

Invited Review

Recent progress and frontiers in the electromagnetic mechanism of surface-enhanced Raman scattering

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ABSTRACT

The electromagnetic (EM) enhancement of the optical responses of molecules close to plasmonic metal nanostructures has been applied for ultra-sensitive detection in vibrational spectroscopy. Recently, the research fields of EM enhancement entered a new regime wherein the enhancement effects are connected to photochemical and photobiological phenomena. For this regime, the conventional theorem used to understand the EM enhancement effect should be re-examined because the experimental conditions are beyond the assumptions in the theorem. Thus, in this review, we firstly overview and summarize the EM mechanism in surface-enhanced Raman scattering (SERS), which is the most general optical response using an EM enhancement, and determine the limitations and problems of the EM mechanism in SERS. Secondly, we discuss the necessity of re-examining the EM mechanism with respect to three breakdowns of the approximations in Fermi's golden rule: the breakdown of the molecular electronic dynamics by the ultra-fast plasmonic de-excitation, the breakdown of the weak coupling between the plasmon and molecular exciton by strong EM enhancement, and the breakdown of the selection rule of SERS by the field-gradient effect. These breakdowns allow the observation and control of molecular functions that remain hidden by previous spectroscopic methods.

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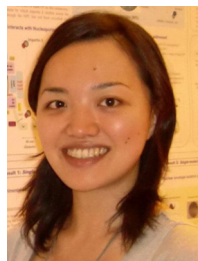
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1. Introduction

Surface-enhanced Raman scattering (SERS) is widely known as an enhancement effect of molecular Raman scattering on a metal surface, particularly plasmonic metals such as silver and gold. Because of the usefulness of SERS, a great number of researchers have exhibited a great zeal to study SERS effects since the technique was discovered. The SERS effect was first detected by Fleischmann et al. in 1974 [1] and correctly interpreted in 1977 by two other groups [2,3]. In these preliminary studies [1–3], electro-chemically roughened silver electrodes were used to amplify the Raman signals from pyridine molecules located on the electrodes. The mechanism of the signal amplification was first ascribed to simple “fractal effects,” i.e., an increase in the effective surface area due to the roughness [4]. However, this hypothesis is clearly interpreted as negative that such a large signal amplification cannot be accounted for by the increase in the surface area alone, and the interaction between the surface plasmon of the roughened metal surfaces and molecules adsorbed was thought to be effective for the signal enhancement [2,3,5,6]. In the late 1990s, a silver colloidal solution was introduced in SERS measurements to achieve a higher enhancement and an enormous amplification of $\sim 10^{10}$, which is sufficient to detect a fluorescent dye, rhodamine 6G (R6G) molecule, at the single-molecule level. This experimental system, called single-molecule SERS (SM-SERS) [7,8], significantly impacted the study of the SERS enhancement mechanism, and helped us to quantitatively understand the fundamentals of SERS.

As the main fundamental of SERS, researchers have discussed two types of SERS enhancement mechanisms: the EM mechanism and chemical enhancement (CE) mechanism [3,9,10]. The EM enhancement, which is caused by the coupling of the incident and Raman EM fields on metallic surfaces with localized surface-plasmon resonances, is thought to be the main contribution in the SERS effect. The CE mechanism is characterized by the shifting of the Raman scattering in non-resonance to that in resonance through the formation of charge transfer complexes between adsorbed molecules and metal surfaces [2,10–15]. Although its existence remains under controversy [4] and its contribution is thought to be far smaller than the EM enhancement, the CE mechanism attracts attention for its potential to achieve plasmonic chemistry, also called “surface plasmon-enhanced photochemical reactions” [16], on the surfaces of plasmonic metal.

In this review article, we focus on the description of the EM mechanism, recent works regarding the mechanism, and future perspectives beyond the EM mechanism. We assume that the readers are familiar with the advanced aspects of SERS spectroscopy, particularly the SERS professionals. In Section 2, we introduce the EM mechanism with a brief history of the discovery of SERS. The recent progresses as well as limitations and problems of the EM mechanism are briefly described. In Section 3, we propose frontiers in the EM mechanism. We connect the EM mechanism to other important research areas, e.g., ultrafast dynamics, strong coupling, and the field-gradient effect by introducing the breakdowns of Fermi’s golden rules. We then conclude this review by showing summary of the EM mechanism.

2. Overview of the electromagnetic mechanism in surface-enhanced Raman scattering

2.1. Brief history of the electromagnetic mechanism study

It is widely accepted that the main origin of SERS enhancement is the EM enhancement effect [4]. Hence, the history of EM enhancement starts at the first moment of the discovery of SERS effect. To the best of our knowledge, the enhancement of the Raman signal on silver nanostructures was first observed by Hendra et al. in 1974, although they did not mention the Raman signal enhancement from a target molecule, pyridine (Fig. 1) [1]. In 1977, Albrecht and Creighton focused on the intense of Raman signal on silver nanostructures using an electrochemical cell similar to Hendra’s and reported the Raman signal enhancement as a new phenomenon (Fig. 2a) [2]. In the same year, Van duyne et al. published a well-organized discussion of the adsorbed pyridine on silver nanostructures (Fig. 2b) [3]. Van duyne et al. also reported in their manuscript that silver nanostructures can yield resonance Raman spectra with a good signal-to-noise ratio, and named the intense of Raman signal as “surface Raman”. In this year, 1977, researchers began attempting to explain the unusual phenomenon of SERS and discussing the EM mechanism of SERS. Moskovits first proposed that the surface roughness of the metal electrode yields an anomalous intensity of the Raman signal and implied that the collective electronic oscillations within a single metal particle, i.e., the plasmon resonance, affect the signal enhancement [5]. In addition, he predicted that the Raman signal enhancement observed in roughened metal electrodes may also occur for colloidal metal particles. This prediction was instantly verified by Creighton et al. using silver and gold hydrosols [17]. After several SERS studies [18–20], one reported that dilute colloidal hydrosols (Fig. 3) [21] exhibit a certain advantage for the SERS study because the system has a critical sensitivity to the signal enhancement: $\sim 10^{10}$ orders of magnitude [22,23]. Note that the highest reported value of the SERS enhancement factor – 10^{14} – represents the product of the EM

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