STUDY OF SOME PHYSICAL PHENOMENA ON THE SURFACE OF SOLIDS

THESIS

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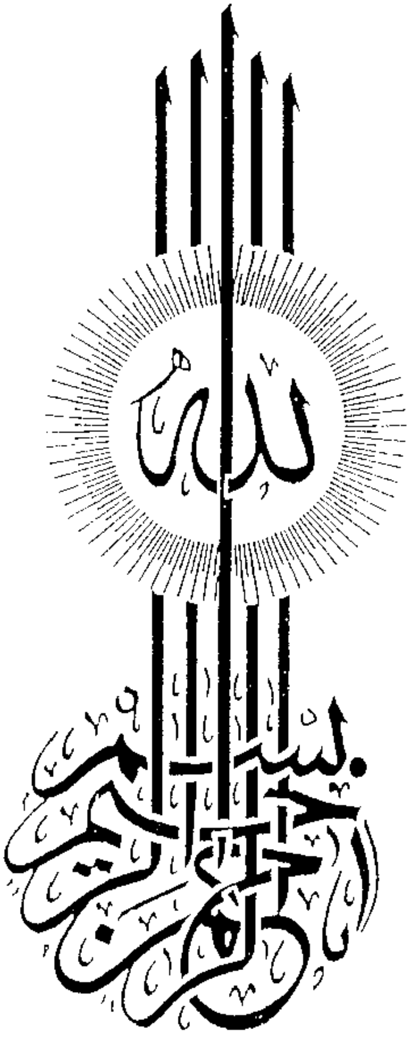
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ABSTRACT

Surface Enhanced Raman Scattering (SERS) of adsorbed molecules of crystal violet (cv) on metal films has been studied. The metal films were silver and gold and of ultrathin thickness to form islands (rough) or of large thickness to form "smooth" surface. The absorption spectra of the bare metal island films as well as the cv coated metal island films were obtained and correlated to the excitation spectra of the surface enhanced Raman vibrational lines. The excitation of the transverse collective electron resonance (localized plasmons), by the incident electromagnetic radiation, has been shown to increase the local field at the adsorbed molecule sites that enhances the absorption and the Raman scattering cross section. The data obtained on the surface enhanced Raman scattering of the adsorbed molecules are in agreement with existing theories of the enhancement phenomena that deal with the nature and structure of the metal substrate and its interaction with adsorbed molecules. We have been able to obtain an estimate of the contribution of the surface roughness to the enhancement process.

CHAPTER I

INTRODUCTION

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INTRODUCTION

Raman spectroscopy has become one of the most valuable tools for the vibrational spectroscopic study of materials particularly after the introduction of lasers. Among other vibrational spectroscopic techniques like infrared transmission(1) or reflection spectroscopy(2), high resolution electron energy loss spectroscopy(3), inelastic electron tunnelling spectroscopy(4), Raman spectroscopy offers several advantages. These include a standard resolution better than 4 cm^{-1}, a free spectral range from about 20-5000 cm^{-1}, and in surface Raman spectroscopy (SRS)(5,6) the possibility to observe adsorbates in situ and at interfaces.

Raman studies are typically performed with laser beams focussed to $5x10^{-3}$ cm^2, for ordinary Raman scattering one usually has something like 10^{15} scattering molecules in the beam cross section. A monolayer on a smooth surface contains on the order of 10^{12} molecules in that area, so the scattered radiation would not be intense enough to be seen. Consequently, it was assumed that it would be impossible to detect the Raman lines in scattering by monolayers and that constituted a major drawback due to the low sensitivity of the method. The difficulty of observing a monolayers were overcome by the discovery in 1977 of surface enhanced Raman scattering (SERS) phenomena where Raman scattering cross section for pyridine molecules adsorbed on Ag electrodes that have been roughened in an electrochemical cell were enhanced by about of factor of 10^6. Since then there has been great research efforts devoted to the study of this phenomena. SERS is not confined to the electrode-electrolyte interface, it has been observed for many molecular species (e.g. pyridine, pyrazine, isonicotinic acid, benzoic acid, etc.) adsorbed on various metals (e.g. Ag, Cu and Au) by various procedures (e.g. electrochemical and chemical deposition from solution, vapour deposition in high vacuum) using continuous and discontinuous (island) evaporated films and colloidal particles or mechanically polished polycrystalline Ag(7). It is generally agreed that the roughness is a necessary condition for SERS.

The current research efforts are aimed to ascertain the macroscopic and microscopic mechanisms responsible for the enormous enhancement in the Raman scattering process. In this thesis we study the enhancement of Raman scattering by molecules adsorbed on metals. We focus our attentions on dye molecules (crystal violet molecules) adsorbed on noble metal island films to elucidate the role of surface roughness and in particular, the role played by the collective electron resonance (e.g. localized plasmons) of the short range structure of the metal island films.

Current theories show that the enhancement of the Raman scattering by molecules adsorbed on metal island films is due to in part to the sizable increase in the effective electric field at the sites of adsorbed molecules when the transverse collective electron resonance is resonantly excited by the incident EM radiation, and in part to the large electric dipole moment for scattered radiation that are induced in the metal islands by the Raman excited molecules.

In this work, we have experimentally investigated these effects on the enhancement of Raman scattering of cv adsorbed on Ag and Au island films. The use of the two metals have allowed us to investigate other theoretical results that indicate the dependence of the enhancement on the nature of the metal substrate, e.g., the imaginary part of the dielectric constant of the metal substrate. Furthermore, we have also studied Raman scattering of adsorbed cv molecules on smooth metal films to obtain an estimates of the contribution of the roughness to the enhancements of the scattering cross section.

In addition, we have studied the optical absorption of our systems in order to farther our understanding of the factors responsible for the enhancement mechanisms.

First, we studied the optical absorption of the bare island film, and then island films coated with the dye monolayers. The data for the bare island films indicate an absorption due to the excitation of the localized plasmons, and the data for the coated films show that the absorption is not simple superposition of the absorption of the island films and the dye due to the interaction of the dye molecules with the metal particles.

The excitation spectra (the variation of the intensity of the surface enhanced Raman vibrational lines with the incident radiation wavelength) show a similar structure to that of the absorption spectra in the region of wavelengths corresponding to the excitation of the transverse collective electron resonance. In addition, there is a large increase in the intensity that correspond to the regular resonance Raman scattering of the molecules.

In Chapter (2), we present a brief review of the existing theoretical models for the enhancement of Raman scattering of molecules adsorbed on metal surfaces.

In Chapter (3), we present the role of surface roughness which includes expressions for the enhancement factors of the incident and scattered radiation fields.

In Chapter (4), the absorption and characteristic of crystal violet are presented.

In Chapter (5), the data on the absorption of the bare island films and the island films coated with the dye molecules as well as a discussion of the interaction of the adsorbate with the metal particles are presented.

In Chapter (6), the spectra for the surface enhanced Raman scattering of the crystal violet adsorbed on glass, metal island films and thick and smooth, Ag and Au films are presented. This is followed by a discussion of the excitation spectra and the effects of the nature of the metal substrate and the cv molecules interaction with the substrate.

In Chapter (7), the concluding remarks of our work are presented.

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CHAPTER 2

THEORETICAL REVIEW

2.1 Raman Scattering Processes

2.2 Surface Enhanced Raman Scattering Processes