

**SURFACE ENHANCED RAMAN AND RESONANCE RAMAN SPECTROSCOPY  
IN A NON-AQUEOUS ELECTROCHEMICAL ENVIRONMENT:  
TRIS(2,2'-BIPYRIDINE)RUTHENIUM(II) ADSORBED ON SILVER FROM ACETONITRILE**

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This letter reports the first observation of both surface enhanced Raman scattering (SERS) and surface enhanced resonance Raman scattering (SERRS) from the transition metal complex tris(2,2'-bipyridine)ruthenium(II),  $\text{Ru}(\text{bpy})_3^{2+}$ , adsorbed on a silver electrode from acetonitrile (ACN). The assignment of these spectra as valid examples of SERS and SERRS in a non-aqueous environment is based on the following criteria: (1) in situ demonstration of monolayer surface coverage of  $\text{Ru}(\text{bpy})_3^{2+}$  using double potential step chronocoulometry (DPSCC); (2) the Raman signals are most intense after surface roughening by anodization; (3) the Raman spectra are potential dependent in the non-faradaic potential region; (4) the measured enhancement factors are greater than  $10^6$ ; (5) the surface spectra are frequency shifted relative to their bulk counterparts; and (6) several other molecules also exhibit non-aqueous SERS and SERRS behavior. These results are highly significant in that the generality of surface enhanced Raman spectroscopy has been extended into the rich domain of non-aqueous electrochemistry.

## 1. Introduction

Surface enhanced Raman scattering (SERS) has been observed for a wide variety of molecules adsorbed on silver, copper, and gold electrodes in aqueous electrochemical environments [1,2]. In contrast, only one very recent example of SERS in a non-aqueous electrochemical environment has been reported [3]. In this work, the most frequently studied SERS adsorbate, pyridine, was found to give intense Raman spectra when adsorbed on anodized (i.e. electrochemically roughened) silver from *N,N'*-dimethylformamide containing tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. Since this observation is without precedent, it is important to confirm this result as a valid example of surface Raman scattering.

In order to demonstrate that a Raman signal detected at the surface of an electrode is a valid example

of SERS, an experimentalist should provide evidence of the following criteria:

(1) The surface coverage of the adsorbate is one monolayer or less. This criterion is particularly important since, of the numerous reports of SERS, only a few have demonstrated that the observed Raman scattering is due to a monolayer or less of the adsorbate. Consequently, there are reports in the literature where normal Raman scattering from a multilayer film have been assigned improperly as SERS.

(2) The intensity of the Raman signal is a function of surface roughness (viz., charge passed during the anodization pretreatment process).

(3) The intensity of the Raman signals are potential dependent even though no faradaic electrochemistry takes place.

(4) The enhancement factor is in the  $10^6$  range for an optimally roughened surface.

(5) The surface Raman spectrum is frequency shifted by  $\approx 1-25 \text{ cm}^{-1}$  relative to the corresponding bulk Raman spectrum.

(6) Chemically dissimilar adsorbates show similar enhancement characteristics.

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The authors of ref. [3] assigned their spectra as valid examples of SERS primarily on the basis of criteria (2), (3), and (5) as well as observation of time dependent changes in the overall signal intensity. While these results are certainly consistent with SERS behavior, they are not complete since criteria (1), (4), and (6) were not demonstrated.

In this letter, we present a more complete data set for the system tris(2,2'-bipyridine)ruthenium(II),  $\text{Ru}(\text{bpy})_3^{2+}$ , adsorbed on a silver electrode from a 0.1 M TBAP/acetonitrile solution. This study, conducted entirely independent of the work in ref. [3], confirms the existence of SERS in a non-aqueous electrochemical environment, as reported in ref. [3]. In addition, we report the first observation of SERS and surface enhanced resonance Raman scattering (SERRS): (1) from the same adsorbate/electrode/electrolyte system and (2) from an electroactive transition-metal complex that exhibits reversible one-electron transfer reactions.

## 2. Experimental

$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  was obtained from G.F. Smith Chemical Company.  $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$  was prepared from the chloride by metathesis with excess  $\text{NaClO}_4$  in a water-ethanol 1:1 mixture and recrystallized twice from this solvent. Polarographic grade tetra-*n*-butylammonium perchlorate (TBAP), the supporting electrolyte, was obtained from Southwestern Analytical Chemicals, Inc. and purified by a double recrystallization from ethyl acetate. The spectroquality acetonitrile from Burdick and Jackson Laboratories, Inc. used was not dried or purified for these initial experiments. All solutions were deaerated by bubbling with prepurified  $\text{N}_2$ .

The Raman spectroelectrochemical cell and the cell used for DPSCC have been described in detail elsewhere [4]. A  $\text{Ag}/\text{Ag}^+$  reference electrode was employed. All reported potentials are expressed as volts versus the standard calomel electrode (SCE) for convenient comparisons to SERS in aqueous solutions.

The silver electrodes were masked with Torr-Seal from Varian Associates to expose an area of  $\approx 0.10 \text{ cm}^2$  for the Raman experiments and  $\approx 0.02 \text{ cm}^2$  for the chronocoulometry measurements. The electrodes were mechanically polished with 0.05 micron alumina from Buehler LTD. To roughen the electrodes for the

SERS experiments, a double potential step waveform from the initial potential  $E_1 = -0.30 \text{ V}$  to  $E_2 = -0.33 \text{ V}$  was applied to the silver electrode in an acetonitrile solution of  $5 \times 10^{-5} \text{ M Ru}(\text{bpy})_3(\text{ClO}_4)_2$  and 0.1 M TBAP. The current passed in the forward step was integrated and the potential returned to  $E_1$  after 25  $\text{mC}/\text{cm}^2$  of charge were passed. The laser was not illuminating the electrode during the application of the double potential step waveform.

Double potential step chronocoulometry measurements [5] (DPSCC) of the surface coverage of  $\text{Ru}(\text{bpy})_3^{2+}$  were made for solutions of  $10^{-3}$  to  $10^{-5} \text{ M Ru}(\text{bpy})_3(\text{ClO}_4)_2$  and 0.1 M TBAP in acetonitrile on both polished electrodes and electrodes roughened by the application of a potential step waveform as described above. The starting potential for the chronocoulometry measurement was varied between  $-0.3$  and  $-0.8 \text{ V}$ . A potential step to a potential 140 mV past the  $1e^-$  or  $2e^-$  reduction of  $\text{Ru}(\text{bpy})_3^{2+}$  of 100 ms duration was applied and 60 points per 1 ms interval were collected. The data were analyzed using Anson plots of the charge  $Q_f$  versus  $t^{1/2}$  for the forward step and of the charge  $Q_r$  versus  $\theta$  for the reverse step [5]. Although it was difficult to achieve diffusion control for the  $1e^-$  reduction without stepping into the  $2e^-$  reduction wave, the measured charge for the  $2e^-$  step was approximately twice that of the  $1e^-$  step.

SER spectra were obtained using a Spex model 1400-II double monochromator with a Coherent Radiation model CR-500K cw krypton ion laser and a HG-2 Jobin-Yvon double monochromator with a Coherent Radiation model CR-3 cw argon ion laser as described elsewhere [1,6]. Data acquisition on the Spex system was by a Ratheon Data Systems model 500 computer and on the Jobin-Yvon system by a Data General Corp. Nova 2. All spectra were obtained with a  $3 \text{ cm}^{-1}$  band pass and calibrated with a neon lamp. Electrochemical instrumentation for cyclic voltammetry and DPSCC, including the potentiostat, integrator, and data acquisition are described elsewhere [7].

## 3. Results

Cyclic voltammograms of  $10^{-3} \text{ M Ru}(\text{bpy})_3^{2+}$  solutions in water and acetonitrile are compared in fig. 1. The three reduction peaks in acetonitrile occur at

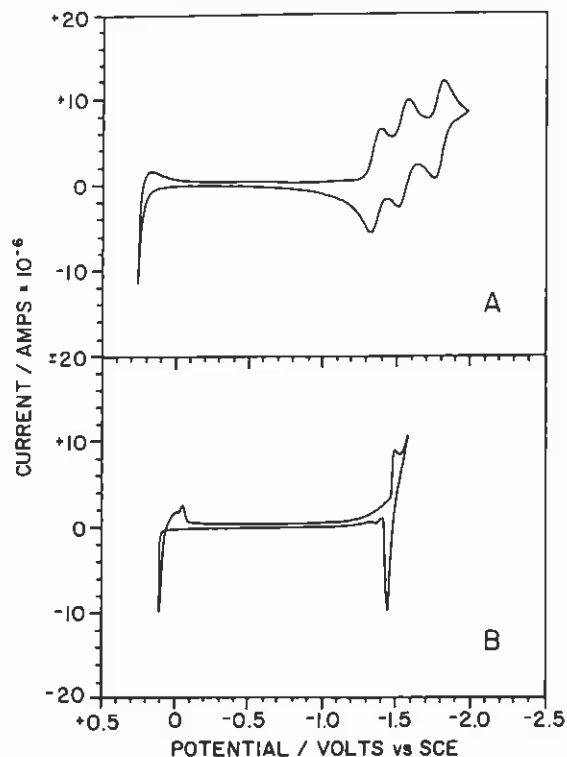


Fig. 1. Cyclic voltammograms. (A) Cyclic voltammogram of  $10^{-3}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  in acetonitrile at a silver electrode with 0.1 M TBAP as the supporting electrolyte. The scan begins at  $-0.6$  V and first moves in the negative direction at  $100$  mV/s. The wave at  $+0.23$  V is the oxidation of the Ag and the three one-electron reductions of  $\text{Ru}(\text{bpy})_3^{2+}$  occur at  $-1.36$ ,  $-1.55$ , and  $-1.79$  V. (B) Cyclic voltammogram of  $10^{-3}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  in water at a silver electrode with 0.1 M NaCl as the supporting electrolyte. The scan begins at  $-0.6$  V and first moves in the negative direction at  $100$  mV/s. The wave at  $+0.05$  V is the oxidation of Ag to AgCl. The wave near  $-1.36$  V is the one-electron reduction of  $\text{Ru}(\text{bpy})_3^{2+}$ , just cathodic of hydrogen evolution.

$-1.36$ ,  $-1.55$  and  $-1.79$  V versus SCE and are associated with the production of  $\text{Ru}(\text{bpy})_3^{1+}$ ,  $\text{Ru}(\text{bpy})_3^0$ , and  $\text{Ru}(\text{bpy})_3^{1-}$ , respectively. Good reversible behavior was observed for all three reductions. Although the deposition of a gold-colored film, attributed to  $\text{Ru}(\text{bpy})_3^0$ , has been reported for platinum electrodes [8], we found no evidence of a similar deposition on silver. In water, only the first reduction of  $\text{Ru}(\text{bpy})_3^{2+}$  occurs cathodic of hydrogen evolution.

The concentration of an electroactive species adsorbed on an electrode surface can be determined pre-

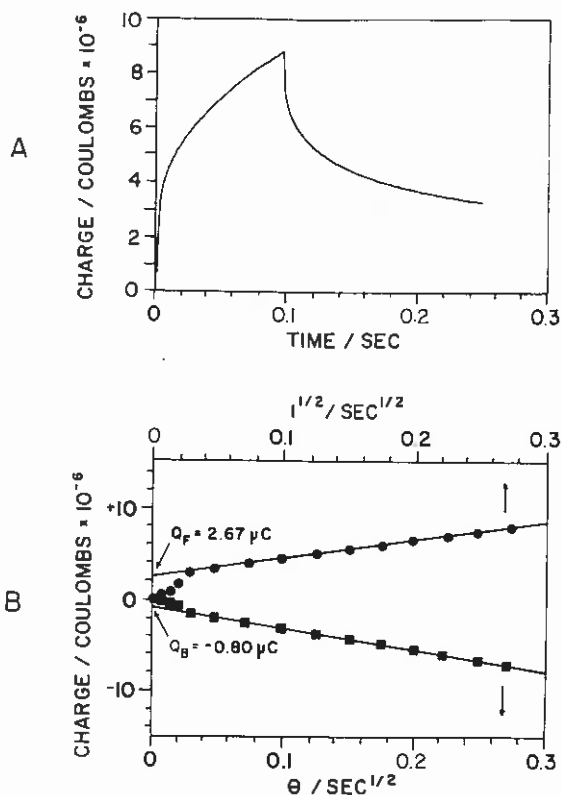


Fig. 2. Double potential step chronocoulometry data. (A) Chronocoulogram for  $10^{-3}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  in acetonitrile at a silver electrode with 0.1 M TBAP as the supporting electrolyte. Starting potential:  $-0.7$  V. Forward step:  $140$  mV past the  $2e^-$  reduction peak potential. Step width:  $100$  ms with  $60$  points at  $1$  ms intervals. (B) Anson plots of  $Q_f$  versus  $t^{1/2}$  (forward) and  $Q_r$  versus  $t$  (reverse) for the data. Only a few of the actual data points are shown.

cisely by DPSCC [5]. An example of the DPSCC data for the adsorption of  $\text{Ru}(\text{bpy})_3^{2+}$  on silver from a  $10^{-3}$  M solution in acetonitrile and the data analysis using Anson plots are shown in fig. 2. The results indicate that  $0.96 \times 10^{14}$  molecules/cm<sup>2</sup> are adsorbed on the electrode. The coverage is constant for potentials between  $-0.3$  and  $-0.8$  V. If the size of the molecule is estimated from the crystal structure of  $\text{trans}[\text{Ru}(\text{bpy})_2(\text{OH}_2)(\text{OH})](\text{ClO}_4)_2$  [9] the measured surface concentration translates to approximately one monolayer of adsorbed  $\text{Ru}(\text{bpy})_3^{2+}$ . As the adsorbate concentration is decreased from  $10^{-3}$  to  $10^{-5}$  M, the surface concentration decreases from  $0.96 \times 10^{14}$  to  $0.75 \times 10^{14}$  molecules/cm<sup>2</sup>.

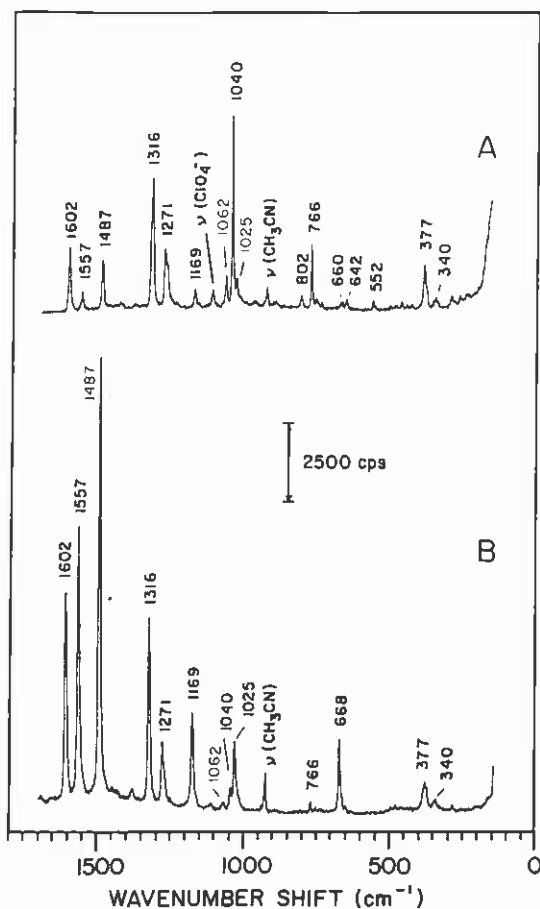


Fig. 3. SER spectra. (A) SER spectrum for  $\text{Ru}(\text{bpy})_3^{2+}$  adsorbed on silver at  $-0.5$  V (SCE). Solution:  $10^{-5}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  and  $0.1$  M TBAP in acetonitrile. Excitation:  $30$  mW  $647.1$  nm. Bandpass:  $3$   $\text{cm}^{-1}$ . Anodization:  $25$   $\text{mC}/\text{cm}^2$  at  $+0.33$  V. (B) Same as (A) except the laser excitation is  $30$  mW  $457.9$  nm.

SER spectra for  $5 \times 10^{-5}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  in acetonitrile for both  $647.1$  and  $457.9$  nm laser excitations are shown in fig. 3. No Raman scattering is observed before the polished electrode is roughened by the anodization procedure described above. The SERS intensities do not decay with time over a period of at least  $6$  h and are weakly potential dependent between  $-0.3$  and  $-0.9$  V. Preliminary attempts to measure the enhancement factor for  $\text{Ru}(\text{bpy})_3^{2+}$  at  $647.1$  nm gave values of greater than  $10^6$  enhancement.

The relative intensities of the SERS at  $647.1$  nm excitation differ significantly from those at  $457.9$  nm. Since the latter wavelength coincides with the energy

of the first electronic transition of the molecule [10], a more accurate description of the scattering observed at  $457.9$  nm is surface enhanced resonance Raman scattering (SERRS). The most intense modes under resonance conditions are the totally symmetric bipyridine vibrations [11], including the C=C and C=N stretches at  $1602$  and  $1557$   $\text{cm}^{-1}$  [12]. At  $647.1$  nm excitation the molecule is in its ground state and the non-totally symmetric modes, including the out-of-plane hydrogen bending vibrations of  $1040$  and  $766$   $\text{cm}^{-1}$  [12], gain intensity with respect to the symmetric vibrations.

The surface Raman scattering can be compared to bulk Raman scattering from a solution of  $10^{-3}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  in acetonitrile. The frequency shifts and the relative intensities of the SERRS at  $457.9$  nm are identical, within the accuracy of the experiment, to bulk resonance Raman scattering (RRS). At  $647.1$  nm, a similar comparison is difficult to make since even a saturated  $\text{Ru}(\text{bpy})_3^{2+}$  solution gives very weak normal Raman scattering (NRS). The most intense peak detected in the NR spectrum was at  $1040$   $\text{cm}^{-1}$ , as it is in the SER spectrum at  $647.1$  nm. An interesting result is that although bulk RRS is a few orders of magnitude more intense than bulk NRS, the intensity of the  $1487$   $\text{cm}^{-1}$  band in the SERR spectrum at  $457.9$  nm is only about twice the intensity of the  $1040$   $\text{cm}^{-1}$  band in the SER spectrum at  $647.1$  nm.

Concerning the generality of SERS in acetonitrile, we have found that molecules similar to  $\text{Ru}(\text{bpy})_3^{2+}$  also give intense SERS, in particular  $\text{Fe}(\text{bpy})_3^{2+}$ ,  $\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})^{2+}$ , and  $\text{Fe}(9,10\text{-phenanthroline})_3^{2+}$ . An unrelated molecule,  $(\text{C}_6\text{H}_5)_3\text{SnCl}$ , dissolves in acetonitrile and the  $(\text{C}_6\text{H}_5)_3\text{Sn}(\text{CH}_3\text{CN})^{1+}$  cation formed also adsorbs on silver to give intense SERS. While the SERS of these cations is detected easily, we have had little success with neutral molecules and few anions that are good Raman scatterers can be dissolved in acetonitrile.

#### 4. Discussion

The  $\text{Ru}(\text{bpy})_3^{2+}/\text{CH}_3\text{CN}/\text{Ag}$  system has the following experimental characteristics:

- (1) DPSCC measurements indicate a surface coverage near one monolayer.
- (2) SERS intensities scale with surface roughness.

(3) The surface Raman spectra are weakly potential dependent.

(4) The enhancement factor is greater than  $10^6$ .

(5) Frequency shifts in the SERS relative to bulk scattering are not observed with the  $3\text{ cm}^{-1}$  resolution of our experiment. A careful study for frequency shifts of less than  $3\text{ cm}^{-1}$  is necessary. However, since  $\text{Ru}(\text{bpy})_3^{2+}$  is a large molecule, it is possible that perturbations on the molecule due to its interaction with the surface produce only very small changes in the frequencies of the various vibrations.

(6) Similar enhancement characteristics are observed for other cations.

The surface coverage of  $\text{Ru}(\text{bpy})_3^{2+}$  is near one monolayer, even in a  $10^{-5}\text{ M}$  solution. This suggests a strong interaction with the surface. It is likely that electrostatic and covalent bonding are both important. Since spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  can be obtained even after the electrode has been thoroughly rinsed, we suggest that  $\text{Ru}(\text{bpy})_3^{2+}$  is bound irreversibly to silver. Chambers and Buck [13] made a similar observation in their report of SERS of ruthenium complexes adsorbed on silver electrodes from aqueous solutions. We speculate that the molecule is oriented with a three-fold axis perpendicular to the surface. This allows three C=C moieties from three different pyridine rings (two bipyridine ligands) to interact with the silver surface.

If  $\text{Ru}(\text{bpy})_3^{2+}$  is adsorbed irreversibly, we expect some of the SERS characteristics to be different from systems with reversible adsorption. For example, the weak potential dependence of the SERS of  $\text{Ru}(\text{bpy})_3^{2+}$  can be attributed to the fact that the coverage in the potential region scanned is nearly constant. In contrast, DPSCC measurements of the coverage of acetylpyridine reversible adsorbed on silver from water show large changes of coverage with potential [4]. Correspondingly, the SER spectra of acetylpyridine are very sensitive to potential.

The observation of SERS from  $\text{Ru}(\text{bpy})_3^{2+}$  provides an important opportunity to study the contribution of resonance enhancement to SERS. The results presented suggest that the surface enhancement of NRS is a few orders of magnitude larger than the surface enhancement of RRS. Quantitative measurements of the relative surface enhancements of NRS and RRS will be important, especially in testing the predictions of various theories [14].

The extension of SERS to non-aqueous electro-

chemical systems leads to some exciting new avenues for SERS research. SERS intensities can be correlated with the dielectric properties of the solvent and various theories tested against the results [14–16]. Many non-aqueous solvents have electrochemical windows that are larger than that of water and therefore the potential dependence of a particular adsorbate may be studied over a greater range without solvent reduction. The larger potential window also increases the variety of electrochemical reactions that are possible. A thorough study of  $\text{Ru}(\text{bpy})_3^{2+}$  and the three one-electron reduction products is in progress, as well as a systematic investigation as to the generality of SERS in non-aqueous electrochemical environments.

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