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Nonstationary CARS by Polaritons

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Abstract

One of the significant problems of molecular spectroscopy is the determination and detailed analysis of how molecular vibrations are dephased. The dephasing of infrared-active (IR-active) vibrations of molecules was investigated by IR absorption spectroscopy. Pulse methods were used to investigate IR-vibrations as well. These methods revealed such coherent nonstationary effects as optical nutation, damping of the free polarization, photon echo, etc. New means of studying dephasing processes were uncovered by the method of nonstationary (time-domain) coherent anti-Stokes Raman scattering (CARS) spectroscopy. However, there are some aspects of CARS that still are not fully covered. One of them is related to Raman scattering by polaritons in dipole-active crystals whereas the second one is the increase of efficiency of CARS (minimization of the wave mismatch, the relationship between pulse width and the relaxation time, etc.). The purpose of the present research to study the case of "extreme" coherency between all interacting pulses (the duration of each pulse is smaller than characteristic times and those pulses are traveling with the same speed) in dipole-active crystals. In this research, we analyzed the process of simultaneous propagation of three waves (anti-Stokes, Stokes, and the pump) under CARS by polaritons. We have found some solutions modeling such simultaneous propagation. We also found the expression for the gain factor for such scattering. The gain factor was evaluated under the assumption of a given stationary pump field. It was shown that the typical values of the relative intensities were consistent with the experimental results.

Keywords

Coherent Anti-Stokes Raman Scattering, Spectroscopy, Polaritons, Stimulated Raman Scattering

1. Introduction

Maker and Terhune were first who demonstrated the CARS technique [1]. In [1] was also shown that the efficiency of the CARS generation is the function of the third-order susceptibilities which were extensively studied in the experiments of the nonlinear properties of solids and liquids [2] [3] [4]. Since then CARS spectroscopy has become a powerful technique in many fields of knowledge such as physics, biology, chemistry, healthcare, etc. [5] [6] [7] [8] [9]. The CARS imaging proved its efficiency in cancer diagnosis as well [10] [11]. Begley *et al.* were among the researches who summarized the important advantages of vibrational spectroscopy based on nonlinear anti-Stokes generation [12] [13] [14]. This technique went to the next level when the ultrashort laser pulses resulted in the possibility of the coherent excitation of multiple Raman modes [15] [16] [17]. For example, the method of nonstationary (time-domain) CARS spectroscopy permitted direct observation of vibration dephasing in an ensemble of atoms or molecules or even in the simplest system-molecular hydrogen [18]. The further increase in efficiency would result from simultaneous propagation in the medium of all interacting waves. In [19] [20] [21] we considered the cases of Raman scattering by polaritons in dipole-active crystals. In this paper, we considered the theoretical modeling of the processes of nonstationary CARS by polaritons in dipole-active crystals.

2. Basic Principles and Equations

In this paper, we consider the nonlinear interaction of four electromagnetic waves: anti-Stokes, Stokes, pump (laser), and polariton. Those waves are assumed to be linearly polarized plane waves. It is also assumed that the nonlinear medium takes a form of a layer bounded by the planes $z = 0$ and $z = L$. The pump wave

$$\vec{E}_l(\vec{r},t) = \hat{e}_l A_l(z,t)\exp\left[i\left(k_l^z z - \omega_l t\right)\right] + c.c. \tag{1}$$

propagates along the z-axis. The subscripts a, l, s, and p denote the anti-Stokes, pump (laser), Stokes, and polariton wave fields, $\omega_{a,l,s,p}$ are the frequencies, $n_{a,l,s,p}$ and $\vec{k}_{a,l,s,p}$ are the refractive indices and the wave vectors in the unpumped medium, and $\hat{e}_{a,l,s,p}$ are the real unit vectors of electromagnetic fields. The nonlinear medium is assumed to be nonmagnetic and transparent at the frequencies $\omega_{a,l,s}$. We use the anti-Stokes, Stokes, and polariton fields in the form

$$\vec{E}_a(\vec{r},t) = \hat{e}_a A_a(z,t)\exp\left[i\left(k_a^z z - \omega_a t\right)\right] + c.c., \tag{2}$$

$$\vec{E}_s(\vec{r},t) = \hat{e}_s A_s(z,t)\exp\left[i\left(k_s^z z - \omega_s t\right)\right] + c.c., \tag{3}$$

$$\vec{E}_p(\vec{r},t) = \hat{e}_p A_p(z,t)\exp\left[i\left(W^z z - \omega_p t\right)\right] + c.c., \tag{4}$$

where $k_{a,s} = q_{a,s} n_{a,s}$; $q_{a,s} = \omega_{a,s}/c$; $W^z = k_l^z - k_s^z$; $\omega_p = \omega_l - \omega_s$.

In the process of CARS, the nonlinear interaction of two electromagnetic waves $\omega_{l,s}$ results in the generation of anti-Stokes and polariton waves. The system of shortened equations for the amplitudes $A_{a,l,s,p}$ is obtained from Maxwell's equations by using the standard approximation of slowly-varying amplitudes [22] and takes the form

$$\frac{\partial A_a}{\partial z}+\frac{1}{v_a^z}\frac{\partial A_a}{\partial t}=i\frac{2\pi\omega_a}{cn_a\cos\left(\theta_a^z\right)}\left\{\chi_a A_l A_p \mathrm{e}^{i\Delta k^z z}+\gamma_a\left(\left|A_l\right|^2+\left|A_s\right|^2\right)A_a\right\}, \tag{5}$$

$$\frac{\partial A_l}{\partial z}+\frac{1}{v_l^z}\frac{\partial A_l}{\partial t}=i\frac{2\pi\omega_l}{cn_l\cos\left(\theta_l^z\right)}\left\{\chi_{l1}A_s A_p+\chi_{l2}A_a A_p^* \mathrm{e}^{-i\Delta k^z z}\right\}, \tag{6}$$

$$\frac{\partial A_s}{\partial z}+\frac{1}{v_s^z}\frac{\partial A_s}{\partial t}=i\frac{2\pi\omega_s}{cn_s\cos\left(\theta_s^z\right)}\left\{\chi_s A_l A_p^*+\gamma_s\left(\left|A_l\right|^2+\left|A_s\right|^2\right)A_s\right\}, \tag{7}$$

$$\frac{\partial A_p^*}{\partial z}+\frac{1}{v_p^z}\frac{\partial A_p^*}{\partial t}=i\frac{q_p^2\varepsilon_p^\infty}{2W^z}\left(\frac{W^2}{q_p^2\varepsilon_p^\infty}-1\right)A_p^*-i\frac{2\pi q_p^2}{W^z}\left\{\chi_{p1}A_l^*A_s+\chi_{p2}A_a^*A_l\mathrm{e}^{i\Delta k^z z}\right\}, \tag{8}$$

where $\chi_a,\chi_{l1,l2},\chi_s,\chi_{p1,p2},\gamma_{a,s}$ are the corresponding tensor contractions of non-resonance quadratic and cubic nonlinear polarizabilities with unit vectors of polarization of interacting waves; e_p^∞ is the non-resonance part of dielectric permeability at frequency ω_p; $v_{a,l,s,p}^z$ are z-components of velocities of waves on $\omega_{a,l,s,p}$; $\Delta k^z\equiv k_l^z+W^z-k_a^z$ is the wave mismatch between the pump, polariton, and anti-Stokes waves.

Given the strong polariton absorption we have [23]

$$\left|\frac{\partial A_p^*}{\partial z}\right|\approx\left|\frac{1}{v_p^z}\frac{\partial A_p^*}{\partial t}\right|\ll\frac{q_p^2\varepsilon_p^\infty}{2W^z}\left(\frac{W^2}{q_p^2\varepsilon_p^\infty}-1\right)A_p^*, \tag{9}$$

so that we can neglect in (8) the terms with the derivatives after which this equation yields

$$A_p^*=\frac{4\pi q_p^2}{\left(W^2-q_p^2\varepsilon_p^\infty\right)}\left(\chi_{p1}A_l^*A_s+\chi_{p2}A_a^*A_l\mathrm{e}^{i\Delta k^z z}\right). \tag{10}$$

If we insert the obtained expression for the amplitude of polariton wave in (5)-(6), we get a system of 3 differential equations for $A_{a,l,s}$ as follows:

$$\frac{\partial A_a}{\partial z}+\frac{1}{v_a^z}\frac{\partial A_a}{\partial t}=i\frac{2\pi\omega_a}{cn_a\cos\left(\theta_a^z\right)}\left\{\frac{4\pi q_p^2\chi_a\chi_{p1}^*}{\left(W^2-q_p^2\varepsilon_p^\infty\right)}A_l^2A_s^*\mathrm{e}^{i\Delta k^z z}+\gamma_{a1}\left|A_l\right|^2A_a+\gamma_a\left|A_s\right|^2A_a\right\}, \tag{11}$$

$$\begin{aligned}\frac{\partial A_l}{\partial z}+\frac{1}{v_l^z}\frac{\partial A_l}{\partial t}=i\frac{2\pi\omega_l}{cn_l\cos\left(\theta_l^z\right)}&\left\{\frac{4\pi q_p^2\left(\chi_{l1}\chi_{p2}^*+\chi_{l2}\chi_{p1}\right)}{\left(W^2-q_p^2\varepsilon_p^\infty\right)}A_aA_l^*A_s\mathrm{e}^{-i\Delta k^z z}\right.\\&\left.+\frac{4\pi q_p^2\chi_{l2}\chi_{p2}}{\left(W^2-q_p^2\varepsilon_p^\infty\right)}\left|A_a\right|^2A_l+\gamma_{l1}\left|A_s\right|^2A_l+\gamma_l\left|A_l\right|^2A_l\right\},\end{aligned} \tag{12}$$

$$\frac{\partial A_s}{\partial z}+\frac{1}{v_s^z}\frac{\partial A_s}{\partial t}=i\frac{2\pi\omega_s}{cn_s\cos\left(\theta_s^z\right)}\left\{\frac{4\pi q_p^2\chi_s\chi_{p2}}{\left(W^2-q_p^2\varepsilon_p^\infty\right)}A_l^2A_a^*\mathrm{e}^{i\Delta k^z z}+\gamma_{s1}\left|A_l\right|^2A_s+\gamma_s\left|A_s\right|^2A_s\right\}, \tag{13}$$

where $q_p \equiv \omega_p / c$, $\gamma_{a1} \equiv \gamma_a + \frac{4\pi q_p^2 \chi_a \chi_{p2}^*}{\left(W^2 - q_p^2 \varepsilon_p^\infty\right)}$, $\gamma_{s1} \equiv \gamma_s + \frac{4\pi q_p^2 \chi_s \chi_{p1}}{\left(W^2 - q_p^2 \varepsilon_p^\infty\right)}$, and $\gamma_{l1} \equiv \gamma_l + \frac{4\pi q_p^2 \chi_{l1} \chi_{p1}^*}{\left(W^2 - q_p^2 \varepsilon_p^\infty\right)}$.

The system (11)-(13) can be simplified if we use new variables

$$A'_a \equiv A_a \mathrm{e}^{-\frac{i\Delta k^z z}{2}} \tag{14}$$

and $$A'_s \equiv A_s \mathrm{e}^{-\frac{i\Delta k^z z}{2}}. \tag{15}$$

The system (11)-(13) in terms of $A'_{a,s}$ can be written as follows:

$$\begin{aligned} &\frac{\partial A'_a}{\partial z} + \frac{1}{v_a^z}\frac{\partial A'_a}{\partial t} + \frac{i\Delta k^z}{2} A'_a \\ &= i\frac{2\pi\omega_a}{cn_a \cos\left(\theta_a^z\right)}\left\{\frac{4\pi q_p^2 \chi_a \chi_{p1}^*}{\left(W^2 - q_p^2 \varepsilon_p^\infty\right)} A_l^2 A_s'^* + \gamma_{a1}\left|A_l\right|^2 A'_a + \gamma_a \left|A_s\right|^2 A'_a\right\}, \end{aligned} \tag{16}$$

$$\begin{aligned} \frac{\partial A_l}{\partial z} + \frac{1}{v_l^z}\frac{\partial A_l}{\partial t} = i\frac{2\pi\omega_l}{cn_l \cos\left(\theta_l^z\right)} &\left\{\frac{4\pi q_p^2\left(\chi_{l1}\chi_{p2}^* + \chi_{l2}\chi_{p1}\right)}{\left(W^2 - q_p^2 \varepsilon_p^\infty\right)} A'_a A'_s A_l^* \right. \\ &\left. + \gamma_{l1}\left|A'_s\right|^2 A_l + \gamma_l \left|A_l\right|^2 A_l + \frac{4\pi q_p^2 \chi_{l2}\chi_{p2}}{\left(W^2 - q_p^2 \varepsilon_p^\infty\right)}\left|A'_a\right|^2 A_l\right\}, \end{aligned} \tag{17}$$

$$\begin{aligned} &\frac{\partial A'_s}{\partial z} + \frac{1}{v_s^z}\frac{\partial A'_s}{\partial t} + \frac{i\Delta k^z}{2} A'_s \\ &= i\frac{2\pi\omega_s}{cn_s \cos\left(\theta_s^z\right)}\left\{\frac{4\pi q_p^2 \chi_s \chi_{p2}}{\left(W^2 - q_p^2 \varepsilon_p^\infty\right)} A_l^2 A_a'^* + \gamma_{s1}\left|A_l\right|^2 A'_s + \gamma_s \left|A'_s\right|^2 A'_s\right\}. \end{aligned} \tag{18}$$

And, finally, if we assume a "week" wave mismatch at Stokes and anti-Stokes frequencies, that is

$$\left|\frac{\partial A'_{a,s}}{\partial z} + \frac{1}{v_{a,s}^z}\frac{\partial A'_{a,s}}{\partial t}\right| \gg \frac{\Delta k^z}{2} A'_{a,s}, \tag{19}$$

then the final system of equations simulating CARS can be expressed as

$$\begin{aligned} &\frac{\partial A'_a}{\partial z} + \frac{1}{v_a^z}\frac{\partial A'_a}{\partial t} \\ &= i\frac{2\pi\omega_a}{cn_a \cos\left(\theta_a^z\right)}\left\{\frac{4\pi q_p^2 \chi_a \chi_{p1}^*}{\left(W^2 - q_p^2 \varepsilon_p^\infty\right)} A_l^2 A_s'^* + \gamma_{a1}\left|A_l\right|^2 A'_a + \gamma_a \left|A'_s\right|^2 A'_a\right\}, \end{aligned} \tag{20}$$

$$\begin{aligned} \frac{\partial A_l}{\partial z} + \frac{1}{v_l^z}\frac{\partial A_l}{\partial t} = i\frac{2\pi\omega_l}{cn_l \cos\left(\theta_l^z\right)} &\left\{\frac{4\pi q_p^2\left(\chi_{l1}\chi_{p2}^* + \chi_{l2}\chi_{p1}\right)}{\left(W^2 - q_p^2 \varepsilon_p^\infty\right)} A'_a A'_s A_l^* \right. \\ &\left. + \frac{4\pi q_p^2 \chi_{l2}\chi_{p2}}{\left(W^2 - q_p^2 \varepsilon_p^\infty\right)}\left|A'_a\right|^2 A_l + \gamma_{l1}\left|A'_s\right|^2 A_l + \gamma_l \left|A_l\right|^2 A_l\right\}, \end{aligned} \tag{21}$$

$$\frac{\partial A_s'}{\partial z}+\frac{1}{v_s^z}\frac{\partial A_s'}{\partial t}$$
$$=i\frac{2\pi\omega_s}{cn_s\cos\left(\theta_s^z\right)}\left\{\frac{4\pi q_p^2\chi_s\chi_{p2}}{\left(W^2-q_p^2\varepsilon_p^\infty\right)}A_l^2A_a'^*+\gamma_{s1}\left|A_l\right|^2A_s'+\gamma_s\left|A_s'\right|^2A_s'\right\}. \tag{22}$$

3. Asymptotic Solutions in a Form of Simultaneously Propagating Waves at Frequencies $\omega_{a,l,s}$

Since we will conduct the numerical analysis of the system (20)-(22) we bring it to unitless form first. To do that we multiply both the left and right part of each equation by the factor z_0/A_0 (A_0 and τ_0 are the peak amplitude and characteristic duration of the pump, $z_0=c\tau_0$). After that, the system (20)-(22) can be reduced to

$$\frac{\partial\tilde{A}_a'}{\partial\tilde{z}}+\frac{1}{\tilde{v}_a^z}\frac{\partial\tilde{A}_a'}{\partial\tilde{t}}=i\left\{C_{a1}\tilde{A}_l^2\tilde{A}_s'^*+C_{a2}\left|\tilde{A}_l\right|^2\tilde{A}_a'+C_{a3}\left|\tilde{A}_s'\right|^2\tilde{A}_a'\right\}, \tag{23}$$

$$\frac{\partial\tilde{A}_l}{\partial\tilde{z}}+\frac{1}{\tilde{v}_l^z}\frac{\partial\tilde{A}_l}{\partial\tilde{t}}=i\left\{C_{l1}\tilde{A}_a'\tilde{A}_s'\tilde{A}_l^*+C_{l2}\left|\tilde{A}_s'\right|^2\tilde{A}_l+C_{l3}\left|\tilde{A}_l\right|^2\tilde{A}_l+C_{l4}\left|\tilde{A}_a'\right|^2\tilde{A}_l\right\}, \tag{24}$$

$$\frac{\partial\tilde{A}_s'}{\partial\tilde{z}}+\frac{1}{\tilde{v}_s^z}\frac{\partial\tilde{A}_s'}{\partial\tilde{t}}=i\left\{C_{s1}\tilde{A}_l^2\tilde{A}_a'^*+C_{s2}\left|\tilde{A}_l\right|^2\tilde{A}_s'+C_{s3}\left|\tilde{A}_s'\right|^2\tilde{A}_s'\right\}, \tag{25}$$

where $\tilde{A}_{a,s}'\equiv\frac{A_{a,s}'}{A_0}$, $\tilde{A}_l\equiv\frac{A_l}{A_0}$, $\tilde{t}\equiv\frac{t}{\tau_0}$, $C_{a1}\equiv\frac{2\pi\omega_a z_0}{cn_a\cos\left(\theta_a^z\right)}\frac{4\pi q_p^2\chi_a\chi_{p1}^*A_0^2}{\left(W^2-q_p^2\varepsilon_p^\infty\right)}$,

$$C_{a2}\equiv\frac{2\pi\omega_a z_0}{cn_a\cos\left(\theta_a^z\right)}\gamma_{a1}A_0^2,\quad C_{a3}\equiv\frac{2\pi\omega_0 z_0}{cn_a\cos\left(\theta_a^z\right)}\gamma_aA_0^2,\quad C_{l2}\equiv\frac{2\pi\omega_l z_0}{cn_l\cos\left(\theta_l^z\right)}\gamma_{l1}A_0^2,$$

$$C_{l3}\equiv\frac{2\pi\omega_l z_0}{cn_l\cos\left(\theta_l^z\right)}\gamma_lA_0^2,\quad C_{l1}\equiv\frac{2\pi\omega_l z_0}{cn_l\cos\left(\theta_l^z\right)}\frac{4\pi q_p^2\left(\chi_{l1}\chi_{p2}^*+\chi_{l2}\chi_{p1}\right)A_0^2}{\left(W^2-q_p^2\varepsilon_p^\infty\right)},$$

$$C_{l4}\equiv\frac{2\pi\omega_l z_0}{cn_l\cos\left(\theta_l^z\right)}\frac{4\pi q_p^2\chi_{l2}\chi_{p2}A_0^2}{\left(W^2-q_p^2\varepsilon_p^\infty\right)},\quad C_{s1}\equiv\frac{2\pi\omega_s z_0}{cn_s\cos\left(\theta_s^z\right)}\frac{4\pi q_p^2\chi_s\chi_{p2}A_0^2}{\left(W^2-q_p^2\varepsilon_p^\infty\right)},$$

$$C_{s2}\equiv\frac{2\pi\omega_s z_0}{cn_s\cos\left(\theta_s^z\right)}\gamma_{s1}A_0^2,\quad C_{s3}\equiv\frac{2\pi\omega_s z_0}{cn_s\cos\left(\theta_s^z\right)}\gamma_sA_0^2.$$

We are looking for stationary solutions as

$$\tilde{A}_{a,s}'\left(\tilde{z},\tilde{t}\right)\equiv B_{a,s}\left(\tilde{\xi}\right)e^{i\Phi_{a,s}\left(\tilde{\xi}\right)}\ \text{and}\ \tilde{A}_l\left(\tilde{z},\tilde{t}\right)\equiv B_l\left(\tilde{\xi}\right)e^{i\Phi_l\left(\tilde{\xi}\right)}, \tag{26}$$

where $\tilde{\xi}\equiv\tilde{t}-\tilde{z}/\tilde{v}^z$; $\tilde{v}^z$ is the velocity of simultaneously propagating waves at the frequencies $\omega_{a,l,s}$; $B_{a,l,s}$ and $\Phi_{a,l,s}$ are the real amplitudes and phases of the waves, respectively. Such a standard procedure of presenting the complex amplitudes of waves in terms of real and imaginary parts results in duplication of the system of (23)-(25):

$$\frac{\mathrm{d}B_a}{\mathrm{d}\tilde{\xi}}=-\kappa_aC_{a1}B_l^2B_s\sin\left(\Phi\right), \tag{27}$$

$$\frac{\mathrm{d}\Phi_a}{\mathrm{d}\tilde{\xi}} = \kappa_a \left\{ C_{a1} \frac{B_l^2 B_s}{B_a} \cos(\Phi) + C_{a2} B_l^2 + C_{a3} B_s^2 \right\}, \tag{28}$$

$$\frac{\mathrm{d}B_l}{\mathrm{d}\tilde{\xi}} = \kappa_l C_{l1} B_a B_s B_l \sin(\Phi), \tag{29}$$

$$\frac{\mathrm{d}\Phi_l}{\mathrm{d}\tilde{\xi}} = \kappa_l \left\{ C_{l1} B_a B_s \cos(\Phi) + C_{l2} B_s^2 + C_{l3} B_l^2 + C_{l4} B_a^2 \right\}, \tag{30}$$

$$\frac{\mathrm{d}B_s}{\mathrm{d}\tilde{\xi}} = -\kappa_s C_{s1} B_l^2 B_a \sin(\Phi), \tag{31}$$

$$\frac{\mathrm{d}\Phi_s}{\mathrm{d}\tilde{\xi}} = \kappa_s \left\{ C_{s1} \frac{B_l^2 B_a}{B_s} \cos(\Phi) + C_{s2} B_l^2 + C_{s3} B_s^2 \right\}, \tag{32}$$

where $\kappa_{a.s.l} \equiv v_{a,s,l}^z v^z \big/ \left(v^z - v_{a,s,l}^z\right)$, $\Phi \equiv 2\Phi_l - \Phi_s - \Phi_a$.

If we introduce the amplitude of simultaneously propagated waves as

$$Q \equiv -\frac{B_a^2}{\kappa_a C_{a1}} = -\frac{B_s^2}{\kappa_s C_{s1}} = \frac{B_l^2}{\kappa_l C_{l1}} \tag{33}$$

we could reduce the system above to

$$\frac{\mathrm{d}Q}{\mathrm{d}\tilde{\xi}} = \alpha Q^2 \sin(\Phi), \tag{34}$$

$$\frac{\mathrm{d}\Phi}{\mathrm{d}\tilde{\xi}} = 2\alpha Q \cos(\Phi) + \beta Q, \tag{35}$$

where

$$\begin{aligned} &\lambda_a^2 = -\kappa_a C_{a1},\ \lambda_l^2 = \kappa_l C_{l1},\ \lambda_s^2 = -\kappa_s C_{s1},\ \alpha \equiv 2\lambda_a \lambda_s \lambda_l^2, \\ &\beta \equiv 2\kappa_l \left(C_{l2}\lambda_s^2 + C_{l3}\lambda_l^2 + C_{l4}\lambda_a^2\right) - \kappa_s \left(C_{s2}\lambda_l^2 + C_{s3}\lambda_s^2\right) - \kappa_a \left(C_{a2}\lambda_l^2 + C_{a3}\lambda_s^2\right). \end{aligned} \tag{36}$$

The system (34)-(35) can be further simplified as follows

$$\frac{\mathrm{d}Q}{\mathrm{d}x} = Q^2 \sin(\Phi), \tag{37}$$

$$\frac{\mathrm{d}\Phi}{\mathrm{d}x} = Q\left(2\cos(\Phi) + \tilde{\beta}\right), \tag{38}$$

where $x \equiv \tilde{\xi}\alpha$, $\tilde{\beta} = \dfrac{\beta}{\alpha}$.

We can reduce the number of equations by using the integral of motion

$$Q = \frac{1}{\sqrt{2\cos(\Phi) + \tilde{\beta}}}, \tag{39}$$

where $Q > 0$, $\tilde{\beta} > 2$.

If we express the phase Φ as the function of Q in (37) we get

$$\int \frac{\mathrm{d}Q}{\sqrt{\left(4 - \tilde{\beta}^2\right)Q^4 + 2\tilde{\beta}Q^2 - 1}} = \frac{1}{2}x \tag{40}$$

The integral on the left can be found as follows:

$$\int \frac{\mathrm{d}Q}{\sqrt{\left(4-\tilde{\beta}^2\right)Q^4+2\tilde{\beta}Q^2-1}} = -\left(i\sqrt{\left(1-\left(\tilde{\beta}-2\right)Q^2\right)\left(1-\left(\tilde{\beta}+2\right)Q^2\right)}\right.$$
$$\left.\times F\left(i\sinh^{-1}\left(\sqrt{\left(2-\tilde{\beta}\right)}Q\left|\frac{\tilde{\beta}-2}{\tilde{\beta}+2}\right.\right)\right)\right)\Big/\sqrt{\left(2-\tilde{\beta}\right)\left(\left(4-\tilde{\beta}^2\right)Q^4+2\tilde{\beta}Q^2-1\right)}, \tag{41}$$

where $F\left(\tilde{x}|m\right)$ is the elliptic integral of the first kind with the parameter $m=k^2$, $\sinh^{-1}\left(\tilde{x}\right)$ is the inverse hyperbolic sine function.

In Figure 1 it is shown that the solution of (37) and (38) exists in the form of pulses. The duration of those pulses can be easily evaluated as follows: first, we assume, that $C_{a1}\approx C_{s1}\approx C_{l1}\approx C$ (in the next topic it is shown that $g\approx C$ where g is the gain factor of Raman scattering) so that the coefficient $\alpha=\lambda_a\lambda_l^2\lambda_s\approx C^2\approx g^2$. The typical values of the gain factor in crystals are of order 10^{-3} cm/MW [24]. Hence, if we consider the pump of the intensity of 10^2 - 10^3 MW and $z=1\,\mathrm{cm}$, then $g\approx 1$.

4. Gain Factor *g*

To show that the system of Equations (5)-(8) is consistent with experimental results for CARS by polaritons we consider the stationary solutions of the coupled wave equations in the constant pump approximation. The system for Stokes and anti-Stokes (20), (22) under the above suggestions can be expressed as

$$\frac{\partial\tilde{A}_s}{\partial\tilde{z}}=iC_{s1}\tilde{A}_a^*\mathrm{e}^{i\Delta k^z z} \tag{42}$$

$$\frac{\partial\tilde{A}_a^*}{\partial\tilde{z}}=-iC_{a1}\tilde{A}_s\mathrm{e}^{-i\Delta k^z z} \tag{43}$$

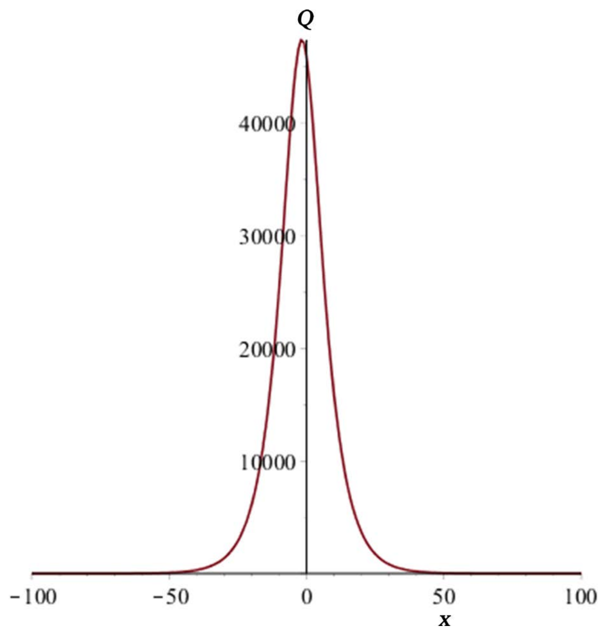

Figure 1. Q versus x.

After introducing new variables

$$F_s \equiv \tilde{A}_s e^{-i\Delta k^z z/2} \quad \text{and} \quad F_a^* \equiv \tilde{A}_a^* e^{i\Delta k^z z/2} \tag{44}$$

the system of differential equations of the first order can be readily transformed to the single differential equation of the second order (for example, for $F_s(z)$) as

$$\frac{\partial^2 F_s}{\partial z^2} + \left(\frac{\Delta k^z}{2}\right)^2 F_s = C_{a1} C_{s1} F_s. \tag{45}$$

We solve this equation by adopting a trial solution for F_s in the form

$$F_s(z) = F_s(0) e^{gz} \tag{46}$$

where g represents a gain factor. Then we substitute (46) into (45) to obtain the approximate value for g as

$$g \approx (C_{a1} C_{s1})^{\frac{1}{2}} \approx C \tag{47}$$

(here we assumed that the pump was strong enough to provide $C_{a1} C_{s1} \gg \left(\frac{\Delta k^z}{2}\right)^2$).

Finally, the expression for g can be reduced to

$$g \approx C \approx 8\pi^2 \omega z_0 \chi^2 A_0^2 / (cn) \tag{48}$$

$$\left(g \approx (C_{a1} C_{s1})^{\frac{1}{2}} = \left(\frac{2\pi\omega_a z_0}{cn_a \cos(\theta_a^z)} \frac{4\pi q_p^2 \chi_a \chi_{p1}^* A_0^2}{(W^2 - q_p^2 \varepsilon_p^\infty)} \frac{2\pi\omega_s z_0}{cn_s \cos(\theta_s^z)} \frac{4\pi q_p^2 \chi_s \chi_{p2} A_0^2}{(W^2 - q_p^2 \varepsilon_p^\infty)} \right)^{1/2} \approx \left(8\pi^2 \omega z_0 / (\varepsilon' nc) \chi^2 A_0^2\right) \approx 8\pi^2 \omega z_0 \chi^2 A_0^2 / (cn) \right).$$

As the experimental data for this gain, we used the following [25]: pulse width of the pulsed Ar^+ laser ≃ 30 ps, the peak output power ≈ 2.5 kW, the wavelength was 514.5 nm, the cross-section ≈ 10^{-18} cm^{-2}, $\gamma_f \approx 10\ \text{cm}^{-1}$, and $\chi \approx 10^{-8}\ \text{esu}$. In [26] the nonlinear medium was zinc blende ZnS, in which the polariton frequencies were in the rage 200 - 400 cm^{-1}. Both the experimental results for the gain factor in [26] and calculations based on (48) have resulted in $g \approx 1$.

5. Conclusion

In this paper, we have found the system of differential equations that model the process of coherent anti-Stokes Raman scattering by polaritons in crystals. We have also found the asymptotic solutions of that system that correspond to the simultaneous propagation of all waves participating in the process of Raman scattering. And, lastly, we showed that the value of such an important feature as the gain factor resulted from that system is consistent with the experimental results.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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