

The Student Seminar Series

Presents a seminar by

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Recent Applications of Surface Enhanced Raman Scattering in Analytical Chemistry

4:00 PM

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Chemistry Building, room 2104

Abstract

A segment of analytical chemists have focused their attention on surface-enhanced Raman scattering (SERS) because of its potential applications in the field of trace analysis. It has been recently reported that SERS could be used as a vapor sensor and a CE (capillary electrophoresis) detector. SERS can be also used for ultra-sensitive analysis including single molecule detection. Interesting applications of SERS for interfacial and surface analysis were also reported. Other groups have reported the application of SERS for bio-imaging and as gene probes for HIV. In this seminar, the SERS mechanism and SERS applications for single molecule detection and interface/thin film analysis will be primarily discussed.

Biography

Jinseok Heo received his B.S. and M.S. degrees in Chemistry at Pohang University of Science and Technology, Korea in 1992 and 1994 respectively. He then worked as an industrial researcher from 1994 to 1999 at Hansol in Korea. He began his graduate studies at Texas A&M in Sep., 2000. Since Aug., 2001 he has been studying for the Ph. D. degree under the direction of Dr. Richard M. Crooks. His dissertation research focuses on the fabrication of micro-channel systems for analytical and bio-analytical applications.

Recent Applications of Surface Enhanced Raman Scattering in Analytical Chemistry

Chem. 681 Student Seminar Series

Nov. 19, 2001

Jinseok Heo

Room 2104

Advisor: Dr. Richard M. Crooks

Introduction

When electromagnetic radiation in the form of light is scattered by matter, photons with higher and lower frequencies than those of the incident light are observed. This is generally referred to as Raman scattering, which was first reported by C.V. Raman in 1928. The frequency difference between the scattered and incident light matches the vibrational or rotational energy levels of the molecules in the matter. Since the advent of laser sources and related optics, Raman spectroscopy has become one of the standard methods for determining molecular composition and orientation analysis, complementing IR spectroscopy. The availability of Raman spectroscopy as a low-limit-of-detection method was limited until surface enhanced Raman scattering (SERS) was reported in 1977 by Van Duyne and Creighton independently [1]. The anomalous Raman signal enhancement, by factors of up to 10^6 , was observed when molecules were adsorbed on a chemically roughened metal substrate. While the SERS mechanism has not been completely resolved, many research groups have been interested in the potential applications of SERS. First of all, molecular structure information can be obtained from SERS spectra, thus offering an advantage over fluorescence methods. It has been recently reported that SERS could be used as a vapor sensor and a CE (capillary electrophoresis) detector to obtain the molecular structure information of the analytes [2-4]. SERS can be also used for ultra-sensitive analysis including single molecule detection, which was shown by the Nie and Kneipp groups [5-11]. Weaver's group has reported interesting applications of SERS for interfacial and surface analysis [12-15]. Other groups have reported the application of SERS for bio-imaging and as gene probes for HIV [16-17]. In this report, the SERS mechanism and SERS applications for single molecule detection and interface/thin film analysis will be primarily discussed.

SERS mechanism [18, 19]

Although the complete SERS mechanism is still controversial, two representative mechanisms, i.e. the “electromagnetic enhancement” and the “chemical enhancement” mechanisms, are known to contribute to the observed overall Raman signal enhancement. Electromagnetic radiation incident on the underlying metal substrate polarizes the metal surface. The collective excitation of the electrons in the near metal surface region is termed a surface plasmon. The collectively oscillating electrons localized in the metal surface, synchronous with the incident electromagnetic light, emit an electromagnetic field. The magnitude of this localized electromagnetic field is proportional to the square of the incident electromagnetic field, leading to an enhancement of the Raman signal from the molecules near the metal surface. Furthermore, the enhanced Raman field from the molecules also polarizes the metal substrate. The induced Raman field from the polarized metal substrate contributes to the final amplified Raman signal. The enhancement factor by electromagnetic enhancement mechanism is approximately $10^6 - 10^7$.

The electromagnetic enhancement mechanism alone is not sufficient to explain the observation that CO and N₂ molecules on the same substrate do not exhibit the same enhancement factor in Raman intensity. In fact, they differ by a factor of 200, despite their similar polarizabilities. This can, however, be explained by the incorporation of the chemical enhancement mechanism. When molecules are chemisorbed on a metal surface, they form new electronic states, i.e. resonant intermediate states during Raman scattering. Charge transfer excitation can occur, from the metal to these new intermediate states or vice versa, with much less energy than between the intrinsic intramolecular states of the adsorbates. Many molecules frequently used in SERS studies have their lowest electronic excitations in the near UV, but this theory shows that charge transfer transitions are possible in the visible region, leading to a surface localized resonance Raman enhancement. This enhancement factor from the chemical enhancement mechanism is $10^2 - 10^3$.

Ag, Au and Cu are frequently used as SERS substrates, because their surface plasmon resonance frequency matches well with the visible frequency used for Raman spectroscopy. The SERS substrate can be prepared by various methods, such as

electrochemical redox reactions, vacuum deposition, lithography, chemical etching, mechanical etching and chemical reduction. The shape, size and dielectric property of the metal, the dielectric property of the medium surrounding the metal and the frequency of the incident light have been shown to affect the overall enhancement in the Raman signal.

Single molecule detection

Generally, the Raman scattering cross-section of a molecule is on the order of $\sim 10^{-30} \text{ cm}^2$ per molecule while its fluorescence cross-section is $\sim 10^{-16} \text{ cm}^2$ per molecule. At least 14 orders of the Raman signal enhancement are needed to overcome the discrepancy between the normal Raman scattering and fluorescence cross-sections. For

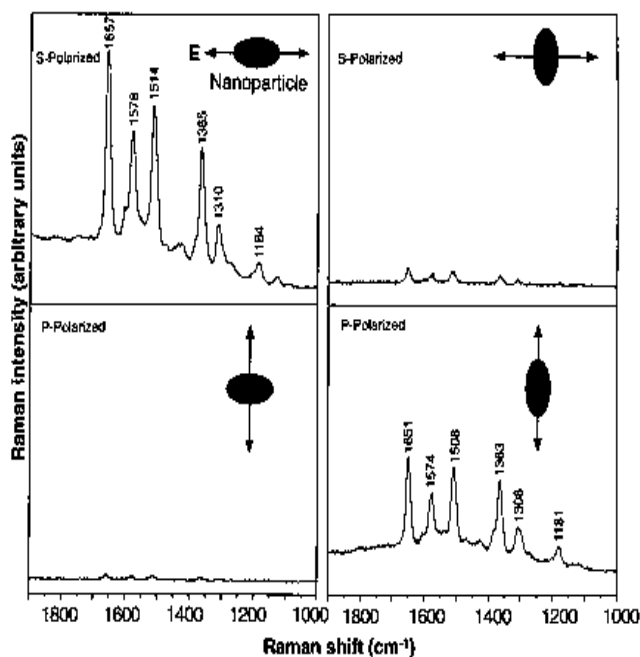


Figure 1. Surface enhanced Raman spectra of R6G obtained with a linearly polarized confocal laser beam from two Ag nanoparticles[7].

the first time, two groups have accomplished an improvement in Raman signal sensitivity by a factor of 10^{14} . Nie et al. were able to detect single molecules by incorporating the SERS and resonance Raman effect. Kneipp et al. have reported the similar magnitudes of Raman signal enhancement by using the SERS method with near-IR laser excitation.

Nie's group observed that a few particles among a large ensemble of Ag colloids modified with R6G (Rhodamine 6G) exhibited

unusually high Raman signal enhancement. These are termed hot particles. Hot particles were carefully analyzed among the large number of silver colloids, which were immobilized on a glass slides [7-9]. By doing this they could remove population-average effects observed in the typical Raman signal measurement, achieving a factor of $10^6 - 10^7$ increase in the Raman signal. Since the number of colloidal particles is much larger than that of analyte molecules, the possibility that more than one molecule is attached to a

colloid is very low. Therefore, the Raman signal obtained from a single Ag colloid will necessarily be that of single R6G molecule. There are two experiments confirming this assumption. First, as shown in fig. 1, the strong polarized nature, characteristic of Raman photons emitted from a single molecule, was observed. This phenomenon is not observed if the Raman signal is population-averaged because of the overall random polarization. Second, sudden spectral intensity fluctuations were observed in the Raman signal. Similar fluctuation phenomena have also been reported in the fluorescence signal of single molecules in low temperature solids [20].

Fig. 2 shows a schematic diagram of the experimental set-up for single molecule detection designed by Kneipp's group. They used a similar method to make single-molecule-attached Ag colloids as the Nie group. The unique attributes of their experiments compared with Nie's group are as follows [5-6]:

First, a similar magnitude of SERS was observed with a near-IR laser source. Second, the single-molecule-attached colloids were not immobilized on the substrate, but confined in

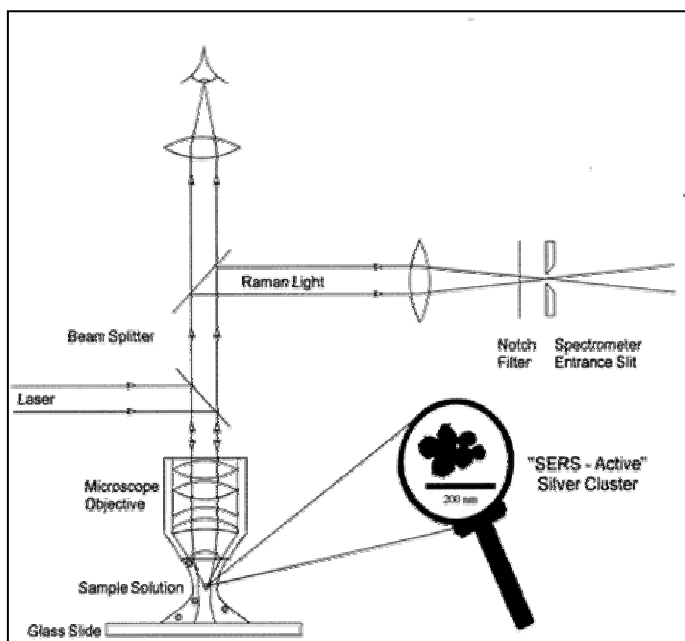


Figure 2. Schematic experimental set up for single molecule SERS[21].

probe volume during data collection time.

a small volume droplet. Since the volume within the focal region and the concentration of clusters are very small, the average number of clusters moving in and out of the probed volume is one or fewer. Third, the evidence for single molecule detection by SERS is that the statistical distribution of Raman signal changes from Gaussian to Poisson when there is one or fewer clusters present in the

Chemical interfaces and thin-film analysis

Adsorbates at the interface between water and metal cannot be easily probed with IR spectroscopy or EELS (Electron Energy Loss Spectroscopy) techniques because water has a strong absorption in the IR region and EELS is not possible under such ambient condition. Thus, Raman spectroscopy can be a preferential choice for those analyses if the sensitivity can be improved. The application of SERS to examine molecules located at metal-water interface will be illustrated in the following section.

The electromagnetic enhancement effect for a Raman signal as a function of distance from the metal nano particle to the probed molecule has the following relationship:

$$I \propto [r/(r+d)]^{12} \quad (1)$$

I : intensity, r : radius of spherical particle, d : distance.

Raman intensity was reported to decrease by less than 10 fold if the distance is below 2 ~

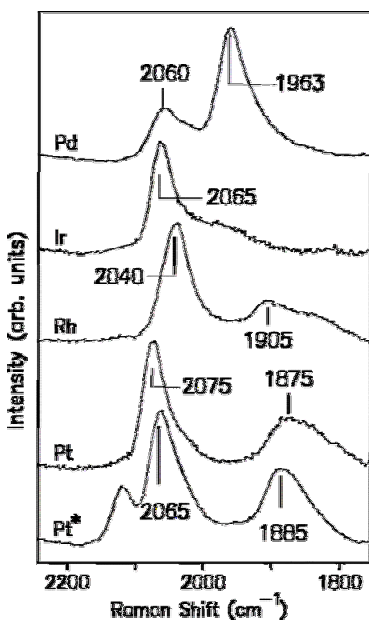


Figure 3. SER spectra in the C-O stretching region for CO layers on transition-metal overlayer films[13].

3 nm [21]. This observation leads to the expectation that molecules adsorbed on the thin metal film coated onto the SERS substrate will still exhibit SERS signals. In other words, the spacer, i.e. the ultrathin film, will not greatly weaken the electromagnetic amplification. If we are interested in the chemistry of adsorbates on the Pt-group metals, the Pt-group metal film can be coated on the SERS substrate such as Ag or Au by electro-deposition method. The important thing is to make pinhole-free thin films on the SERS substrate because the exposed SERS substrate can complicate Raman spectra [13]. Fig. 3 shows the SERS spectra in the C-O stretching region for CO layers formed on transition metal thin layers and the additional peak (Fig. 3-Pt*) was observed when the film contained pin-holes. Fig. 4 shows the SERS spectra of

benzonitrile and toluene on a Pd thin film, coated onto a Au substrate. In this aqueous solution we can determine that toluene is chemisorbed on the Pd surface via the benzene ring while benzonitrile is chemisorbed on the surface via the nitrile by observing the ring

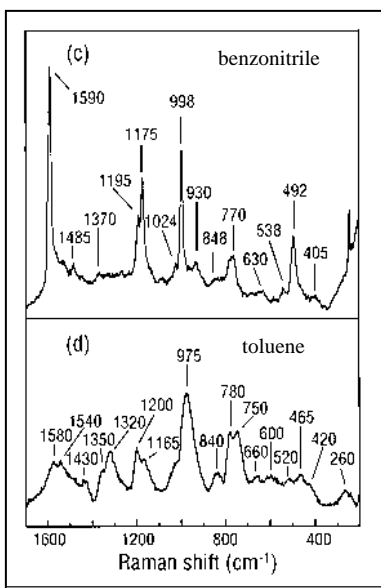


Figure 4. SERS spectra for aromatic molecules adsorbed on Pt- group overlayer films[12].

modes of toluene are frequency-shifted and broadened but those of benzonitrile are not [12]. This experiment shows that SERS is very useful for elucidating chemistry occurring at the interface.

Future of SERS

As discussed in previous sections, the SERS method has the distinct advantages of offering structural information along with increased sensitivity in the field of trace analysis. However, the SERS method has a limitation in that some molecules do not exhibit any SERS enhancement, which is not yet fully explained by the current SERS mechanisms. A better understanding of the SERS mechanism is still required to apply SERS into the diverse fields of trace analysis.

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