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ON THE THEORY OF STIMULATED COMBINATION (RAMAN) RADIATION

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A number of problems in the theory of two-quantum processes, particularly stimulated combination radiation (stimulated Raman effect), are considered. Fluctuation-dissipation theorems are derived which relate the stimulated two-quantum emission with fluctuations when an external sinusoidal signal is present. With the aid of these theorems it is possible to relate the spectral intensities of the spontaneous and induced Raman emission. The theory developed is applied to study the interaction of electromagnetic waves, taking into account stimulated Raman emission, and to derive the conditions for self-excitation of a Raman laser. The relation between Raman and parametric systems is considered.

1. INTRODUCTION

WITH the development of the technology of coherent optical generators (lasers), the experimental observation of various multi-quantum processes of optical emission and absorption has become possible. In particular double absorption of light from a laser [1,2], and stimulated Raman emission in organic liquids[3], have been observed. Spontaneous Raman emission (also called combination scattering or combination radiation) was first observed by Mandelstam and Landsberg [4] in solids and by Raman and Krishnan [5] in liquids as early as 1928.

Of the numerous works devoted to two-quantum processes we cite only the book by Placzek [6] and the work of Göppert-Mayer.[7] These authors calculate the probability of two-quantum processes assuming discrete atomic (or molecular) spectra and a continuous spectrum for the radiation field.

In the present work (Sec. 2) a theory of two-quantum processes is constructed without these limitations (suitable in particular for coherent electromagnetic signals); a general treatment is given of the behavior when external forces are present in an arbitrary quantum system having resonant absorption (Sec. 3). An analogue of the fluctuation-dissipation theorem is derived which relates the noise when an external force is present to the susceptibility of the system in the presence of the same force (Sec. 4). Further (Sec. 6), the interaction of electromagnetic waves taking into account stimulated Raman radiation is considered, and the conditions of self-excitation are derived (Sec. 7) for a Raman laser (the functioning of such a laser is based on the phenomenon of stimulated Raman emission). A comparison of Raman and parametric systems is made in Sec. 8.

2. TWO-QUANTUM PROCESSES

The following elementary two-quantum processes are possible:[6,7]

a) Double emission and absorption: a molecule goes from a lower state E_1 to an upper E_2 with the absorption of two photons, or from an upper to a lower state with emission (spontaneous and stimulated) of two photons. The frequencies of the photons ω_1 and ω_2 here satisfy the relation (expressing the law of conservation of energy)

$$E_2 - E_1 = \hbar\omega_1 + \hbar\omega_2;$$

b) Raman emission and absorption; a molecule goes from a lower state to an upper with emission (spontaneous or stimulated) of one photon (frequency ω_2) and absorption of another photon of frequency $\omega_1 > \omega_2$—a Stokes process. If the molecule was originally in the upper state, then the photon of larger frequency ω_1 is emitted—an anti-Stokes process. The frequencies of the signals ω_1 and ω_2 satisfy the relation

$$E_2 - E_1 = \hbar\omega_1 - \hbar\omega_2.$$

In order to find the intensity of the emission from processes of types a) and b) we consider the stimulated and spontaneous emission of a system which is under the influence of an external field whose energy of interaction with the system has the form[1]

$$\hat{V}_1 = \sum_l \hat{V}^l e^{-i\omega_l t}.$$

The radiation field of the other signal will be described quantum-mechanically. Then the complete Hamiltonian of the system is

$$\hat{H} = \hat{H}_0 + \hat{V}_1(t) + \frac{1}{2}\sum_\nu (\hat{p}_\nu^2 + \omega_\nu^2 \hat{q}_\nu^2) - \sum_\nu \hat{B}_\nu \hat{q}_\nu, \qquad (1)$$

where $\hat{H}_0$ is the Hamiltonian of the unperturbed molecular system and the quantity $\hat{B}_\nu$ has the form

$$\hat{B}_\nu = \sum_{s=1}^{n} \frac{e_s}{m_s c} (\hat{\mathbf{p}}_s \mathbf{A}_\nu(s)),$$

e_s, m_s, $\hat{\mathbf{p}}_s$ are the charge, mass and momentum of the s-th particle of the molecule, and $\mathbf{A}_\nu(s)$ is the value of the eigen vector $\mathbf{A}_\nu$ of the ν-th mode of the radiation field at the site of the s-th particle. We neglect terms quadratic in the particle charge, since these terms are not essential for the processes considered.

The intensity of the radiation of the ν-th mode of the radiation field is determined by the operator

$$\frac{d\hat{H}_\nu}{dt} \equiv \frac{d}{dt}\left\{\frac{1}{2}(\hat{p}_\nu^2 + \omega_\nu^2 \hat{q}_\nu^2)\right\} = \frac{i}{\hbar}[\hat{H}, \hat{H}_\nu] = \hat{B}_\nu \hat{p}_\nu. \qquad (2)$$

We average this expression with respect to the density matrix of the entire system (with Hamiltonian H). The equation for the density matrix in the interaction representation, with the interaction as $\hat{V}_2 = -\sum_\nu \hat{B}_\nu \hat{q}_\nu$, has the form

$$i\hbar\, \partial\hat{\rho}/\partial t = [\hat{V}_2, \hat{\rho}].$$

The mean value of the emission intensity accurate to terms of second order in $\hat{V}_2$ assumes the form (see [8])[2]

$$\frac{d\bar{H}_\nu}{dt} = \overline{B_\nu(t)}\;\overline{p_\nu(t)} + \frac{i}{\hbar}\sum \int_0^t \{\overline{B_\nu(t) B_\lambda(t_1)}\;\overline{p_\nu(t)\, q_\lambda(t_1)} - \overline{B_\lambda(t_1) B_\nu(t)}\;\overline{q_\lambda(t_1)\, p_\nu(t)}\}\, dt_1. \qquad (3)$$

In distinction from the corresponding expression in a paper by one of the authors,[8] the variation of $\hat{B}_\nu(t)$ with time is also determined by the external field $\hat{V}_1(t)$.

We shall in what follows be interested in the second term in (3) which gives the spontaneous and stimulated emission (or absorption) which does not depend on the phase relation between the unperturbed radiation field (p_ν, q_ν) and $B_\nu(t)$. After averaging over a time much larger than the period of the radiation, and remembering that the correlation function $\overline{p_\lambda(t_1)\, q_\nu(t)}$ satisfies the conditions taken in [8], we obtain the radiation intensity as

$$I_\nu \equiv \frac{d\bar{H}_\nu}{dt} = \frac{1}{2}\int_0^t \cos\omega_\nu(t - t_1)\, \{\overline{B_\nu(t) B_\nu(t_1)} + \overline{B_\nu(t_1) B_\nu(t)}\}\, dt_1 - i\left(n_\nu + \frac{1}{2}\right)\int_0^t \sin\omega_\nu(t - t_1)\, [\overline{B_\nu(t), B_\nu(t_1)}]\, dt_1, \qquad (4)$$

where $\overline{B_\nu(t) B_\nu(t_1)}$ is the part of this correlation function which depends only on the difference $t - t_1$, and $(N_\nu + 1/2)\hbar\omega_\nu = \overline{H}_\nu$.

It now remains to calculate $\hat{B}_\nu(t)$. Since we assume that the field $V_1(t)$ is small enough, we limit ourselves to the first order approximation in $\hat{V}_1(t)$:

$$B_\nu^{(1)}(t)_{nm} = \sum_l e^{i(\omega_{mn} - \omega_l)t} b_{\nu nm}^l, \qquad (5)$$

$$b_{\nu nm}^l = \sum_{k,l}\left\{\frac{B_{\nu nk} V_{km}^l}{\hbar}\zeta(\omega_l - \omega_{km}) - \frac{V_{nk}^l B_{\nu km}}{\hbar}\zeta(\omega_l - \omega_{nk})\right\}, \qquad (6)$$

where the function $\zeta(x)$ has the form $\zeta(x) = P/x - i\pi\delta(x)$ (P/x is the principal value of $1/x$). From the definition (5) and the fact that $\hat{B}_\nu^{(1)}$ is Hermitian it follows that $b_{\nu nm}^l = (b_{\nu mn}^{-l})^*$.

Under the assumption that the density matrix of the unperturbed molecule is diagonal, the part of the correlation that depends only on the difference $t - t_1$, $\overline{B_\nu^{(1)}(t) B_\nu^{(1)}(t_1)}$ has the form

$$\overline{B_\nu^{(1)}(t)\, B_\nu^{(1)}(t_1)} = \sum_{n,k,l} \rho_n b_{\nu nk}^l b_{\nu kn}^{-l} e^{i(\omega_{nk} - \omega_l)(t - t_1)}, \qquad (7)$$

where the ρ_n are the populations of the levels in the unperturbed molecule. Substituting (7) in (4) and considering a time interval $t \gg \tau_c = 1/\delta\omega$ (where $\delta\omega$ characterizes the spectrum of the molecule or the field) we obtain the required formula for the radiation intensity for two-quantum and Raman processes;[3]

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[1] Thus we describe one of the fields acting on the system classically. If we have in mind the powerful field of a laser this can always be done, since, for sufficiently strong fields, quantum effects can be neglected.

[2] Just as in [8], the assumption is made that at the time t = 0 the density matrix of the system has the form $\hat{\rho} = \hat{\rho}_m \hat{\rho}_f$, where ρ_m is the density matrix of the molecular system with Hamiltonian $\hat{H}_0$, and $\hat{\rho}_f$ is the density matrix of the radiation field.

[3] The remaining terms of the type $B_\nu^{(0)}(t) B_\nu^{(1)}(t_1)$ and $B_\nu^{(0)}(t) B_\nu^{(2)}(t_1)$ give no contribution to the time-averaged radiation intensity (3), if $\omega_\nu \neq \omega_{nm}$, which we further assume.

$$I_\nu = \pi \sum_{n,k,l} |b^l_{\nu nk}|^2 \delta (\omega_{nk} + \omega_\nu - \omega_l) \{\rho_n + \bar{n}_\nu (\rho_n - \rho_k)\}. \tag{8}$$

In the particular case of a field of one frequency ω_1 acting on a molecular system, we have $V_1 = V_1^1 \exp(-i\omega_1 t) + V_1^{-1} \exp(i\omega_1 t)$ (l assumes the values ± 1). It follows from (8) that the radiation frequencies ω_ν can assume the values $\omega_\nu = \omega_{kn} \pm \omega_1$. The upper sign refers to double and the lower to Raman emission or absorption.

3. GENERAL CONSIDERATION OF THE BEHAVIOR OF SYSTEMS IN EXTERNAL FIELDS

We consider an arbitrary molecular system with Hamiltonian $\hat{H}_0$ in the presence of external forces whose effect is taken into account by the interaction energy

$$\hat{V} = \sum_l \hat{V}^l e^{-i\omega_l t}.$$

The steady-state response of the system as the mean value of the quantity $\langle \hat{x}_a(t) \rangle \equiv \overline{x_a(t)}$ can in the general case be written as

$$\overline{x_a(t)} = \sum \chi_{ab}(\omega_l)\, f^l_b e^{-i\omega_l t} + \sum \chi_{abc}(\omega_s, \omega_l)\, f^s_b f^l_c e^{-i(\omega_s+\omega_l)t} + \sum \chi_{abcd}(\omega_s, \omega_l, \omega_r)\, f^s_b f^l_c f^r_d e^{-i(\omega_s+\omega_l+\omega_r)t} \tag{9}$$

(where the summation is made over all indices except a), if $\hat{V}^l$ is of the form

$$\hat{V}^l = -\sum f^l_a \hat{x}_a. \tag{10}$$

Here $\chi_{ab}(\omega_l)$ is the usual susceptibility of the system. The processes of parametric interaction of three electromagnetic vibrations and of frequency doubling [9-11] are associated with the third rank tensor $\chi_{abc}(\omega_s, \omega_l)$ (we shall call it the cross-susceptibility tensor). The processes of parametric interaction of four vibrations, of frequency tripling, and, as we shall see below, of two-quantum processes, are associated with the fourth rank cross-susceptibility tensor $\chi_{abcd}(\omega_s, \omega_l, \omega_r)$.

The tensors χ_{abc} and χ_{abcd} can be expressed in terms of the density matrix of the unperturbed molecular system. To do this we solve the equation for the density matrix in the interaction representation to terms of third order in $\hat{V}$. This solution has the form

$$\hat{\rho}(t) = \hat{\rho}(-\infty) + \hat{\rho}^{(1)} + \hat{\rho}^{(2)} + \hat{\rho}^{(3)} + \ldots,$$

where, under the assumption that $\hat{\rho}(-\infty)$ is diagonal,

$$\rho^{(1)}_{mn} = \hbar^{-1} \sum V^l_{mn} (\rho_n - \rho_m)\, \zeta(\omega_l - \omega_{mn})\, e^{i(\omega_{mn}-\omega_l)t}, \tag{11}$$

$$\rho^{(2)}_{mn} = \hbar^{-2} \sum V^s_{mk} V^l_{kn} [(\rho_n - \rho_k)\, \zeta(\omega_l - \omega_{kn}) - (\rho_k - \rho_m)\, \zeta(\omega_s - \omega_{mk})] \times \zeta(\omega_l + \omega_s - \omega_{mn}) \exp[i(\omega_{mn} - \omega_l - \omega_s)t], \tag{12}$$

$$\begin{aligned}\rho^{(3)}_{mn} = \hbar^{-3} \{V \textstyle\sum^r_{mp} V^s_{pk} V^l_{kn} & [(\rho_n - \rho_k)\, \zeta(\omega_l - \omega_{kn}) \\ & - (\rho_k - \rho_p)\, \zeta(\omega_s - \omega_{pk})]\ \zeta(\omega_l + \omega_s - \omega_{pn}) \\ & - V^s_{mk} V^l_{kp} V^r_{pn} [(\rho_p - \rho_k)\, \zeta(\omega_l - \omega_{kp}) \\ & - (\rho_k - \rho_m)\, \zeta(\omega_s - \omega_{mk})] \\ & \times \zeta(\omega_l + \omega_s - \omega_{mp})\} \exp[i(\omega_{mn} - \omega_s - \omega_l - \omega_r)t] \\ & \times \zeta(\omega_r + \omega_l + \omega_s - \omega_{mn});\end{aligned} \tag{13}$$

The summation is carried out over all indices except m and n.

Hence, under condition (10) we find explicit expressions for the quantities[4] χ_{abc} and χ_{abcd}:

$$\begin{aligned}\chi_{abc}(\omega_s, \omega_l) & = \hbar^{-2} \frac{P_1}{2!} \sum_{n,m,k} x_{anm} x_{bmk} x_{ckn} [(\rho_n - \rho_k)\, \zeta(\omega_l - \omega_{kn}) \\ & - (\rho_k - \rho_m)\, \zeta(\omega_s - \omega_{mk})]\, \zeta(\omega_l + \omega_s - \omega_{mn}),\end{aligned} \tag{14}$$

$$\begin{aligned}\chi_{abcd}(\omega_s, \omega_l, \omega_r) = -\hbar^{-3} \frac{P_2}{3!} \sum_{m,p,k,n} & \zeta(\omega_s + \omega_l + \omega_r - \omega_{mn}) \\ & \times \{x_{amp} x_{bpk} x_{ckn} x_{anm} [(\rho_n - \rho_k)\, \zeta(\omega_l - \omega_{kn}) \\ & - (\rho_k - \rho_p)\, \zeta(\omega_s - \omega_{pk})]\ \zeta(\omega_l + \omega_s - \omega_{pn}) \\ & - x_{amk} x_{ckp} x_{dpn} x_{anm} [(\rho_p - \rho_k)\, \zeta(\omega_l - \omega_{kp}) \\ & - (\rho_k - \rho_m)\, \zeta(\omega_s - \omega_{mk})]\, \zeta(\omega_l + \omega_s - \omega_{mp})\},\end{aligned} \tag{15}$$

where P_1 and P_2 denote the operations of summing the permutations of, respectively, (s, b), (l, c) and (s, b), (l, c), (r, d).

A number of symmetry properties of the tensors χ_{abc} and χ_{abcd} follow from these expressions. We shall not deal with these at present, but proceed to the relation between the tensor χ_{abcd} and two-quantum processes. It is possible to associate with the tensor χ_{abcd} the susceptibility at a frequency ω_2 under the influence of fields of frequency ω_l. This susceptibility (its imaginary part) determines the absorption (positive or negative) of a weak field of frequency ω_2 when other fields of frequencies ω_l are present (for the latter we take into account the squares of the amplitudes).

The response at frequency ω_2, as is seen from (9), is obtained under the condition

$$\omega_s + \omega_l + \omega_r = \omega_2 \tag{16}$$

(the analogous condition in the second term of (9) can be satisfied only in the degenerate case [5] $\omega_s = -\omega_2$, $\omega_l = 2\omega_2$). Using directly (13) and condition (16), we find the response at the frequency ω_2 to be

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[4] We use the fact that $\langle x_a(t) \rangle = \mathrm{Sp}\, \hat{\rho}\hat{x}_a$.

[5] This case will be discussed in Sec. 8.

$$\begin{aligned}\overline{x_a}(t) &= \sum \rho_{mn}^{(3)} x_{anm} e^{i\omega_{mn}t} = \hbar^{-3}\sum e^{-i\omega_2 t}\zeta(\omega_2-\omega_{mn})\,x_{anm}\\ &\times \{V_{mp}^{r}V_{pk}^{s}V_{kn}^{l}\,[(\rho_n-\rho_k)\,\zeta(\omega_l-\omega_{kn})-(\rho_k-\rho_p)\\ &\times\zeta(\omega_s-\omega_{pk})]\,\zeta(\omega_l+\omega_s-\omega_{pn})\\ &-V_{mk}^{s}V_{kp}^{l}V_{pn}^{r}\,[(\rho_p-\rho_k)\,\zeta(\omega_l-\omega_{kp})-(\rho_k-\rho_m)\\ &\times\zeta(\omega_s-\omega_{mk})]\,\zeta(\omega_l+\omega_s-\omega_{mp})\}+\text{comp. conj}\end{aligned}$$

where the summation is made over all indices.

We shall be further interested in the imaginary part of the susceptibility at the frequency ω_2. We retain only the resonance terms which satisfy the condition for two-quantum processes

$$\omega_l+\omega_s=\omega_{12}. \tag{17}$$

The molecular levels satisfying (17) can be numerous in the system; it is, therefore, necessary to retain the summation over 1 and 2. If the disposition of the levels is such that the indices l and s in (17) assume the values −1 and 2, then Raman emission (absorption) occurs; double emission (absorption) will take place if l and s are different but of the same sign.

Using the definition of the susceptibility $\chi_{aa}(\omega_2)$

$$\overline{x_a(t)}=(\chi_{aa}f_a^{(2)}e^{-i\omega_2 t}+\overset{*}{\chi}_{aa}f_a^{(-2)}e^{i\omega_2 t}),$$

condition (10) for the weak field of frequency ω_2 and condition (17), we obtain, after straightforward manipulation, the imaginary part of the susceptibility as

$$\begin{aligned}\chi''_{aa}(\omega_2) &= -\frac{\pi}{\hbar}\sum_{1,2}(\rho_1-\rho_2)\,|A_{21}^{l}|^2\,\delta(\omega_l+\omega_2-\omega_{12}),\\ A_{21}^{l} &= (A_{12}^{-l})^{*}=\hbar^{-1}\sum_{k}[V_{k2}^{l}x_{a1k}\zeta(\omega_l-\omega_{k2})\\ &-V_{1k}^{l}x_{ak2}\zeta(\omega_l-\omega_{1k})].\end{aligned} \tag{18}$$

We have used the assumption (see the third footnote) that ω_l and ω_s do not coincide with resonance frequencies of the system.

In Raman emission ($l = -1$) the susceptibility at frequency ω_2, as is easily seen from (18), will be negative if $\omega_2 < \omega_1$, and if the molecular system in its initial state is not excited ($\omega_{12} < 0$ and $\rho_2 < \rho_1$). If $\omega_2 > \omega_1$, then $\chi''_a(\omega_2) > 0$ ($\omega_{12} > 0$ and $\rho_1 < \rho_2$). If, on the other hand, the system is excited, the susceptibility at the smaller frequency ($\omega_2 < \omega_1$) is positive, but is negative at the larger ($\omega_2 > \omega_1$). It is clear that the first and second cases consist of stimulated Stokes and anti-Stokes emission.

The sign of the susceptibility for double ($l = 1$) emission (absorption) does not depend on the ratio between ω_1 and ω_2; in the case of an excited molecular system ($\omega_{12} > 0$ and $\rho_2 < \rho_1$) the susceptibility is negative (stimulated double emission); in the case of an unexcited molecular system double absorption occurs.

The intensity of the two-quantum process is essentially determined, as is seen from formula (18), by the matrix elements of the dipole moment x_{a1k} and x_{ak2}, and is not determined by the matrix element of the transition between the initial and final states. For molecular systems possessing central symmetry this means that only levels having equal parity (levels between which transitions are forbidden) participate in a two-quantum transition. Levels with parity different from the parity of the initial and final states are the intermediate levels k (so-called alternative restriction [6]).

It is interesting to note that (18) is of a completely general character, since we made in essence no assumptions of any sort about the character of the "molecular system" or about the forces acting on it. The conclusions derived about the sign of χ''_{aa} are also valid for classical but non-linear systems. It can be shown directly that an anharmonic oscillator with characteristic frequency ω_0 has, under the influence of an external field at frequency $\omega_1 > \omega_0$, a negative susceptibility at the frequency $\omega_1 - \omega_0$, i.e., under such conditions it is unstable with respect to external excitations (see Sec. 8).

In concluding this section we note that the efficiency of a two-quantum process increases greatly if there is the additional resonance $\omega_l - \omega_{k2} = 0$ or $\omega_l - \omega_{1k} = 0$. These conditions signify that for double absorption (emission) the "intermediate" level k lies between the initial and final levels, and for the Raman process that the level k lies either above or below levels 1 and 2. The latter case corresponds to the situation occurring in the resonant interaction of two coherent signals on a three-level quantum system (maser).

We note an important relation stemming from formula (18). With equal amplitudes at frequencies $\omega_1 - \omega_0$ and $\omega_1 + \omega_0$ (where ω_0 is a resonance frequency of the system)

$$\chi''(\omega_1-\omega_0)=-\chi''(\omega_1+\omega_0). \tag{19}$$

The other important relation stemming from (18) has the form

$$\begin{gathered}P_1/\omega_1+P_2/\omega_2=0;\\ P_1=\tfrac{1}{2}\omega_1\chi''(\omega_1)\,|f^{(1)}|^2,\qquad P_2=\tfrac{1}{2}\omega_2\chi''(\omega_2)\,|f^{(2)}|^2,\end{gathered} \tag{20}$$

where P_1, P_2 are the mean powers absorbed at the frequencies ω_1 and ω_2 when fields of these frequencies are present (and there are no other sources of absorption at these frequencies).

4. THE FLUCTUATION-DISSIPATION THEOREM IN THE PRESENCE OF EXTERNAL FORCES

We shall relate the steady-state fluctuations in our system, when an external force is present, with the susceptibility (18) in the presence of the same force. The spectrum of the steady-state fluctuations of the quantities described by the operator $\hat{x}_a(t)$ is, according to [12], defined in the following way:

$$\frac{1}{2}\langle \hat{x}_{a\omega}\hat{x}_{a\omega'} + \hat{x}_{a\omega'}\hat{x}_{a\omega}\rangle = (x_a^2)_\omega \cdot \delta(\omega + \omega'). \tag{21}$$

On the left-hand side of (21) we retain only those terms which appear in the presence of the interaction and are proportional to $\delta(\omega + \omega')$ (the steady-state part of the fluctuations). We use (5) applied to the operator $\hat{x}_a(t)$ and take the Fourier transform of the matrix elements

$$(x_{a\omega}^{(1)})_{nm} = \frac{1}{2\pi}\int_{-\infty}^{\infty} x_{anm}^{(1)}(t)\, e^{i\omega t}dt = \sum_l A_{nm}^l \delta(\omega_{nm} - \omega_l + \omega), \tag{22}$$

$$A_{nm}^l = \hbar^{-1}\sum_{kl}\{x_{ank}V_{km}^l \zeta(\omega_l - \omega_{km}) - V_{nk}^l x_{akm}\zeta(\omega_l - \omega_{nk})\} \tag{23}$$

Substituting (22) into the left-hand side of (21) and retaining only terms proportional to $\delta(\omega + \omega')$, we obtain for the spectral density of the fluctuations when forces with frequencies ω_l are present

$$(x_a^{(1)\,2})_\omega = \frac{1}{2}\sum_{1,2,l}(\rho_1 + \rho_2)\,|A_{21}^l|^2\,\delta(\omega_l + \omega - \omega_{12}). \tag{24}$$

Comparing this with (18) we find that, if the molecular system without the external force is in a state of thermodynamic equilibrium (at temperature T), then the following fluctuation-dissipation theorems apply:

$$(x_a^{(1)2})_{\omega_2} = \frac{\hbar}{2\pi}\,\frac{1 + \exp[\hbar(\omega_1 - \omega_2)/kT]}{1 - \exp[\hbar(\omega_1 - \omega_2)/kT]}\,\chi''_{aa}(\omega_2) \tag{25}$$

for Raman processes ($l = -1$) and

$$(x_a^{(1)\,2})_{\omega_2} = \frac{\hbar}{2\pi}\,\frac{1 + \exp[\hbar(\omega_1 + \omega_2)/kT]}{1 - \exp[\hbar(\omega_1 + \omega_2)/kT]}\,\chi''_{aa}(\omega_2) \tag{26}$$

for double absorption ($l = 1$).

These theorems and their derivation are analogous to the usual Callen-Welton fluctuation-dissipation theorem (see [13,12]). It is seen from (25) that when $\omega_1 > \omega_2$ the susceptibility is negative, as also follows from the results of the preceding section (molecular system not excited).

With the aid of the fluctuation-dissipation theorems here established, it is possible as a particular case to relate the spectral intensity of the spontaneous emission to the imaginary part of the susceptibility $\chi''_{aa}(\omega_2)$. To do this we rewrite the spectral intensity of the spontaneous emission ($n_{\overline{\nu}} = 0$) (8) as

$$I_\nu^{\text{sp}} = \frac{\pi}{2}\sum_{n,k,l}|b_{\nu nk}^l|^2\,\delta(\omega_{nk} + \omega_\nu - \omega_l) \times \{(\rho_n + \rho_k) + (\rho_n - \rho_k)\}. \tag{27}$$

We eliminate $(\rho_n + \rho_k)$ and $(\rho_n - \rho_k)$ from (27), (18) and (24), taking as x_a the projection of the dipole moment (dipole approximation $B_\nu = \dot{d}\cdot A_\nu/c$). We then obtain

$$I_\nu^{\text{sp}} = (A_\nu^2\omega_\nu^2/c^2)\{\pi\,(d_a^2)_{\omega_\nu} - \tfrac{1}{2}\hbar\chi''_{aa}(\omega_\nu)\},$$

where A_ν is the projection of A on the direction $\dot{d}_a$. The spontaneous emission thus consists of two parts. One part is related to the fluctuations of the dipole moment and the other to the emission or absorption of the vacuum fluctuations (for more details see [8]).

Using the fluctuation-dissipation theorem (25) we find a relation between the spontaneous emission and the susceptibility $\chi''_{aa}(\omega_2)$ (for Raman emission):

$$I_\nu^{\text{sp}} = (A_\nu^2\omega_\nu^2/c^2)\chi''_{aa}(\omega_\nu)\{\exp[-\hbar(\omega_1 - \omega_2)/kT] - 1\}^{-1}.$$

Thus, by using experimental data on the Raman effect we can determine $\chi''_{aa}(\omega_\nu)$, which characterizes the stimulated Raman emission (or absorption).

5. STIMULATED RAMAN EMISSION IN THE VIBRATIONAL SPECTRUM

To calculate the Raman emission susceptibility $\chi''_{aa}(\omega_2)$ specifically it is necessary to use the kinetic equations which determine the behavior of a molecular system, taking into account dissipative processes in the molecular system. Such a kinetic equation has been derived in the works of one of us [13], and under the assumptions defined has the form

$$\dot{\sigma}_{mn} + i\omega_{mn}\sigma_{mn} + \frac{i}{\hbar}[\hat{V}, \hat{\sigma}]_{mn} = \begin{cases} \sum(w_{km}\sigma_{kk} - w_{mk}\sigma_{mm}), & m = n \\ -\tau_{mn}^{-1}\sigma_{mn}, & m \neq n \end{cases}, \tag{28}$$

where $w_{km} = w_{mk}\exp(-\hbar\omega_{mk}/kT)$ is the probability of a transition in unit time from the state k to the state m, and τ_{mn} is in a number of cases defined by the relation $\tau_{mn}^{-1} = \Sigma(w_{mk} + w_{nk}) = \tau_{nm}^{-1}$. In particular dissipative processes can arise from spontaneous emission; in this case

w_{km} is the probability of spontaneous emission (T = 0). Equation (28) can also include dissipative processes such as spin-lattice relaxation in the molecular system itself.

It can be shown that using the kinetic equation leads to the conclusion that it is necessary, in the formulae given above for χ''_{aa}, to replace the corresponding $\zeta(\omega_l - \omega_{kn})$ by the function6)

$$(\omega_l - \omega_{kn} + i\tau_{kn}^{-1})^{-1}, \tag{29}$$

and the δ function by

$$\{\pi\tau_{kn}\,[(\omega_l - \omega_{kn})^2 + \tau_{kn}^{-2}]\}^{-1}. \tag{30}$$

We consider the particular but important case when the eigen frequencies of the molecular system $\omega_{21} = \omega_0$, which satisfy the resonance conditions (17), are much smaller than the frequencies for the virtual transitions ω_{k1} and ω_{k2} and the corresponding frequency differences ($\omega_l - \omega_{k2}$) and ($\omega_l - \omega_{1k}$). Such a spectrum is possessed, for example, by the molecule of a liquid (or an ion in a crystal), when the vibrations of the molecule (ion) are taken into consideration. We note that the Raman effect was in fact first observed in the vibrational levels of molecules of liquids and of solids.[4,5] The theory of this phenomenon (the so-called theory of polarizability) was developed by Placzek.[6] In this section we calculate the polarizability7) of a molecular system under the assumptions of this theory:

$$\omega_0 \ll \omega_{k1},\, \omega_{k2}; \quad \omega_0 \ll \omega_l - \omega_{k2}. \tag{31}$$

For convenience we replace the indices 1 and 2 by 0s and 0,s + 1, and k by ks′. The polarizability of the system (18) using (29) and (30) we write as (s, s′ are the vibrational sub-levels of the electronic levels 0 and k8))

$$\chi''_{aa}(\omega_2) = \frac{1}{\hbar}\sum_s (\rho_{0s} - \rho_{0,s+1})\,|A^l_{0,s+1;0s}|^2 \frac{\tau^{-1}}{(\omega_l + \omega_2 - \omega_{12})^2 + \tau^{-2}}; \tag{32}$$

$$A^l_{0,s+1;0s} = \frac{1}{\hbar}\sum_{ks'}\left(\frac{V^l_{ks';0,s+1}x_{a0s,ks'}}{(\omega_l - \omega_{ks';0,s+1})} - \frac{V^l_{0s,ks'}x_{aks';0,s+1}}{(\omega_l - \omega_{0s;ks'})}\right). \tag{33}$$

Because of the large frequency differences [see (31)] we omit the corresponding relaxation time in the function ζ. In the case considered the interaction energy with the external field has the form

$$V^l = -\mathbf{E}^l\mathbf{d} \equiv -\sum_b \mathbf{E}^l_b \mathbf{d}_b, \quad b = x, y, z,$$

where $\mathbf{E}^l$ is the electric field of frequency ω_l, and d is the dipole moment of the molecule.

We make a series of transformations (taking (31) into account) and introduce the molecular polarizability (χ''_{aa}, which is the usual one and not that in the presence of the field of frequency ω_l) due to the electrons with the nuclear positions fixed. We expand the matrix element for this polarizability, taken with respect to the vibrational states s and s + 1, in terms of the normal vibrations of the nuclei, and limit ourselves to the first derivative only (just as was done by Placzek[6]). Finally, we obtain for the Raman emission polarizability ($l = -1$) for one molecule at thermodynamic equilibrium the following formula:

$$\chi''_{aa}(\omega_2) = -\frac{1}{\hbar}\left|\sum E_b^{(-1)}\frac{\partial\alpha_{ab}}{\partial q_s}\right|^2 \frac{\hbar}{2\omega_0}\frac{\tau^{-1}}{(\omega_1 - \omega_2 - \omega_0)^2 + \tau^{-2}} \tag{34}$$

(here τ^{-1} is the line width corresponding to the vibrational transitions).

6. THE INTERACTION OF ELECTROMAGNETIC WAVES TAKING INDUCED RAMAN EMISSION INTO ACCOUNT

As has been established above, negative absorption arises at the frequency $\omega_2 = \omega_1 - \omega_0$ when a signal with frequency $\omega_1 > \omega_0$ acts on a molecular system in a state of thermodynamic equilibrium. Thus, the electromagnetic wave of frequency ω_2 will be amplified as it passes through the medium due to the attenuation of the wave of frequency $\omega_1 > \omega_2$. We consider this process in more detail.

Let two plane travelling waves propagate along the z axis and let them have identical polarizations (along the x axis). Maxwell's equations, after eliminating the magnetic field from them, give the wave equation

$$\operatorname{rot}\operatorname{rot}\mathbf{E} + \frac{1}{c^2}\frac{\partial^2(\varepsilon\mathbf{E})}{\partial t^2} = -\frac{4\pi}{c^2}\frac{\partial^2\mathbf{P}^{NL}}{\partial t^2}. \tag{35*}$$

Here $\mathbf{P}^{NL}$ is the non-linear part of the polarization [see (9)] where the x_a become the components of the polarization and the f_a become the components of the electric field. We have taken the linear part of the polarization into account in the definition of the dielectric permittivity. At present we shall include only that part of $\mathbf{P}^{NL}$ that is

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6) Here the matrix elements x_{amn} will be taken with respect to the unperturbed molecular functions ignoring dissipative processes.

7) Up till now we have taken χ to mean the susceptibility in the generalized sense, since no specific properties of the molecular system were used. The latter could be paramagnetic, dielectric, or even mechanical. In this section we shall take χ to mean the polarizability of a dielectric.

8) The system is in the electronic ground state 0.

*rot = curl.

associated with the induced Raman emission and absorption.

In the steady-state case for an isotropic medium (the latter assumption is made for simplicity), Eq. (30) for the field of frequency ω_2 assumes the form

$$\frac{\partial^2 E_x^{(2)}}{\partial z^2} + \frac{\varepsilon\omega_2^2}{c^2} E_x^{(2)} + \frac{4\pi\omega_2^2}{c^2} P_x^{NL}(\omega_2) = 0; \tag{36}$$

$$E_x^{(2)} = \operatorname{Re}\{A_2(z)\, e^{i(k_2z-\omega_2t}\}, \quad k_2 = \varepsilon\omega_2/c; \tag{37}$$

$$P_x^{NL}(\omega_2) = \operatorname{Re}\{\chi(\omega_2, E_x^{(1)}(z))\, A_2 e^{i(k_2z-\omega_2t)}\}. \tag{38}$$

We introduce the notation

$$\chi''(\omega_2, E_x^{(1)}(z)) = -\delta\, |A_1|^2, \tag{39}$$

where δ is defined by (18), and A_1 is the complex amplitude of the wave $E_x^{(1)}(Z)$. Substituting (37)—(39) in (36), assuming that $A_2(z)$ changes slowly compared with e^{ikz} (in view of the smallness of the non-linear effects), and putting $\chi'(\omega_2) = 0$ (we consider the case of exact resonance), we obtain the equation for the amplitude:

$$\frac{\partial A_2}{\partial z} - \frac{2\pi\omega_1^2}{k_2c^2}\,\delta\,|A_1|^2 A_2 = 0. \tag{40}$$

Here $\delta > 0$ (since $\omega_1 > \omega_2$). Similarly we obtain (using (19)) for the amplitude A_1:

$$\frac{\partial A_1}{\partial z} + \frac{2\pi\omega_1^2}{k_1c^2}\,\delta\,|A_2|^2 A_1 = 0.$$

We further introduce the energy flux densities along the z axis:

$$S_1 = \frac{c^2k_1}{8\pi\omega_1}|A_1|^2, \qquad S_2 = \frac{c^2k_2}{8\pi\omega_2}|A_2|^2,$$

for which we obtain from (39) and (40) the equations

$$\frac{\partial S_2}{\partial z} - \beta\omega_2 S_1 S_2 = 0, \qquad \frac{\partial S_1}{\partial z} + \beta\omega_1 S_1 S_2 = 0;$$

$$\beta = \frac{32\pi^2\omega_2\omega_1}{k_1k_2c^4}. \tag{41}$$

From (41) follows the integral of motion:

$$I = \frac{S_1(z)}{\omega_1} + \frac{S_2(z)}{\omega_2} = \frac{S_1(0)}{\omega_1} + \frac{S_2(0)}{\omega_2}. \tag{42}$$

This equality is a consequence of the general property (20). Eliminating S_1 from (41) and (42) we obtain for S_2 a solution of the form

$$S_2(z) = \frac{S_2(0)\,[1 + \omega_1S_2(0)/\omega_2S_1(0)]\exp\{\beta[\omega_2S_1(0) + \omega_1S_2(0)]\,z\}}{1 + [\omega_1S_1(0)/\omega_2S_2(0)]\exp\{\beta[S_1(0)\,\omega_2 + \omega_1S_2(0)]\,z\}}. \tag{43}$$

Thus, the energy flux in the wave with frequency ω_2 grows monotonically from the limiting value $S_2(0)$ to $S_2(\infty) = \omega_2S_1(0)/\omega_1 + S_2(0)$. Meanwhile, as follows from (42), the energy flux in the wave with frequency ω_1 decreases to zero. It is interesting to note that the energy from wave A_1 is not transferred completely to wave A_2 but only the fraction ω_2/ω_1; the remaining fraction of the energy $1 - \omega_2/\omega_1 = \omega_0/\omega_1$ is spent in losses in the medium, and particularly in spontaneous emission of frequency ω_0. We might add that (42) can be interpreted as a law of conservation of the total number of quanta of frequencies ω_1 and ω_2: all the quanta $\hbar\omega_1$ are transformed into quanta $\hbar\omega_2$; at each such transition part of the energy $\hbar\omega_1 - \hbar\omega_2$ is dissipated in absorption in the molecular system.

We estimate the characteristic length l along the z axis within which there is a significant transformation of energy. It follows from (43), (42), and (39) that

$$l^{-1} = 4\pi\omega_2c^{-1}\delta\,|A_1|^2 = 4\pi\omega_2c^{-1}\,|\chi''(\omega_2, |A_1|^2)|. \tag{44}$$

Numerical estimates, and a comparison with the characteristic length for parametric interaction, will be made below.

7. RAMAN LASER

The phenomenon of stimulated Raman emission may be used to construct quantum amplifiers and generators. The first attempt to realize an optical quantum generator based on stimulated Raman emission was made by Eckhard, Hellwarth, McClung, Schwarz, Weiner, and Woodbury.[3] The results of the preceding section provide in essence the theory of a travelling wave quantum amplifier. In this section we consider the condition of self-excitation for a Raman laser. We shall here neglect the reverse reaction of the excited field of frequency ω_2 on the pump field of frequency $\omega_1 > \omega_2$.

We expand the electromagnetic field inside the cavity in terms of the complex eigen functions of the cavity $\mathbf{E}_\nu$ and $\mathbf{H}_\nu$:

$$\mathbf{E} = \sum_\nu a_\nu \mathbf{E}_\nu e^{-i\omega_\nu t}, \quad H = \sum a_\nu \mathbf{H}_\nu e^{-i\omega_\nu t}, \tag{45}$$

with the normalization condition

$$\int \mathbf{E}_\nu \mathbf{E}_{\nu'}\,dv = \int \mathbf{H}_\nu \mathbf{H}_{\nu'}\,dv = 4\pi\hbar\omega_\nu\delta_{\nu\nu'} \tag{46}$$

the quantities $a_\nu a_\nu^*$ signify the mean numbers of photons of energy $\hbar\omega_\nu$. Substituting the series (45) into Maxwell's equation (for simplicity we consider the isotropic case and ignore dispersion in the medium), we obtain equations for the amplitudes a_ν

$$\frac{da_\nu}{dt} + \frac{1}{2}\frac{\omega_\nu}{Q_\nu}a_\nu = -\frac{i}{2\hbar\omega_\nu^2}\int \ddot{\mathbf{P}}\mathbf{E}_\nu e^{i\omega_\nu t}\,dv, \tag{47}$$

into which we have introduced attenuation in a phenomenological way (by means of the quality factor Q_ν).

We substitute into (47) an expression for the non-linear part of the polarization $\mathbf{P}^{NL}$ in the form

$$\mathbf{P}^{NL} = \sum \chi\,(\omega_\nu, |A_1|^2)\, a_\nu \mathbf{E}_\nu e^{-i\omega_\nu t}, \tag{48}$$

where $|A_1|^2$ is the square of the complex amplitude of the field with frequency ω_1; this quantity does not depend on z and t in our approximation. From (46)—(48) it is not difficult to obtain the condition for self-excitation of a Raman laser in the form

$$Q_\nu^{-1} \leqslant |4\pi\chi''(\omega_\nu, |A_1|^2)|;$$

of all the frequencies $\omega_\nu \approx \omega_2 = \omega_1 - \omega_0$, that one is excited for which the quality factor Q_ν is a maximum.

To estimate the quantity χ'' we use formula (18), taking into account (29) and (30); as a result we find

$$4\pi\chi'' \sim \frac{4\pi d^2 T_2}{\hbar} N \frac{d^2 |A_1|^2}{\hbar^2\omega^2}, \tag{49}$$

where d, T_2, and ω are, respectively, characteristic values of the matrix element of the dipole moment, of the relaxation time of the molecular system τ_{mn}, and of the frequency differences in formula (18), and N is the corresponding difference of populations. If we put $d \sim 10^{-18}$ cgs esu, $T_2 = 10^{-11}$ sec, $N \sim 10^{22}$ cm^{-3}, $\omega \approx 10^{15}$ sec^{-1} and $Q_\nu = 10^7$, then the self-excitation condition is satisfied under a pump field of order 3 kV/cm.

We estimate the pump field for a Raman laser working in benzene (992 cm^{-1} line). To do this we use formula (34) for χ'' applied to the vibrational spectrum. Experimental data on the intensity of the Raman effect, taken, for example, from the work of Savin and Sobel'man,[14] allow us to estimate the quantity $(\partial\alpha_{ab}/\partial q_s)\hbar/2\omega_0$ which appears to be of order 0.5×10^{-50} cgs esu (the scattering cross section at $\lambda = 0.5\mu$ is 0.7×10^{-25} cm^2). The self-excitation condition for a Raman laser in benzene ($N = 10^{22}$ cm^{-3}, $T_2 = 0.2 \times 10^{-11}$ sec) will be satisfied if the pump field attains the value $E \sim 6$ kV/cm. In practice this field might be larger—the approximate nature of the estimate must be remembered.

8. CONCLUSION. COMPARISON WITH PARAMETRIC SYSTEMS

In Secs. 3 and 4 of the present paper a number of general relations were obtained referring to an arbitrary system on which external forces act. It was shown in particular that if the system considered has an eigen frequency ω_0 and if a force with frequency $\omega_1 > \omega_0$ acts on the system, then negative absorption arises at the frequency $\omega_2 = \omega_1 - \omega_0 < \omega_1$, i.e., instability of the system relative to the effect of a force at a frequency ω_2 is possible. In particular such an instability can occur in a plasma on which an electromagnetic field acts. In Sec. 4 fluctuation-dissipation theorems were derived which relate the noise arising in the system when an external field is present with the susceptibility of the system. A fluctuation-dissipation theorem can be used to calculate the noise properties of a Raman laser.

It is of interest to compare the Raman excitation of a system, as considered above, with parametric excitations. The qualitative features of such a comparison can be understood most easily in a discrete (point) model. To begin with we consider a typical situation corresponding to a parametric pump.[15] A pump field of frequency ω_1 acts on a non-linear element. Associated with this non-linear element are two RLC circuits: the "signal" and "idler" frequencies of which ω_2 and ω_0 satisfy the relation $\omega_1 = \omega_2 + \omega_0$. Under the conditions defined self-excitation occurs (or additional negative resistance appears) simultaneously in both circuits. The occurrence of negative resistances or the corresponding instabilities is a consequence of the parametric interaction of the fields in both circuits. In particular, if one of the circuits, for example the "idler," is removed from the system, then the other circuit will not be excited. Thus, parametric excitation is associated not with the non-linear element alone, but is a property of the electromagnetic system also, i.e., the system of circuits.

We now consider Raman excitation of a system. Here a field ω_1 also acts on a non-linear element (possessing a resonance frequency ω_0). Negative resistance then appears at the frequency $\omega_2 = \omega_1 - \omega_0$; however, this is the resistance of the non-linear element itself in the presence of the pump. This resistance can now be connected to any circuit with frequency ω_2 and instability will arise there. Thus, in the case of Raman excitation, the appearance of negative resistance is a property of the non-linear element itself in the presence of the pump.

It is easy to establish the relation between parametric and Raman excitations. To do this it is sufficient in the first case to consider as a non-linear system a molecular system together with an idler circuit of frequency ω_0. In such a system the pump field with frequency ω_1 causes negative resistance, which appears if we connect a trial circuit of frequency $\omega_2 = \omega_1 - \omega_0$. Parametric excitation can be considered as stimulated Raman emission in the "idler" circuit ω_0.

In fact, parametric interaction is associated, as has been remarked already, with the second term in expansion (9). The responses at the frequencies ω_0 and ω_1 have the forms

$$x(\omega_0) = \chi(\omega_1, -\omega_2) f^{(1)} f^{(-2)} e^{-i\omega_0 t},$$

$$x(\omega_1) = \chi(\omega_1, -\omega_0) f^{(1)} f^{(-0)} e^{-i\omega_2 t}. \tag{50}$$

The field at frequency ω_0 is in the steady-state condition

$$f^{(-0)} = \alpha x^*(\omega_0) = \alpha\chi^*(\omega_1, -\omega_2) f^{(1)*} f^{(-2)*} e^{i\omega_0 t}, \tag{51}$$

where α is some coefficient determined in particular by the electrodynamics of the circuits. Substituting (51) in the second equality of (50) we obtain

$$x(\omega_2) = \alpha\chi(\omega_1, -\omega_0)\chi^*(\omega_1, -\omega_0) \,|f^{(1)}|^2 f^{(2)} e^{-i\omega_2 t},$$

where the quantity

$$\tfrac{1}{2}\alpha\chi(\omega_1, -\omega_0)\chi^*(\omega_1, -\omega_2)\,|f^{(1)}|^2$$

signifies the susceptibility at the frequency ω_2 and, according to the general theory, the imaginary part of this quantity should be negative when $\omega_1 > \omega_2$. It can be shown that specific calculation leads to the correct value of the negative resistance which arises in parametric systems.

It is clear that one can also say that Raman excitation coincides with parametric if as "idler" circuit one takes the "circuit" of the molecular system. From this point of view one can understand why equation (20), which is one of the possible Manley-Rowe [16] relations, is satisfied. As an example of such a molecular system circuit one can take the anharmonic oscillator on which a force with frequency ω_1 acts. Negative resistance should then appear at frequency ω_2. Let x be the coordinate of the anharmonic oscillator; then

$$\ddot{x} + \omega_0^2 x + \alpha\dot{x} - \lambda x^2 = f_1 \cos\omega_1 t + f_2\cos(\omega_2 t + \theta);$$

It is not difficult to satisfy oneself that the solution of this equation, accurate up to $f_1^2 f_2$, has at frequency ω_2 the form

$$x(\omega_2) = \frac{f_2 e^{-i\theta}}{2(\omega_0^2 - \omega_2^2)} + \frac{\lambda^2 f_1^2 f_2 e^{-i\theta}}{2(\omega_0^2 - \omega_1^2)^2(\omega_0^2 - \omega_2^2)^2[\omega_0^2 - (\omega_1 - \omega_2)^2 + i(\omega_1 - \omega_2)\alpha]}.$$

Hence we obtain the susceptibility at frequency ω_2 as

$$\chi(\omega_2) = \frac{1}{\omega_0^2 - \omega_2^2} + \frac{\lambda^2 f^2{}_1[\omega_0 - (\omega_1 - \omega_2) - i\alpha/2]}{2(\omega_0^2 - \omega_1^2)^2(\omega_0^2 - \omega_2^2)\,\omega_0\{[\omega_0 - (\omega_1 - \omega_2)]^2 + \alpha^2/4\}}.$$

As one would expect, the imaginary part of this susceptibility is negative. For more detail on the classical interpretation of stimulated Raman emission, see the work of Platonenko and Khokhlov.[17]

We now compare parametric interaction of electromagnetic waves in a non-linear dielectric, discussed by Khokhlov[9] and by Bloembergen and co-workers,[10] with Raman interaction, treated in Sec. 6 of the present paper. While efficient parametric interaction requires the phase-matching condition $\mathbf{k}(\omega_1) + \mathbf{k}(\omega_2) = \mathbf{k}(\omega_1 + \omega_2)$ to be satisfied, spatial synchronism is not necessary for the accomplishment of Raman interaction, as follows from Sec. 6. It is interesting to compare the lengths in which significant transformation of energy takes place for Raman interaction (l_k) [see (49) and (44)] and parametric (l_p) interaction (see [10]). It is not difficult to obtain the ratio of the lengths in order of magnitude as

$$l_p/l_k = dA_1\hbar^{-1}T_2. \tag{52}$$

Here we took the dipole moments of the molecular system and the molecular concentrations to be equal for both interaction cases. It is seen from (52) that, although Raman interaction is an effect of higher order (see formula (9)) than parametric, for a sufficiently strong field $A_1 \sim \hbar T_2^{-1} d^{-1}$ the characteristic lengths become equal. A field of the appropriate magnitude (30 kV/cm) can be obtained with the aid of lasers.

We dwell briefly on the properties of the susceptibility in the degenerate case when $\omega_2 = \omega_1/2$. As follows from formula (9), a response at frequency $\omega_1/2$ appears even in the second order of perturbation theory. However, in this case the susceptibility of the system depends essentially on the phase relations between the pump field (ω_1) and the signal field (ω_2). In other words, the second term in (9) cannot give a negative resistance which is independent of the phase relation. Such a situation is typical of the parametric phase-matched amplifier. In distinction from this the third term in expression (9) (the Raman susceptibility) defines a negative resistance which does not depend on the phase relation of the pump field (ω_1) and the signal field at frequency $\omega_1/2$. Such a difference is associated with the fact that for the Raman interaction the idler circuit (the molecular system) and the signal frequency circuit are by no means identical, as they are in the case of phase-matched parametric amplifiers.

In conclusion we note that using stimulated Raman emission at frequency $\omega_2 = 2\omega_1$ (the anti-Stokes component) we can perform frequency doubling inside the laser itself, since in the latter the molecular system finds itself in an inverted state.

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[1] W. Kaiser and C. G. B. Garrett, Phys. Rev. Letters **7**, 229 (1961).

[2] I. D. Abella, Phys. Rev. Letters 9, 453 (1962).

[3] Eckhardt, Hellwarth, McClung, Schwarz, Weiner, and Woodbury, Phys. Rev. Letters **9**, 455 (1962).

[4] G. Landsberg and L. Mandelstam, Naturwissenschaften **16**, 557, 772 (1928).

[5] C. V. Raman and K. S. Krishnan, Nature **121**, 501 (1928).

[6] G. Placzek, (Rayleigh Scattering and the Raman Effect) (Russ. Transl.) ONTI, Khar'kov (1935).

[7] M. Göppert-Mayer, Ann. Physik 9, 273 (1931).

[8] V. M. Faĭn, Izv. Vuzov, Radiofizika **6**, 207 (1963).

[9] R. V. Khokhlov, Radiotekhnika i élektronika **6**, 1116 (1961); S. A. Akhmanov and R. V. Khokhlov, JETP **43**, 351 (1962), Soviet Phys. JETP **16**, 252 (1963).

[10] Armstrong, Bloembergen, Ducuing and Pershan, Phys. Rev. **127**, 1918 (1962).

[11] V. I. Karpman, JETP **44**, 1307 (1963), Soviet Phys. JETP **17**, 882 (1963).

[12] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Gostekhizdat (1957).

[13] V. M. Faĭn, JETP **42**, 1075 (1962), Soviet Phys. JETP **15**, 743 (1962). UFN **79**, 641 (1963), Soviet Phys. Uspekhi **6**, 294 (1963).

[14] F. A. Savin and I. I. Sobel'man, Optika i spektroskopiya **7**, 740 (1959).

[15] S. Bloom and K.K.N. Chang, R.C.A. Reveiw **18**, 578 (1957).

[16] J. M. Manley and H. E. Rowe, Proc. Inst. Radio Engrs. **44**, 904 (1956).

[17] V. T. Platonenko and R. V. Khokhlov, JETP **46**, 555 (1964), this issue, p. 378.

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