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A STUDY ON SURFACE-ENHANCED HYPER-RAMAN SCATTERING OF BASIC FUCHSIN ADSORBED ON THE SILVER COLLOID*

PAN DUO-HAI(潘多海)
Department of Physics, Shaanxi Normal University, Xi'an 710062, China

ZHANG PENG-XIANG(张鹏翔)
Institute of Physics, Academia Sinica, Beijing 100080, China

LI XIANG-SHENG(李祥生), MIAO RUN-CAI(苗润才), and HUAN YI-XIAN(郇宜贤)
Department of Physics, Shaanxi Normal University, Xi'an 710062, China

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This paper presents the surface-enhanced hyper-Raman scattering (SEHRS) effect of basic fuchsin (BF) adsorbed on the silver colloid. On the basis of the absorption spectra, a new absorption band at 1000 nm has been observed in the case of BF adsorption on the silver colloid. The result indicates that surface electromagnetic enhancement also appears at the incident photon frequency in the near-IR region, which plays an important role in the SEHRS signals. The electromagnetic enhancement factor (2.0×10^4) is estimated by using electromagnetic model. Additionally, surface-enhanced second-harmonic generation (SHG) effect in the cases of pure silver colloid, silver colloid plus adsorbed molecule and KCl solution has been detected.

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I. INTRODUCTION

Hyper-Raman scattering is a nonlinear optical process involving virtual transitions of two photons from the incident beam (with photon energy $h\nu_0$) and the emission of one photon (with photon energy $h(2\nu_0-\nu_R)$, where ν_R is the molecular vibrational frequency). Its main attraction lies in its particular section rules: all IR-active vibrational modes are hyper-Raman allowed and those modes inactive in both Raman and IR (i.e. the silent modes) may be active in hyper-Raman scattering. As a result, hyper-Raman scattering is capable of providing new vibrational information which is not obtainable from IR and Raman spectroscopy. However, hyper-Raman scattering is intrinsically very weak (10^6 times weaker than Raman). This fact has severely hindered its development into a practical spectroscopic technique[1].

Since the discovery and development of surface-enhanced Raman scattering (SERS), the idea of using surface enhancement to study hyper-Raman scattering has been appealing. The first surface-enhanced hyper-Raman scattering (SEHRS) effect was observed by Murphy[2] in 1981. Because of enormously amplified hyper-Raman cross-section for molecules adsorbed on the roughened silver surface, SEHRS effect has attracted considerable attention.

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Some studies of SEHRS have been carried out for dye molecules in silver colloid[3] and for pyridine on a silver electrode[4]. Recently, Yu and co-workers[5] have reported SEHRS of non-centrosymmetric molecules adsorbed on silver colloid. Their results demonstrate that SEHRS may eventually be developed as a valuable spectroscopic technique. However, the mechanism of surface hyper-Raman scattering enhancement is still incompletely understood, in particular, the importance of surface electromagnetic enhancement in the near-IR region has not been proved both experimentally and theoretically[6].

In this paper, surface-enhanced hyper-Raman scattering and SHG of basic fuchsin (BF) adsorbed on the silver colloid are reported. Furthermore, the influence of surface EM enhancement in the near-IR on the SEHRS signals is discussed. Finally, the enhancement factor of SEHRS is estimated.

II. EXPERIMENTAL

The silver colloid was prepared in the way as described in Ref.[7]. SEHRS and SHG were excited by a Q-switched Nd:YAG laser. The 1.064 μm fundamental output consists of 10 ns pulse width with a repetition rate of 10 Hz and an output energy 3 mJ per pulse. Scattered light was focused into a monochrometer with a photomultiplier tube. The spectra were recorded on a X-Y recorder before being processed by a boxcar averager. An Ar^+ laser was employed to provide a visible excitation for obtaining SERS. The absorption spectrum was detected with a UV-visible spectrophotometer (HITACHI, U-2000).

III. RESULTS AND DISCUSSION

The aqueous solution containing 1 ml of 5×10^{-6} M BF and 0.1 ml of 1.0 M KCl was added to 2 ml of silver colloid. In Fig.1 are shown the SEHRS and SERS spectra of BF adsorbed on the silver colloid. The frequencies of bands and their relative intensities are given in Table 1. In our experiment, the hyper-Raman scattering of bulk BF is not observed, even with high-power excitation and densely concentrated BF solution. It is suggested that the hyper-Raman cross-section of molecule is amplified due to its adsorption on silver surface. The BF molecule has a low symmetry, and for this reason the SEHRS and SERS spectra are similar in relative intensity and frequency (Table 1). On the other hand, we find some important distinctions between the two spectra. In comparison with SERS, the realtive intensities of SEHRS lines of 564, 1298 and 1589 cm^{-1} are clearly changed, and two new bands appear at 1407 and 1706 cm^{-1}. The redistribution of relative intensity is due to different excitations for SEHRS and SERS. BF is widely employed as a biological stain and exhibits an optical absorption maximum at 540 nm (Fig. 2). Therefore, the two photons at 532 nm can show resonance effect for adsorbed molecule, i.e. resonant surface-enhanced

hyper-Raman scattering. According to albrecht's theory[1], the enhancement of signals varies with the frequency of band. This is in agreement with Baranov's report[3]. Although the vibrational assignments for the two new bands have not been made, our preliminary analysis of the SEHRS signals suggests that SEHRS can provide new information about molecular structure.

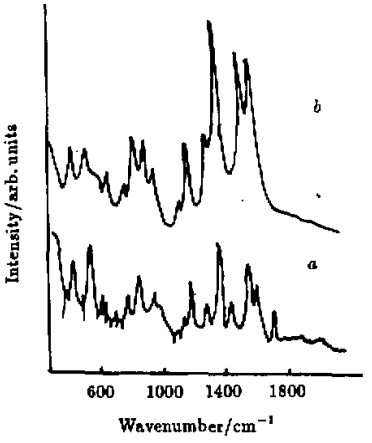

Fig. 1. Surface-enhanced hyper-Raman and surface-enhanced Raman spectra of BF adsorbed on Ag colloid. Curve *a* indicates SEHRS; curve *b* indicates SERS, 488.0 nm/60 mW.

Table 1. Surface-enhanced Raman and hyper-Raman bands/cm^{-1}.

SERS	SEHRS	SERS	SEHRS
420 w	424 w	564 w	564 w
640 w	–	821 w	821 w
908 s	908 m	950 m	956 w
1087 w	–	1175 s	1172 s
1298 m	1292 w	1370 vs	1370 vs
–	1407 w	1520 vs	1518 vs
1589 vs	1582 m	–	1706 w

Notes: w=weak, m=medium, s=strong, vs=very strong.

Surface-enhanced SHG effect of BF in the silver colloid has also been observed (not shown here). The surface-enhanced SHG in silver colloid after addition of BF and KCl is about 200 times as intense as the SHG from pure silver colloid. The result shows that surface-enhanced SHG effect arises not only from the silver particle, but also from molecular specificity. As has been reported previously by Shen[6], the surface nonlinear polarizability may be affected by interactions between molecule and metal surface, which lead to the enhancement of SHG. From the fact we have observed, we conclude that surface-enhanced SHG can also provide a useful probe to study the interactions between molecule and metal surface.

Because hyper-Raman scattering is a nonlinear optical process, the mechanism of enhancement of SEHRS should differ from that of SERS. Let us consider the contribution of local electromagnetic field enhancement. The mathematical expression of EM enhancement factor of SEHRS is given by

$$G = R^2(\nu_0)R(2\nu_0 - 2\nu_R) ,$$

where $R(\nu)$ is the EM amplification factor at the frequency ν. If the resonant conditions at the incident and emitted photon energy are simutaneously satisfied, it predicts a sharp increase of SEHRS intensity.

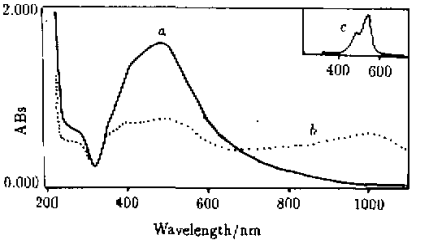

Fig. 2. Absorption spectra. Curves a, b and c indicate the spectra of silver colloid, silver colloid / BF / KCl, and 5×10^{-6} M BF solution, respectively.

Some experiments and calculations showed that excitation wavelength in visible region is required to observe SERS on Ag substrates. We wonder if the EM enhancement exists in the near-IR excitation. In order to obtain further evidence, we measured the absorption spectra of pure silver colloid and BF in the silver colloid (Fig.2). The absorption maximum of silver colloid is at 474 nm. When the silver colloid is mixed with BF and KCl solution (the condition in Fig.1), a new strong absorption band at 1000 nm is detected, which is caused by the aggregation of colloidal particles[9]. In this case a larger value of $R^2(\nu_0)$ at 1.064 μm may be obtained. It is shown that surface EM enhancement in the near-IR excitation also appears under a certain conditon, which is necessary for obtaining SEHRS signal. This conclusion may provide valuable insight into the mechanism of surface-enhanced Fourier transform (FT) Raman scattering in the near-IR region. Another source of enhancement is the EM enhancement at the emitted hyper-Raman photon energies, which is similar to the case of SERS.

To further estimate EM enhancement, we make the assumption of an approximately spherical symmetry at the surface of the colloid particles within aggregates. In what follows, we assume a fixed orientation of molecules with respect to the local surface normal (e.g. edge-on adsorption). Under these conditions, the enhancement of β_{222} component of the hyper polarizability is larger than that of others. This point has been made by Golab *et al.*[4] for pyridine adsorbed to a silver electrode. From EM model[10], the enhancement factor of SEHRS is

$$G = |1 + 2g|^4|1 + 2g'|^2 ,$$

$g = [\varepsilon(\omega_0 - \varepsilon]/[\varepsilon(\omega_0) + \chi\varepsilon_0]$ and $g' = [\varepsilon(\omega_s) - \varepsilon_0]/[\varepsilon(\omega_s) + \chi\varepsilon_0]$, where ε and ε_0 are the dielectric constants of the particle and the ambient medium, respectively, and χ is an adjustable parameter, which is related to the aggregation of silver particles. In our experiment, for

the case that we take χ=19 the plasma resonance is shifted to 1000 nm. Using the data in Ref.[11], we can write $\varepsilon_0 = -58 + 0.6i$, $\varepsilon(\omega_s)$=12.86+0.4i for $\omega_s = 2\omega_0 - 1000\,\mathrm{cm}^{-1}$, and $\varepsilon_0 = 1.77$ is the dielectric constant of water. Substituting the proper values into the equation, we find $G = 2.0 \times 10^4$ and $R^2(\nu_0)/R(2\nu_0 - \nu_R)$=140. It can be seen that surface EM enhancement at the incident photon frequency (1.064 μm) is the major contribution to the observed SEHRS signal intensity.

Furthemore, the existence of the stable surface complex composed of adsorbed molecules, Cl^{-1} ions and Ag atoms may lead to a charge-transfer effect. A further increase in hyper-Raman cross-section is postulated through the chemical effect[9], and the typical estimates are about $10^2 - 10^3$. Considering simultaneously the EM enhancement and chemical effects, we obtain the factor of SEHRS enhancement is about $10^6 - 10^7$. It is comparable to or higher than that of SERS. Interestingly, a surprising large enhancement factor of 10^{13} was determined by Golab and co-workers[4] from the electrode SEHRS. The conclusion is considerably different from ours. This is due to the difference of the surface substrates. Comparison of SEHRS and SERS signals reveals that the enhancement value we have estimated is certainly reasonably.

IV. CONCLUSIONS

In this paper, surface-enhanced hyper-Raman scattering from BF adsorbed on the silver colloid has been observed. Comparing with the SERS spectrum of adsorbed molecule, we find that SEHRS can provide new vibrational information unobtainable by using Raman or SERS method.

With the aid of absorption spectra and EM theory, we have confirmed that the surface EM enhancement at the incident photon frequency in near-IR is the major contribution to the observed SEHRS signals. Combining electromagnetic enhancement and chemical effect leads us to the conclusion that SEHRS enhancement factor is approximately $10^6 - 10^7$.

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REFERENCES

[1] D. A. Long, Raman Spectroscopy (McGraw-Hill, New York, 1977), chap. 8.
[2] D. V. Murphy, K. U. von Raben, R. K. Chang and P. B. Dorain, *Chem. Phys. Lett.*, **45**(1982), 502.
[3] A. V. Baranov and Ya. S. Bobovich, *JETP Lett.*, **36**(1982), 339.
[4] J. T. Golab, J. R. Sprague, K. T. Carron, G. C. Schatz and R. P. Van Duyne, *J. Chem. Phys.*, **88**(1988), 7942.
[5] N. T. Yu, S. Nie and L. A. Lipscomb, *J. Raman Spectrosc.*, **21**(1990), 797.
[6] D. H. Pan, Y. X. Huan and P. X. Zhang, *Physics*, **21**(1992), 344 (in Chinese).
[7] D. H. Pan, Y. X. Huan and P. X. Zhang, *Acta Physica Sinica*, **41**(1992), 1096 (in Chinese).
[8] Y. R. Shen, *J. Van. Soc. Technol.*, **B31**(1985), 1644.
[9] M. Moskovits, *Rev. Mod. Phys.*, **57**(1985), 783.
[10] M. Moskovits, *J. Phys. Chem.*, **88**(1984), 5526.
[11] P. B. Johnson and R. W. Chrity, *Phys. Rev.*, **B6**(1970), 4370.