

SERS INVESTIGATION OF DISSOLUTION OF GOLD IN CYANIDE

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Keywords: *SERS, gold, cyanide*

Abstract: SERS provides an excellent in-situ method of observing in real-time the vibrational characteristics of surface species during electrochemically controlled gold dissolution in cyanide solution.

The SERS technique allows rapid acquisition of spectra during voltammetric scans, allowing vibrational characteristics of surface and solution species to be observed in real-time during electrochemical events.

Potential dependent SERS scans show a variation of vibrational frequency with potential, known as Stark-tuning. This phenomenon provides qualitative information regarding the nature of the chemical bonding and orientation of the surface species. A significant variation of Raman background intensity is also seen during the acquisition of potentiodynamic SERS spectra. Elucidation of relationships between the Raman background and optical properties of the adsorbate-modified gold surface may facilitate the development of a novel surface-sensitive technique.

Cyclic voltammetry in pH 11 buffered 0.01 mol dm⁻³ NaCN solutions show a solution cyanide species Stark-tuning linearly at 55 cm⁻¹V⁻¹ with ν_{CN} ranging from 2075 cm⁻¹ at -1.4 V, to 2105 cm⁻¹. Adsorption is evidenced at the onset of cyanidation, -0.8 V, by the appearance of low frequency modes ν_{AuC} , 350 cm⁻¹ and δ_{AuCN} , 290 cm⁻¹. Passivation of the oxidation is seen at -0.2 V, with a decrease in Stark-tuning of ν_{CN} . At +0.7 V ν_{CN} reaches a limiting value of 2130 cm⁻¹, attributable to a surface adsorbed cyanoaurous species.[1] With increased potential, the band was seen to disappear concurrently with the low frequency modes. A new band was seen to emerge at 2165 cm⁻¹ attributable to cyanate species, followed by surface cyanide bands at 2110 cm⁻¹ and the appearance of low frequency bands at 580 cm⁻¹ attributable to ν_{AuO} .

In the reverse (negative going) direction, electrochemical evidence of an oxide layer remained until a reduction potential of +0.2 V was reached. Below this potential a rapid oxidation was observed, with the return of both the solution species and adsorbed dicyanoaurate. An increase in SERS intensity was observed during the reverse scan. Three linear Stark-tuning ν_{CN} curves were seen during the ramp. These may be tentatively assigned to the adsorbed cyanate, adsorbed cyanide and a cyanide complex.

Observed electrochemical behavior of the dissolution process in the presence of impurities agreed with the results of Jeffrey and Ritchie in their system purity studies, with respect to peak positions for Ag & Pb impurities in the cyanide system.[2,3] However, no spectroscopic evidence was found for the existence of a passivating AuCN surface polymer as suggested by these authors.[4] This may be attributed to the use of AR grade reagents during this work, rather than the high purity reagents employed by Jeffrey & Ritchie.

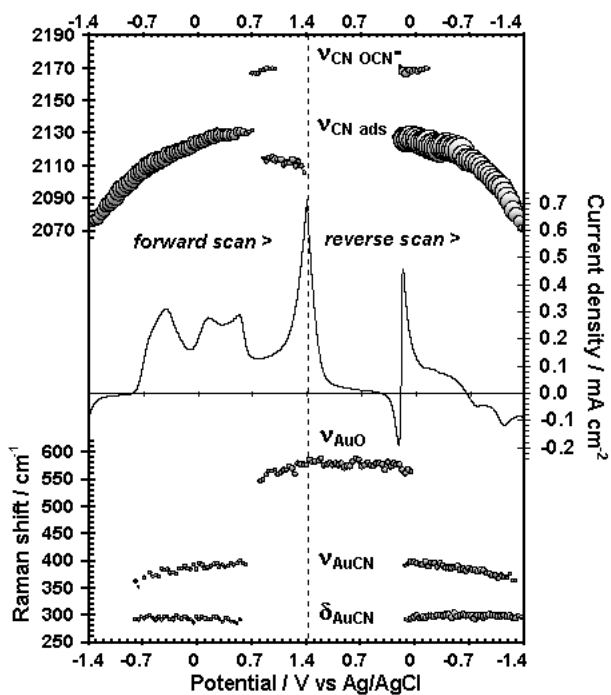


Figure 1 CV SERS for gold in cyanide

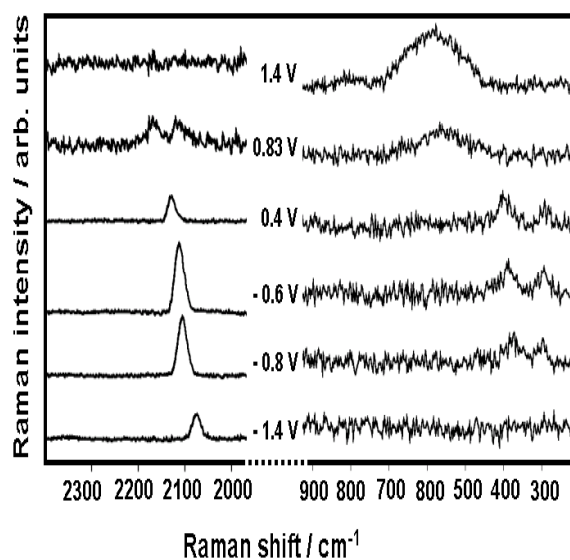


Figure 2 Raman spectra acquired at various potentials during the cyclic voltammogram.

References

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