Nonlinear Optics at Surfaces and in Composite Materials

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1 Introduction

It is well known that surfaces and interfaces play a very important role, for example in chemistry, biology... In physics, they put a limit on the dimensions of crystals, for example, therefore breaking the translational invariance usually assumed, leading to the existence of surface states. One could cite many more examples. They are used in industrial processes such as mineral extraction or heterogeneous catalysis. They have already been studied for a long time by chemists using sophisticated tools such as electron diffraction [1]. However it is only recently that they entered the nonlinear optical domain.

We will concentrate on two areas and leave aside other active fields such as surface polaritons. First, the presence of interfaces may lead to dramatic effects such as the resonances that are encountered in Surface Enhanced Raman Scattering or in linear properties (the dielectric anomaly) of metal colloids. In this paper, we will arbitrarily consider spontaneous Raman scattering as a nonlinear process on the basis that it is a two photon transition. Secondly, the nonlinear properties of a surface or of an adsorbed molecular monolayer are interesting as such. For example, second harmonic generation has recently proven, as we shall see, to be a powerful tool to study surfaces.

This chapter is organized as follows. In section 2, we will deal with Surface Enhanced Raman Scattering. Section 3 will be devoted to Second Harmonic Generation by surfaces and molecular monolayers and its applications. Finally, in section 4, we will discuss the nonlinear optical properties of composite materials, restricting ourselves to the recent studies of optical phase conjugation in metal colloids and in semiconductor-doped glasses. Although the properties of composite materials are often strongly related to the presence of interfaces between the two-component media, specific models have been developed to explain their properties and the field of nonlinear optics in composite materials will undoubtedly grow in the next years.

2 Surface Enhanced Raman Scattering

2.1 Description of SERS and possible explanations

The Raman spectrum of a molecular monolayer is too weak to be observed under normal conditions. In order to observe it, a ~ 3 orders of magnitude enhancement is needed. In the early 1970's, people were thinking of two possibilities to circumvent this difficulty, (1) increasing the surface area and consequently the number density, (2) utilizing resonant Raman scattering thus increasing the scattering cross section. The first observation of the Raman spectrum of a molecular monolayer (pyridine adsorbed on anodized silver) was reported by Fleishmann, Hendra and McQuillan in 1974 [2]. They believed they had increased the number density by roughening the substrate. The fact that a new effect (SERS) had been discovered was realized independently by Jeanmaire and Van Duyne [3] and Albrecht and Creighton [4] in 1976-77. In fact, the Raman cross section is enhanced by about 6 orders of magnitude in this case.
Fig. 1. Part of a setup with which SERS can be observed. The silver substrate is placed inside an electrolytic cell containing an aqueous KCl solution (0.1 M) and pyridine (0.05 M). SCE is a saturated calomel electrode.

The enhancement phenomenon is fairly easy to observe with the setup shown in fig. 1. A freshly polished silver electrode is immersed in an electrolytic cell together with a platinum counter-electrode and a reference saturated calomel electrode (SCE). The electrolyte is a 0.1 M KCl aqueous solution. One then performs an oxidation - reduction cycle. For example, the silver electrode being first positively polarized, a ~ 500 μA per cm² of electrode current is run. Silver is oxidized according to

$$\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + e^-$$

After 2 minutes, the applied voltage is inverted: silver chloride is then reduced with complete charge recovery

$$\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$$

This oxidation - reduction cycle with a charge transfer of ~ 60 mC/cm² has roughened (anodized) the silver surface. Pyridine is then added to the solution (0.05 mole/liter) and the silver electrode negatively biased in order to have $V_{\text{Ag-SCE}} = -0.6 \text{V}$ where $V_{\text{Ag-SCE}}$ is the measured voltage difference between the silver electrode and the SCE one. An Ar⁺ laser beam (typically 30 mW at $\lambda = 0.5145 \text{ μm}$) is focused on the silver electrode by a cylindrical lens. The laser spot (a narrow vertical line) is imaged onto the entrance slit of a double monochromator equipped with a conventional detection system for Raman spectroscopy. The lines at 1006 and 1037 cm⁻¹ are then readily observable. Several other lines may also be observed. For example, at $V_{\text{Ag-SCE}} = -0.8 \text{V}$, the line at 1215 cm⁻¹ is also very intense. To get an estimate of the enhancement effect, one may shift the silver electrode out of the laser beam. Then, only the pyridine molecules contained in the solution contribute to the Raman signal which is ~ 500 to 1000 times weaker. To sum up, pyridine molecules adsorbed on a rough silver surface have Raman scattering cross sections about 6 orders of magnitude larger than the same molecules dissolved in water. This is, as it was first observed, the new effect now known as SERS.

It was soon realized that many other molecules exhibit the same effect when adsorbed on anodized silver. Other metallic substrates also lead to a similar enhancement, for example, gold and copper in the red part of the spectrum [5]. Most studies have been performed in an electrochemical environment but the effect may be observed under other conditions, for example for pyridine adsorbed on cold and rough silver in a vacuum chamber or for the silver - CN system at room temperature and in ambient air.

When the existence of this new effect was generally accepted, people started thinking about what could be the origin of the enhancement. The surface area increases only by a small factor, on the order of 2 to 3, on roughening. Therefore it is the Raman cross section which is enhanced. In the simple case of an isotropic molecule, the cross section $d\sigma/d\omega$ is given by: