

## 4. THIRD-ORDER NONLINEAR PROCESSES

### 4.1. Third-Order Nonlinear Susceptibility & Classification

$$\mathbf{P}^{NL} = \epsilon_0 \left[ \chi^{(2)} : \vec{E}\vec{E} + 4\chi^{(3)} : \vec{E}\vec{E}\vec{E} + \dots \right] \quad (4.1.1)$$

Note that  $\chi^{(3)} = \chi'^{(3)}/\epsilon_0$  as defined in the text.  $\chi'^{(3)}$  is a tensor of the fourth rank:

$$\chi'_{jklm}{}^{(3)}(\omega_4; \omega_1, \omega_2, \omega_3),$$

e.g. when  $\omega_4 = \omega_1 + \omega_2 - \omega_3$

$$\begin{aligned} P_j^{(3)}(\vec{r}, \omega_4) = & \frac{6}{4} \times 4\epsilon_0 \sum_k \sum_l \sum_m \chi'_{jklm}{}^{(3)}(\omega_4; \omega_1, \omega_2, -\omega_3) \times \\ & \times E_k(\omega_1) E_l(\omega_2) E_m^*(\omega_3) e^{i(\vec{k}_1 + \vec{k}_2 - \vec{k}_3) \cdot \vec{r}} \end{aligned} \quad (4.1.2)$$

The numerical coefficients 6/4 arise because of 1/2 factors in the definition of the field amplitudes (note: we have three fields on the right hand side and one field on the left hand side  $\rightarrow$  two fields with each contributing 1/2) and because we have already summed over these permutations (totally 6) of frequencies and polarization subscripts that are equivalent.

The third-order susceptibility is responsible for great many kinds of nonlinear processes as compared with second-order susceptibility.

In particular,

$$\chi'^{(3)}(\omega_1; \omega_1, 0, 0):$$

DC Kerr Effect

(the change of linear dielectric constant  $\epsilon_{jn}$  for optical field  $\omega_1$  under action of DC field)

$$\chi'^{(3)}(\omega_1; \omega_1, \omega_1, -\omega_1):$$

Nonlinear Refractive Index at the Frequency of

the field: self-focusing, self-phase modulation, soliton pulses, optical bistability, nonlinear interface effect, also, saturable absorption and two-photon absorption

$$\chi'^{(3)}(2\omega_1; \omega_1, \omega_1, 0):$$

DC field-induced second harmonic generation (DC anharmonicity)

$\chi^{(3)}(3\omega_I; \omega_I, \omega_I, \omega_I)$ : third harmonic generation

$\chi^{(3)}(\omega_S; \omega_S, \omega_I, -\omega_I)$ : stimulated Raman scattering (Stokes component)  
 In stimulated Raman scattering, a photon of frequency  $\omega$  is annihilated and a photon at the Stokes shifted frequency  $\omega_S = \omega_I - \omega_V$  is created, leaving the molecule (or atom) in an excited state with energy  $\hbar\omega_V$ .

The excitation energy usually corresponds to the vibrational energy of molecules and acts as a reservoir of energy which can amplify waves at certain frequency. The vibrational frequency  $\omega_V$  is unique for each atom group. Therefore, Raman spectroscopy can be used to identify trace of chemicals and is one of the important tools for environmental study. The efficiency of stimulated Raman scattering can be quite large, with often 10% or more of the power of the incident light being converted to the Stokes frequency. This high efficiency occurs as a result of the stimulation by an intense laser beam. In contrast, the efficiency of spontaneous Raman scattering is typically many orders of magnitude smaller.

$\chi^{(3)}(2\omega_I - \omega_2; \omega_I, \omega_I, -\omega_2)$ : coherent — anti-Stokes Raman scattering; four-wave mixing  
 Coherent anti-Stokes frequency  $\omega_A = 2\omega_I - \omega_2$  is again generated through Raman scattering. However, this time the output frequency  $\omega_A$  is increased by  $\omega_V = \omega_I - \omega_2$  where  $\omega_I$  is the laser frequency and  $\omega_2 = \omega_S$ .

$\chi^{(3)}(\omega_I + \omega_2 \pm \omega_3; \omega_I, \omega_2, \pm\omega_3)$ : sum and difference frequency generation

The purely third-order nonlinearity is possible (as opposed to second order) in isotropic media or in central-symmetric crystals.

#### 4.2. Classical Model: Third-Order Nonlinearity in a Forced Oscillator

We will now consider an ensemble of undamped oscillators, each with the equation of motion

$$\frac{d^2 r}{dt^2} + \omega_0^2 r - \xi r^3 = -e E_x(t)/m \quad (4.2.1)$$

For the sake of simplicity, we assume now that there is no loss (the term  $\alpha \dot{x}$  is absent or our frequency is far from the resonance); this assumption always gives good results when all the frequencies involved are far from the linear resonance.

For  $E_x(t) = E_0 \cos \omega t$ , we first obtain the approximate i.e. linear ( $\xi = 0$ ) solution

$$r_1(t) = -\frac{(e/m)E_0 \cos \omega t}{(\omega_0^2 - \omega^2)} \quad (4.2.2)$$

In a perturbation analysis we use this as the amplitude of the cubic term and look for the solution of:

$$\frac{d^2 r_3}{dt^2} + \omega_0^2 r_3 - \xi r_1^3 = 0$$

or

$$\begin{aligned} \frac{d^2 r_3}{dt^2} + \omega_0^2 r_3 &= -\frac{\xi(e/m)^3 E_0^3 \cos^3 \omega t}{(\omega_0^2 - \omega^2)^3} \\ &= -\frac{3}{4} \frac{\xi(e/m)^3 E_0^3}{(\omega_0^2 - \omega^2)^3} \cos \omega t - \frac{\xi(e/m)^3 E_0^3}{4(\omega_0^2 - \omega^2)^3} \cos 3\omega t \end{aligned} \quad (4.2.3)$$

Thus,  $r(t) = r_1 + r_3 = x_1 \cos \omega t + x_2 \cos 3\omega t$  where

$$x_1 = -\frac{(e/m)E_0}{(\omega_0^2 - \omega^2)} \left\{ 1 + \frac{3}{4} \frac{\xi(e/m)^2 E_0^2}{(\omega_0^2 - \omega^2)^3} \right\} \quad (4.2.4)$$

and

$$x_2 = -\frac{\xi(e/m)^3 E_0^3}{4(\omega_0^2 - \omega^2)^3 (\omega_0^2 - (3\omega)^2)} \quad (4.2.5)$$

The polarization of the ensemble of N oscillators is  $-eNr$ . It has a nonlinear component (proportional to  $x_2$ ) at the frequency  $3\omega$  that couples to the third harmonic radiation field. In terms of the nonlinear polarization vector, we have a

$$P^{(3)}(3\omega) = \frac{\xi (e/m)^3 e N E_0^3}{(\omega_0^2 - \omega^2)^3 (\omega_0^2 - (3\omega)^2)} \quad (4.2.6)$$

Notice that it also has a nonlinear component at the frequency  $\omega$ . This corresponds to a change in the index of refraction seen by the fundamental and

is proportional to the fundamental intensity itself. The nonlinear polarization vector is

$$P^{(3)}(\omega) = \frac{3\xi (e/m)^3 e N E_0^3}{(\omega_0^2 - \omega^2)^4} \quad (4.2.7)$$

It contributes to self-phase modulation, self-focusing, and the optical Kerr coefficient. If both  $\omega$  and  $3\omega$  are much less than  $\omega_0$  (and all other contributing resonances)

$$P^{(3)}(\omega) = 3P^{(3)}(3\omega) \quad (4.2.8)$$

Similar to Chapter 2, we can roughly estimate the magnitude of  $\chi^{(3)}$  with a given lattice spacing  $a \approx N^{-1/3}$  where  $N$  is the number of atoms per unit volume. We postulate that the nonlinear and linear forces become comparable when the amplitude of oscillations  $r$  approaches the lattice spacing  $a$ , i.e. in Eq. (4.2.1)  $\omega_0^2 a \approx \xi a^3 \rightarrow \xi = (\omega_0/a)^2$ . Therefore,

$$\chi^{(3)} \approx \frac{\xi e^4 N}{m^3 \omega_0^8 \epsilon_0} \rightarrow \chi^{(3)} = \frac{e^4}{m^3 \omega_0^6 a^5 \epsilon_0} \quad (4.2.9)$$

For  $\lambda_0 \sim 1000\text{\AA}$ ,  $a \sim 2\text{\AA}$  and  $m = 9.1 \times 10^{-31} \text{ kg}$ , we obtain

$$\chi^{(3)} = 6.85 \times 10^{-24} (\text{m/V})^2 = 5.16 \times 10^{-17} (\text{cm}^2/\text{W})$$

### 4.3. Third Harmonic Generation (THG)

Third harmonic generation (THG) is allowed in centrosymmetric as well as non-centrosymmetric materials. THG has been demonstrated in a number of solid and liquid systems; but the greatest interest has been directed to vapor phase systems where THG can be used to generate coherent radiation in the vacuum ultraviolet.

The third order susceptibility defined such that

$$P^{(3)}(3\omega) = \epsilon_0 \chi^{(3)}(3\omega; \omega, \omega, \omega) E(\omega) E(\omega) E(\omega).$$

For plane wave with the beam at  $\omega$  nondepleted, we only need to solve the envelope equation for the 3rd harmonic wave

$$\frac{dE(3\omega)}{dz} = -j \frac{3\omega \chi^{(3)}(3\omega)}{2n_3 c_0} E^3(\omega) e^{j\Delta kz} \quad (4.3.1)$$

where  $\Delta k = k_3 - 3k_1$ ,  $k_3 = n_3 3\omega/c_0$ ,  $k_1 = n_1 \omega/c_0$ ,  $n_3 = n(3\omega)$  and  $n_1 = n(\omega)$ .

$$I(3\omega, l) = \frac{n_3}{2\eta_0} \left\{ \frac{3\omega \chi^{(3)}(3\omega)}{2c_0 n_3} \right\}^2 l^2 I^3(\omega) \left\{ \frac{2\eta_0}{n_1} \right\}^3 \sin^2 \left\{ \frac{\Delta kl}{2} \right\} \left/ \left\{ \frac{\Delta kl}{2} \right\}^2 \right. \quad (4.3.2)$$

The conversion efficiency is for phase matched (i.e.  $\Delta k = 0$ )

$$\frac{I(3\omega, l)}{I(\omega)} = \left\{ \frac{3\omega \chi^{(3)}(3\omega) \eta_o}{c_o} \right\}^2 l^2 \frac{I^2(\omega)}{n_3 n_1^3} \quad (4.3.3)$$

One may show that, analogously to Eq. (3.4.4), if  $\chi^{(3)}(\omega_1 + \omega_2 + \omega_3; \omega_1, \omega_2, \omega_3) \approx \chi^{(3)}(\omega_4 - \omega_1 - \omega_2; \omega_1, -\omega_2, -\omega_3) = \dots$  one has again Manley-Rowe relations valid:

$$\frac{d}{dz} \frac{dI_1}{dz} = \frac{1}{\omega_2} \frac{dI_2}{dz} = \frac{1}{\omega_3} \frac{dI_3}{dz} = -\frac{1}{\omega_4} \frac{dI_4}{dz} \quad (4.3.3)$$

#### 4.4. THG in Vapors

It can be shown [Armstrong et al., Phys. Rev. 127, 1918 (1962); see also Bloembergen's book] that the nonlinear susceptibility of quantum multilevel system for third harmonic generation is

$$\chi^{(3)}(3\omega) = \frac{N}{\hbar^3} \sum_g \sum_{abc} u_{ga} u_{ab} u_{bc} u_{cg} \rho_{gg} A_{abc} \quad (4.4.1)$$

where  $N$  is the density of atoms/unit volume,  $\rho_{gg}$  is the probability of occupancy of the ground state  $g$ , the  $\mu_{ij}$  are the dipole matrix elements between the  $ij$  states and  $A_{abc}$  are the frequency factors (without the resonant damping terms):

$$A_{abc} = \frac{1}{(\omega_{ag} - 3\omega)(\omega_{bg} - 2\omega)(\omega_{cg} - \omega)} + \frac{1}{(\omega_{ag} + 3\omega)(\omega_{bg} + 2\omega)(\omega_{cg} + \omega)} + \frac{1}{(\omega_{ag} + \omega)(\omega_{bg} + 2\omega)(\omega_{cg} - \omega)} + \frac{1}{(\omega_{ag} + \omega)(\omega_{bg} - 2\omega)(\omega_{cg} - \omega)} \quad (4.4.2)$$

which is valid only for THG in an isotropic medium. In the general case ( $C_I$  symmetry and  $\omega_4 = \omega_1 + \omega_2 + \omega_3$ ) there are 81 terms, but this particular example indicates the kind of resonant terms that appear.