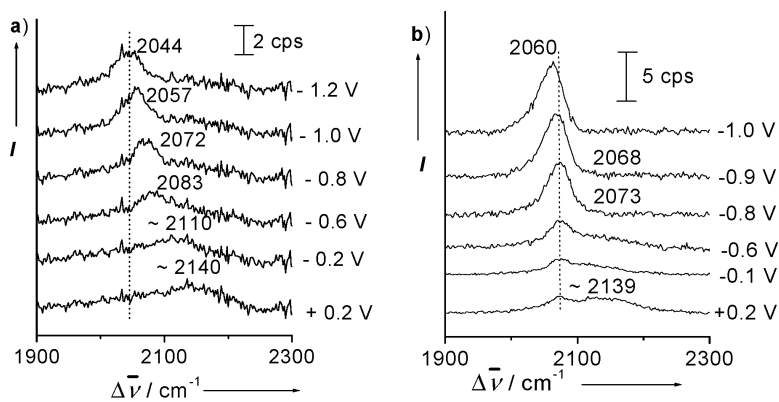


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Surface-Enhanced Raman Scattering in the Ultraviolet Spectral Region: UV-SERS on Rhodium and Ruthenium Electrodes

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The theory and experiment in surface-enhanced Raman scattering (SERS) and surface-enhanced resonance Raman scattering (SERRS) have advanced steadily with innovative and extensive analytical applications in surface science,¹ electrochemistry,^{2,3} biology,^{4,5} and materials research.⁶ Recently, it has been realized that specific metal nanostructures^{7,8} may enhance the Raman cross section by as much 14 orders of magnitude, which can be of the same order of magnitude or even greater than the best fluorescence cross section, allowing one to detect the spectrum of the single molecule.^{7–12} The most successful metal nanostructures for SERS or SERRS down to the single molecule detection level are silver and gold nanostructures.^{7–13} However, the search for a new enhancing substrate has continued, and SERS on a variety of rough surfaces has been reported; most notably, the weak SERS effect has also been generated directly on transition metals: Fe, Co, Ni, Ru, Rh, Pd, and Pt.¹⁴ It has been applied successfully in surface adsorption, electrocatalysis, and corrosion of diverse transition-metal-based substrates.¹⁵

The above exciting progress has revived interest in SERS study. For some time, we have been exploring the possibility of generating SERS by ultraviolet light excitation. Although several thousand papers have been published, the excitation lines have only covered the visible spectrum up to the near-infrared region, from 450 to 1064 nm.^{16–19} There are inherent difficulties in the UV-SERS experiment that could explain the absence of these data in the SERS literature. Electromagnetic enhancements are rather small in the ultraviolet region where damping is generally large due to interband transitions. For instance, the best enhancers in the visible and near-infrared, silver and gold, do not produce SERS with 325 nm laser excitation. Our experiments using electrochemically prepared surfaces and silver and gold island films tested with highly sensitive confocal Raman microscopy failed to produce SERS from the surface species. However, the same molecules exhibit high SERS activity using the visible excitation on these substrates. Because the optical property of the transition metal is different from that of silver and gold, it is worth it to test UV-SERS of transition metals. In this study, we report the first ultraviolet surface-enhanced Raman scattering (UV-SERS) spectra of molecules adsorbed onto rough rhodium (Rh) and ruthenium (Ru) metal surfaces.

Recently, a technique was developed to roughen Rh surfaces.²⁰ The rough topography was clearly seen in the AFM image of the Rh electrode where a cauliflower-like structure is apparent. Each cauliflower has a dimension of about 100 nm and consists of many nanoparticles in the range of 20–40 nm.²⁰ A Rh electrode so prepared was found to enhance the Raman signal of adsorbed species when they were excited with the 325 nm laser line. The UV-SERS experiments were carried out using a UV-vis R1000

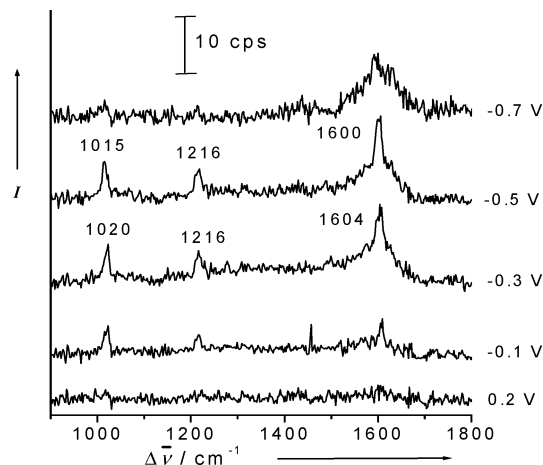


Figure 1. UV-SERS spectra of pyridine on a Rh electrode recorded at five different applied potentials.

Renishaw micro-Raman system equipped with a UV-enhanced CCD detector. The 325 nm laser line from the He–Cd laser was used for excitation. Pyridine, the most studied molecule in SERS,^{16–18} was used to first test SERS on the roughened Rh electrode. The potential-sequenced SERS spectra of the adsorbed pyridine are shown in Figure 1. The UV-SERS spectrum shows three Raman bands at 1015, 1216, and 1600 cm^{-1} that can be safely assigned to a_1 vibrational modes.¹⁶ The UV-SERS provides a different relative intensity pattern from that of the visible SERS, and frequencies are slightly shifted from those of pyridine in solution. The electrode potential dependence of the spectra is further evidence of adsorbed surface species.

In the present work, it is also important to ensure that the UV-SERS can be extended to the study not only of pyridine but also of more general and important organic and inorganic molecules having smaller Raman scattering cross sections. The two potential-sequenced spectra of SCN^- anion adsorbed respectively onto roughened Rh and Ru electrodes are presented in Figure 2. The Raman band due to the CN stretching vibration of adsorbed SCN^- is observed in the 2044–2140 cm^{-1} region and critically depends on the substrate and applied potential. The center of the vibrational band shifts to higher frequency with more positive values of the electrode potential, indicating the strong metal–adsorbate interaction.¹⁵

The claim to surface enhancement in the UV region has to be supported by some estimation of the enhancement factor.¹⁵ To this end, and using the spectrum obtained at -0.2 V shown in Figure 2a, the enhancement factor for Rh was estimated to be about 100 (see the Supporting Information). Our observation seems to violate the commonly accepted frame that Au, Ag, and Cu have higher SERS activity than other metals. However, after the dielectric

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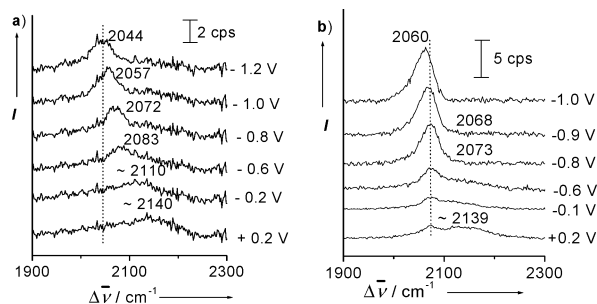


Figure 2. UV-SERS spectra of SCN^- on Rh (a) and Ru (b) electrodes as a function of the applied potential.

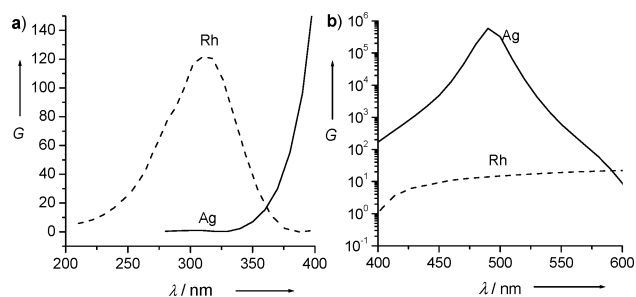


Figure 3. Enhancement factor computations for Ag and Rh spheroids in the UV spectral region (a) and the visible region (b) of the EM spectrum.

function $\epsilon(\omega)$ in the UV region was carefully analyzed, it can be seen that both real and imaginary parts of $\epsilon(\omega)$ for Rh and a number of transition metals (e.g., Ru, Co, and Fe) strongly suggest the possibility of UV-SERS activity, much in the same fashion as the optical properties led to the excellent visible SERS-active metals, Ag, Au, and Cu.

On the basis of the electromagnetic (EM) model,¹⁸ a simple calculation of the wavelength-dependent enhancement factor for Rh and Ag was carried out using the method described by Zeman and Schatz.²¹ The results for a metal spheroid with a 3:1 aspect ratio (semimajor axis $a = 45$ nm and semiminor axis $b = 15$ nm) are shown in Figure 3. It can be seen that the surface-averaged enhancement factor (G) for Ag in the visible light region (as high as 10^6) decreases sharply when the excitation frequencies are from the UV spectral region. The EM approach allows one to notice that a large increase of the local electromagnetic field at the surface of the metal nanostructures (much smaller than the λ of the incident radiation) can be realized due to the excitation of the dipole particle plasmon resonances.^{18,22} The dielectric function of the metal, being the response function to the incident electric field, determines the spectral region of SERS activity for any particular shape and size of the metal particle. Therefore, it can be seen in Figure 3 that there is no enhancement effect for Ag in the region around 325 nm. However, the enhancement factor calculated for Rh spheroid shows a maximum to be ca. 10^2 in the UV region around 325 nm. This preliminary theoretical calculation is in agreement with the experimental data and provides a rationale to explain why some transition metals, instead of the typical SERS metals, may present observable SERS activity in the UV region. The theoretical approach could offer new physical insight into the SERS/SERRS phenomenon. It will allow the investigation of molecules and nanostructures under a new experimental condition including UV-SERS active materials that may or may not be SERS active in the visible or near-infrared region of the EM spectrum.

In light of the new experimental evidence of UV-SERS achieved with the 325 nm laser excitation, it seems appropriate to highlight the differences between UV-SERS and resonance Raman scattering (RRS),²³ a powerful technique rapidly becoming a commonplace

for catalytic studies in the UV. RRS has been successfully applied in the UV as an analytical technique for catalyst characterization, and occasionally for characterization of the adsorbate.²⁴ At present, the use of RRS in the UV as an analytical technique is limited and in the hands of specialized groups. However, the advent of tunable UV-lasers and a compact UV-Raman system may change that. The use of RRS for the detection of adsorbates on catalytic surfaces in the UV faces the interference from the signal of species from the bulk phase that may absorb in the spectral region of excitation. In this regard, UV-SERS, like SERS in the visible, with its unique surface-selectivity has a great potential in UV surface and interfacial science to study a wide variety of adsorbed molecular systems on metal nanoparticles. As in the visible, where RRS, SERS, and SERRS are clearly recognized and well separated, in the ultraviolet these techniques have their own strength and limitations. Hopefully, UV-SERS will develop side by side with RRS and SERRS, facilitated by the fast development of commercial low cost UV laser and UV-Raman systems. UV-SERS, RRS, and SERRS will be further applied in fields that include electrochemistry, biomedicine, and catalysis, as well as nanostructures and the theoretical investigation of SERS itself.

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Supporting Information Available: Detailed experimental section of UV-SERS of rhodium and ruthenium and the calculated enhancement factor (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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