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Effects of photon density of states on Raman scattering in mesoscopic structures

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Photon density of states (DOS) effects on spontaneous Raman scattering in certain mesoscopic structures are outlined. Similar to spontaneous emission spontaneous Raman scattering should experience modification if DOS redistribution over frequency and solid angle occurs. In continuous media DOS dependence on dimensionality $d=3,2,1$ results in different power dependencies of scattering rate on refraction index n and frequency ω in the form $(n\omega)^d$. Photon DOS effects can be purposefully used to enhance Raman signals in molecular spectroscopy using purely dielectric structures.

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Spontaneous emission and scattering of light is not an intrinsic property of atoms, molecules, clusters, nanocrystals, and macroscopic solids but is essentially a result of their interaction with zero electromagnetic fields (electromagnetic vacuum). Therefore the probability of spontaneous photon emission/scattering for a given frequency is directly proportional to the density of electromagnetic modes [photon density of states (DOS)] at this frequency. In a mesoscopic structure with dielectric properties varying on a photon wavelength scale, photon DOS modifies resulting in modification of spontaneous emission probability and radiative lifetime of a given quantum system with respect to a dielectrically homogenous space. Since the prediction by Purcell[1] the role of photon DOS effects on *spontaneous emission* of light has been recognized and established in different mesoscopic structures, namely, microcavities,[2–4] photonic crystals,[5–9] metal-dielectric interfaces,[10] refractive media,[11] dielectric slabs,[12] and biomembranes.[13] However, to the author's best knowledge, possible photon DOS effects on *spontaneous Raman scattering* of light have not been considered to date in spite of the wide research on Raman scattering of molecules adsorbed at complicated interfaces. In this paper, the effect of photon DOS on spontaneous Raman scattering is outlined and considered with respect to a few model dielectric mesoscopic structures for which spectral distribution of photon DOS has been examined.

Consider Raman scattering of light with frequency ω' by a molecule in a continuous medium. Probability W of scattering into a mode with frequency ω in terms of the perturbation theory is given by the known formula[14]

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

where $N(\omega'),N(\omega)$ are photon numbers with frequencies ω',ω; S is a transition matrix element; and $D(\omega)$ is the density of photon states, i.e., a number of electromagnetic modes in a unit volume in the frequency interval $(\omega,\omega+d\omega)$. 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 latter process has the probability proportional to $D(\omega)/4\pi$ where the coefficient $1/4\pi$ means the photon DOS is calculated per unit solid angle. In a vacuum one has

$$D(\omega)=\frac{\omega^2}{2\pi^2c^3} \tag{2}$$

with c being the speed of light in vacuum. In a medium other than three-dimensional (3D) space with dielectric permittivity $\varepsilon=1$ the photon DOS function is to be calculated explicitly to give the correct spontaneous Raman-scattering probability.

Consider a few simple cases starting from continuous media with different material parameters and geometry. Expression (2) comes from DOS versus wave number dependence $D_3(k)$ inherent in a 3D space,

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

using the relation

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

and the dispersion law for electromagnetic (EM) waves in a continuous homogeneous medium $\omega(k)=ck/n$ with refraction index $n=1$. This means the Raman-scattering rate should modify even in the case of a homogeneous 3D medium if the latter possesses a finite dielectric permittivity. One can see that in this case the $W(\omega',\omega)$ value for spontaneous scattering appears to be proportional to n^3, i.e.,

$$W(\omega',\omega)=\frac{1}{\hbar^2}\omega' N(\omega')|S|^2\frac{1}{4\pi}\frac{\omega^3}{c^3}n^3. \tag{5}$$

Equation (5) can be easily verified experimentally if a spontaneous Raman signal from the same molecules is detected using a number of different solutions provided the values influencing the transition matrix element remain constant. However, to the author's knowledge no systematic experiment of this type has been reported to date in spite of a wide routine application of Raman spectroscopy in molecular science.

Photon DOS can be explicitly calculated in continuous media with lower dimensionality, such as, e.g., very thin dielectric slabs or very fine dielectric wires. In cases of ideal 2D and 1D media, the photon DOS versus wave number k read

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

Note that functions $D_i(k)$ are the same for all classical waves and quantum particles (see, e.g., Refs. 15 and 16) whereas $D_i(\omega)$ functions are specific for every wave/particle because of the specific dispersion laws.

For continuous homogeneous 2D and 1D media with $n=\text{const}$ one has

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

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

$$W_2(\omega',\omega)=\frac{1}{\hbar^2}\omega' N(\omega')|S|^2\frac{1}{2}\frac{\omega^2 n^2}{c^2}, \tag{8}$$

$$W_1(\omega',\omega)=\frac{2\pi}{\hbar^2}\omega' N(\omega')|S|^2\frac{\omega n}{c}. \tag{9}$$

These examples show that in continuous dielectric media photon DOS effects result from dependence of scattering rate upon dimensionality and refractive index of a medium. Note that for low-dimensional structures the known relation $W(\omega',\omega)\propto\omega^4$ which holds if $\omega-\omega'\ll\omega$ is no longer valid. One has $W_2(\omega',\omega)\propto\omega^3$ and $W_1(\omega',\omega)\propto\omega^2$ relations instead. Generally, in low-dimensional structures with dimensionality $d=1,2,3$ a dependence of scattering rate on refraction index n and frequency ω can be written in the form

$$W(\omega',\omega,n,d)\propto\omega'(n\omega)^d, \tag{10}$$

which reads $W\propto\omega^{d+1}n^d$ when $\omega-\omega'\ll\omega$ which is valid for typical experiments in the optical range. Schematics of DOS functions in continuous three- and two-dimensional media with various refraction indices are displayed in Fig. 1.

In a medium other than a continuous one, a molecule (or another object containing large number of atoms but small in size as compared to photon wavelengths, e.g., a semiconductor nanoparticle, or quantum dot) will interact with an EM vacuum with probability determined by the *local* density of photon states in the vicinity of a molecule position. In this case to get a $W(\omega',\omega)$ value the local DOS is to be calculated explicitly. In a mesoscopic structure possessing inhomogeneity of a dielectric function on a scale comparable to photon wavelengths the local density of states is a complicated function of frequency and coordinate. According to the sum rule derived by Barnett and Loudon,[17] photon density of states redistributes within the frequency spectrum, the total integral DOS being constant. To illustrate the DOS effect on Raman scattering in heterogeneous structures consider the two cases of mesoscopic structures for which photon DOS behavior is qualitatively understood. The first example refers to a medium with periodic variation of the n value in space (so-called *photonic crystals*). In this case a dip in $D(\omega)$ in the band-gap region coexists with enhanced $D(\omega)$ values outside the gap as shown by dashed lines in Fig. 1 (see, e.g., Refs. 9, 18, and 19, and references 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 an incomplete angular-dependent band gap develops.[9] 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 a two-dimensional photonic band gap in the x-y plane, spontaneous Raman scattering will be inhibited in the x-y plane but enhanced in the direction along the z axis as shown schematically in Fig. 2. This is the case of porous structures with periodically arranged columnar pores, such as, e.g., porous alumina obtained by electrochemical etching of aluminum. Recently reported enhancement of luminescence of various probes in such structures[20] is an indicative hint to search for Raman enhancement in the same structures. For a multilayer dielectric stack an analytical solution for DOS has been derived.[19] Simple analysis showed that in dielectric multilayer structures relative variation of $D(\omega)$ by about two orders of 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 redistributions of spontaneous scattering probabilities.

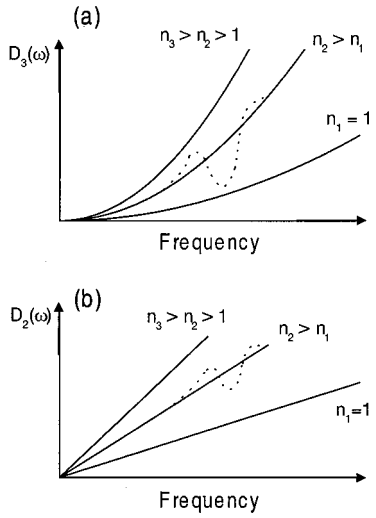

FIG. 1. Density of photon states in (a) three-dimensional and (b) two-dimensional space. Solid lines correspond to continuous media with various refraction indices. Dashed lines show redistribution of density of states in photonic band-gap structures.

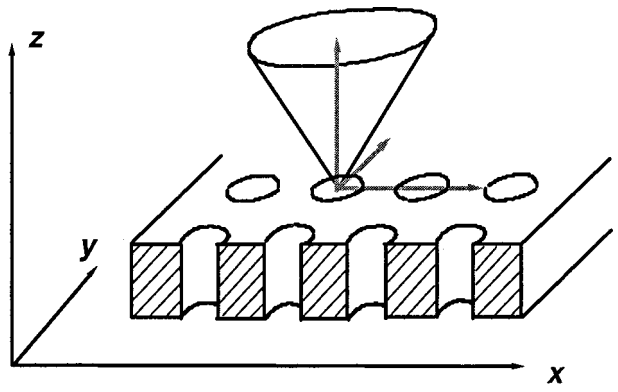

FIG. 2. Possible observation of Raman-scattering enhancement due to photon density of states in a purely dielectric structure. A slab of porous dielectric with regular pores forms a photonic band gap in the *x*-*y* plane with subsequent inhibition of spontaneous scattering within this plane and solid angles adjacent to the plane. At the same time scattering into solid angles adjacent to the *z* axis are expected to show enhancement because of angular redistribution of photon density of states.

The second example relates to microcavities. In spherical and planar microcavities as well as in Fabry-Perot interferometers photon DOS concentrates in resonant modes. In these structures, spontaneous scattering into resonant modes becomes more favorable. As far as we know, though enhanced Raman scattering into resonant cavity modes was known for microdroplets since 1975,[21–24] to the author's knowledge it has not been recognized as a particular manifestation of the general DOS effect and no extension to other mesoscopic structures has been outlined. Probably, a photon DOS effect did manifest itself in the recent experiments[25] though it is hard to be identified unambiguously because of the metal fractal effects involved.

The above examples illustrate photon DOS effects on spontaneous Raman scattering in dielectric structures. It is reasonable to make two comments concerning possible DOS effects in strong Raman-scattering enhancement [so-called surface-enhanced Raman scattering (SERS)] observed in metal-dielectric structures such as island films, etched electrodes, and colloidal aggregates.[26] First, in SERS-active metal-dielectric structures with complicated topology resulting in drastic redistribution of EM field in space, photon DOS will redistribute as well. This will result in angular and frequency redistributions of Raman-scattering rates. DOS redistribution may readily occur in periodic metal nanostructures which were reported to exhibit superior enhancement of Raman signals of molecules adsorbed thereon.[27,28] Second, a combination of DOS enhancement mechanisms in porous dielectric structures with overall SERS effects in the presence of metal nanocolloids can be purposefully used in challenging experiments of single molecule detection by means of Raman spectroscopy.[29]

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 experimental manifestations are discussed. The consideration is hoped to stimulate experiments aimed at establishing 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. The effects can be purposefully used to enhance Raman signals in molecular spectroscopy using purely dielectric structures, thus avoiding charge-transfer processes inherent in metal-dielectric substrates.

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