A quantum mechanical theory of stimulated resonance Raman scattering taking full account of the effects of the incident and scattered radiation on the state and properties of the molecules is developed. The resulting formulas enable the amplification of the scattered radiation and the attenuation of the incident flux to be determined. The conditions under which stimulated Raman scattering produces amplification of radiation are formulated. The range of applicability of the theory, not taking account of the effects of radiation on the properties of the material is discussed.

Several papers on the quantum mechanical theory of stimulated Raman scattering (SRS) have appeared recently [1-4]. They deal with several of the major properties of the SRS phenomenon, but their results are generally applicable only in cases of medium strength scattering in the absence of resonance. Their extension to the case of resonance scattering is not possible, since the above authors have derived their formulas without taking full account of the effect of the incident and scattered radiation on the state and properties of the scattering molecules [5]. In fairness it must be noted that in contrast to [1-3], small fields are not assumed in [4]. This enabled the author of the latter paper to make allowance for certain saturation effects. He did, however, assume the absence of resonance between the frequencies of the field and the characteristic frequencies of the molecules. This renders the results of [4] inapplicable in the case of resonance SRS.

The present paper concerns the characteristic features of first-order SRS which arise upon transition from non-resonance to resonance scattering. No limitations are imposed as regards the magnitude of the radiation field. As in [1-4], we shall describe the state of the scattering molecules by means of the density matrix $\rho$ whose elements $\rho_{ij}$ practically always (in the optical frequency range) [6] satisfy the equations

$$\frac{d\rho_{ij}}{dt} = \sum_k V_{ik} \rho_{kj} - \sum_k \rho_{ik} V_{kj} + \sum_h d_{ik} \rho_{hh} + \sum_k d_{kh} \rho_{kh},$$

$$\frac{d\rho_{ij}}{dt} = \sum_k V_{ik} \rho_{kj} - \sum_k \rho_{ik} V_{kj} - \gamma_{ij} \rho_{ij}.$$

Here $d_{ik}$ are the nonoptical transition probabilities; $\gamma_{ij}$ is the parameter representing the difference between the phases of the states $i$ and $j$, which is usually manifested as the spectral width of the transition $i \rightarrow j$; $V_{ik}$ are the elements of the radiation-molecule interaction matrix, which in the dipole approximation are given by the formula

$$V_{ik} = -\frac{1}{\hbar} \rho_{ik} E e^{i\omega_{ik} t},$$

where $\rho_{ik}$ and $\omega_{ik}$ are the dipole moment and frequency of the transition $i \rightarrow k$; $E$ is the electric intensity of the radiation field at the center point of the molecule. In considering stimulated interaction of radiation and matter there is no need to quantize the field [6]. Hence, $E$ in (3) can be considered as a classical function of time and coordinates, and the spontaneous transition probabilities can be assumed to be contained in $\gamma_{ij}$ and $d_{ik}$. In computing SRS it is sufficient to assume that the electromagnetic field is made up of two waves,

$$E = \Re (e_1 E_1 e^{i\omega_1 t} + e_2 E_2 e^{i\omega_2 t}),$$

whose frequency difference, to within the line width, is equal to one of the characteristic frequencies of the molecule,

$$\omega_1 - \omega_2 \approx \omega_{21};$$

where $e_1$ and $e_2$ are the polarization vectors.

The simplest model of the material taking part in this phenomenon is a three-level system in which the difference between the energies of the two lower levels determines the frequency $\omega_{21}$. Without limiting the generality of our conclusions, we can assume that $\rho_{21} = 0$ and that $|\omega_{31} - \omega_{32}| < \omega_3 + \omega_f$. With these assumptions systems (1) and (2) becomes

$$\frac{d\rho_{11}}{dt} = 2\Re (V_{31} \rho_{31} e^{i(\omega_3 - \omega_1) t} - (d_{21} + d_{13}) \rho_{11} + d_{21} \rho_{22} + d_{31} \rho_{33}),$$

where $d_{1k}$ and $d_{2k}$ are the nonoptical transition probabilities; $\gamma_{ij}$ is the parameter representing the difference between the phases of the states $i$ and $j$, which is usually manifested as the spectral width of the transition $i \rightarrow j$; $V_{ik}$ are the elements of the radiation-molecule interaction matrix, which in the dipole approximation are given by the formula

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whose frequency difference, to within the line width, is equal to one of the characteristic frequencies of the molecule,

$$\omega_1 - \omega_2 \approx \omega_{21};$$

where $e_1$ and $e_2$ are the polarization vectors.
\[ \frac{d \rho_{31}}{dt} = V_{31}^+ e^{-i (\omega_{31} - \omega_1) t} (\rho_{11} - \rho_{33}) + V_{32}^- e^{i (\omega_{32} - \omega_2) t} \rho_{21} = \gamma_{31} \rho_{31}, \]  
(6b)

\[ \frac{d \rho_{21}}{dt} = V_{21}^+ e^{-i (\omega_{21} - \omega_2) t} (\rho_{33} - \rho_{22}) + V_{31}^- e^{-i (\omega_{31} - \omega_1) t} \rho_{11} = \gamma_{21} \rho_{21}, \]  
(6c)

\[ \frac{d \rho_{33}}{dt} = V_{33}^- e^{-i (\omega_{33} - \omega_3) t} (\rho_{33} - \rho_{22}) - V_{13}^- e^{-i (\omega_{13} - \omega_1) t} \rho_{13} = \gamma_{33} \rho_{33}, \]  
(6d)

\[ \frac{d \rho_{22}}{dt} = -2 \text{Re} (V_{32}^- e^{-i (\omega_{22} - \omega_2) t} \rho_{22}) - \frac{d_{12}^+ \gamma_{22} + d_{13} \gamma_{11} + d_{23} \gamma_{23}}{d_{32} + d_{33}}, \]  
(6e)

\[ \frac{d \rho_{22}}{dt} = -2 \text{Re} (V_{32}^- e^{-i (\omega_{22} - \omega_2) t} \rho_{22}) - \frac{d_{12} \gamma_{22} + d_{23} \gamma_{33} + d_{12} \gamma_{11}}{d_{32} + d_{33}}, \]  
(6f)

where

\[ V_{3j}^+ = -\left( V_{3j} \right)^* = -\frac{1}{2i \hbar} (p_{3j} e_i^j) E_j. \]  
(7)

In system (6) we have omitted the rapidly oscillating terms with the sum frequencies \( \omega_{ij} + \omega_j \) and with the frequencies \( \omega_{31} - \omega_2, \omega_{22} - \omega_1 \); we have also taken account of the fact that \( \rho_{ij} = \rho_{ji}^* \) and \( \rho_{ii} = 0 \).

Now, substituting

\[ \gamma_{3j} = \rho_{3j} e^{-i (\omega_{3j} - \omega_3) t}; \quad \rho_{21} = \rho_{21} e^{-i (\omega_{21} - \omega_2 + \omega_1) t} \]  
(8)

in (6), we readily obtain a system of linear differential equations with constant coefficients. Although this system cannot be solved generally, its solution for the steady state is quite simple. After elimination of the nondiagonal matrix elements it reduces to the solution of an algebraic system of the form

\[ (a_1 + d_{31}) \rho_{33} + (d_{32} + S) \rho_{22} - (d_{12} + d_{13} + a_1 + S) \rho_{11} = 0, \]  
(9a)

\[ (a_2 + d_{22}) \rho_{33} - (d_{23} + d_{21} + a_2 + S) \rho_{22} + (d_{12} + S) \rho_{11} = 0, \]  
(9b)

\[ \rho_{11} + \rho_{22} + \rho_{33} = 1. \]  
(9c)

In deriving (9) we have replaced the equation which follows from (6e) by the normalization condition (\( S p = 1 \)) for the matrix \( \rho \) and introduced the notation

\[ \alpha_j = B_j u_j - \gamma_j, \]  
(10)

\[ B_j = \frac{4 \pi}{h^2} \frac{\left| (p_{3j} e_i^j) \right|^2 \gamma_{3j}}{\gamma_{3j}^2 + (\omega_{3j} - \omega_j)^2}, \]  
(11)

\[ S_j = \frac{8 \pi^2}{h^4} u_i u_z \text{Re} \left\{ \frac{1}{Q + \gamma_{21} + i (\omega_{21} - \omega_1 + \omega_2)} \right\} \times \]  
(12a)

\[ \times \left( \frac{\left| (p_{23} e_i^3) (p_{21} e_i^1) \right|^2}{\gamma_{31} + i (\omega_{31} - \omega_1)} \right) \right\}, \]  
(12b)

\[ Q = \frac{2 \pi}{h^2} \frac{\left| (p_{31} e_i^1) \right|^2 \mu_1}{\gamma_{32} - i (\omega_{32} - \omega_2)} + \frac{2 \pi}{h^2} \frac{\left| (p_{32} e_i^2) \right|^2 \mu_2}{\gamma_{31} + i (\omega_{31} - \omega_1)} \]  
(13)

\[ + \frac{2 \pi}{h^2} \frac{\left| (p_{31} e_i^1) \right|^2 \mu_1}{\gamma_{32} - i (\omega_{32} - \omega_2)} + \frac{2 \pi}{h^2} \frac{\left| (p_{32} e_i^2) \right|^2 \mu_2}{\gamma_{31} + i (\omega_{31} - \omega_1)}. \]  
(14)