Incoherent subharmonic light scattering in isotropic media


Laboratory for High Intensity Optics, Shanghai Institute of Optics and Fine Mechanics,
Chinese Academy of Sciences, Shanghai 201800, PR China

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Abstract

Incoherent subharmonic light scattering in isotropic media is a new kind of nonlinear light scattering, which involves single input photon and multiple output photons of equal frequency. We investigate theoretically the dependence of the subharmonic scattering intensity on the hyperpolarizability of molecules and the incident intensity using nonlinear optics theory similar to that used for Hyper-Rayleigh scattering and degenerate optical parametric oscillators. It is derived that the subharmonic scattering intensities grow exponentially or superexponentially with the hyperpolarizability of molecules and the incident intensity.

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1. Introduction

Light scattering arises when the electric susceptibility of a medium varies in time or in space or both [1]. Linear light scattering involves individual input and output photons, which is governed by the linear electric susceptibility $\chi^{(1)}$. Nonlinear light scattering involves multiple photons, which is governed by the nonlinear electric susceptibility $\chi^{(N)}$. The scattering is coherent while the light emitted from different points in the medium interferes constructively. The scattering is incoherent while the light interferes randomly. Among the well-investigated coherent nonlinear light scattering, there are second harmonic generation (SHG) [2] where two input photons of frequency $\omega$ are composite to give one output photon of frequency $2\omega$, and degenerate optical parametric oscillators (DOPO) [3,4] where a single input photon of frequency $\omega$ splits into two or more photons of equal frequency $\omega/n$ ($n \geq 2$). Both SHG and DOPO are intensively investigated experimentally and theoretically. They play an important role in the generation of new laser spectral lines. With two or more input photons of frequency $\omega$ composing one single output photon of frequency $n\omega$, similar to coherent harmonic generation, the incoherent harmonic light scattering, which is known as Hyper-Rayleigh scattering (HRS), received an in-depth study in the past 40 years both experimentally and theoretically [5–15]. HRS was first detected from H$_2$O, CCl$_4$, and fused quartz by Terhune et al. [5], and further studied by Klays and Persoons [7] to determine the first hyperpolarizability $\beta$ of nonlinear optical molecules. HRS technique now becomes the most popular manner to accurately get the first hyperpolarizability $\beta$ of organic molecules [7,8] and inorganic nanomaterials including semiconductors [11] and metals [12,13].

Up to now, incoherent nonlinear subharmonic scattering (subharmonic scattering, SHS) is still a strange concept, which involves single input photon of frequency $\omega$ and multiple output photons of equal frequency $\omega/n$ ($n \geq 2$) and bears an analogy with DOPO. The nonlinear scattering generated in the solution containing Ag nanoparticles by resonant excitations was investigated experimentally by Jiang et al. [16,17]. In the conducted experiments, a resonant excitation of wavelength $\lambda$ may result in a nonlinear scattering peak at wavelength $\lambda/2$ or $2\lambda$, which namely is HRS or second subharmonic scattering. However, the nonlinear optics description similar to that used for HRS has not been constructed for SHS so far. Compared with well-investigated incoherent HRS and coherent nonlinear scattering, incoherent SHS is still lacking in elementary investigations.

In this work, we investigate theoretically incoherent SHS in isotropic media. We formulate the dependence of the scattering...
tering intensity on the hyperpolarizability of molecules and the incident intensity using the classical nonlinear optics theory similar to that used for HRS and DOPO. The technique for detecting the generation of incoherent SHS is discussed.

2. Theoretical description

In the intense incident field, the induced dipole moment for a single molecule can be expanded as a power series of the inducing optical field strength \( E \) [2],

\[
p_i = a_0 E_1 + \beta_{ikl} E_i E_j E_k E_l + \cdots ,
\]

where \( a_0 \) is the component of the linear polarizability tensor \( \alpha \), \( \beta_{ikl} \) is the \( ikl \) component of the first hyperpolarizability tensor \( \beta \), which determines the second-order optical nonlinearity, \( \gamma_{ijkl} \) is the \( ijkl \) component of the second hyperpolarizability tensor \( \gamma \), which determines the third-order optical nonlinearity. A repeated subscript implies summation over the three components.

For the second-subharmonic scattering (SSHS) signal, i.e., \( \omega_s = \omega/2 \) (\( \omega_i \) and \( \omega \) are the frequency of the scattered wave and incident wave, respectively), the Fourier amplitude of the induced dipole moment for a single molecule at \( \omega/2 \) is then

\[
p_s(\omega_i, \omega) = \beta_{ikl} (\omega_i - \omega/2) E_i E_k E_l(\omega/2).
\]

Considering the resemble between SHS and DOPO, we derive the dependence of the scattering intensity on the hyperpolarizability of molecules and the incident intensity in a similar way to that used for DOPO [3]. The difference between the theory for coherent DOPO and incoherent SHS is that, in the coherent scattering the electric-field vector component of SHS in different directions and different molecules are interfering, while in the incoherent scattering it is that the scattered intensities of SHS in different directions and different molecules are adding simply. In the usual slowly varying envelope and a small signal approximation, the non-linear coupling equation takes the form

\[
\frac{dE(\omega/2)}{dt} = g_2 E(\omega) E^*(\omega/2),
\]

where

\[
g_2 = g_2(\omega_i - \omega/2) \exp(-ik_s \Delta K) f_{\text{loc}}(\omega, \omega/2),
\]

\( k_s \) is a wave vector from an arbitrary origin to a fixed point in the scattering unit. Where \( E(\omega/2) \) and \( E(\omega) \) are the electric-field phasor components of the subharmonic and fundamental waves, respectively. \( k_s(\omega/2) \) and \( K(\omega) \) are the modulus of the wave vector corresponding to the subharmonic and fundamental waves, respectively. \( \Delta K = 2K(\omega/2) - K(\omega) \). \( \theta \) is the angle between \( k_s \) and \( E(\omega) \). \( f_{\text{loc}}(\omega, \omega/2) \) contains the local-field corrections.

For further investigation in the following section, we express the incident and scattering waves in the form

\[
E(\omega_i) = A(\omega_i) \exp[i\Phi_\omega(\omega_i)],
\]

\[
E(\omega_i) = A(\omega) \exp[i\Phi_\omega(\omega_i)],
\]

where \( A(\omega_i) \) and \( A(\omega) \) are the amplitudes of the SHS and incident waves, respectively. \( \Phi_\omega(\omega_i) \) and \( \Phi_\omega(\omega) \) are their respective phases. Substituting the above two equations into Eq. (2), we obtain

\[
\frac{dA(\omega_i)}{dt} = g_2^* A(\omega_i) A(\omega) \exp[i\Phi_\omega(\omega_i)],
\]

where \( g_2^* \) is the corresponding constant. \( g_2^* = g_2 \exp[i\Phi_\omega - 2\Phi_\omega(\omega_i)] \). We get

\[
A(\omega_i) = c_2 \exp[G_2 \beta A(\omega)],
\]

where \( c_2 \) is the initial noise level, \( G_2 = \int dk_s g_2^* \).

An isotropic medium consists of a large number of randomly oriented molecules. Assuming the molecules in the scattering volume are completely independent, the total intensity is proportional to the sum of the intensity scattered by the individual molecules. Considering a time average over the period of incident radiation, the SSHS intensity \( I(\omega_i/2) \) is of the form

\[
I(\omega_i/2) = N \int \frac{d\Omega}{4\pi} |A(\omega)|^2 \exp[iK(\omega_i/2) - K(\omega)],
\]

where \( \Omega \) denotes the solid angles of the molecule. \( C \) is a proportionality constant containing the initial noise level and geometrical factors. \( N \) is the number density of sample molecules. \( \beta_{\text{SSHS}} \) is the average first hyperpolarizability for isotropic media which is transformed from \( \beta \) by averaging the products of the direction cosines over all directions [18]. \( K_s \) contains \( G_2 \) and the averages of the products of the direction cosines. \( I(\omega) \) denotes the incident intensity. In the processing of Eq. (5), we take the light intensity equal to the square of the electric amplitude, which neglects constant coefficients but does not change the final expressions formally.

Eq. (5) shows that the SSHS intensity grows exponentially with \( \beta_{\text{SSHS}} \) and \( \sqrt{\rho_0} \), which is different from the dependence for HRS where the HRS intensity grows quadratically with \( \beta_{\text{SSHS}} \) and \( I(\omega) \).

For the third-subharmonic scattering (TSHS), i.e., \( \omega_s = \omega^3 \), the Fourier amplitude of the induced dipole moment for a single molecule at \( \omega/3 \) is of the form

\[
p(\omega/3) = g_3^* E(\omega) E(\omega)^* E(\omega^3/4).
\]

Similar to SSHS, we obtain

\[
\frac{dE(\omega/3)}{dt} = g_3^* E(\omega) E(\omega)^* E(\omega^3/4).
\]
where

\[ g_3 = \sin \theta \frac{\hbar (\omega/3)^3}{2} \exp(-i \omega K) f_n \left( \omega, \frac{\omega}{3} \right). \]

Introducing phases and amplitudes as

\[ E(\omega) = A(\omega) \exp(i \phi_3), \]

Then from Eq. (6) we get

\[ \frac{dI(\omega/3)}{d\omega} = g_3 \gamma_3 A(\omega) A^* \left( \frac{\omega}{3} \right), \]  
(7)

where \( g_3 = g_3 \exp(i \phi_3 - 3 \phi_3) \). Then

\[ A \left( \frac{\omega}{3} \right) = \frac{1}{\{1/c_3\} - G_3 Y_3}, \]  
(8)

where \( c_3 \) is the initial noise level, \( G_3 = \int \omega g_3^3. \) Thus,

\[ I \left( \frac{\omega}{3} \right) = N \int_2^\omega d\Omega \mathcal{A}^2 \left( \frac{\omega}{3} \right) \]  

\[ = CnN \left[ \frac{1}{c_3} - K_3 \gamma_3 N \hbar \sqrt{\frac{\Omega}{\omega}} \right]^{2/3} \]  
(9)

\( \gamma_3 N \) is the average second hyperpolarizability for isotropic media which is transformed from \( \chi^0 \) by averaging the products of the direction cosines over all directions. \( C_3 \) is a proportionality constant containing geometrical factors. \( K_3 \) contains \( G_3 \) and the averages of the products of the direction cosines.

In conclusion, we have first investigated incoherent SHS by using classical nonlinear optics theory. The dependence of the SHS intensity on the hyperpolarizability of optical molecules and incident intensity has been derived. It is found that the subharmonic scattering intensities grow exponentially or superexponentially with the hyperpolarizability of molecules and the incident intensity.

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References


