SURFACE ENHANCED RAMAN SPECTROSCOPY: A RE-EXAMINATION OF THE ROLE OF SURFACE ROUGHNESS AND ELECTROCHEMICAL ANODIZATION

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To date all surface enhanced Raman spectroscopy (SERS) studies have been carried out on rough metal surfaces. This has resulted in the general impression that surface roughness is an absolute prerequisite for the observation of SERS. In this paper we demonstrate, at least for the case of SERS at the solid–liquid interface (i.e., an electrochemical cell) that neither surface roughness (viz., quasi-spherical particles >250 Å in diameter) or electrochemical anodization are prerequisites to SERS observation. For the model system, Ag/0.05 M pyridine/0.1 M KCl/H₂O, an enhancement factor of ca. 10⁴ is observed on “smooth”, unanodized surfaces implying a maximum roughness contribution to the overall enhancement of only about ca. 10². The observation of SERS on “smooth” surfaces is not restricted to pyridine since it can also be observed in the system Ag/0.005 M Pt(CN)₃⁻/0.1 M SO₄²⁻/H₂O. These results strongly support the hypothesis that the overall SERS enhancement of 10⁶ is the product of 10⁴ enhancement from a roughness independent mechanism (e.g., image-dipole mechanism) and a 10² enhancement from a roughness dependent mechanism (e.g., the development of geometrically defined electromagnetic resonances near rough solid surfaces – “lightning rod mechanism”).

1. Introduction

Surface roughness has played a major role in the experimental and conceptual development of the surface sensitive, inelastic light scattering technique now known as surface enhanced Raman spectroscopy (SERS) [1]. For example, in the first successful applications of normal Raman spectroscopy (NRS) to the study of adsorbates on metal surfaces, Fleischmann and coworkers [2–7] prepared high surface area silver substrates by repetitive anodization or oxidation–reduction cycles (ORC) using silver working electrodes in an electrochemical cell containing aqueous Cl⁻ supporting electrolyte. The anodization process involves an oxidation half-cycle in which Ag is dissolved to form AgCl multilayers on the electrode surface. On the reduction half-cycle, AgCl is reversibly reconverted to Ag metal. The ORC

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results in substantial surface roughening due to the spatially non-uniform nature of
the nucleation and growth phenomena associated with metal deposition on
electrodes [8]. The successful observation of NR spectra from pyridine on Ag was
attributed to the increased surface number density of Raman scatterers in the focal
spot of the exciting laser beam resulting from the microscopic area increase on
these roughened electrode surfaces.

Jeanmaire and Van Duyne [9,10] repeated the Ag/pyridine Raman scattering
experiment as a function of the charge passed (viz., charge is proportional to the
number of monolayers of silver dissolved) in the oxidation half-cycle of the ORC
roughening process. It was found that the intensity of the pyridine surface Raman
signals increased as less and less roughening was carried out over the range of
1000 millicoulombs (mC) per cm² of geometric surface area (this was comparable
to the extent of surface roughening used in ref. [3]) to 50 mC cm⁻². In the range of
50–25 mC cm⁻², which corresponds to ca. 200–100 monolayers of Ag dissolved,
the Raman intensity peaked and then decreased over the range 25–1 mC cm⁻². On
the basis of these data it was concluded that surface area changes alone could not
account either for the magnitude of the extraordinarily large Raman intensities ob-
erved or their dependence on anodization. In addition it was demonstrated quan-
titatively that under optimized experimental conditions (viz., electrode potential =
−0.6 V versus SCE, bulk pyridine concentration = 0.05 M or greater, bulk chloride
ion concentration = 0.10 M, and ionization charge = 25 mC cm⁻²), the surface
Raman intensities were enhanced by a factor of 10⁶ compared to the bulk signals.
Albrecht and Creighton [11] independently reported intensity enhancements on
the order of 10⁵ for the Ag/pyridine system. Subsequently, several other groups of
investigators reported similar results and extended the range of SERS observations
to include silver single crystal electrodes, silver thin film electrodes, and the first
observations of a diatomic, inorganic anion adsorbed on silver [12–21]. An exten-
sive review of the early experimental development of SERS, including these results
has been presented [1].

SERS is now rapidly becoming established as a promising new tool for the
detailed characterization of a wide variety of interfacial systems including the
solid–liquid (electrolyte) interface (viz., electrochemical cells [22–49]); the solid–ultrahigh vacuum (UHV) interface [50–60]; the solid–solid (tunnel junction) inter-
face [61–63]; and the solid (island film)–condensed phase interface [68–70].
This broad collection of studies carried out over the last two years clearly indicates
that SERS is a very general technique for the study of molecular structure and, to
some extent, the dynamics of molecules adsorbed on metal surfaces.

These investigations have stimulated a great deal of controversy over the origin
of the repeatedly demonstrated 10⁵–10⁶ fold enhancement of the Raman scat-
tering intensities for adsorbed molecules. Although there is no broad consensus yet
as to the origin of SERS, the careful re-examination of the optics of surfaces
spawned by the unexpected discovery of SERS has produced a wide spectrum of
tentative or postulated explanations [71–99] as well as a group of experimental ob-
servations that, in many cases, have been widely reproduced and can therefore constitute a yardstick by which theory can be tested. The set of experiments that presently defines the SERS phenomenon are (from this author's perspective):

(1) SERS exists. It is not a phantom phenomenon.

(2) SERS has been observed for more than 50 different molecules and ions both organic and inorganic) adsorbed on Ag. Adsorbed water has now been observed [49].

(3) SERS has been observed for several different molecules and ions on Cu [32,47], Au [32] and possibly liquid Hg [67].

(4) The metal substrates may be polycrystalline bulk metal, single crystal bulk metal, vapor deposited thin films, etc. [1].

(5) The magnitude and laser excitation wavelength, $\omega_L$, dependence of the SERS enhancement factor, $\epsilon(\hbar \omega_L)$, is critically dependent on the optical properties of the substrate metal and, to a first approximation, independent of the properties of the adsorbate molecule [47]. The last part of this statement applies only to cases where the laser excitation wavelength is far removed from direct electronic resonance with an electronic transition localized on the adsorbate (i.e., conventional resonance Raman spectroscopy (RRS)).

(6) The values of $\epsilon(\omega_L)$ scale in the order Ag (ca. $10^6$) > Cu (ca. $(1-5) \times 10^5$) > Au (ca. $10^5$) at the value of $\omega_L$ that maximizes the enhancement. The numbers quoted are for anodized, polycrystalline or thin film electrodes [32,47].

(7) The magnitude of $\epsilon(\omega_L)$ can definitely be modulated by the surface topological properties (i.e., surface roughness or morphology) of the substrate. The scale of the surface roughness is extremely important in determining the overall nature of the SERS observables [81].

(8) The enhanced Raman lines are accompanied by a broad background continuum [71,81].

(9) Total SERS enhancements approaching $10^{10}$ can be observed by superimposing the enhancement due to conventional RRS on the SERS enhancement [1,9].

(10) The total SERS enhancement can be increased by the deliberate excitation of plasmon surface polariton (PSP) resonances for molecules adsorbed on metal diffraction gratings [57,62,65,66].

Although much progress toward a more complete understanding of SERS has been made recently, there are still a number of nagging and persistent questions that must be resolved. One of the most difficult has been the role of surface roughness, the scale of surface roughness most relevant to SERS, and, for experiments carried out in electrochemical cells, the role of the ORC that produces the roughness. Many SERS researchers have now concluded that roughness on the scale of ca. 250 Å to ca. 5000 Å (i.e., the order to the wavelength of the exciting radiation), is required to observe SERS [31,38,52,53, 62,72,84,93,95,98,99]. Others conclude that the required scale of roughness is in the "submicroscopic" range of ca. 25 to 250 Å [22,81], while still others feel that the "atomic" scale roughness contributed by adatoms, clusters, and surface defects (viz., <ca. 25 Å) is the most important
[37,41]. Roughness greater than the wavelength of the exciting radiation has been excluded by most workers as being an essential component of SERS, although if it is present in a regular topological array such as a diffraction grating, then SERS intensities can be modulated by the deliberate excitation of PSP resonances as mentioned above.

In this paper, we would like to address the surface roughness question for the specific case of SERS on Ag electrodes in electrochemical cells. We restrict our discussion to this case only because of the confines of our experimental experience and our belief that the various factors involved in the overall phenomenon of SERS may not operate equally in all interfacial environments. It has been repeatedly stated by some of the most prominent SERS researchers that have used electrochemical cells as their vehicle for SERS study, that the electrochemical anodization step that produces surface roughness is an absolute or essential prerequisite to the observation of SERS in this interfacial environment [15,18,19,25,28,29,31,32,38,40,49]. We wish to take issue with this statement and hopefully to present experimental evidence to the contrary. As a result of this study we are now able to state with confidence that: (1) the electrochemical anodization or ORC is NOT required for the observation of SERS; (2) surface roughness on the scale of 250–500 Å or greater is NOT required for the observation of SERS in electrochemical cells, (3) the presence of surface roughness on the scale of 250 to ca. 3000 Å definitely influences the magnitude of the total observed SERS enhancement factor; (4) surface roughness on the scale of 250 to ca. 3000 Å contributes a maximum increase in the underlying SERS enhancement of \(10^2\) and may be as small as \(2 \times 10^1\).

2. Experimental

All SER spectra were acquired using 60–100 mW of laser power from the 514.5 nm line of a Coherent Radiation Laboratories Model CR-3 argon ion laser. The double monochromator, detection electronics, and computer-based data acquisition system have been described [1,9,10].

The SERS electrochemical cell used in this study is a modified version of the one described previously [1]. This modification was made to the holder for the polycrystalline, Ag working electrode. The electrodes used here are Ag slugs cut from a 6.3 mm dia. rod. These were expoxied (Varian Torr-Seal) into an electrode holder fabricated from fiber-glass epoxy resin. This electrode holder also served as the mount for mechanically polishing the Ag specimen. The electrode holder was mounted in the glass envelop of the SERS electrochemical cell in such a way that it could be positioned at various distances from the optically flat front window of the cell (0.5–5.0 mm).

The polycrystalline Ag electrodes were very carefully polished first with emery paper then with a series of aqueous alumina slurries starting with a particle size of 0.3 μm and finishing with a particle size of 0.05 μm. The actual size of the alumina particles used in the final polishing step was smaller than the nominal 0.05 μm since
the alumina powder was suspended in H₂O and only the smallest particles (i.e. those that did not settle out) were used. Following the polishing step, the electrodes were ultrasonically cleaned in deionized water and dried in a stream of prepurified nitrogen. Electrode surfaces prepared in this manner were examined both before and after SERS experiments with an optical microscope, scanning electron microscope (SEM, JEOL Model JSM-50A), and a scanning Auger microprobe (SAM, Physical Electronics Industries, Inc., Model 590A) in order to establish the surface topography and the elemental surface composition. Auger electron spectra (AES) were recorded using a primary beam voltage of 2 keV at 50 nA of beam current with the analyzer modulated at 6 eV. The base pressure for all of the UHV surface analyses was 1 × 10⁻⁹ Torr.

Two chemical systems were chosen for this SERS investigation on "smooth", unanodized, mechanically polished Ag electrodes. These were:
System I: Ag/0.05M pyridine/0.10M KCl/H₂O;
System II: Ag/0.005M Pt(CN)²⁻/0.10M K₂SO₄/H₂O.
System I was chosen because it has become the defacto model system for all SERS studies. System II was chosen to illustrate that the conclusions we have reached are more general than for the pyridine model system alone. In addition, the tetracyanoplatinate (i.e., TCP²⁻) system has the very desirable property for the present investigation that the SERS detected adsorption isotherm for TCP²⁻ on Ag saturates at a bulk TCP²⁻ concentration of only 0.005M. This is an order of magnitude less than that for pyridine so that the contribution of bulk NR scattering to the total observed SERS signal is very much less. This helps considerably in facilitating the detection of weak SERS signals.

All solutions were prepared with distilled, deionized water (Milli-Q, Millipore Corp.). Pyridine (Gold-label 99+%) was used as freshly received from Aldrich Chemical Co. The K₂Pt(CN)₄ used was a gift from Dr. Joel S. Miller of the Occidental Petroleum Corp. and is gratefully acknowledged. All other materials were standard reagent grade chemicals. All solutions were thoroughly deoxygenated with prepurified nitrogen prior to the immersion of any of the carefully prepared Ag surfaces.

For comparison purposes a few standard SERS measurements were made on anodized electrodes. For these experiments a single double potential step (E₁ = -0.6 V versus SCE and E₂ = +0.15 V versus SCE) anodization pulse was used for System I. Adsorbate was present in the electrochemical cell at the time of the electrode anodization but 514.5 nm laser light was rigorously excluded from illuminating the electrode surface. The charge passed in the forward step and the reverse step of the anodization was recorded. Only experiments in which the charge recovery is 100 ± 0.5% are accepted as valid. A few experiments were also carried out using the triangular anodization waveform preferred by some SERS researchers [16,18,29,31,37].
3. Results and discussion

The objective of these experiments is to demonstrate that it is, in fact, possible to observe SERS in an electrochemical cell on a surface where no intentional roughening is carried out. In this study, we have attempted to prepare as smooth a Ag surface as possible by mechanical polishing and then to observe SERS after immersion into pyridine and aqueous electrolyte at $-0.6$ V versus SCE (i.e., the potential at which the SERS signal is at maximum intensity) with no anodization or ORC. A preliminary version of this experiment had actually been carried out previously by our group and published in the review article (see p. 140, fig. 12 of ref. [1]). The SERS spectrum on an unanodized, mechanically polished electrode has probably been overlooked because there was no accompanying surface roughness characterization, surface elemental composition characterization, and no definitive proof that this was a surface and not a bulk signal. In the experiments which follow we will attempt to rectify this situation and demonstrate that the unanodized electrode experiment in ref. [1] was in fact valid.

3.1. SEM and AES characterization of mechanically polished, unanodized, silver electrodes both before and after SERS experiments

The four panels in fig. 1 are SEM topography images of polycrystalline silver electrodes prepared under different conditions.

Fig. 1d is an image of an anodized silver electrode prepared with 3 triangular wave anodization cycles. In each the potential was scanned at 3.0 mV s$^{-1}$ from a starting potential of $-0.6$ V versus SCE to a final potential of $+0.15$ V versus SCE and back. In each cycle 100 mC cm$^{-2}$ (viz., ca. 400 monolayers of Ag) of charge was passed in each half-cycle. The specimen was not exposed to the laser beam during anodization. The extremely rough surface produced in this manner is similar to that described by Hexter et al. [29] and produces SERS with an enhancement factor of ca. $(2-3) \times 10^4$ as discussed elsewhere [1]. We also point out that on this very rough surface, but not on surfaces roughened by $<50$ mC cm$^{-2}$ ORC's, Blondeau and co-workers recently claim to have found evidence of multilayer adsorption in the pyridine model system [26]. If these investigators are correct, the enhancement factor for SERS on surfaces such as those shown in fig. 1d will be decreased.

Fig. 1c is an SEM image of an optimally anodized silver electrode prepared with a single, double potential step anodization pulse in which 20 mC cm$^{-2}$ of charge (i.e., 80 monolayers) were passed in each half-cycle. This is precisely the type of anodization (i.e., roughening) that gives the maximum SERS intensity corresponding to an enhancement factor of $10^6$ at $\omega_L = 514.5$ nm. The type of surface roughness generated in this procedure is very similar, if not identical, to that shown by workers at Bell Laboratories [101]. This roughness can be characterized as very nearly hemi-spheroidal with a distribution of diameters ranging from 250 Å (the resolution limit of our SEM) to ca. $(3-4) \times 10^3$ Å. The hemi-spheroids are not com-
Fig. 1. SEM topography images of the silver electrodes: (a) carefully polished, unanodized surface after a SERS experiment; (b) carefully polished, unanodized surface before the SERS experiment, latex calibration spheres are shown covering part of this surface (1000 ± 50 Å and 4800 ± 100 Å); (c) after 20 mC/cm² single double potential step anodization, not exposed to the laser beam; (d) after 3 triangular waves anodization cycles with 100 mC/cm² per cycle, not exposed to the laser beam. The electrons were incident on the sample at an angle of 65°.
Table 1
AES peak-to-peak intensity ratios for the main surface contaminants for various sample pre-treatment

<table>
<thead>
<tr>
<th>Q (mC/cm²)</th>
<th>Anodization mode</th>
<th>AES intensity ratio</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>S/Ag</td>
</tr>
<tr>
<td>0</td>
<td>none</td>
<td>0.3</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>0.1</td>
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<td>300</td>
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a) Possible carbon signal at ~270 eV was quantitated by correction for overlap with the silver transition at 266 eV.

pletely overlapping although there are regions of clustering. In addition, the hemi-spheroids appear to be in contact with the “smooth” ground plane of Ag. The lateral distances between hemi-spheroids range from contact to a few μm. AES analysis of this surface revealed that the relative Auger intensities of S/Ag, C/Ag, and Ω/Ag decreased considerably after anodization, confirming the previous observations of Hexter et al. [29] that the redeposited Ag was cleaner after anodization. Table 1 summarizes the AES results for no anodization, a 20 mC cm⁻² double-potential step anodization, and the 300 mC cm⁻², three-cycle triangular wave anodization. The AES intensity ratios were calculated from peak to peak heights for the following transitions: S = 152 eV, O = 503 eV, C = 272 eV, and Ag = 356 eV. Standard element to element sensitivity factors were taken into account in computing these ratios. All anodized surfaces are cleaner than the unanodized. Thus there are more Ag atoms on the surface in the anodized case than the unanodized case. This may explain some recently obtained results in this laboratory which show that the surface coverage of an electro-active pyridine as measured by double potential step chronocoulometry [102] (viz., 4-cyanopyridine) on Ag is greater by a factor of 3–5 on an anodized surface than an unanodized one [103].

Fig. 1b shows the SEM image for an unanodized, mechanically polished Ag electrode before any SERS experiment. In order to provide a calibration for the surface roughness seen in fig. 1c, latex calibration spheres of known sizes are superimposed on the “smooth” surface in fig. 1b. The calibration spheres were overcoated with ca. 120 Å of gold to improve the SEM contrast ratio. Since the SEM pictures shown in figs. 1b and 1c were made under identical experimental conditions, one can clearly see that there is no roughness in fig. 1b with hemi-spheroidal character on the scale of 250 Å or greater.

Fig. 1a shows the SEM photograph of the mechanically polished, unanodized Ag surface after completion of a SERS experiment in which the surface was never exposed to a potential more positive than −0.6 V versus SCE but was immersed into the 0.05M pyridine/0.10M KCl/H₂O electrolyte and then exposed to ca. 100 mW of 514.5 nm laser light. We conclude that no hemi-spheroidal surface
roughness has been either photochemically or electrochemically generated during the course of the SERS experiment.

It is probably obvious to the reader but we state it here for clarity: In none of these experiments can we discuss surface roughness smaller than 250 Å. Even this figure may be slightly pushing the resolution of the SEM used in this work.

3.2. SERS of Ag/pyridine on unanodized, mechanically polished electrodes

Fig. 2 shows a SERS experiment with the Ag/pyridine model system on a mechanically polished, unanodized silver surface whose roughness features are identical to those shown in fig. 1a. This experiment was carried out in a conventional SERS electrochemical cell where the surface of the Ag electrode was placed 3.0 mm behind the optically flat front window of the cell. In this configuration the laser beam must traverse a 3.0 mm solution layer before reaching the electrode surface. This incident beam excites both bulk pyridine molecules in solution and adsorbed on the surface. In addition, the specularly reflected beam exits the cell through the 3.0 mm solution path and excites still more bulk phase pyridine molecules. When we attempted to detect the potential dependent displacement of pyridine from the electrode surface which, of course, is a prerequisite observation for a Raman signal to be characterized as [1], we failed. As shown in fig. 2b, there is a very substantial residual Raman signal at 0.0 V versus SCE. In fact, there is very

Fig. 2. Effect of potential on SER spectra of pyridine from a solution of 0.05M pyridine and 0.1M KCl and from the surface of an unanodized silver electrode: (a) −0.6 V, the overlapping peaks from the surface and from the solution, the 1006 cm⁻¹ surface peak is slightly shifted to the higher energy side; (b) 0.0 V, the 1006 cm⁻¹ surface peak disappears, whereas the solution peak remains (electrode ~3 mm away from the window). Laser power = 60 mW at 514.5 nm, counting intervals 8 s, scan speed 0.033 A/s, slit width 2 cm⁻¹.

Fig. 3. Effect of potential on SER spectra of pyridine adsorbed on a carefully polished, unanodized silver electrode from a solution of 0.05M pyridine and 0.4M KCl. Electrode potentials are: (a) −0.6 V; (b) 0.0 V versus SCE. Electrode ca. 0.5 mm from the window. Laser power = 60 mW at 514.5 nm, counting intervals 4 s, scan speed 0.0625 A/s, slit width 2 cm⁻¹.
little difference between the signals at $-0.6$ V versus SCE where SERS should maximize and near 0.0 V versus SCE where it should minimize. On careful scrutiny, however, we observed that the linewidth of the observed Raman signal was different at the two potentials and the frequencies were slightly but reproducibly shifted with respect to each other. This observation lead us to conclude that if we were seeing any SERS signal at all, it was reasonably weak and was superimposed on the NR scattering from bulk aqueous pyridine. This conclusion was further supported by the fact that the line shapes in fig. 2a were not symmetric as would be the case if the SERS and NRS were superimposed.

In order to test this conclusion, we conducted the experiment whose results are shown in fig. 3. This is an identical experiment to that depicted in fig. 2 with the exception that the Ag working electrode has now been moved as close as possible to the rear surface of the optically flat cell window. We estimate that this distance was 0.5 mm. In this way, the bulk contribution to the total Raman signal should be minimized, thus spatially discriminating in favor of the SERS signal. Under these quasi-thin layer electrochemical conditions [104], the expected SERS dependence on applied potential was observed. At $-0.6$ V versus SCE (fig. 3a) the totally symmetric ring breathing modes of pyridine are clearly seen [viz., $\nu_1 = 1006$ cm$^{-1}$ and $\nu_{12} = 1035$ cm$^{-1}$]. The mode number scheme is that of ref. [100]. These signals are ca. 100 counts/s above the background. Under similar experimental conditions the SERS signals obtained from a surface such as that shown in fig. 1c would produce $10^4$ counts/s above background corresponding to an $\epsilon(\hbar\omega_L) = 10^6$. Thus we conclude that this SERS signal represents an enhancement factor of ca. $10^4$ assuming that a monolayer of pyridine is adsorbed on the Ag surface. As expected for a true SERS signal, its intensity drops below background level when pyridine is desorbed by potentiostatting at $E = 0.0$ V versus SCE [1,9].

To further confirm the observation of a true SERS signal for the Ag pyridine system on "smooth", unanodized, but mechanically polished electrodes, the depolarization ratios for $\nu_1$ and $\nu_{12}$ modes were measured. As shown for the first time in refs. [1,9] the depolarization ratios for these modes should be approximately equal to or greater than 0.6 (i.e., depolarized) for SERS as compared to the bulk pyridine NRS values of ca. 0.03–0.01 (i.e., polarized). Fig. 4 shows the SERS for the same experiment as fig. 3 where the polaroid analyzer was oriented parallel (fig. 4a) and then perpendicular (fig. 4b) to the vertically polarized (i.e., p-polarized) incident laser beam. The calculated depolarization ratios were $\rho_{1006} = 0.8$ and $\rho_{1035} = 0.6$. These results further substantiate our claim for the observation of true SERS signals on Ag electrodes that have no surface roughness features greater than 250–500 Å.

3.3. SERS of Ag/Pt(CN)$_2^-$ on unanodized, mechanically polished electrodes

A frequent criticism voiced in the early days of SERS was: "SERS is interesting but does it work for anything besides pyridine on silver". This notion has now been
thoroughly dispelled for adsorbates on rough electrodes [22-49]. To avoid that potential criticism of this work, with respect to the observation of SERS on surfaces without surface roughness features on the scale greater than 250 Å, an experiment with a radically different adsorbate was carried out.

Allen [105,107] has shown that many metal complexes adsorb on silver electrodes and give rise to very intense SERS. Tetracyanoplatinate ion is one of these adsorbates and has been fairly thoroughly characterized. It has been found that for Ag electrodes subjected to a 20 mC cm$^{-2}$ double potential step anodization (fig. 1c, surface roughness) an intense SERS band in the CN stretching region is observed at 2165 cm$^{-1}$. Furthermore, since TCP$^{2-}$ is an anionic adsorbate, it is expected to have a very different potential dependence to its adsorption isotherm as compared to a neutral molecule such as pyridine. Based on the usual models of the electrical double layer, one would anticipate that TCP$^{2-}$ would be most strongly adsorbed at potentials positive of the point of zero charge (pzc) which occurs at ca. –0.7 V versus SCE on Ag [1], and minimally adsorbed at potentials negative of the pzc. This is exactly what has been found by Allen for TCP$^{2-}$ on anodized Ag electrodes. The SERS signal at 2165 cm$^{-1}$ is most intense at potentials near –0.13 V versus SCE (viz., positive of the pzc) and cannot be observed at potentials more negative than ca. –1.0 V versus SCE (viz., negative of the pzc).

Fig. 5a shows the SERS of TCP$^{2-}$ adsorbed on an unanodized, mechanically
polished Ag electrode with the surface roughness features shown in fig. 1a. The surface Raman signal peaks at 2170 cm$^{-1}$ and is most intense at $-0.13$ V versus SCE. This signal cannot be observed at potentials negative of $-1.0$ V versus SCE as shown in fig. 5b. The companion polarization studies have been carried out but are not shown as a figure here. The measured depolarization ratio for the 2170 cm$^{-1}$ vibrational feature of TCP$^{2-}$ on Ag is 0.60 confirming its SERS identity.

3.4. Qualitative theory/experiment comparison

The significance of the results presented here is their relationship to the present state of theoretical understanding of the SERS phenomenon. As indicated above, there is currently a wide spectrum of SERS theories and enhancement mechanisms being discussed in the literature [71–99]. Although many of the theories are not yet sufficiently advanced in their development to make specific predictions that can be rigorously tested by experiment, one characteristic of SERS addressed by all of the theoretical suggestions so far is that of surface roughness and its role in the enhancement process. The theories can be divided into two categories based on roughness: (1) theories in which roughness is absolutely required in order to achieve the enhancement and (2) roughness independent theories. In this latter category it should be recognized that there is nothing to prevent a superposition of a roughness dependent enhancement mechanism on top of an underlying roughness independent mechanism. In the former category it should be understood that different scales of surface roughness are deemed important by different theorists.

The roughness dependent enhancement mechanisms and the roughness scales thought to be important are: (1) conventional surface plasmon (i.e., PSP) models — submicroscopic (viz., 25–250 Å roughness) as well as microscopic (250 Å to 1 μm roughness) [62,94,98]; (2) electron–hole pair excitations in the metal, and charge transfer excitations between the metal and the adsorbate — submicroscopic roughness [22,81]; (3) geometrically defined electromagnetic resonances (i.e., collective electron resonances) — submicroscopic and microscopic roughness [72,84,91,95,98,99]; (4) a special case of the electron–hole pair excitation model in which it is believed atomic scale roughness (i.e., <25 Å) couples the adsorbate and the e–h pair [37,41]. The roughness independent enhancement mechanisms are: (1) modulated reflectance models [87,96] and (2) image field (or dipole) models [73,75–78,82,97].

The results we have presented here allow one to place an upper limit on the magnitude of the SERS enhancement in electrochemical cells contributed by roughness features in the 250–3000 Å range. At most this type of roughness can contribute an enhancement of $10^2$ since we are, in fact, able to observe SERS in electrochemical cells on surfaces without these roughness features. Furthermore, if the coverage of pyridine or Pt(CN)$_2$$^-$. turns out to be less than a monolayer on these un-anodized surfaces, this factor could be reduced even further. On the basis of our double potential step chronocoulometry measurements of the coverage of 4-cyano-
pyridine on anodized and unanodized surfaces, we estimate that there may be as much as five times the coverage on the rough surface. This would have the effect of reducing the contribution of roughness to an enhancement factor of only 20 times. In addition, we note that this conclusion is in agreement with a recent theoretical model combining the image dipole and geometrically defined electromagnetic resonance ideas [106]. Also we note that our estimate of the roughness contribution is in agreement with the experimental observations of Kirtley et al., who have sown enhancement variation of 20–100 between PSP resonance conditions and off-resonance conditions [61–63]. Thus we conclude that SERS enhancements of ca. $10^4$ must be explained by invoking theories that either do not require roughness greater than 250 Å to achieve their enhancement or roughness dependent theories which involve smaller roughness scales. Combined SERS and surface roughness characterization measurements that probe this question on the submicroscopic scale are crucial to the further comparison of theory and experiment.

The results presented here on relatively smooth electrodes do impact on SERS measurements in UHV [52,53] that claim the requirement for roughness on the 500 Å scale. We conclude that these measurements should either be reexamined or that there is a fundamental difference in the mix of SERS enhancement mechanisms operative in UHV as compared to electrochemical cells.

Finally, we comment on the role of electrochemical anodization. Since none of the SERS spectra presented in figs. 2–5 involved anodized electrodes we hope that this finally puts to rest the idea that an ORC pretreatment is an absolute prerequisite for the observation of SERS in electrochemical cells. Furthermore, we point out that Allen [47,107] has recently shown that SERS spectra can be observed for may different adsorbates on unanodized copper electrodes as well. In addition to the practical significance of not requiring anodization for SERS observation, we would like to point out that Otto’s adatom hypothesis should be re-examined in light of these new results since he interprets many features of the electrochemical SERS experiment in terms of adatoms produced by the anodization pretreatment. Since we do not anodize, we are not producing large surface concentrations of adatoms. Thus it may be that adatom contributions to the SERS enhancement are less than or equal to $10^2$ as well. If this were the case, then one might conclude that the $10^2$ enhancement contribution produced in electrochemical SERS experiments following anodization and roughening would he shared between adatom and collective electron resonance mechanisms.

4. Conclusions

The conclusions resulting from this study of electrochemical SERS on unanodized, mechanically polished silver electrodes may be summarized as follows:

(1) The electrochemical anodization or ORC is *not absolutely* required or essential to the observation of SERS in electrochemical cells.
(2) Surface roughness on the scale of 250–500 Å, which represents the lower resolution limit of the electron microscope available to us, or greater is not absolutely required or essential for the observation of SERS in electrochemical cells.

(3) Surface roughness on the microscopic scale (viz., 250–3000 Å) definitely modulates the observed SERS intensities but removal of this scale of roughness does not completely remove the SERS enhancement.

(4) We are able to semi-quantitatively estimate the relative magnitudes of the SERS enhancement contributed by roughness greater than 250–500 Å and that contributed by roughness below this scale or by smooth surfaces. This estimate is:

\[ \epsilon_{\text{roughness}} > 250 \text{--} 500 \text{Å} = \sim 10^2 \text{ (max.),} \]
\[ \epsilon_{\text{roughness}} < 250 \text{--} 500 \text{Å} = \sim 10^4 \text{ (min.),} \]
\[ \epsilon_{\text{total}} = 10^6. \]

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