

Possible effects of redistributed photon density of states on Raman scattering enhancement in mesoscopic structures

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ABSTRACT

Modification of photon density of states (DOS) is considered as an essential factor of modified Raman scattering in mesoscopic media with complicate spatial dependence of dielectric function on a scale of incident/scattered photon wavelengths. Possible contribution of redistributed photon DOS over frequency spectrum in mesoscopic metal-dielectric structures to surface enhancement of Raman scattering (SERS) by adsorbed molecules is outlined. Considerable growth of DOS for a certain mode increase spontaneous scattering rate to this mode which in turn promotes stimulated Raman scattering to the same mode. Therefore total effect of DOS on scattering rate can be higher than DOS increase in a given mesoscopic medium versus vacuum.

Keywords: mesoscopic structures, low-dimensional systems, Raman scattering, photonic crystals, microcavities, surface enhanced Raman scattering

1. INTRODUCTION

In mesoscopic metal-dielectric structures, molecules adsorbed at rough metal surfaces with characteristic size of metal particles (clusters, islands or rods) in submicrometer range exhibit drastic enhancement of Raman scattering. Surface enhanced Raman scattering (SERS) is known since 1974 and was the subject of extensive research in 80-ies^{1,2}. Recent pioneering works on single molecule detection by means of SERS^{3,4} provided an evidence that local enhancement factor of scattering rate (up to 10^{14} - 10^{15} times) is significantly greater than previously observed ensemble averaged enhancement factor on the order of 10^6 - 10^{10} . These findings did stimulate further experimental studies and discussions aimed at establishing the mechanisms of huge local enhancement factors in SERS⁵⁻⁸. The existing models include two basically different considerations. The first one is "physical" enhancement mechanism whereas the second one is referred to as "chemical" mechanism. Physical mechanism implies redistribution of incident $E(\omega)$ and scattered $E(\omega')$ fields in space over surface in the vicinity of a given molecule adsorbed at metal particle (cluster, island, rod etc.). It results in formation of hot spots where electromagnetic fields $E(\omega)$ and $E(\omega')$ can drastically (up to 10^6) increase as compared to an average field value. In many experiments on SERS not only absolute values of scattered intensity increases but shape of Raman spectrum exhibits differences from that obtained for the same molecules in solutions. In other words, different Raman lines experience different enhancement factors. In a number of cases, new lines appear in SERS spectrum which are not intrinsically inherent in adsorbed molecules. Spectral modifications of Raman signal are usually attributed to chemical mechanisms, i. e. bonding interaction between an adsorbed molecule and surface metal atoms and charge transfer processes between a molecule and metal surface.

In this communication, one more physical mechanism of Raman scattering enhancement and Raman spectrum reshaping is outlined which can contribute significantly both to intensities and relative weights of different Raman lines resulting from intrinsic molecular vibrational states. The mechanism is based on contribution of photon density of states (DOS) to probability of spontaneous Raman scattering. To date modification of *spontaneous emission* of light due to DOS redistribution⁹ is well established and recognized in different mesoscopic structures, namely microcavities¹⁰⁻¹², photonic crystals¹³⁻¹⁸, heterostructures and interfaces¹⁹, dielectric slabs²⁰, biomembranes²¹. However to the author's knowledge

photon DOS effect on spontaneous scattering of light in mesoscopic structures has not been widely recognized to date and has not been involved in the SERS theory.

2. RAMAN SCATTERING IN MEDIA WITH DIFFERENT DIMENSIONALITIES

Consider Raman scattering of light with frequency ω by a molecule in a continuous medium. Probability W of scattering into mode with frequency ω' in terms of the perturbation theory is given by the known formula²²

$$W(\omega, \omega') = \frac{2\pi^2}{\hbar^2} \omega \omega' N(\omega) |S|^2 \left[N(\omega') + \frac{1}{4\pi} \frac{\omega'^2}{2\pi^2 c^3} \right] \quad (1)$$

where $N(\omega)$, $N(\omega')$ are photon numbers with frequencies ω , ω' , S is transition matrix element, and c is speed of light in vacuum. The two terms in this formula determined by the first and the second terms in the brackets correspond to stimulated and spontaneous scattering processes, respectively. The value

$$D_3(\omega) = \frac{\omega'^2}{2\pi^2 c^3} \quad (2)$$

is density of photon states (electromagnetic modes) in a continuous three-dimensional ($3d$) medium per unit frequency interval in a unit volume. Therefore the second term in the square brackets of Eq. (1) is photon density of states in a unit solid angle. Proportionality of spontaneous scattering probability to the density of photon states implies that similar to spontaneous emission spontaneous scattering of light results from stimulated process due to interaction of a molecule with zero electromagnetic (EM) fields (electromagnetic vacuum). Similar to spontaneous emission, modification of spontaneous Raman scattering probability should be expected in a medium other than a continuous $3d$ -medium.

Expression (2) comes from DOS versus wavenumber dependence

$$D_3(k) = \frac{k^2}{2\pi^2} \quad (3)$$

using the relation

$$D(\omega) = D(k) \frac{dk}{d\omega} \quad (4)$$

and the dispersion law for EM-waves in a continuous homogeneous medium

$$\omega(k) = ck / n \quad (5)$$

with refraction index $n = 1$. In cases of $2d$ - and $1d$ -media, the photon DOS versus wavenumber k functions read

$$D_2(k) = \frac{k}{2\pi}, D_1(k) = \frac{1}{\pi} \quad (6)$$

Note that functions $D(k)$ are the same for all classical waves and quantum particles (see, e.g. ref. 23, 24) whereas $D(\omega)$ functions are specific for every wave/particle because of the specific dispersion laws.

For continuous homogeneous $2d$ - and $1d$ -media with $n = 1$ one has

$$D_2(\omega) = \frac{\omega}{2\pi c^2}, D_1(\omega) = \frac{1}{\pi c}. \quad (7)$$

These expressions are to be inserted instead of Eq.(3) in Eq. (1) to calculate Raman scattering probability in homogeneous low-dimensional media. In $2d$ -structures one should also replace solid angle 4π by 2π . In $1d$ -structures 4π should be replaced by 1. Then probability of scattering in $2d$ and $1d$ cases takes the form

$$W_{2d}(\omega, \omega') = \frac{2\pi^2}{\hbar^2} \omega\omega'N(\omega)|S|^2 \left[N(\omega') + \frac{1}{2\pi} \frac{\omega'}{2\pi c^2} \right], \quad (8)$$

$$W_{1d}(\omega, \omega') = \frac{2\pi^2}{\hbar^2} \omega\omega'N(\omega)|S|^2 \left[N(\omega') + \frac{1}{\pi c} \right]. \quad (9)$$

Note, that in a medium with refractive index different from $n = 1$, a substitution $c \rightarrow c/n$ is to be made in Eqs. (1), (8), (9).

These examples show that in continuous dielectric media photon density of states effect results in dependence of scattering rate upon dimensionality and refractive index of a medium. Note that for low-dimensional structures in the limit of small $N(\omega')$ values the known relation $W(\omega, \omega') \propto \omega^4$ which holds if $\omega - \omega' \ll \omega$ is no longer valid. One has $W_{2d}(\omega, \omega') \propto \omega^3$ and $W_{1d}(\omega, \omega') \propto \omega^2$ relations instead.

3. RAMAN SCATTERING IN PHOTONIC CRYSTALS AND MICROCAVITIES

In a medium other than a continuous one, a molecule will interact with EM-vacuum with probability determined by the *local* density of photon states in the vicinity of a molecule position. In this case to get $W(\omega, \omega')$ value local DOS is to be calculated explicitly. In a mesoscopic structure possessing inhomogeneity of dielectric function (and of refractive index) on a scale comparable to photon wavelengths the local density of states is a complicate function of frequency and coordinate. According to the sum rule derived by Barnett and Loudon^{25,26}, photon density of states redistributes within frequency spectrum, the total integral DOS being constant.

To illustrate the DOS effect on Raman scattering consider simple cases of mesoscopic structures with known behavior of $D(\omega)$ for photons. In media with *periodic variation* of n value in space (so called "*photonic crystals*") a dip in $D(\omega)$ in the band gap region coexists with enhanced $D(\omega)$ values outside the gap (see, e.g. ref. 17,27 and refs. therein). Therefore, in a photonic crystal spontaneous Raman scattering should be inhibited for frequencies within the gap and enhanced in the ranges adjacent to the gap region. In dielectric structures with three-dimensional periodicity of n with materials available to date only incomplete angular dependent band gap develops^{17,28}. In this case spontaneous Raman scattering intensity will redistribute both over frequency and over solid angle in proportion to DOS redistribution. In three-dimensional mesoscopic structures with two-dimensional photonic band gap in x - y -plane, spontaneous Raman scattering will be inhibited along directions normal to z -axis but enhanced in the direction along z -axis. For a multilayer stack, an analytical solution for DOS has been derived²⁷. Simple analysis showed that in dielectric structures relative variation of $D(\omega)$ by about 2 orders of the magnitude occurs. It is expected to be even higher in metal-dielectric structures. This example shows that photonic band gap structures can be purposefully used for Raman scattering enhancement by means of frequency and angular redistribution of spontaneous scattering probabilities.

In *microcavities* and Fabry–Perot interferometers photon DOS concentrates in resonant modes. In these structures, spontaneous scattering into resonant modes becomes more favorable. The only experiment on systematic observation of cavity DOS on Raman scattering has been reported recently by Hennrich *et al*²⁹. Probably, photon DOS effect did manifest itself in the other recent experiments though it has not been discussed and identified because of the other factors involved, namely metal fractal effects⁵ and porosity³⁰.

4. POSSIBLE DOS EFFECTS IN SURFACE ENHANCED RAMAN SCATTERING

It is clear from the above consideration that in SERS-active metal-dielectric structures with complicate topology (fractal clusters, island films, granular structures of coinage metals) exhibiting drastic redistribution of EM-field in space photon DOS will redistribute as well. This will result in angular and frequency redistribution of Raman scattering rates. Not only increase of the term related to DOS in Eq.(1) will contribute to higher SERS probability. Increase in scattered photon number $N(\omega')$ due to the DOS term will in its turn stimulate Raman scattering described by the term proportional to $N(\omega')$. For this reason absolute value of SERS enhancement factor due to the DOS effect will be greater than DOS enhancement. A kind of internal feedback and instability may develop with stimulated scattering initiated by enlarged spontaneous scattering rate. Therefore "hot spots" can develop at the surface not only with respect to field amplitudes but with respect to DOS and scattering rates as well.

Though explicit quantitative analysis of DOS effect in SERS-active metal-dielectric structures remains for further studies, two comments are worth to be stated on SERS understanding and applications. First, photon DOS effect can (at least partially) contribute to the giant local enhancement of Raman scattering reported for single molecule experiments^{3,4,7,8}. Stimulated scattering promoted by high spontaneous scattering rate can be the reason of superlinear intensity dependence of Raman scattering recently observed for single molecules by Brus with coworkers³¹. Second, in the view of the above discussion reshaping of Raman spectra in SERS experiments as compared to ordinary Raman spectra of the same molecules does not necessarily originate from chemical bonding and charge transfer states at molecule-metal interface. Reshaping may result from photon DOS redistribution. Therefore in many instances, even reshaped Raman spectra if containing only intrinsic vibrational lines, can give true insight at molecular structure and should not be ignored in analytical applications.

5. CONCLUSION

In conclusion, the role of modified photon density of states in Raman scattering in mesoscopic low-dimensional and heterogeneous structures is outlined and its possible contribution to giant enhancement of Raman scattering probabilities in metal-dielectric structures and to Raman spectra reshaping is discussed. The consideration is believed to stimulate experiments aimed at establishing of photon density of states effects in model mesoscopic structures for which photon density of states is well known, e.g. in photonic crystals and microcavities.

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