Available online at www.sciencedirect.com

SCIENCE DIRECT®

Current Applied Physics 6 (2006) 411–414

Current Applied Physics
An official journal of the KPS

www.elsevier.com/locate/cap
www.kps.or.kr

Plasmon resonances of silver colloids studied by surface enhanced Raman spectroscopy

E.C. Le Ru *, M. Dalley, P.G. Etchegoin

The MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences,
Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand

Abstract

It is shown that surface enhanced Raman scattering (SERS) average signals and fluctuations can be used to characterize the spectral dependence of plasmon resonances, and are particularly sensitive to the local fields, as opposed to other optical techniques. SERS can be used to probe both the plasmon resonances and the mechanisms of optical amplification.

PACS: 78.67.−n; 78.20.Bh; 78.67.Bf; 73.20.Mf

Keywords: Surface enhanced Raman spectroscopy; Plasmon; Metallic surfaces; Local field

1. Introduction

Surface enhanced Raman scattering (SERS) [1] can become an analytical tool with many applications. There is renewed interest in SERS for its potential to observe single molecules [2]. Despite this, the mechanisms responsible for SERS are still not fully understood.

The large optical enhancements in SERS are believed to be due to single or collective plasmon resonances. The SERS signal intensity is given by

$$I_{\mathrm{SERS}} = M(\omega_{\mathrm{L}})M(\omega_{\mathrm{R}})I_{\mathrm{RS}}, \tag{1}$$

where I_{RS} is the signal in non-SERS conditions, ω_{L} and ω_{R} are the frequencies of the exciting laser and of the emitted photon, respectively, and $M(\omega)$ is the local field intensity enhancement due to plasmon resonances:

$$M(\omega) = \left|\frac{E_{\mathrm{loc}}(\omega)}{E_0}\right|^2. \tag{2}$$

Plasmon resonances of SERS active media are usually characterized by the optical extinction, although it is very difficult to extract from these measurements in the far-field information about local field enhancements. Near field techniques can be used to probe the local field [3] but are not always applicable.

Here, we show that SERS can be used as a probe of plasmon resonances. In Eq. (1), the SERS signal gives an indirect measurement of the resonance profile. One advantage is that it directly probes the local field at the metallic surface, where the molecules are adsorbed. A potential problem is that the signal usually comes from several molecules with different field enhancements, a situation avoided when single molecule SERS is possible. Also, the measurement is indirect since we measure a convolution at two frequencies. For a typical dye the Raman shifts of the main peaks range from 400 to 1800 cm^{-1} for Stokes (S) processes. To extend this, it is also possible to measure anti-Stokes processes (AS). Finally, it is also possible to look at overtones. Using lasers at 514 and 633 nm, most of the visible wavelengths can then be probed. In this work, we studied SERS from Rhodamine 6G (RH6G) in colloidal silver solutions. The fluctuations of the signal

---

* Corresponding author. Fax: +64 44635237.
E-mail addresses: eric.leru@vuw.ac.nz (E.C. Le Ru), Pablo.Etchegoin@vuw.ac.nz (P.G. Etchegoin).

1567-1739/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cap.2005.11.030

show evidence of underlying plasmon resonances; the average signals enable us to characterize them further. The results are discussed and compared to extinction measurements.

2. Experimental details and results

Ag-colloids were prepared according to Ref. [4] (average diameter: ~50 nm, conc.: ~10^{11} colloids/cm^3). Samples

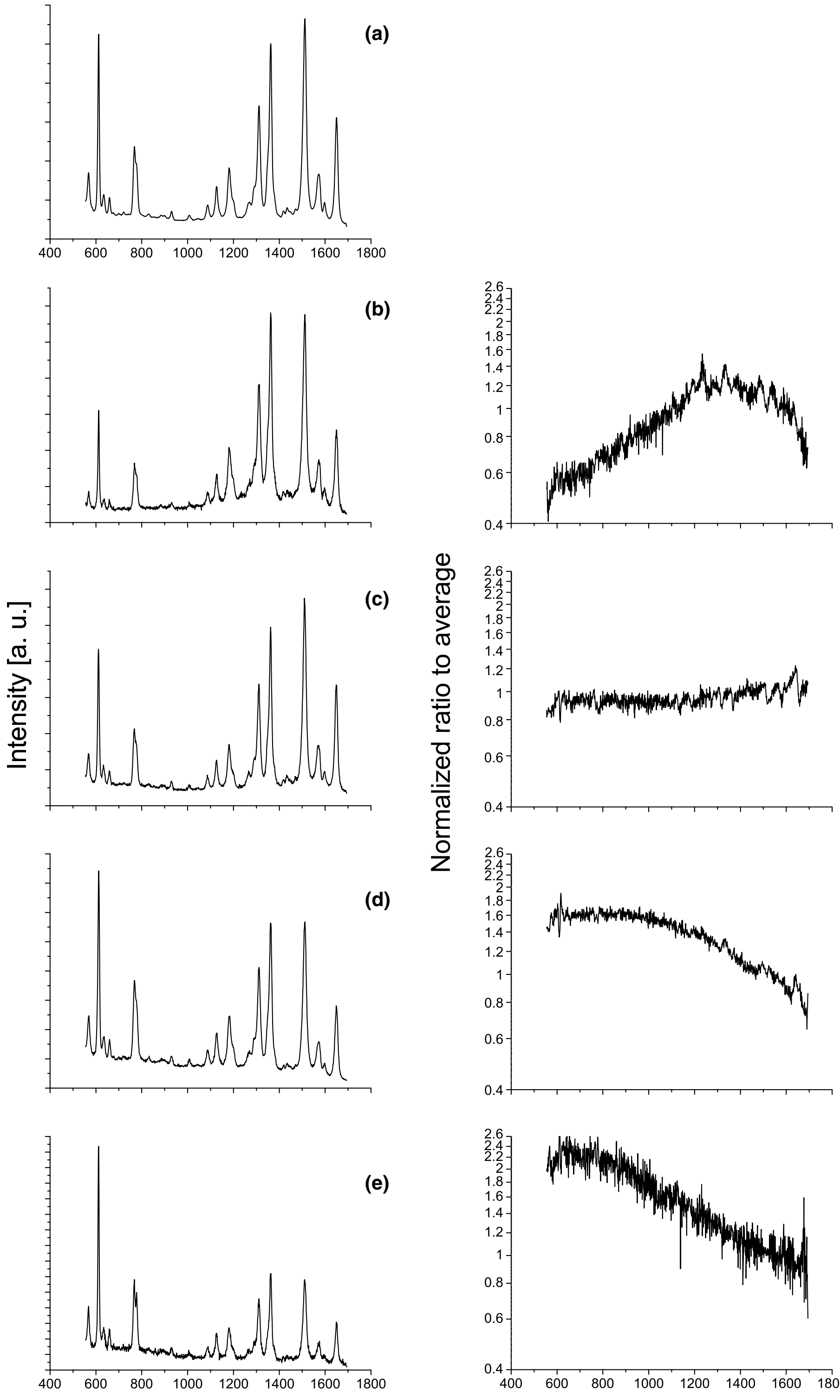

Fig. 1. Fluctuations of the Stokes SERS spectra of RH6G in Ag-colloids. (a) Average signal; (b)–(e) individual events (integration ~50 ms). The right hand side shows the ratio of the signal of these events to the average signal.

were prepared by mixing 0.5 mL of colloids with 0.5 mL of 20 mM KCl (reducing the Coulombic interaction and increasing the occurrence of coupled plasmon resonances). RH6G was added to a final concentration of 200 nM. SERS experiments were performed on a Raman microscope with a ×100 immersion objective. Samples were measured with 633 nm (HeNe) or 514 nm (Ar^+) lasers (2 mW). A strong SERS signal is observed for integration times of 50 ms. The scattering volume contains on average only one or two colloids at a time; they do not have time to diffuse in or out in 50 ms. Each event corresponds to the observation of one particular colloid configuration. Large temporal fluctuations of the signal are observed, reflecting the diversity of colloidal shape, size, configurations, and plasmon resonances. We show in Fig. 1 four individual events, along with the average signal obtained for the Stokes Raman at 633 nm. The SERS signal fluctuates both in the absolute and relative intensities of the peaks [5,6], with an underlying Raman background signal which shows the same fluctuations as the main peaks. In Fig. 1, we also plot for each event the ratio of the intensity over the average vs. Raman shift. The integrated intensities of the spectra have been normalized to give ratios ~1. These ratios show a smooth variation as function of wavelength, suggesting that there are relatively broad resonances which favor different parts of the spectra. The laser is fixed here at 633 nm, and $M(\omega_L)$ is constant for a given event. Also, we observe in each event the average signal from a large number of molecules, ruling out the possibility that the fluctuations are the result of various orientations of the probe. Fluctuations must therefore be a direct result of different $M(\omega_R)$'s with respect to the average, due to different aggregate size, shape, and orientation. The window we probe here is from 653 nm (500 cm^{-1}) to 710 nm (1700 cm^{-1}) and the ratio of intensity between these two extremes can change by a factor of 10 from one event to another (see for example, in Fig. 1b and e). Some events (such as d and e) show stronger enhancements on the low wavelength side, while others (such as b) show the opposite.

Still, we can only infer here changes in $M(\omega)$ with respect to the average. Hereafter, we look at other regions of the spectra to gain information on M vs. λ. To do so, we need to know the expected value of the relative intensity of the peaks (in the absence of a resonance); a very difficult undertaking in general. There is, however, one situation where we know the ratio of these peaks: the Stokes and anti-Stokes processes exhibit the same cross sections and their ratios should only be dictated by temperature. The theoretical AS/S ratio for a given peak of energy E is given by

$$R_{\text{theo}}(E) = \left(\frac{\omega_{AS}}{\omega_S}\right)^4 \exp\left(-\frac{E}{kT}\right), \tag{3}$$

where T is the temperature, k the Boltzmann constant, $\hbar\omega_S = \hbar\omega_L - E$ and $\hbar\omega_{AS} = \hbar\omega_L + E$. The pre-factor here is ~1. In Fig. 2, we plot average AS/S ratios for various peaks for both 633 and 514 nm excitation, with the theoretical value for $T = 300$ and $T = 400$ K. Although heating is possible in both cases, it is unlikely to be more dominant in the 633 nm case. We conclude that the AS/S ratios are higher than expected for 633 nm while they are lower for 514 nm. Such anomalies have been reported before [7–9], and they are another effect of the underlying enhancement factor variation. Taking this into account, we have

$$R = \frac{M(\omega_{AS})}{M(\omega_S)} R_{\text{theo}}. \tag{4}$$

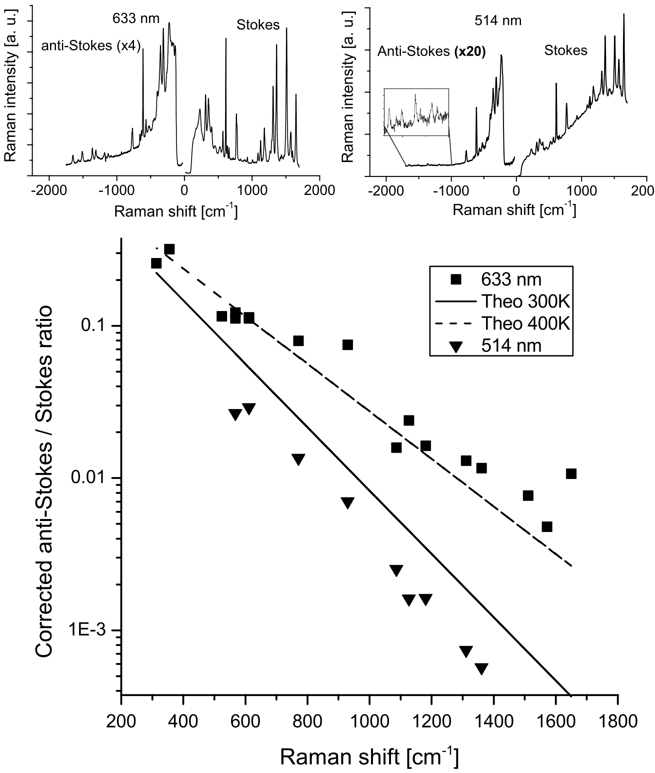

Fig. 2. AS/S ratios of various Raman peaks of RH6G along with the theoretical ratios at 300 and 400 K. Data have been corrected to account for the ω^4 pre-factor (see text). The insets at the top show the spectra at 633 and 514 nm from which the ratios were measured.

We conclude that for 633 nm (514 nm), $M(\omega)$ is larger (smaller) on the AS side, $\lambda < 633$ nm (514 nm) than on the Stokes side, $\lambda > 633$ nm (514 nm); i.e. the maximum of M occurs somewhere in between 514 and 633 nm.

We can probe further this region by looking at the overtones. The average overtone spectra for 514 and 633 nm are shown in Fig. 3; peaks can easily be assigned, except for the 3400 cm^{-1} peak associated with O–H or N–H stretch. The overtones signal is clearly much stronger with 514 nm excitation (spanning the region from around 580 to 620 nm) rather than with 633 nm excitation (where it is beyond 750 nm). This is another confirmation that the average underlying resonance shows a maximum around 580 nm. We note also that anti-Stokes overtone signals are not observed with both lasers.

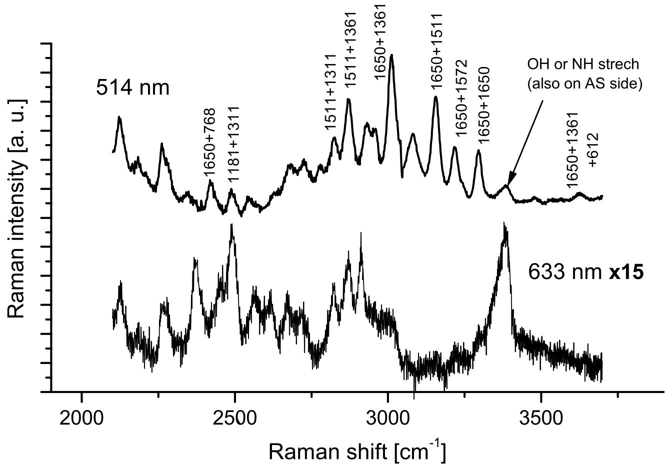

Fig. 3. SERS spectra in the overtones region for 633 and 514 nm excitation. The assignment of some of the peaks to specific overtones is also indicated.

3. Discussion and conclusions

We were able to deduce qualitatively the profile of the average underlying SERS resonance in our colloidal samples with a maximum in the region 550–600 nm. This resonance is broad and shows variation of at most one or two orders of magnitude across the whole visible range. A possible average resonance profile is shown schematically in Fig. 4. In fact, plasmon resonances would be expected to lead to sharper resonances. What we observe is an average resonance; the result of a distribution of much sharper fluctuating resonances. In fact, analyzing the fluctuations for short integration times (such as in Fig. 1) can also shed light on these individual resonances. For example, we observe events of both types (b) and (e) (see Fig. 1) with a large SERS intensity, indicating that there are individual resonances peaking on both sides of the Stokes region at 633 nm. For the 514 nm laser, high intensity events tend to show a higher signal on the high energy peaks (not shown here), indicating that most individual resonances peak at a wavelength longer than the Stokes region for 514 nm.

Interesting is the comparison of this resonance with the extinction spectrum, shown in Fig. 4. The SERS resonance is strongly red-shifted compared to the extinction spectrum. The SERS resonance is sensitive to the local field enhancements and it is not directly visible in the extinction. It also occurs at a longer wavelengths mainly as a result of coupled plasmon resonances. The latter are believed to lead to red-shifted resonances with large local field enhancements. SERS is highly sensitive and a good probe for them. Extinction spectra are dominated by single colloids resonances. Coupled plasmons are better studied by SERS in this respect.

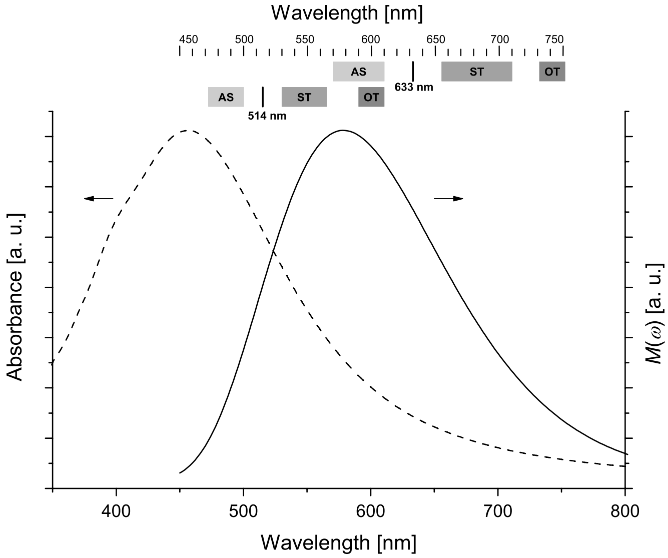

Fig. 4. Schematic of the average resonance profile deduced from SERS measurements (solid line) and measured extinction spectrum (dashed line). The top part shows the position of each Raman window, anti-Stokes (AS), Stokes (ST), and overtones (OT) for 514 and 633 nm excitation.

In closing, we showed that fluctuations of the SERS signals can be used to characterize the distribution of plasmon resonances in colloidal solutions. A careful analysis of the average SERS signals at various excitations enables us to deduce qualitatively the profile of the plasmon resonances contributing to SERS. Our results suggest that this is dominated by coupled plasmon resonances which do not appear in extinction spectra. We believe that this method not only helps to characterize the plasmon resonances, but it is also useful for the understanding of the mechanisms of SERS enhancements.

References

[1] M. Moskovits, Rev. Mod. Phys. 57 (1985) 783.
[2] S. Nie, S.R. Emory, Science 275 (1997) 1102.
[3] P. Zhang, T.L. Haslett, C. Douketis, M. Moskovits, Phys. Rev. B 57 (1998) 15513.
[4] P.C. Lee, D. Meisel, J. Phys. Chem. 86 (1982) 3391.
[5] A. Weiss, G. Haran, J. Phys. Chem. B 105 (2001) 12348.
[6] K.A. Bosnick, J. Jiang, L.E. Brus, J. Phys. Chem. B 106 (2001) 8096.
[7] K. Kneipp, Y. Wang, H. Kneipp, I. Itzkan, R.R. Dasri, M.S. Feld, Phys. Rev. Lett. 76 (1996) 2444.
[8] R.C. Maher, L.F. Cohen, P. Etchegoin, H.J.N. Hartigan, R.J.C. Brown, M.J.T. Milton, J. Chem. Phys. 120 (2004) 11746.
[9] R.C. Maher, M. Dalley, E.C. Le Ru, L.F. Cohen, P.G. Etchegoin, H. Hartigan, R.J.C. Brown, M.J.T. Milton, J. Chem. Phys. 121 (2004) 8901.