

films which are thin (compared with the penetration depth) for temperatures ranging from T_c down to $0.18 T_c$, the lowest available temperature, in disagreement with the theory of Bardeen⁸ but in agreement with that of Nambu and Tuan.⁹

We have applied the theory of BRT,¹³ which is based on BCS, to our data on thin films of Pb, Sn, and In, on the assumption that their theory is valid for $H \neq 0$ with a suitable field-dependent gap parameter $\epsilon_0(H)$. At $T = 0.65 T_c$, the function $\epsilon_0(H)$ which results from our analysis is essentially identical to that predicted by GLG and experimentally found in tunnel measurements. At lower temperatures ($0.36 T_c$), our $\epsilon_0(H)$ computed with the aid of BRT is different, indicating a breakdown of the GLG theory for $T \ll T_c$, or possibly a failure of the method of data analysis via BRT.

By varying the relative orientation of the direction of heat flow and the applied magnetic field in the plane of the experimental films, we unsuccessfully sought evidence for vestiges of the $\mathbf{p}_F \cdot \mathbf{v}$ term in the excitation spectrum of a current-carrying superconductor, predicted by Bogoliubov.¹⁴ Since the experimental conditions differed radically from those envisioned by Bogoliubov, this negative result is not surprising.

Application of magnetic fields at various angles up to 90° with respect to the film plane still produced surprisingly well defined thermodynamic transitions, although H_c was reduced considerably below the parallel field value. The transition in a perpendicular field appeared to be second-order even for films of thickness up to 4000 \AA , whose parallel field transition was definitely first order. The perpendicular critical field values and the angular dependence of H_c seem to be explained satisfactorily by the theory of Tinkham.³¹

Lead films gave results qualitatively similar to indium and tin films, but quantitatively the form of the derived $\epsilon_0(H)$ at low temperatures was different from that of tin and indium. We suspect that this is connected with the well-known peculiarities in the thermal properties of superconducting lead.

ACKNOWLEDGMENTS

Thanks are due to I. F. Silvera for measuring the effect of atmospheric oxidation on the optical transmissivity of our Pb films. One of us (D.M.) would like to thank Dr. K. G. Ramanathan for the hospitality of the National Physical Laboratory of India during the preparation of the manuscript.

Higher Order Coherent Raman Effects*

C. L. TANG

Raytheon Research Division, Waltham, Massachusetts

(Received 8 January 1964)

With the recently available very intense coherent maser light, interesting higher order coherent Raman effects have been observed in solids, liquids, and gases. Garmire, Pandarese, and Townes have given a phenomenological theory of these higher order coherent Raman effects. In this paper a somewhat more detailed theory of these effects is given. The analysis is based on a perturbation solution of the Boltzmann equation for the density matrix of the Raman active medium. General expressions for all the relevant induced dipole moments and absorbed or emitted Stokes and anti-Stokes radiations in the ordinary or higher order coherent Raman processes are given. These cover a great variety of possible experimental situations. Several specific simple examples are studied in some detail and the results of the phenomenological theory are reproduced from the general results given here.

I. INTRODUCTION

THE first-order Raman effects have been investigated extensively in the past both experimentally and theoretically. With the recently available very intense maser light, interesting higher order coherent Raman effects in solids,¹ liquids,² and gases³ have also

* Work supported in part by Contract No. AF 19(628)-3862, AFCRL, Hanscom Field, Bedford, Massachusetts.

¹ G. Eckardt, D. P. Bortfeld, and M. Geller, *Appl. Phys. Letters* **3**, 137 (1963).

² B. Stoicheff, Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 1963 (unpublished); *Phys. Letters* **7**, 186 (1963); H. J. Zeiger, P. E. Tannenwald, S. Kern, and R. Herendeen, *Phys. Rev. Letters* **11**, 419 (1963).

³ R. W. Mink, R. W. Terhune, and W. G. Rado, *Appl. Phys. Letters* **3**, 181 (1963).

been observed. Garmire, Pandarese, and Townes⁴ give a detailed macroscopic theory of these higher order coherent Raman effects, particularly those through excitation of intense coherent molecular oscillations at infrared frequencies. Many interesting conclusions were drawn from the theory and some of these have already been observed experimentally. In this paper an attempt is made to give a somewhat more detailed analysis of the same effects on the basis of the quantum-mechanical Boltzmann equation for the density matrix characterizing the Raman-active medium and to include in the theory the effects of various relaxation processes.

⁴ E. Garmire, F. Pandarese, and C. H. Townes, *Phys. Rev. Letters* **11**, 160 (1963).

The effects of spatial dispersion⁵ are not, however, explicitly taken into account in the calculations here. This may be a serious omission in some cases involving liquids and solids, but in the cases of gases it is most likely not. When spatial dispersion effects are neglected, a local description of the Raman-active dielectric medium is possible. The study of the various higher order coherent Raman effects can then be carried out in several steps.

In the first step, we consider a volume of the dielectric with linear dimensions large compared with the intermolecular spacings but small compared with the wavelengths of the interacting photons and the coherent molecular vibrational waves (or other polarization waves). Within a volume of this size, the radiation fields can be assumed coherent and uniform, and the medium can be characterized by a spatially independent density matrix. The quantum-mechanical Boltzmann equation governs the time response of the density matrix due to the applied fields. The average induced dipole moment per molecule or molecular oscillations in the medium produced in various Raman processes can be obtained from the corresponding higher order terms in the perturbation solution of the Boltzmann equation. From these one can determine the frequencies of the Raman-scattered Stokes and anti-Stokes radiations and the rate at which they are absorbed or emitted locally. In Sec. II an explicit formulation of the problem in terms of the density matrix is given along with a formal procedure for obtaining the appropriate perturbation solution.

In the second step, we consider a volume of the dielectric medium with linear dimensions large compared with the wavelengths of all the waves of interest but still small compared with the distances over which the amplitudes and phases of the waves change appreciably. The harmonic spatial dependences of all the waves can therefore be directly introduced into the various expressions obtained in the previous step. When macroscopic spatially coherent effects are considered, one assumes a fixed phase for each of the electromagnetic waves. Upon averaging the resulting expressions over such a volume, one obtains the conditions under which each Stokes or anti-Stokes radiation will be absorbed or amplified on the average. These include the so-called phase-matching conditions which give the propagation vectors of the Stokes and anti-Stokes radiations.

In the final step, one may consider questions which are only significant on dimensional scales over which the amplitudes and phases of the various waves vary appreciably. These involve questions such as energy transport, boundary effects, geometrical effects, etc.

In the present study we do not, however, go beyond the second step in any detail. The primary concern here is in the intrinsic properties of the higher order coherent

Raman processes as discussed by Garmire, Pandarese, and Townes.

The above assumptions and basic steps are implicit in the calculations and discussions given below.

II. THE DENSITY-MATRIX EQUATION

We ignore first the spatial dependence in all the variables. Under the usual assumptions,⁶ the quantum-mechanical Boltzmann equation for the density matrix is

$$\partial\rho/\partial t = -(i/\hbar)[H, \rho] - \frac{1}{2}[\Gamma(\rho - \bar{\rho}) + (\rho - \bar{\rho})\Gamma], \quad (2.1)$$

where the total Hamiltonian

$$H = H_0 + V = H_0 - \mathbf{p} \cdot \mathbf{E} \quad (2.1a)$$

is the sum of the unperturbed Hamiltonian of the molecule, H_0 , and the interaction energy of the molecules with the total electric field, \mathbf{E} . In a representation in which H_0 is diagonal, Γ , which characterizes phenomenologically the effects of various relaxation processes, is a diagonal matrix $\Gamma_{mn} = \gamma_m \delta_{mn} \cdot \mathbf{1}$, where $\mathbf{1}$ is a unit matrix with the dimensionality of the corresponding eigenvalue of H_0 . The matrix $\bar{\rho}$ is diagonal, and the diagonal elements are proportional to the thermal equilibrium populations of the corresponding energy levels at a given temperature T in the absence of V , or

$$\bar{\rho} = \exp(-H_0/kT) / \text{Trace}[\exp(-H_0/kT)]. \quad (2.1b)$$

$\rho(t)$ determines the average induced electric dipole moment, $\mathbf{p}(t)$, per molecule:

$$\mathbf{p}(t) = \text{Tr}[\mathbf{p}\rho(t)], \quad (2.2)$$

where \mathbf{p} is the electric dipole operator.

In studying Raman effects we consider three energy levels, ϵ_1 , ϵ_2 , and ϵ_3 , of the molecules (Fig. 1) where level 1 is the ground state and level 2 could be a vibrational level, a rotational level, or an electronic level if electronic Raman effects are considered. Level 3 is the intermediate state. All these levels will in general be degenerate. For the basic first-order Raman process, it is sufficient to assume that the total electric field consists of two components:

$$\mathbf{E}(t) = [\mathbf{E}_a e^{i\omega_a t} + \mathbf{E}_a^* e^{-i\omega_a t}] + [\mathbf{E}_b e^{i\omega_b t} + \mathbf{E}_b^* e^{-i\omega_b t}]. \quad (2.3a)$$

The elements of interest in the perturbation term V of the total Hamiltonian are assumed to be:

$$\begin{aligned} V_{1\alpha, 1\beta} &= V_{2\alpha, 2\beta} = V_{3\alpha, 3\beta} = V_{1\alpha, 2\beta} = 0, \\ V_{1\alpha, 3\beta} &= V_{1\alpha, 3\beta}^{(a)} e^{i\omega_a t} + V_{1\alpha, 3\beta}^{(a)*} e^{-i\omega_a t}, \\ V_{2\alpha, 3\beta} &= V_{2\alpha, 3\beta}^{(b)} e^{i\omega_b t} + V_{2\alpha, 3\beta}^{(b)*} e^{-i\omega_b t}, \end{aligned} \quad (2.3b)$$

for ω_a and ω_b sufficiently close to the correspond-

⁵ See, for example, J. J. Hopfield and D. G. Thomas, Phys. Rev. **132**, 563 (1963).

⁶ R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948); W. E. Lamb, Jr., *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1960), Vol. II, p. 435; Third International Symposium on Quantum Electronics, Paris, France, 1963 (unpublished).

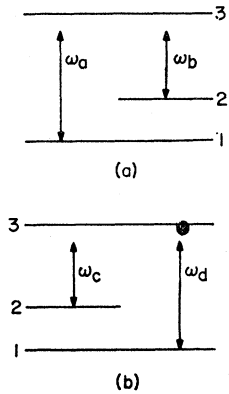


FIG. 1. Schematic diagram of energy levels and fields involved in (a) ordinary and (a), (b) higher order Raman processes.

ing transition frequencies $\omega_{31} = \hbar^{-1}(\epsilon_3 - \epsilon_1)$ and $\omega_{32} = \hbar^{-1}(\epsilon_3 - \epsilon_2)$, and

$$V_{m\alpha, n\beta}^{(a,b)} = -\langle m, \alpha | \mathbf{p} \cdot \mathbf{E}_{a,b} | n, \beta \rangle. \quad (2.3c)$$

In Eqs. (2.3b) and (2.3c), α and β designate the degenerate states of the energy levels ϵ_m and ϵ_n , respectively. We also assume that

$$\omega_a - \omega_b \approx \hbar^{-1}(\epsilon_2 - \epsilon_1) = \omega_{21}, \quad (2.3d)$$

but ω_a and ω_b are not so near the corresponding transition frequencies that the direct processes become important.

As in the usual theory⁷ of ordinary Raman effects for a single molecule, which is based on the perturbation solution of Schrödinger's equation, we obtain the steady-state solution of the Boltzmann equation (2.1) by perturbation techniques.⁸ Specifically, we formally expand the elements of the density matrix:

$$\rho_{m\alpha, n\beta} = \rho_{m\alpha, n\beta}^{(0)} + \rho_{m\alpha, n\beta}^{(1)} + \cdots + \rho_{m\alpha, n\beta}^{(j)} + \cdots \quad (2.4)$$

in successive orders of approximation corresponding to ascending powers of the amplitude of the electric field. The lowest order term

$$\rho_{m\alpha, n\beta}^{(0)} = \frac{1}{T_{mn}} \int^t \exp\left(i\omega_{mn} + \frac{1}{T_{mn}}\right) \times (t' - t) \bar{\rho}_{m\alpha, n\beta} dt', \quad (2.5)$$

which would simply be equal to $\bar{\rho}_{m\alpha, n\beta}$ if the latter is purely diagonal and time-independent. In Eq. (2.5)

$$T_{mn}^{-1} = \frac{1}{2}(\gamma_m + \gamma_n), \quad (2.6)$$

which is independent of the degeneracy indices α and β .

⁷ See, for example, M. Göppert-Mayer, *Ann. Phys.* **9**, 273 (1931); G. Placzek, *Handbuch der Radiologie* (Akademische Verlagsgesellschaft Leipzig, 1934), Vol. VI, Part II, pp. 209-347. For more recent studies in connection with maser work see, for example, A. Javan, *J. Phys. Radium* **19**, 806 (1958).

⁸ C. L. Tang and H. Statz, *Phys. Rev.* **128**, 1013 (1962); H. Statz and C. L. Tang, Third International Symposium on Quantum Electronics, Paris, France, 1963 (unpublished).

The successive terms, i.e., $j \geq 1$:

$$\rho_{m\alpha, n\beta}^{(j)} = -\frac{i}{\hbar} \sum_{l, \gamma} \int^t \exp\left(i\omega_{mn} + \frac{1}{T_{mn}}\right) (t' - t) \times [V_{m\alpha, l\gamma} \rho_{l\gamma, n\beta}^{(j-1)} - \rho_{m\alpha, l\gamma}^{(j-1)} V_{l\gamma, n\beta}] dt'. \quad (2.7)$$

This series solution, (2.4)-(2.7), is formally identical to that used in the study of nonlinear interaction of oscillating modes in a gas maser, or in similar problems, where the nonlinearity is due to multiple successive single-photon processes.^{6,8,9} Raman processes are true multiple-photon processes.

Mathematically, the distinction is quite simple, and it lies in how the intermediate steps in the iterations implied in (2.7) are carried out, apart from the resonance conditions. Very briefly, in the successive single-photon process, one calculates alternately the off-diagonal and the diagonal elements in the successive steps of (2.7) (see Ref. 8). In the ordinary Raman process, as in the situation depicted in Fig. 1(a), in which simultaneous absorption of a photon at ω_a and emission of a photon at ω_b occur, one calculates, for example, the second-order term $\rho_{1\alpha, 2\beta}^{(2)}$ directly from $\rho_{1\alpha, 3\gamma}^{(1)}$ and $\rho_{3\gamma, 2\beta}^{(1)}$. This will become clearer in the following sections.

III. ORDINARY COHERENT RAMAN EFFECTS

In the ordinary Raman process, only two photons are involved as shown in Fig. 1(a). Following the usual procedure,⁸ we obtain from Eqs. (2.7), (2.5), (2.3b), and (2.1b) the lowest order terms in the perturbation expansions of the off-diagonal elements of the density matrix

$$\rho_{1\alpha, 3\gamma}^{(1)} = -\frac{i\Delta\bar{\rho}_{31}T_{13}V_{1\alpha, 3\gamma}^{(a)}e^{i\omega_a t}}{\hbar[1+i(\omega_a - \omega_{31})T_{13}]}, \quad (3.1a)$$

$$\rho_{2\beta, 3\gamma}^{(1)} = -\frac{i\Delta\bar{\rho}_{32}T_{23}V_{2\beta, 3\gamma}^{(b)}e^{i\omega_b t}}{\hbar[1+i(\omega_b - \omega_{32})T_{23}]}, \quad (3.1b)$$

where

$$\Delta\bar{\rho}_{mn} \equiv \bar{\rho}_{m\alpha, m\alpha} - \bar{\rho}_{n\beta, n\beta} \equiv \bar{\rho}_{mm} - \bar{\rho}_{nn} \quad (3.2)$$

for any α and β . $\Delta\bar{\rho}_{mn}$ is diagonal and is independent of the degeneracy indices by virtue of (2.1b). Substituting (3.1a) and (3.1b) into (2.7), we obtain for the second-order term in the off-diagonal matrix element

$$\rho_{1\alpha, 2\beta}^{(2)} = \sum_{\gamma} \frac{V_{1\alpha, 3\gamma}^{(a)} V_{3\gamma, 2\beta}^{(b)*} T_{12} e^{i(\omega_a - \omega_b)t}}{\hbar^2 [1+i(\omega_a - \omega_b - \omega_{21})T_{12}]} \times \left[\frac{\Delta\bar{\rho}_{32}T_{23}}{1-i(\omega_b - \omega_{32})T_{23}} + \frac{\Delta\bar{\rho}_{31}T_{13}}{1+i(\omega_a - \omega_{31})T_{13}} \right]. \quad (3.3)$$

In the proper limits this term corresponds to the second-

⁹ B. Senitzky, G. Gould, and S. Cutler, *Phys. Rev.* **130**, 1460 (1963); H. Haken and H. Sauerman, *Z. Physik* **173**, 261 (1963); N. Bloembergen and Y. R. Shen, *Phys. Rev.* **133**, A37 (1964).

order term in the perturbed wave function of the Schrödinger equation in the theory of ordinary Raman effects for a single molecule.⁷ It contains all the necessary information for calculating the coherent molecular oscillations excited by the light waves. If electronic Raman processes are being considered and dipole transitions between levels 1 and 2 are allowed, it describes the induced dipole moment oscillating at $\omega_{21} = \omega_a - \omega_b$ produced by the light waves at ω_a and ω_b .

This coherently driven molecular oscillation described by $\rho_{1\alpha,2\beta}^{(2)}$ gives rise to a third-order term $\rho_{1\alpha,3\gamma}^{(3)}$, which results in an oscillating dipole moment per molecule at ω_a :

$$\begin{aligned} \mathbf{p}_a^{(3)} &= \sum_{\alpha, \gamma} [\mathbf{p}_{3\gamma,1\alpha} \rho_{1\alpha,3\gamma}^{(3)} + \rho_{3\gamma,1\alpha}^{(3)} \mathbf{p}_{1\alpha,3\gamma}] \\ &= \sum_{\gamma, \alpha, \gamma', \beta} i\chi_a \mathbf{p}_{3\gamma,1\alpha} V_{1\alpha,3\gamma'}^{(a)} V_{3\gamma',2\beta}^{(b)*} V_{2\beta,3\gamma}^{(b)} \\ &\quad \times e^{i\omega_a t} + \text{c.c.}, \quad (3.4a) \end{aligned}$$

where

$$\begin{aligned} \chi_a &= \frac{T_{12} T_{13}}{\hbar^3 [1 + i(\omega_a - \omega_b - \omega_{21}) T_{12}] [1 + i(\omega_a - \omega_{31}) T_{13}]} \\ &\quad \times \left[\frac{\Delta \bar{\rho}_{32} T_{23}}{1 - i(\omega_b - \omega_{32}) T_{23}} + \frac{\Delta \bar{\rho}_{31} T_{13}}{1 + i(\omega_a - \omega_{31}) T_{13}} \right], \quad (3.4b) \end{aligned}$$

and an oscillating dipole moment at ω_b :

$$\begin{aligned} \mathbf{p}_b^{(3)} &= \sum_{\beta, \gamma} [\mathbf{p}_{3\gamma,2\beta} \rho_{2\beta,3\gamma}^{(3)} + \rho_{3\gamma,2\beta}^{(3)} \mathbf{p}_{2\beta,3\gamma}] \\ &= \sum_{\gamma, \beta, \gamma', \alpha} i\chi_b \mathbf{p}_{3\gamma,2\beta} V_{2\beta,3\gamma'}^{(b)} V_{3\gamma',1\alpha}^{(a)*} V_{1\alpha,3\gamma}^{(a)} \\ &\quad \times e^{i\omega_b t} + \text{c.c.}, \quad (3.4c) \end{aligned}$$

where

$$\begin{aligned} \chi_b &= \frac{T_{12} T_{23}}{\hbar^3 [1 - i(\omega_a - \omega_b - \omega_{21}) T_{12}] [1 + i(\omega_b - \omega_{32}) T_{23}]} \\ &\quad \times \left[\frac{\Delta \bar{\rho}_{32} T_{23}}{1 + i(\omega_b - \omega_{32}) T_{23}} + \frac{\Delta \bar{\rho}_{31} T_{13}}{1 - i(\omega_a - \omega_{31}) T_{13}} \right], \quad (3.4d) \end{aligned}$$

with the help of (3.3), (2.7), (2.3b), and (2.2). Not all the terms in the sums over the degeneracy indices in (3.4a) and (3.4c), as well as (3.3), are nonzero. Many will vanish of course due to selection rules or other special circumstances.

These dipole moments at frequencies ω_a and ω_b , $\mathbf{p}_a^{(3)}$ and $\mathbf{p}_b^{(3)}$, induced in the Raman process will lead to energy exchange between the molecules and the oscillating electric fields at the corresponding frequencies. The average absorbed power is equal to the time average of the scalar product of the rate of decrease of the dipole moment and the corresponding oscillating component of the electric field. We obtain from (3.4a) for the average power absorbed per molecule at the frequency ω_a

$$P_a = \text{Re} \left\{ \sum_{\gamma, \alpha, \gamma', \beta} 2\omega_a \chi_a V_{3\gamma,1\alpha}^{(a)*} V_{1\alpha,3\gamma'}^{(a)} \right. \\ \left. \times V_{3\gamma',2\beta}^{(b)*} V_{2\beta,3\gamma}^{(b)} \right\}. \quad (3.5)$$

Similarly, from (3.4c) the average absorbed power per molecule at ω_b is

$$P_b = \text{Re} \left\{ \sum_{\gamma, \beta, \gamma', \alpha} 2\omega_b \chi_b V_{3\gamma,2\beta}^{(b)*} V_{2\beta,3\gamma'}^{(b)} \right. \\ \left. \times V_{3\gamma',1\alpha}^{(a)*} V_{1\alpha,3\gamma}^{(a)} \right\}. \quad (3.6)$$

We next introduce the spatial dependence of the perturbation terms $V^{(a)}$ and $V^{(b)}$ into (3.5) and (3.6) and obtain the absorbed power averaged over a volume large compared with all the wavelengths of interest but small compared with the distances over which the amplitudes and phases of the waves vary appreciably. We consider homogeneous plane waves:

$$\begin{aligned} V_{1\alpha,3\beta}^{(a)} &= \bar{V}_{1\alpha,3\beta}^{(a)} e^{-i\mathbf{k}_a \cdot \mathbf{r}}, \\ V_{2\alpha,3\beta}^{(b)} &= \bar{V}_{2\alpha,3\beta}^{(b)} e^{-i\mathbf{k}_b \cdot \mathbf{r}}, \end{aligned} \quad (3.7)$$

where \mathbf{r} is the position vector of the average molecules characterized by the density matrix and $\bar{V}_{m\alpha, n\beta}^{(a,b)}$ is spatially independent but complex.

Substituting (3.7) into (3.5) and (3.6) and averaging over \mathbf{r} , we obtain the average power per unit volume absorbed at the frequency ω_a :

$$\langle P_a \rangle_{\mathbf{r}} = \text{Re} \left\{ \sum_{\gamma, \alpha, \gamma', \beta} 2N\omega_a \chi_a \bar{V}_{3\gamma,1\alpha}^{(a)*} \bar{V}_{1\alpha,3\gamma'}^{(a)} \right. \\ \left. \times \bar{V}_{3\gamma',2\beta}^{(b)*} \bar{V}_{2\beta,3\gamma}^{(b)} \right\}, \quad (3.8a)$$

and that at ω_b :

$$\langle P_b \rangle_{\mathbf{r}} = \text{Re} \left\{ \sum_{\gamma, \beta, \gamma', \alpha} 2N\omega_b \chi_b \bar{V}_{3\gamma,2\beta}^{(b)*} \bar{V}_{2\beta,3\gamma'}^{(b)} \right. \\ \left. \times \bar{V}_{3\gamma',1\alpha}^{(a)*} \bar{V}_{1\alpha,3\gamma}^{(a)} \right\}, \quad (3.8b)$$

where N is the density of the active molecules coupled to the fields. In both cases the final results are independent of the propagation vectors. Unlike the higher order Raman effects which will be considered in the following section, there are no phase matching conditions here. The average absorptions per unit volume, (3.8a) and (3.8b), are always directly proportional to the local absorptions (3.6a) and (3.6b).

On the other hand, substituting (3.7) into (3.3), we have

$$\begin{aligned} \rho_{1\alpha,2\beta}^{(2)} &= \sum_{\gamma} \frac{\bar{V}_{1\alpha,3\gamma}^{(a)} \bar{V}_{3\gamma,2\beta}^{(b)*} T_{12}}{\hbar^2 [1 + i(\omega_a - \omega_b - \omega_{21}) T_{12}]} \\ &\quad \times \left[\frac{\Delta \bar{\rho}_{32} T_{23}}{1 - i(\omega_b - \omega_{32}) T_{23}} + \frac{\Delta \bar{\rho}_{31} T_{13}}{1 + i(\omega_a - \omega_{31}) T_{13}} \right] \\ &\quad \times \exp i[(\omega_a - \omega_b)t - (\mathbf{k}_a - \mathbf{k}_b) \cdot \mathbf{r}], \quad (3.9) \end{aligned}$$

which means the molecular-oscillation wave (or other polarization waves) produced in the coherent Raman process has a propagation vector equal to $\mathbf{k}_a - \mathbf{k}_b$.

If ω_a designates the primary light, say the maser light at ω_l , then (3.8b) describes the first Stokes radiation at

$\omega_{S_1} = \omega_b$:

$$\langle P_{S_1} \rangle_r = \text{Re} \left\{ \sum_{\gamma, \beta, \gamma', \alpha} 2N\omega_{S_1} \chi_{S_1} \bar{V}_{3\gamma, 2\beta}^{(S_1)*} \bar{V}_{2\beta, 3\gamma'}^{(S_1)} \right. \\ \left. \times \bar{V}_{3\gamma', 1\alpha}^{(I)*} \bar{V}_{1\alpha, 3\gamma}^{(I)} \right\}, \quad (3.10a)$$

where

$$\chi_{S_1} = \frac{T_{12}T_{23}}{\hbar^3 [1 - i(\omega_l - \omega_{S_1} - \omega_{21})T_{12}] [1 + i(\omega_{S_1} - \omega_{32})T_{23}]} \\ \times \left[\frac{\Delta\bar{\rho}_{32}T_{23}}{1 + i(\omega_{S_1} - \omega_{32})T_{23}} + \frac{\Delta\bar{\rho}_{31}T_{13}}{1 - i(\omega_l - \omega_{31})T_{13}} \right]. \quad (3.10b)$$

If ω_b designates the primary light, say the maser light at ω_l , then (3.8a) describes the anti-Stokes radiation at $\omega_{AS} = \omega_a$:

$$\langle P_{AS} \rangle_r = \text{Re} \left\{ \sum_{\gamma, \alpha, \gamma', \beta} 2N\omega_{AS} \chi_{AS} \bar{V}_{3\gamma, 1\alpha}^{(AS)*} \bar{V}_{1\alpha, 3\gamma'}^{(AS)} \right. \\ \left. \times \bar{V}_{3\gamma', 2\beta}^{(I)*} \bar{V}_{2\beta, 3\gamma}^{(I)} \right\}, \quad (3.10c)$$

where

$$\chi_{AS} = \frac{T_{12}T_{13}}{\hbar^3 [1 + i(\omega_{AS} - \omega_l - \omega_{21})T_{12}] [1 + i(\omega_{AS} - \omega_{31})T_{13}]} \\ \times \left[\frac{\Delta\bar{\rho}_{32}T_{23}}{1 - i(\omega_l - \omega_{32})T_{23}} + \frac{\Delta\bar{\rho}_{31}T_{13}}{1 + i(\omega_{AS} - \omega_{31})T_{13}} \right]. \quad (3.10d)$$

Equations (3.10a)–(3.10d) contain all the information about the Stokes and anti-Stokes radiations in the ordinary Raman process. These expressions are very general though somewhat complicated. In order to see the physical interpretations of these results better, we consider some simple limiting cases.

We first simplify the χ 's. Let us assume that

$$T_{13}, T_{23} \rightarrow \infty \quad (3.11)$$

and

$$\Delta\bar{\rho}_{32} \approx -\bar{\rho}_{22}, \quad \Delta\bar{\rho}_{31} \approx -\bar{\rho}_{11}. \quad (3.12)$$

Therefore, we have from (3.10b):

$$\lim_{T_{13}, T_{23} \rightarrow \infty} \chi_{S_1} = \frac{1}{\hbar^3} \left[\frac{T_{12} + iT_{12}^2(\omega_l - \omega_{S_1} - \omega_{21})}{1 + (\omega_l - \omega_{S_1} - \omega_{21})^2 T_{12}^2} \right] \\ \times \left[\pi\delta(\omega_{S_1} - \omega_{32}) - iP \frac{1}{\omega_{S_1} - \omega_{32}} \right] \\ \times \left[-\bar{\rho}_{22}\pi\delta(\omega_{S_1} - \omega_{32}) + i\bar{\rho}_{22}P \frac{1}{\omega_{S_1} - \omega_{32}} \right. \\ \left. - \bar{\rho}_{11}\pi\delta(\omega_l - \omega_{31}) - i\bar{\rho}_{11}P \frac{1}{\omega_l - \omega_{31}} \right], \quad (3.13a)$$

where P in (3.13a) designates principal values. The δ -functions' contributions correspond to the effects of the single-photon processes between levels 1 or 2 and 3. These effects are usually not considered as a part of the

Raman process. One should note, however, that a clear-cut distinction can easily be made only in the case $T_{13}, T_{23} \rightarrow \infty$. Experimentally, in the cases where the Raman processes are important, the direct single-photon processes usually are not, so that one does not have to make a distinction and both the δ -function contributions and the principal value signs in (3.13a) can be omitted:

$$\chi_{S_1} = -\frac{1}{\hbar^3(\omega_{S_1} - \omega_{32})} \left[\frac{T_{12}}{1 + (\omega_l - \omega_{S_1} - \omega_{21})^2 T_{12}^2} \right. \\ \left. + i \frac{(\omega_l - \omega_{S_1} - \omega_{21})T_{12}^2}{1 + (\omega_l - \omega_{S_1} - \omega_{21})^2 T_{12}^2} \right] \\ \times \left[\frac{\bar{\rho}_{11}}{\omega_l - \omega_{31}} - \frac{\bar{\rho}_{22}}{\omega_{S_1} - \omega_{32}} \right]. \quad (3.13b)$$

We also assume that the primary light is linearly polarized in, say the \hat{z} direction

$$\mathbf{E}_l = \hat{z} E_l e^{-i\mathbf{k}_l \cdot \mathbf{r}}, \quad (3.14a)$$

and that the Stokes radiation is

$$\mathbf{E}_{S_1} = [\sin\theta_{S_1} \hat{x} + \cos\theta_{S_1} \hat{z}] \bar{E}_{S_1} \\ \times \exp(-i\mathbf{k}_{S_1} \cdot \mathbf{r} + i\psi_{S_1}). \quad (3.14b)$$

With (3.13b), (3.14a) and (3.14b), (3.10a) and (3.10b) can be readily evaluated if, for example, levels 1 and 2 are nondegenerate; one obtains for the Stokes radiation the familiar result⁴:

$$\langle P_{S_1} \rangle_r = -\frac{2N(\bar{\rho}_{11} - \bar{\rho}_{22})\omega_{S_1}T_{12}}{9\hbar^3\Delta_1^2[1 + (\omega_l - \omega_{S_1} - \omega_{21})^2 T_{12}^2]} \\ \times |\mathbf{p}_{13}|^2 |\mathbf{p}_{23}|^2 \bar{E}_l^2 \bar{E}_{S_1}^2 \cos^2\theta_{S_1}, \quad (3.15a)$$

where $\Delta_1 = \omega_{31} - \omega_l \approx \omega_{32} - \omega_{S_1}$ near the resonance peak at $\omega_l - \omega_{S_1} \approx \omega_{21}$ and $|\mathbf{p}_{mn}|$ is the magnitude of the reduced matrix element of the operator \mathbf{p} . Since $\bar{\rho}_{11} > \bar{\rho}_{22}$, $\langle P_{S_1} \rangle_r \leq 0$, and Stokes radiation is emitted. It is emitted in all directions with the radiation pattern determined by the angle, θ_{S_1} , between the polarizations of the maser light and the Stokes light according to $\cos^2\theta_{S_1}$.

Similarly, one obtains for the absorbed anti-Stokes radiation per unit volume⁴:

$$\langle P_{AS} \rangle_r = \frac{2N(\bar{\rho}_{11} - \bar{\rho}_{22})\omega_{AS}T_{12}}{9\hbar^3\Delta_2^2[1 + (\omega_l - \omega_{S_1} - \omega_{21})^2 T_{12}^2]} \\ \times |\mathbf{p}_{13}|^2 |\mathbf{p}_{23}|^2 \bar{E}_l^2 \bar{E}_{AS}^2 \cos^2\theta_{AS}, \quad (3.15b)$$

where $\Delta_2 = \omega_{31} - \omega_{AS} \approx \omega_{32} - \omega_l$. It is clear from (3.15b) that anti-Stokes radiation is always absorbed.

These are only some special cases. A great variety of more complicated situations may arise in experiments and the general expressions (3.10a)–(3.10d) must then be used.

IV. HIGHER ORDER COHERENT RAMAN PROCESSES

A. General Theory

In the higher order Raman processes more than two photons are involved simultaneously. Let there be photons at angular frequencies ω_c and ω_d as shown in Fig. 1(b) in addition to the photons at ω_a and ω_b as shown in Fig. 1(a).

Physically, a light wave at ω_c , propagating through a medium which is being modulated by coherent molecular oscillations, excited by two other light waves at ω_a and ω_b as described by the second order off-diagonal density matrix element $\rho_{1\alpha,2\beta}^{(2)}$, (3.3), will induce an oscillating dipole moment at $\omega_d = \omega_c + (\omega_a - \omega_b)$. Similarly, the light wave at ω_d can induce an oscillating dipole moment at $\omega_c = \omega_d - (\omega_a - \omega_b)$. Both are higher order Raman effects. This is not unlike the double-resonance effects¹⁰ where the coherence between levels 1 and 2 is induced directly by an applied field of angular frequency ω_{21} . In the present case, this coherence is

$$\mathbf{p}_{d-a+b}^{(3)} = \sum_{\gamma, \beta, \gamma', \alpha} i\chi_{d-a+b} \mathbf{p}_{3\gamma, 2\beta} V_{2\beta, 3\gamma'}^{(b)} V_{3\gamma', 1\alpha}^{(a)*} V_{1\alpha, 3\gamma}^{(d)} e^{i(\omega_d - \omega_a + \omega_b)t} + \text{c.c.}, \quad (4.2a)$$

where

$$\chi_{d-a+b} = \frac{T_{12}T_{23}}{\hbar^3 [1 - i(\omega_a - \omega_b - \omega_{21})T_{12}] [1 + i(\omega_d - \omega_a + \omega_b - \omega_{32})T_{23}]} \left[\frac{\Delta\bar{\rho}_{32}T_{23}}{1 + i(\omega_b - \omega_{32})T_{23}} + \frac{\Delta\bar{\rho}_{31}T_{13}}{1 - i(\omega_a - \omega_{31})T_{13}} \right], \quad (4.2b)$$

and the induced dipole moment per molecule at $\omega_c + (\omega_a - \omega_b)$:

$$\mathbf{p}_{c+a-b}^{(3)} = \sum_{\gamma, \alpha, \gamma', \beta} i\chi_{c+a-b} \mathbf{p}_{3\gamma, 1\alpha} V_{1\alpha, 3\gamma'}^{(a)} V_{3\gamma', 2\beta}^{(b)*} V_{2\beta, 3\gamma}^{(c)} e^{i(\omega_c + \omega_a - \omega_b)t} + \text{c.c.}, \quad (4.3a)$$

where

$$\chi_{c+a-b} = \frac{T_{12}T_{13}}{\hbar^3 [1 + i(\omega_a - \omega_b - \omega_{21})T_{12}] [1 + i(\omega_c + \omega_a - \omega_b - \omega_{31})T_{13}]} \left[\frac{\Delta\bar{\rho}_{32}T_{23}}{1 - i(\omega_b - \omega_{32})T_{23}} + \frac{\Delta\bar{\rho}_{31}T_{13}}{1 + i(\omega_a - \omega_{31})T_{13}} \right]. \quad (4.3b)$$

Let the primary light be the maser light at ω_l ; we can study all the higher order Stokes and anti-Stokes radiations with the help of (4.2a), (4.2b), (4.3a), and (4.3b).

1. First Stokes Radiation

The following combination of frequencies can lead to the first Stokes radiation in the higher order Raman process involving four photons:

$$\omega_a = \omega_{AS}, \quad \omega_b = \omega_l, \quad \omega_d = \omega_l, \quad (4.4)$$

and

$$\omega_c = \omega_d - \omega_a + \omega_b = \omega_l - \omega_{AS} + \omega_l = \omega_{S1}.$$

Substituting (4.4) into (4.2a) and (4.2b), we obtain the induced dipole moment per molecule at ω_{S1} produced in the process:

$$\mathbf{p}_{S1}^{(3)} = \sum_{\gamma, \beta, \gamma', \alpha} i\chi_{S1} \mathbf{p}_{3\gamma, 2\beta} V_{2\beta, 3\gamma'}^{(l)} V_{3\gamma', 1\alpha}^{(AS)*} \times V_{1\alpha, 3\gamma}^{(l)} e^{i\omega_{S1}t} + \text{c.c.}, \quad (4.5a)$$

¹⁰ F. Bitter, Phys. Rev. **76**, 833 (1949).

induced by two applied fields at ω_a and ω_b , where $\omega_a - \omega_b \approx \omega_{31} - \omega_{32} = \omega_{21}$.

Mathematically, the presence of two additional oscillating fields adds new elements in the perturbation term, V , in the total Hamiltonian for the density-matrix equation:

$$V_{1\alpha, 3\beta}^{(d)} e^{i\omega_d t} + V_{1\alpha, 3\beta}^{(d)*} e^{-i\omega_d t}, \quad (4.1a)$$

and

$$V_{2\alpha, 3\beta}^{(c)} e^{i\omega_c t} + V_{2\alpha, 3\beta}^{(c)*} e^{-i\omega_c t}. \quad (4.1b)$$

In the perturbation solution of the density-matrix equation, a third-order term in the off-diagonal density-matrix element $\rho_{1\alpha, 3\gamma}^{(3)}$ appears which comes from substituting into (2.7) the second-order off-diagonal elements $\rho_{1\alpha, 2\beta}^{(2)}$ and $\rho_{2\beta, 1\alpha}^{(2)}$ and the new perturbation terms given in (4.1b). Similarly, a third-order term $\rho_{2\beta, 3\gamma}^{(3)}$ appears. These give rise to new induced dipole terms.

From (2.2), (2.7), (3.3), and (4.1a), we then obtain the average induced dipole moment per molecule at $\omega_d - (\omega_a - \omega_b)$:

where

$$\chi_{S1}' = \frac{T_{12}T_{23}}{\hbar^3 [1 - i(\omega_{AS} - \omega_l - \omega_{21})T_{12}] [1 + i(\omega_{S1} - \omega_{32})T_{23}]} \times \left[\frac{\Delta\bar{\rho}_{32}T_{23}}{1 + i(\omega_l - \omega_{32})T_{23}} + \frac{\Delta\bar{\rho}_{31}T_{13}}{1 - i(\omega_{AS} - \omega_{31})T_{13}} \right] \quad (4.5b)$$

and use is made of the fact that $\omega_{AS} - \omega_l = \omega_l - \omega_{S1}$.

Following exactly the same steps as used in the previous section, we find the average absorbed power per molecule:

$$P_{S1}' = \text{Re} \left\{ \sum_{\gamma, \beta, \gamma', \alpha} 2\omega_{S1} \chi_{S1}' V_{3\gamma, 2\beta}^{(S1)*} V_{2\beta, 3\gamma'}^{(l)} \times V_{3\gamma', 1\alpha}^{(AS)*} V_{1\alpha, 3\gamma}^{(l)} \right\}. \quad (4.6)$$

By introducing the plane-wave spatial dependence of the fields, (3.7) and

$$V_{1\alpha, 3\gamma}^{(AS)} = \bar{V}_{1\alpha, 3\gamma}^{(AS)} \exp(-i\mathbf{k}_{AS} \cdot \mathbf{r}) \quad (4.7)$$

into (4.6) and then averaging over \mathbf{r} , we obtain the

average absorbed power per unit volume:

$$\langle P_{S_1'} \rangle_r = \text{Re} \left\{ \sum_{\gamma, \beta, \gamma', \alpha} 2N\omega_{S_1} \chi_{S_1'} \bar{V}_{3\gamma, 2\beta}^{(S_1)*} \bar{V}_{2\beta, 3\gamma'}^{(l)} \right. \\ \left. \times \bar{V}_{3\gamma', 1\alpha}^{(AS)*} \bar{V}_{1\alpha, 3\gamma}^{(l)} \right\} \delta_{\mathbf{k}_l + \mathbf{k}_l' - \mathbf{k}_{S_1} - \mathbf{k}_{AS}}. \quad (4.8)$$

In contrast to the ordinary Raman processes, in the present case there is a phase matching condition⁴:

$$\mathbf{k}_l + \mathbf{k}_l' - \mathbf{k}_{S_1} - \mathbf{k}_{AS} = 0 \quad (4.8a)$$

in order for the higher order coherent Raman process to take place. Whether (4.8) corresponds to absorption or emission will depend upon the detailed nature of the molecular states and the relative phases of the fields involved, as expressed in the bracketed factor in (4.8). We shall examine some special cases later.

2. First Anti-Stokes Radiation

For the first anti-Stokes radiation we take the following combination of frequencies in (4.3a) and (4.3b):

$$\omega_a = \omega_l, \quad \omega_b = \omega_{S_1}, \quad \omega_c = \omega_l, \quad (4.9)$$

and

$$\omega_d = \omega_l + \omega_l - \omega_{S_1} = \omega_{AS}.$$

The induced dipole moment per molecule at ω_{AS} produced in the higher order Raman process is

$$\mathbf{p}_{AS'}^{(3)} = \sum_{\gamma, \alpha, \gamma', \beta} i \chi_{AS'} \mathbf{p}_{3\gamma, 1\alpha} V_{1\alpha, 3\gamma'}^{(l)} V_{3\gamma', 2\beta}^{(S_1)*} \\ \times V_{2\beta, 3\gamma}^{(l)} e^{i\omega_{AS}t} + \text{c.c.}, \quad (4.10a)$$

where

$$\chi_{AS'} = \frac{T_{12} T_{13}}{\hbar^3 [1 + i(\omega_l - \omega_{S_1} - \omega_{21}) T_{12}] [1 + i(\omega_{AS} - \omega_{31}) T_{13}]} \\ \times \left[\frac{\Delta \bar{\rho}_{32} T_{23}}{1 - i(\omega_{S_1} - \omega_{32}) T_{23}} + \frac{\Delta \bar{\rho}_{31} T_{13}}{1 + i(\omega - \omega_{31}) T_{13}} \right] \quad (4.10b)$$

from (4.9) and (4.3a) and (4.3b). The average absorbed power per molecule is then

$$P_{AS'} = \text{Re} \left\{ \sum_{\gamma, \alpha, \gamma', \beta} 2\omega_{AS} \chi_{AS'} V_{3\gamma, 1\alpha}^{(AS)*} V_{1\alpha, 3\gamma'}^{(l)} \right. \\ \left. \times V_{3\gamma', 2\beta}^{(S_1)*} V_{2\beta, 3\gamma}^{(l)} \right\}. \quad (4.11)$$

Upon introducing the spatial dependence of the fields, (3.7) and (4.7), and averaging over \mathbf{r} , we obtain the absorbed power per unit volume:

$$\langle P_{AS'} \rangle_r = \text{Re} \left\{ \sum_{\gamma, \alpha, \gamma', \beta} 2N\omega_{AS} \chi_{AS'} \bar{V}_{3\gamma, 1\alpha}^{(AS)*} \bar{V}_{1\alpha, 3\gamma'}^{(l)} \right. \\ \left. \times \bar{V}_{3\gamma', 2\beta}^{(S_1)*} \bar{V}_{2\beta, 3\gamma}^{(l)} \right\} \delta_{\mathbf{k}_l + \mathbf{k}_l' - \mathbf{k}_{S_1} - \mathbf{k}_{AS}}. \quad (4.12)$$

Again, one has the phase matching condition, (4.8a).⁴

$$\begin{aligned} \sum &= \sum_{\gamma, \beta, \gamma', \alpha} \bar{V}_{3\gamma, 2\beta}^{(S_1)*} \bar{V}_{2\beta, 3\gamma'}^{(l)} \bar{V}_{3\gamma', 1\alpha}^{(AS)*} \bar{V}_{1\alpha, 3\gamma}^{(l)} \\ &= \sum_{\alpha, \beta} \bar{E}_l^2 \bar{E}_{S_1} \bar{E}_{AS} e^{-i\psi_{S_1} - i\psi_{AS}} \langle 2, \beta | T(1, 0) | 3, \beta \rangle \langle 1, \alpha | T(1, 0) | 3, \alpha \rangle \\ &\quad \times [\langle 3, \alpha | T(1, 0) | 2, \beta \rangle \cos \theta_{S_1} + (1/\sqrt{2}) (\langle 3, \alpha | T(1, -1) | 2, \beta \rangle - \langle 3, \alpha | T(1, 1) | 2, \beta \rangle) \sin \theta_{S_1}] \\ &\quad \times [\langle 3, \beta | T(1, 0) | 1, \alpha \rangle \cos \theta_{AS} - (1/\sqrt{2}) (\langle 3, \beta | T(1, 1) | 1, \alpha \rangle (\sin \theta_{AS} \cos \phi_{AS} + i \sin \theta_{AS} \sin \phi_{AS}) \\ &\quad + (1/\sqrt{2}) \langle 3, \beta | T(1, -1) | 1, \alpha \rangle (\sin \theta_{AS} \cos \phi_{AS} - i \sin \theta_{AS} \sin \phi_{AS})], \quad (4.16) \end{aligned}$$

3. Higher Order Stokes and Anti-Stokes Radiations

By taking suitable combinations of frequencies, properties of successive higher orders of Stokes and anti-Stokes radiations can be studied in much the same way using (4.2a), (4.2b), (4.3a), and (4.3b).

For example, for the second Stokes radiation, one takes the following independent combinations of frequencies:

$$\omega_a = \omega_l, \quad \omega_b = \omega_{S_1}, \quad \omega_d = \omega_{S_1}, \quad (4.13a)$$

$$\omega_c = \omega_d - \omega_a + \omega_b = \omega_{S_1} - (\omega_l - \omega_{S_1}) = \omega_{S_2};$$

and

$$\omega_a = \omega_{AS}, \quad \omega_b = \omega_l, \quad \omega_d = \omega_{S_1}, \quad (4.13b)$$

$$\omega_c = \omega_{S_1} - (\omega_{AS} - \omega_l) = \omega_{S_2}.$$

Physically, these correspond to the cases where a light wave at ω_{S_1} propagates in a medium which is modulated by the coherent molecular oscillations excited by two other light waves at ω_l and ω_{S_1} , (4.13a), or ω_{AS} and ω_l , (4.13b). As a result, absorption or emission at ω_{S_2} may take place. It is now obvious how the absorbed powers could be calculated. It may be of interest to look at the phase matching conditions.

It can be shown readily that for the first case, (4.13a), the phase matching condition is⁴

$$\mathbf{k}_{S_1} + \mathbf{k}_{S_1}' - \mathbf{k}_l - \mathbf{k}_{S_2} = 0; \quad (4.14a)$$

and for the second case, (4.13b), it is

$$\mathbf{k}_{AS} - \mathbf{k}_l - \mathbf{k}_{S_1} + \mathbf{k}_{S_2} = 0. \quad (4.14b)$$

It is clear that the general results given can be readily applied to a great variety of interesting experimental situations. We now study some specific simple cases.

B. Special Examples

Consider the first Stokes radiation in the higher order process. As in Sec. III, let us assume again that all the light waves are linearly polarized:

$$\bar{V}^{(l)} = p_z \bar{E}_l, \quad (4.15a)$$

$$\bar{V}^{(S_1)} = (p_x \sin \theta_{S_1} + p_z \cos \theta_{S_1}) \bar{E}_{S_1} e^{i\psi_{S_1}}, \quad (4.15b)$$

$$\bar{V}^{(AS)} = (p_x \sin \theta_{AS} \cos \phi_{AS} + p_y \sin \theta_{AS} \sin \phi_{AS} \\ + p_z \cos \theta_{AS}) \bar{E}_{AS} e^{i\psi_{AS}}, \quad (4.15c)$$

in a suitably chosen coordinate system. With (4.15a)–(4.15c), we can evaluate the sums in (4.8), assuming that level 2 is a vibrational level; for example,

where the tensor operators are

$$T(1,0) = p_z, \quad T(1,-1) = \frac{1}{\sqrt{2}}p_x + \frac{i}{\sqrt{2}}p_y, \quad T(1,1) = -\frac{1}{\sqrt{2}}p_x + \frac{i}{\sqrt{2}}p_y. \quad (4.16a)$$

If, furthermore, levels 1 and 2 are nondegenerate, Eq. (4.16) simplifies to

$$\Sigma = \frac{1}{9} |p_{13}|^2 |p_{23}|^2 \bar{E}_i^2 \bar{E}_{S_1} \bar{E}_{AS} e^{-i\psi_{S_1} - i\psi_{AS}} \cos\theta_{S_1} \cos\theta_{AS}. \quad (4.16b)$$

Assuming in addition that $T_{13}, T_{23} \rightarrow \infty$ and none of the single-photon frequencies are very near any of the transition frequencies, substituting (4.16b) into (4.8) and (4.5b), and taking the proper limits, we obtain for the average absorbed first Stokes radiation per unit volume:

$$\langle P_{S_1}' \rangle_r = -\frac{2N(\bar{\rho}_{11} - \bar{\rho}_{22})\omega_{S_1} T_{12} |p_{13}|^2 |p_{23}|^2 \bar{E}_i^2 \bar{E}_{S_1} \bar{E}_{AS}}{9\hbar^3 [1 + (\omega_{AS} - \omega_l - \omega_{21})^2 T_{12}^2] \Delta_1 \Delta_2} \cos\theta_{S_1} \cos\theta_{AS} \\ \times [\cos(\psi_{S_1} + \psi_{AS}) + T_{12}(\omega_{AS} - \omega_l - \omega_{21}) \sin(\psi_{S_1} + \psi_{AS})] \delta_{\mathbf{k}_l + \mathbf{k}_l' - \mathbf{k}_{S_1} - \mathbf{k}_{AS}}, \quad (4.17)$$

where in the denominator, as before,

$$\Delta_1 = \omega_{32} - \omega_{S_1} \quad \text{and} \quad \Delta_2 = \omega_{32} - \omega_l \approx \omega_{31} - \omega_{AS}.$$

On resonance,⁴ one has absorption of the first Stokes radiation, or $\langle P_{S_1}' \rangle_r \geq 0$, if $\pi/2 < (\psi_{S_1} + \psi_{AS}) < 3\pi/2$, and emission of the first Stokes radiation, or $\langle P_{S_1}' \rangle_r \leq 0$, if $-\pi/2 < (\psi_{S_1} + \psi_{AS}) < \pi/2$.

Under similar circumstances, one finds the absorbed anti-Stokes radiation per unit volume:

$$\langle P_{AS}' \rangle_r = \frac{2N(\bar{\rho}_{11} - \bar{\rho}_{22})\omega_{AS} T_{12} |p_{13}|^2 |p_{23}|^2 \bar{E}_i^2 \bar{E}_{S_1} \bar{E}_{AS}}{9\hbar^3 [1 + (\omega_{AS} - \omega_l - \omega_{21})^2 T_{12}^2] \Delta_1 \Delta_2} \cos\theta_{S_1} \cos\theta_{AS} \\ \times [\cos(\psi_{S_1} + \psi_{AS}) - T_{12}(\omega_{AS} - \omega_l - \omega_{21}) \sin(\psi_{S_1} + \psi_{AS})] \delta_{\mathbf{k}_l + \mathbf{k}_l' - \mathbf{k}_{S_1} - \mathbf{k}_{AS}}, \quad (4.18)$$

where, in the denominator, use is made of the fact that

$$\omega_l - \omega_{31} \approx \omega_{S_1} - \omega_{32} \quad \text{and} \quad \omega_{AS} - \omega_{31} \approx \omega_l - \omega_{32}.$$

Therefore, on resonance, when $\pi/2 < (\psi_{S_1} + \psi_{AS}) < 3\pi/2$, $\langle P_{AS}' \rangle_r \leq 0$, and one has emission of anti-Stokes radiation; when $-\pi/2 < (\psi_{S_1} + \psi_{AS}) < \pi/2$, $\langle P_{AS}' \rangle_r \geq 0$ and one has absorption of anti-Stokes radiation.⁴

It follows also from (4.17) and (4.18) that on resonance and when the phase matching condition is satisfied

$$\langle P_{AS}' \rangle_r \cdot \omega_{AS}^{-1} = -\langle P_{S_1}' \rangle_r \cdot \omega_{S_1}^{-1}, \quad (4.19)$$

which is similar to the so-called Manley-Row relation, well-known in the theory of parametric amplifiers in microwave tube work and derived classically.¹¹

One should note also that when, for example, three photons are simultaneously involved in the higher order Raman process, the net absorption of the first Stokes radiation is not just $\langle P_{S_1}' \rangle_r$. It should be $\langle P_{S_1}' \rangle_r$

plus $\langle P_{S_1}' \rangle_r$, since both terms could be of the same order of magnitude. Similarly, the net absorption of anti-Stokes radiation is the sum of $\langle P_{AS}' \rangle_r$ and $\langle P_{AS}' \rangle_r$. An examination of these expressions shows that when $\bar{E}_{S_1} > \bar{E}_{AS}$ one could have coherent amplification of anti-Stokes radiation of the right phase.

It is clear that specific results for other higher order Stokes and anti-Stokes radiations can be obtained in much the same way.

Most of the results and conclusions obtained in these simple examples, as well as those given in the previous section, have been given and discussed in detail in Ref. 4 on the basis of a phenomenological theory. In more complicated cases, the general results given in Sec. IIIA, as well as those given in Sec. II, will have to be used.

ACKNOWLEDGMENTS

The author would like to thank Dr. S. Kern for an interesting discussion on his experimental work and Dr. H. Stutz for helpful discussions.

¹¹ P. K. Tien and H. Suhl, Proc. IRE 46, 700-706 (1958), with references to the original work of Manley and Row.