VI
Coupled Maxwell-Bloch Equations for Pulsed Raman Transitions

B. W. Shore, R. Sacks and T. Kart

Lawrence Livermore National Laboratory

UCID--21078

DE87 013572

Abstract

As part of a comprehensive examination of equations describing pulsed laser propagation, this memo presents the coupled partial differential equations that describe the propagation of radiation pulses through a vapor of randomly placed molecules that respond by Raman excitation.

Section VI.1 summarizes the equations that describe the propagation of plane-wave pulse envelopes, of various carrier frequencies, and the transfer of energy out of an incident pulse and into other frequencies (the Stokes and anti-Stokes lines), as expressed by a gain matrix and mode velocity matrix.

Section VI.2 examines the molecular expectation values needed for the gain and velocity matrices, using molecular basis states with well defined angular momentum, as befits diatomic molecules.

Section VI.4 summarizes the molecular equations of motion, under the influence of the pulse-mode electric fields. The formulas make use of irreducible tensor representations of the various operators. The molecular excitation equation is the density matrix equation, in state-multipole representation, appropriate to the effective two-photon Hamiltonian of Raman excitation.

Section VI.3 applies these results to a two-level molecule in the presence of pump, Stokes, and anti-Stokes radiation.

Section VI.5 presents perturbation-theory approximations for the molecular equations for a two-level molecule (allowing degeneracy).

Section VI.6 presents steady-state solutions to these two-level perturbation equations, for arbitrary electric-field polarizations, and examines the Stokes-antiStokes coupling and the Stokes gain matrix.

This work was performed under the auspices of the United States Department of Energy by the Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTINGUISHED

§VI.1. The Field Mode Equations

We have introduced a mode expansion for the positive frequency part of the solenoidal electric field,

$$E^{(+)}(r,t) = \frac{1}{2} \sum_{\lambda} e(\lambda) \mathcal{E}_{\lambda}(r,t) \exp[ik_{\lambda} \cdot r - i\omega_{\lambda} t] \quad (VI.1-1)$$

thereby defining pulse amplitudes $\mathcal{E}_{\lambda}(r,t)$ modulating carrier plane waves. We introduced a similar expansion for the polarization field,

$$P^{(+)}(r,t) = \frac{1}{2} \sum_{\lambda} e(\lambda) \mathcal{P}_{\lambda}(r,t) \exp[ik_{\lambda} \cdot r - i\omega_{\lambda} t]. \quad (VI.1-2)$$

We introduced a set of molecular basis states, for a molecule with center of mass at R , by means of the expansion

$$\Psi(R,t) = \sum_p \psi_p C_p(R,t) \exp[iK_p \cdot R - iW_p t] + \sum_q \psi_q C_q(R,t) \exp[iK_q \cdot R - iW_q t] \quad (VI.1-3)$$

thereby partitioning the molecular basis states into two sets, the Q states that are far from resonance and the P states that are close to resonance, either by one photon or two photon processes. With these expansions the induced dipole moment for a single molecular species can be expressed (by adiabatic elimination) as [Multiple species require suitable sums over separate species]

$$\begin{aligned} \langle d^{(+)}(r,t) \rangle = \frac{1}{2} \sum_{pp'} \rho_{pp'}(r,t) \langle p' | X(\omega_{\lambda}) | p \rangle \cdot e(\lambda) \mathcal{E}_{\lambda}(r,t) \\ \times \exp[i(K_p - K_{p'} + k_{\lambda}) \cdot r] \exp[-i(W_p - W_{p'} + \omega_{\lambda}) t] \end{aligned} \quad (VI.1-4)$$

where $X(\omega)$ is the frequency-dependent polarizability operator, defined by Cartesian components

$$\langle p' | X_{ij}(\omega) | p \rangle = \sum_q \left[\frac{\langle p' | d_i | q \rangle \langle q | d_j | p \rangle}{\hbar(W_q - W_p - \omega)} + \frac{\langle p' | d_j | q \rangle \langle q | d_i | p \rangle}{\hbar(W_q - W_{p'} + \omega)} \right]. \quad (VI.1-5)$$

From the definition of the polarization field $P(r,t)$ as the density of dipole moments, or $P = \mathcal{N} \langle d \rangle$, it follows that the polarization mode envelope is

$$\begin{aligned} \mathcal{P}_\lambda(r,t) = \mathcal{N}(r,t) \sum_{pp'} \rho_{p'p}(r,t) \langle \mathbf{p} | \mathbf{X}(\omega_\lambda) | \mathbf{p}' \rangle \cdot \mathbf{E}(\lambda, \lambda') \mathcal{E}_\lambda(r,t) \\ \times \exp[i(\mathbf{K}_{p'} - \mathbf{K}_p + \mathbf{k}_\lambda - \mathbf{k}_\lambda) \cdot \mathbf{r}] \exp[-i(W_{p'} - W_p + \omega_\lambda - \omega_\lambda)t] \end{aligned} \quad (\text{VI.1-6})$$

This formula introduces the field polarization tensor $\mathbf{E}(\lambda', \lambda)$, with Cartesian components $E_{ij}(\lambda', \lambda)$:

$$\mathbf{E}(\lambda', \lambda) = \mathbf{e}(\lambda')^* \mathbf{e}(\lambda), \quad E_{ij}(\lambda', \lambda) = e_i(\lambda'^*) e_j(\lambda). \quad (\text{VI.1-7})$$

Using this expression for the polarization field we find that the field envelope functions $\mathcal{E}_\lambda$, for plane-wave slowly-varying envelopes, in the absence of single-photon resonances, obey the mode equations

$$\left[\hat{\mathbf{k}}_\lambda \cdot \nabla + \frac{1}{v_{\lambda\lambda}(r,t)} \frac{\partial}{\partial t} \right] \mathcal{E}_\lambda(r,t) = \sum_{\lambda' \neq \lambda} \left[G_{\lambda\lambda'}(r,t) - \frac{1}{v_{\lambda\lambda'}(r,t)} \frac{\partial}{\partial t} \right] \mathcal{E}_{\lambda'}(r,t). \quad (\text{VI.1-8})$$

The elements of the gain matrix $G_{\lambda\lambda'}$ and the mode-velocity inverse $1/v_{\lambda\lambda'}$ that appear in this equation are each complex-valued functions of position and time, given (with the neglect of $\{W_{p'}/\omega_\lambda\}$ by the expressions

$$\begin{aligned} G_{\lambda\lambda'}(r,t) = \frac{2\pi i \omega_\lambda}{c \eta_\lambda} \mathcal{N}(r,t) \sum_{pp'} \rho_{p'p}(r,t) \langle \mathbf{p} | \mathbf{X}(\omega_\lambda) | \mathbf{p}' \rangle \cdot \mathbf{E}(\lambda, \lambda') \left[1 - \frac{2i\Gamma_{pp'}}{\omega_\lambda} \right] \\ \times \exp[i(\mathbf{K}_{p'} - \mathbf{K}_p + \mathbf{k}_\lambda - \mathbf{k}_\lambda) \cdot \mathbf{r}] \exp[-i(W_{p'} - W_p + \omega_\lambda - \omega_\lambda)t] \end{aligned} \quad (\text{VI.1-9})$$

$$\begin{aligned} \frac{1}{v_{\lambda\lambda'}(r,t)} = \frac{1}{c \eta_\lambda} \frac{4\pi \mathcal{N}(r,t)}{c \eta_\lambda} \sum_{pp'} \delta(W_{p'} - W_p) \rho_{p'p}(r,t) \langle \mathbf{p} | \mathbf{X}(\omega_\lambda) | \mathbf{p}' \rangle \cdot \mathbf{E}(\lambda, \lambda') \\ \times \left[1 - \frac{i\Gamma_{pp'}}{\omega_\lambda} \right] \exp[i(\mathbf{K}_{p'} - \mathbf{K}_p + \mathbf{k}_\lambda - \mathbf{k}_\lambda) \cdot \mathbf{r}] \exp[-i(W_{p'} - W_p + \omega_\lambda - \omega_\lambda)t] \end{aligned} \quad (\text{VI.1-10a})$$

The diagonal elements of $G_{\lambda\lambda'}$ are needed to define the refractive index, but do not occur explicitly in the propagation equation. The diagonal elements of $1/v_{\lambda\lambda'}$ are

$$\frac{1}{v_{\lambda\lambda}(r,t)} = \frac{\eta_\lambda}{c} \left[1 - \frac{i}{\eta_\lambda \omega_\lambda} \frac{\partial}{\partial t} 4\pi \chi_{\lambda\lambda}(r,t) \right]$$

$$= \frac{1}{c\eta_\lambda} + \frac{4\pi\mathcal{N}(r,t)}{c\eta_\lambda} \sum_{pp'} \delta(W_p - W_{p'}) \rho_{p'p}(r,t) \langle p | X(\omega_\lambda) | p' \rangle : E(\lambda, \lambda) \\ \times \left[1 - \frac{i(\Gamma_{pp})}{\omega_\lambda} \right] \exp[i(\mathbf{K}_{p'} - \mathbf{K}_p) \cdot \mathbf{r}] \quad (\text{VI.1-10b})$$

(Note that the off-diagonal elements of $1/v$ are smaller than the diagonal elements by the ratio $4\pi\chi/(1 + 4\pi\chi)$). In producing these results we have taken the relationship between k_λ and ω_λ to be a slowly varying function of space and time,

$$ck_\lambda = \omega_\lambda \eta_\lambda(r,t) \quad (\text{VI.1-11})$$

where the refractive index is

$$\eta_\lambda(r,t) \approx 1 + 2\pi\mathcal{N}(r,t) \sum_{pp'} \delta(W_p - W_{p'}) \rho_{p'p}(r,t) \langle p | X(\omega_\lambda) | p' \rangle : E(\lambda, \lambda) \\ \times \left[1 - \frac{i2\Gamma_{pp}}{\omega_\lambda} \right] \exp[i(\mathbf{K}_{p'} - \mathbf{K}_p) \cdot \mathbf{r}] \quad (\text{VI.1-12})$$

[This definition of η_λ eliminates the occurrence of diagonal elements of the gain matrix G in the propagation equations]. Molecular properties enter these expressions as time- and space-varying elements of the density matrix $\rho_{pp'}$ (both diagonal and off-diagonal elements occur) and in fixed values of matrix elements of the polarizability operator. The formulas rely on adiabatic elimination to produce a Raman Hamiltonian and a polarizability operator $X(\omega_\lambda)$, but they do not assume that molecular response to the radiation is either weak or steady. The complete description of radiation propagation must combine these equations for field modes with equations for molecular excitation, either dynamic (i.e. the Schrödinger equation) or steady-state.

§VI.2. The Expectation Values

The connection between the polarization field $\mathbf{P}$ and the electric field $\mathbf{E}$ is established by a constitutive relationship that expresses a macroscopic average over microscopic properties. When the medium consists of independent molecules, as we are assuming, the needed average involves a quantum mechanical expectation value. For Raman processes we wish to evaluate the following molecular expectation value:

$$\langle \hat{X}(\lambda, \lambda') \rangle = \sum_{pp'} \rho_{p'p} \langle p | \hat{X} | p' \rangle \epsilon(\lambda, \lambda'). \quad (\text{VI.2-1})$$

As presented here, the summation requires a sum over magnetic sublevels as well as levels. (When Doppler distributions or other distributions of species are present, the expectation value must include an appropriate sum or integral.) Using tensor operators to express the polarization tensor ϵ and the polarizability operator $\hat{X}$ we write this as

$$\langle \hat{X}(\lambda, \lambda') \rangle = \sum_{pp'kq} \rho_{p'p} \langle p | \hat{X}^{(k)}_q | p' \rangle \epsilon(\lambda, \lambda')^{(k)}_{-q} \quad (\text{VI.2-2})$$

We complete the angular momentum description by introducing state multipoles to describe the density matrix. Then the sums over magnetic quantum numbers can be carried out, and the expectation value may be written

$$\langle \hat{X}(\lambda, \lambda') \rangle = \sum_{kqpJp'J'} (-1)^{J'-J'} \frac{\langle pJ || \hat{X}^{(k)} || p'J' \rangle}{\sqrt{2k+1}} \epsilon(\lambda, \lambda')^{(k)}_q \rho(p'J', pJ)^{(k)}_q \quad (\text{VI.2-3})$$

Let us introduce the notation

$$\langle \hat{X}(p, p'; \lambda, \lambda') \rangle = \sum_{kq} (-1)^{J_p - J_{p'}} \frac{\langle p || \hat{X}^{(k)} || p' \rangle}{\sqrt{2k+1}} \epsilon(\lambda, \lambda')^{(k)}_q \rho(p', p)^{(k)}_q \quad (\text{VI.2-4})$$

where now p, p' denote level labels rather than state labels. That is, the labels p and p' now refer to levels with different energies. Let us also assume that the phase $K_{p,r}$ does not depend on the magnetic quantum number of state p . This assumption allows us to express the polarization envelope, the gain matrix, the inverse velocity matrix, and the refractive index as

$$\begin{aligned} \mathcal{P}_\lambda(r, t) = & \mathcal{A}^*(r, t) \sum_{\lambda' p p'} \langle \hat{X}(p, p'; \lambda, \lambda') \rangle \mathcal{E}_{\lambda'}(r, t) \\ & \times \exp[i(K_{p'} - K_p + k_{\lambda'} - k_\lambda) \cdot r] \exp[-i(W_{p'} - W_p + \omega_{\lambda'} - \omega_\lambda)t] \end{aligned} \quad (\text{VI.2-5})$$

$$G_{\lambda\lambda'}(r,t) = \frac{2\pi\omega_\lambda}{c\eta_\lambda} \gamma(r,t) \sum_{pp'} \langle \hat{X}(p,p';\lambda,\lambda') \rangle \left[1 - \frac{2i\Gamma_{pp'}}{\omega_\lambda} \right] \\ \times \exp[i(\mathbf{K}_p - \mathbf{K}_{p'} + \mathbf{k}_\lambda) \cdot \mathbf{r}] \exp[-i(W_{p'} - W_p + \omega_\lambda - \omega_{\lambda'})t] \quad (\text{VI.2-6})$$

$$\frac{1}{v_{\lambda\lambda'}(r,t)} = \frac{1}{c\eta_\lambda} + \frac{4\pi\gamma(r,t)}{c\eta_\lambda} \sum_p \langle \hat{X}(p,p;\lambda,\lambda) \rangle \left[1 - \frac{i\Gamma_{pp}}{\omega_\lambda} \right] \\ \eta_\lambda(r,t) \simeq 1 + 2\pi\gamma(r,t) \sum_p \langle \hat{X}(p,p;\lambda,\lambda) \rangle \left[1 - \frac{i2\Gamma_{pp}}{\omega_\lambda} \right] \quad (\text{VI.2-7})$$

The expectation values $\langle X \rangle$ are to be understood as including sums or integrals over molecular species.

The Dipole Moment

As a result of the pulsed excitation, molecules will possess induced dipole moments. These moments will affect collisions, which are no longer between unpolarized molecules. To evaluate the expectation value of the dipole moment of a molecule whose center of mass is located at position $\mathbf{R}$ we first write the molecular dipole moment operator as a sum of vector components,

$$\mathbf{d} = \sum_q \mathbf{e}(q) d \cdot \mathbf{e}(q)^* \quad (\text{VI.2-8})$$

Then we have

$$\langle d^{(+)}(\mathbf{R},t) \rangle = \sum_q \mathbf{e}(q) \frac{1}{2} \sum_{pp'\lambda'} \rho_{pp'}(\mathbf{R},t) \langle p' | \mathbf{X}(\omega_\lambda) | p \rangle : \mathbf{E}(q,\lambda) \mathcal{G}_\lambda(r,t) \\ \times \exp[i(\mathbf{K}_p - \mathbf{K}_{p'} + \mathbf{k}_\lambda) \cdot \mathbf{R}] \exp[-i(W_{p'} - W_p + \omega_\lambda)t] \\ = \sum_q \mathbf{e}(q) \frac{1}{2} \sum_{pp'\lambda'} \langle \hat{X}(p',p; q,\lambda) \rangle \mathcal{G}_\lambda(\mathbf{R},t) \\ \times \exp[i(\mathbf{K}_p - \mathbf{K}_{p'} + \mathbf{k}_\lambda) \cdot \mathbf{R}] \exp[-i(W_{p'} - W_p + \omega_\lambda)t] \quad (\text{VI.2-9})$$

We can use this expression to evaluate the dipole moment at a fixed position after the conclusion of a pulse. At later times this dipole moment moves along a classical tra-

jectory (the path of the center of mass). To calculate the effect of a bath of such moving dipole moments upon a given test particle we must average collision trajectories (between individual bath particles and the test particle) over an ensemble of initial conditions.

§VI.3 Two-Level System

Let us consider the example of a two-level molecule together with three radiation modes, a pump (P), a Stokes (S) and an anti-Stokes (A) mode. The relevant frequencies are

$$\omega_S = \omega_P - (W_2 - W_1), \quad \omega_A = \omega_P + (W_2 - W_1) \quad (VI.3-1)$$

That is, the energy difference $W_2 - W_1$ can simultaneously equal the pump-Stokes and the anti-Stokes-pump frequency differences:

$$\omega_P - \omega_S = \omega_A - \omega_P = W_2 - W_1. \quad (VI.3-2)$$

Such equality is not possible for the wavevector differences in the presence of dispersion. Let us choose the molecular phase vectors $\mathbf{K}_2$ and $\mathbf{K}_1$ such that

$$\mathbf{k}_P - \mathbf{k}_S = \mathbf{K}_2 - \mathbf{K}_1. \quad (VI.3-3)$$

Then the anti-Stokes-pump wavevector difference introduces a phase, $\Delta\mathbf{k}$, defined by the formula

$$\mathbf{k}_A - \mathbf{k}_P = \mathbf{K}_2 - \mathbf{K}_1 - \Delta\mathbf{k}. \quad (VI.3-4)$$

In the plane-wave approximation we write the needed phase as

$$(2\mathbf{k}_P - \mathbf{k}_S - \mathbf{k}_A) \cdot \mathbf{r} = \Delta\mathbf{k} \cdot \mathbf{z}. \quad (VI.3-5)$$

For a two-level system the expressions for refractive index and mode velocity become

$$\eta_\lambda(\mathbf{r}, t) \simeq 1 + 2\pi\mathcal{N}(\mathbf{r}, t) \left[\langle \hat{X}(1, 1; \lambda, \lambda) \rangle \left[1 - \frac{i(\Gamma_{11})}{\omega_\lambda} \right] + \langle \hat{X}(2, 2; \lambda, \lambda) \rangle \left[1 - \frac{i(\Gamma_{22})}{\omega_\lambda} \right] \right] \quad (VI.3-6)$$

$$\frac{1}{v_\lambda(\mathbf{r}, t)} = \frac{1}{c\eta_\lambda} + \frac{4\pi\mathcal{N}(\mathbf{r}, t)}{c\eta_\lambda} \left[\langle \hat{X}(1, 1; \lambda, \lambda) \rangle \left[1 - \frac{i(\Gamma_{11})}{\omega_\lambda} \right] + \langle \hat{X}(2, 2; \lambda, \lambda) \rangle \left[1 - \frac{i(\Gamma_{22})}{\omega_\lambda} \right] \right] \quad (VI.3-7)$$

while the gain matrix is

$$G_{\lambda\lambda'}(\mathbf{r}, t) = \frac{2\pi i \omega_\lambda}{c\eta_\lambda} \mathcal{N}(\mathbf{r}, t) \langle \hat{X}(1, 2; \lambda, \lambda') \rangle \left[1 - \frac{2i\Gamma_{21}}{\omega_\lambda} \right]$$

$$\times \exp[i(\mathbf{K}_1 - \mathbf{K}_2 + \mathbf{k}_\lambda - \mathbf{k}_{\lambda'}) \cdot \mathbf{r}] \exp[-i(W_1 - W_2 + \omega_{\lambda'} - \omega_\lambda)t]$$

$$+ \frac{2\pi i \omega_\lambda}{c \eta_\lambda} \mathcal{N}(r,t) \langle \hat{X}(2,1;\lambda,\lambda') \rangle \left[1 - \frac{2i\Gamma_{12}}{\omega_\lambda} \right] \\ \times \exp[i(\mathbf{K}_2 - \mathbf{K}_1 + \mathbf{k}_\lambda - \mathbf{k}_{\lambda'}) \cdot \mathbf{r}] \exp[-i(W_2 - W_1 + \omega_\lambda - \omega_{\lambda'})t]. \quad (\text{VI.3-8})$$

As an example, with pump (P) and Stokes (S) pulses we have

$$G_{SP}(r,t) = \frac{2\pi i \omega_S}{c \eta_S} \mathcal{N}(r,t) \langle \hat{X}(2,1;S,P) \rangle \left[1 - \frac{2i\Gamma_{12}}{\omega_S} \right] \quad (\text{VI.3-9a})$$

$$G_{PS}(r,t) = \frac{2\pi i \omega_P}{c \eta_P} \mathcal{N}(r,t) \langle \hat{X}(1,2;P,S) \rangle \left[1 - \frac{2i\Gamma_{21}}{\omega_P} \right] \quad (\text{VI.3-9b})$$

plus terms that contain rapidly varying factors $\exp[\pm i(W_2 - W_1)t]$ and which are therefore not included in the slowly varying approximation. The addition of antistokes pulses introduces the matrix elements

$$G_{PA}(r,t) = \frac{2\pi i \omega_P}{c \eta_P} \mathcal{N}(r,t) \langle \hat{X}(2,1;P,A) \rangle \left[1 - \frac{2i\Gamma_{12}}{\omega_P} \right] \exp(-\Delta k \cdot z) \quad (\text{VI.3-9c})$$

$$G_{AP}(r,t) = \frac{2\pi i \omega_A}{c \eta_A} \mathcal{N}(r,t) \langle \hat{X}(1,2;A,P) \rangle \left[1 - \frac{2i\Gamma_{21}}{\omega_A} \right] \exp(-\Delta k \cdot z). \quad (\text{VI.3-9d})$$

The elements G_{AS} and G_{SA} involve phase factors $\exp[\pm 2i(W_2 - W_1)t]$ and so they are omitted. The elements G_{PP} , G_{SS} and G_{AA} are all set to zero by our choice of η_P , η_S and η_A . For a single species, the required expectation values are

$$\langle \hat{X}(2,1;\lambda,\lambda') \rangle = \sum_{kq} (-1)^{J_2 - J_1} \frac{(2\|X^{(k)}\|1)}{\sqrt{2k+1}} \epsilon(\lambda', \lambda)^{(k)}_q \rho(1, 2)^{(k)}_q \quad (\text{VI.3-10a})$$

$$\langle \hat{X}(1,1;\lambda,\lambda) \rangle = \sum_{kq} \frac{(1\|X^{(k)}\|1)}{\sqrt{2k+1}} \epsilon(\lambda, \lambda)^{(k)}_q \rho(1, 1)^{(k)}_q \quad (\text{VI.3-10b})$$

For rotational transitions or rotational-vibrational transitions in spinless diatomic molecules $k = 0$ or 2 ; only $k = 2$ contributes to the off-diagonal elements of $X^{(k)}_q$. Note that the group velocity and the refractive index depend upon the sum of populations in each of the two levels.

The coupled equations for the three waves are

$$\begin{aligned}
 \left[\frac{\partial}{\partial z} + \frac{1}{v_{PP}} \frac{\partial}{\partial t} \right] \mathcal{E}_P &= G_{PS} \mathcal{E}_S + G_{PA} \mathcal{E}_A + \frac{1}{v_{PS}} \frac{\partial}{\partial t} \mathcal{E}_S + \frac{1}{v_{PA}} \frac{\partial}{\partial t} \mathcal{E}_A \\
 \left[\frac{\partial}{\partial z} + \frac{1}{v_{SS}} \frac{\partial}{\partial t} \right] \mathcal{E}_S &= G_{SP} \mathcal{E}_P + \frac{1}{v_{SP}} \frac{\partial}{\partial t} \mathcal{E}_P \\
 \left[\frac{\partial}{\partial z} + \frac{1}{v_{AA}} \frac{\partial}{\partial t} \right] \mathcal{E}_A &= G_{AP} \mathcal{E}_P + \frac{1}{v_{AP}} \frac{\partial}{\partial t} \mathcal{E}_P
 \end{aligned}
 \tag{VI.2-17}$$

These equations apply to pulses or to steady radiation. In the latter case we can introduce a steady-state molecular response and express the gain matrix elements in terms of products of various field amplitudes.

§VI.4. The Molecule Equations

We convert the Schrödinger equation into a set of equations for probability amplitudes, from which we adiabatically eliminated the Q states, to obtain an effective Schrödinger equation for the P states alone. The Schrödinger equation for these states is

$$\frac{d}{dt} C_p(r,t) = -i \sum_p W_{p'p}(r,t) C_p(r,t). \quad (VI.4-1)$$

With the neglect of direct dipole transitions between P states the effective Hamiltonian $W(r,t)$ is due to polarizability. The Raman Hamiltonian may be written as

$$\begin{aligned} \hbar W_{p'p}(r,t) = & -\frac{1}{4} \langle p' | X(\tilde{\omega}) | p \rangle \sum_{\lambda\lambda'} \langle \lambda', \lambda \rangle \mathcal{E}_{\lambda'}(r,t)^* \mathcal{E}_{\lambda}(r,t) \\ & \times \exp[i(K_p - K_{p'} + k_{\lambda} - k_{\lambda'}, r)] \exp[-i(W_p - W_{p'} + \omega_{\lambda} - \omega_{\lambda'})t] \end{aligned} \quad (VI.4-2)$$

The Liouville equation for the density matrix is

$$\frac{\partial}{\partial t} \rho_{pp'}(r,t) = -i \sum_s [W_{ps}(r,t) \rho_{sp'}(r,t) - \rho_{ps}(r,t) W_{p's}(r,t)] \quad (VI.4-3)$$

This is the equation in the Dirac picture, without relaxation. As exhibited here the labels include magnetic sublevels. We can, instead, describe the system with state multipoles $\rho(p,p')^{(k)}_q$. For that purpose we write the Raman Hamiltonian as

$$\hbar W_{p'p}(r,t) = -\frac{1}{4} \sum_{kq} (-1)^q \langle p' | X(\tilde{\omega})^{(k)}_q | p \rangle F(p',p)^{(k)}_{-q} \quad (VI.4-4)$$

where the fields enter as the bilinear form

$$\begin{aligned} F(p',p)^{(k)}_{-q} = & \sum_{\lambda\lambda'} \langle \lambda', \lambda \rangle^{(k)}_{-q} \mathcal{E}_{\lambda'}(r,t)^* \mathcal{E}_{\lambda}(r,t) \\ & \times \exp[i(K_p - K_{p'} + k_{\lambda} - k_{\lambda'}, r)] \exp[-i(W_p - W_{p'} + \omega_{\lambda} - \omega_{\lambda'})t]. \end{aligned} \quad (VI.4-5)$$

For rotational or rotation-vibration transitions in spinless diatomic molecules only the tensors of order $k = 0$ and $k = 2$ are required. In the rotating wave approximation the sum over modes is restricted by the condition that the exponentiated phase be small. This means

$$W_{p'} - W_p \simeq \omega_{\lambda} - \omega_{\lambda'}. \quad (VI.4-6)$$

and so we can write, within the RWA,

$$F(p',p)^{(k)}_{-q} = \sum_{\lambda\lambda'} \epsilon(\lambda',\lambda)^{(k)}_{-q} \mathcal{E}_{\lambda'}^* \mathcal{E}_{\lambda} \delta(W_p - W_{p'} + \omega_{\lambda} - \omega_{\lambda'}) \\ \times \exp[i(K_p - K_{p'} + k_{\lambda} - k_{\lambda'}) \cdot r]. \quad (VI.4-7)$$

When level p' lies above level p , then frequency ω_{λ} , associated with amplitude $\mathcal{E}_{\lambda}$, is the larger of the two frequencies.

Stokes and Anti-Stokes Fields

As an example, consider a two-level system (possibly degenerate) in which there are pulses at pump (P), Stokes (S) and anti-Stokes (A) frequencies. Take, as above,

$$K_2 - K_1 = k_p - k_s, \quad \Delta k z \equiv (2k_p - k_s - k_A) \cdot r. \quad (VI.4-8)$$

Then we have the RWA

$$F(1,2)^{(k)}_{-q} = \sum_{\lambda\lambda'} [\epsilon(P,S)^{(k)}_{-q} \mathcal{E}_P^* \mathcal{E}_S + \epsilon(A,P)^{(k)}_{-q} \mathcal{E}_A^* \mathcal{E}_P \exp(i\Delta k z)] \quad (VI.4-9a)$$

$$F(2,1)^{(k)}_{-q} = \sum_{\lambda\lambda'} [\epsilon(S,P)^{(k)}_{-q} \mathcal{E}_S^* \mathcal{E}_P + \epsilon(P,A)^{(k)}_{-q} \mathcal{E}_P^* \mathcal{E}_A \exp(-i\Delta k z)] \quad (VI.4-9b)$$

$$F(1,1)^{(k)}_{-q} = \sum_{\lambda\lambda'} [\epsilon(P,P)^{(k)}_{-q} |\mathcal{E}_P|^2 + \epsilon(S,S)^{(k)}_{-q} |\mathcal{E}_S|^2 + \epsilon(A,A)^{(k)}_{-q} |\mathcal{E}_A|^2] \\ = F(2,2)^{(k)}_{-q} \quad (VI.4-9c)$$

The sums still go over whatever polarization modes occur.

Molecular Equations for Two-Level System

Let us consider the state-multipole equations for a two-level molecule. Consider an interaction Hamiltonian of the form

$$H^I = - \frac{1}{4} X^{(0)}_0 F^{(0)}_0 - \frac{1}{4} \sum_q (-1)^q X^{(2)}_q F^{(2)}_{-q} \quad (VI.4-10)$$

where $F^{(k)}$ is a combination of fields and $X^{(k)}$ is a molecular operator. Specifically, we take the field portion to be that of Stokes, anti-Stokes, and Pump waves, so that $F(2,2)^{(k)}_q = F(1,1)^{(k)}_q$. Then in the Dirac picture the equation for coherences (with simple relaxation) is

$$\hbar \frac{\partial}{\partial t} \rho(2,1)^{(K)}_Q = -\hbar \Gamma(2,1)^{(K)}_Q \rho(2,1)^{(K)}_Q \quad (VI.4-11)$$

$$+ \frac{1}{4} i \sum_{K'Q'} \rho(2,1)^{(K')}_{Q'} \sum_{kq} (-1)^{J_1+J_2+Q'+k} \sqrt{2K+1} \sqrt{2K'+1} \begin{Bmatrix} K' & k & K \\ Q' & q & -Q \end{Bmatrix} F(1,1)^{(k)}_{-q} \\ \times \left[\begin{Bmatrix} K' & k & K \\ J_2 & J_1 & J_2 \end{Bmatrix} (2||X^{(k)}||2) - (-1)^{K+K'+k} \begin{Bmatrix} K' & k & K \\ J_1 & J_2 & J_1 \end{Bmatrix} (1||X^{(k)}||1) \right] \\ + \frac{1}{4} i \sum_{K'Q'kq} (-1)^{J_1+J_2+Q'+k} \sqrt{2K+1} \sqrt{2K'+1} \begin{Bmatrix} K' & k & K \\ Q' & q & -Q \end{Bmatrix} F(2,1)^{(k)}_{-q} (2||X^{(k)}||1) \\ \times \left[\begin{Bmatrix} K' & k & K \\ J_2 & J_1 & J_2 \end{Bmatrix} \rho(1,1)^{(K')}_{Q'} - (-1)^{K+K'+k} \begin{Bmatrix} K' & k & K \\ J_1 & J_2 & J_2 \end{Bmatrix} \rho(2,2)^{(K')}_{Q'} \right]$$

The equation for populations and polarizations is

$$\hbar \frac{\partial}{\partial t} \rho(1,1)^{(K)}_Q = -\hbar \Gamma(1,1)^{(K)}_Q \rho(1,1)^{(K)}_Q \quad (VI.4-12)$$

$$+ \frac{1}{4} i \sum_{qK'Q'} (-1)^{2J_1+Q'} \sqrt{2K+1} \sqrt{2K'+1} \begin{Bmatrix} K' & 2 & K \\ Q' & q & -Q \end{Bmatrix} \begin{Bmatrix} K' & 2 & K \\ J_1 & J_1 & J_2 \end{Bmatrix} \\ \times [F(1,2)^{(2)}_{-q} (1||X^{(2)}||2) \rho(2,1)^{(K')}_{Q'} \\ - (-1)^{K+K'} \rho(1,2)^{(K')}_{Q'} F(2,1)^{(2)}_{-q} (2||X^{(2)}||1)]$$

These are the equations that must be solved, for each multipole order of coherence and polarization, to describe transient excitation of a two-level molecule in the presence of relaxation.

§VI.5. Perturbation Theory

Consider first-order perturbation theory applied to these equations. Initially the only nonzero state multipoles are the populations, i.e. the multipoles $\rho(n,n)^{(0)}_0$. The connection between populations P_n and the state multipoles is

$$P_n = \sqrt{2J_n+1} \rho(n,n)^{(0)}_0 \quad (\text{VI.5-1})$$

We consider only those state multipoles that are connected to these by a single interaction. Those equations form the first-order perturbation equations for state multipoles.

Interaction Parameters

It proves useful to parameterize the interaction between the molecule and pairs of field amplitudes by generalizations of the Rabi frequency and detuning. For this purpose we define the energies

$$\hbar\Omega(2,1)_q = \frac{1}{4} (-1)^q F(2,1)^{(2)}_{-q} \frac{(2||X^{(2)}||1)}{\sqrt{5}} \quad (\text{VI.5-2})$$

$$\hbar\tilde{\Omega}_q = \frac{1}{4} (-1)^q F(1,1)^{(2)}_{-q} (-1)^{J_1+J_2}$$

$$\times \left[\left\{ \begin{matrix} 2 & 2 & 2 \\ J_1 & J_1 & J_1 \end{matrix} \right\} (2||X^{(2)}||2) - \left\{ \begin{matrix} 2 & 2 & 2 \\ J_1 & J_2 & J_1 \end{matrix} \right\} (1||X^{(2)}||1) \right]$$

$$\hbar\Delta_{2,1} = \frac{1}{4} F(1,1)^{(0)}_0 \left[\frac{(2||X^{(0)}||2)}{\sqrt{2J_2+1}} - \frac{(1||X^{(0)}||1)}{\sqrt{2J_1+1}} \right]$$

More specifically, these frequencies can be written

$$\hbar\Omega(2,1)_q = \frac{1}{4} (-1)^q \frac{(2||X^{(2)}||1)}{\sqrt{5}} \quad (\text{VI.5-3})$$

$$\times \sum_{\lambda\lambda'} [E(S,P)^{(2)}_{-q} \mathcal{E}_S^* \mathcal{E}_P + E(P,A)^{(2)}_{-q} \mathcal{E}_P^* \mathcal{E}_A \exp(-i\Delta kz)]$$

$$\hbar \bar{\Omega}_q = \frac{1}{4} (-1)^q (-1)^{J_1+J_2} \left[\left\{ \begin{matrix} 2 & 2 & 2 \\ J_2 & J_1 & J_2 \end{matrix} \right\} (2 \| X^{(2)} \| 2) - \left\{ \begin{matrix} 2 & 2 & 2 \\ J_1 & J_2 & J_1 \end{matrix} \right\} (1 \| X^{(2)} \| 1) \right]$$

$$\times \sum_{\lambda \lambda'} [\epsilon(P, P)^{(2)}_{-q} |\mathcal{E}_P|^2 + \epsilon(S, S)^{(2)}_{-q} |\mathcal{E}_S|^2 + \epsilon(A, A)^{(2)}_{-q} |\mathcal{E}_A|^2]$$

$$\hbar \Delta_{21} = \frac{1}{4} \left[\frac{(2 \| X^{(0)} \| 2)}{\sqrt{2J_2+1}} - \frac{(1 \| X^{(0)} \| 1)}{\sqrt{2J_1+1}} \right]$$

$$\times \frac{-1}{\sqrt{3}} \sum_{\lambda} [|\mathcal{E}_P|^2 + |\mathcal{E}_S|^2 + |\mathcal{E}_A|^2]$$

For pure rotational transitions in spinless Σ -state molecules the reduced matrix elements may be written

$$(2 \| X^{(0)} \| 2) = -\sqrt{2J_1+1} \sqrt{3} \bar{a} \quad (\text{VI.5-4})$$

$$(2 \| X^{(2)} \| 1) = \sqrt{\frac{2}{3}} (-1)^{J_2} \begin{Bmatrix} J_1 & 2 & J_2 \\ 0 & 0 & 0 \end{Bmatrix} \sqrt{2J_1+1} \sqrt{2J_2+1} \gamma. \quad (\text{VI.5-5})$$

Therefore this case gives the following expressions:

$$\hbar \Omega(2,1)_q = \frac{1}{4} (-1)^q F(2,1)^{(2)}_{-q} \gamma \sqrt{\frac{2}{3}} (-1)^{J_2} \begin{Bmatrix} J_1 & 2 & J_2 \\ 0 & 0 & 0 \end{Bmatrix} \sqrt{2J_1+1} \sqrt{2J_2+1} \quad (\text{VI.5-6})$$

$$\hbar \bar{\Omega}_q = \frac{1}{4} (-1)^q F(1,1)^{(2)}_{-q} \gamma \sqrt{\frac{2}{3}} (-1)^{J_1+J_2}$$

$$\times \left[\begin{Bmatrix} 2 & 2 & 2 \\ J_2 & J_1 & J_2 \end{Bmatrix} \begin{Bmatrix} J_2 & 2 & J_2 \\ 0 & 0 & 0 \end{Bmatrix} - \begin{Bmatrix} 2 & 2 & 2 \\ J_1 & J_2 & J_1 \end{Bmatrix} \begin{Bmatrix} J_1 & 2 & J_1 \\ 0 & 0 & 0 \end{Bmatrix} \right]$$

$$\hbar \Delta_{21} = 0$$

Perturbation Equations

The first of the required perturbation equations is that for the quadrupole coherences,

$$\begin{aligned} \frac{\partial}{\partial t} \rho(2,1)^{(2)}_Q &= -i [\Delta_{21} - i\Gamma_{21}] \rho(2,1)^{(2)}_Q + i \Omega(2,1)_Q \left[\frac{P_1}{\tilde{\omega}_1} - \frac{P_2}{\tilde{\omega}_2} \right] \\ &+ i \sum_{Q'q} \rho(2,1)^{(2)}_{Q'} \cdot 5 \left\{ \begin{matrix} 2 & 2 & 2 \\ Q' & q & -Q \end{matrix} \right\} \tilde{n}_q \end{aligned} \quad (VI.5-7)$$

Here $\tilde{\omega}_n = (2J_n+1)$ is the statistical weight of level n . Because we are using the Dirac picture the detuning that appears in this equation is the dynamic Stark shift Δ_{21} . Note that the connection amongst the coherences is produced by the frequency Ω , which is smaller than the frequency $\Omega(2,1)$ that provides the connection with populations. With the consideration of these coherences the populations obey the equation

$$\frac{\partial}{\partial t} P_1 = -\Gamma_{11} P_1 + i \sum_{Q'} (-1)^{J_1-J_1} \{ \Omega(1,2)_{-Q'} \rho(2,1)^{(2)}_{Q'} - \rho(1,2)^{(2)}_{-Q'} \Omega(2,1)_{Q'} \} \quad (VI.5-8)$$

and the alignments obey the equation

$$\begin{aligned} \frac{\partial}{\partial t} \rho(1,1)^{(2)}_Q &= -\Gamma(1,1)^{(2)}_Q \rho(1,1)^{(2)}_Q \\ &+ i \sum_{qQ'} (-1)^{2J_1+Q} 5\sqrt{5} \left\{ \begin{matrix} 2 & 2 & 2 \\ Q' & q & -Q \end{matrix} \right\} \left\{ \begin{matrix} 2 & 2 & 2 \\ J_1 & J_1 & J_2 \end{matrix} \right\} \\ &\times [\Omega(1,2)_q \rho(2,1)^{(2)}_{Q'} - \rho(1,2)^{(2)}_{Q'} \Omega(2,1)_q]. \end{aligned} \quad (VI.5-9)$$

No other state multipoles need be considered in this approximation.

§VI.6. Steady State Solutions

To solve the coherence equation we should introduce linear combinations of multipoles with different Q' . Suppose we ignore this requirement for the moment. (This is equivalent to assuming that the damping Γ is much larger than the mixing Ω). Then we have the steady-state approximation

$$\rho(2,1)^{(2)}_q = \Omega(2,1)_q \frac{1}{\Delta'_{21} - i\Gamma_{21}} \left[\frac{P_1}{\tilde{\omega}_1} - \frac{P_2}{\tilde{\omega}_2} \right]. \quad (\text{VI.6-1})$$

Using the definition of $\Omega(2,1)_q$ we write the quadrupole coherences as

$$\rho(2,1)^{(2)}_q = + \frac{1}{4} (-1)^q F(2,1)^{(2)}_{-q} \frac{(2||X^{(2)}||1)}{\sqrt{5}} \left[\frac{P_1}{\tilde{\omega}_1} - \frac{P_2}{\tilde{\omega}_2} \right] \frac{1}{\hbar(\Delta'_{21} - i\Gamma_{21})} \quad (\text{VI.6-1})$$

$$\rho(1,2)^{(2)}_q = - \frac{1}{4} (-1)^q F(1,2)^{(2)}_{-q} \frac{(1||X^{(2)}||2)}{\sqrt{5}} \left[\frac{P_1}{\tilde{\omega}_1} - \frac{P_2}{\tilde{\omega}_2} \right] \frac{1}{\hbar(\Delta'_{12} - i\Gamma_{12})}. \quad (\text{VI.6-2})$$

The detuning Δ'_{21} is the sum of Stark shifts from orders $k = 0$ and $k = 2$:

$$\Delta'_{21} = \Delta_{21} - 5 \begin{pmatrix} 2 & 2 & 2 \\ q & 0 & q \end{pmatrix} \tilde{\Omega}_0 \quad (\text{VI.6-3})$$

The fields enter this expression as

$$F(2,1)^{(k)}_{-q} = \sum_{\lambda_1 \lambda_2} \epsilon(\lambda_2, \lambda_1)^{(k)}_{-q} \mathcal{E}_2^* \mathcal{E}_1 \\ \times \exp[-i(W_1 - W_2 + \omega_1 - \omega_2)t] \exp[i(K_1 - K_2 + k_1 - k_2) \cdot r]. \quad (\text{VI.6-4})$$

In the RWA this expression becomes

$$F(2,1)^{(k)}_{-q} = \sum_{\lambda_1 \lambda_2} \epsilon(\lambda_2, \lambda_1)^{(k)}_{-q} \mathcal{E}_2^* \mathcal{E}_1 \delta(W_1 - W_2 + \omega_1 - \omega_2) \exp[i(K_1 - K_2 + k_1 - k_2) \cdot r]. \quad (\text{VI.6-5})$$

We use the more general expression in the expectation value for $\langle X \rangle$ with the result

$$\begin{aligned} \langle \hat{X}(1,2;\lambda,\lambda') \rangle &= \frac{1}{2} \left[\frac{P_1}{\bar{\omega}_1} - \frac{P_2}{\bar{\omega}_2} \right] \frac{(-1)^{J_2-J_1}}{\hbar(\Delta'_{21} - i\Gamma_{21})} \frac{1}{2} (1||X^{(2)}||2) (2||X^{(2)}||1) \\ &\times \sum_q (-1)^q \in(\lambda,\lambda')^{(2)}_q F(2,1)^{(2)}_{-q} \end{aligned} \quad (V1.6-6)$$

This can be written more explicitly as

$$\begin{aligned} \langle \hat{X}(1,2;\lambda_4,\lambda_3) \rangle &= \left[\frac{P_1}{\bar{\omega}_1} - \frac{P_2}{\bar{\omega}_2} \right] \frac{i}{4\hbar(\Gamma_{21} + i\Delta'_{21})} \frac{1}{2} (1||X^{(2)}||2)^2 \\ &\times \sum_q (-1)^q \in(\lambda_4,\lambda_3)^{(2)}_q \sum_{\lambda_1,\lambda_2} \in(\lambda_4,\lambda_1)^{(2)}_{-q} \mathcal{E}_2^* \mathcal{E}_1 \\ &\times \exp[i(K_1 - K_2 + k_1 - k_2).r] \exp[-i(W_1 - W_2 + \omega_1 - \omega_2)t] \end{aligned} \quad (V1.6-7)$$

Multilevel Results

In the more general multilevel case this expression becomes

$$\begin{aligned} \langle \hat{X}(p,p';\lambda_4,\lambda_3) \rangle &= i \left[\frac{P_p}{\bar{\omega}_p} - (P_{p'}) \frac{1}{\bar{\omega}_{p'}} \right] \frac{1}{4\hbar(\Gamma_{pp'} + i\Delta_{pp'})} \sum_k \frac{(p'||X^{(k)}||p)^2}{2k+1} \\ &\times \sum_{\lambda_1,\lambda_2} \in(\lambda_4,\lambda_3)^{(k)} \in(\lambda_1,\lambda_1)^{(k)} \mathcal{E}_2^* \mathcal{E}_1 \\ &\times \exp[i(K_p - K_{p'} + k_1 - k_2).r] \exp[-i(W_p - W_{p'} + \omega_1 - \omega_2)t] \end{aligned} \quad (V1.6-8)$$

The diagonal elements are given by the expression

$$\langle \hat{X}(p,p;\lambda_4,\lambda_3) \rangle = (p||X^{(0)}||p) \in(\lambda_4,\lambda_3)^{(0)}_0 \frac{P_p}{2J_p+1} \quad (V1.6-9)$$

These are to be used for the polarization envelope

$$\begin{aligned} \mathcal{P}_\lambda(r,t) &= \mathcal{N}(r,t) \sum_{pp'\lambda'} \langle \hat{X}(p,p';\lambda,\lambda') \rangle \mathcal{E}_\lambda(r,t) \\ &\times \exp[i(K_p - K_{p'} + k_\lambda - k_{\lambda'}) . r] \exp[-i(W_p - W_{p'} + \omega_\lambda - \omega_{\lambda'})t] \end{aligned} \quad (V1.6-10)$$

and with the gain matrix

$$G_{\lambda\lambda'}(r,t) = \frac{2\pi i \omega_\lambda}{c \eta_\lambda} \mathcal{N}(r,t) \sum_{pp'} \langle \hat{X}(p,p';\lambda,\lambda') \rangle \left[1 - \frac{2\Gamma_{pp'}}{\omega_\lambda} \right] \\ \times \exp[i(\mathbf{k}_{p'} - \mathbf{k}_p + \mathbf{k}_\lambda - \mathbf{k}_{\lambda'}) \cdot \mathbf{r}] \exp[-i(W_{p'} - W_p + \omega_\lambda - \omega_{\lambda'})t]. \quad (VI.6-10)$$

The resulting gain matrix is

$$G_{\lambda\lambda'}(r,t) = \frac{2\pi i \omega_\lambda}{c \eta_\lambda} \mathcal{N}(r,t) \sum_{pp'} \left[1 - \frac{2\Gamma_{pp'}}{\omega_\lambda} \right] \left[\frac{P_{p'}}{\tilde{\omega}_{p'}} - \frac{P_p}{\tilde{\omega}_p} \right] \frac{1}{4\hbar(\Gamma_{pp'} + i\Delta_{pp'})} \\ \times \sum_k \frac{(p' || X^{(k)} || p)^2}{2k+1} \sum_{\lambda_1 \lambda_2} \epsilon(\lambda, \lambda')^{(k)} \epsilon(\lambda_2, \lambda_1)^{(k)} \mathcal{E}_2^* \mathcal{E}_1 \quad (VI.6-11)$$

$$\times \exp[i(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_\lambda - \mathbf{k}_{\lambda'}) \cdot \mathbf{r}] \exp[-i(W_{p'} - W_p + \omega_\lambda - \omega_{\lambda'})t] \exp[-i(W_p - W_{p'} + \omega_1 - \omega_2)t].$$

The Mode Sources

In steady state we can collect both diagonal and off-diagonal elements of the gain matrix into a source term $\mathcal{J}_\lambda$ and write

$$\left[\hat{\mathbf{k}}_\lambda \cdot \nabla + \frac{1}{c} \frac{\partial}{\partial t} \right] \mathcal{E}_\lambda(r,t) = \mathcal{J}_\lambda(r,t) \quad (VI.6-12)$$

where the source term for mode λ is

$$\mathcal{J}_\lambda(r,t) = \sum_{\lambda'} G_{\lambda\lambda'}(r,t) \mathcal{E}_{\lambda'}(r,t). \quad (VI.6-13)$$

From the steady-state result above we find (with the neglect of Γ compared with ω_λ and the neglect of Δ compared with Γ) that the source term is

$$\mathcal{J}_\lambda = \frac{\pi \omega_\lambda}{2\hbar c \eta_\lambda} \sum_{pp'} \left[\frac{\mathcal{N}_{p'}}{\tilde{\omega}_{p'}} - \frac{\mathcal{N}_p}{\tilde{\omega}_p} \right] \frac{1}{\Gamma_{pp'}} \frac{1}{6} (p' || X^{(2)} || p)^2 \quad (VI.6-14) \\ \times \sum_{\lambda_1 \lambda_2 \lambda_3} \epsilon(\lambda, \lambda_3)^{(2)} \epsilon(\lambda_2, \lambda_1)^{(2)} \mathcal{E}_3 \mathcal{E}_2^* \mathcal{E}_1 \exp[i(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_\lambda) \cdot \mathbf{r}]$$

$$\times \exp[-i(W_p - W_{p'} + \omega_1 - \omega_2)t] \exp[-i(W_{p'} - W_p + \omega_3 - \omega_\lambda)t]$$

For the RWA two-level system this gives

$$\begin{aligned} \mathcal{J}_\lambda = & \frac{\pi\omega_\lambda}{2\hbar c\eta_\lambda} \left[\frac{\mathcal{N}_1}{\tilde{\omega}_1} - \frac{\mathcal{N}_2}{\tilde{\omega}_3} \right] \frac{1}{\Gamma_{12}} \frac{1}{6} (2\|X^{(2)}\|1)^2 \\ & \times \sum_{\lambda_1 \lambda_2 \lambda_3} \epsilon(\lambda, \lambda_3)^{(2)} \epsilon(\lambda_2, \lambda_1)^{(2)} \mathcal{E}_3 \mathcal{E}_1^* \mathcal{E}_\lambda \exp[i(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_\lambda) \cdot \mathbf{r}] \\ & \times [- \delta(W_1 - W_2 + \omega_1 - \omega_2) \exp[-i(W_2 - W_1 + \omega_3 - \omega_\lambda)t] \\ & + \delta(W_2 - W_1 + \omega_1 - \omega_2) \exp[-i(W_1 - W_2 + \omega_3 - \omega_\lambda)t]] \end{aligned}$$

In particular, for Stokes, Pump and anti-Stokes pulses (each in a single direction but possibly with different polarizations) we have, using the RWA and with $\Delta k_z = (2k_p - k_S - k_A) \cdot \hat{z}$,

$$\begin{aligned} \mathcal{J}_S = & \frac{\pi\omega_S}{2\hbar c\eta_S} \left[\frac{\mathcal{N}_1}{\tilde{\omega}_1} - \frac{\mathcal{N}_2}{\tilde{\omega}_3} \right] \frac{1}{\Gamma_{12}} \frac{1}{6} (2\|X^{(2)}\|1)^2 \quad (\text{VI.6-15}) \\ & \times [\epsilon(S, P)^{(2)} \epsilon(P', S')^{(2)} \mathcal{E}_P \mathcal{E}_{P'}^* \mathcal{E}_S + \epsilon(S, P)^{(2)} \epsilon(A, P')^{(2)} \mathcal{E}_P \mathcal{E}_A^* \mathcal{E}_P \exp[i\Delta k_z]] \\ \mathcal{J}_A = & - \frac{\pi\omega_A}{2\hbar c\eta_A} \left[\frac{\mathcal{N}_1}{\tilde{\omega}_1} - \frac{\mathcal{N}_2}{\tilde{\omega}_3} \right] \frac{1}{\Gamma_{12}} \frac{1}{6} (2\|X^{(2)}\|1)^2 \\ & \times [\epsilon(A, P)^{(2)} \epsilon(P', A')^{(2)} \mathcal{E}_P \mathcal{E}_{P'}^* \mathcal{E}_A + \epsilon(A, P)^{(2)} \epsilon(S, P')^{(2)} \mathcal{E}_P \mathcal{E}_S^* \mathcal{E}_P \exp[i\Delta k_z]] \\ \mathcal{J}_P = & \frac{\pi\omega_P}{2\hbar c\eta_P} \left[\frac{\mathcal{N}_1}{\tilde{\omega}_1} - \frac{\mathcal{N}_2}{\tilde{\omega}_3} \right] \frac{1}{\Gamma_{12}} \frac{1}{6} (2\|X^{(2)}\|1)^2 \\ & \times [- \mathcal{E}_{P'} [\epsilon(P, S)^{(2)} \epsilon(S', P')^{(2)} \mathcal{E}_S \mathcal{E}_S^* + \epsilon(P, A)^{(2)} \epsilon(A', P')^{(2)} \mathcal{E}_A \mathcal{E}_A^*] \\ & - [\epsilon(P, S)^{(2)} \epsilon(P', A)^{(2)} - \epsilon(P, A)^{(2)} \epsilon(P', S)^{(2)}] \mathcal{E}_A \mathcal{E}_{P'}^* \mathcal{E}_S \exp[-i\Delta k_z]] \end{aligned}$$

When only single polarizations are present for each mode the plane-wave coupled equations that result from these expressions are of the form discussed by Bloembergen (1971):

$$\frac{\partial}{\partial z} \mathcal{E}_S = \frac{\pi\omega_S}{2c\eta_S} [\chi(\text{SPPS}) \mathcal{E}_P \mathcal{E}_P^* \mathcal{E}_S + \chi(\text{SPAP}) (\mathcal{E}_P)^2 \mathcal{E}_A^* \exp(i\Delta k z)] \quad (\text{VI.6-16})$$

$$\frac{\partial}{\partial z} \mathcal{E}_A^* = -\frac{\pi\omega_A}{2c\eta_A} [\chi(\text{APPA}) \mathcal{E}_P \mathcal{E}_P^* \mathcal{E}_A^* - \chi(\text{PAPS}) (\mathcal{E}_P^*)^2 \mathcal{E}_S \exp(-i\Delta k z)]$$

$$\frac{\partial}{\partial z} \mathcal{E}_P = -\frac{\pi\omega_P}{2c\eta_P} [\chi(\text{PSSP}) \mathcal{E}_S \mathcal{E}_S^* \mathcal{E}_P - \chi(\text{PAAP}) \mathcal{E}_A \mathcal{E}_A^* \mathcal{E}_P]$$

where

$$\chi(\lambda_1, \lambda_2, \lambda_1) = \left[\frac{\mathcal{N}_1}{\tilde{\omega}_1} - \frac{\mathcal{N}_2}{\tilde{\omega}_2} \right] \frac{1}{\hbar\Gamma_{12}} \quad \frac{1}{6} (2\|X^{(2)}\|1)^2 \in(\lambda_1, \lambda_2)^{(2)} \in(\lambda_2, \lambda_1)^{(2)} \quad (\text{VI.6-17})$$

These are the coupled equations that are used to deduce Stokes-anti-Stokes coupling, and the suppression of Stokes gain when $\Delta k = 0$.

To evaluate the angular parts we can use the formula

$$[A^{(1)} \chi B^{(1)}]^{(2)} [C^{(1)} \chi D^{(1)}]^{(2)} = \frac{1}{2} (A.C)(B.D) + \frac{1}{2} (A.D)(B.C) - \frac{1}{2} (A.B)(C.D). \quad (\text{VI.6-18})$$

When only single polarizations are present in each mode this formula gives the expression for the vector source term,

$$\mathcal{J}_S \mathbf{e}(S) = \frac{\pi\omega_S}{12\hbar c\eta_S} \left[\frac{\mathcal{N}_1}{\tilde{\omega}_1} - \frac{\mathcal{N}_2}{\tilde{\omega}_2} \right] \frac{1}{\Gamma_{12}} \quad \frac{1}{6} (2\|X^{(2)}\|1)^2 \quad (\text{VI.6-19})$$

$$\begin{aligned} & \times [\mathcal{E}_S \mathcal{E}_P \mathcal{E}_P^* \{ 3\mathbf{e}(P)^* \cdot (P.S) + 3\mathbf{e}(S) \cdot (P^* . P) - 2\mathbf{e}(P) \cdot (P^* . S) \} \\ & + \mathcal{E}_P \mathcal{E}_A^* \mathcal{E}_P \exp[i(2k_P - k_A - k_S).r] \{ 3\mathbf{e}(A)^* \cdot (P.P) + \mathbf{e}(P) \cdot (A^* . P) \}] \end{aligned}$$

$$\mathcal{J}_A \mathbf{e}(S) = -\frac{\pi\omega_A}{12\hbar c\eta_A} \left[\frac{\mathcal{N}_1}{\tilde{\omega}_1} - \frac{\mathcal{N}_2}{\tilde{\omega}_2} \right] \frac{1}{\Gamma_{12}} \quad \frac{1}{6} (2\|X^{(2)}\|1)^2$$

$$\begin{aligned} & \times [\mathcal{E}_A \mathcal{E}_P \mathcal{E}_P^* \{ 3\mathbf{e}(P)^* \cdot (P.A) + 3\mathbf{e}(A) \cdot (P^* . P) - 2\mathbf{e}(P) \cdot (P^* . A) \} \\ & + \mathcal{E}_P \mathcal{E}_S^* \mathcal{E}_P \exp[i(2k_P - k_A - k_S).r] \{ 3\mathbf{e}(S)^* \cdot (P.P) + \mathbf{e}(P) \cdot (S^* . P) \}] \end{aligned}$$

$$\mathcal{J}_P \mathbf{e}(P) = \frac{\pi\omega_P}{12\hbar c\eta_P} \left[\frac{\mathcal{N}_1}{\tilde{\omega}_1} - \frac{\mathcal{N}_2}{\tilde{\omega}_2} \right] \frac{1}{\Gamma_{12}} \quad \frac{1}{6} (2\|X^{(2)}\|1)^2$$

$$\begin{aligned} & \times [-\mathcal{E}_S \mathcal{E}_S^* \mathcal{E}_P [3\mathbf{e}(S) \cdot (\mathbf{P} \cdot \mathbf{S}) + 3\mathbf{e}(P) \cdot (\mathbf{S}^* \cdot \mathbf{S}) - 2\mathbf{e}(S) \cdot (\mathbf{S}^* \cdot \mathbf{P})] \\ & + \mathcal{E}_A \mathcal{E}_A^* \mathcal{E}_P [3\mathbf{e}(A) \cdot (\mathbf{P} \cdot \mathbf{A}) + 3\mathbf{e}(P) \cdot (\mathbf{A}^* \cdot \mathbf{A}) - 2\mathbf{e}(A) \cdot (\mathbf{A}^* \cdot \mathbf{P})] \end{aligned}$$

Here $(\mathbf{A} \cdot \mathbf{B})$ denotes the product of two unit vectors, $\mathbf{e}(\mathbf{A}) \cdot \mathbf{e}(\mathbf{B})$. These are the Stokes and anti-Stokes angular factors used by Venkin et al.

The Stokes Gain Coefficient

When there is no anti-Stokes pulse the equations for the quasi-stationary pump and Stokes waves may be written in the traditional form (cf. Penzkofer et al)

$$\left[\frac{\partial}{\partial z} + \gamma_S \right] I_S = g_S I_S I_P \quad (\text{VI.6-20})$$

$$\left[\frac{\partial}{\partial z} + \gamma_P \right] I_P = -\frac{\omega_P}{\omega_S} g_S I_S I_P$$

where the intensities are

$$I_S = \frac{c\eta_S}{8\pi} |\mathcal{E}_S|^2, \quad I_P = \frac{c\eta_P}{8\pi} |\mathcal{E}_P|^2. \quad (\text{VI.6-21})$$

It follows that the Stokes gain coefficient is obtained as

$$g_S = \frac{8\pi}{c} \frac{\pi\omega_S}{c\eta_S\eta_P} \left[\frac{\mathcal{N}_1}{\tilde{\omega}_1} - \frac{\mathcal{N}_2}{\tilde{\omega}_2} \right] \frac{1}{\Gamma_{12}} \frac{1}{8} (2|X^{(2)}||1\rangle)^2 \Theta(S, P)^{(2)} \quad (\text{VI.6-22})$$

where $\Theta(\lambda, \lambda')^{(k)}$ is the angular distribution function of Yuratich and Hanna,

$$\Theta(\lambda, \lambda')^{(k)} = \epsilon(\lambda, \lambda')^{(k)} \cdot \epsilon(\lambda', \lambda)^{(k)}. \quad (\text{VI.6-23})$$

The full-width at half-maximum of the profile function is $\Delta\omega = 2\Gamma_{12}$. One can also write

$$g_S = \frac{8\pi}{c} \frac{\pi\omega_S}{6c\eta_S\eta_P} \left[\frac{\mathcal{N}_1}{\tilde{\omega}_1} - \frac{\mathcal{N}_2}{\tilde{\omega}_2} \right] \frac{1}{\hbar\Gamma_{12}} \frac{1}{8} (2|X^{(2)}||1\rangle)^2 [3(P \cdot S)^2 + 3 - 2|(P^* \cdot S)|^2]. \quad (\text{VI.6-24})$$

For co-linearly polarized Stokes and pump this becomes

$$g_S = \frac{8\pi}{3} \frac{\pi\omega_S}{c^2\eta_S\eta_P} \left[\frac{\mathcal{N}_1}{\tilde{\omega}_1} - \frac{\mathcal{N}_2}{\tilde{\omega}_2} \right] \frac{1}{\hbar\Gamma_{12}} \frac{2}{5} (2|X^{(2)}||1\rangle)^2 \quad (\text{VI.6-25})$$

For the case of pure rotational transitions in a spinless Σ -state molecule this expression becomes

$$g_S = \frac{8\pi}{3} \frac{\pi\omega_S}{c^2\eta_S\eta_P} \left[\frac{\mathcal{N}_1}{\tilde{\omega}_1} - \frac{\mathcal{N}_2}{\tilde{\omega}_2} \right] \frac{1}{\hbar\Gamma_{12}} \frac{2}{5} (2\|X^{(2)}\|_1)^2 \quad (\text{VI.6-25})$$

For the case of pure rotational transitions in a spinless Σ -state molecule this expression becomes

$$g_S = \frac{8\pi}{3} \frac{\pi\omega_S}{c^2\eta_S\eta_P} \left[\mathcal{N}_1 - \frac{\tilde{\omega}_1}{\tilde{\omega}_2} \mathcal{N}_2 \right] \frac{1}{\hbar\Gamma_{12}} \frac{4}{15} (2J_2+1) \begin{pmatrix} J_1 & 2 & J_2 \\ 0 & 0 & 0 \end{pmatrix}^2 \gamma^2$$

For thermal populations this formula reads

$$g_S = \frac{8\pi}{3} \frac{\pi\omega_S}{c^2\eta_S\eta_P} \frac{\mathcal{N} \exp(-E_2/kT)}{\mathcal{Z}(T)} \left[1 - \exp\left[\frac{E_1-E_2}{kT}\right] \right] \frac{1}{\hbar\Gamma_{12}} \\ \times \frac{4}{15} (2J_2+1)(2J_1+1) \begin{pmatrix} J_1 & 2 & J_2 \\ 0 & 0 & 0 \end{pmatrix}^2 \gamma^2$$

where $\mathcal{Z}(T)$ is the partition function at temperature T . For example, the transition $J_1 = J \rightarrow J_2 = J+2$ has the gain

$$g_S = \frac{8\pi}{3} \frac{\pi\omega_S}{c^2\eta_S\eta_P} \left[\mathcal{N}_1 - \frac{2J+1}{2J+5} \mathcal{N}_2 \right] \frac{1}{\hbar\Gamma_{12}} \frac{4}{5} \frac{(J+1)(J+2)}{(2J+1)(2J+3)} \gamma^2 \\ = \frac{8\pi}{3} \frac{\pi\omega_S}{c^2\eta_S\eta_P} \frac{\mathcal{N} \exp(-E_1/kt)}{\mathcal{Z}(T)} \left[1 - \exp\left[\frac{E_1-E_2}{kT}\right] \right] \frac{1}{\hbar\Gamma_{12}} \frac{4}{5} \frac{(J+1)(J+2)}{2J+3} \gamma^2$$

This is equivalent to the expression given by Herring et al.