Appendix A

Theory of z-scan technique

1. Closed aperture

For a cubic nonlinear medium, the index of refraction is

\[ n = n_0 + \frac{n_2}{2} |E|^2 = n_0 + \Delta n \]  \hspace{1cm} (A1)

\( n_2 \) represents nonlinear refractive index. Suppose a Gaussian beam in TEM\(_{00} \) mode having beam waist \( \omega_0 \) is incident on the medium. The electric field for the incident beam is given by

\[ E(z, r, t) = E_0(t) \cdot \frac{\omega_0}{w(z)} \exp \left[ -\frac{r^2}{\omega^2(z)} - \frac{ikr^2}{2R(z)} e^{-i\phi(z,t)} \right] \]  \hspace{1cm} (A2)

with \( E_0 \), the electric field at focus

\[ \omega^2(z) = \omega_0^2 \left( 1 + \frac{z^2}{z_0^2} \right), \text{ radius of beam} \]

\[ R(z) = z \left( 1 + \frac{z^2}{z_0^2} \right), \text{ the radius of curvature of the wavefront at position } z \]

\[ z_0 = \frac{k\omega_0^2}{2}, \text{ Rayleigh range} \]

\[ k = \frac{2\pi}{\lambda}, \text{ the wave vector and} \]

\( e^{-i\phi(z,t)} \) represents the radially uniform phase variation.

Using slowly varying envelope approximation, the radial phase shift \( \Delta \phi(r) \) as a function of position \( z \) is obtained from the following two equations that represent the Gaussian beam propagation through the sample.

\[ \frac{d\Delta \phi}{dz} = \Delta n.k \]  \hspace{1cm} (A3)

and \[ \frac{dI}{dz} = -\alpha I \]  \hspace{1cm} (A4)
Here $\alpha$ contains both the linear and nonlinear absorption terms. For cubic nonlinearity and negligible nonlinear absorption, the solution of equations (A3) and (A4) gives the phase variation $\Delta \phi(z,r,t,L)$ at the exit of the medium of length $L$.

$$\Delta \phi(z,r,t,L) = \Delta \phi(z,t,L) \exp \left[ -\frac{2r^2}{\omega^2(z)} \right]$$  \hspace{1cm} (A5)

with $\Delta \phi(z,t,L) = \frac{\Delta \phi_0(t,L)}{1 + \frac{z^2}{z_0^2}}$

and $\Delta \phi_0(t,L)$, the on-axis phase variation at the beam waist is written as

$$\Delta \phi_0(t,L) = k \Delta n L_{\text{eff}}$$  \hspace{1cm} (A6)

Here $L_{\text{eff}} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}$ is effective thickness, $\alpha_0$ is the linear absorption coefficient. The complex electric field at the exit of the sample is given by the relation

$$E_z(z,r,t) = E(z,r,t) e^{-\frac{\alpha_0 L}{z} \alpha \Delta \phi(z,r,t)}$$  \hspace{1cm} (A7)

Using Gaussian decomposition method and far-field condition (Distance between sample and aperture plane $>> z_0$) the on-axis normalized transmittance $T(z,\Delta \phi_0)$ and peak-valley transmittance change $\Delta T_{p,v}$ is given by

$$T(z,\Delta \phi_0) = \frac{[E(z,r=0,\Delta \phi)]^2}{[E(z,r=0,\Delta \phi_0 = 0)]^2} = 1 - \frac{4\Delta \phi_0 \frac{z}{z_0}}{\left( \frac{z}{z_0} \right)^2 + 9 \left( \frac{z}{z_0} \right)^2 + 1}$$  \hspace{1cm} (A8)

and $\Delta T_{p,v} = 0.406 (1 - S)^{0.25} |\Delta \phi_0|$, for $|\Delta \phi_0 | \leq \pi$  \hspace{1cm} (A9)

Here $S$ is the aperture transmittance. Using equation (A6) and (A9), the nonlinear refractive index is calculated in closed aperture $z$-scan system.
2. Open aperture

The absorption coefficient \( \alpha \) for a third order nonlinear medium can be written in terms of linear absorption coefficient \( \alpha_0 \) and nonlinear absorption coefficient \( \beta \) as

\[
\alpha = \alpha_0 + \beta I
\]  \hspace{1cm} (A10)

Considering nonlinear absorption, the solution of equations (A3) and (A4) gives the following intensity distribution at exit of the sample.

\[
I_e(z, r, t) = \frac{I(z, r, t)e^{-\alpha L}}{1 + q(z, r, t)}
\]  \hspace{1cm} (A11)

Here \( q(z, r, t) = \beta I(z, r, t) L_{\text{eff}} \). By integrating equation (A11) over \( z \) and \( r \), the total power transmitted through the sample is given as

\[
P(z, t) = P_i(t) e^{-\alpha L} \frac{\ln[1 + q_0(z, t)]}{q_0(z, t)}
\]  \hspace{1cm} (A12)

with \( P_i(t) = \frac{\pi \alpha_0^2 I_0}{2} \),

\[
q_0(z, t) = \frac{\beta I_0 L_{\text{eff}} \xi_0^2}{z^2 + \xi_0^2}
\]

For \( |q_0| < 1 \), the integration of equation (A12) gives transmittance and normalized transmittance (\( \Delta T \)) difference between baseline and peak/dip as

\[
T(z, S = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z, 0)]^m}{(m+1)^{3/2}}
\]

\[
\text{and} \quad \Delta T = \frac{\beta I_0 L}{2\sqrt{2}}
\]  \hspace{1cm} (A13)

Equation (A14) is used for estimation of nonlinear absorption coefficient in open aperture z-scan.
Appendix B

Degenerate four-wave mixing

1. Wave equation for phase conjugation

Let the input optical field propagating along z-axis is represented by

\[ E_1(\omega) = a_1 A_1(z) e^{-i(\omega - k_1)z}, \]

\[ E_2(\omega) = a_2 A_2(z) e^{-i(\omega - k_2)z}, \]

\[ E_3(\omega) = a_3 A_3(z) e^{-i(\omega - k_3)z} \]  \hspace{1cm} (B1)

Here \( a_1, a_2, a_3 \) are the unit vectors along the light polarization direction of wave, \( \omega \) is angular frequency, \( A_1, A_2, \) and \( A_3 \) are amplitude functions of pump beams and \( k \) is the wave vector of optical field. According to the principle of FWM, the forth conjugate wave is generated through third order nonlinear polarization \( (P^{(3)}) \) of medium. The wave equation for the amplitude of the generated wave \( (E_4) \) is

\[ \Delta^2 E_4 + \frac{n_2}{c^2} \frac{\partial^2 E_4}{\partial t^2} = -\frac{4\pi}{c^2} \frac{\partial^2 P^{(3)}}{\partial t^2} \]  \hspace{1cm} (B2)

Using slowly varying amplitude approximation \( \left( \left| \frac{d^2 A_4}{dz^2} \right| \ll \left| k \frac{dA_4}{dz} \right| \right) \) and \( E_4(\omega) = a_4 A_4(z) e^{i(\omega - k_4)z} \) as a solution for wave equation, the following coupled equations are obtained

\[ \frac{dA_4(z)}{dz} = i\kappa A_4^*(z) \]  \hspace{1cm} (B3)

\[ \frac{dA_4^*(z)}{dz} = i\kappa^* A_4(z) \]  \hspace{1cm} (B4)
Here $A_j^*$ is complex conjugate of input probe wave, $\kappa = \frac{\omega}{2n_0c} \chi^{(3)} A_i A_2$ is coupling coefficient. For boundary conditions $A_j(0) \neq 0$ and $A_j(L) = 0$, the solution of coupled equations (B3) and (B4) are

$$A_j(z) = \frac{\cos[|\kappa|(z - L)]}{\cos(|\kappa|L)} A_j(0)$$  \hspace{1cm} (B5)

$$A_j(z) = i\kappa \frac{\sin[|\kappa|(z - L)]}{|\kappa|} \frac{A_j^*(0)}{\cos(|\kappa|L)}$$  \hspace{1cm} (B6)

For above two waves, the output amplitudes are

$$A_j(L) = \frac{1}{\cos(|\kappa|L)} A_j(0)$$  \hspace{1cm} (B7)

$$A_j(0) = \frac{i\kappa}{|\kappa|} \tan(|\kappa|L) A_j^*(0)$$  \hspace{1cm} (B8)

Equations (B7) and (B8) shows that generated wave is proportional to complex conjugate of probe beam $A_j(0)$.

2. **Intensity of phase conjugate wave**

In order to evaluate third order nonlinear susceptibility $\chi^{(3)}$, equation (B8) has been used. For $|\kappa|L << 1$ equation (B8) becomes

$$A_j(0) = -i\kappa L A_j^*(0) = -i \frac{\omega}{2n_0c} L \chi^{(3)} A_i A_2 A_j^*(0)$$  \hspace{1cm} (B9)

The intensity of a wave of amplitude $A$ is given by

$$I = \frac{1}{2} \varepsilon_0 c n_0 |A|^2$$  \hspace{1cm} (B10)
Substituting equation (B10) in equation (B9), the relation between $\chi^{(3)}$ and intensities of pump, probe and conjugate beams is

$$I_c = \left( \frac{\omega L \chi^{(3)}}{\varepsilon_0 c^2 n_0^2} \right)^2 J_f I_b I_p \tag{B11}$$

For an absorbing material having linear absorption $\alpha_0$, the above relation becomes

$$I_c = e^{-\alpha_0 L} \left( 1 - e^{-\alpha_0 L} \right)^2 \left( \frac{\omega L \chi^{(3)}}{\varepsilon_0 \alpha_0 c^2 n_0^2} \right) J_f I_b I_p \tag{B12}$$
Appendix C

Measurement of harmonic generation in reflection

The second order nonlinear polarization \( P^{(2)} \) is given by the relation

\[
P^{(2)} = \chi^{(2)} E^2
\]  \hspace{1cm} (C1)

Here \( E \) is the beam field inside the sample that is related to the incident field \( E_i \) by Fresnel formula given as

\[
E = E_i \cdot \frac{2 \cos \theta_i}{\cos \theta_i + \varepsilon_1^{1/2} \left(1-\sin^2 \theta_i\right)^{1/2}}
\]  \hspace{1cm} (C2)

\( \theta_i \) is the angle of incidence and \( \varepsilon_1^{1/2} \) is the linear refractive index of medium at frequency \( \omega \). Using boundary conditions, the solution of wave equation gives the amplitude of reflected \( A_s^R \) and transmitted \( A_r^T \) second harmonic wave.

\[
A_s^R = A_r^T - \frac{4\pi P^{(2)}}{\varepsilon_2 - \varepsilon_1} \]

\[
\varepsilon_2^{1/2} \cos \theta^T A_r^T = \frac{4\pi P^{(2)}}{\varepsilon_2 - \varepsilon_1} \varepsilon_1^{1/2} \cos \theta^s - A_s^R \cos \theta^R
\]  \hspace{1cm} (C3)

\[
A_s^R = -\frac{4\pi P^{(2)}}{\varepsilon_2 - \varepsilon_1} \left[ \varepsilon_2^{1/2} \cos \theta^T - \varepsilon_1^{1/2} \cos \theta^s \right]
\]

The conservation of tangential component of momentum provides relation between angles of reflection and refraction as

\[
\sin \theta_s^R = \sin \theta^s,
\]
\[
\sin \theta_r^T = \varepsilon_1^{1/2} \sin \theta,
\]
\[
\sin \theta^T = \varepsilon_1^{-1/2} \sin \theta^i
\]  \hspace{1cm} (C6)
Finally, the amplitude of reflected second harmonic wave obtained from equations (C1), (C2), (C5) and (C6) is given by

$$\left| A_2^R \right|^2 = \left| \chi^{(2)} \right|^2 F_2^R (\theta, \varepsilon) |A|^4$$

(C7)

Here factor $F_2^R (\theta, \varepsilon)$ given by equation (C8) is dependent on angle of incidence and linear refractive index of the medium, $\varepsilon_1^{1/2}$ at $\omega$ and $\varepsilon_2^{1/2}$ at $2\omega$.

$$F_2^R (\theta, \varepsilon) = \frac{256\pi^2 \cos^4 \theta_i}{\left| \cos \theta_i + \left( \varepsilon_1 - \sin^2 \theta_i \right)^{1/2} \right|^4 \left| \cos \theta_i + \left( \varepsilon_2 - \sin^2 \theta_i \right)^{1/2} \right|^4 \left( \varepsilon_1 - \sin^2 \theta_i \right)^{1/2} + \left( \varepsilon_2 - \sin^2 \theta_i \right)^{1/2} \right|^2}$$

(C8)

Similarly, the amplitude of reflected third harmonic wave is given by

$$\left| A_3^R \right|^2 = \left| \chi^{(3)} \right|^2 F_3^R (\theta, \varepsilon) |A|^6$$

(C9)

Here

$$F_3^R (\theta, \varepsilon) = \frac{1024\pi^2 \cos^6 \theta_i}{\left| \cos \theta_i + \left( \varepsilon_1 - \sin^2 \theta_i \right)^{1/2} \right|^6 \left| \cos \theta_i + \left( \varepsilon_3 - \sin^2 \theta_i \right)^{1/2} \right|^6 \left( \varepsilon_1 - \sin^2 \theta_i \right)^{1/2} + \left( \varepsilon_3 - \sin^2 \theta_i \right)^{1/2} \right|^2}$$

(C10)

$\varepsilon_3^{1/2}$ represents linear refractive index at third harmonic wavelength. Equations (C7) and (C9) are used for estimation of second and third order nonlinear susceptibility.