CHAPTER I

INTRODUCTION

1.1 GENERAL

1.2 DISCOVERY OF SERS

1.3 NATURE OF SERS

1.4 SCOPE OF SERS

REFERENCES
1.1 General

When an intense beam of monochromatic light is allowed to pass through a substance in the solid, liquid or gaseous state, the molecules of the substance will scatter the light. The scattered light contains some additional frequencies above and below that of the incident frequency. This phenomenon is known as the Raman scattering which provides valuable information about the structure and properties of the molecules being irradiated. The difference between the frequency of the incident light and that of the Raman lines is called the Raman shift. This Raman shift corresponds to the vibrational (also rotational and electronic in particular cases) frequencies present in the molecules of the sample.

The Raman process itself—inelastic light scattering by molecular vibrations—is inherently weak. Only a small fraction, $10^{-6}$ or so, of the photons incident on a sample are Raman scattered. Thus a major limitation of the conventional Raman method is its low sensitivity. Recently, the Raman technique has enjoyed an increased interest among the spectroscopists following the observation of enormous Raman enhancement for some molecules adsorbed on special metal surfaces. There are certain molecules which when adsorbed on specially prepared metal surfaces or on metal colloids exhibit inordinate Raman signals whose intensity is $\approx 10^2 - 10^6$ times larger than the normal Raman signals. This enormous increase
in Raman signal arises from a surface enhancement process and the phenomenon has been christened as Surface Enhanced Raman Scattering (SERS).

1.2. Discovery of SERS

In 1974, Fleischmann et al [1] reported strongly enhanced Raman scattering from pyridine molecules adsorbed from aqueous solution onto silver electrode surface that had been roughened electrochemically by successive oxidation-reduction cycles. They apparently believed that the inordinate signal strength is coming due to a large increase in the electrodes' surface area. In 1977, Jeanmair et al [2] and independently Albrecht et al [3] first recognized that the large intensity could not be accounted for by the increase in surface area alone. They showed that the increase in SERS signals obtained by roughening the electrode surface area too slightly is equal to that obtained by extending the electrodes' surface area ten times.

Almost all early studies on SERS were performed with pyridine on roughened silver electrodes. Since then the effect has been reported for a few hundred molecules adsorbed on Ag, Au, Cu, Li, Na, K, In, Al, pl and Rh. Silver is the most studied and the most efficient SERS metal, although the alkalis seems to produce SERS signals rivaling that of silver.
1.3 Nature of SERS

Surface-enhanced Raman scattering (SERS) was first detected in pyridine, $C_5\text{NH}_5$, adsorbed at silver electrodes. If one starts with a smooth silver electrode, e.g. a silver deposited at room temperature, a strong Raman signal from the vibrational lines of pyridine appears only after an electrochemical oxidation-reduction cycle. After analyzing the results of all experiments on SERS, it has been widely accepted that the surface roughness is a pre-requisite for SER effect. When appropriately roughened, a silver surface can induce a SERS enhancement factor of $10^6$, whereas a mirror-like smooth silver surface produces only 400-fold Raman enhancement [4]. The dependence of the SERS enhancement on surface roughness exhibits different excitation profiles for different surface preparations. For silver colloids and arrays of posts of definite shape and size the maximum enhancement was reported at a particular excitation frequency.

The SERS phenomenon has excitation characteristics that are similar to those observed with Normal Raman Scattering (NRS). The intensity of the scattered light is dependent on that of the incident light. The scattered light is depolarized even with molecules such as pyridine, which exhibits highly polarized NRS.

The SERS effect appears to occur under specific experimental conditions based on (a) special requirements on the
dielectric constant and (b) the morphology of the surface under study. Selection criteria of the type of substrates and media that are SERS active are based on several considerations. The type of the metal on the surfaces is an important factor. The SERS phenomenon occurs mostly on specific metallic surfaces. Silver exhibits the strongest enhancement effects followed by copper and gold.

In SERS, the Raman selection rules are relaxed, as detected for pyrazine on silver by Dornhaus et al [7] and Erdheim et al [8] and for benzene on silver by Moskovits and DiLella [9]. Normally forbidden bands arise in the spectrum of an adsorbed molecule due to the reduction in the symmetry of the molecule after a strong bond formation with the surface [10]. The appearance of Raman forbidden lines may also come due to the steep electric field gradient that exists near an illuminated metal surface.

1.4 Scope of SERS

The discovery of the SERS effect has stimulated an immense interest in fundamental research. Raman spectroscopy as a probe of surface structure and dynamics has developed its potential due to SERS. Besides producing much affinity in Raman spectroscopy of surfaces, the discovery of SERS has animated and resurrected the activity in classical electrostatic and
electromagnetic theory, especially as applied to small particles; in the problem of radiating multipoles near metal surfaces, in the optical properties of small particles and in the generation of surface plasmons. It has encouraged the experiments like second-harmonic generation from molecules at surfaces by bringing the general area of surface-photon interactions to the foreground. Theoretical and experimental investigations of the properties of metallic gratings and molecules placed near them has greatly increased due to the continuous interest in SERS. The discovery of SERS has also renewed interest in the properties of aqueous metal sols, a well-established field of science that had fallen on hard times. This renaissance coincided to some extent with a growing interest in non-metal colloids such as those of polymers.

One important new direction in experimental SERS has been the successful union of the Langmuir-Blodgett technique and surface-enhanced spectroscopy. There was a great need in the field of Langmuir-Blodgett (LB) mololayers for a sensitive method for characterization of monolayers and interfaces consisting of LB films. SERS has emerged as a powerful technique for spectroscopic characterization of LB layers [11].

An interesting application of SERS has been recently developed in the field of photographic sciences. Since SERS allows structurally sensitive investigations of adsorbed molecules in very low concentrations, SERS spectra of sensitizing dyes can
be recorded which give information about the chemical structure of these molecules as well as their adsorption behaviour, aggregation and formation of radicals. Moreover, the SERS enhancement factor shows correlations to photographically important properties of silver halide emulsion and of the sensitizing dyes [12, 13].
Reference


