 2060 cm^{-1}
even at potentials as negative as -1000 mV. An alternative explanation
is that feature III is associated chiefly with solution thiocyanate (for
which ν_{CN} = 2060 cm^{-1}) which is removed by adsorption as S-bound thiocyanate
as the potential is altered from -900 mV to markedly more positive values.
This would obviously account for the absence of the band in the SER spectra
at negative potentials. Such a band is expected in SNIFTIRS as well as
EMIRS since the potential modulation required to eliminate the effects of
baseline drift (*vide supra*) also gives the solution in the thin-layer cavity
insufficient time to equilibrate entirely with the surrounding reservior during
each potential excursion. Adsorption of thiocyanate at the more positive
potential should therefore be accompanied by a positive-going SNIFTIRS band,
reflecting the loss of solution thiocyanate within the thin-layer cavity.

Although·the positive band (feature III) is much more pronounced than the negative bands associated with S-bound thiocyanate (feature II, Figs. 2,3), this can be accounted for if the molar absorptivity of ν_{CN} for S-bound adsorbed thiocyanate, ε_{NCS-}, is appropriately smaller than for uncoordinated thiocyanate, ε_{NCS}, as well as for the N-bound form, ε_{SCN-}. At least for bulk-phase thiocyanate complexes, typically $\varepsilon_{NCS-} \sim 0.2\ \varepsilon_{NCS} \sim 0.1\ \varepsilon_{SCN-}$;[8,18] moreover, for $Au(SCN)_4^{-}$, $\varepsilon_{NCS-} \sim 0.1\ \varepsilon_{NCS}$.[18a] Therefore the S-bound adsorption of a given amount of free thiocyanate from the thin solution layer is anticipated to yield a substantially (ca. tenfold) larger positive band at 2060 cm^{-1} than the accompanying negative SNIFTIRS band, in correspondence with the experimental data. The low-frequency shoulder on feature III at around 2040-2050 cm^{-1}, seen most clearly with roughened gold (Fig. 3B,C) may well be due to reorientation of a small amount of N-bound thiocyanate present at -900 mV.

Admittedly, the assignment of the main feature III to loss of N-bound thiocyanate is in itself also in harmony with the data in Figs. 2 and 3. A

marked decrease in the intensity of feature III is, however, obtained when more dilute (0.1 m$\underline{M}$ NCS⁻) solutions are employed and the electrode is pushed against the optical window so to minimise the thin-layer volume adjacent to the surface. This is consistent with the assignment of feature III to solution thiocyanate, but not with the adsorbed N-bound thiocyanate since the latter should be unaffected by the quantity of thiocyanate available for adsorption upon stepping to more positive potentials.

Taken together, then, the SERS and SNIFTIRS data both indicate the presence of S-bound thiocyanate at potentials less negative than ca. -400 mV, whereas some evidence suggests that the N-bound orientation may form at far negative potentials. The strong preference of the gold surface for the former thiocyanate orientation is expected both from chemical bonding[19] and electrostatic arguments, the latter predicting S-bonding at positively charged surfaces since the sulfur atom carries most of the negative charge.[8] Given that the potential of zero charge (p.z.c.) of polycrystalline gold is around -50 mV vs. s.c.e. in the absence of specific adsorption[20] and that a thiocyanate monolayer should shift this at least ca. 500 mV more negative,[11] extensive N-binding is expected to be restricted only to very negative potentials. It is also possible that both N- and S-binding occurs at more negative potentials with the thiocyanate lying flat on the surface; this geometry can account for the lack of a 2060 cm⁻¹ peak in the SER spectra since such "bridging" thiocyanate usually yields a ν_{CN} band above 2100 cm⁻¹.[8]

Given the large (60-70 cm⁻¹) increase of ν_{CN} upon S-bound adsorption of thiocyanate, the close (within 5 cm⁻¹) agreement in the frequencies of the major species seen by the Raman and infrared probes, as well as the similarities of the latter at smooth and roughened electrodes, suggest

that the gold surface sites probed by SERS are chemically similar to the average or predominant sites that are presumably sensed by infrared spectroscopy. Close similarities have also been obtained between the SER and infrared spectra of cyanide on silver,[4a,21] although parallel data sets using the same conditions for both techniques were apparently not obtained.

It will clearly be necessary, however, to examine systematically a number of systems under identical conditions in this manner before any sweeping conclusions can be drawn. Nevertheless, for substrates where Raman as well as infrared techniques can be employed, the strengths and limitations of the two methods are such that we anticipate that they will supply valuable complementary information.
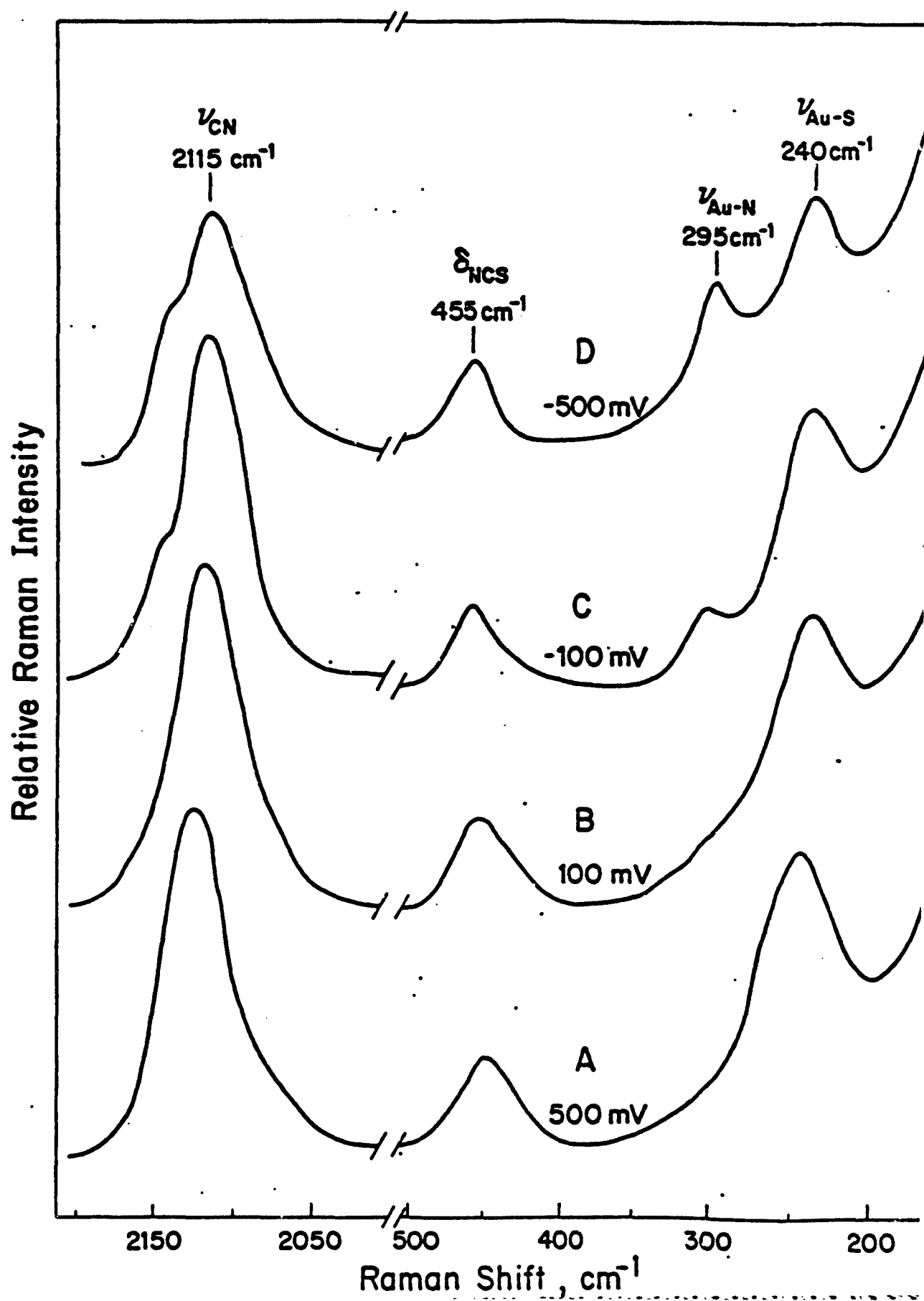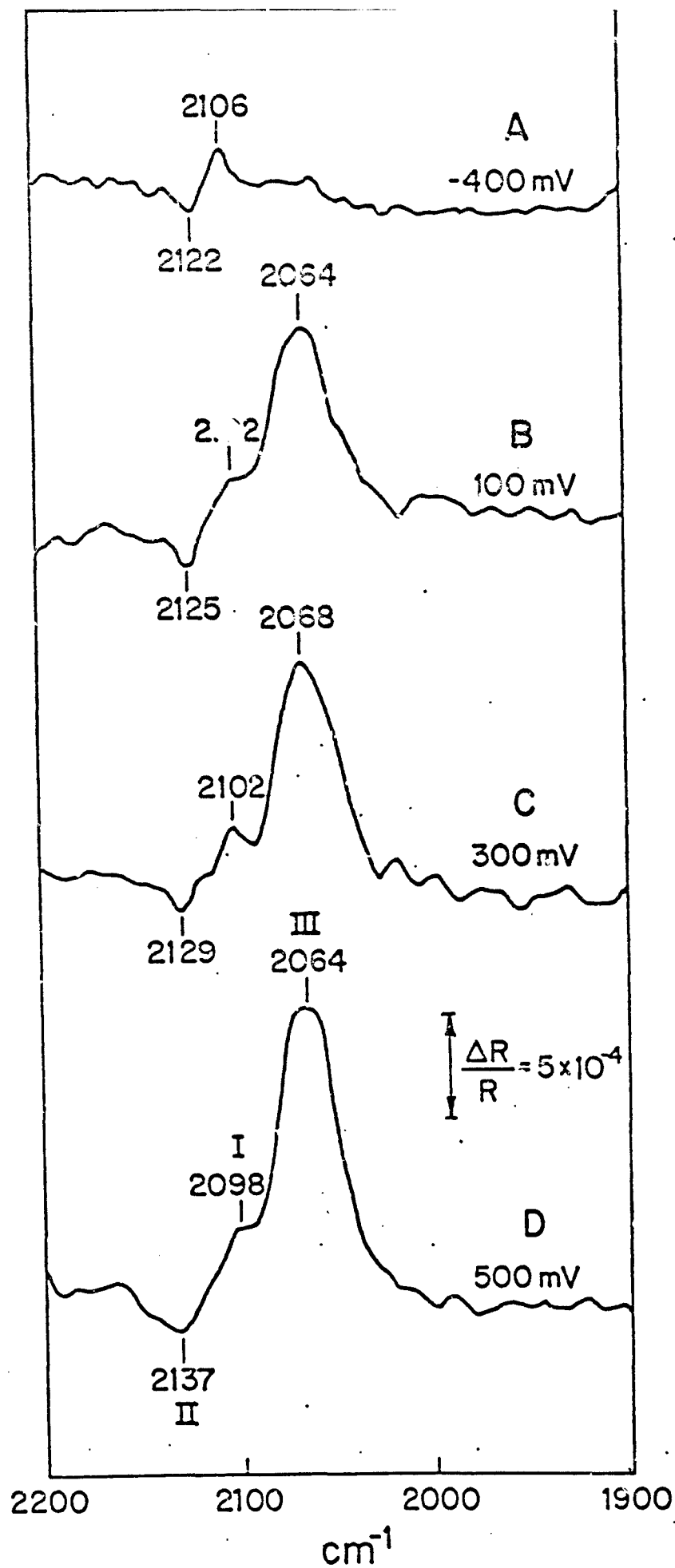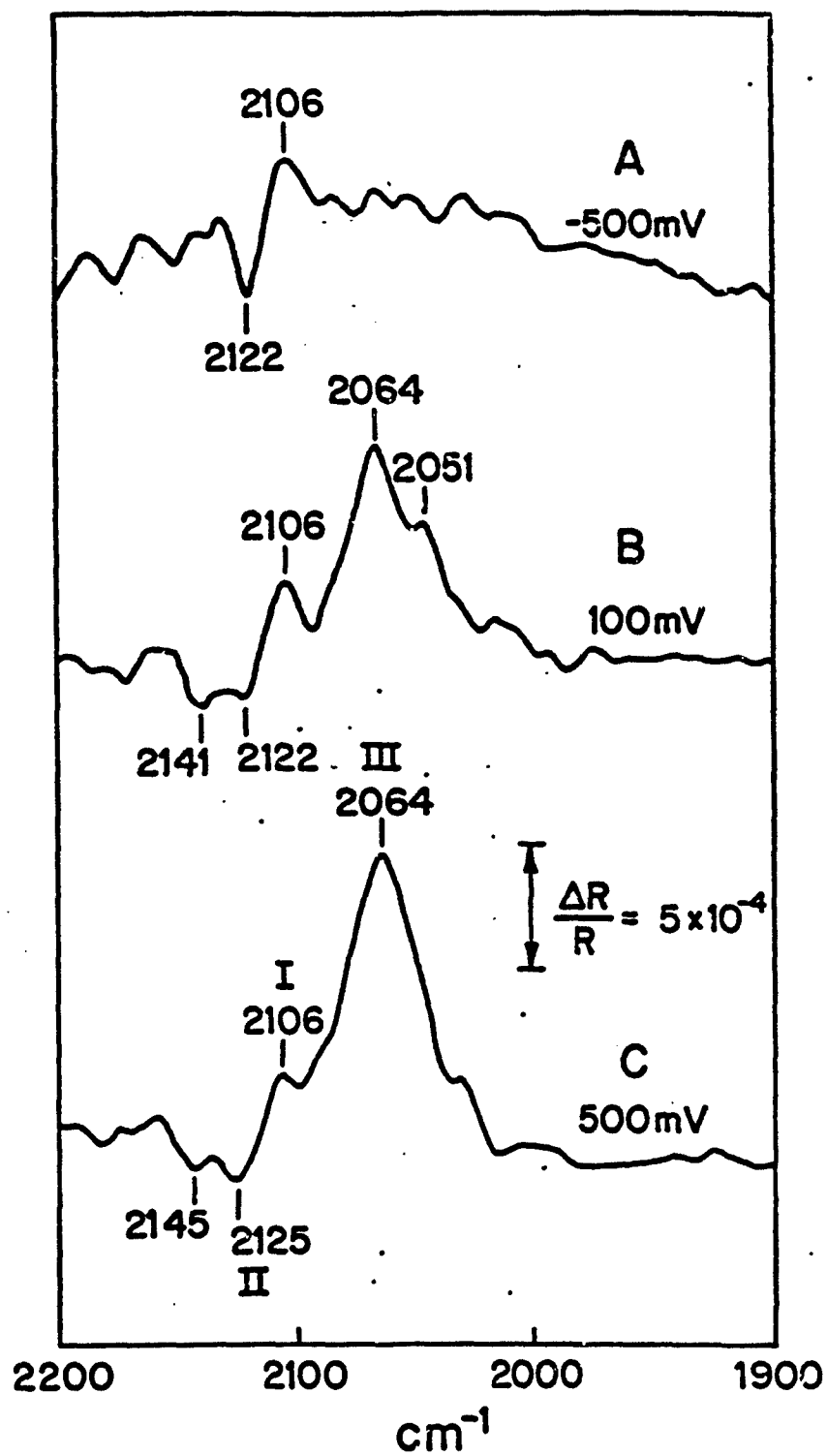
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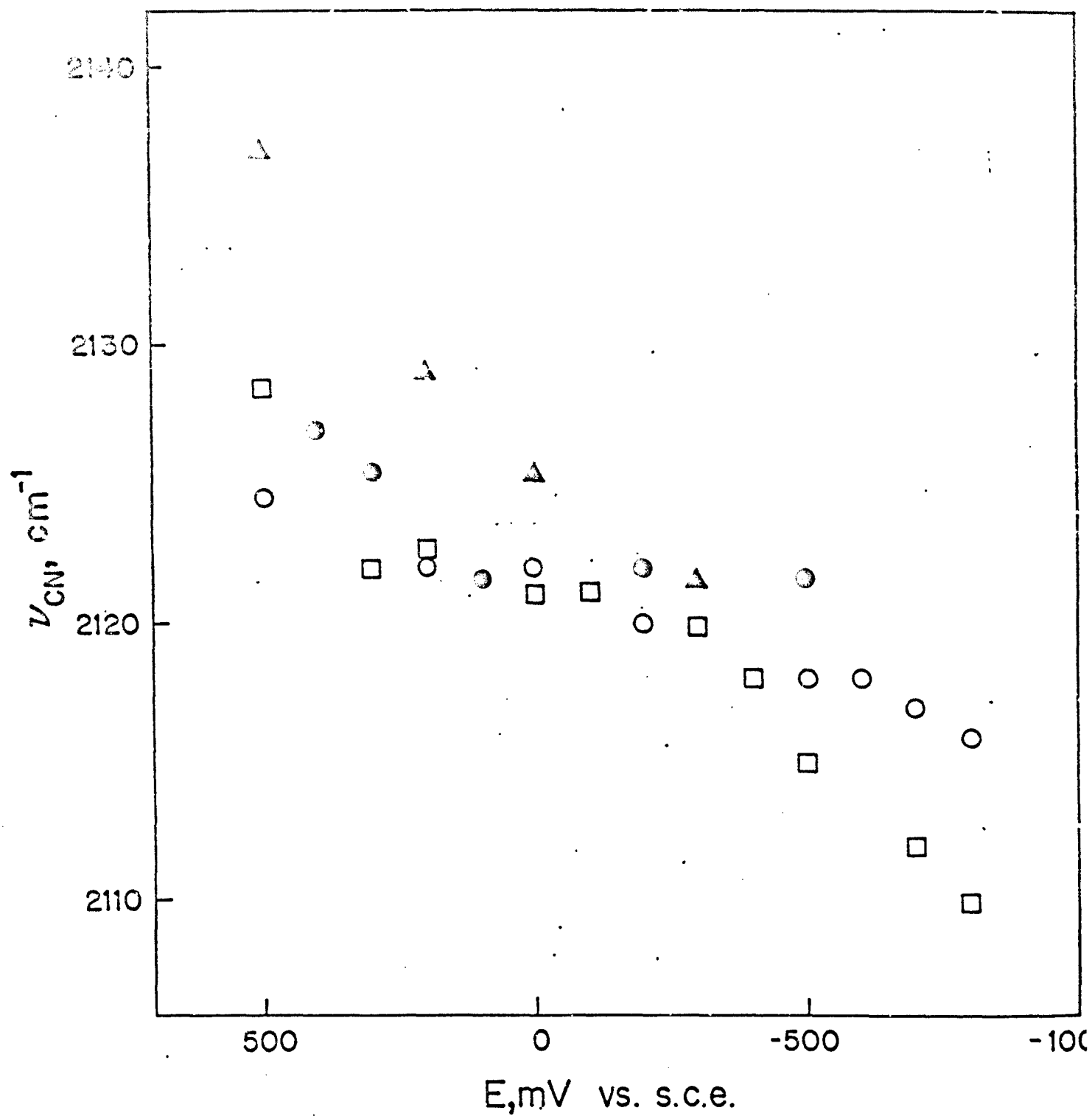
ν_{CN}
2115 cm⁻¹

δ_{NCS}
455 cm⁻¹

ν_{Au-N}
295 cm⁻¹

ν_{Au-S}
240 cm⁻¹

D
−500 mV

C
−100 mV

B
100 mV

A
500 mV

Relative Raman Intensity

2150   2050   500   400   300   200

Raman Shift , cm⁻¹

2106

2122

A

−400 mV

2064

2. 2

B

100 mV

2125

2068

2102

C

300 mV

2129

III

2064

$\dfrac{\Delta R}{R} = 5 \times 10^{-4}$

I

2098

D

500 mV

2137

II

2200   2100   2000   1900

cm⁻¹

Figure 1

SER spectra for adsorbed thiocyanate at gold-aqueous interface at four electrode potentials as indicated (vs. s.c.e.). Solution contained 1 mM NaNCS in 0.5 M Na$_2$SO$_4$. Raman excitation was 50 mW spot focussed (ca. 2 mm diameter) on gold surface; spectral band-pass was 5 cm^{-1}. Typical peak intensity of ν_{CN} band was 3 x 10^3 counts sec^{-1} versus background.

Figure 2

SNIFTIR spectra for thiocyanate at an electropolished gold-aqueous interface, using -900 mV vs s.c.e. as the reference potential, to four more positive potentials as indicated. Solution contained 1 mM NaNCS in 0.5 M Na$_2$SO$_4$. Spectra are an average of 1024 normalized scans at each potential.

Figure 3

SNIFTIR spectra for thiocyanate as in Figure 2, but using roughened gold under conditions used to generate the corresponding SER spectra in Figure 1.

Figure 4

The frequency of the C-N stretching mode for adsorbed thiocyanate at gold, ν_{CN}, obtained from SERS (open symbols) and SNIFTIRS (closed symbols) plotted against electrode potential, E. Circles are peak values of ν_{CN} obtained from SERS or SNIFTIRS data at roughened gold; closed triangles are corresponding SNIFTIRS data at smooth gold. Open squares are average values of ν_{CN} obtained from SERS (see text).