Chapter 12

SURFACE-ENHANCED RAMAN SCATTERING

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1. INTRODUCTION

In 1928, Sir C.V. Raman documented the phenomenon of inelastic light scattering\(^1\). Radiation scattered by molecules contains photons with the same frequency as the incident radiation, but may also contain photons with changed or shifted frequency. This effect is very weak - approximately one photon out of a million (0.0001\%) will scatter from that sample at a wavelength slightly shifted from the original wavelengths. The process was later named after him, with the shifting of frequency referred to as the Raman effect and the frequently-shifted light as Raman radiation. Raman spectroscopy is based on vibrational transitions that yield very narrow spectral features which are characteristic of the investigated sample. Thus, it has long been regarded as a valuable tool for the identification of chemical and biological samples as well as the elucidation of molecular structure, surface processes, and interface reactions. Despite such advantages, Raman scattering suffers the disadvantage of extremely poor efficiency. Compared to luminescence-based processes Raman spectroscopy has an inherently small cross-section (e.g. \(10^{-30}\) cm\(^2\) per molecule), thus precluding the possibility of analyte detection at low concentration levels without special enhancement processes. Some modes of signal enhancement have included resonance Raman scattering and nonlinear processes such as coherent anti-Stokes Raman scattering. However, the need for high-power, multiple-wavelength excitation sources has limited the widespread use of these techniques.

Nevertheless, there has been a renewed interest in Raman techniques in the past two decades due to the discovery of the surface-enhanced Raman scattering (SERS) effect, which results from the adsorption of molecules on specially textured metallic surfaces. This large enhancement was first

reported in 1974 by Fleischmann and coworkers, who observed the effect for pyridine molecules adsorbed on electrochemically-roughened silver electrodes\(^2\). It was initially believed that the enhancement resulted from the increased surface area produced by the electrochemical roughening, giving rise to increased probed sample density. The teams of Jeanmaire and Van Duyne\(^3\), and Albrecht and Creighton\(^4\) later confirmed the enhancement (up to \(10^8\)) but attributed the effect to more complex surface enhancement processes, which continue to be the subject of intense theoretical studies. Following the first observations of the SERS effect in the 1970’s, there have been an extensive amount of fundamental research and theoretical studies on the SERS effect. During a period between the mid-1970s and the early 1980’s, this early enthusiasm for SERS decreased and did not lead to practical applications because the Raman enhancement effect had been observed for only a limited number of molecules. Most studies had involved samples at concentrations between \(10^{-1}\) and \(10^{-3}\) M, which are well above the useful concentration ranges for trace analysis. Most fundamental studies were also limited to a few highly polarizable small molecules, such as pyridine, benzoic acid and its derivatives, or some ionic species such as the cyanide radical CN\(^-\) and the anion of dithiozone. It was even thought that the SERS effect occurs only for a few molecules (such as pyridine) only under specific experimental conditions.

The "Renaissance" of SERS started only in the mid-1980’s. In 1984, our laboratory first reported the general applicability of SERS as an analytical technique, and the possibility of SERS measurement for a variety of chemicals including several homocyclic and heterocyclic polyaromatic compounds using solid substrates covered with silver-coated nanospheres were first reported\(^5\). For the following two decades, SERS has been accepted as a general phenomenon and research activities in this field has regained explosive interest. More recent reports have cited SERS enhancements from \(10^{13}\) to \(10^{15}\), thus demonstrating the potential for single-molecule detection with SERS\(^6\)-\(^10\).

Because of the aggressive development of SERS substrates and application to a wide range of chemicals, the potential of SERS as a routine analytical technique was recognized by the mid-1980s. The SERS technique has since continued to receive increased interest, as is evidenced by the large numbers of papers and review articles\(^11\)-\(^22\). Furthermore, the scope of SERS has been extended to include other surface-enhanced spectroscopies such as surface-enhanced second-harmonic generation\(^23\) and surface-enhanced hyper-Raman scattering\(^24\).

A host of biological compounds (e.g., proteins, amino acids, lipids, fats, fatty acids, DNA, RNA, antibodies, enzymes) have been studied via SERS. The extensive progress in the development of dependable SERS substrates over the past few decades has promoted the application of SERS in the rapidly expanding field of biotechnology, as is demonstrated in several