CONTRIBUTION TO THE THEORY OF STIMULATED RAMAN SCATTERING EXCITED BY PICOSECOND PULSES

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SRS under local nonstationary conditions is investigated. To this end, the Maxwell equations and the kinetic equations for the density matrix are solved by successive approximations. It is demonstrated in the zeroth approximation that inverted population of the vibrational levels can be produced and used to amplify the anti-Stokes radiation along the axis or to amplify the signal at the molecule-vibration frequency. In first-order approximation, conditions for the appearance of discrete broadening of the lines in the SRS spectra are established and analyzed.

INVESTIGATIONS of SRS with the aid of picosecond pulses[1] have been recently initiated[1]. The SRS has in this case a non-stationary character. This occurs as a result of the group delay of the waves (wave nonstationarity) and also in the case when the laser pulse duration τ_L is shorter than the transverse-relaxation time T_2 (local nonstationarity). In the general case, when $\tau_L \lesssim T_2$, it is necessary to take into account the occurrence of both local and wave nonstationarity.

Nonstationary SRS can be described by a coupled system of nonlinear Maxwell's equations and kinetic equations for the density matrix:

$$\dot{R}_{21} + \frac{1}{T_2} R_{21} = -\frac{i}{\hbar} V_{21}^0 \Delta(t), \tag{1a}$$

$$\dot{R}_{12} + \frac{1}{T_2} R_{12} = \frac{i}{\hbar} V_{12}^0 \Delta(t), \tag{1b}$$

$$\dot{\Delta} = \frac{2i}{\hbar}(V_{21}^0 R_{12} - V_{12}^0 R_{21}) + \frac{1}{T_1}(\Delta^e - \Delta), \tag{1c}$$

$$\left(\frac{\partial}{\partial z} + \frac{1}{U_S}\frac{\partial}{\partial t} + \beta_S\right) F_S = -2\pi i N \frac{\omega_S}{\varepsilon U_S} p_S^{NL}, \tag{1d}$$

$$\left(\frac{\partial}{\partial z} + \frac{1}{U_L}\frac{\partial}{\partial t} + \beta_L\right) F_L = -2\pi i N \frac{\omega_L}{\varepsilon U_L} p_L^{NL}, \tag{1e}$$

where the Hamiltonian of the interaction of the field with the molecule is

$$\hat{V}_{12} = -\hat{\alpha}_{12} E E^*, \quad V_{12}^0 = -\alpha_{12} F_L^* F_S, \tag{2}$$

$\hat{\alpha}$ is the polarizability operator, the indices 1 and 2 label the ground and first-excited vibrational states of the molecule,

$$E = F_L(z, t) e^{-i\omega_L t} + F_S(z, t) e^{-i\omega_S t} + \text{c.c.}, \tag{3}$$

$\omega_L - \omega_S = \omega_{21}$ is the molecule vibration frequency, and the indices L and S pertain to the laser and Stokes radiation, respectively,

$$P^{NL}(\omega_S) = \alpha_{12}(E + E^*)(\rho_{12} + \rho_{21}) = p_S^{NL} e^{-i\omega_S t}, \quad \rho_{12} = R_{12} e^{i(\omega_L - \omega_S)t} \tag{4}$$

F, R, and p_α^{NL} (α = L, S) are the amplitudes of the field, the density matrix, and the nonlinear polarization, Δ^e is proportional to the equilibrium population difference of the vibrational levels, N is the number of molecules per unit volume, T_1 is the longitudinal relaxation time, β and U are the losses and the velocity of light in the medium, and ϵ is the dielectric constant.

The wave nonstationarity sets in already at $\tau_L \approx 10^{-10}$ sec. The condition $\tau_L \gg T_2$ ($T_2 \approx 10^{-11}$–10^{-12} sec) remains in force here, so that the field amplitude in the equation for the density matrix can be regarded as independent of the time. This case makes it possible to solve separately the systems of equations for the density matrix and Maxwell's equations. An investigation of the wave nonstationarity for SRS was carried out in[2] by exactly solving the system of equations for the amplitudes of the laser (L) and Stokes (S) fields. It was shown that the wave group delay effect decreases the SRS gain.

In[3,4] they investigated the case $\tau_L \approx T_2$ assuming the laser field to be given and under the condition $\Delta = \Delta^e$. These limitations have made it possible to reduce the system (1) to a hyperbolic equation that can be integrated by the Riemann method. It was shown there that the SRS gain decreases with decreasing laser-pulse duration and as the Stokes pulse propagates in the medium it broadens and its maximum becomes delayed.

The present paper is devoted to SRS under conditions of local nonstationarity ($\tau_L \ll T_2, T_1$). It will be shown below that under these conditions there exists a possibility of obtaining inverted population of the vibrational levels, of observing anti-Stokes radiation along the axis, and obtaining a discretely broadened spectrum of the SRS lines.

Let us proceed to solve the system (1). It is impossible to obtain its exact solution, and we therefore use the method of successive approximations[5]:

$$\begin{aligned} F_\alpha(t) &= F_\alpha^{(0)}(t) + F_\alpha^{(1)}(t) + \dots, \\ \rho_{12}(t) &= \rho_{12}^{(0)}(t) + \rho_{12}^{(1)}(t) + \dots, \\ \Delta(t) &= \Delta^{(0)}(t) + \Delta^{(1)}(t) + \dots \end{aligned} \tag{5}$$

In the zeroth approximation we shall assume that the fields of the L and S radiations are given functions of the time and do not depend on z. In this case the system (1) reduces to the system (1a)–(1c) for the density matrix. Assuming for simplicity that the L or S radiation is in the form of rectangular pulses:

$$F_\alpha^{(0)}(t) = \begin{cases} F_{\alpha 0}^{(0)} \text{ for } 0 \leqslant t \leqslant \tau & (\alpha = L, S) \\ 0 \text{ for t outside this interval} \end{cases}$$

we obtain from (1a) and (1b)

$$R_{21}^{(0)} = \frac{i}{\hbar}\alpha_{12}F_{L0}^{(0)}F_{S0}^{(0)*}\int_0^t \exp\left\{-\frac{1}{T_2}(t-\tau)\right\}\Delta^{(0)}(\tau)\,d\tau,$$
$$R_{12}^{(0)} = (R_{21}^{(0)})^*. \tag{6}$$

Substituting these expressions in (1c), we obtain an integro-differential equation describing the motion of the difference of the populations of the vibrational levels:

$$\dot{\Delta}^{(0)} + \frac{1}{T_1}\Delta^{(0)} = \frac{1}{T_1}\Delta^e - 4\alpha_{12}^2\hbar^{-2}|F_{L0}^{(0)}|^2|F_{S0}^{(0)}|^2 \times \int_0^t \exp\left\{-\frac{1}{T_2}(t-\tau)\right\}\Delta^{(0)}(\tau)\,d\tau. \tag{7}$$

We solve this equation with the aid of the Laplace transformation. The obtained transform is

$$\mathcal{F}(p) = \frac{\Delta^e(a/p+1)(p+b)}{(p+a)(p+b)+\lambda^2}, \tag{8}$$

from which we obtain the inverse transform

$$\Delta^{(0)}(t) = \Delta^e\left\{\frac{e^{-\gamma t}}{\Gamma}\left[(a+b)-\gamma\left(1+\frac{ab}{ab+\lambda^2}\right)\right]\operatorname{sh}\Gamma t + e^{-\gamma t}\left[1-\frac{ab}{ab+\lambda^2}\right]\operatorname{ch}\Gamma t + \frac{ab}{ab+\lambda^2}\right\}, \tag{9}$$

where

$$a = T_1^{-1}, \quad b = T_2^{-1}, \quad \gamma = {}^1/_2(T_1^{-1}+T_2^{-1}),$$
$$\Gamma = \left\{\left(\frac{T_2-T_1}{2T_2T_1}\right)^2 - \lambda^2\right\}^{1/2}, \quad \lambda = \frac{2\alpha_{12}|F_{L0}^{(0)}||F_{S0}^{(0)}|}{\hbar}. \tag{10}$$

Let us investigate the behavior of the population difference of the vibrational levels $\Delta^{(0)}$ in the case when the durations of the L and S pulses are much shorter than the times of longitudinal and transverse relaxations: $\tau_L \ll T_2$, T_1 and $1/T_2T_1 < \lambda^2$. This enables us to neglect the influence of the relaxation processes on $\Delta^{(0)}$ compared with the influence of the L and S fields. Then it follows from (9) that

$$\Delta^{(0)}(t) = \Delta^e\cos\lambda t, \tag{11}$$

whence, under the condition

$$\lambda t = (2n+1)\pi, \quad n = 0, 1, 2, \ldots \tag{12}$$

we get $\Delta^{(0)} = -\Delta^e$.

In other words, as the result of the SRS that occurs under conditions of local nonstationarity, it is possible to produce inverted population of the vibrational levels. We note that the condition (12) is the analog of the condition for producing pulsed inversion in the theory of two-level lasers[6].

We shall show that the produced inverted population of the vibrational levels can be used to amplify anti-Stokes SRS radiation in the forward direction or to amplify a signal at the molecule-vibration frequency. Let us assume that a medium with initial levels

$$\Delta(0) = -\Delta^e, \quad \rho_{12}(0) = \rho_{21}(0) = 0, \tag{13}$$

is subjected to the action of a laser pulse with duration $\tau_L > T_2$, T_1. The Hamiltonian of the interaction of the field with the molecule is given by (2), and the field itself is chosen in the form

$$E = F_L(z,t)e^{-i\omega_L t} + F_{AS}(z,t)e^{-i\omega_{AS}t} + \text{к.с.} \tag{14}$$

If the change of the populations of the vibrational levels is determined mainly by the relaxation processes and not by the field, then the polarization obtained by solving the system of equations (1a)–(1c) and also from (4) and (14) is given by

$$P^{NL}(\omega_{AS}) = \frac{i}{\hbar}\frac{\alpha_{12}^2}{T_2^{-1}}\Delta|F_{L0}|^2F_{AS}e^{-i\omega_{AS}t}, \tag{15}$$

where

$$\Delta = \Delta^e(1-2e^{-t/T_1}) < 0. \tag{16}$$

For amplification of the anti-Stokes radiation to occur, it is necessary to have Δ smaller than a certain critical value $\Delta' = -\eta\Delta^e$ $(0 < \eta < 1)$. It follows therefore that the system will amplify the anti-Stokes radiation after inversion for a time interval satisfying the inequality

$$0 < t'/T_1 < \ln[2/(1+\eta)]. \tag{17}$$

We note the following with respect to the amplification of the signal at the molecule-vibration frequencies: the inversion of the vibrational-level population by pumping with nonstationary SRS radiation uncovers a possibility of obtaining new laser transitions at these frequencies. The priming signal can be obtained by parametric interaction of L and S waves. In the case when the active medium consists of non-polar molecules, the medium, together with the cell where the priming pulse is produced, should be placed in a constant electric field in order to lift the alternative forbiddenness[7]. If the duration of the priming signal exceeds T_2, then the time of its amplification is determined by (17).

Let us return to the investigation of nonstationary SRS. We employ the values of $R_{12}^{(0)}$, $R_{21}^{(0)}$, and $\Delta^{(0)}$ obtained by us to calculate the susceptibility of SRS occurring under local nonstationary conditions. From (3), (4), (6), and (11) it follows that

$$\chi_S'' = -\frac{1}{\hbar}\alpha_{12}^2\Delta^eN\frac{\sin\lambda t}{\lambda}. \tag{18}$$

Let us show that the oscillations of the nonstationary Raman susceptibility cause the presence of additional lines in the SRS spectrum. To this end, in first order of the employed method, we investigate the spatial and temporal behavior of the Stokes-radiation amplitude.

Substitution of (4) in (1d) with allowance for (5) under the condition $\beta_S = \beta_L = 0$ yields

$$\left(\frac{\partial}{\partial z}+\frac{1}{U_S}\frac{\partial}{\partial t}\right)F_S^{(1)} = -2\pi iN\frac{\omega_S}{U_S\varepsilon}\alpha_{12}(E^{(0)}+E^{(0)*})(\rho_{12}^{(0)}+\text{к.с.}).$$

Using now (6) and (11), we get

$$\left(\frac{\partial}{\partial z}+\frac{1}{U_S}\frac{\partial}{\partial t}\right)F_S^{(1)} = |F_S^{(0)}|\frac{2\pi N\alpha_{12}^2\Delta^e\omega_S|F_L^{(0)}|^2}{\hbar U_S\varepsilon}\frac{\sin\lambda t}{\lambda}.$$

Solving this equation, we obtain ultimately

$$F_S^{(1)} = |F_S^{(0)}|\frac{2\pi N\alpha_{12}^2\Delta^e\omega_S|F_L^{(0)}|^2}{\hbar U_S\varepsilon\lambda}z\sin\lambda t,$$
$$I_S = |F_S^{(0)}+F_S^{(1)}|^2 \approx |F_S^0|^2\left\{1+\frac{4\pi N\alpha_{12}^2\Delta^e\omega_S|F_L^{(0)}|^2}{\hbar\varepsilon U_S\lambda}z\sin\lambda t\right\}. \tag{19}$$

It follows therefore that there appear in the spectrum, besides the Stokes line, also lines shifted relative

to the Stokes line by a frequency $\Omega = \pm\lambda/2\pi$. The next-higher approximations establish the presence in the spectrum of SRS lines with frequencies $\nu_S \pm n\Omega$, n = n = 0, 1, 2, ... Thus, in SRS under local nonstationary conditions, it is possible to observe an enriched spectrum of SRS lines.

The mechanism considered above for the discrete broadening of the lines in the nonstationary SRS spectra is connected with oscillations of the Raman susceptibility χ_S'', which in turn are due to periodic changes in the population difference of the vibrational levels $\Delta^{(0)}(t)$. In addition to this mechanism, oscillations of χ_S'' are caused by the influence of the quadratic Stark effect on the SRS. When the energy of the picosecond pulse is low, there may also be no appreciable change in $\Delta^{(0)}$: $\Delta^{(0)} = 0$, $\Delta^{(0)} = \Delta^e$. Then only the second mechanism is effective. This case was considered by Shimoda[8], who investigated the formation of a discrete structure of SRS lines in CS_2. Shimoda believes that self-modulation of the pulse occurs in self-focusing in the thin short-lived filaments, owing to the oscillations of χ_S''. The nature of these oscillations is not indicated in[8], although it is obvious that they are connected with the influence of the Stark effect on the SRS in the absence of relaxation and under the condition $\Delta = \Delta^e$.

We can take the Stark effect into account in the present analysis by retaining in the left-hand sides of (1a) and (1b), respectively, terms of the type $+i(V_{11} - V_{22})R_{21}^{(0)}/\hbar$ and $-i(V_{11} - V_{22})R_{12}^{(0)}/\hbar$, with

$$V_{11} - V_{22} = \Delta\alpha(|F_{L_0}^{(0)}|^2 + |F_{S_0}^{(0)}|^2),$$

where $\Delta\alpha = \alpha_{11} - \alpha_{22}$ is the difference of the polarizabilities in the ground and first-excited vibrational states. Repeating now the calculation used above to derive (11) and (18), we obtain for $\Delta^{(0)}(t)$ and χ_S'' the following expressions:

$$\Delta^{(0)}(t) = \Delta^e \frac{\mu^2 + \lambda^2 \cos \zeta t}{\zeta^2}, \tag{20}$$

$$\chi_S'' = -\frac{\alpha_{12}^2 \Delta^e N}{\hbar\zeta} \sin \zeta t, \tag{21}$$

where

$$\mu = \Delta\alpha(|F_{L0}^{(0)}|^2 + |F_{S0}^{(0)}|^2)/\hbar, \quad \zeta = (\mu^2 + \lambda^2)^{1/2}.$$

It follows from (20) that the condition for the inverted population of the vibrational levels in nonstationary SRS takes in the general case the form

$$\zeta t = (2n+1)\pi, \quad n = 0, 1, \ldots, \tag{22a}$$

$$\lambda > \mu. \tag{22b}$$

We note that the condition (22b) can be satisfied if the coefficient of conversion of L radiation into S radiation is sufficiently high (e.g., $|F_S^{(0)}|^2 \approx 0.1\,|F_L^{(0)}|^2$) and as the result of the fact that $\Delta\alpha \ll \alpha_{12}$. (The expansion of $\Delta\alpha$ in powers of the normal coordinate Q yields $\Delta\alpha = (\partial^2\alpha/\partial Q^2)_0 Q^2$, whence $\Delta\alpha \ll \alpha_{12} = (\partial a/\partial Q)_0 Q$, where $Q = \sqrt{\hbar/2m\omega}$.)

The formula (21) for χ_S'' is a generalization of the results of Shimoda[8] (formula (11)) and of the present paper (formula (18)). The analog of formula (11) of[8] follows from (21) at $\lambda = 0$ (or $\Delta^{(0)} = \Delta^e$), and then the oscillations of χ_S'' are connected only with the influence of the Stark effect on the SRS.

Let us present estimates. In the case of gases (by way of an example we consider hydrogen: $\nu_{21} = 4155\ cm^{-1}$, $N \approx 10^{19}\ cm^{-3}$, $T_2 \approx 10^{-9}$ sec, and $\nu_S \approx 2.5 \times 10^{14}\ sec^{-1}$) exposed to radiation from a neodymium laser with $\tau_L \approx 10^{-10}$ sec at $F_L^{(0)} \approx 3 \times 10^4$ cgs esu, $F_S^{(0)} \approx 0.3\,F_L^{(0)}$, $\alpha_{12} = (\partial a/\partial Q)_0 Q \approx 10^{-25}\ cm^3$ ($(\partial\alpha/\partial Q)_0 \approx 1.2 \times 10^{-16}$ cgs esu[7], and $Q \approx 10^{-9}$ cgs esu) we obtain an oscillation frequency $\Omega \approx 0.3\ cm^{-1}$. On the basis of (22b) we assume that the main contribution to the oscillation frequency is made by the population-oscillation mechanism. Since $T_2 = 10^{-9}$ sec, the condition $\Omega T_2 \gg 1$ is satisfied, and consequently a discrete structure of the L and S lines should be observed in the SRS spectra of hydrogen.

In the case of a liquid (CS_2: $\nu_{21} = 656\ cm^{-1}$, $N \approx 5 \times 10^{21}\ cm^{-3}$, $T_2 = 5 \times 10^{-11}$ sec, $\epsilon \approx 2.6$, $\nu_S \approx 3 \times 10^{14}\ sec^{-1}$) at $F_L^{(0)} \approx 10^5$ cgs esu, $F_S^{(0)} \approx 0.3\,F_L^{(0)}$, $\alpha_{12} \approx 6 \times 10^{-26}\ cm^3$ ($\partial\alpha/\partial Q \approx 1.5 \times 10^{-16}$ cgs esu, $Q \approx 4 \times 10^{-10}$ cgs esu) the frequency Ω turns out to be $\Omega \approx 1.8\ cm^{-1}$.

We note that from the condition $F_S^{(1)} \ll F_S^{(0)}$ and from (19) it follows that the nonstationary process occurs in a thin layer of matter with thickness $l \approx 0.5$ cm in a gas and $t \approx 5 \times 10^{-3}$ cm in a liquid. The same estimates can be arrived at by starting from qualitative considerations. Under local nonstationary conditions, the conversion of L radiation into S radiation occurs at a distance comparable with the length of the L pulse. Since the energy of the depleted L pulse then becomes lower than the SRS threshold energy, then the L and S pulses will pass through the remainder of the cell without being appreciably altered. Consequently, the distance over which the non-stationary SRS takes place can be estimated at $l \approx c\tau_L$. Starting from $\tau_L \ll T_2$, we assume that the gas and the liquid are irradiated by pulses with $\tau_L \approx 10^{-10}$ sec and $\tau_L \approx 5 \times 10^{-13}$ sec, respectively. We then have for gases $l \approx 3$ cm and for liquids $l \approx 10^{-2}$ cm.

As already mentioned, the presence of oscillations leads to a discrete structure of the lines in the SRS. A similar phenomenon was observed by Bol'shov et al.[9] In a single picosecond pulse of duration $\tau_L \approx 3 \times 10^{-12}$ sec and a power on entering the cell $\approx 250\ GW/cm^2$ ($F_L = 2 \times 10^4$ cgs esu), self-focusing and a fine structure of the SRS lines in CS_2 were observed. Unfortunately, the result of this experiment was not estimated in[9]. Nonetheless, since $\tau_L \ll T_2$, it can be assumed that the SRS occurred in this case under conditions of local nonstationarity, and consequently the mechanism proposed in our paper is one of the causes of the observed fine structure, in addition to the other mechanisms discussed in[9].

The estimates given above for $F_L^{(0)}$ can be regarded as not overvalued in comparison with the experimental data of Bol'shov et al.[9], since the pump intensity can increase by several orders of magnitude in the case of self-focusing in thin filaments[10].

A fine structure of SRS and pump lines was observed also in C_6H_6, CS_2, and in the field of ordinary nanosecond pulses (see the bibliography in[9]). In this case the cause of the fine structure may be nonstationary processes occurring in SRS in the case of self focusing in thin filaments, with a pulse duration shorter than the relaxation time[8]. An analogous effect of amplitude modulation of the light pulse takes place also when

an intense L pulse passes through a resonantly absorbing medium. In particular, Hocker and Tang[11] observed, in the passage of a CO_2-laser pulse through SF_6, damped oscillations near the leading front of the pulse. These oscillations are likewise attributed by the cited authors to oscillations of the populations, and their damping is attributed to relaxation processes.

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