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Theoretical Development of Third-Order Susceptibility as Related to Coherent Anti-Stokes Raman Spectroscopy (CARS)

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The basic theory for coherent anti-stokes Raman spectroscopy has been developed by two methods: a classical approach and a quantum mechanical development. Standard methods of perturbation theory, Maxwell's equation, harmonic oscillator approximation, and density matrix theory are applied to the third-order nonlinear effect of generating anti-Stokes photons from the mixing of two intense laser beams. Each mathematical step has been explicitly included in the derivations comparisons between the expressions obtained here and those published in the literature

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20. Abstract (Continued)

are made. Where possible, clarification with respect to differences of factors of "2" or "3" which appear in various references have been included.

Finally, the application of these derivations to problems involving the use of CARS as an analytical and spectroscopic tool are discussed in some detail. For example, the possibility of signal improvement by electronic resonance enhancement is explored. Also, the effects of tight focusing, phase matching, band shape, etc. are discussed in some detail.

CONTENTS

THEORETICAL DEVELOPMENT OF THIRD-ORDER SUSCEPTIBILITY AS RELATED TO COHERENT ANTI-STOKES RAMAN SPECTROSCOPY (CARS)

I. INTRODUCTION

It is well known that in Raman scattering there is a shift in frequency associated with the scattering process. If light with photon energy $\hbar\omega$ is scattered by a system with energy E, conservation of energy requires

$$\hbar\omega + E = \hbar\omega' + E' \quad ,$$

where $\hbar$ is Planck's constant divided by 2π, ω is the angular frequency of the radiation, and the primes denote the values of the quantities after scattering. This shows that if $E < E'$, then $\omega' < \omega$ and the radiation produces a spectral line down-shifted in frequency (Stokes line), while the reverse condition produces an up-shifted (anti-Stokes) spectral line. Since its discovery in 1928 by C. V. Raman, this process has been extensively developed as a technique for spectral analysis.

In general, the Raman scattering cross sections are quite small and, hence, the lines are extremely weak with the anti-Stokes lines even weaker than the Stokes lines for large Raman shifts. This made Raman spectroscopy difficult and tedious until the development of the laser with its single, intense frequency of coherent radiation. However, conventional Raman spectroscopy has never been noted as a sensitive technique, and Raman signals are often obscurred by laser-induced fluorescence or chemiluminescence in practical applications,such as the study of natural products, combustion analysis, etc. A relatively new kind of Raman spectroscopy based on a nonlinear optics principle called Coherent Anti-Stokes Raman Spectroscopy (CARS) offers a hope of overcoming some of these problems.

Coherent anti-Stokes emission was first observed by Terhune and Maker (1, 2), but its application to Raman spectroscopy has been hindered by the requirement for high peak power, tunable laser sources. This deficiency is now being met with the rapid growth of nitrogen pumped and solid-state laser pumped dye laser sources, so that it is now important to exploit the method for its advantages over conventional

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Raman spectroscopy, which for gas diagnostics have been recently proposed (3 - 5) and discussed (6 - 8) in the literature.

Being basically a Raman process, CARS is characterized by a third-order, nonlinear susceptibility. However, the existing literature on nonlinear susceptibility is so abundant, with different notations and treatments, that it is very easy to become confused. Quoted results differing by factors of 2, 3, 4, and 6 are quite common. For example, Maker and Terhume (2) give for the 992 cm^{-1} mode of benzene a χ_R equal to 1.2 X $10^{-12} cm^3/erg$, while Levenson and Bloembergen (9) give χ_R equal to 0.46 X $10^{-12} cm^3/erg$. In discussing particular physical processes, some authors use the classical harmonic oscillator form of the susceptibility, while others use the quantum mechanical, dipole transition form. Thus, it was felt that in order to aid the development of CARS as a spectroscopic technique for gas diagnostics, a pedagogical paper describing the application of Maxwell's equations and standard perturbation theory to the polarization expression in order to calculate third-order, nonlinear susceptibilities, which are related to the CARS efficiency, would be helpful. It is also the purpose of this report to describe the experimental and analytical implications of the theory so developed. However, before we embark on the development of the basic theory, let us first give a very brief introduction to the CARS process.

If two high-powered lasers, at least one of which should be tunable, are impinged on a material, the high field strengths present develop a third-order, nonlinear response from the medium such that two photons of one laser are mixed with one photon of the other laser to generate photons in the anti-Stokes region or:

$$2\omega_\ell - \omega_s = \omega_{as}$$

, where ω_ℓ is one laser frequency, ω_s is the other (usually tunable and is Stokes shifted with respect to ω_ℓ), and ω_{as} is the new emission which is generated at the anti-Stokes side of ω_ℓ. The emission is in the form of a coherent, laser-like beam which can be very intense.

This emission is often many orders of magnitude greater than ordinary Raman spectroscopy, and its coherency allows high collection efficiency and excellent discrimination against interfering spontaneous effects such as luminescence. Observation of the emission in the anti-Stokes region discriminates against laser-induced fluorescence.

II. Maxwell's Equations and Nonlinear Polarization

The propagation of electromagnetic waves through a medium is governed by Maxwell's equations, which for a nonmagnetic medium containing no free charges or currents, is given by (10)

$$\underset{\sim}{\nabla}\times\underset{\sim}{\nabla}\times\underset{\sim}{E}+\frac{1}{c^2}\partial_t^2\underset{\sim}{E}=-\frac{4\pi}{c^2}\partial_t^2\underset{\sim}{P} \qquad (1)$$

where E is the electric intensity of the field, P is the polarization induced by the field, c the velocity of light. The tilde below a quantity is used to denote a vector quantity since the AIP style Manual requires this notation in manuscripts to instruct the editor and compositor that the quantity should be set in bold print signifying a vector quantity. This eliminates having two notations, one for the reader and one for the editor. Since in general the total field E is composed of many frequencies, it is convenient to introduce the Fourier transform and thereby obtain an equation for each frequency component. Thus let

$$P(t)=\int_{-\infty}^{\infty}P(\omega)e^{-i\omega t}d\omega \qquad E(t)=\int_{-\infty}^{\infty}E(\omega)e^{-i\omega t}d\omega \qquad (2)$$

with inverse transforms

$$P(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}P(t)e^{i\omega t}dt \qquad E(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}E(t)e^{i\omega t}dt \qquad (3)$$

It is shown in Appendix A that for P(t) and E(t) to be real, the Fourier components obey the restrictions

$$P(-\omega)=P^*(\omega) \qquad E(-\omega)=E^*(\omega) \qquad (4)$$

where $P^*(\omega)$ is the complex conjugate of $P(\omega)$. Introducing eqs. (2) into eq. (1) gives the wave equation for each frequency component.

$$\underset{\sim}{\nabla}\times\underset{\sim}{\nabla}\times\underset{\sim}{E}(\omega)-\frac{\omega^2}{c^2}\underset{\sim}{E}(\omega)=4\pi\frac{\omega^2}{c^2}\underset{\sim}{P}(\omega) \qquad (5)$$

For weak fields $P(\omega)$ will be linear in $E(\omega)$; that is, a linear relation exists between the two and can be represented by

$$\underset{\sim}{P}_L(\omega) = \chi_L(\omega)\underset{\sim}{E}(\omega) \tag{6}$$

where the subscript L denotes linear. The proportionality factor $\chi_L(\omega)$ is called the linear susceptibility and is a characteristic of the medium. However, for intense fields the polarization $P(\omega)$ can be induced by fields at different frequencies. This can be represented by writing

$$\underset{\sim}{P}(\omega) = \underset{\sim}{P}_L(\omega) + \underset{\sim}{P}^{NL}(\omega) \tag{7}$$

where the superscript NL denotes nonlinear. Substituting this into eq. (5) and using equation (6) gives

$$\underset{\sim}{\nabla} \times \underset{\sim}{\nabla} \times \underset{\sim}{E}(\omega) - \frac{\omega^2}{c^2}\left(1 + 4\pi\chi_L(\omega)\right)\underset{\sim}{E}(\omega) = 4\pi\frac{\omega^2}{c^2}\underset{\sim}{P}^{NL}(\omega) \tag{8}$$

Introducing the dielectric constant $\epsilon(\omega)$ defined by

$$\epsilon(\omega) = 1 + 4\pi\chi_L(\omega) \tag{9}$$

into eq. (8) gives

$$\underset{\sim}{\nabla} \times \underset{\sim}{\nabla} \times \underset{\sim}{E}(\omega) - \frac{\omega^2}{c^2}\epsilon(\omega)\underset{\sim}{E}(\omega) = 4\pi\frac{\omega^2}{c^2}\underset{\sim}{P}^{NL}(\omega) \tag{10}$$

The nonlinear polarization $\underset{\sim}{P}^{NL}(\omega)$ on the right side is the induced polarization resulting from all fields leading to an ω dependence. Therefore, a relation between P^{NL} and the applied field E is needed.

In Appendix B a field expansion for the polarization P(t) in terms of the field E(t) is assumed of the form (11)

$$P(t) = P^{(1)}(t) + P^{(2)}(t) + \cdots + P^{(r)}(t) + \cdots \tag{11}$$

where $P^{(1)}(t)$ is linear in E(t), $P^{(2)}(t)$ is quadratic in E(t), etc. It is shown that this then leads to the Fourier component

$$\underset{\sim}{P}^{(r)}(\omega) = \underset{\approx}{\chi}^{(r)}(-\omega+\omega_1+\omega_2+\cdots+\omega_r) \mid \underset{\sim}{E}(\omega_1)\underset{\sim}{E}(\omega_2)\cdots\underset{\sim}{E}(\omega_r) \tag{12}$$

where $\underset{\approx}{\chi}^{(r)}$ is the generalized susceptibility tensor of rank r + 1 and the bar denotes tensor product. The χ will denote a tensor of rank greater than two. A delta function dependence $\delta(-\omega + \omega_1 + \cdot \cdot \cdot + \omega_r)$ is implied in the susceptibility. When $r \neq 1$, the polarization $\underset{\sim}{P}^{(r)}(\omega)$ of equation (12) is to be used for $\underset{\sim}{P}^{NL}(\omega)$ in eq. (10). In component form eq. (12) becomes

$$P_\mu^{(r)}(\omega) = \chi^{(r)}_{\mu\alpha_1\alpha_2\cdots\alpha_r}(-\omega+\omega_1+\omega_2+\cdots+\omega_r)E_{\alpha_1}(\omega_1)E_{\alpha_2}(\omega_2)\cdots E_{\alpha_r}(\omega_r) \tag{13}$$

As noted in Appendix B, $\chi^{(r)}$ is invariant with respect to the r! permutations of the pairs $\alpha_1\ \omega_1$, $\alpha_2\ \omega_2$, . . ., $\alpha_r \omega_r$. Thus the order of the fields can be disregarded by inserting r! on the right side of eq. (13). Also, if n frequencies are equal, the right side must be divided by n!. This results in

$$P_\mu^{(r)}(\omega) = \frac{r!}{n!}\chi^{(r)}_{\mu\alpha_1\alpha_2\cdots\alpha_r}(-\omega+\omega_1+\omega_2+\cdots+\omega_r)E_{\alpha_1}(\omega_1)\cdots E_{\alpha_r}(\omega_r) \tag{14}$$

Examples are

$$\begin{aligned}
P^{(2)}(\omega) &= 2\chi^{(2)}(-\omega+\omega_1+\omega_2)E(\omega_1)E(\omega_2)\\
P^{(2)}(\omega) &= \chi^{(2)}(-\omega+2\omega_1)E^2(\omega_1)\\
P^{(3)}(\omega) &= 6\chi^{(3)}(-\omega+\omega_1+\omega_2+\omega_3)E(\omega_1)E(\omega_2)E(\omega_3)\\
P^{(3)}(\omega) &= 3\chi^{(3)}(-\omega+\omega_1+2\omega_2)E(\omega_1)E^2(\omega_2)\\
P^{(3)}(\omega) &= \chi^{(3)}(-\omega+3\omega_1)E^3(\omega_1)
\end{aligned} \tag{15}$$

This is consistant with the scheme outlined by Terhune and Maker (12). This same result can also be obtained by assuming a series expansion of the polarization P(ω) in powers of the field E(ω), thus

$$P(\omega) = \chi^{(1)}(\omega)E(\omega) + \chi^{(2)}(\omega)E^2(\omega) + \chi^{(3)}(\omega)E^3(\omega) + \cdots \tag{16}$$

Then considering the second order field to be composed of two fields at frequencies ω_1 and ω_2 gives

$$[E(\omega_1)+E(\omega_2)]^2 = E^2(\omega_1)+E^2(\omega_2)+2E(\omega_1)E(\omega_2) \tag{17}$$

Likewise, considering the third order field to be composed of three fields at frequencies ω_1, ω_2, and ω_3 gives

$$[E(\omega_1)+E(\omega_2)+E(\omega_3)]^3 = E^3(\omega_1)+E^3(\omega_2)+E^3(\omega_3)+3E^2(\omega_1)E(\omega_2)+ \\ 3E^2(\omega_1)E(\omega_3)+\cdots+6E(\omega_1)E(\omega_2)E(\omega_3) \tag{18}$$

and so on. However, if equations (16) through (18) are used with trigonometric functional dependence in the fields, then because in general

$$\begin{aligned} \cos^2\omega_i &= \tfrac{1}{2}(1+\cos 2\omega_i) \\ \cos^3\omega_i &= \tfrac{1}{4}(3\cos\omega_i+\cos 3\omega_i) \end{aligned} \tag{19}$$

the polarizations must be defined as 13

$$P(\omega) = \chi^{(1)}(\omega)E(\omega)+2\chi^{(2)}E^2(\omega)+4\chi^{(3)}E^3(\omega)+\cdots \tag{20}$$

Since $\underset{\approx}{\chi}^{(r)}$ in eq. (12) is a tensor of rank r + 1 and is characteristic of the medium, it must display the symmetry properites of the medium it describes. However, the transformations governing the symmetry properties of the susceptibility will not be treated here, and the reader is referred to the literature(11,14,15).

Equation (12) now shows how the susceptibility is to be treated, and equation (10) shows how it is used in describing wave propagation through media. However, neither equation gives an explicit form for the nonlinear susceptibility. There are basically two methods used to derive $\underset{\approx}{\chi}^{(r)}$: a classical approach based on polarizability and a quantum approach based on dipole transitions. Each method will be described and, in particular, expressions for the third order nonlinear susceptibility $\underset{\approx}{\chi}^{(3)}(-\omega+2\omega_\ell-\omega_s)$ will be obtained, where ω_ℓ and ω_s are the two frequency components of the applied E field.

III. The Classical Approach to Susceptibility

In the linear interaction of a wave with matter, the polarization is related to the applied field through

$$P = \chi E$$

where χ is the linear susceptibility. Also, if a wave interacts with a bound system, it is expected that a dipole moment $\underset{\sim}{d} = -e\underset{\sim}{r}$ would be imposed on the system. If there are N such systems per unit volume and the polarization P is considered the total dipole moment per unit volume, then the above becomes

$$P = N d = \chi E \tag{21}$$

If the bound system is represented by a harmonic oscillator, its equation of motion is (16)

$$\ddot{q} + \Gamma \dot{q} + \omega_0^2 q = -\frac{e}{m} E \tag{22}$$

where q is its displacement from equilibrium, E is the applied field, and Γ describes the damping of the oscillator. The solution of this equation is

$$q = \frac{-e/m\, E}{\omega_0^2 - \omega^2 - i\omega\Gamma} \tag{23}$$

Then by eq. (21) the polarization is

$$P = \frac{N e^2/m\, E}{\omega_0^2 - \omega^2 - i\omega\Gamma} \tag{24}$$

and the linear susceptibility is

$$\chi = \frac{N e^2/m}{\omega_0^2 - \omega^2 - i\omega\Gamma} \tag{25}$$

A nonlinearity in the oscillation will lead to higher order nonlinear susceptibilities. This can be described by introducing an anharmonic term into the oscillator equation. Thus the equation of motion becomes

$$\ddot{q} + \Gamma \dot{q} + \omega_0^2 q + \lambda q^2 = -\frac{e}{m} E \tag{26}$$

A perturbation solution (17) to this equation can be found by assuming a solution of the form

$$q = q_1 + \lambda q_2 + \lambda^2 q_3 + \cdots \tag{27}$$

with

$$q^2 = q_1^2 + 2\lambda q_1 q_2 + \lambda^2 (q_2^2 + 2 q_1 q_3) + \cdots \tag{28}$$

Substituting eq. (27) into eq. (26) and equating terms independent of λ gives

$$\ddot{q}_1 + \Gamma \dot{q}_1 + \omega_0^2 q_1 = -\frac{e}{m} E \tag{29}$$

Letting the applied field E be the sum of two fields at frequencies ω_ℓ and ω_s

gives

$$E = E_l + E_s \tag{30}$$

where

$$E_l = \frac{1}{2} E_l^0 e^{i(k_l \cdot r - \omega_l t)} + c.c.$$

$$E_s = \frac{1}{2} E_s^0 e^{i(k_s \cdot r - \omega_s t)} + c.c. \tag{31}$$

Substituting eqs. (30) and (31) into equation (29) gives

$$q_1 = -\frac{e}{2m}\left(E_l^0 \frac{e^{i(k_l \cdot r - \omega_l t)}}{\omega_0^2 - \omega_l^2 - i\omega_l \Gamma} + E_s^0 \frac{e^{i(k_s \cdot r - \omega_s t)}}{\omega_0^2 - \omega_s^2 - i\omega_s \Gamma} + c.c. \right) \tag{32}$$

Equating terms in λ gives

$$\ddot{q}_2 + \Gamma \dot{q}_2 + \omega_0^2 q_2 = -q_1^2 \tag{33}$$

The q_1^2 term will lead to exponentials depending on $2\omega_l$, $2\omega_s$, and $\omega_l \pm \omega_s$.

Assuming a solution of the form

$$q_2 = \frac{1}{2} q_2^0 e^{i(k_l \cdot r - k_s \cdot r - \omega_l t + \omega_s t)} + c.c. \tag{34}$$

gives

$$q_2 = -\frac{e^2}{2m^2}\left(E_l^0 E_s^{0*} \frac{e^{i(k_l \cdot r - k_s \cdot r - \omega_l t + \omega_s t)}}{D(\omega_l - \omega_s) D(\omega_l) D^*(\omega_s)} + c.c. \right) \tag{35}$$

where

$$D(\omega) \equiv \omega_0^2 - \omega^2 - i\omega\Gamma \tag{36}$$

Equating terms in λ^2 gives

$$\ddot{q}_3 + \Gamma \dot{q}_3 + \omega_0^2 q_3 = -2 q_1 q_2 \tag{37}$$

Again, the term on the right side will lead to the mixing of frequencies.

Assuming a particular solution of the form

$$q_3 = \frac{1}{2} q_3^0 e^{i(k_{as} \cdot r - \omega_{as} t)} + c.c. \tag{38}$$

where

$$k_{as} = 2k_\ell - k_s$$

$$\omega_{as} = 2\omega_\ell - \omega_s \tag{39}$$

gives

$$q_3 = -\frac{e^3}{2m^3}\left(E_\ell^{0\,2} E_s^{0\,*} \frac{e^{i(k_{as}\cdot r - \omega_{as} t)}}{D(\omega_{as}) D^2(\omega_\ell) D(\omega_\ell - \omega_s) D^*(\omega_s)} + \mathrm{c.c.}\right) \tag{40}$$

This term will then give a dipole moment d = -eq and a polarization P = Nd, which when compared with

$$P^{(3)}(\omega_{as}) = 3\chi^{(3)}(\omega_{as}) E_\ell E_\ell E_s^* \tag{41}$$

gives the third order susceptibility

$$3\chi^{(3)}(\omega_{as}) = \frac{N\lambda^2\, e^4/m^3}{D(\omega_{as}) D^2(\omega_\ell) D(\omega_\ell - \omega_s) D^*(\omega_s)} \tag{42}$$

Equation (41), along with eq. (42), is then to be substituted into the right side of eq. (10) to describe the polarization of waves with frequency $\omega_{as} = 2\omega_\ell - \omega_s$. The susceptibility is multiplied by three as indicated by eqs. (15) and (18).

A method (18) similar to the above is to introduce the nonlinearity into the driving force instead of the potential. An applied field E acting on a system will induce a polarizability d(q) which can be expanded about its equilibrium value giving

$$\alpha(q) = \alpha_0 + q \left.\frac{\partial\alpha}{\partial q}\right|_0 + \cdots \tag{43}$$

The energy W of the system is

$$W = -\frac{1}{2}\alpha E^2 \tag{44}$$

so that the force F is

$$F = -\frac{\partial W}{\partial q} = \frac{1}{2}\frac{\partial\alpha}{\partial q} E^2 \tag{45}$$

Thus a system described by the harmonic oscillator equation gives

$$\ddot{q} + \Gamma\dot{q} + \omega_0^2 q = F/m = \frac{1}{2m}\frac{\partial\alpha}{\partial q}E^2 \tag{46}$$

Assuming an applied field composed of two frequencies gives

$$E = E_\ell + E_s \tag{47}$$

where

$$\begin{aligned} E_\ell &= \tfrac{1}{2}E_\ell^0\, e^{i(k_\ell\cdot r - \omega_\ell t)} + c.c. \\ E_s &= \tfrac{1}{2}E_s^0\, e^{i(k_s\cdot r - \omega_s t)} + c.c. \end{aligned} \tag{48}$$

Substituting eqs. (47) and (48) into eqs. (46) and keeping only those terms with frequency dependence ± $(\omega_\ell - \omega_n)$ gives

$$q = \frac{1}{4m}\frac{\partial\alpha}{\partial q}\left(E_\ell^0 E_s^{0*}\,\frac{e^{i(k_\ell\cdot r - k_s\cdot r - \omega_\ell t + \omega_s t)}}{D(\omega_\ell - \omega_s)} + c.c.\right) \tag{49}$$

where $D(\omega_\ell - \omega_s)$ is defined in eq. (36). As before, the susceptibility is given by

$$\chi = N\alpha = N\left(\alpha_0 + q\,\frac{\partial\alpha}{\partial q}\Big|_0\right) \tag{50}$$

where $N\alpha_0$ is equal to the linear susceptibility. Using $P = \chi E$ along with eqs. (50) and (48) gives on keeping the terms with frequency dependence ± $(2\omega_\ell - \omega_s)$

$$P^{(3)}(\omega_{as}) = \frac{N}{8m}\left(\frac{\partial\alpha}{\partial q}\right)_0^2\left(E_\ell^{0\,2}E_s^{0*}\,\frac{e^{i(k_{as}\cdot r - \omega_{as}t)}}{D(\omega_\ell - \omega_s)} + c.c.\right) \tag{51}$$

where again

$$\begin{aligned} k_{as} &\equiv 2k_\ell - k_s \\ \omega_{as} &\equiv 2\omega_\ell - \omega_s \end{aligned} \tag{52}$$

This gives a third order nonlinear susceptibility of the form

$$3\chi^{(3)}(\omega_{as}) = \frac{N}{m}\left(\frac{\partial\alpha}{\partial q}\right)_0^2\frac{1}{D(\omega_\ell - \omega_s)} \tag{53}$$

A treatment similar to this, but using first order perturbation theory is noted in Appendix C.

IV. The Quantum Mechanical Approach to Suceptibility

Explicit expressions for the susceptibility tensor can be derived quantum mechanically by use of the density matrix method. Normally a state vector describing a system in quantum mechanics can be expanded in a series of eigen vectors of an operator. The coefficients a_n of the expansion are then related to the probability of finding the system in one of the eigenstates. Transitions from one state to another are determined by the equation of motion whose solution depends on the intiial values of the expansion coefficients. However, if precise values for the coefficients are not known, but certain average values can be ascertained, then a density matrix ρ_{mn} can be defined as

$$\rho_{mn} = \overline{a_n^* a_m}$$

where the bar denotes an average and the asterisk denotes the complex conjugate. Then if some aspect of a system is described by a matrix $\underset{\approx}{Q}$, it can be shown (19) that the average value of the expectation value of $\underset{\approx}{Q}$ is given by the trace of the matrix product $\underset{\approx}{\rho}\underset{\approx}{Q}$; that is, if $\bar{Q}$ denotes the average value of the expectation value of $\underset{\approx}{Q}$, then

$$\bar{Q} = Tr(\underset{\approx}{\rho}\underset{\approx}{Q})$$

Since the trace of a matrix is defined as the sum of terms along its main diagonal, the above equation in component form is

$$\bar{Q} = \sum_{mn} \rho_{mn} Q_{nm}$$

To apply the density matrix to the problem of determining the sysceptibility of a system, recall that the susceptibility χ is defined through the polarization P. If the polarization is taken to be the number of dipole moments per unit volume, then there results

$$P = Nd$$

where N is the number density of dipoles with moment d. A matrix d_{nm} can then be associated with the dipole moment due to a transition from a state m to a state n whose average value of the expectation value is given by

$$\bar{d} = \mathrm{Tr}(\underline{\rho}\,\underline{d})$$

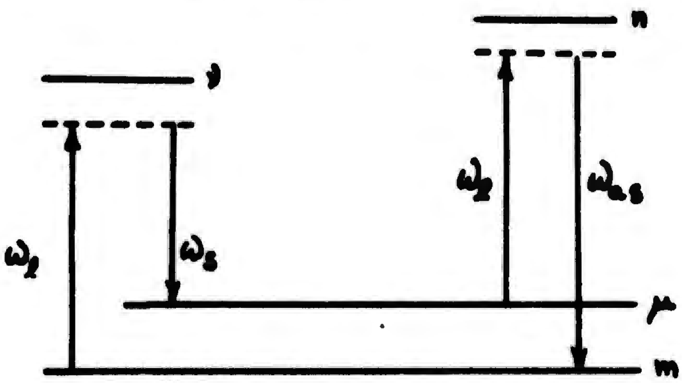
In Appendix D the equation of motion for the density matrix is derived in terms of a Hamiltonian H. Then assuming that the system is perturbed by a dipole interaction, a perturbation solution of the equation of motion is given. In Apprndix E an example is given of finding the susceptibility tensor from the perturbation solution of the equation of motion of the density matrix. In particular, the case is considered of two waves of frequency ω_ℓ and ω_s incident on a medium. The third order susceptibility $\chi^{(3)}(\omega_{as})$ at the anti-Stokes frequency $\omega_{as} = 2\omega_\ell - \omega_s$ is then obtained. The result is

$$\begin{aligned}
\chi^{(2)}(-\omega_{as}+2\omega_\ell-\omega_s) = -\frac{N}{4\hbar^3}\sum_{mn\mu\nu}\Bigg\{ & \left(\frac{\overset{0}{\rho}_{nn}-\overset{0}{\rho}_{\nu\nu}}{\omega_{n\nu}+\omega_s} - \frac{\overset{0}{\rho}_{\nu\nu}-\overset{0}{\rho}_{\mu\mu}}{\omega_{\nu\mu}-\omega_\ell}\right)\frac{\underline{d}_{mn}\underline{d}_{n\nu}\underline{d}_{\nu\mu}\underline{d}_{\mu m}}{(\omega_{n\mu}-\Delta)(\omega_{nm}-\omega_{as})} \\
& + \left(\frac{\overset{0}{\rho}_{nn}-\overset{0}{\rho}_{\nu\nu}}{\omega_{n\nu}-\omega_\ell} - \frac{\overset{0}{\rho}_{\nu\nu}-\overset{0}{\rho}_{\mu\mu}}{\omega_{\nu\mu}+\omega_s}\right)\frac{\underline{d}_{mn}\underline{d}_{\nu\mu}\underline{d}_{n\nu}\underline{d}_{\mu m}}{(\omega_{n\mu}-\Delta)(\omega_{nm}-\omega_{as})} \\
& + \left(\frac{\overset{0}{\rho}_{nn}-\overset{0}{\rho}_{\nu\nu}}{\omega_{n\nu}-\omega_\ell} - \frac{\overset{0}{\rho}_{\nu\nu}-\overset{0}{\rho}_{\mu\mu}}{\omega_{\nu\mu}-\omega_\ell}\right)\frac{\underline{d}_{mn}\underline{d}_{\mu m}\underline{d}_{\nu\mu}\underline{d}_{n\nu}}{(\omega_{n\mu}-2\omega_\ell)(\omega_{nm}-\omega_{as})} \\
& + \left(\frac{\overset{0}{\rho}_{\nu\nu}-\overset{0}{\rho}_{mm}}{\omega_{\nu m}+\omega_s} - \frac{\overset{0}{\rho}_{\mu\mu}-\overset{0}{\rho}_{\nu\nu}}{\omega_{\mu\nu}-\omega_\ell}\right)\frac{\underline{d}_{mn}\underline{d}_{\nu m}\underline{d}_{\mu\nu}\underline{d}_{n\mu}}{(\omega_{\mu m}-\Delta)(\omega_{nm}-\omega_{as})} \\
& + \left(\frac{\overset{0}{\rho}_{\nu\nu}-\overset{0}{\rho}_{mm}}{\omega_{\nu m}-\omega_\ell} - \frac{\overset{0}{\rho}_{\mu\mu}-\overset{0}{\rho}_{\nu\nu}}{\omega_{\mu\nu}-\omega_\ell}\right)\frac{\underline{d}_{mn}\underline{d}_{n\mu}\underline{d}_{\mu\nu}\underline{d}_{\nu m}}{(\omega_{\mu m}-2\omega_\ell)(\omega_{nm}-\omega_{as})} \\
& + \left(\frac{\overset{0}{\rho}_{\nu\nu}-\overset{0}{\rho}_{mm}}{\omega_{\nu m}-\omega_\ell} - \frac{\overset{0}{\rho}_{\mu\mu}-\overset{0}{\rho}_{\nu\nu}}{\omega_{\mu\nu}+\omega_s}\right)\frac{\underline{d}_{mn}\underline{d}_{\mu\nu}\underline{d}_{n\mu}\underline{d}_{\nu m}}{(\omega_{\mu m}-\Delta)(\omega_{nm}-\omega_{as})}\Bigg\}
\end{aligned} \qquad (54)$$

where the $\overset{0}{\rho}_{\alpha\alpha}$ are initial values of the density matrix for the level α, $\Delta = \omega_\ell - \omega_s$ and $\underline{d}_{\alpha\beta}$ is the matrix components of the dipole moment $\underline{d}$.

We shall now attempt to simplify equation (54) in order to better understand the resonant enhancements and perturbations of neighboring electronic levels. First, let us consider the following simple energy level scheme for a molecule:

Figure 1



Here, m is the ground state of the molecule, μ is an excited vibrational level and ν and n are two electronic levels within the species. First, we shall assume that all molecules are in the ground state. This assumption causes all density elements $\overset{\bullet}{\rho}_{\alpha\alpha}$ to vanish except $\overset{\bullet}{\rho}_{mm}$ since m is the ground state. Hence, only the last three terms of equation (54) survive. It should be noted that two of these terms are the only ones which contain the CARS resonance denominator, $(\omega_{\mu m} - \Delta)$. This denominator becomes very small as $\Delta = \omega_\ell - \omega_s \rightarrow \omega_{as}$ or, in other words, $\chi^{(3)}\ \omega_{as}$ increases rapidly as ω_s is tuned such that the difference in frequency between the two laser beams approaches a Raman resonance in the medium. Equation (54) can now be written as:

$$\chi^{(3)}(\omega_{as}) = \frac{N}{4\hbar^3} \sum_{\nu n} \frac{1}{\omega_{nm} - \omega_{as}} \left\{ \frac{1}{\omega_{\mu m} - \Delta} \left[\frac{\overset{\bullet}{\rho}_{mm}}{\omega_{\nu\mu} + \omega_\ell} \underset{\sim}{d}_{mn} \underset{\sim}{d}_{\nu m} \underset{\sim}{d}_{\mu\nu} \underset{\sim}{d}_{n\mu} + \frac{\overset{\bullet}{\rho}_{mm}}{\omega_{\nu m} - \omega_\ell} \underset{\sim}{d}_{mn} \underset{\sim}{d}_{\mu n} \underset{\sim}{d}_{n\mu} \underset{\sim}{d}_{\nu m} \right] + \chi_R \right\} + \chi^{el} \qquad (54a)$$

where χ_R is a sum of all the off-resonant, vibrational and electronic contributions to the susceptibility. It also includes small contributions from the terms which were assumed negligible ($\rho_{\alpha\alpha} = 0$) and resonances with other electronic transitions (fifth term in equation (54)). The overall minus sign was taken inside the summations.

In the past it has been assumed that χ_R (the residual resonance term) can be simply lumped into χ^{el} to give an overall background contribution to the susceptibility. This assumption can lead to a misinterpretation regarding electronic resonance enhancement. As can be clearly seen for equation (54a), the CARS term can be enhanced by the electronic resonance denominator. However, χ_R is equally enhanced. If $(\omega_{nm} - \omega_{as})^{-1} \cdot \chi_R$ is much smaller than χ^{el}, enhancement of the CARS signal above the background will take place because χ^{el} is the main contribution to the background. If χ_R, however, is large, then it will dominate over χ^{el}, and the background signal will increase at the same rate as the signal and the CARS emission will not be effectively enhanced. It is therefore important to know the conditions under which χ_R becomes unusually high in order to avoid such situations. One condition appears in the fifth term of equation (54). This term will make a large contribution to χ_R when the laser frequency, ω_ℓ, lies in the vicinity of another electronic resonance. It is also clear that the two photon contributions (third term in equation (54) will be large when twice the laser frequency approaches the electronic transition $\omega_{n\nu}$, especially for situations where molecules are excited. Thus, it appears that one might expect the greatest possible resonance enhancement from electronic states by allowing ω_{as} to encroach upon an electronic transition and to avoid two photon effects and electronic resonance coincidences with the exciting laser frequencies. It should be emphasized that this is a recommended approach as a first attempt at electronic resonance enhancement. Since enhancement is a very complicated process for complex molecules, enhancement may be found with ω_ℓ as well.

V. Application to Coherent Anti-Stokes Raman Spectroscopy

Consider the case where two optical beams of frequencies ω_ℓ and ω_s are incident on a sample, as shown in Figure 2.

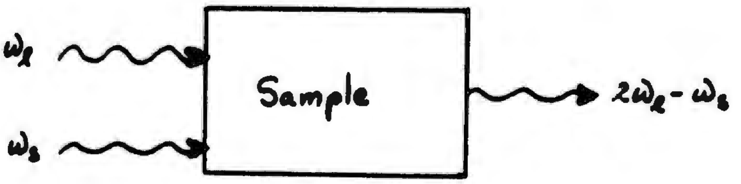


Figure 2

Due to the third-order susceptibility of the sample, a beam nearly collinear with the incident beams is generated at the frequency $2\omega_\ell - \omega_s$. The level diagram for the process is shown schematically in Figure 3, with the scattering process occurring instantaneously.

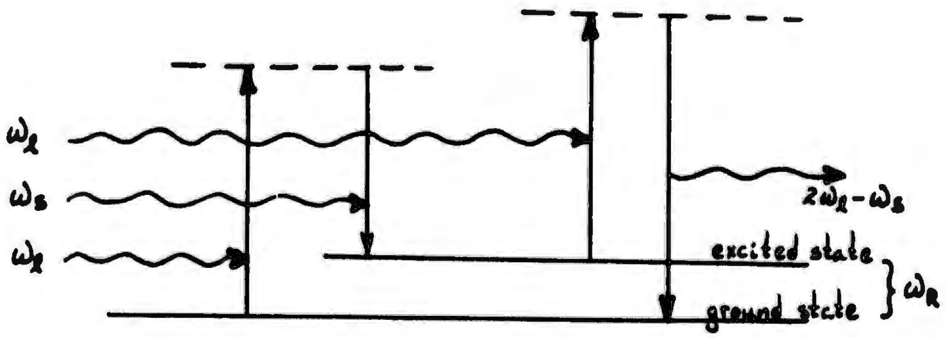


Figure 3

If ω_ℓ is fixed and ω_s is varied, then when the difference $\Delta = \omega_\ell - \omega_s$ equals the frequency of a vibrational transition of the sample, say ω_R, the nonlinear susceptibility is resonantly enhanced, and a greatly increased output signal is generated at the anti-Stokes frequency $\omega_{as} = 2\omega_\ell - \omega_s = \omega_\ell + \omega_R$.

To understand the generation of the anti-Stokes wave, let the two incident waves be represented by plane waves propagating in the Z direction with propagation vectors k_ℓ and k_s and with general forms given by

$$E_i = \frac{1}{2} E_i^0 e^{i(k_i z - \omega_i t)} + c.c. \qquad , \; i = \ell, s \tag{55}$$

Then from Section II, the polarization is given by

$$P(2\omega_\ell - \omega_s) = \frac{3}{8} \chi^{(3)} E_\ell^{0\,2} E_s^{0\,*} e^{i(2k_\ell z - k_s z - 2\omega_\ell t + \omega_s t)} + c.c. \tag{56}$$

which generates an anti-Stokes wave satisfying the wave equation

$$\underset{\sim}{\nabla} \times \underset{\sim}{\nabla} \times \underset{\sim}{E}(\omega_{as}) - \frac{\omega_{as}^2}{c^2} \epsilon(\omega_{as}) \underset{\sim}{E}(\omega_{as}) = \frac{4\pi\omega_{as}^2}{c^2} \underset{\sim}{P}(2\omega_\ell - \omega_s) \tag{57}$$

Using the identity $\underset{\sim}{\nabla} \times \underset{\sim}{\nabla} \times \underset{\sim}{E} = \underset{\sim}{\nabla}(\underset{\sim}{\nabla} \cdot \underset{\sim}{E}) - (\underset{\sim}{\nabla} \cdot \underset{\sim}{\nabla}) \underset{\sim}{E}$ and the condition $\underset{\sim}{\nabla} \cdot \underset{\sim}{E} = 0$ for a charge-free region, the wave equation becomes

$$(\underset{\sim}{\nabla} \cdot \underset{\sim}{\nabla}) \underset{\sim}{E}(\omega_{as}) + \frac{\omega_{as}^2}{c^2} \epsilon(\omega_{as}) \underset{\sim}{E}(\omega_{as}) = -\frac{4\pi\omega_{as}^2}{c^2} \underset{\sim}{P}(2\omega_\ell - \omega_s) \tag{58}$$

Since the propagation is in the Z direction, this becomes

$$\frac{\partial^2}{\partial z^2} E(\omega_{as}) + \frac{\omega_{as}^2}{c^2} \epsilon(\omega_{as}) E(\omega_{as}) = -\frac{4\pi\omega_{as}^2}{c^2} P(2\omega_\ell - \omega_s) \tag{59}$$

Assuming the form

$$E(\omega_{as}) = \frac{1}{2} E_{as}^0 e^{i(k_{as} z - \omega_{as} t)} + c.c. \tag{60}$$

$$\frac{\partial}{\partial z} E(\omega_{as}) = \frac{1}{2}\Big[\frac{\partial E^{\circ}_{as}}{\partial z} e^{i(k_{as}z - \omega_{as}t)} + c.c. \qquad (61)$$

$$+ ik_{as}E^{\circ}_{as} e^{i(k_{as}z - \omega_{as}t)} + c.c. \Big]$$

$$\frac{\partial^2}{\partial z^2} E(\omega_{as}) = \frac{1}{2}\Big[\frac{\partial^2 E^{\circ}_{as}}{\partial z^2} e^{i(k_{as}z - \omega_{as}t)} + c.c.$$

$$+ 2ik_{as}\frac{\partial E^{\circ}_{as}}{\partial z} e^{i(k_{as}z - \omega_{as}t)} + c.c. \qquad (62)$$

$$- k_{as}^2 E^{\circ}_{as} e^{i(k_{as}z - \omega_{as}t)} + c.c. \Big]$$

Choosing $k_{as}^2 = \frac{\omega_{as}^2}{c^2} E\ (\omega_{as})$ and ignoring the second-order derivatives, since $\left|\frac{\partial^2 E^{\circ}_{as}}{\partial z^2}\right| << k_{as}\left|\frac{\partial E^{\circ}_{as}}{\partial z}\right|$ if the variation of the amplitude over one wavelength is small, gives

$$ik_{as}\frac{\partial E^{\circ}_{as}}{\partial z} = -4\pi\frac{\omega_{as}^2}{c^2}P(2\omega_R - \omega_s)e^{-i(k_{as}z - \omega_{as}t)}$$

or

$$\frac{\partial E^{\circ}_{as}}{\partial z} = 4\pi i \frac{\omega_{as}}{c\, n_{as}} P(2\omega_{\ell}-\omega_{s})\, e^{-i(k_{as}z-\omega_{as}t)} \tag{63}$$

where n_{as} is the index of refraction at the frequency ω_{as}. Substituting the expression for the polarization into the above and integrating over the sample length gives

$$E^{\circ}_{as} = \frac{\pi i\, \omega_{as}}{2c\, n_{as}} E_{\ell}^{\circ 2} E_{s}^{\circ *} \int_{0}^{L} 3\chi^{(3)}(\omega_{as})\, e^{i\Delta k z}\, dz \tag{64}$$

where $\Delta k = 2k_{\ell} - k_{s} - k_{as}$ is the phase matching condition, and it has been assumed that E°_{ℓ} and E°_{s} are slowly varying throughout the sample. Since the time averaged intensity is related to the electric field through

$$I = \frac{c}{8\pi} |E^{\circ}|^{2} \tag{65}$$

the intensity of the generated anti-Stokes wave is given by

$$I(\omega_{as}) = \left(\frac{4\pi^{2}\omega_{as}}{c^{2} n_{as}}\right)^{2} I_{\ell}^{2} I_{s} \left| \int_{0}^{L} 3\chi^{(3)} e^{i\Delta k z}\, dz \right|^{2} \tag{66}$$

The susceptibility can be gotten by using a harmonic oscillator model for the optical transition. From Section III the susceptibility was found to be

$$3\chi^{(3)} = \frac{N}{m}\left(\frac{\partial \alpha}{\partial q}\right)^{2} \frac{1}{D(\omega_{\ell}-\omega_{s})} \tag{67}$$

From ordinary scattering theory the differential cross section is given by (20)

$$\frac{d\sigma}{d\Omega} = \frac{\omega_{\ell}^{4}}{c^{4}} (\alpha')^{2} \tag{68}$$

where α' is the polarizability matrix element of the Raman transition and is defined through

$$\alpha = \alpha_0 + \alpha' = \alpha_0 + \frac{\partial\alpha}{\partial q} q \qquad (69)$$

Assuming the classical and quantum mechanical normal coordinate q to be the same, there results

$$q^2 = \frac{\hbar}{2m\omega_0}$$

and (21)

$$\frac{d\sigma}{d\Omega} = \frac{\omega_s^4}{c^4}\left(\frac{\partial\alpha}{\partial q}\right)^2 \frac{\hbar}{2m\omega_0} \qquad (70)$$

Substituting this into equation (67) for the susceptibility gives

$$3\chi^{(3)}(\omega_{as}) = \frac{2Nc^4}{\hbar\omega_s^4}\frac{d\sigma}{d\Omega}\left[\frac{\omega_0}{\omega_0^2-(\omega_l-\omega_s)^2-i\Gamma(\omega_l-\omega_s)}\right] \qquad (71)$$

Letting $\Delta\omega = \omega_0 - (\omega_l - \omega_s)$ or $\omega_l - \omega_s = \omega_0 - \Delta\omega$ and dividing the above by $\omega_l - \omega_s$ gives

$$3\chi^{(3)}(\omega_{as}) = \frac{2Nc^4}{\hbar\omega_s^4}\frac{d\sigma}{d\Omega}\left[\frac{\frac{\omega_0}{\omega_0-\Delta\omega}}{\frac{\omega_0}{\omega_0-\Delta\omega}-(\omega_0-\Delta\omega)-i\Gamma}\right] \qquad (72)$$

But, if $\frac{\Delta\omega}{\omega_0} \ll 1$, then

$$\frac{1}{\omega_0-\Delta\omega} = \frac{1}{\omega_0}\left(1-\frac{\Delta\omega}{\omega_0}\right)^{-1} \approx \frac{1}{\omega_0}\left(1+\frac{\Delta\omega}{\omega_0}\right)$$

and the above becomes

$$3\chi^{(3)}(\omega_{as}) \approx \frac{2Nc^4}{\hbar\omega_s^4}\frac{d\sigma}{d\Omega}\left[\frac{1+\frac{\Delta\omega}{\omega_0}}{\omega_0\left(1+\frac{\Delta\omega}{\omega_0}\right)-\omega_0+\Delta\omega-i\Gamma}\right]$$

or

$$3\chi^{(3)}(\omega_{as}) \approx \frac{2Nc^4}{\hbar\omega_s^4}\frac{d\sigma}{d\Omega}\left[\frac{1}{2\Delta\omega - i\Gamma}\right] \qquad (73)$$

We shall now attempt to calculate a relation for efficiency of the CARS generation for focused and unfocused beams. For unfocused beams assuming plane waves we need to evaluate the integral on equation (66). If we first assume that both exciting lasers have identical beam diameters and that phase-matching is achieved, then $\Delta k = 0$ and the integration of equation (66) is trivial, yielding for the CARS efficiency, ϵ:

$$\epsilon = \frac{I(\omega_{as})}{I(\omega_s)} = \frac{P(\omega_{as})/A}{P(\omega_s)/A} = \left(\frac{4\pi^2\omega_{as}}{c^2 n_{as}}\right)^2 \left|3\chi^{(3)}\right|^2 I_\ell^2 L^2 \qquad (74)$$

which is identical to that derived by Taran, et al. (3).† This relation says that anti-Stokes mixing will continue to grow rapidly (as the square of the interaction length), as the beems pass through the medium. Actually, only a certain maximum conversion can take place because the three beams gradually slip out of phase and destructively interfere as the beams propagate at slightly different phase velocities, i. e. the index of refraction in the medium is different at the three frequencies (dispersion). Let us now integrate equation (66) assuming $\Delta k \neq 0$. Since Δk is not a function of Z for simple applications, the integration is again quite easy. The result is:

$$\epsilon = \frac{P(\omega_{as})}{P(\omega_s)} = \left(\frac{4\pi^2\omega_{as}}{c^2 n_{as}}\right)^2 \left|3\chi^{(3)}\right|^2 I_\ell^2 L^2 \left[\frac{\sin(\Delta k L/2)}{(\Delta k L/2)}\right]^2 \qquad (75)$$

This equation is identical to the phase-matched relation for efficiency (equation (74)) except for the factor in brackets. This factor is a typical function

† Taran, et al. incorporate the factor of three within their expression for susceptibility.

found in nonlinear optics and is called the sinc function. Note that $\Delta k = o$, the sinc function becomes unity, and equation (75) reduces to equation (74) as expected. However, for nonzero values of Δk the growth of anti-Stokes emission is reduced. Let us now examine this situation more carefully. From equation (75) it is seen that peak conversion efficiency occurs for $\Delta k\, L/2 = (n - 1/2)\pi$, where $\Delta k \neq o$ but constant, L, the interaction length, is varying and n is a positive, nonzero integer. Thus, for nonzero values of Δk the efficiency of the CARS process does not grow as L^2 but instead reaches a maximum in a periodic fashion. The length of path to reach this first maximum (for n = 1) is called the coherence length or $\Delta k\, L_c/2 = \pi/2$. Hence, the coherence length, $L_c = \pi/\Delta k$. Now equation (75) can be rewritten as:

$$\epsilon = \left(\frac{4\pi^2 \omega_{as}}{c^2 n_{as}}\right)^2 \left|3\chi^{(3)}\right|^2 I_\ell^2 \left(\frac{2L_c}{\pi}\right)^2 \sin^2\left(\frac{L}{L_c}\cdot\frac{\pi}{2}\right) \tag{76}$$

For maximum conversion efficiency then $L = L_c$, and equation (76) becomes:

$$\epsilon_{max} = \left(\frac{4\pi^2 \omega_{as}}{c^2 n_{as}}\right)^2 \left|3\chi^{(3)}\right|^2 I^2 \left(\frac{2L_c}{\pi}\right)^2 \tag{77}$$

Now, comparing the relation for phase-matched efficiency (equation (74)) with the maximum conversion efficiency for $\Delta k \neq o$, we see that ϵ has decreased by the factor $(2/\pi)^2$ over the interaction length $L = L_c$. The functional dependences of efficiency on interaction length, L, and coherence length, L_c, are illustrated in Figure 4.

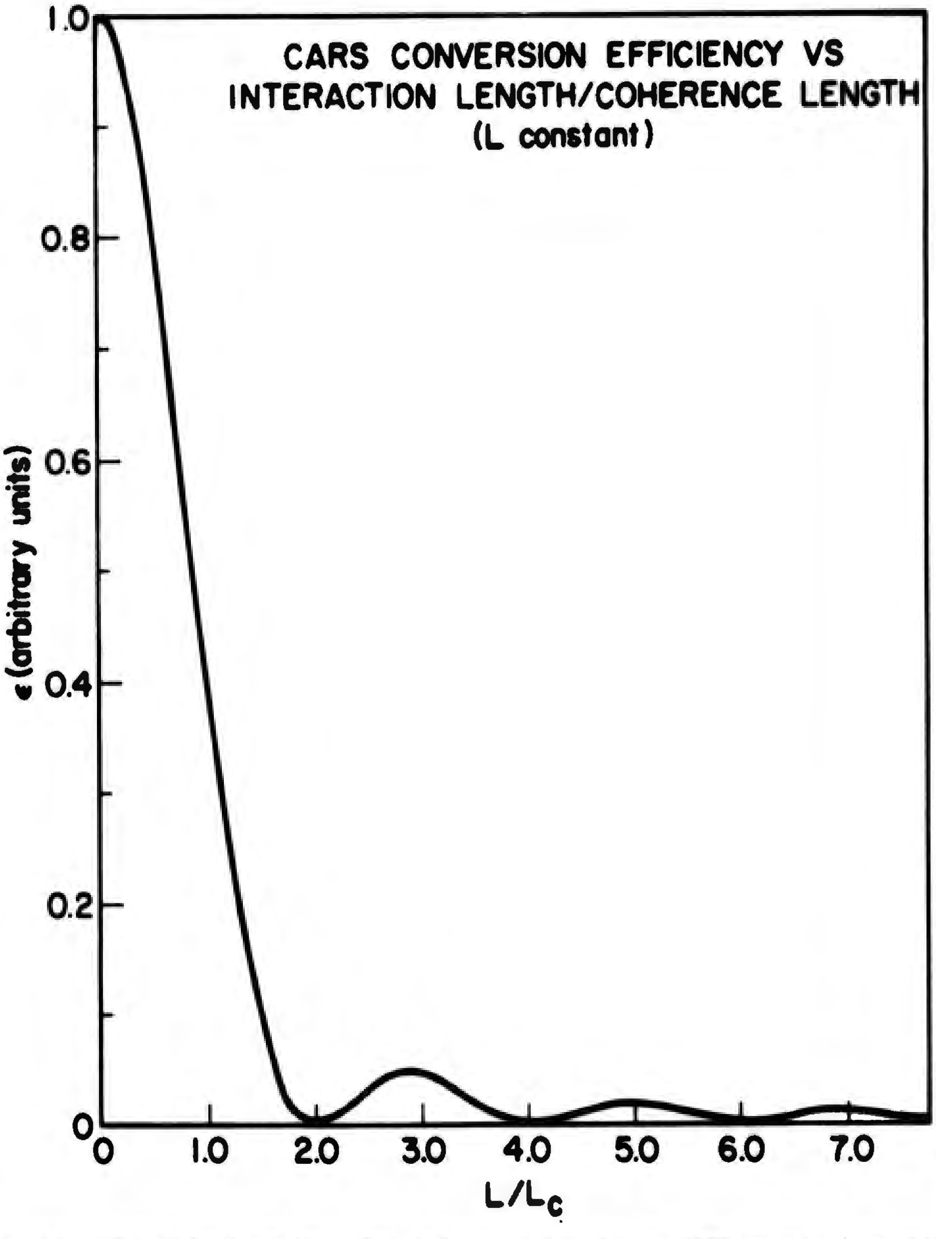


Fig. 4a. The effect of changing coherence length on CARS conversion efficiency for constant interaction length. Clearly the phase-matched condition ($\Delta k = 0$, $L_c = \infty$) gives the greatest conversion efficiency.

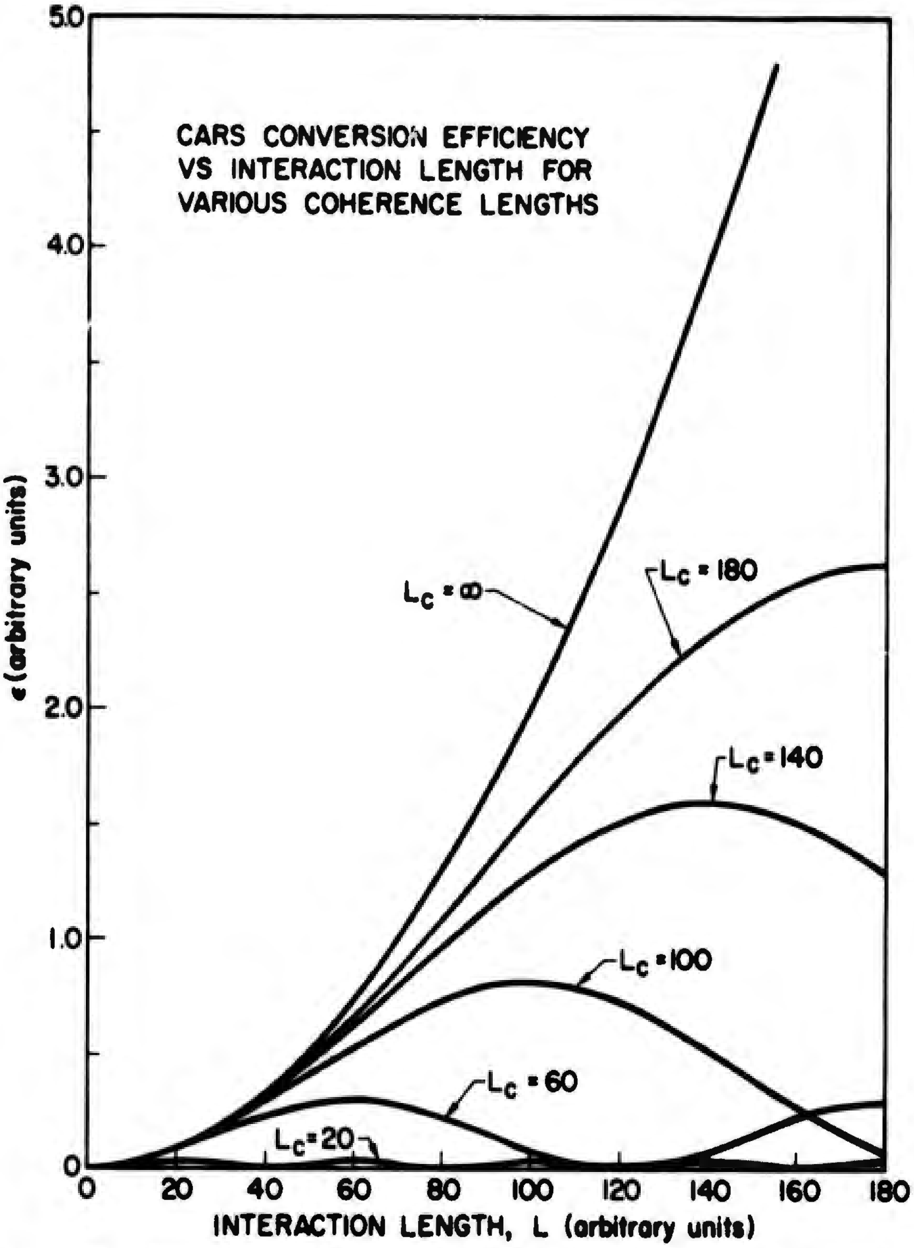


Fig. 4b. The effect of changes in interaction length on CARS efficiency for various coherence lengths.

Let us now examine the Δk or the coherence length in more detail. Actually, k is a vector, the momentum vector, the magnitude of which is $|\mathbf{k}_i| = n_i \omega_i / c$, where n_i is the index of refraction at ω_i, the angular frequency of the i^{th} wave. If the CARS signal is generated at $\omega_{as} = 2\omega_\ell - \omega_s$, the momentum vectors must also follow a similar relation for phase matching, i. e. $\mathbf{k}_{as} = 2\mathbf{k}_\ell - \mathbf{k}_s$. The magnitudes of the vectors will not obey this relation for a dispersive medium and collinear beams. There will therefore be a momentum mismatch or $\Delta k = 2k_\ell - k_s - k_{as}$. For liquids Δk is quite large or, to state another way, the coherence length is quite short (millimeters). For gases the coherence lengths can be quite long (several centimeters to many meters for rarified gas). One method for overcoming the momentum mismatch is to cross the beams at some angle, θ. In Figure 5 we see how phase matching can be achieved by this method.

Infinite interaction lengths cannot be obtained by crossing the beams, since the lasers will not spatially overlap over long paths. However, in condensed media the coherence length is usually shorter than the effective interaction length of the crossed beams, and it is more advantageous to cross the beams. As will be shown shortly, it is even more important to focus the beams to achieve even greater efficiencies and, in this case, only short interaction lengths can be achieved anyway.

The coherence length can be calculated by the following relation which was obtained by assuming a truncated series expansion of refractive index with respect to frequency:

$$L_c \approx \frac{\pi c}{\omega_v^2 (2n' + \omega_\ell n'')} \qquad (78)$$

where ω_v is the vibrational resonance frequency and n' and n" are the first and second derivatives of refractive index with respect to frequency (in radians per

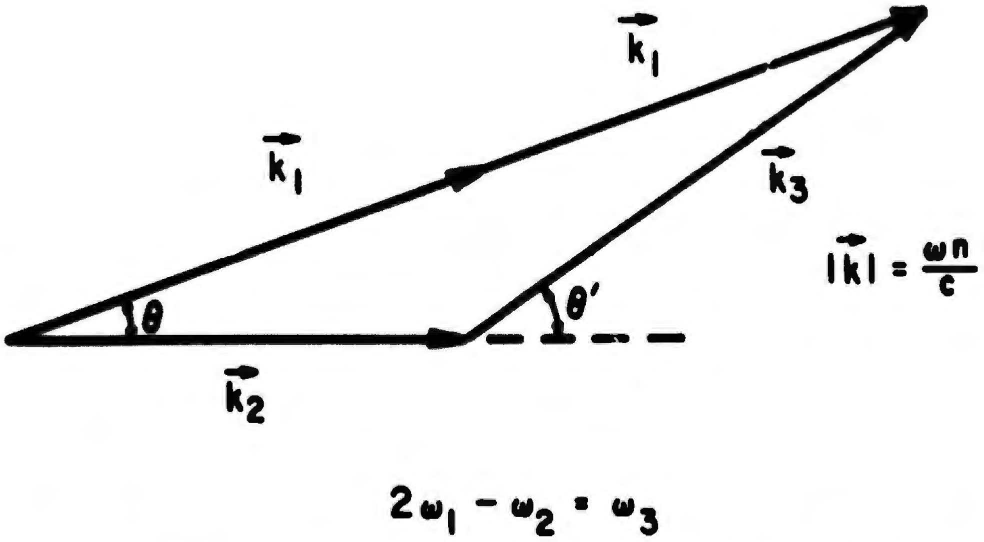


Fig. 5. Phase-matching condition for CARS. $\vec{k}_1 = \vec{k}_\ell$, $\vec{k}_2 = \vec{k}_s$ and $\vec{k}_3 = \vec{k}_{as}$. The phase-matching angle θ is ~ $\theta'/2$.

second), respectively. Similarly, if the refractive indices at the three frequencies are known, then the crossing angle can be calculated from the following formula from simple geometry:

$$\cos\theta = \frac{4\omega_\ell \omega_s n_{as}^2 - 4\omega_\ell^2 (n_{as}^2 - n_\ell^2) - \omega_s^2 (n_{as}^2 - n_s^2)}{4\omega_\ell n_\ell \omega_s n_s} \tag{79}$$

Let us now reexamine equation (78). For a particular medium n' and n" are constants, and the coherence length is determined by the inverse of the vibrational frequency squared, assuming that ω_ℓ is constant and ω_s is tuned, that is: $L_c \propto 1/\omega_v^2$. The coherence length decreases rapidly with vibrational frequency. However, efficiency decreases as the square of the coherence length. Hence, maximum CARS signal in the nonphased matched condition decreases as the fourth power of vibrational frequency or $\epsilon_{max} \propto 1/\omega_v^4$. Actually, this dependence is not quite as strong as it appears since there are other frequency factors contained within ϵ_{max}.

As was indicated previously, the third-order nonlinear susceptibility, $\chi^{(3)}$, is composed of a resonant part and a nonresonant part. The resonant part is itself made up of two components, a real portion, χ', and an imaginary portion, χ'', or

$$\chi^{(3)} = \chi' + \chi'' + \chi^{nR}(el) \tag{80}$$

χ^{NR} (el) is a real quantity and is due to the electronic contribution to the susceptibility. Typically, χ^{NR} (el) is orders of magnitude smaller than the resonant susceptibility for intense transitions in pure materials. However, for a dilute mixture or for a very weak transition, there is a point where the resonant component contributes little to the overall susceptibility. For H_2 mixed with N_2, for instance, Taran, et al. (3) found that at 10 - 100 ppm the resonant signal from H_2 became lost in the background generated in the bulk gas N_2 (1 atm). In Figure 6 we have plotted the functional forms of the resonant susceptibilities and their squares. It is to be remembered that the square of the absolute value of the susceptibility is directly related to the intensity of the CARS signal. In Figure 7 we plot the behavior of the CARS signal when the nonresonant part of the susceptibility is added to the resonant part. Note that as χ^{NR} (el) acquires a larger part of the total susceptibility, the shape of the band begins to look like the real part of the susceptibility and the center of the resonance now shifts from the central maximum to a frequency midway between the maximum and the minimum point. The reason for this change in shape is clearly seen from the following equations:

$$\chi^{(3)} = (\chi' + \chi^{NR}(el)) + \chi'' \qquad (81)$$

where the two real parts of the susceptibility are lumped together. The CARS signal is directly related to the square of the modulus or absolute value of the susceptibility

$$\begin{aligned} I(\omega_{as}) \propto |\chi^{(3)}|^2 &= \left|(\chi' + \chi^{NR}(el)) + \chi''\right|^2 \\ &= (\chi' + \chi^{NR}(el))^2 + (\chi'')^2 \qquad (82) \\ &= (\chi')^2 + (\chi'')^2 + (\chi^{NR}(el))^2 + 2\chi'\chi^{NR}(el) \end{aligned}$$

Thus, for a resonant material in low concentration $(\chi')^2$ and $(\chi'')^2$ are negligibly small and $(\chi^{NR}\,(el))^2$ is a large constant background. The last term then causes I (ω_{as}) to assume the shape of χ' (see Figure 6). A similar effect occurs from somewhat distant resonances. For close neighbors the CARS again produces a unique result not found in conventional spectroscopy. In this case, the negative part of χ' in one resonance cancels all or part of the positive part of the

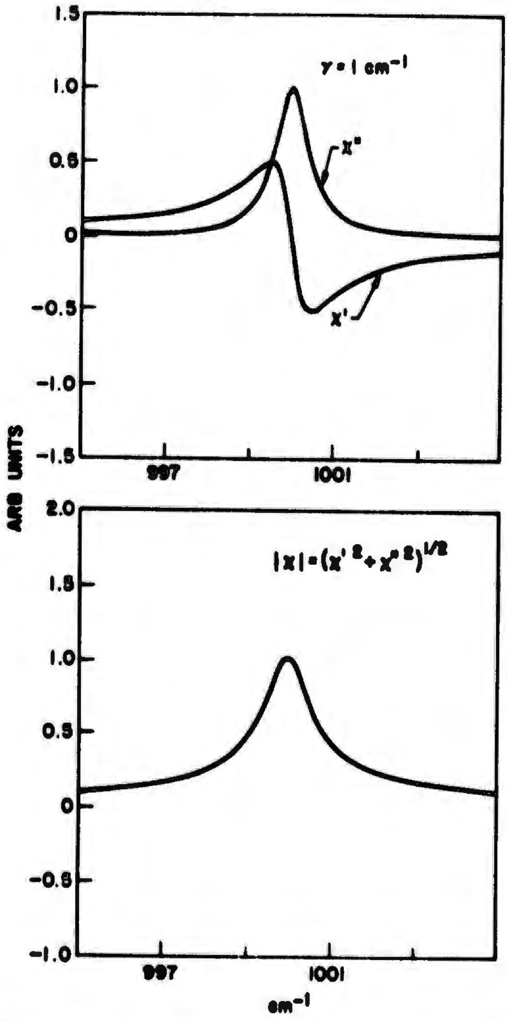


Fig. 6a. In the upper curve the real (χ') and imaginary (χ'') parts of the third-order nonlinear susceptibility are plotted for a resonance centered at 1000 cm^{-1} Raman shift and 1.0 cm^{-1} line width (FWHM). Note that χ' becomes negative or the high-frequency side of the resonance. The lower curve is the absolute value or modulus of $\chi^{(3)}$.

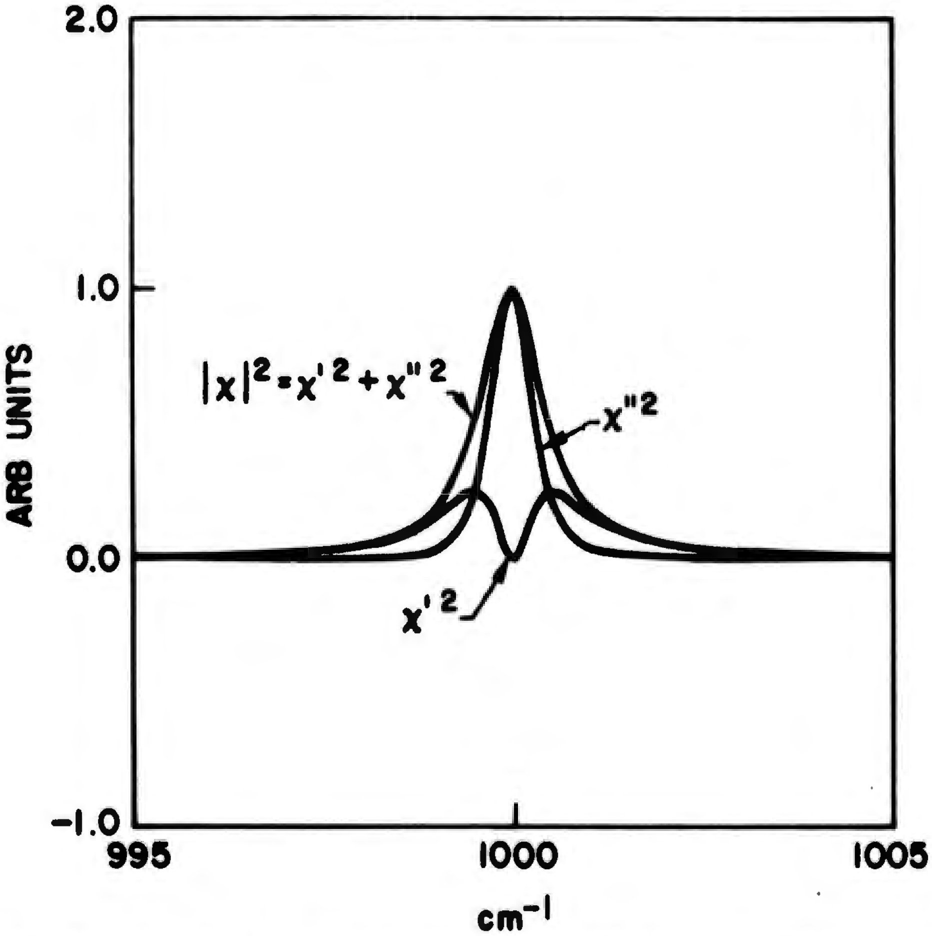


Fig. 6b. In this plot we display the squares of the total susceptibility and the squares of the real and imaginary parts for the resonance described in Fig. 6a.

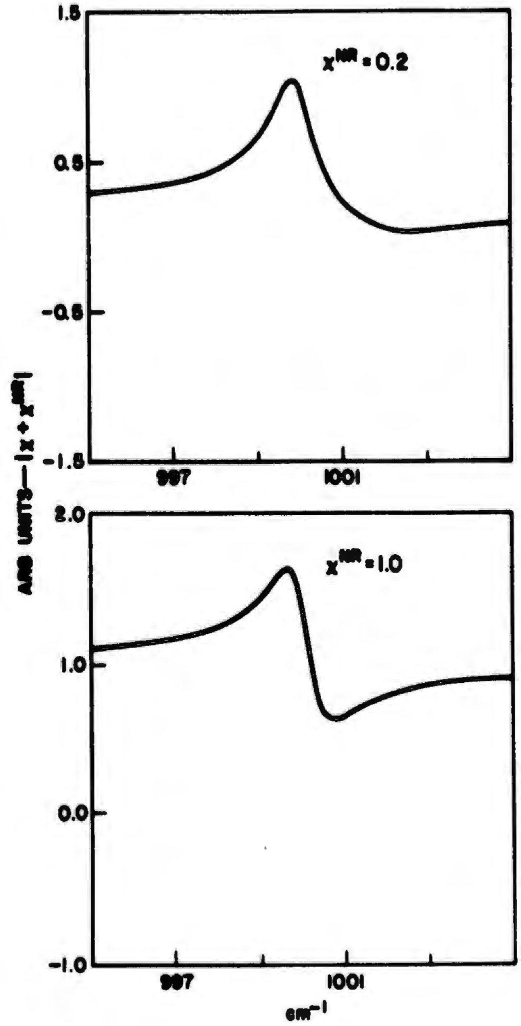
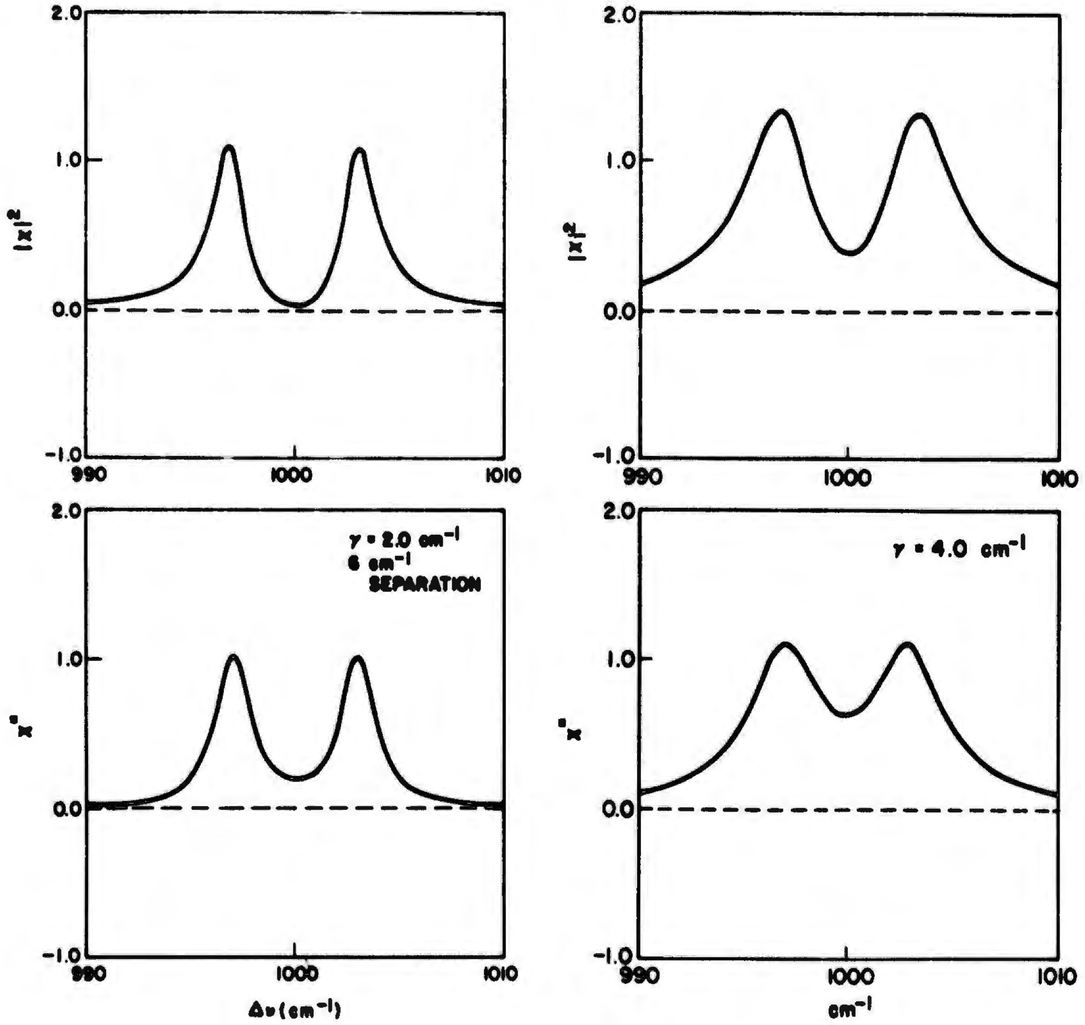
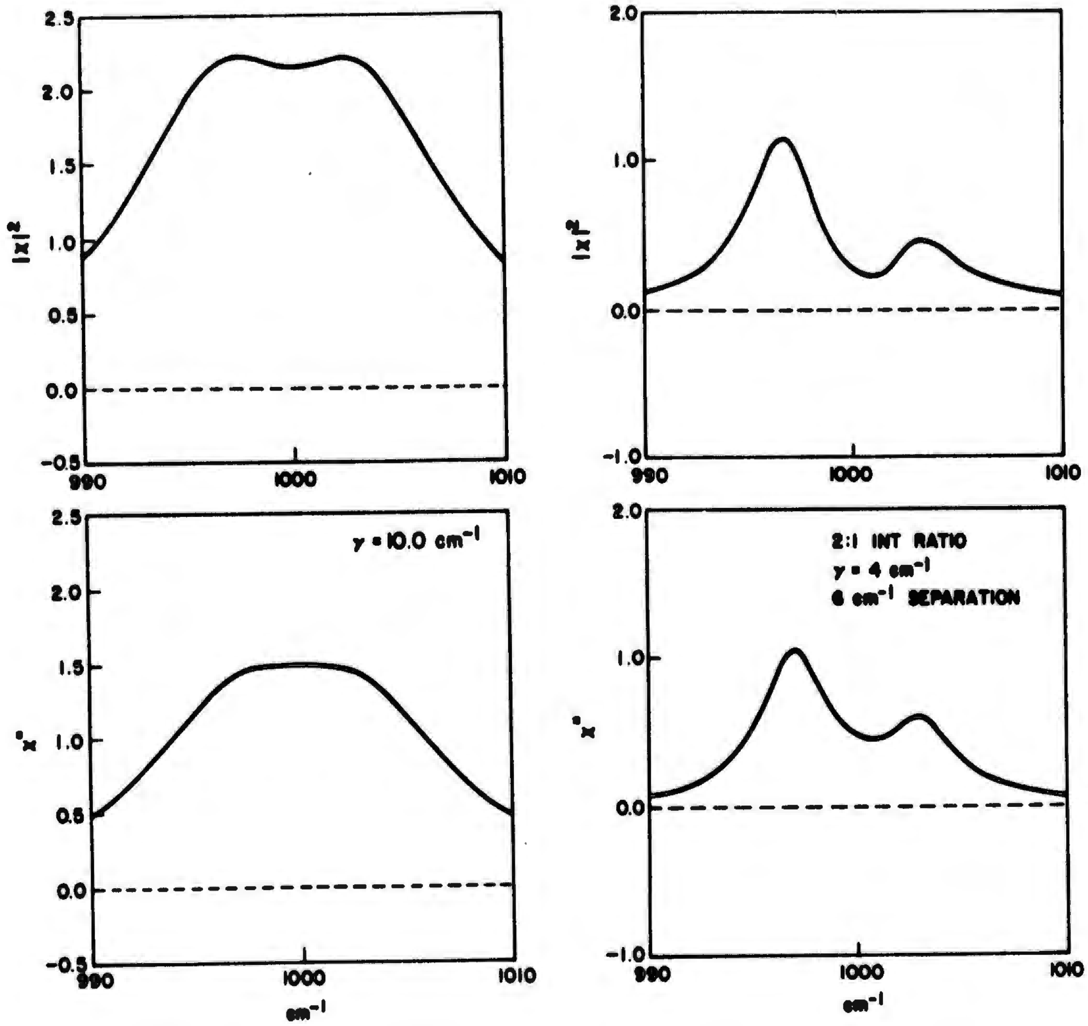


Fig. 7. In Fig. 6a and 6b we assumed that the background, nonresonant susceptibility, χ^{NR}, is negligible. In this figure we show the effects of added background susceptibility. Note that as χ^{NR} becomes relatively large in comparison with the resonant susceptibility, the CARS emission takes on a minimum which becomes identical to the shape of χ' at the limit of very large χ^{NR}.


2.0
1.0
0.0
-1.0
$|\chi|^2$
990
1000
1010
γ = 2.0 cm^{-1}
6 cm^{-1}
SEPARATION
χ''
$\Delta\nu$ (cm^{-1})
γ = 4.0 cm^{-1}
cm^{-1}

(a)

(b)



(c) (d)

Figs. 8a, b, c, and d. The next four figures show the effective improvement that CARS spectra have on band separation. The increased separation is the result of the presence of negative susceptibility in $|X|^2$ (which is related to CARS signal). Normal Raman spectroscopy (related to X'') has no such component. The overlapping bands in the illustration are separated by 6 cm^{-1}, but the line widths (FWHM) of the peaks are increased from 2.0 cm^{-1} in Fig. 8a to 10 cm^{-1} in Fig. 8c. In Fig. 8d this effect is still evident for bands of unequal intensity.

other. This effect causes an overall decrease in the resonant susceptibility between the resonances, the net effect of which is a better separation of neighboring peaks by CARS than is normal Raman (see Figure 8).

A more general comparison of CARS with normal Raman may be seen by the following. Normal Raman is really a special case of stimulated Raman effect where the exponential buildup of Raman gain is not observed for very small light intensities. Normal Raman, or more generally stimulated Raman, intensity is related to the imaginary part of the susceptibility χ'' (and not the real part which is a measure of the nonlinear refractive index). Thus, normal Raman is directly proportional to χ'', whereas CARS is related to $|\chi|^2$:

$$I_{Raman} \propto \sum_i \chi_i'', \text{ whereas } I_{CARS} \; |\sum_i \chi_i|^2$$

In other words, normal Raman is a simple sum of resonances, whereas CARS has strong interactive components generated by the cross terms in the expression for I_{CARS}. Such strong interactions make CARS rather unique compared with normal spectroscopy.

Equations (74 - 77) were obtained assuming plane waves and collimated laser beams. From the properties of gaussian beams (24), it is known that the focal region of a focused beam can be approximated by a cylinder of plane or collimated waves of diameter d and length $\pi d^2/2$. The length of the focal region is sometime called the confocal parameter, b. The reader is referred to Figure 9. Now let us return to equation (74), which was derived for plane waves and insert for the intensity, I_ℓ, its equivalent of power per unit area, P_L/A, where A is the area of

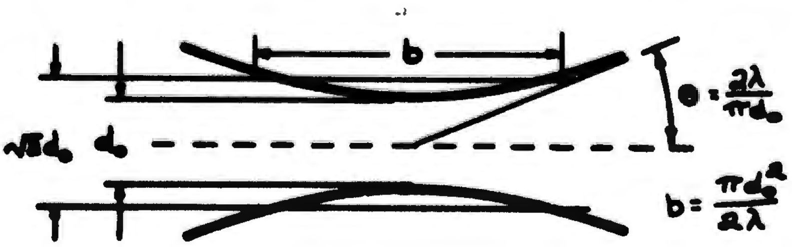


Fig. 9. Gaussian beam parameters of a focused laser beam. d_o is the minimum beam diameter, b is the confocal parameter.

the focal region or $A = \pi(d/2)^2$. We will also replace the interaction length, L, with the length of the approximately cylindrical focal region (confocal parameter, b); thus:

$$\epsilon = \frac{P(\omega_{as})}{P(\omega_s)} = \left(\frac{4\pi^2\omega_{as}}{c^2 n_{as}}\right)^2 \left|\chi^{(3)}\right|^2 \frac{P_\ell^2}{\pi^2 (d/2)^4} \left(\frac{\pi d^2}{2\lambda_\ell}\right)^2 \text{, or}$$

$$\epsilon = \left(\frac{8\pi^2\omega_{as}}{\lambda_\ell c^2 n_{as}}\right)^2 \left|\chi^{(3)}\right|^2 P_\ell^2 \text{, or alternately} \tag{83}$$

$$\epsilon = \left(\frac{16\pi^3}{\lambda_\ell \lambda_{as} n_{as} c}\right)^2 \left|\chi^{(3)}\right|^2 P_\ell^2$$

Equation (83) assumes that we are phase matched ($\Delta k = 0$ or that $b < L < L_c$). If this condition is not satisfied, equation (83) must be replaced by equation (76) for the nonphase-matched case. Note that equation (83) is not a function of the focal length of the focusing lens. This is because the length of the focal region, b, decreases as rapidly as the area of the beam decreases for tighter focusing; hence, there appears to be little dependence on focusing. However, equation (83) assumes we are phase-matched throughout the focal region. For materials with short coherence lengths, such as condensed media, loose focusing can result in a focal region longer than the coherence length. Hence, tighter focusing will then achieve higher efficiencies until $b << L_c$. Beyond this point, little is gained by tighter focusing. For gases especially at low (total) pressures, coherence lengths are quite large (of the order of 100 cm at one atmosphere pressure). Unless high spatial resolution is desired, this model predicts that tight focusing in gases is not necessary for maximum efficiency provided that the beams are mixed over the focal region and that the $b << L_c$. Typical confocal parameters of unfocused lasers are of the order of 100 cm.

Therefore, for most gases at pressures less than one atmosphere, one can attain as much CARS conversion efficiency using unfocused beams (mixed in the gas over the confocal parameter) as can be obtained by focusing tightly, according to this simple model.

As was mentioned earlier, one method for phase matching is to cross the beams. However, because of beam "walk off", one cannot achieve infinitely long coherence lengths by this method. In fact, if the beams have an effective overlap region smaller than one coherence length, it may not improve the efficiency to cross the beams in order to achieve phase matching. Let us now consider Figure 10 for two crossed beams:

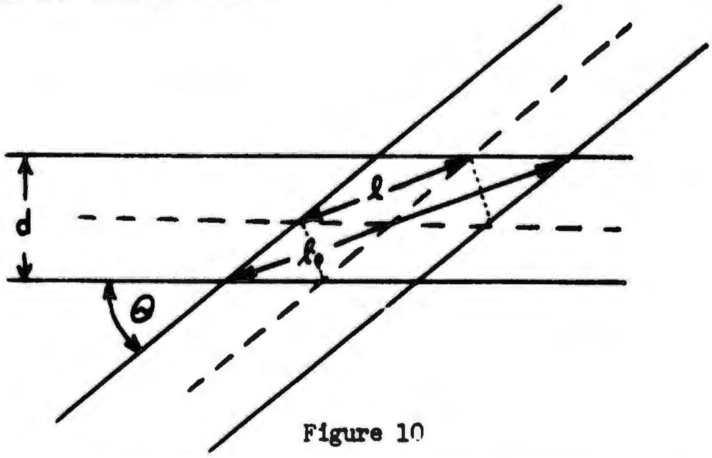


Figure 10

both of diameter d and crossed at angle θ. The interaction length is a volume resembling the shape of an ellipsoid of length, l_0. At the end of the interaction length, conversion to CARS signal should be very low because only the edges of the gaussian beams are overlapped (at this point, the intensity of each beam is only about 10% of the peak or the rate of CARS signal generation will be ~ 0.2% of that at the point of maximum overlap). Thus, an effective interaction length, ℓ, can be approximated by assuming that it begins where the edge of one beam crosses the center of the other, as illustrated in Figure 10. For small angles ($\theta < 10^\circ$), $\ell \sim d/\theta$ (θ in radians). Now we need to compare ℓ with the confocal parameter, b, as follows:

$$\frac{\ell}{b} = \frac{2\lambda}{\theta \pi d} \; (\theta \text{ in radians}) \quad \text{or} \quad = \frac{360\lambda}{\theta \pi^2 d} \; (\theta \text{ in degrees}) \qquad (84)$$

Since the CARS signal is reduced by the factor $(2/\pi)^2$ for generation over one coherence length compared with the phase-matched condition, this quantity should be incorporated into equation (84) to give some indication of whether crossing the beams is of any advantage (provided $b \lesssim$ Lc). Thus,

$$f = \frac{\ell}{b}\left(\frac{\pi}{2}\right)^2 = \frac{\pi\lambda}{2\theta d} \; (\theta \text{ in radians}) \quad \text{or} \quad = \frac{90\lambda}{\theta d} \; (\theta \text{ in degrees}) \qquad (85)$$

For values of $f > 1$, it is an advantage to cross the beams. For values of $f < 1$, the beam walk-off is appreciable, and it is better to transmit the beams collinearly or at some reduced crossing angle θ. Let us now evaluate f for a typical case, say benzene, for the vibrational mode at 1000 cm^{-1} (see references 6 and 7). The crossing angle for phase matching is about 1.3° ($\lambda_\ell \simeq 500$ nm) and $d \sim 10$ μm (for a lens of $f \simeq 5$ cm and an original beam diameter of ~ 1 mm)

$$f = \frac{(90)(500 \times 10^{-9} \text{ m})}{(1.3)(10 \times 10^{-6} \text{ m})} \sim 3$$

Hence, it is an advantage to cross the beams. This calculation is also in agreement with the observation that conversion with collinear interaction was smaller by an order of magnitude than phase matching by introducing a crossing angle.

In the previous paragraphs, it was assumed that the focus of the laser beams may be approximated by a cylindrical focal region. This simple model predicted that focusing was not a particular advantage for CARS efficiency as long as the confocal parameter was smaller than the coherence length. Bjorkland (25), however, has made a more precise calculation for CARS efficiency. His computations predict that focusing does achieve higher efficiencies. Shaub (26) has recently rederived these relations and has verified the strong dependence of CARS efficiency on focusing.

VI. Summary

In the previous sections we have outlined the basis for the theory behind Coherent Anti-Stokes Raman Spectroscopy and have shown the unusual features of the resulting spectra which are clearly unique as compared with conventional spectroscopy. By CARS, Raman spectra are really measurements of both bulk and molecular (microscopic) properties. The intensities one achieves with this method, however, can be truly astounding compared with normal Raman spectroscopy. For high-pressure gases (~ 1 atm) with narrow lines and for some liquids, the efficiencies are very high (~ 1%) with watts to kilowatts of peak power in the form of a coherent laser-like beam in the anti-Stokes region. These properties clearly make the method ideally suited for recording Raman spectra of fluorescent samples (as is often encountered with biological samples and natural products) and in situations where background luminescence is a problem (photochemistry, plasmas, discharges, etc.). High-resolution spectroscopy is another area where CARS is clearly advantageous. One of the most serious problems with CARS is background generation via the nonresonant susceptibility. The background is, in some respects, similar to fluorescence in normal Raman spectroscopy and at present limits the sensitivity.

Fertile and extremely useful areas of research in CARS will surely include means for reducing or eliminating background susceptibility, investigation into the use of depolarization measurements in structural chemistry, better susceptibility measurements, effects of pressure and neighboring resonances on band shapes, studies in electronic resonance enhancement, problems associated with saturation and the effects of turbulence and mie scattering, etc. on CARS efficiencies. With regerd to future applications, CARS has already been shown to be useful in profiling temperatures and number densities in flames. Such studies will certainly increase as the demand for new diagnostic tools for combustion applications increases. Another area of research for which CARS has applications is in laser diagnostics, analysis of discharges, plasmas, and atmospheric chemistry. The method is already finding utility in obtaining spectra on biological samples. Future research into the use of CARS for studying surfaces, fluctuation phenomena, reaction dynamics, photochemistry, kinetics, relaxation and energy transfer is just a partial list. CARS will clearly be a valuable method for making measurements in a wide variety of chemical, physical and engineering applications.

References

1. R. W. Terhune
Bull. Am. Phys. Soc 8, 359 (1963)

2. P. D. Maker and R. W. Terhune
Phys. Rev. 137, A801 (1965)

3. P. R. Regnier and J. P. E. Taran
Appl. Phys. Lett. 23, 240 (1973)

4. P. R. Regnier, F. Moya and J. P. E. Taran
AIAA Jour. 12, 826 (1974)

5. F. Moya, S. A. J. Druet and J. P. E. Taran
Optics Comm. 13, 169 (1975)

6. R. F. Begley, A. B. Harvey, R. L. Byer and B. S. Hudson
Amer. Lab. 6, 11 (1974)

7. R. F. Begley, A. B. Harvey and R. L. Byer
Appl. Phys. Lett. 25, 387 (1974)

8. R. F. Begley, A. B. Harvey, R. L. Byer and B. S. Hudson
J. Chem. Phys. 61, 2466 (1974)

9. M. D. Levenson and N. Bloembergen
J. Chem. Phys. 60, 1323 (1974)

10. M. Born and E. Wolf
Principles of Optics, Pergamon Press, N. Y. (1959)

11. P. N. Butcher
Nonlinear Optical Phenomena, Ohio State Univ. Press, Columbus, Ohio (1965)

12. R. W. Terhune and P. D. Maker
Chapter 4 of Lasers, Vol. 2, ed. by A. K. Levine; Marcel Dekker Publ. (1968)

13. R. W. Minck, R. W. Terhune and C. C. Wong
App. Optics 5, 1595 (1966)

14. R. A. Soref and H. W. Moos
J. Appl. Phys. 35, 2152 (1964)

15. R. K. Chang, J. Ducuing and N. Bloembergen
Phys. Rev. Lett. 15, 415 (1965)

16. R. Loudon
Quantum Theory of Light, Oxford Univ. Press (1973)

17. N. Bloembergen
Nonlinear Optics, Benjamin Inc., N. Y. (1965)

18. E. Garmire, F. Pandarese and C. H. Townes
Phys. Rev. Lett. 11, 160 (1973)

19. A. S. Davydov
Quantum Mechanics, NED Press, Ann Arbor, Michigan (1966)

20. I. I. Sobel'man
Introduction to the Theory of Atomic Spectra Ch. 9, Pergamon Press, N. Y. (1972)

21. M. Maier, W. Kaiser and J. A. Giordmaine
Phys. Rev. 177, 580 (1969)

22. G. Hergberg
Infrared and Raman Spectra of Polyatomic Molecules, Chapter III, Section 2, Van Nostrand, Inc., Princeton, N. J. (1960)

23. D. Marcuse
Engineering Quantum Electrodynamics, Harcourt, Brace and World, Inc., N. Y. (1970)

24. H. Kogalnik and T. Li
Proc. IEEE, 54, 1312 (1966)

25. G. C. Bjorklund, IEEE J. Quantum Electron. QE-11, 287 (1975); Bell Lab Report, TM 74-133-23 (1974); Microwave Lab Report No. 2339, Stanford Univ. (1974)

26. W. M. Shaub, "CARS Power Generation With Focused Pump Beams," to be published

Appendix A

Reality of E(t) and P(t)

Let the field E(t) be represented by

$$E(t) = \int_{-\infty}^{\infty} E(\omega) e^{-i\omega t} d\omega \tag{A1}$$

with inverse transform

$$E(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} E(t) e^{i\omega t} dt \tag{A2}$$

Taking the complex conjugate of equation (A2) gives

$$E^*(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} E^*(t) e^{-i\omega t} dt \tag{A3}$$

while letting $\omega \to -\omega$ in equation (A2) gives

$$E(-\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} E(t) e^{-i\omega t} dt \tag{A4}$$

Comparing equations (A3) and (A4) it is seen that for $E^*(t) = E(t)$; that is, E(t) real, then

$$E(-\omega) = E^*(\omega) \tag{A5}$$

The same is true for P(t).

Appendix B

Field Expansion of the Polarization

To get a relation between $\underset{\sim}{P}^{NL}(t)$ and the applied field $\underset{\sim}{E}(t)$ assume[11]

$$\underset{\sim}{P}(t) = \underset{\sim}{P}^{(1)}(t) + \underset{\sim}{P}^{(2)}(t) + \cdots + \underset{\sim}{P}^{(r)}(t) + \cdots \qquad \text{(B1)}$$

where $\underset{\sim}{P}^{(1)}(t)$ is linear in $\underset{\sim}{E}(t)$, $\underset{\sim}{P}^{(2)}(t)$ is quadratic in $\underset{\sim}{E}(t)$, etc. According to the principle of time invariance, the dynamical properties of the medium are assumed independent of time. Thus, if $\underset{\sim}{E}(t)$ results in a $\underset{\sim}{P}(t)$, then $\underset{\sim}{E}(t + T)$ must result in $\underset{\sim}{P}(t + T)$, where T is an arbitrary time displacement. Since $\underset{\sim}{P}^{(1)}(t)$ is linear in $\underset{\sim}{E}(t)$, assume the most general possible linear relation between them; namely

$$\underset{\sim}{P}^{(1)}(t) = \int_{-\infty}^{\infty} \underset{\approx}{\varphi}^{(1)}(t,\tau) | \underset{\sim}{E}(\tau)\, d\tau \qquad \text{(B2)}$$

where $\underset{\approx}{\varphi}^{(1)}(t,\tau)$ is a second rank tensor and the bar denotes a tensor expansion. Replacing t by t + T in eq. (B2) gives

$$\underset{\sim}{P}^{(1)}(t+T) = \int_{-\infty}^{\infty} \underset{\approx}{\varphi}^{(1)}(t+T,\tau) | \underset{\sim}{E}(\tau)\, d\tau \qquad \text{(B3)}$$

But by the principle of t invariance, $\underset{\sim}{P}^{(1)}(t + T)$ must be the same polarization induced by a field $\underset{\sim}{E}(t + T)$. Thus replacing $\underset{\sim}{E}(\tau)$ by $E(\tau + T)$ in equation (B2) gives

$$\underset{\sim}{P}^{(1)}(t+T) = \int_{-\infty}^{\infty} \underset{\approx}{\varphi}^{(1)}(t,\tau) | \underset{\sim}{E}(\tau+T)\, d\tau$$

Letting $\tau \to \tau - T$ results in

$$\underset{\sim}{P}^{(1)}(t+T) = \int_{-\infty}^{\infty} \underset{\approx}{\varphi}^{(1)}(t,\tau-T) | \underset{\sim}{E}(\tau)\, d\tau \qquad \text{(B4)}$$

Comparing eqs. (B3) and (B4) gives

$$\underset{\approx}{\varphi}^{(1)}(t+T,\tau) = \underset{\approx}{\varphi}^{(1)}(t,\tau-T) \qquad \text{(B5)}$$

Setting t = 0 and T = t gives

$$\underset{\approx}{\varphi}^{(1)}(t,\tau) = \underset{\approx}{\varphi}^{(1)}(0,\tau-t) \tag{B6}$$

Thus $\underset{\approx}{\varphi}^{(1)}(t,\tau)$ depends only on the difference τ - t and a new notation can be introduced to explicitly display this dependence; namely

$$\underset{\approx}{\varphi}^{(1)}(t,\tau) = \underset{\approx}{R}^{(1)}(t-\tau) \tag{B7}$$

Introducing this into eq. (B2) gives

$$\underset{\sim}{P}^{(1)}(t) = \int_{-\infty}^{\infty} \underset{\approx}{R}^{(1)}(t-\tau) | \underset{\sim}{E}(\tau) d\tau \tag{B8}$$

The function $\underset{\approx}{R}^{(1)}(t - \tau)$ is the linear polarization response function of the medium with the restriction:

1) $\underset{\approx}{R}^{(1)}(t - \tau) = 0$ when $t<\tau$ to ensure that $\underset{\sim}{P}^{(1)}(t)$ depends only on the fields when the time is less than t. This is the causality condition
2) $\underset{\approx}{R}^{(1)}(t - \tau)$ is real to ensure that $\underset{\sim}{P}^{(1)}(t)$ is real when $\underset{\sim}{E}(t)$ is real (the reality condition).

For the quadratic polarization $\underset{\sim}{P}^{(2)}(t)$, assume

$$\underset{\sim}{P}^{(2)}(t) = \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \, \underset{\underset{\sim}{\approx}}{\varphi}^{(2)}(t,\tau_1,\tau_2) | \underset{\sim}{E}(\tau_1)\underset{\sim}{E}(\tau_2) \tag{B9}$$

where $\underset{\underset{\sim}{\approx}}{\varphi}^{(2)}(t,\tau_1,\tau_2)$ is a third rank tensor and $\underset{\sim}{\approx}$ denotes a tensor of rank equal to 3. However, writing $\underset{\underset{\sim}{\approx}}{\varphi}^{(2)}$ as the sum of a symmetric and antisymmetric part gives

$$\varphi^{(2)}_{\mu\alpha\beta}(t,\tau_1,\tau_2) = S^{(2)}_{\mu\alpha\beta}(t,\tau_1,\tau_2) + A^{(2)}_{\mu\alpha\beta}(t,\tau_1,\tau_2) \tag{B10}$$

where

$$S^{(2)}_{\mu\alpha\beta}(t,\tau_1,\tau_2) = \frac{1}{2}\left\{ \varphi^{(2)}_{\mu\alpha\beta}(t,\tau_1,\tau_2) + \varphi^{(2)}_{\mu\beta\alpha}(t,\tau_2,\tau_1) \right\} \tag{B11}$$

$$A^{(2)}_{\mu\alpha\beta}(t,\tau_1,\tau_2) = \frac{1}{2}\left\{ \varphi^{(2)}_{\mu\alpha\beta}(t,\tau_1,\tau_2) - \varphi^{(2)}_{\mu\beta\alpha}(t,\tau_2,\tau_1) \right\} \tag{B12}$$

Writing equation (B9) in component form results in

$$P_\mu^{(2)}(t)=\int_{-\infty}^{\infty}d\tau_1\int_{-\infty}^{\infty}d\tau_2\,\varphi_{\mu\alpha\beta}^{(2)}(t,\tau_1,\tau_2)E_\alpha(\tau_1)E_\beta(\tau_2) \tag{B13}$$

Permuting $\alpha\tau_1$ and $\beta\tau_2$ gives

$$P_\mu^{(2)}(t)=\int_{-\infty}^{\infty}d\tau_1\int_{-\infty}^{\infty}d\tau_2\,\varphi_{\mu\beta\alpha}^{(2)}(t,\tau_2,\tau_1)E_\beta(\tau_2)E_\alpha(\tau_1) \tag{B14}$$

Adding this to eq. (B13) and using (B10) gives

$$\begin{aligned}2P_\mu^{(2)}(t)=\int_{-\infty}^{\infty}d\tau_1\int_{-\infty}^{\infty}d\tau_2\Big\{&S_{\mu\alpha\beta}^{(2)}(t,\tau_1,\tau_2)+A_{\mu\alpha\beta}^{(2)}(t,\tau_1,\tau_2)\\&+S_{\mu\beta\alpha}^{(2)}(t,\tau_2,\tau_1)+A_{\mu\beta\alpha}^{(2)}(t,\tau_2,\tau_1)\Big\}\end{aligned}$$

or

$$P_\mu^{(2)}(t)=\int_{-\infty}^{\infty}d\tau_1\int_{-\infty}^{\infty}d\tau_2\,S_{\mu\alpha\beta}(t,\tau_1,\tau_2)$$

Therefore the antisymmetric part makes no contribution to $P_\mu^{(2)}(t)$ and is therefore arbitrary. It is standard to set the antisymmetric part to zero, giving

$$\varphi_{\mu\alpha\beta}^{(2)}(t,\tau_1,\tau_2)=\varphi_{\mu\beta\alpha}^{(2)}(t,\tau_2,\tau_1) \tag{B15}$$

Applying the principle of t-invariance, gives

$$\underset{\approx}{\varphi}^{(2)}(t+T,\tau_1,\tau_2)=\underset{\approx}{\varphi}^{(2)}(t,\tau_1-T,\tau_2-T)$$

setting t = 0 and letting T = t gives

$$\underset{\approx}{\varphi}^{(2)}(t,\tau_1,\tau_2)=\underset{\approx}{\varphi}^{(2)}(0,t-\tau_1,t-\tau_2)$$

and again the notation for explicit time difference dependence can be introduced as

$$\underset{\approx}{\varphi}^{(2)}(t,\tau_1,\tau_2)=\underset{\approx}{R}^{(2)}(t-\tau_1,t-\tau_2) \tag{B16}$$

Substituting eq. (B16) into eq. (B9) gives

$$\underset{\sim}{P}^{(2)}(t)=\int_{-\infty}^{\infty}d\tau_1\int_{-\infty}^{\infty}d\tau_2\,\underset{\approx}{R}^{(2)}(t-\tau_1,t-\tau_2)\vert\underset{\sim}{E}(\tau_1)\underset{\sim}{E}(\tau_2) \tag{B17}$$

The function $\underset{\approx}{R}^{(2)}(t-\tau_1,\ t-\tau_2)$ is the quadratic polarization response function which vanishes when $t-\tau_1$, or $t-\tau_2$ is negative. $\underset{\approx}{R}^{(2)}$ is real and is invariant under the interchange of $\alpha\tau_1$ and $\beta\tau_2$.

Extending this to the rth order in $\underset{\sim}{P}^{(r)}(t)$ gives

$$\underset{\sim}{P}^{(r)}(t)=\int_{-\infty}^{\infty}d\tau_1\cdots\int_{-\infty}^{\infty}d\tau_r\,\underset{\approx}{R}^{(r)}(\tau_1,\cdots,\tau_r)\,|\,\underset{\sim}{E}(t-\tau_1)\cdots\underset{\sim}{E}(t-\tau_r) \tag{B18}$$

or in component form

$$P_{\mu}^{(r)}(t)=\int_{-\infty}^{\infty}d\tau_1\cdots\int_{-\infty}^{\infty}d\tau_r\,R_{\mu\alpha_1\cdots\alpha_r}^{(r)}(\tau_1,\cdots,\tau_r)E_{\alpha_1}(t-\tau_1)\cdots E_{\alpha_r}(t-\tau_r) \tag{B19}$$

where $\underset{\approx}{R}^{(r)}$ is a tensor of rank r + 1 and is real. It vanishes when any of the τ's are negative and it is invariant under of the r! permutations of the pairs $\alpha_1\tau_1,\cdots,\alpha_r\tau_r$ Substituting the Fourier transform

$$\underset{\sim}{E}(t)=\int_{-\infty}^{\infty}\underset{\sim}{E}(\omega)\,e^{-i\omega t}\,d\omega \tag{B20}$$

into eq. (B19) gives

$$\underset{\sim}{P}^{(r)}(t)=\int_{-\infty}^{\infty}d\omega_1\cdots\int_{-\infty}^{\infty}d\omega_r\,\underset{\approx}{\chi}^{(r)}(\omega_1,\cdots,\omega_r)\,|\,\underset{\sim}{E}(\omega_1)\cdots\underset{\sim}{E}(\omega_r)\,e^{-it\sum_{m=1}^{r}\omega_m} \tag{B21}$$

where

$$\underset{\approx}{\chi}^{(r)}(\omega_1,\cdots,\omega_r)=\int_{-\infty}^{\infty}d\tau_1\cdots\int_{-\infty}^{\infty}d\tau_r\,\underset{\approx}{R}^{(r)}(\tau_1,\cdots,\tau_r)\,e^{i\sum_{m=1}^{r}\omega_m\tau_m} \tag{B22}$$

As in Appendix A, reality implies that

$$\left[\underset{\approx}{\chi}^{(r)}(\omega_1,\cdots,\omega_r)\right]^{*}=\underset{\approx}{\chi}^{(r)}(-\omega_1^{*},\cdots,-\omega_r^{*}) \tag{B23}$$

and in component notation

is invariant under all r! permutations of the pairs $\alpha_1\omega_1,\cdots,\alpha_r\omega_r$.

Taking the inverse transform of eq. (B21) using

$$P(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} P(t)\, e^{i\omega t}\, dt$$

gives

$$\underset{\sim}{P}^{(r)}(\omega) = \int_{-\infty}^{\infty} d\omega_1 \cdots \int_{-\infty}^{\infty} d\omega_r\, \underset{\approx}{\chi}^{(r)}(\omega_1, \cdots, \omega_r) \,|\, \underset{\sim}{E}(\omega_1) \cdots \underset{\sim}{E}(\omega_r)\, \delta\left(-\omega + \sum_{m=1}^{r} \omega_m\right)$$

The argument of the $\underset{\approx}{\chi}^{(r)}$ can be augmented to include the delta function dependence as

$$\underset{\sim}{P}^{(r)}(\omega) = \underset{\approx}{\chi}^{(r)}(\omega = \omega_1 + \omega_2 + \cdots + \omega_r) \,|\, \underset{\sim}{E}(\omega_1) \cdots \underset{\sim}{E}(\omega_r) \qquad \text{(B24)}$$

or

$$\underset{\sim}{P}^{(r)}(\omega) = \underset{\approx}{\chi}^{(r)}(-\omega + \omega_1 + \omega_2 + \cdots + \omega_r) \,|\, \underset{\sim}{E}(\omega_1) \cdots \underset{\sim}{E}(\omega_r) \qquad \text{(B25)}$$

With $r \neq 1$, eqs. (B24) or (B25) are to be used on the right side of eq. (10). Using the symmetry properties of the $\underset{\approx}{\chi}$; namely that $\chi^{(r)}_{\mu\alpha_1\cdots\alpha_r}(\omega_1, \cdots, \omega_r)$ is invariant under all r! permutations of the pairs $\alpha_1\omega_1, \alpha_2\omega_2, \cdots, \alpha_r\omega_r$, equation (B25) becomes

$$P^{(r)}_{\mu}(\omega) = r!\, \chi^{(r)}_{\mu\alpha_1\cdots\alpha_r}(-\omega + \omega_1 + \omega_2 + \cdots + \omega_r)\, E_{\alpha_1}(\omega_1) \cdots E_{\alpha_r}(\omega_r) \qquad \text{(B26)}$$

if all frequencies are different. If some frequencies are equal, then in general

$$P^{(r)}_{\mu}(\omega) = \frac{r!}{n!}\, \chi^{(r)}_{\mu\alpha_1\cdots\alpha_r}(-\omega + \omega_1 + \cdots + \omega_r)\, E_{\alpha_1}(\omega_1) \cdots E_{\alpha_r}(\omega_r) \qquad \text{(B27)}$$

where n is the number of equal frequencies. For example,

$$P^{(2)}(\omega) = 2\chi^{(2)}(-\omega + \omega_1 + \omega_2)\, E(\omega_1) E(\omega_2)$$

while

$$P^{(2)}(\omega) = \chi^{(2)}(-\omega + 2\omega_1)\, E^2(\omega_1)$$

Likewise

$$P^{(3)}(\omega) = 6\chi^{(3)}(-\omega + \omega_1 + \omega_2 + \omega_3)\, E(\omega_1) E(\omega_2) E(\omega_3)$$

while

$$P^{(3)}(\omega) = 3\chi^{(3)}(-\omega + \omega_1 + 2\omega_2)\, E(\omega_1) E^2(\omega_2)$$

and

$$P^{(3)}(\omega) = \chi^{(3)}(-\omega + 3\omega_1)\, E^3(\omega_1)$$

Appendix C

Phenomenological Approach

Raman-type nonlinearities are third-order effects requiring a third-order perturbation treatment. However, a phenomenological approach (22) can be taken using a first-order perturbation theory. An interaction Hamiltonian of the form

$$H_{int} = -\underset{\sim}{d}'\cdot\underset{\sim}{E} \tag{C1}$$

is introduced with an effective dipole moment $\underset{\sim}{d}'$ to obtain the Raman effect. This moment is induced by the applied electric field E so that

$$\underset{\sim}{d}' = \underset{\approx}{\alpha}\,\underset{\sim}{E} \tag{C2}$$

where α is the polarizability of the molecule. The polarizability can be expanded in a Taylor series in terms of the molecular coordinates as

$$\alpha_{\mu\nu} = \alpha^{0}_{\mu\nu} + \sum_{\lambda} \frac{\partial\alpha_{\mu\nu}}{\partial q_{\lambda}} q_{\lambda} \tag{C3}$$

and the derivative evaluated at equilibrium. Then the interaction Hamiltonian becomes

$$H_{int} = -\sum_{\mu} \left\{ \sum_{\nu} \left[\alpha^{0}_{\mu\nu} + \sum_{\lambda} \frac{\partial\alpha_{\mu\nu}}{\partial q_{\lambda}} q_{\lambda} \right] E_{\mu} \right\} E_{\nu} \tag{C4}$$

The first term in $\alpha^{0}_{\mu\nu}$ does not contribute to Raman scattering, but the second term gives Raman scattering in the first order of perturbation theory. The transition probability is then given in terms of

$$\langle \varphi_f | H_{int} | \varphi_i \rangle$$

where φ_i and φ_f are the initial and final states of the system, respectively. These states refer only to the vibrational states of the molecule and the value of $\frac{\partial\alpha_{\mu\nu}}{\partial q_{\lambda}}$ are obtained from experiments.

Appendix D

The Density Matrix and the Perturbation Solution to Its Equation of Motion

Assume a system is described by a state vector $|\psi\rangle$ and can be expanded in a series of eigenvetors $|\varphi_n\rangle$ of some operator as

$$|\psi\rangle = \sum_{n=0}^{\infty} a_n |\varphi_n\rangle \tag{D1}$$

The expectation value of an operator $\hat{Q}$ will then be

$$\langle\psi|\hat{Q}|\psi\rangle = \sum_{n,m=0}^{\infty} a_n^* a_m \langle\varphi_n|\hat{Q}|\varphi_m\rangle \tag{D2}$$

Assume that the precise values for the a's are not known but only certain average values. Then the average value of the expectation value will be

$$\bar{Q} = \overline{\langle\psi|\hat{Q}|\psi\rangle} = \sum_{nm} \overline{a_n^* a_m} \langle\varphi_n|\hat{Q}|\varphi_m\rangle \tag{D3}$$

where the bar denotes an average. With

$$Q_{nm} \equiv \langle\varphi_n|\hat{Q}|\varphi_m\rangle \tag{D4}$$

$$\rho_{mn} \equiv \overline{a_n^* a_m} \tag{D5}$$

eg. (D3) becomes

$$\bar{Q} = \sum_{n,m=0}^{\infty} \rho_{mn} Q_{nm} \tag{D6}$$

Noting that the form

$$\sum_n \rho_{\mu n} Q_{n\nu}$$

if just the $\mu\nu$ element of the matrix product $\underset{\sim}{\rho}\underset{\sim}{Q}$, the form

$$\sum_n \rho_{mn} Q_{nm}$$

is the mm element of the main diagonal of the matrix product $\underset{\sim}{\rho}\underset{\sim}{Q}$. Therefore, the form

$$\sum_{n,m=0}^{\infty} \rho_{mn} Q_{nm}$$

is, by definition, the trace of the matrix product $\underset{\approx}{\rho}\underset{\approx}{Q}$ and the average value of the expectation value of $\hat{Q}$ is

$$\bar{Q} = \mathrm{Tr}\,(\underset{\approx}{\rho}\underset{\approx}{Q}) \tag{D7}$$

Since

$$|\psi\rangle = \sum_n a_n |\varphi_n\rangle$$

multiplication by $\langle\varphi_m|$ gives

$$\langle\varphi_m|\psi\rangle = \sum_n a_n \langle\varphi_m|\varphi_n\rangle = \sum_n a_n \delta_{mn}$$

or

$$a_m = \langle\varphi_m|\psi\rangle$$

This allows the density matrix ρ_{mn} to be written as

$$\rho_{mn} = \overline{a_n^* a_m} = \overline{\langle\psi|\varphi_n\rangle\langle\varphi_m|\psi\rangle} \tag{D8}$$

which gives for $\bar{Q}$ from eq. (D6)

$$\bar{Q} = \sum_{mn} \overline{\langle\psi|\varphi_n\rangle\langle\varphi_n|\hat{Q}|\varphi_m\rangle\langle\varphi_m|\psi\rangle}$$

or

$$\bar{Q} = \overline{\langle\psi|\hat{Q}|\psi\rangle} \tag{D9}$$

showing that eq. (D3) is independent of the choice of the set of eigenvectors $|\varphi_n\rangle$. Assign a probability w_ν to the occurrence of a certain state $|\psi_\nu\rangle$, which is the same as for the occurrence of the set of coefficients $a_n^{(\nu)}$. Then from eq. (D8)

$$\rho_{mn} = \sum_\nu a_n^{(\nu)*} a_m^{(\nu)} w_\nu = \langle\varphi_m| \sum_\nu |\psi_\nu\rangle w_\nu \langle\psi_\nu|\varphi_n\rangle$$

which defines the density operator $\hat{\rho}$ as (19)

$$\hat{\rho} = \sum_\nu |\psi_\nu\rangle w_\nu \langle\psi_\nu| \tag{10}$$

Taking the time derivative of eq. (D10) and using the Schroedinger equation $i\hbar\partial_t|\psi\rangle = H|\psi\rangle$ gives the equation of motion of the density operator

$$i\hbar\partial_t \hat{\rho} = -[\hat{\rho}, H] \tag{D11}$$

or in matrix form

$$i\hbar\partial_t \rho_{nm} = \sum_\nu H_{n\nu}\rho_{\nu m} - \sum_\nu \rho_{n\nu} H_{\nu m} \tag{D12}$$

A perturbation solution to the equation of motion of the density matrix (23) will now be developed. This solution will then be used to find the average value of the dipole moment $\underset{\sim}{d} = -e\underset{\sim}{r}$ which in turn allows an explicit expression to be obtained for the susceptibility tensor.

Let the Hamiltonian H be expressed as

$$H = H_0 - \underset{\sim}{d}\cdot\underset{\sim}{E} \tag{D13}$$

where H_0 is the unperturbed part describing the system when the field E is off. Using an energy representation such that

$$H|W_m\rangle = (H_0 - \underset{\sim}{d}\cdot\underset{\sim}{E})|W_m\rangle = W_m|W_m\rangle - \underset{\sim}{d}\cdot\underset{\sim}{E}|W_m\rangle$$

where W_m is the eigenvalue of the state W_m , gives for eq. (D12)

$$i\hbar\partial_t \rho_{nm} = \sum_\nu \left\{ W_n\langle W_n|W_\nu\rangle\rho_{\nu m} - \langle W_n|\underset{\sim}{d}\cdot\underset{\sim}{E}|W_\nu\rangle\rho_{\nu m} \right\}$$
$$- \sum_\nu \left\{ \rho_{n\nu} W_m \langle W_\nu|W_m\rangle - \rho_{n\nu}\langle W_\nu|\underset{\sim}{d}\cdot\underset{\sim}{E}|W_m\rangle \right\}$$

which, by orthognality, becomes

$$\partial_t \rho_{nm} = \frac{W_n - W_m}{i\hbar}\rho_{nm} + \frac{1}{i\hbar}\sum_\nu \left\{ \rho_{n\nu}(\underset{\sim}{d}\cdot\underset{\sim}{E})_{\nu m} - (\underset{\sim}{d}\cdot\underset{\sim}{E})_{n\nu}\rho_{\nu m} \right\} \tag{D14}$$

where $(\underset{\sim}{d}\cdot\underset{\sim}{E})_{\alpha\beta} \equiv \langle\alpha|\underset{\sim}{d}\cdot\underset{\sim}{E}|\beta\rangle$. Letting $\frac{W_n - W_m}{\hbar} = \omega_{nm}$, eq. (D14)

becomes

$$\partial_t \rho_{nm} = -i\omega_{nm}\rho_{nm} + \frac{1}{i\hbar}\sum_\nu (\rho_{n\nu}\underset{\sim}{d}_{\nu m} - \underset{\sim}{d}_{n\nu}\rho_{\nu m})\cdot\underset{\sim}{E} \tag{D15}$$

Now changing to the interaction picture through

$$\rho_{nm}^{(I)} \equiv \sigma_{nm} = \langle W_n| e^{iH_0 t/\hbar}\hat{\rho}\, e^{-iH_0 t/\hbar}|W_m\rangle = e^{i\omega_{nm}t}\rho_{nm}$$

gives

$$\rho_{nm} = e^{-i\omega_{nm}t}\sigma_{nm} \tag{D16}$$

Thus eq. (D15) becomes

$$\partial_t \sigma_{nm} = \frac{1}{i\hbar}\sum_\nu (\sigma_{n\nu}\underset{\sim}{d}_{\nu m} e^{i\omega_{\nu m}t} - \underset{\sim}{d}_{n\nu}\sigma_{\nu m} e^{i\omega_{n\nu}t})\cdot\underset{\sim}{E} \tag{D17}$$

where $\omega_{nm}-\omega_{n\nu}=\omega_{\nu m}$ was used. Equation (D17) is now the equation of motion of the density matrix in the interaction picture. Using the initial conditions

$$\sigma^{(0)}_{nm} = \sigma^{(0)}_{nn}\,\delta_{nm} \tag{D18}$$

in eq. (D17) give a first order term

$$\sigma^{(1)}_{nm} = \frac{1}{i\hbar}(\sigma^{0}_{nn}-\sigma^{0}_{mm})\,\underset{\sim}{d}_{nm}\cdot\int_{-\infty}^{\infty}\underset{\sim}{E}\,e^{i\omega_{nm}t_1}dt_1 \tag{D19}$$

Substituting this back into eq. (D17) gives the second order term

$$\sigma^{(2)}_{nm} = \frac{1}{(i\hbar)^2}\sum_{\nu}\int_0^t\Big\{\underset{\sim}{E}\cdot\underset{\sim}{d}_{\nu m}(\sigma^{0}_{nn}-\sigma^{0}_{\nu\nu})e^{i\omega_{\nu m}t_2}\int_0^{t_2}\underset{\sim}{E}\cdot\underset{\sim}{d}_{n\nu}\,e^{i\omega_{n\nu}t_1}dt_1$$

$$-\,\underset{\sim}{E}\cdot\underset{\sim}{d}_{n\nu}(\sigma^{0}_{\nu\nu}-\sigma^{0}_{mm})e^{i\omega_{n\nu}t_2}\int_0^{t}\underset{\sim}{E}\cdot\underset{\sim}{d}_{\nu m}\,e^{i\omega_{\nu m}t_1}dt_1\Big\}dt_2 \tag{D20}$$

Substituting this back into eq. (D17) gives the third order term

$$\sigma^{(3)}_{nm} = \frac{1}{(i\hbar)^3}\sum_{\mu}\int_0^t\underset{\sim}{d}_{\mu m}\cdot\underset{\sim}{E}\,e^{i\omega_{\mu m}t_3}\sum_{\nu}\int_0^t\Big\{\underset{\sim}{E}\cdot\underset{\sim}{d}_{\nu\mu}(\sigma^{0}_{nn}-\sigma^{0}_{\nu\nu})e^{i\omega_{\nu\mu}t_2}$$

$$\cdot\int_0^{t_2}\underset{\sim}{E}\cdot\underset{\sim}{d}_{n\nu}\,e^{i\omega_{n\nu}t_1}dt_1-\underset{\sim}{E}\cdot\underset{\sim}{d}_{n\nu}(\sigma^{0}_{\nu\nu}-\sigma^{0}_{\mu\mu})e^{i\omega_{n\nu}t_2}$$

$$\cdot\int_0^{t_2}\underset{\sim}{E}\cdot\underset{\sim}{d}_{\nu\mu}\,e^{i\omega_{\nu\mu}t_1}dt_1\Big\}dt_2-\underset{\sim}{E}\cdot\underset{\sim}{d}_{n\mu}\,e^{i\omega_{n\mu}t_3}\sum_{\nu}\int_0^{t_3}\Big\{\underset{\sim}{E}\cdot\underset{\sim}{d}_{\nu m} \tag{D21}$$

$$\cdot(\sigma^{0}_{\mu\mu}-\sigma^{0}_{\nu\nu})e^{i\omega_{\nu m}t_2}\int_0^{t_2}\underset{\sim}{E}\cdot\underset{\sim}{d}_{\mu\nu}\,e^{i\omega_{\mu\nu}t_1}dt_1-\underset{\sim}{E}\cdot\underset{\sim}{d}_{\mu\nu}(\sigma^{0}_{\nu\nu}-\sigma^{0}_{mm})$$

$$\cdot\,e^{i\omega_{\mu\nu}t_2}\int_0^{t_2}\underset{\sim}{E}\cdot\underset{\sim}{d}_{\nu m}\,e^{i\omega_{\nu m}t_1}dt_1\Big\}dt_2\Big\}dt_3$$

and so forth. Thus the general solution is

$$\sigma_{nm} = \sigma_{nm}^{(0)} + \sigma_{nm}^{(1)} + \sigma_{nm}^{(2)} + \sigma_{nm}^{(3)} + \cdots \qquad \text{(D22)}$$

Appendix E

The Susceptibility Tensor at the Anti-Stokes Frequency $\omega_{as}=2\omega_\ell-\omega_s$

Let the applied field E be composed of two fields E_ℓ and E_s. Then it is necessary to consider products of the form

$$E_\ell E_\ell E_s\ ,\ E_\ell E_s E_\ell\ ,\ E_s E_\ell E_\ell$$

in eq. (D21). Letting

$$E_\ell = \frac{\hat{e}_\ell}{2}\left(E_\ell^0\, e^{i(k_\ell\cdot r-\omega_\ell t)}+c.c.\right)$$

$$E_s = \frac{\hat{e}_s}{2}\left(E_s^0\, e^{i(k_s\cdot r-\omega_s t)}+c.c.\right)$$

where $\hat{e}_\ell$ and $\hat{e}_s$ are unit vectors in the field directions, the integrals of the first term of $\sigma_{nm}^{(3)}$ with the form $E_\ell E_\ell E_s$ are

$$\frac{1}{2^3}\int_0^t\int_0^{t_3}\int_0^{t_2} dt_1 dt_2 dt_3 \left\{e^{i(\omega_{\mu m}-\omega_\ell)t_3}e^{ik_\ell\cdot r}+e^{i(\omega_{\mu m}+\omega_\ell)t_3}e^{-ik_\ell\cdot r}\right\}$$

$$\cdot\left\{e^{i(\omega_{\nu\mu}-\omega_\ell)t_2}e^{ik_\ell\cdot r}+e^{i(\omega_{\nu\mu}+\omega_\ell)t_2}e^{-ik_\ell\cdot r}\right\}$$

$$\cdot\left\{e^{i(\omega_{n\nu}-\omega_s)t_1}e^{ik_s\cdot r}+e^{i(\omega_{n\nu}+\omega_s}\quad e^{-ik_s\cdot r}\right\}$$

Considering only terms like $e^{\pm i(k_{as}\cdot r-\omega_{as}t)}$, where

$$k_{as}=2k_\ell-k_s$$

$$\omega_{as}=2\omega_\ell-\omega_s$$

gives

$$\frac{1}{2^3}\int_0^t\int_0^{t_3}\int_0^{t_2} dt_1 dt_2 dt_3 \left\{e^{ik_{as}\cdot r}e^{i(\omega_{\mu m}-\omega_\ell)t_3+i(\omega_{\nu\mu}-\omega_\ell)t_2+i(\omega_{n\nu}+\omega_s)t_1}\right.$$

$$\left.+e^{-ik_{as}\cdot r}e^{i(\omega_{\mu m}+\omega_\ell)t_3+i(\omega_{\nu\mu}+\omega_\ell)t_2+i(\omega_{n\nu}-\omega_s)t_1}\right\}$$

Doing the integrals, the first term of $\sigma_{nm}^{(3)}$ with form $E_\ell E_\ell E_s$ is

$$(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{\eta\mu}(\hat{e}_s\cdot\underline{d})_{n\nu}(\sigma^0_{nn}-\sigma^0_{\nu\nu})\frac{1}{(2i)^3}E_\ell^{0^2}E_s^{0*}e^{i\omega_{nm}t}$$

$$\cdot\left\{e^{i(k_{as}\cdot r-\omega_{as}t)}\left(\frac{1}{(\omega_{n\nu}+\omega_s)(\omega_{\eta\mu}-\omega_\ell+\omega_s)(\omega_{nm}-2\omega_\ell+\omega_s)}\right)\right.$$

$$\left.+\,e^{-i(k_{as}\cdot r-\omega_{as}t)}\left(\frac{1}{(\omega_{n\nu}-\omega_s)(\omega_{\eta\mu}+\omega_\ell-\omega_s)(\omega_{nm}+2\omega_\ell-\omega_s)}\right)\right\}$$

The integrals of the first term of $\sigma^{(3)}_{nm}$ with form $E_\ell E_s E_\ell$ give

$$(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_s\cdot\underline{d})_{\eta\mu}(\hat{e}_\ell\cdot\underline{d})_{n\nu}(\sigma^0_{nn}-\sigma^0_{\nu\nu})\frac{1}{(2i)^3}E_\ell^{0^2}E_s^{*}e^{i\omega_{nm}t}$$

$$\cdot\left\{e^{i(k_{as}\cdot r-\omega_{as}t)}\left(\frac{1}{(\omega_{n\nu}-\omega_\ell)(\omega_{\eta\mu}-\omega_\ell+\omega_s)(\omega_{nm}-2\omega_\ell+\omega_s)}\right)\right.$$

$$\left.+\,e^{-i(k_{as}\cdot r-\omega_{as}t)}\left(\frac{1}{(\omega_{n\nu}+\omega_\ell)(\omega_{\eta\mu}+\omega_\ell-\omega_s)(\omega_{nm}+2\omega_\ell-\omega_s)}\right)\right\}$$

The integrals of the first term of $\sigma^{(3)}_{nm}$ with form $E_s E_\ell E_\ell$ give

$$(\hat{e}_s\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{\eta\mu}(\hat{e}_\ell\cdot\underline{d})_{n\nu}(\sigma^0_{nn}-\sigma^0_{\nu\nu})\frac{1}{(2i)^3}E_\ell^{0^2}E_s^{0*}e^{i\omega_{nm}t}$$

$$\cdot\left\{e^{i(k_{as}\cdot r-\omega_{as}t)}\left(\frac{1}{(\omega_{n\nu}-\omega_\ell)(\omega_{\eta\mu}-2\omega_\ell)(\omega_{nm}-2\omega_\ell+\omega_s)}\right)\right.$$

$$\left.+\,e^{-i(k_{as}\cdot r-\omega_{as}t)}\left(\frac{1}{(\omega_{n\nu}+\omega_\ell)(\omega_{\eta\mu}+2\omega_\ell)(\omega_{nm}+2\omega_\ell-\omega_s)}\right)\right\}$$

Thus the total contribution from the first term is

$$\frac{1}{(2i)^3}\frac{1}{(i\hbar)^3}\sum_{\mu\nu} E_\ell^{0\,2} E_s^{0\,*} e^{i\omega_{nm}t}\Big\{ e^{i(k_{as}\cdot r-\omega_{as}t)}(\sigma^0_{nn}-\sigma^0_{\nu\nu})$$

$$\cdot\left[\frac{(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{\nu\mu}(\hat{e}_s\cdot\underline{d})_{n\nu}}{(\omega_{n\nu}+\omega_s)(\omega_{n\mu}-\omega_\ell+\omega_s)(\omega_{nm}-2\omega_\ell+\omega_s)}+\frac{(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_s\cdot\underline{d})_{\nu\mu}(\hat{e}_\ell\cdot\underline{d})_{n\nu}}{(\omega_{n\nu}-\omega_\ell)(\omega_{n\mu}-\omega_\ell+\omega_s)(\omega_{nm}-2\omega_\ell+\omega_s)}\right.$$

$$\left.+\frac{(\hat{e}_s\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{\nu\mu}(\hat{e}_\ell\cdot\underline{d})_{n\nu}}{(\omega_{n\nu}-\omega_\ell)(\omega_{n\mu}-2\omega_\ell)(\omega_{nm}-2\omega_\ell+\omega_s)}\right]+e^{-i(k_{as}\cdot r-\omega_{as}t)}(\sigma^0_{nn}-\sigma^0_{\nu\nu})$$

$$\cdot\left[\frac{(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{\nu\mu}(\hat{e}_s\cdot\underline{d})_{n\nu}}{(\omega_{n\nu}-\omega_s)(\omega_{n\mu}+\omega_\ell-\omega_s)(\omega_{nm}+2\omega_\ell-\omega_s)}+\frac{(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_s\cdot\underline{d})_{\nu\mu}(\hat{e}_\ell\cdot\underline{d})_{n\nu}}{(\omega_{n\nu}+\omega_s)(\omega_{n\mu}+\omega_\ell-\omega_s)(\omega_{nm}+2\omega_\ell-\omega_s)}\right.$$

$$\left.+\frac{(\hat{e}_s\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{\nu\mu}(\hat{e}_\ell\cdot\underline{d})_{n\nu}}{(\omega_{n\nu}+\omega_\ell)(\omega_{n\mu}+2\omega_\ell)(\omega_{nm}+2\omega_\ell-\omega_s)}\right]\Big\}$$

Integrals of the second term of $\sigma^{(3)}_{nm}$ of the form $E_\ell E_\ell E_s$, $E_\ell E_s E_\ell$ and $E_s E_\ell E_\ell$ give to total contribution

$$\left(\frac{1}{2i}\right)^3\left(\frac{1}{i\hbar}\right)^3\sum_{\mu\nu} E_\ell^{0\,2}E_s^{0*}e^{i\omega_{nm}t}(\sigma^0_{\nu\nu}-\sigma^0_{\mu\mu})\left\{e^{i(k_{as}\cdot r-\omega_{as}t)}\left[\frac{(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{n\nu}(\hat{e}_s\cdot\underline{d})_{\nu\mu}}{(\omega_{\nu\mu}+\omega_s)(\omega_{n\mu}-\omega_\ell+\omega_s)(\omega_{nm}-2\omega_\ell+\omega_s)}\right.\right.$$

$$+\frac{(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_s\cdot\underline{d})_{n\nu}(\hat{e}_\ell\cdot\underline{d})_{\nu\mu}}{(\omega_{\nu\mu}-\omega_\ell)(\omega_{n\mu}-\omega_\ell+\omega_s)(\omega_{nm}-2\omega_\ell+\omega_s)}+\left.\frac{(\hat{e}_s\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{n\nu}(\hat{e}_\ell\cdot\underline{d})_{\nu\mu}}{(\omega_{\nu\mu}-\omega_\ell)(\omega_{n\mu}-2\omega_\ell)(\omega_{nm}-2\omega_\ell+\omega_s)}\right]$$

$$+e^{-i(k_{as}\cdot r-\omega_{as}t)}\left[\frac{(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{n\nu}(\hat{e}_s\cdot\underline{d})_{\nu\mu}}{(\omega_{\nu\mu}-\omega_s)(\omega_{n\mu}+\omega_\ell-\omega_s)(\omega_{nm}+2\omega_\ell-\omega_s)}\right.$$

$$\left.\left.+\frac{(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_s\cdot\underline{d})_{n\nu}(\hat{e}_\ell\cdot\underline{d})_{\nu\mu}}{(\omega_{\nu\mu}+\omega_\ell)(\omega_{n\mu}+\omega_\ell-\omega_s)(\omega_{nm}+2\omega_\ell-\omega_s)}+\frac{(\hat{e}_s\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{n\nu}(\hat{e}_\ell\cdot\underline{d})_{\nu\mu}}{(\omega_{\nu\mu}+\omega_\ell)(\omega_{n\mu}+2\omega_\ell)(\omega_{nm}+2\omega_\ell-\omega_s)}\right]\right\}$$

Integrals in the third term of $\sigma_{nm}^{(3)}$ of the form $E_\ell E_\ell E_s$, $E_\ell E_s E_\ell$ and $E_s E_\ell E_\ell$ give the total contribution of

$$\frac{1}{(2i)^3}\frac{1}{(i\hbar)^3}\sum_{\mu\nu} E_\ell^{0\,2}E_s^{0*}e^{i\omega_{nm}t}(\sigma^0_{\mu\mu}-\sigma^0_{\nu\nu})\left\{e^{i(k_{as}\cdot r-\omega_{as}t)}\left[\frac{(\hat{e}_\ell\cdot\underline{d})_{n\mu}(\hat{e}_\ell\cdot\underline{d})_{\nu m}(\hat{e}_s\cdot\underline{d})_{\mu\nu}}{(\omega_{\mu\nu}+\omega_s)(\omega_{\mu m}-\omega_\ell+\omega_s)(\omega_{nm}-2\omega_\ell+\omega_s)}\right.\right.$$

$$+\frac{(\hat{e}_\ell\cdot\underline{d})_{n\mu}(\hat{e}_s\cdot\underline{d})_{\nu m}(\hat{e}_\ell\cdot\underline{d})_{\mu\nu}}{(\omega_{\mu\nu}-\omega_\ell)(\omega_{\mu m}-\omega_\ell+\omega_s)(\omega_{nm}-2\omega_\ell+\omega_s)}+\left.\frac{(\hat{e}_s\cdot\underline{d})_{n\mu}(\hat{e}_\ell\cdot\underline{d})_{\nu m}(\hat{e}_\ell\cdot\underline{d})_{\mu\nu}}{(\omega_{\mu\nu}-\omega_\ell)(\omega_{\mu m}-2\omega_\ell)(\omega_{nm}-2\omega_\ell+\omega_s)}\right]$$

$$+e^{-i(k_{as}\cdot r-\omega_{as}t)}\left[\frac{(\hat{e}_\ell\cdot\underline{d})_{n\mu}(\hat{e}_\ell\cdot\underline{d})_{\nu m}(\hat{e}_s\cdot\underline{d})_{\mu\nu}}{(\omega_{\mu\nu}-\omega_s)(\omega_{\mu m}+\omega_\ell-\omega_s)(\omega_{nm}+2\omega_\ell-\omega_s)}\right.$$

$$+\frac{(\hat{e}_\ell\cdot d)_{n\mu}(\hat{e}_s\cdot d)_{\nu m}(\hat{e}_\ell\cdot d)_{\mu\nu}}{(\omega_{\mu\nu}+\omega_\ell)(\omega_{\mu m}+\omega_\ell-\omega_s)(\omega_{nm}+2\omega_\ell-\omega_s)}+\frac{(\hat{e}_s\cdot d)_{n\mu}(\hat{e}_\ell\cdot d)_{\nu m}(\hat{e}_\ell\cdot d)_{\mu\nu}}{(\omega_{\mu\nu}+\omega_\ell)(\omega_{\mu m}+2\omega_\ell)(\omega_{nm}+2\omega_\ell-\omega_s)}\Bigg]\Bigg\}$$

Integrals of the fourth term in $\sigma_{nm}^{(3)}$ of the form $E_\ell E_\ell E_s$, $E_\ell E_s E_\ell$ and $E_s E_\ell E_\ell$ give a total contribution of

$$\left(\frac{1}{2i}\right)^3\left(\frac{1}{i\hbar}\right)^3\sum_{\mu\nu}E_\ell^{0\,2}E_s^{0\,*}e^{i\omega_{nm}t}(\sigma^0_{\nu\nu}-\sigma^0_{mm})$$

$$\cdot\Bigg\{e^{i(k_{as}\cdot r-\omega_{as}t)}\Bigg[\frac{(\hat{e}_\ell\cdot d)_{n\mu}(\hat{e}_\ell\cdot d)_{\mu\nu}(\hat{e}_s\cdot d)_{\nu m}}{(\omega_{\nu m}+\omega_s)(\omega_{\mu m}-\omega_\ell+\omega_s)(\omega_{nm}-2\omega_\ell+\omega_s)}$$

$$+\frac{(\hat{e}_\ell\cdot d)_{n\mu}(\hat{e}_s\cdot d)_{\mu\nu}(\hat{e}_\ell\cdot d)_{\nu m}}{(\omega_{\nu m}-\omega_\ell)(\omega_{\mu m}+\omega_s-\omega_\ell)(\omega_{nm}-2\omega_\ell+\omega_s)}+\frac{(\hat{e}_s\cdot d)_{n\mu}(\hat{e}_\ell\cdot d)_{\mu\nu}(\hat{e}_\ell\cdot d)_{\nu m}}{(\omega_{\nu m}-\omega_\ell)(\omega_{\mu m}-2\omega_\ell)(\omega_{nm}-2\omega_\ell+\omega_s)}\Bigg]$$

$$+e^{-i(k_{as}\cdot r-\omega_{as}t)}\Bigg[\frac{(\hat{e}_\ell\cdot d)_{n\mu}(\hat{e}_\ell\cdot d)_{\mu\nu}(\hat{e}_s\cdot d)_{\nu m}}{(\omega_{\nu m}-\omega_s)(\omega_{\mu m}+\omega_\ell-\omega_s)(\omega_{nm}+2\omega_\ell-\omega_s)}$$

$$+\frac{(\hat{e}_\ell\cdot\underline{d})_{n\mu}(\hat{e}_s\cdot\underline{d})_{\mu\nu}(\hat{e}_\ell\cdot\underline{d})_{\nu m}}{(\omega_{\mu m}+\omega_\ell)(\omega_{\mu m}-\omega_s+\omega_\ell)(\omega_{nm}+2\omega_\ell-\omega_s)}+\frac{(\hat{e}_s\cdot\underline{d})_{n\mu}(\hat{e}_\ell\cdot\underline{d})_{\mu\nu}(\hat{e}_\ell\cdot\underline{d})_{\nu m}}{(\omega_{\nu m}+\omega_\ell)(\omega_{\mu m}+2\omega_\ell)(\omega_{nm}+2\omega_\ell-\omega_s)}\Bigg]\Bigg\}$$

Introducing the notation

$$2\omega_\ell-\omega_s=\omega_{as}$$
$$\omega_\ell-\omega_s=\Delta$$

and transforming back to Schroedinger picture through

$$\rho_{nm}=\sigma_{nm}e^{-i\omega_{nm}t}$$

the total result for the third order density matrix is

$$\rho^{(3)}_{nm}=\frac{1}{(2i)^3}\frac{1}{(i\hbar)^3}\sum_{\mu\nu}E_\ell^{0\,2}E_s^{0*}\left\{\frac{e^{i(k_{as}\cdot r-\omega_{as}t)}}{\omega_{nm}-\omega_{as}}\right.\left\{(\rho^0_{nn}-\rho^0_{\nu\nu})\left(\frac{(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{\nu\mu}(\hat{e}_s\cdot\underline{d})_{n\nu}}{(\omega_{n\nu}+\omega_s)(\omega_{n\mu}-\Delta)}\right.\right.$$

$$+\frac{(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_s\cdot\underline{d})_{\nu\mu}(\hat{e}_\ell\cdot\underline{d})_{n\nu}}{(\omega_{n\nu}-\omega_\ell)(\omega_{n\mu}-\Delta)}+\left.\frac{(\hat{e}_s\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{\nu\mu}(\hat{e}_\ell\cdot\underline{d})_{n\nu}}{(\omega_{n\nu}-\omega_\ell)(\omega_{n\mu}-2\omega_\ell)}\right)$$

$$-(\rho^0_{\nu\nu}-\rho^0_{\mu\mu})\left(\frac{(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{n\nu}(\hat{e}_s\cdot\underline{d})_{\nu\mu}}{(\omega_{\nu\mu}+\omega_s)(\omega_{n\mu}-\Delta)}+\frac{(\hat{e}_\ell\cdot\underline{d})_{\mu m}(\hat{e}_s\cdot\underline{d})_{n\nu}(\hat{e}_\ell\cdot\underline{d})_{\nu\mu}}{(\omega_{\nu\mu}-\omega_\ell)(\omega_{n\mu}-\Delta)}\right.$$

$$\left.+\frac{(\hat{e}_s\cdot\underline{d})_{\mu m}(\hat{e}_\ell\cdot\underline{d})_{n\nu}(\hat{e}_\ell\cdot\underline{d})_{\nu\mu}}{(\omega_{\nu\mu}-\omega_\ell)(\omega_{n\mu}-2\omega_\ell)}\right)-(\rho^0_{\mu\mu}-\rho^0_{\nu\nu})\left(\frac{(\hat{e}_\ell\cdot\underline{d})_{n\mu}(\hat{e}_\ell\cdot\underline{d})_{\nu m}(\hat{e}_s\cdot\underline{d})_{\mu\nu}}{(\omega_{\mu\nu}+\omega_s)(\omega_{\mu m}-\Delta)}\right.$$

$$+\frac{(\hat{e}_\ell\cdot\underline{d})_{n\mu}(\hat{e}_s\cdot\underline{d})_{\nu m}(\hat{e}_\ell\cdot\underline{d})_{\mu\nu}}{(\omega_{\mu\nu}-\omega_\ell)(\omega_{\mu m}-\Delta)}+\left.\frac{(\hat{e}_s\cdot\underline{d})_{n\mu}(\hat{e}_\ell\cdot\underline{d})_{\nu m}(\hat{e}_\ell\cdot\underline{d})_{\mu\nu}}{(\omega_{\mu\nu}-\omega_\ell)(\omega_{\mu m}-2\omega_\ell)}\right)$$

$$+\left(\rho^{0}_{\nu\nu}-\rho^{0}_{mm}\right)\Bigg(\frac{(\hat{e}_l\cdot\underline{d})_{n\mu}(\hat{e}_l\cdot\underline{d})_{\mu\nu}(\hat{e}_s\cdot\underline{d})_{\mu m}}{(\omega_{\nu m}+\omega_s)(\omega_{\mu m}-\Delta)}+\frac{(\hat{e}_l\cdot\underline{d})_{n\mu}(\hat{e}_s\cdot\underline{d})_{\mu\nu}(\hat{e}_l\cdot\underline{d})_{\nu m}}{(\omega_{\nu m}-\omega_l)(\omega_{\mu m}-\Delta)}$$

$$+\frac{(\hat{e}_s\cdot\underline{d})_{n\mu}(\hat{e}_l\cdot\underline{d})_{\mu\nu}(\hat{e}_l\cdot\underline{d})_{\nu m}}{(\omega_{\nu m}-\omega_l)(\omega_{\mu m}-2\omega_l)}\Bigg)\Bigg\}+\frac{e^{-i(k_{as}\cdot r-\omega_{as}t)}}{\omega_{nm}+\omega_{as}}\Bigg\{\left(\rho^{0}_{nn}-\rho^{0}_{\nu\nu}\right)$$

$$\cdot\Bigg(\frac{(\hat{e}_l\cdot\underline{d})_{\mu m}(\hat{e}_l\cdot\underline{d})_{\nu\mu}(\hat{e}_s\cdot\underline{d})_{n\nu}}{(\omega_{n\nu}-\omega_s)(\omega_{n\mu}+\Delta)}+\frac{(\hat{e}_l\cdot\underline{d})_{\mu m}(\hat{e}_s\cdot\underline{d})_{\nu\mu}(\hat{e}_l\cdot\underline{d})_{n\nu}}{(\omega_{n\nu}+\omega_l)(\omega_{n\mu}+\Delta)}$$

$$+\frac{(\hat{e}_s\cdot\underline{d})_{\mu m}(\hat{e}_l\cdot\underline{d})_{\nu\mu}(\hat{e}_l\cdot\underline{d})_{n\nu}}{(\omega_{n\nu}+\omega_l)(\omega_{n\mu}+2\omega_l)}\Bigg)-\left(\rho^{0}_{\nu\nu}-\rho^{0}_{\mu\mu}\right)\Bigg(\frac{(\hat{e}_l\cdot\underline{d})_{\mu m}(\hat{e}_l\cdot\underline{d})_{n\nu}(\hat{e}_s\cdot\underline{d})_{\nu\mu}}{(\omega_{\nu\mu}-\omega_s)(\omega_{n\mu}+\Delta)}$$

$$+\frac{(\hat{e}_l\cdot\underline{d})_{\mu m}(\hat{e}_s\cdot\underline{d})_{n\nu}(\hat{e}_l\cdot\underline{d})_{\nu\mu}}{(\omega_{\nu\mu}+\omega_l)(\omega_{n\mu}+\Delta)}+\frac{(\hat{e}_s\cdot\underline{d})_{\mu m}(\hat{e}_l\cdot\underline{d})_{n\nu}(\hat{e}_l\cdot\underline{d})_{\nu\mu}}{(\omega_{\nu\mu}+\omega_l)(\omega_{n\mu}+2\omega_l)}\Bigg)$$

$$-\left(\rho^{0}_{\mu\mu}-\rho^{0}_{\nu\nu}\right)\Bigg(\frac{(\hat{e}_l\cdot\underline{d})_{n\mu}(\hat{e}_l\cdot\underline{d})_{\nu m}(\hat{e}_s\cdot\underline{d})_{\mu\nu}}{(\omega_{\mu\nu}-\omega_s)(\omega_{\mu m}+\Delta)}+\frac{(\hat{e}_l\cdot\underline{d})_{n\mu}(\hat{e}_s\cdot\underline{d})_{\nu m}(\hat{e}_l\cdot\underline{d})_{\mu\nu}}{(\omega_{\mu\nu}+\omega_l)(\omega_{\mu m}+\Delta)}$$

$$+\frac{(\hat{e}_s\cdot\underline{d})_{n\mu}(\hat{e}_l\cdot\underline{d})_{\nu m}(\hat{e}_l\cdot\underline{d})_{\mu\nu}}{(\omega_{\mu\nu}+\omega_l)(\omega_{\mu m}+2\omega_l)}\Bigg)+\left(\rho^{0}_{\nu\nu}-\rho^{0}_{mm}\right)\Bigg(\frac{(\hat{e}_l\cdot\underline{d})_{n\mu}(\hat{e}_l\cdot\underline{d})_{\mu\nu}(\hat{e}_s\cdot\underline{d})_{\nu m}}{(\omega_{\nu m}-\omega_s)(\omega_{\mu m}+\Delta)}$$

$$+\frac{(\hat{e}_l\cdot\underline{d})_{n\mu}(\hat{e}_s\cdot\underline{d})_{\mu\nu}(\hat{e}_l\cdot\underline{d})_{\nu m}}{(\omega_{\nu m}+\omega_l)(\omega_{\mu m}+\Delta)}+\frac{(\hat{e}_s\cdot\underline{d})_{n\mu}(\hat{e}_l\cdot\underline{d})_{\mu\nu}(\hat{e}_l\cdot\underline{d})_{\nu m}}{(\omega_{\nu m}+\omega_l)(\omega_{\mu m}+2\omega_l)}\Bigg)\Bigg\}\Bigg\}$$

The polarization vector $\underset{\sim}{P}_{as}$ at the anti-Stokes frequency is given by

$$\underset{\sim}{P}_{as} = N\,\mathrm{Tr}(\rho_{nm}\underset{\sim}{d}_{mn}) = N\sum_{mn}\rho_{nm}\underset{\sim}{d}_{mn}$$

The terms in the second exponential term can be rearranged and, since there is a sum over m and n, the permutation (mn) introduced to give the form

$$\frac{e^{-i(k_{as}\cdot r-\omega_{as}t)}}{\omega_{mn}+\omega_{as}}\Bigg\{(\rho^{0}_{\nu\nu}-\rho^{0}_{nn})\Bigg(\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\mu}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu\nu}(\hat{e}_s\cdot\underset{\sim}{d})_{\nu n}}{(\omega_{\nu n}-\omega_s)(\omega_{\mu n}+\Delta)}$$

$$+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\mu}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu n}(\hat{e}_s\cdot\underset{\sim}{d})_{\mu\nu}}{(\omega_{\nu n}+\omega_\ell)(\omega_{\mu n}+\Delta)}+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu n}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu\nu}(\hat{e}_s\cdot\underset{\sim}{d})_{m\mu}}{(\omega_{\nu n}+\omega_\ell)(\omega_{\mu n}+2\omega_\ell)}$$

$$-(\rho^{0}_{\mu\mu}-\rho^{0}_{\nu\nu})\Bigg(\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\mu}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu n}(\hat{e}_s\cdot\underset{\sim}{d})_{\mu\nu}}{(\omega_{\mu\nu}-\omega_s)(\omega_{\mu n}+\Delta)}+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\mu}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu\nu}(\hat{e}_s\cdot\underset{\sim}{d})_{\nu n}}{(\omega_{\mu\nu}+\omega_\ell)(\omega_{\mu n}+\Delta)}$$

$$+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu n}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu\nu}(\hat{e}_s\cdot\underset{\sim}{d})_{m\mu}}{(\omega_{\mu\nu}+\omega_\ell)(\omega_{\mu n}+2\omega_\ell)}\Bigg)-(\rho^{0}_{\nu\nu}-\rho^{0}_{\mu\mu})\Bigg(\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu n}(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\nu}(\hat{e}_s\cdot\underset{\sim}{d})_{\nu\mu}}{(\omega_{\nu\mu}-\omega_s)(\omega_{m\mu}+\Delta)}$$

$$+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu n}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu\mu}(\hat{e}_s\cdot\underset{\sim}{d})_{m\nu}}{(\omega_{\nu\mu}+\omega_\ell)(\omega_{m\mu}+\Delta)}+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\nu}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu\mu}(\hat{e}_s\cdot\underset{\sim}{d})_{\mu n}}{(\omega_{\nu\mu}+\omega_\ell)(\omega_{m\mu}+2\omega_\ell)}+(\rho^{0}_{mm}-\rho^{0}_{\nu\nu})$$

$$\cdot\Bigg(\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu n}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu\mu}(\hat{e}_s\cdot\underset{\sim}{d})_{m\nu}}{(\omega_{m\nu}-\omega_s)(\omega_{m\mu}+\Delta)}+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu n}(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\nu}(\hat{e}_s\cdot\underset{\sim}{d})_{\nu\mu}}{(\omega_{m\nu}+\omega_\ell)(\omega_{m\mu}+\Delta)}$$

$$+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\nu}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu\mu}(\hat{e}_s\cdot\underset{\sim}{d})_{\mu n}}{(\omega_{m\nu}+\omega_\ell)(\omega_{m\mu}+2\omega_\ell)}\Bigg)\Bigg\}$$

Since $\omega_{\alpha\beta}=-\omega_{\beta\alpha}$, this can be written as

$$\frac{e^{-i(k_{as}\cdot r-\omega_{as}t)}}{\omega_{nm}-\omega_{as}}\Bigg\{(\rho^{0}_{nn}-\rho^{0}_{\nu\nu})\Bigg(\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\mu}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu\nu}(\hat{e}_s\cdot\underset{\sim}{d})_{\nu n}}{(\omega_{n\nu}+\omega_s)(\omega_{n\mu}-\Delta)}+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\mu}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu n}(\hat{e}_s\cdot\underset{\sim}{d})_{\mu\nu}}{(\omega_{n\nu}-\omega_\ell)(\omega_{n\mu}-\Delta)}$$

$$+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu n}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu\nu}(\hat{e}_s\cdot\underset{\sim}{d})_{n\mu}}{(\omega_{n\nu}-\omega_\ell)(\omega_{n\mu}-2\omega_\ell)}-(\rho^0_{\nu\nu}-\rho^0_{\mu\mu})\left(\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{n\mu}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu n}(\hat{e}_s\cdot\underset{\sim}{d})_{\mu\nu}}{(\omega_{\nu\mu}+\omega_s)(\omega_{n\mu}-\Delta)}\right.$$

$$+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{n\mu}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu\nu}(\hat{e}_s\cdot\underset{\sim}{d})_{\nu n}}{(\omega_{\nu\mu}-\omega_\ell)(\omega_{n\mu}-\Delta)}+\left.\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu n}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu\nu}(\hat{e}_s\cdot\underset{\sim}{d})_{n\mu}}{(\omega_{\nu\mu}-\omega_\ell)(\omega_{n\mu}-2\omega_\ell)}\right)-(\rho^0_{\mu\mu}-\rho^0_{\nu\nu})$$

$$\cdot\left(\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu n}(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\nu}(\hat{e}_s\cdot\underset{\sim}{d})_{\nu\mu}}{(\omega_{\mu\nu}+\omega_s)(\omega_{\mu m}-\Delta)}+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu n}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu\mu}(\hat{e}_s\cdot\underset{\sim}{d})_{m\nu}}{(\omega_{\mu\nu}-\omega_\ell)(\omega_{\mu m}-\Delta)}+\right.$$

$$+\left.\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\nu}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu\mu}(\hat{e}_s\cdot\underset{\sim}{d})_{\mu n}}{(\omega_{\mu\nu}-\omega_\ell)(\omega_{\mu m}-2\omega_\ell)}\right)+(\rho^0_{\nu\nu}-\rho^0_{mm})\left(\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu n}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu\mu}(\hat{e}_s\cdot\underset{\sim}{d})_{m\nu}}{(\omega_{\nu m}+\omega_s)(\omega_{\mu m}-\Delta)}\right.$$

$$+\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu n}(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\nu}(\hat{e}_s\cdot\underset{\sim}{d})_{\nu\mu}}{(\omega_{\nu m}-\omega_\ell)(\omega_{\mu m}-\Delta)}+\left.\frac{(\hat{e}_\ell\cdot\underset{\sim}{d})_{m\nu}(\hat{e}_\ell\cdot\underset{\sim}{d})_{\nu\mu}(\hat{e}_s\cdot\underset{\sim}{d})_{\mu n}}{(\omega_{\nu m}-\omega_\ell)(\omega_{\mu m}-2\omega_\ell)}\right)\Bigg\}$$

Comparing this term by term with the first exponential term it is seen that they are complex conjugates of each other since $(\hat{e}_\ell\cdot\underset{\sim}{d})^*_{\nu\mu}=(\hat{e}_\ell\cdot\underset{\sim}{d})_{\mu\nu}$, etc. Thus

$$\underset{\sim}{P}(\omega_{as})=Re\left\{(((\underset{\approx}{\chi}^{(3)}(\omega_{as})\cdot\underset{\sim}{E}(\omega_\ell))\cdot\underset{\sim}{E}(\omega_\ell))\cdot\underset{\sim}{E}^*(\omega_s))\right\}$$

where

$$\underset{\approx}{\chi}^{(3)}(\omega_{as})=-\frac{N}{4\hbar^3}\sum_{mn\mu\nu}\left\{\left(\frac{\rho^0_{nn}-\rho^0_{\nu\nu}}{\omega_{n\nu}+\omega_s}-\frac{\rho^0_{\nu\nu}-\rho^0_{\mu\mu}}{\omega_{\nu\mu}-\omega_\ell}\right)\frac{\underset{\sim}{d}_{mn}\underset{\sim}{d}_{n\nu}\underset{\sim}{d}_{\nu\mu}\underset{\sim}{d}_{\mu m}}{(\omega_{n\mu}-\Delta)(\omega_{nm}-\omega_{as})}\right.$$

$$+\left(\frac{\rho^{0}_{nn}-\rho^{0}_{\nu\nu}}{\omega_{n\nu}-\omega_{l}}-\frac{\rho^{0}_{\nu\nu}-\rho^{0}_{\mu\mu}}{\omega_{\nu\mu}+\omega_{s}}\right)\frac{\underset{\sim}{\mu}_{mn}\underset{\sim}{\mu}_{\nu\mu}\underset{\sim}{\mu}_{n\nu}\underset{\sim}{\mu}_{\mu m}}{(\omega_{n\mu}-\Delta)(\omega_{nm}-\omega_{as})}$$

$$+\left(\frac{\rho^{0}_{nn}-\rho^{0}_{\nu\nu}}{\omega_{n\nu}-\omega_{l}}-\frac{\rho^{0}_{\nu\nu}-\rho^{0}_{\mu\mu}}{\omega_{\nu\mu}-\omega_{l}}\right)\frac{\underset{\sim}{\mu}_{mn}\underset{\sim}{\mu}_{\mu m}\underset{\sim}{\mu}_{\nu\mu}\underset{\sim}{\mu}_{n\nu}}{(\omega_{n\mu}-2\omega_{l})(\omega_{nm}-\omega_{as})}$$

$$+\left(\frac{\rho^{0}_{\nu\nu}-\rho^{0}_{mm}}{\omega_{\nu m}+\omega_{s}}-\frac{\rho^{0}_{\mu\mu}-\rho^{0}_{\nu\nu}}{\omega_{\mu\nu}-\omega_{l}}\right)\frac{\underset{\sim}{\mu}_{mn}\underset{\sim}{\mu}_{\nu m}\underset{\sim}{\mu}_{\mu\nu}\underset{\sim}{\mu}_{n\mu}}{(\omega_{\mu m}-\Delta)(\omega_{nm}-\omega_{as})}$$

$$+\left(\frac{\rho^{0}_{\nu\nu}-\rho^{0}_{mm}}{\omega_{\nu m}-\omega_{l}}-\frac{\rho^{0}_{\mu\mu}-\rho^{0}_{\nu\nu}}{\omega_{\mu\nu}-\omega_{l}}\right)\frac{\underset{\sim}{\mu}_{mn}\underset{\sim}{\mu}_{n\mu}\underset{\sim}{\mu}_{\mu\nu}\underset{\sim}{\mu}_{\nu m}}{(\omega_{\mu m}-2\omega_{l})(\omega_{nm}-\omega_{as})}$$

$$+\left(\frac{\rho^{0}_{\nu\nu}-\rho^{0}_{mm}}{\omega_{\nu m}-\omega_{l}}-\frac{\rho^{0}_{\mu\mu}-\rho^{0}_{\nu\nu}}{\omega_{\mu\nu}+\omega_{s}}\right)\frac{\underset{\sim}{\mu}_{mn}\underset{\sim}{\mu}_{\mu\nu}\underset{\sim}{\mu}_{n\mu}\underset{\sim}{\mu}_{\nu m}}{(\omega_{\mu m}-\Delta)(\omega_{nm}-\omega_{as})}\Bigg\}$$