NL response from molecular orientation

examples: CS_2, nitrobenzene, N_2 ...

2 cases: induced dipole moment, permanent dipole

Classical analysis: induced dipole moment: $\vec{p} = \alpha \vec{E} \rightarrow \chi = N\alpha$

model molecule as uniaxial ellipsoid = prolate spheroidal

$\alpha_3 > \alpha_1 \quad \alpha_1 = \alpha_2$

polarizability larger along long axis

- molecules are randomly oriented - due to collisional thermalization
- apply E-field → torque → alignment

torque $\vec{\tau} = \vec{p} \times \vec{E}$

energy $dU = -\vec{p} \cdot d\vec{E}$

$= -p_3 dE_3 - p_1 dE_1$

DC field, induced dipole moment:

$\vec{p} = \overleftrightarrow{\alpha} \cdot \vec{E} = \alpha_1 E_1 \hat{x} + \alpha_3 E_3 \hat{z}$ in coord sys. of molecule.

so $dU = -\alpha_3 E_3 dE_3 - \alpha_1 E_1 dE_1$

integrate:

$$U = -\frac{1}{2}(\alpha_3 E_3^2 + \alpha_1 E_1^2)$$

$$= -\frac{1}{2}(\alpha_3 E_0^2 \cos^2\theta + \alpha_1 E_0^2 \sin^2\theta)$$

$$= -\frac{1}{2}\alpha_1 E_0^2 - \frac{1}{2}(\alpha_3 - \alpha_1) E_0^2 \cos^2\theta$$

AC field

$$E_0^2 \rightarrow E_0^2 (e^{-i\omega t} + e^{i\omega t})^2 = E_0^2 (2 + \underbrace{2\cos 2\omega t}_{\text{molecule too slow}})$$

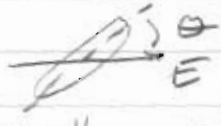
$\therefore$ use time avg field $\overline{E^2}$ $\qquad \therefore$ avg out

energy of the induced dipole of molecule in AC field:

$$U(\theta) = \alpha_1 E_0^2 - (\alpha_3 - \alpha_1) E_0^2 \cos^2\theta$$

for $\alpha_3 - \alpha_1 > 0$ U decreases as $\theta \to 0$

θ = angle btw $\vec{E}$ and molecule z-axis



average over all angles to get mean $\langle U \rangle$

angular distribution is given by Boltzmann.

$\exp(-U(\theta)/kT)$

then $\langle U \rangle = -\frac{1}{2} |E|^2 \langle \alpha \rangle$

and $n^2 = 1 + \chi = 1 + N\langle \alpha \rangle$

Avg over Boltzmann:

$$\langle f(\theta) \rangle = \frac{\int f(\theta) e^{-U(\theta)/kT} \, d\Omega}{\int e^{-U(\theta)/kT} \, d\Omega}$$

$d\Omega = \sin\theta \, d\theta \, d\phi$

Let $U(\theta) = -J \cos^2\theta \cdot kT$ ignore constant part

$J = \frac{1}{2}(\alpha_3 - \alpha_1) \vec{E}_0^2 / kT$

calculate $\langle \cos^2\theta \rangle = \dfrac{\int_0^\pi \cos^2\theta \, e^{+J\cos^2\theta} \sin\theta \, d\theta}{\int_0^\pi e^{J\cos^2\theta} \sin\theta \, d\theta}$

for $J \ll 1$ (low intens),

$\langle \cos^2\theta \rangle \to \frac{1}{3}$

$n_0^2 = 1 + N\left(\frac{1}{3}\alpha_3 + \frac{2}{3}\alpha_1\right)$

$n(I)$ increases w/ I but saturates

linear for low I.

Check assumptions:

1) low density : ok for gases

for liquids, Lorentz-Lorenz law

$$\frac{n^2-1}{n^2+1} = \frac{1}{3} N \langle \alpha \rangle$$

→ local field corr. factor for n_2 : $\left(\frac{n_0^2+2}{3}\right)^4$

for CS_2 max $\delta n = 0.58$

$n_2 \approx 3 \times 10^{-19}\ m^2/W = 3 \times 10^{-15}\ cm^2/W$

~ 10x higher than glass

2) time response: assumptions.

- molecule has time to move. (~ ps)
- enough collisions to randomize (dep. on density)

pump-probe → periodic alignment, damped by collisions.
molecular response best described coherently thru QM.

3) linear polarization

for arbitrary polarization → tensor analysis

→ $B/A = 6$ (vs. 1 in electronic resp.)

$\frac{\delta n_{linear}}{\delta n_{circ}} \approx 4$ for mol. orientation

$\approx 3/2$ electronic

4) dipole moment: permanent dipole $U(\theta) = -p_0 E \cos\theta$

$n_2 < 0$ in this case.

Thermal NL effects.

$$n = n_0 + \left(\frac{dn}{dT}\right) T_\ell \qquad T_\ell = \Delta T \text{ from laser.}$$

dn/dT can be + (typ) or −

here we're working with a coupled eqn:

$$\underbrace{(\rho_0 C)}_{\text{spec. heat}} \frac{\partial T_\ell}{\partial t} - \underbrace{K}_{\text{therm. conductivity}} \nabla^2 T_\ell = \underbrace{Q}_{\text{heat source}} = \alpha I(r)$$

α → abs. coeff't

time response: scale eqn.

$$\rho_0 C \frac{T_\ell}{\tau} \approx \frac{K T_\ell}{R^2} \rightarrow \tau \sim \frac{\rho_0 C R^2}{K}$$

typ. 1 sec. for macroscopic beams ~ 1 mm

100 μs for small beams 10 μm.

Notes: dn/dT, C, K vary with temperature in most materials

→ cryo cooling sapphire

decrease ΔT and increase time response

> $n(r)$ again leads to thermally induced lens

- impt. in amplifiers.

For cw beams, assume steady state.

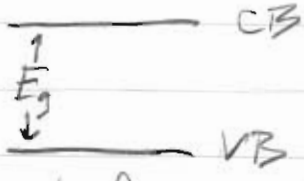
$$-K \nabla^2 T_\ell = \alpha I(r) \qquad I(r)$$

$$K \frac{T_\ell}{R^2} \approx \alpha I_0 \qquad T_\ell \sim \frac{\alpha I_0 R^2}{K}$$

$$\Delta n \sim T_\ell \, dn/dT \rightarrow \text{effective } n_2$$

- very strong NL effects for cw
- must solve coupled eqns in general
  - can use limiting forms of eqn for fast or slow t.

Semiconductor nonlinearity



1) treat free carrier effects:

N_c = cond. band electron density

$$\frac{dN_c}{dt} = \underbrace{\alpha \frac{I}{\hbar\omega}}_{\text{linear absorption}} - \frac{N_c - N_c^{(0)}}{\tau_R}$$

τ_R → recombination CB → VB

τ_R is typically longer than pulse.

use modified plasma refr. index:

$$\varepsilon(\omega) = \varepsilon_b - \frac{\omega_p^2}{\omega(\omega + i/\tau)}$$

ε_b → dielectric const from bound charges.

τ → collision, ohmic term

$$\omega_p^2 = \frac{N_c e^2}{\varepsilon_0 m}$$

m → use effective mass of e^- or h^+

2) exciton effects.

e-h pairs can bind weakly (exciton)

N_c high, free electrons screen charges

→ removal of exciton states, Δn

3) saturation / bleaching

fill all available states → no more absorption

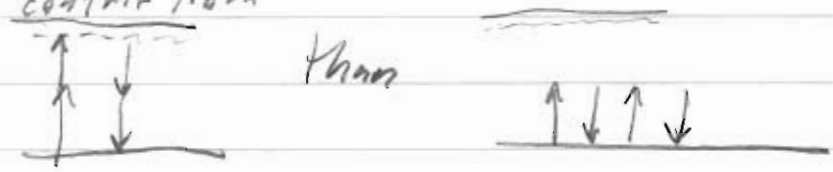
- fast recovery if $E \gg E_g$: e^- to bottom of CB

4) band gap shifting : lower E_g for high N_c

multiphoton effects

- 2PA possible for $E_{in} > E_g/2$
- for $E_{in} < E_g/2$ → near resonance

∴ larger contrib from



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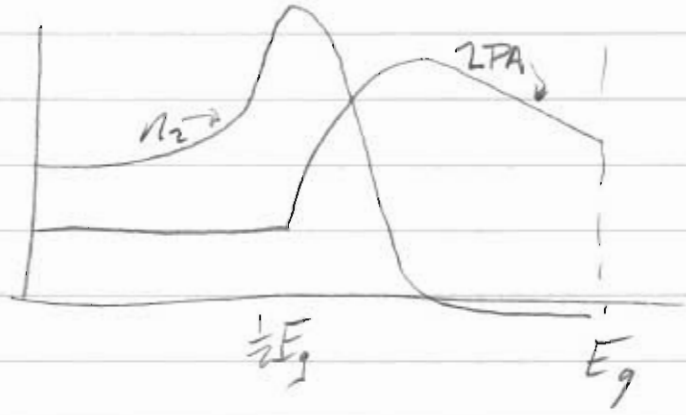

note $n_2 < 0$ for some range.