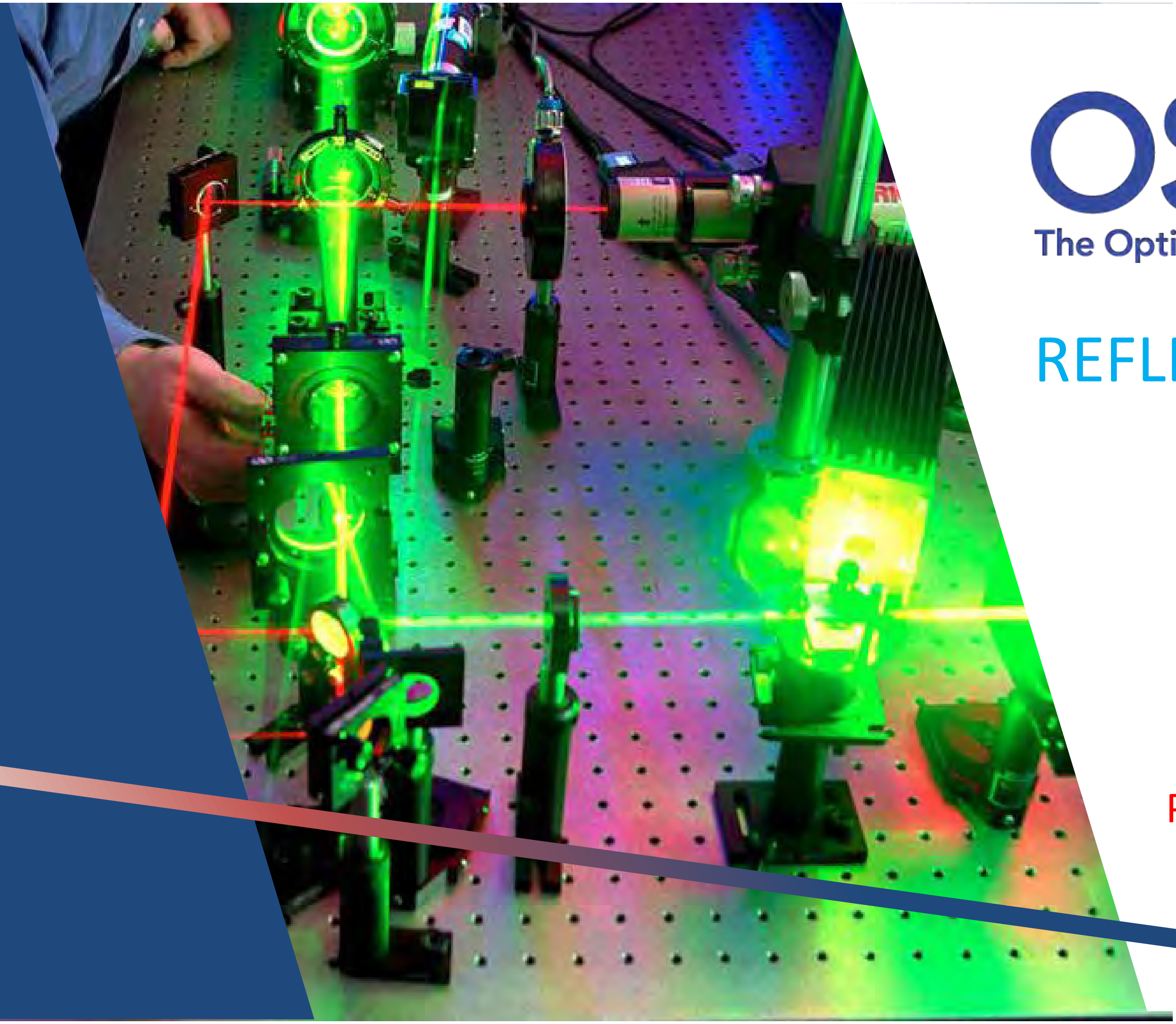
**Siegman 2016, ICFO Barcelona**

**Characterization and Modeling of Nonlinear Optical Materials for Various Applications**

It is necessary to fully understand the nonlinear optical (NLO) response of materials in order to design useful nonlinear optical devices, e.g. all-optical switches. I will present the basics for understanding nonlinear absorption (NLA) and nonlinear refraction (NLR) from various mechanisms in a variety of materials including semiconductors, solvents, organic dyes and even gases. I will also draw similarities between the light-matter interactions in different materials. I will then describe methods that have been developed to unravel the various NLO responses that can occur simultaneously in materials that have plagued the literature leading to apparent orders of magnitude discrepancies. Among these are Z-scan which can separately determine the sign and magnitude of NLA and NLR, but is a single-beam method that gives no information about the temporal response. Complementary to this are pump-probe techniques for NLA which yield the temporal response. Our new beam-deflection technique gives the temporal response of the NLR. Its high sensitivity (as small as $\lambda$/20,000 phase shift) allows measurements of gases. The spectral properties of these various NLO responses is key to their understanding. The nonlinear Kramers-Kronig relations linking the dispersion of nonlinear refraction to the spectrum of nonlinear absorption will also be described in an intuitive manner. This leads us to look at nondegenerate nonlinearities, i.e. where the frequencies used for these 2-photon processes are unequal. For semiconductors we find that by going to extremely nondegenerate photons (energy ratio ~10), the 2-photon absorption is enhanced by 2-3 orders of magnitude. This allows for 2-photon LIDAR imaging and even the possibility of a 2-photon laser.

L – R, Marlan Scully (my mentor) Steve Jacobs, Tony Siegman

Tony Siegman, Chris Dainty & I organized 1st OSA School
Changchun, China, August, 2011



OSA® The Optical Society | 100 Since 1916

# REFLECTING A CENTURY OF INNOVATION

Presenter: Eric Van Stryland
ICFO, Barcelona
2016


FREEFORM SURFACES | ADEN MEINEL | OPTICS IN RUSSIA
OPN
Optics & Photonics News
September 2012 | Vol. 23 No. 9
An OSA Member Benefit
CREOL@25
www.creol.ucf.edu
CREOL at 25
A Full Spectrum of Achievements
OSA


@25
e in Optics and Photonics


Charles Townes
Nico Bloem-bergen

# Characterization and Modeling of Nonlinear Optical Materials for Various Applications

Eric Van Stryland, CREOL
The College of Optics and Photonics
University of Central Florida

www.creol.ucf.edu

**Books on nonlinear optics: NOT A COMPLETE LISTING!**

"The Principles of Nonlinear Optics", Y.R. Shen, Wiley
"The Elements of Nonlinear Optics", Butcher and Cotter, Cambridge
"Applied Nonlinear Optics", F. Zernike and J. Midwinter, Wiley
"Nonlinear Fiber Optics", G.P. Agrawal, Academic Press
"Introduction to Nonlinear Laser Spectroscopy", M. Levenson, Academic Press
"Solitons and Nonlinear Wave Equations", R. Dodd et. al., Academic Press
"Optical Phase Conjugation", R.A. Fisher, Academic Press
"Principles of Phase Conjugation", B.Ya. Zel'dovich, N.F. Pilipetsky and V.V. Shkunov, Springer Verlag
"Nonlinear Optics and Quantum Electronics", M. Schubert and B. Wilhelmi, Wiley
"Optics and Nonlinear Optics of Liquid Crystals", I.C. Khoo and S.T. Wu, World Scientific
"Nonlinear Optical Parametric Processes in Liquids and Gases", J. Reintjes, Academic Press
“Contemporary Nonlinear Optics”, Agrawal and Boyd, Academic Press

"Nonlinear Optics", George & Robert Stegeman, Wiley 2012

“Optical bistability: controlling light with light”, H. Gibbs Academic Press
“Refractive nonlinearity of wide-band semiconductors and applications”, A.A. Borshch, M. Brodin, V. Volkov, Harwood academic publishers

**Compendia of articles on nonlinear optics:**

“Nonlinear Optics”, N. Bloembergen, Frontiers in Physics, A lecture and reprint series, W.A. Benjamin, Inc.
"Nonlinear Optics", P. Harper and B.S. Wherrett, Academic Press
“Nonlinear Optical Materials”, edited by H. Kuhn and J. Robillard, CRC Press
"Nonlinear Optical Properties of Organic Molecules and Crystals", V’s I and II, D.S. Chemla and J. Zyss, Academic Press
“Self-focusing: past and present” Ed. R. Boyd, S. Lukishova, R. Shen, Topics in Applied Physics 114, Springer
“Molecular nonlinear optics” Ed. J. Zyss, Academic Press
“Multiphoton processes”, Ed J. Eberly, P. Lambropoulos, Wiley
“Advances in multi-photon processes and spectroscopy” ed. S.H. Lin, A.A. Villaeys, Y. Fujimura, Vol. 15, World Scientific Press
“Beam shaping and control with nonlinear optics”, Ed. F. Kajzar, R. Reinisch, NATO ASI Series B: Physics Vol. 369, Plenum
“Nonlinear Photonic crystals”, E. R. Slusher, B. Eggleton, Springer
“Nonlinear optics of organic molecules and polymers”, Ed. H.S. Nalwa, S. Miyata, CRC Press
“Organic materials for nonlinear optics, Ed. R. Hann, D. Bloor, Royal Society of Chemistry
“Handbook of Nonlinear Optical Crystals”, V.G. Dmitirev, G.G. Gurzadyan, D.N. Nikogosyan, Springer
“Susceptibility tensors for nonlinear optics”, S.V. Popov, Yu.P. Svirko, N.I. Zheludev, Institute of Physics
Nonlinear optical properties of organic and polymeric materials”, Ed. D. Williams, ACS symposium series 233
“Nonlinear optical properties of liquid crystals and polymer dispersed liquid crystals”, F. Simoni, World Scientific
CRC Handbook of Laser Science and Technology, Supplement 2: Optical Materials
“Characterization techniques and tabulations for organic nonlinear optical materials”, Ed. M. Kuzyk, C. Dirk, Marcel Dekker

Peter Franken et al PRL SHG 1961
my 1st job

Father of Nonlinear Optics (NLO)
OSA R.W. Wood Prize,
died 1991

http://prola.aps.org/pdf/PRL/v7/i4/p118_1

VOLUME 7, NUMBER 4 PHYSICAL REVIEW LETTERS AUGUST 15, 1961

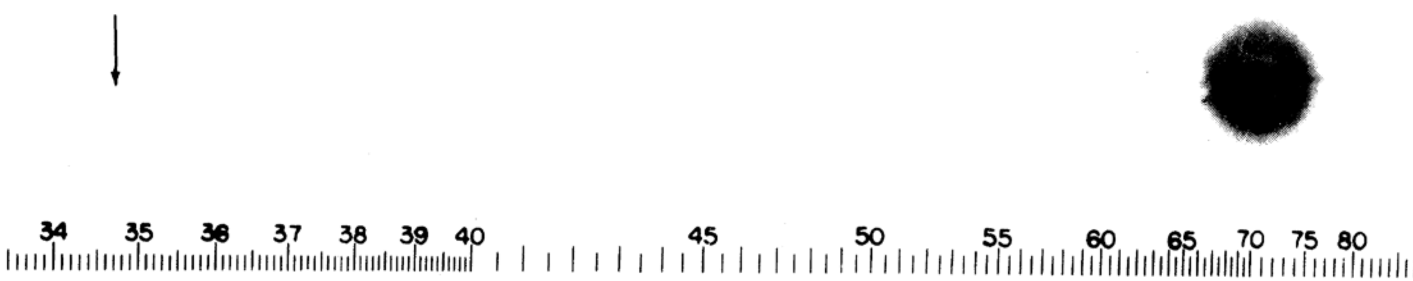
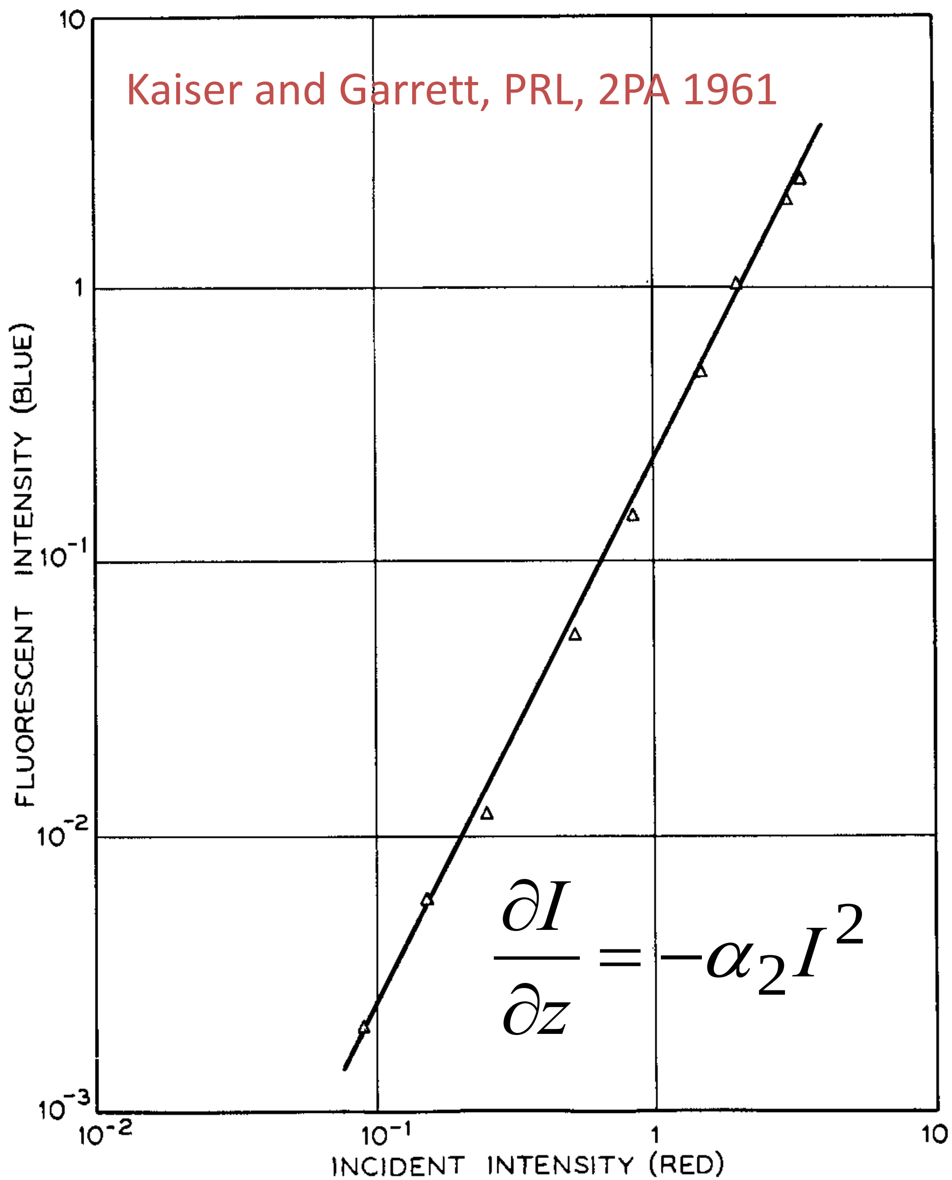



FIG. 1. A direct reproduction of the first plate in which there was an indication of second harmonic. The wavelength scale is in units of 100 A. The arrow at 3472 A indicates the small but dense image produced by the second harmonic. The image of the primary beam at 6943 A is very large due to halation.

http://prola.aps.org/pdf/PRL/v7/i6/p229_1

VOLUME 7, NUMBER 6 PHYSICAL REVIEW LETTERS SEPTEMBER 15, 1961

Kaiser and Garrett, PRL, 2PA 1961




$$\frac{\partial I}{\partial z} = -\alpha_2 I^2$$

**Maria Goeppert Mayer**

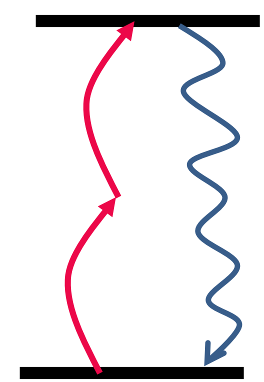
2nd Female Nobel Prize for Physics

Theory of 2-Photon Absorption, 1931

FIG. 2. Blue fluorescent intensity of sample versus incident red intensity.

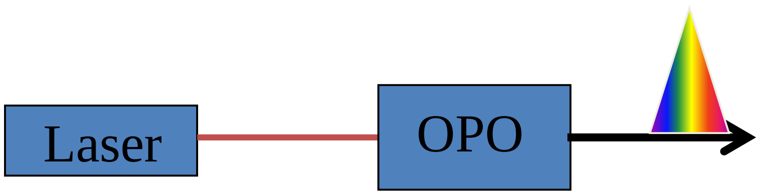
Slope is ~2

WHY?

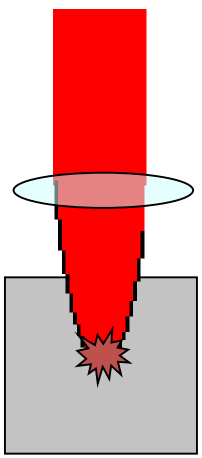


# Is Nonlinear Optics Good For Anything?

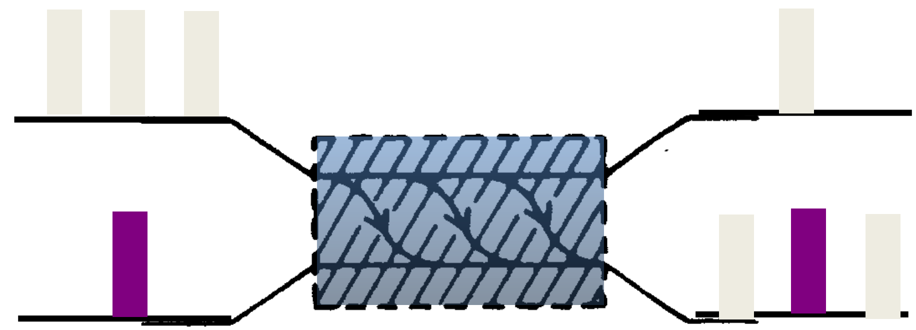
Tunable Generation of New Frequencies



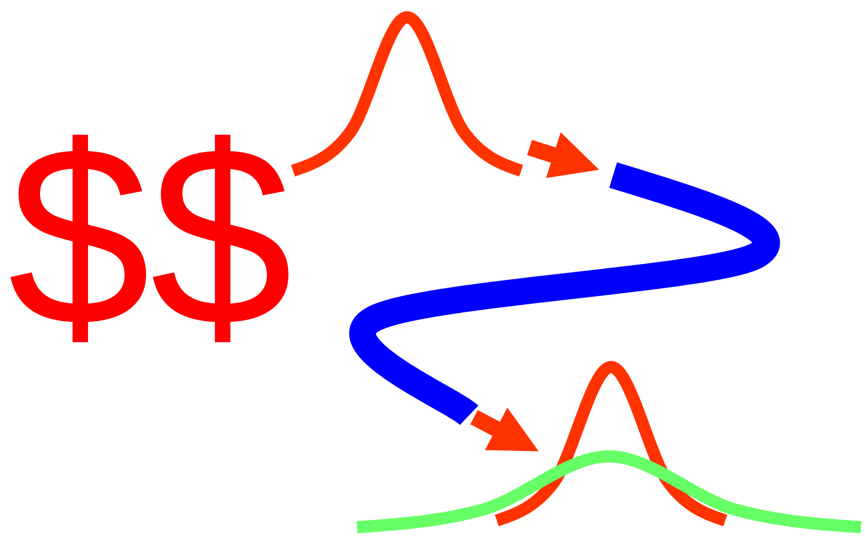

Local Multi-Photon Activated Chemistry



All-Optical Switching



Optical Communication




Kerr-Lens modelocked lasers!

# Do you always need high fields to see NLO effects?

# What is NLO? (besides new ω's)

Light-induced change in optical "constants"

*α=α(I), n=n(I) :* in NLO both *α* and ***n*** are important

e.g. photochromic sunglasses, mirage

What information is needed?

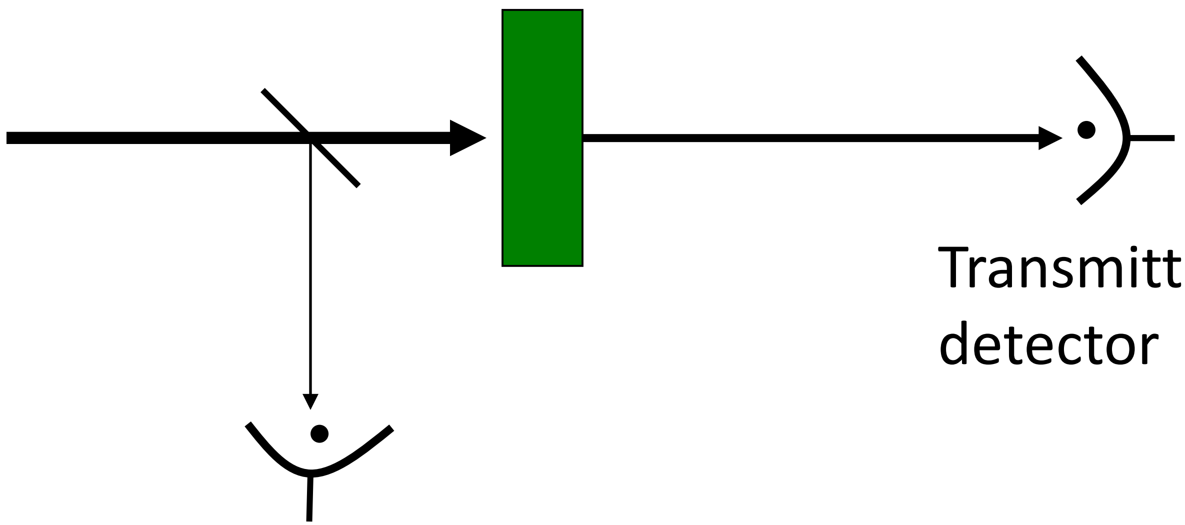
Dominant nonlinearity (if one)

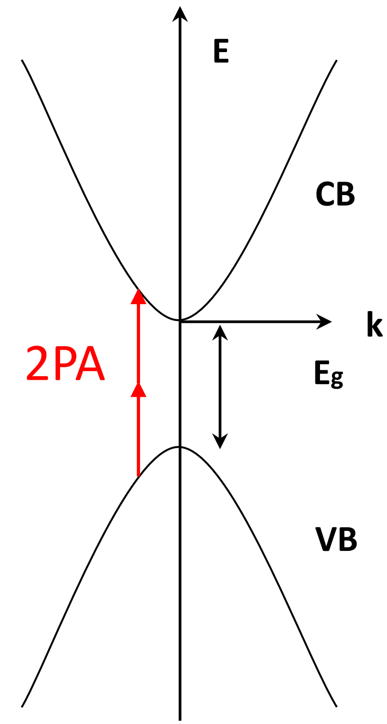
Depends on many parameters $t_p$, $w_0$, … λ

Several experiments varying parameters are needed to unravel physics and determine coefficients.

## "λ" Nonlinear Spectroscopy Enabled by "tunable" sources

# Nonlinear Transmittance



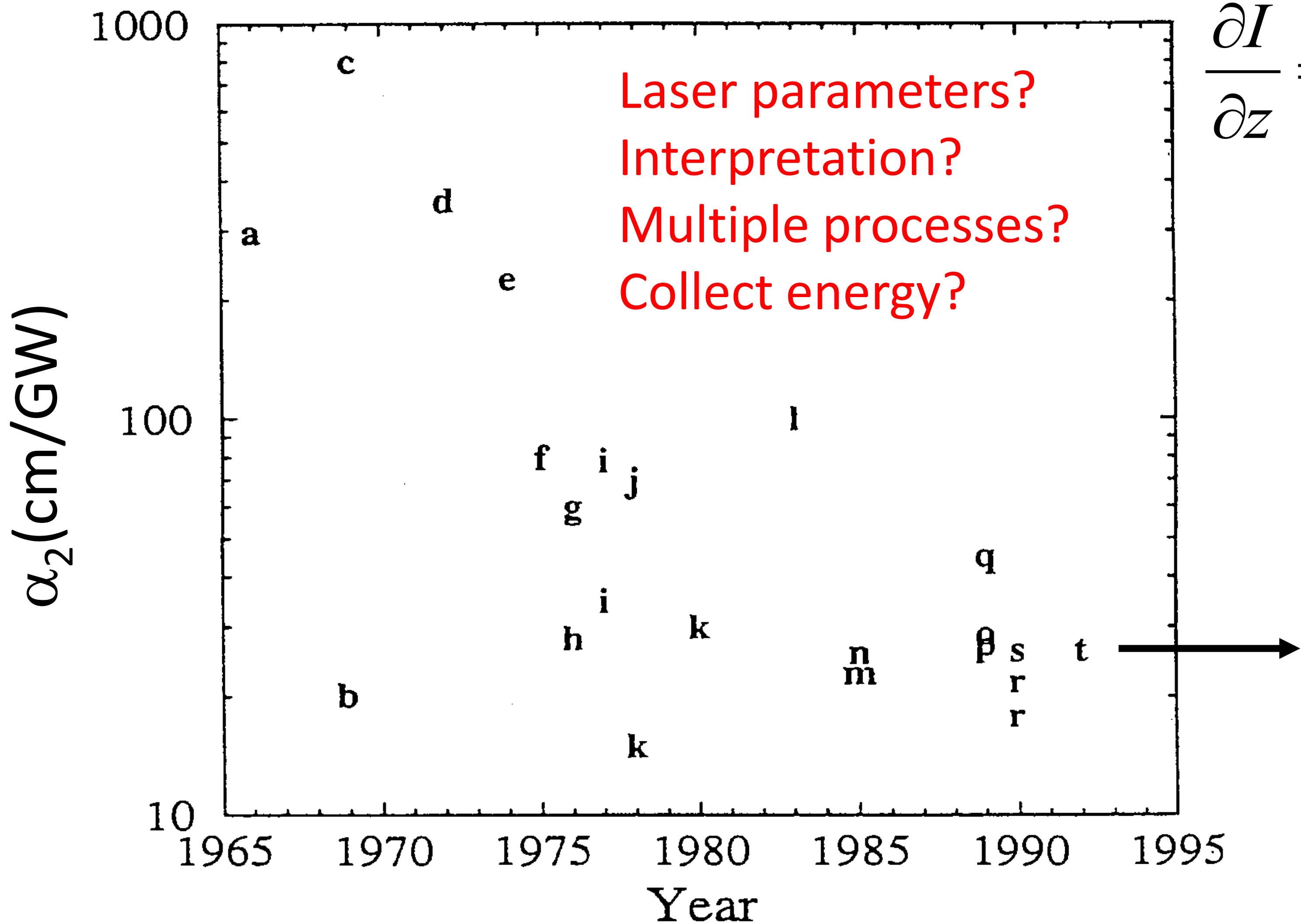




$$T = \frac{\text{Energy Transmitted}}{\text{Energy In}}$$

$$\frac{\partial I}{\partial z} = -\alpha_2 I^2$$

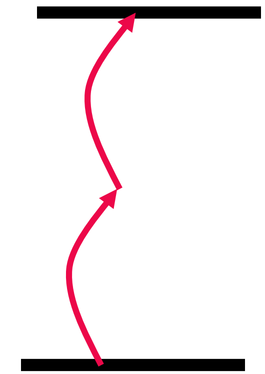
# Materials Characterization

## Reported value of 2PA coefficient of GaAs at 1μm vs. year

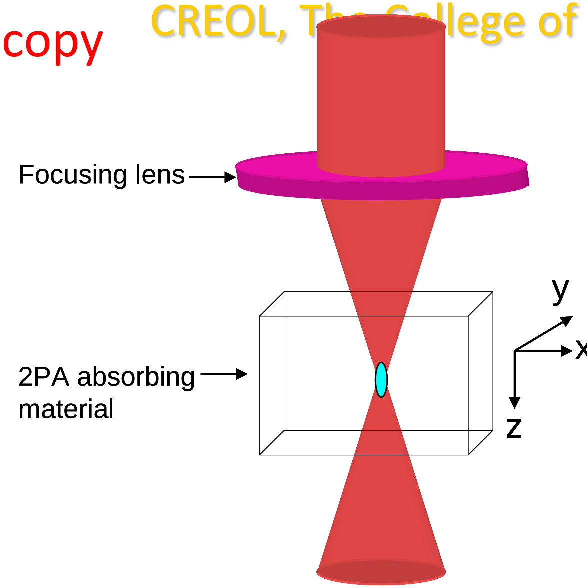



Laser parameters?
Interpretation?
Multiple processes?
Collect energy?

$$\frac{\partial I}{\partial z} = -\alpha_2 I^2$$



Opt. Lett. 10, 490 (1985)



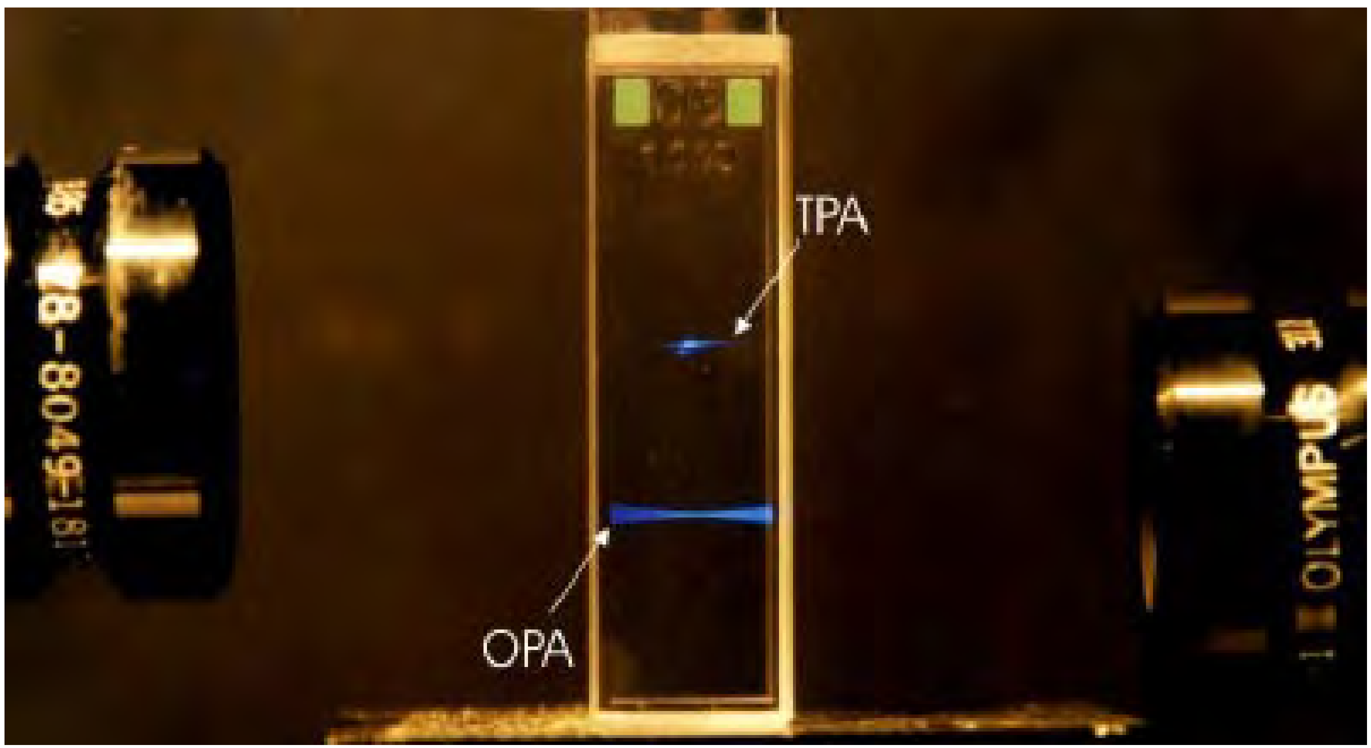

$I \propto z^{-2}$

↓

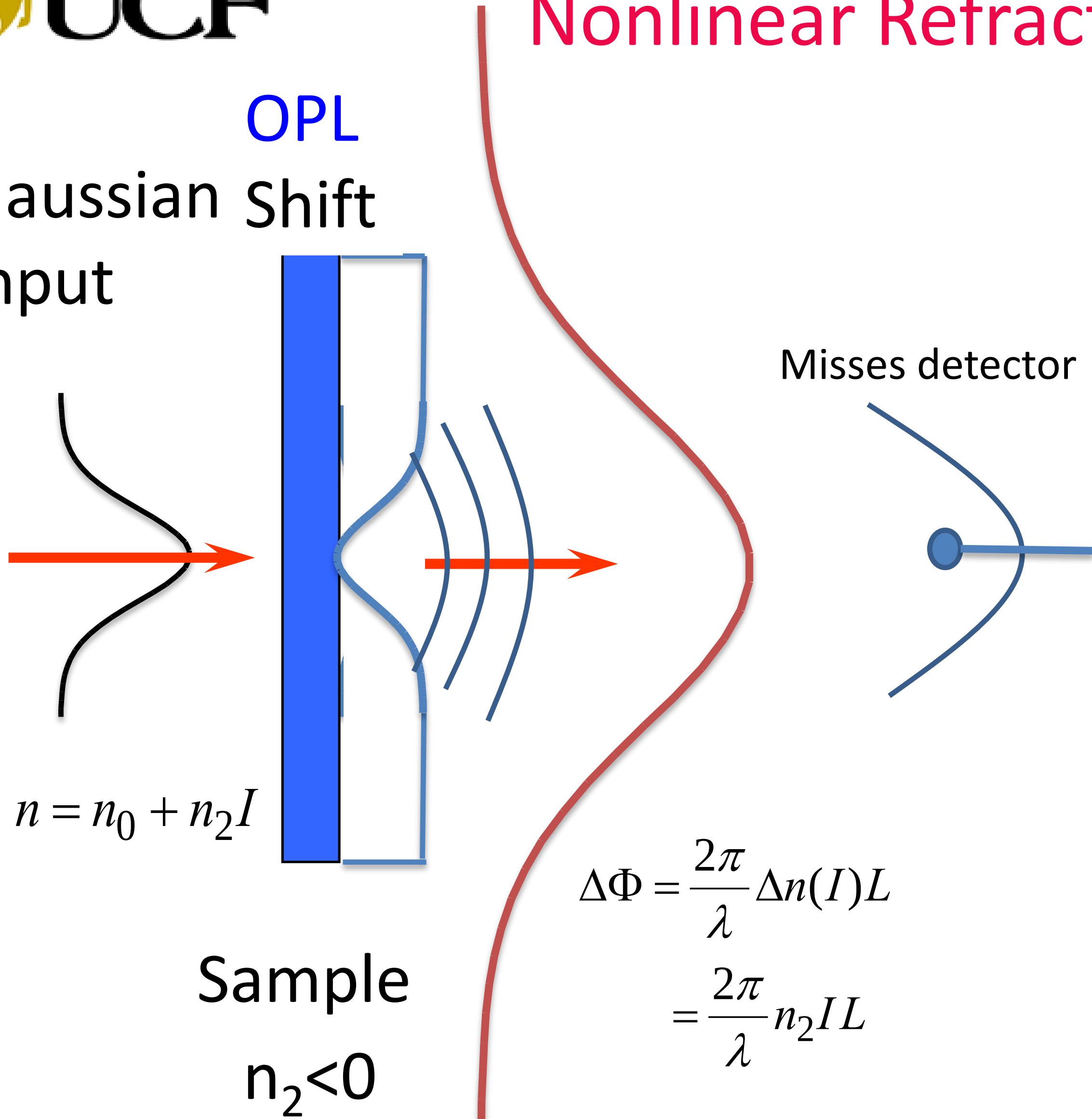
$2PA \propto I^{2}$

↓

$2PA \propto z^{-4}$



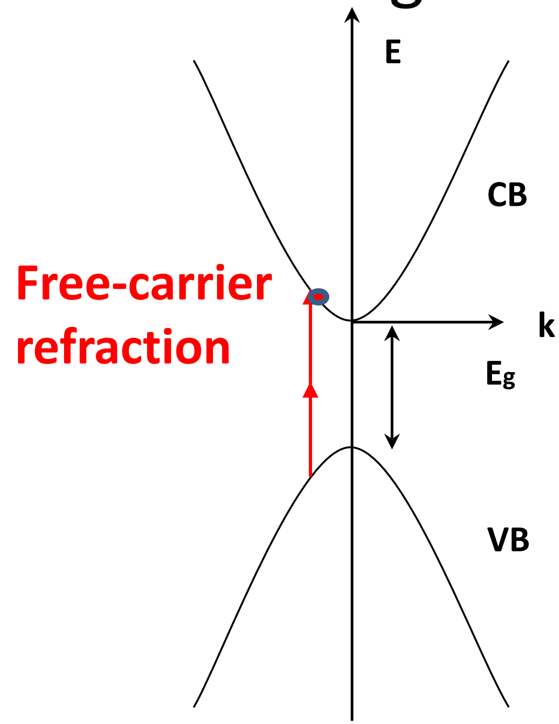
# Nonlinear Refraction

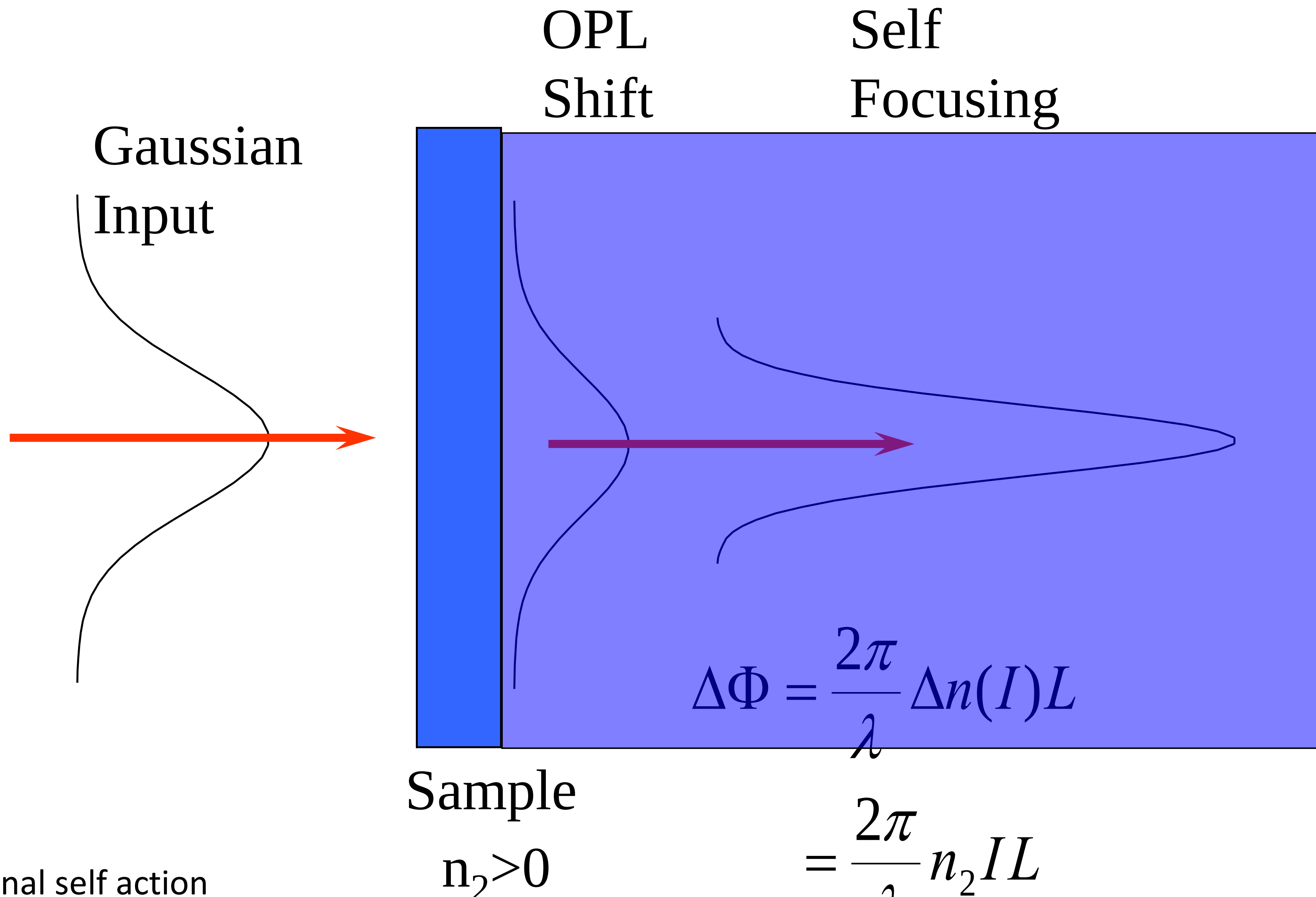



$$n = n_0 + n_2 I$$

$$\Delta\Phi = \frac{2\pi}{\lambda}\Delta n(I)L = \frac{2\pi}{\lambda}n_2 I L$$

Self de-focusing






$$\Delta\Phi = \frac{2\pi}{\lambda}\Delta n(I)L = \frac{2\pi}{\lambda} n_2 I L$$

External self action
- Kaplan

# Normally "see" linear media

$D = \varepsilon_0 E + P$ *P* is a materials property for small $E$, $P = \varepsilon_0 \chi^{(1)} E$

But, for $E \approx E_{atom} \approx \frac{1}{4\pi\varepsilon_0}\frac{e}{a_0^2} \approx 5x10^{11}\frac{V}{m}$ ; where $a_0$=Bohr radius

$$P \approx \varepsilon_0(\chi^{(1)} : E + \quad \chi^{(2)} : EE + \quad \chi^{(3)} : EEE + \quad \ldots \quad )$$

## Nico Bloembergen

**Nicolaas Bloembergen** (Dordrecht, March 11, 1920). PhD from Univ. of Leiden in 1948 - left the war ravaged Netherlands in 1945 for graduate studies at Harvard. Six weeks earlier Harvard Professor Edward Purcell discovered NMR. Nico shared the 1981 Nobel Prize in Physics with Arthur Schawlow and Kai Siegbahn for laser spectroscopy.

the first two terms are comparable when

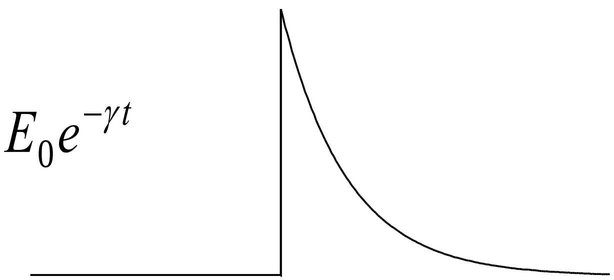
$$\chi^{(2)} \approx \frac{\chi^{(1)}}{E_{atom}} \approx \frac{1}{E_{atom}} \approx 2x10^{-12}\frac{m}{V} \approx 2\frac{pm}{V}$$

BUT $$P(t) = \varepsilon_0 \int_{-\infty}^{\infty} dt' \chi_e(t-t') E(t')$$

For example $\chi_e(t) = \chi_0 e^{-\gamma t}$

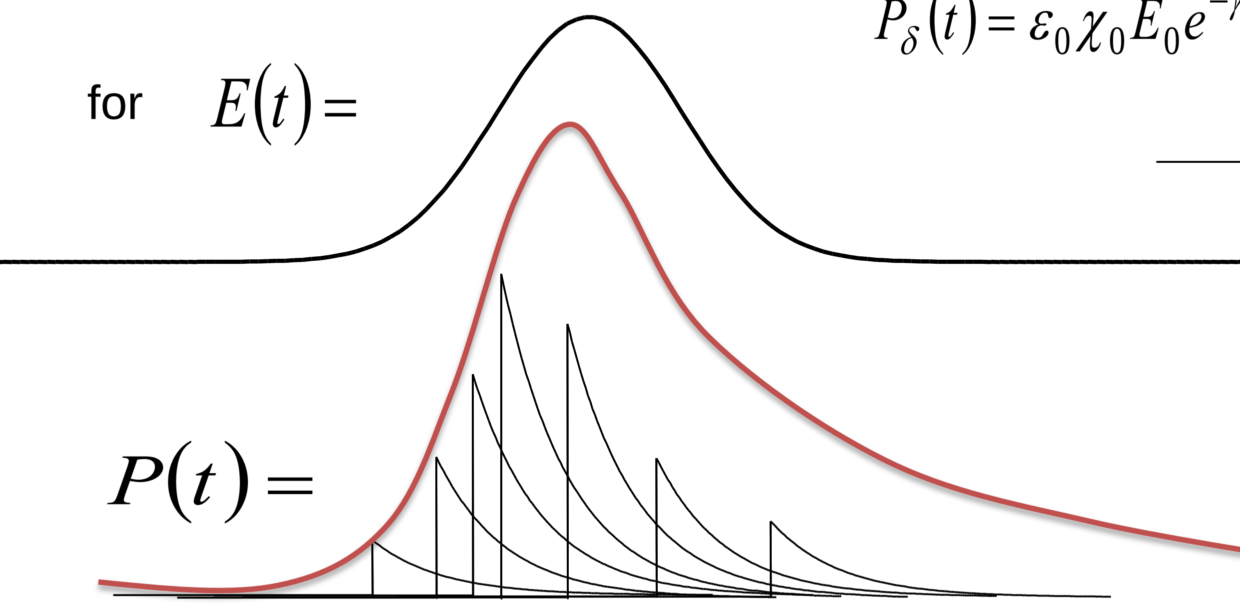
$$P(t) = \varepsilon_0 \int_{-\infty}^{\infty} \chi_0 e^{-\gamma(t-t')} E(t') dt'$$ for $E(t') = E_0 \delta(t')$

$$P_\delta(t) = \varepsilon_0 \chi_0 E_0 e^{-\gamma t}$$



for $E(t) =$

$P(t) =$



BUT $$P_i(\vec{r},t) = \varepsilon_0 [\int_{-\infty}^{t} \chi_{ij}^{(1)}(t-t')E_j(t')dt'$$

$$+ \int_{-\infty}^{t}\int_{-\infty}^{t} \chi_{ijk}^{(2)}(t-t',t-t'')) \, E_j(t')E_k(t'')dt'dt''$$

$$+ \int_{-\infty}^{t}\int_{-\infty}^{t}\int_{-\infty}^{t} \chi_{ijk\ell}^{(3)}(t-t',t-t'',t-t''') \, E_j(t')E_k(t'')E_\ell(t''')dt'dt''dt''' + \ldots]$$

---

$$P(t) \approx \varepsilon_0(\chi^{(1)} : E + \quad \chi^{(2)} : EE + \quad \chi^{(3)} : EEE + \quad \ldots \quad )$$

only for ‘ultrafast’ bound-electronic nonlinearities far from resonance (note: this is in the time domain)

$$P(\omega) = \varepsilon_0 \chi^{(1)}(\omega) E(\omega)$$ etc. in frequency domain

I will discuss ultrafast nonlinear absorption and refraction but also mention other ‘slower’ NLO responses and how this has led to some major discrepancies in the literature.

Actually:

BUT
$$P_i(\vec{r},t)=\varepsilon_0[\int_{-\infty}^{\infty}\int_{-\infty}^{t}\chi_{ij}^{(1)}(\vec{r}-\vec{r}';t-t')E_j(\vec{r}',t')d\vec{r}'dt'$$

$$+\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{t}\int_{-\infty}^{t}\chi_{ijk}^{(2)}(\vec{r}-\vec{r}',\vec{r}-\vec{r}'';t-t',t-t''))$$

$$\text{x } E_j(\vec{r}',t')E_k(\vec{r}'',t'')d\vec{r}'d\vec{r}''dt'dt''$$

$$+\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{t}\int_{-\infty}^{t}\int_{-\infty}^{t}\chi_{ijk\ell}^{(3)}(\vec{r}-\vec{r}',\vec{r}-\vec{r}'',\vec{r}-\vec{r}''';t-t',t-t'',t-t''')$$

$$x\, E_j(\vec{r}',t')E_k(\vec{r}'',t'')E_\ell(\vec{r}''',t''')d\vec{r}'d\vec{r}''d\vec{r}'''dt'dt''dt'''+...]$$

---

$$P\approx\varepsilon_0(\chi^{(1)}:E+\quad\chi^{(2)}:EE+\quad\chi^{(3)}:EEE+\quad...\quad)$$

only for ‘ultrafast’ bound-electronic nonlinearities far from resonance

This equation includes the possibility of nonlocal nonlinearities, e.g. thermal, where light at one position changes the abs. or index, at another position – for thermal this occurs by heat diffusion.

For ultrafast, bound-electronic nonlineairites

$$P \approx \varepsilon_0(\chi^{(1)} : E + \quad \chi^{(2)} : EE + \quad \chi^{(3)} : EEE + \quad \ldots \quad )$$

$P \approx \varepsilon_0(\chi^{(1)} : E)$ $\cos\omega t : \omega$ $\chi^{(1)}$ gives α and $n_0$

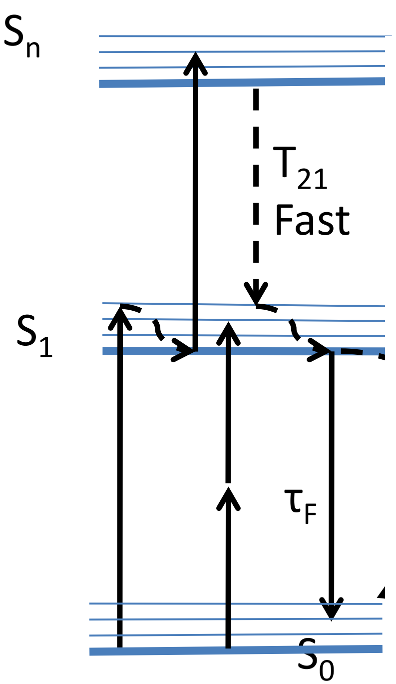
$P \approx \varepsilon_0(\chi^{(2)} : EE\ )$ $\cos^2\omega t : 0, 2\omega$ $\chi^{(2)}$ gives SHG and OPO's etc.

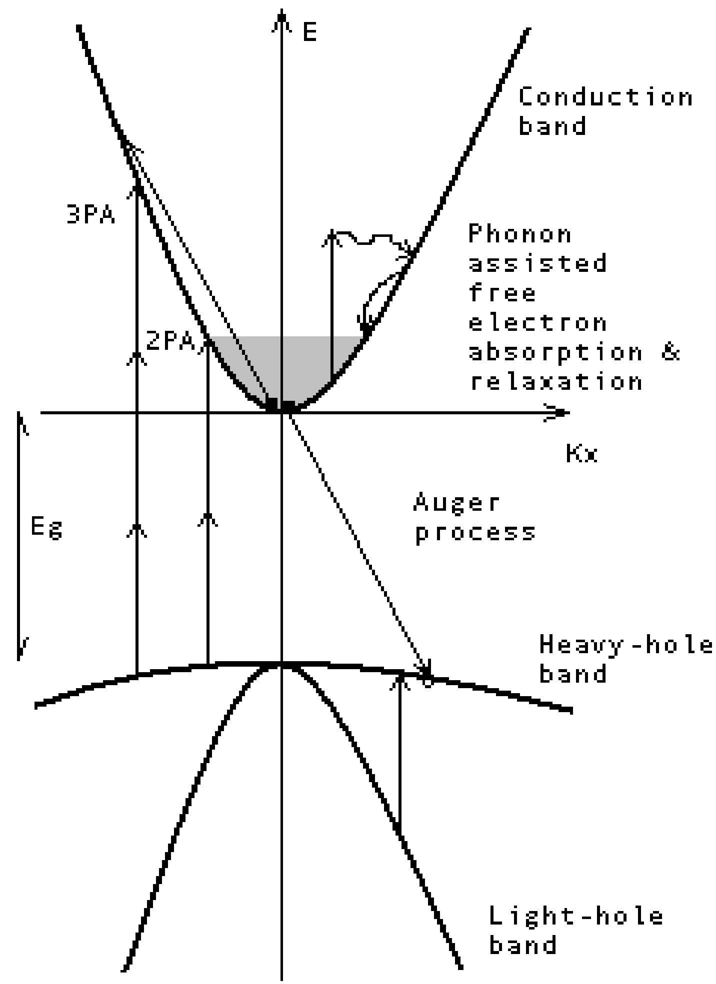
$P \approx \varepsilon_0(\chi^{(3)} : EEE\ )$ $\cos^3\omega t : \omega, 3\omega$ $\chi^{(3)}$ gives 2PA and $n_2$ & THG & etc. etc. etc.

I'll talk about 2PA and $n_2$, but also other NLA and NLR mechanisms not described well by $\chi^{(3)}$

$$\frac{\partial I}{dz} = -\frac{\omega\mu_0}{n^2}\left(\operatorname{Im}\chi_{eff}^{(3)}\right)I^2 \equiv -\alpha_2 I^2 \qquad \frac{\partial\varphi}{dz} = \frac{\omega\mu_0}{2n^2}\left(\operatorname{Re}\chi_{eff}^{(3)}\right)I \equiv k_0 n_2 I$$

# Typical processes for
# NL Absorption
# NL Refraction




Organics

Solvents

Semiconductors

# Facilities





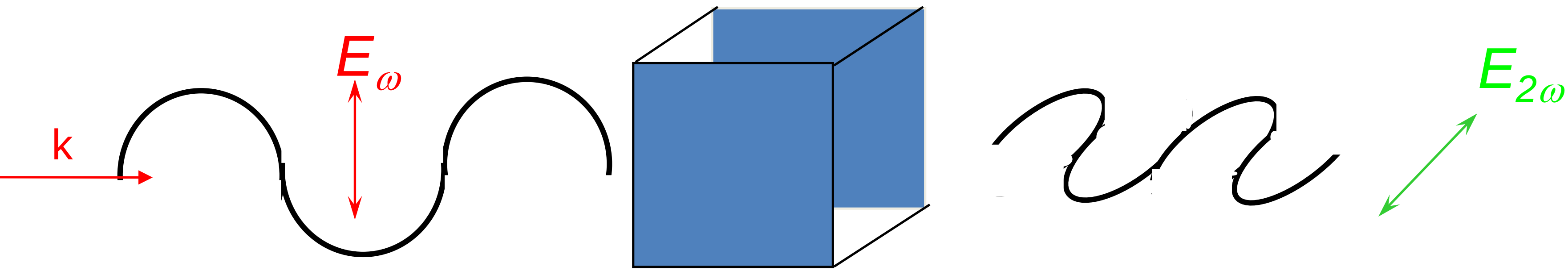
- Tunable femtosecond OPG/A 250 nm -11μm
- Tunable picosecond OPG/A – 450 nm - 18 μm
- Tunable nanosecond OPO – 450 nm – 1.7 μm

# Outline

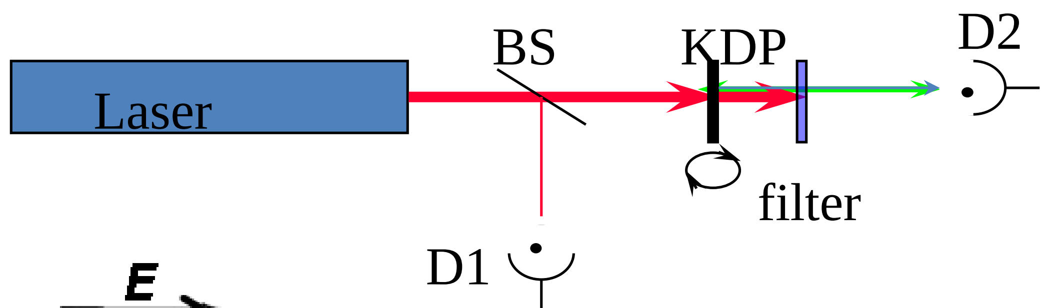
- Z-scan
  - WLC Z-scan
  - Seeded WLC
- Kramers-Kronig
  - Nondegenerate nonlinearities
- ISRE-Intermediate-State Resonance Enhancement
  - Gated Detection with ND 2PA
  - see IR with wide gap - IR 3D imaging
- Beam deflection – $CS_2$
- Organics
- Cascaded 2nd-order nonlinearities
- Bloembergen’s expansion

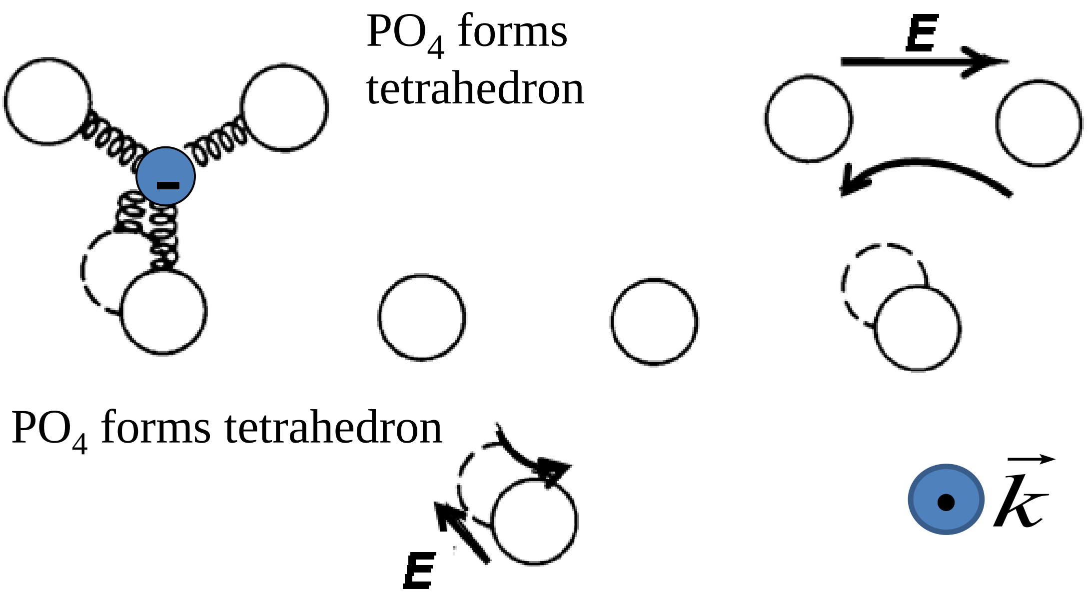
Nonlinear spectroscopy

# $\omega \rightarrow$ SHG $2\omega \rightarrow$



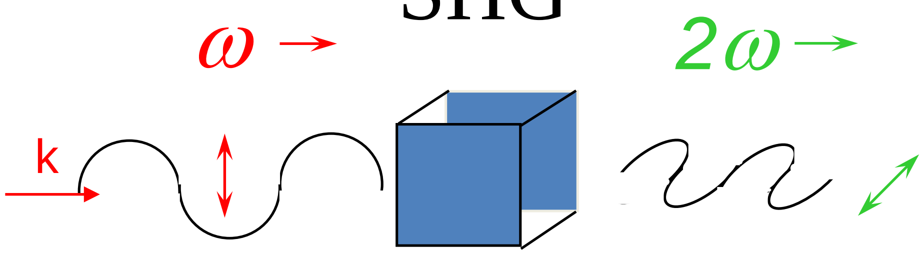

lattice without inversion symmetry



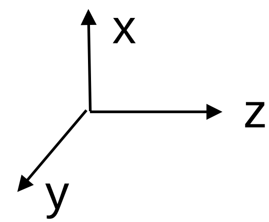




$e^-$'s have small mass and can respond in <fsec, "ultrafast" bound electronic response "instantaneous" - not really, have dispersion, linear & nonlinear. Nuclei move slower.

# SHG

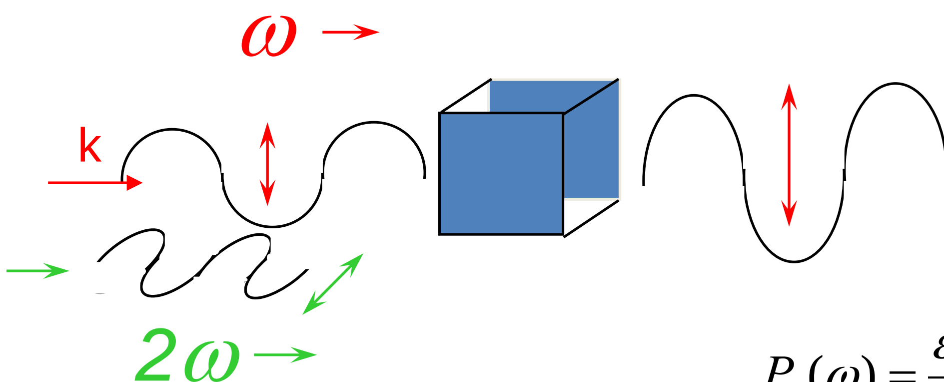



One input along principal axis
One 'eignemode' input

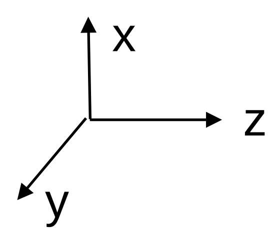



$$P_y(2\omega) = \frac{\varepsilon_0}{2}\chi_{yxx}(2\omega;\omega,\omega)E_x(\omega)E_x(\omega)$$

# DFG –down conversion




Two inputs along principal axes
Two 'eigenmode' inputs




$$P_x(\omega) = \frac{\varepsilon_0}{2}\chi_{xxy}(\omega;-\omega,2\omega)2E_x^*(\omega)E_y(2\omega)$$

$$\chi_{yxx}(2\omega;\omega,\omega) = \chi_{xxy}(\omega;-\omega,2\omega)$$

Wave Equation $$\nabla^2 E - \frac{1}{c^2}\frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P}{\partial t^2} = \mu_0 \frac{\partial^2 P_L}{\partial t^2} + \mu_0 \frac{\partial^2 P_{NL}}{\partial t^2}$$

---

$$P = \varepsilon_0\left(1+\chi^{(1)}\right)E - \varepsilon_0 E = \varepsilon_0\left(1+\chi^{(1)\prime} + i\chi^{(1)\prime\prime}\right)E - \varepsilon_0 E$$
$$= \varepsilon_0 n^2 E + i\varepsilon_0 \chi^{(1)\prime\prime} E - \varepsilon_0 E$$

---

1D $$\frac{\partial^2 E}{\partial z^2} - \left(\frac{n}{c}\right)^2 \frac{\partial^2 E}{\partial t^2} - i\frac{\chi^{(1)\prime\prime}}{c^2}\frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P_{NL}}{\partial t^2}$$

linear
losses

$E = \frac{1}{2}\mathcal{E}(z,t)e^{i(kz-\omega t)} + c.c.$ where $\mathcal{E}(z,t)$ is the SVE. The same for $\mathcal{P}_{NL}(z,t)$

$P = \frac{1}{2}\mathcal{P}_{NL}(z,t)e^{i(k_{NL}z-\omega t)} + c.c.$ $\omega$ Could be $2\omega$, $\omega_1 + \omega_2$ or …

$$\frac{\partial^2 E}{\partial t^2} = \frac{\partial}{\partial t}\left\{\left[\frac{\partial \mathcal{E}}{\partial t} - i\omega\mathcal{E}\right]\frac{e^{i(kz-\omega t)}}{2}\right\} + cc = \left[\frac{\partial^2 \mathcal{E}}{\partial t^2} - \omega^2\mathcal{E} - 2i\omega\frac{\partial \mathcal{E}}{\partial t}\right]\frac{e^{i(kz-\omega t)}}{2} + cc$$

$$\frac{\partial^2 E}{\partial z^2} = \left[ \frac{\partial^2 \mathcal{E}}{\partial z^2} - k^2 E + 2ik \frac{\partial \mathcal{E}}{\partial z} \right] \frac{e^{i(kz-\omega t)}}{2} + cc$$

Neglect 2nd derivatives of SV quantities & other small terms SVEA=SVAP

Plug into 1D Eq. $\frac{\partial^2 E}{\partial z^2} - \left(\frac{n}{c}\right)^2 \frac{\partial^2 E}{\partial t^2} - i \frac{\chi^{(1)"}}{c^2} \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P_{NL}}{\partial t^2}$

$$\left\{ -k^2 \mathcal{E} + 2ik \frac{\partial \mathcal{E}}{\partial z} + \left[ \left(\frac{n}{c}\right)^2 + i \frac{\chi^{(1)"}}{c^2} \right] \left[ \omega^2 \mathcal{E} + 2i\omega \frac{\partial \mathcal{E}}{\partial t} \right] \right\} \frac{e^{i(kz-\omega t)}}{2}$$

$$= -\mu_0 \left[ \omega^2 \mathcal{P}_{NL} + 2i\omega \frac{\partial \mathcal{P}_{NL}}{\partial t} \right] \frac{e^{i(k'z-\omega t)}}{2}$$

Note the $k'$ or $k_{NL}$

neglect

Neglect product

$$2ik \frac{\partial \mathcal{E}}{\partial z} + 2i\omega \left(\frac{n}{c}\right)^2 \frac{\partial \mathcal{E}}{\partial t} + i \frac{\chi^{(1)"}}{c^2} \omega^2 \mathcal{E} = -\mu_0 \omega^2 \mathcal{P}_{NL} e^{i(k'-k)z}$$

Linear loss

$k = n$“$\omega$”$/c$ ; whatever “$\omega$” is

$k$ goes with $\mathcal{E}$ and $k'$ goes with $\mathcal{P}_{NL}$

$$\frac{\partial \mathcal{E}}{\partial z} + \left(\frac{n}{c}\right)\frac{\partial \mathcal{E}}{\partial t} + \frac{\chi^{(1)}{}'' \omega}{2nc}\mathcal{E} = i\frac{\mu_0 \omega c}{2n}\mathcal{P}_{NL} e^{i(k'-k)z} = i\frac{\omega}{2n\varepsilon_0 c}\mathcal{P}_{NL} e^{i(k'-k)z}$$

$\alpha/2$ or $\alpha = \chi^{(1)''}\omega/nc$

i.e. long pulse

If the pulse duration is such that $1/L >> n/(ct_p)$, we can neglect the $\frac{n}{c}\frac{\partial}{\partial t}$ term wrt, $\frac{\partial}{\partial z}$ and then: $\left(\frac{\partial}{\partial z} + \frac{\alpha}{2}\right)E = i\frac{\omega}{2nc\varepsilon_0}P_{NL} e^{i(k'-k)z}$

Otherwise, change coordinate systems to travel

along with the pulse, $\tau \equiv t - \frac{nz}{c}$, the retarded time.

$$\tau \equiv t - \frac{nz}{c}; \quad z \equiv z'; \quad \mathcal{E}(z,t) \rightarrow \mathcal{E}(z',\tau) \qquad \text{etc.}$$

This will eliminate the d/dt term.

# Important result from SVEA

$$2ik\frac{\partial \mathcal{E}}{\partial z} = -\mu_0 \omega^2 \mathcal{P}_{NL} e^{i\left(\vec{k}' - \vec{k}\right)\cdot\vec{z}}$$

$k = n$"$\omega$"$/c$ ; whatever "$\omega$" is

$k$ goes with $\mathcal{E}$ and $k'$ goes with $\mathcal{P}_{NL}$

Where $\mathcal{E}$ and $\mathcal{P}_{NL}$ are slowly varying quantities,

i.e., no cos($kz$-$\omega t$).

# Important result

$$2ik\frac{\partial\mathcal{E}}{\partial z} = -\mu_0\omega^2\mathcal{P}_{NL}e^{i(k'-k)z}$$

$k=n$"$\omega$"$/c$ ; whatever "$\omega$" is

$k$ goes with $\mathcal{E}$ and $k'$ goes with $\mathcal{P}_{NL}$

Using proper factors of 2 in susceptibility expansion

$$2ik_{2\omega}\frac{\partial\mathcal{E}_{2\omega}}{\partial z} = -\mu_0(2\omega)^2\varepsilon_0\chi^{(2)}\mathcal{E}_\omega\mathcal{E}_\omega e^{i(2k_\omega-k_{2\omega})z}$$

$$\frac{\partial\mathcal{E}_{2\omega}}{\partial z} = i\frac{\omega\chi^{(2)}}{2cn_{2\omega}}\mathcal{E}_\omega\mathcal{E}_\omega e^{i\Delta k z}$$

similarly

$$\frac{\partial\mathcal{E}_{\omega}}{\partial z} = i\frac{\omega\chi^{(2)}}{2cn_{\omega}}\mathcal{E}_{2\omega}\mathcal{E}_{-\omega} e^{-i\Delta k z}$$

We'll use these later for cascading.

# For $\chi^{(3)}$ giving "self" nonlinearities

$$2ik_\omega \frac{\partial \mathcal{E}_\omega}{\partial z} \approx -\mu_0 \omega^2 \varepsilon_0 \chi^{(3)} \mathcal{E}_\omega \mathcal{E}_\omega \mathcal{E}_{-\omega} \qquad \vec{k} = \vec{k}'$$

$$\frac{\partial \mathcal{E}_\omega}{\partial z} = i \frac{\omega}{2n_0 c} \chi^{(3)} \mathcal{E}_\omega \left|\mathcal{E}_\omega\right|^2$$

Slowly varying

$$\mathcal{E}_\omega = \sqrt{I} e^{i\varphi} \qquad \Rightarrow \frac{\partial I}{\partial z} = -\frac{\omega \mu_0}{n_0^2} \operatorname{Im} \chi^{(3)} I^2 \equiv -\alpha_2 I^2$$

and

$$\frac{\partial \varphi}{\partial z} = \frac{\omega \mu_0}{2n_0^2} \operatorname{Re} \chi^{(3)} I \equiv k_0 n_2 I$$

$$E(z,t) = A(z,t)e^{i\varphi(z,t)}$$

$$\chi^{(3)} = \chi_r^{(3)} + i\chi_i^{(3)} = \mathrm{Re}\,\chi_{eff}^{(3)} + i\,\mathrm{Im}\,\chi_{eff}^{(3)}$$

$$\frac{\partial E}{dz} + \frac{n}{c}\frac{\partial E}{dt} = i\frac{\omega}{2nc}\chi^{(3)}\frac{|E|^2}{2}E$$

$$\frac{\partial A}{dz} + i\frac{\partial \varphi}{dz}A + \frac{n}{c}\frac{\partial A}{dt} + \frac{in}{c}\frac{\partial \varphi}{dt}A = i\frac{\omega}{2nc}\chi^{(3)}\frac{A^3}{2}$$

Show 2PF movie

Kevin Belfield

$$\mathrm{Re}: \frac{\partial A}{dz} + \frac{n}{c}\frac{\partial A}{dt} = -\frac{\omega}{2nc}\chi_i^{(3)}\frac{A^3}{2}; \qquad \chi_i^{(3)} = \mathrm{Im}\,\chi_{eff}^{(3)}$$

$$\mathrm{Im}: A\frac{\partial \varphi}{dz} + \frac{An}{c}\frac{\partial \varphi}{dt} = \frac{\omega}{2nc}\chi_r^{(3)}\frac{A^3}{2}; \qquad \chi_r^{(3)} = \mathrm{Re}\,\chi_{eff}^{(3)}$$

$$\frac{\partial A^2}{dz} + \frac{n}{c}\frac{\partial A^2}{dt} = -\frac{\omega}{2nc}\chi_i^{(3)}A^4 \qquad \times\left\{\frac{c\varepsilon_0 n}{2}\right\}$$

$$\Rightarrow \frac{\partial I}{dz} + \frac{n}{c}\frac{\partial I}{dt} = -\frac{\omega}{2nc}\chi_i^{(3)}\frac{I^2 2}{c\varepsilon_0 n} = -\frac{\omega}{n^2c^2\varepsilon_0}\chi_i^{(3)}I^2 \equiv -\alpha_2 I^2 = -\frac{\omega}{n^2c^2\varepsilon_0}\left(\frac{3}{2}\chi_i^{(3)}{}_{xxxx}\right)I^2$$

And $\beta$ is often used in place of $\alpha_2$ as the two-photon absorption coefficient (2PA)
TPA is used by most people except me! Since 3PA…..

usually $\frac{\partial}{dz} \rangle\rangle \frac{1}{c}\frac{\partial}{dt} \Rightarrow \frac{\partial I}{dz} = -\alpha_2 I^2$

but can always go to the retarded frame as we did before.

$$\alpha_2 = \frac{\omega}{n^2 c^2 \varepsilon_0}\chi_i^{(3)}$$ where $\chi_i^{(3)}$ is Im$\chi_{eff}$

For example $\alpha_2 = \frac{\omega}{n^2 c^2 \varepsilon_0}\chi_i^{(3)} = \frac{3\omega}{2n^2c^2\varepsilon_0}\mathrm{Im}\,\chi_{xxxx}^{(3)}$ for light pol. in x at 1 wavelength

---

And for the real part of $\chi^{(3)}$

$$A\frac{\partial\varphi}{dz} + \frac{A}{c}\frac{\partial\varphi}{dt} = \frac{\omega}{2nc}\chi_r^{(3)}\frac{A^3}{2}; \qquad \chi_r^{(3)} = \mathrm{Re}\,\chi_{eff}^{(3)} \qquad \text{drop } \frac{\partial}{\partial t}$$

$$\Rightarrow \frac{\partial\varphi}{dz} = \frac{\omega}{2nc}\chi_r^{(3)}\frac{A^2}{2} \equiv k_0 n_2 \frac{A^2}{2} = k_0 n_2 \left\langle E^2 \right\rangle_t$$

$$n_2 \equiv \frac{\chi_r^{(3)}}{2n}$$ $n_2$ in m$^2$/V$^2$

or

$$\Rightarrow \frac{\partial\varphi}{dz} = \frac{\omega}{2nc}\chi_r^{(3)}\frac{2I}{2cn\varepsilon_0} = \frac{\omega}{2n^2c^2\varepsilon_0}\chi_r^{(3)} I$$

$$\frac{\partial\varphi}{dz} = \frac{\omega}{c}\frac{1}{2n^2c\varepsilon_0}\chi_r^{(3)} I \equiv k_0 n_2 I$$

$$n_2 = \frac{\chi_r^{(3)}}{2n^2c\varepsilon_0}$$ $n_2$ in m$^2$/W

$n_2$ is used in several unit systems, e.g. $n_2(esu) = \frac{cn_0}{40\pi} n_2(m^2/W)$

Units are understood from the context of the equation (but not always!).
e.g. above, the LHS uses <|*E*|$^2$> while the RHS uses *I*

$$\frac{\partial \varphi}{dz} = k_0 n_2 \left\langle E^2 \right\rangle_t \qquad \frac{\partial \varphi}{dz} = k_0 n_2 I$$

Unfortunately the literature is a mess for $n_2$ and even worse for $\chi^{(3)}$.

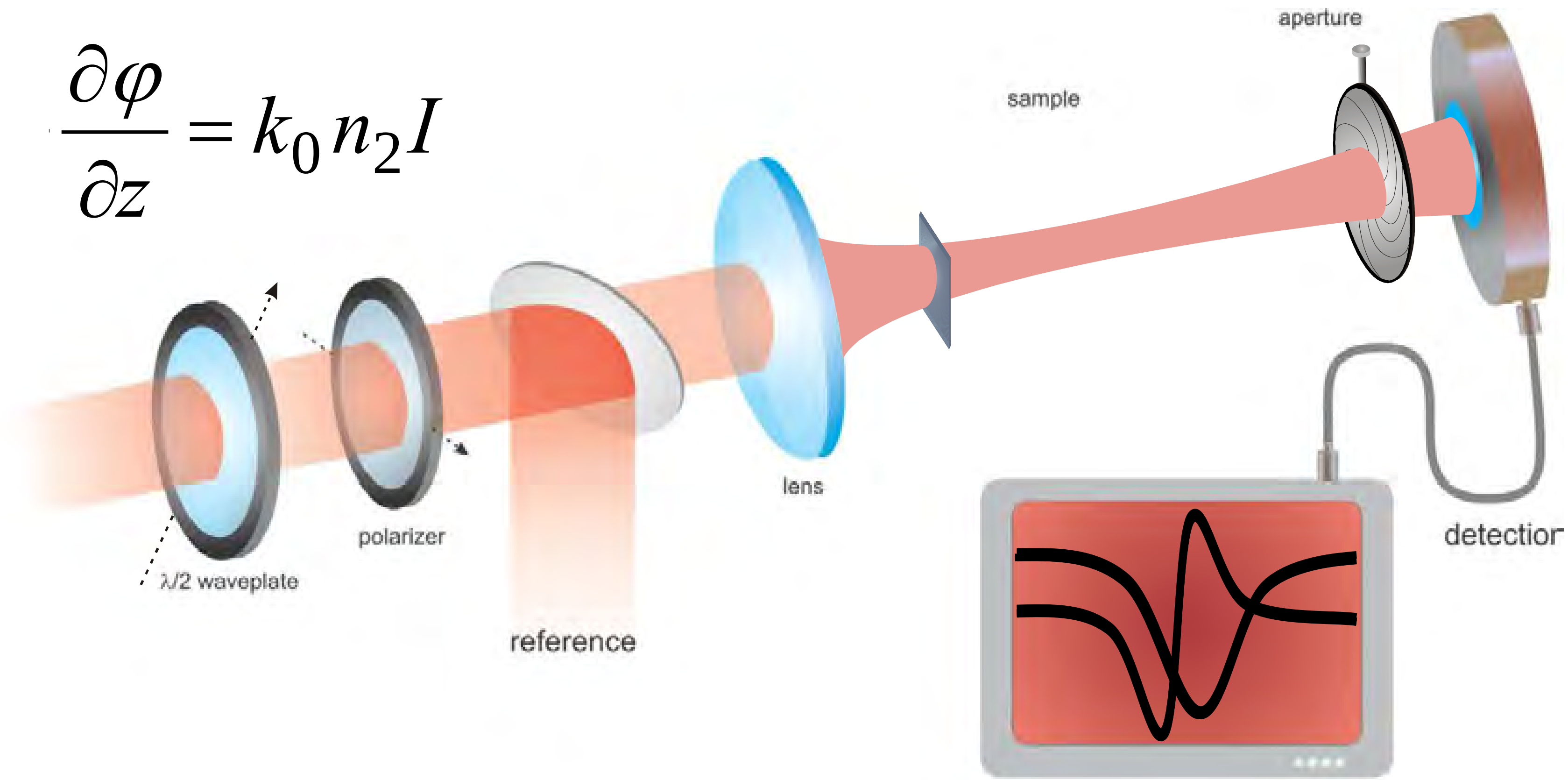
$$n_2(esu) = \frac{cn_0}{40\pi} n_2(m^2/W)$$

Useful for converting different author's papers in the literature
But – then trying to figure out factors of 2 is still a nightmare!

# Nonlinear Spectroscopy Techniques

- **<u>Z-Scan</u>** measures nonlinear absorption (e.g. 2PA) and nonlinear refraction simultaneously of various materials using a single beam

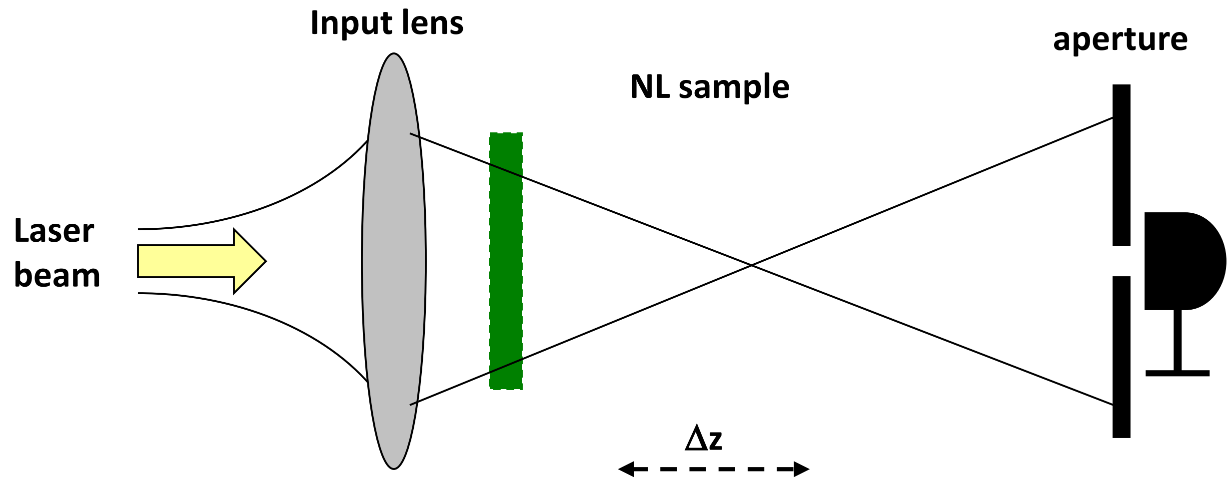
$$\frac{\partial \varphi}{\partial z} = k_0 n_2 I$$



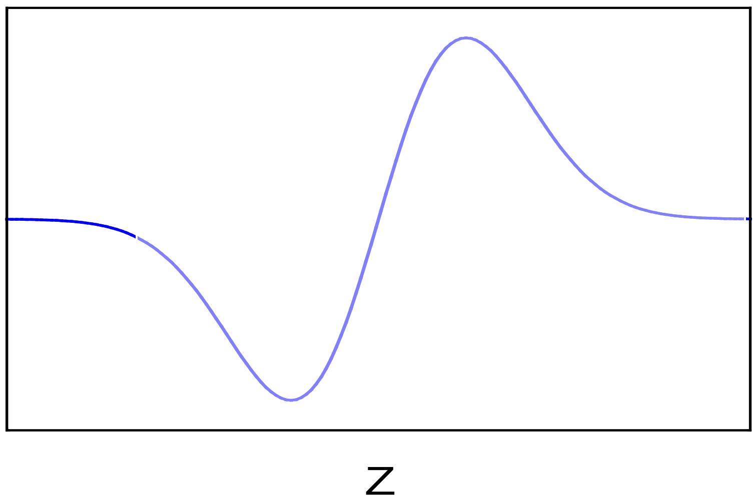

M. Sheik-Bahae, …, D.J. Hagan, & <u>E.W. Van Stryland</u>, *IEEE J. Quantum Electron.* **26**, 760 (1990)

>4400 citations

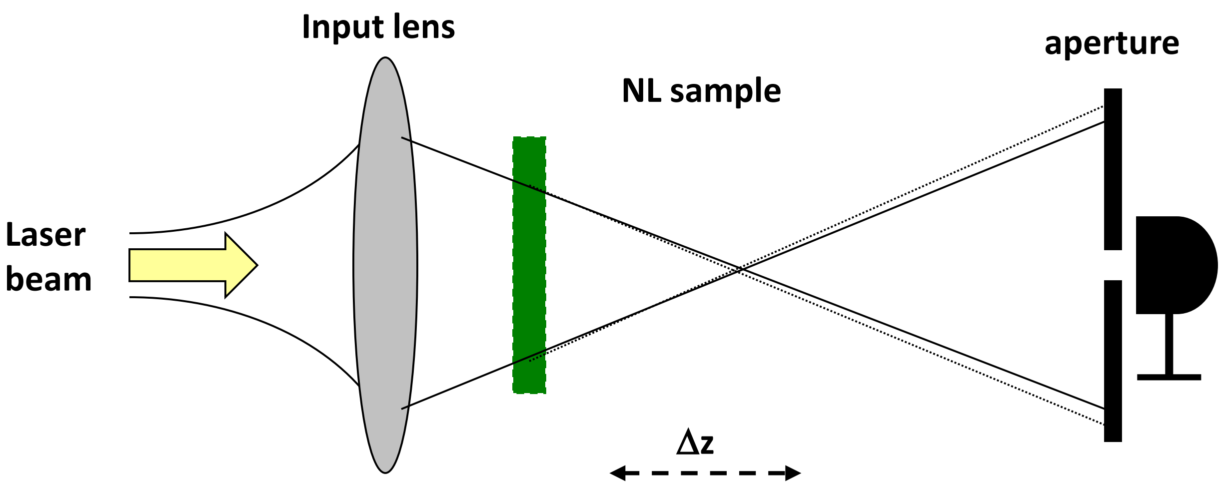
# “Closed” aperture Z-Scan

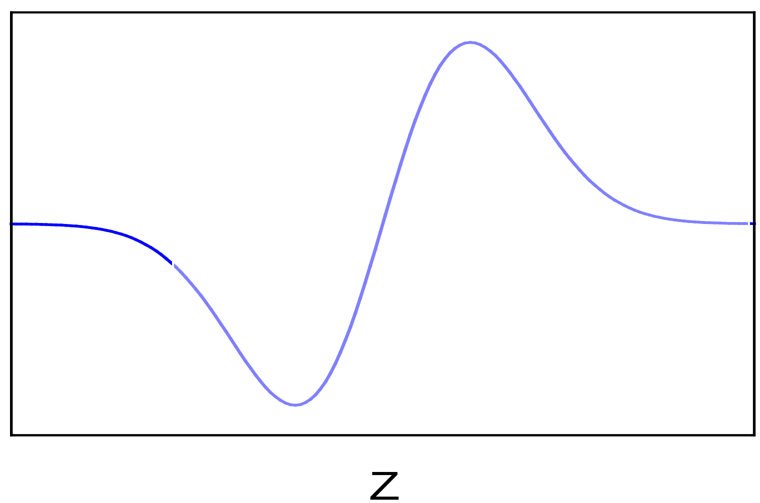


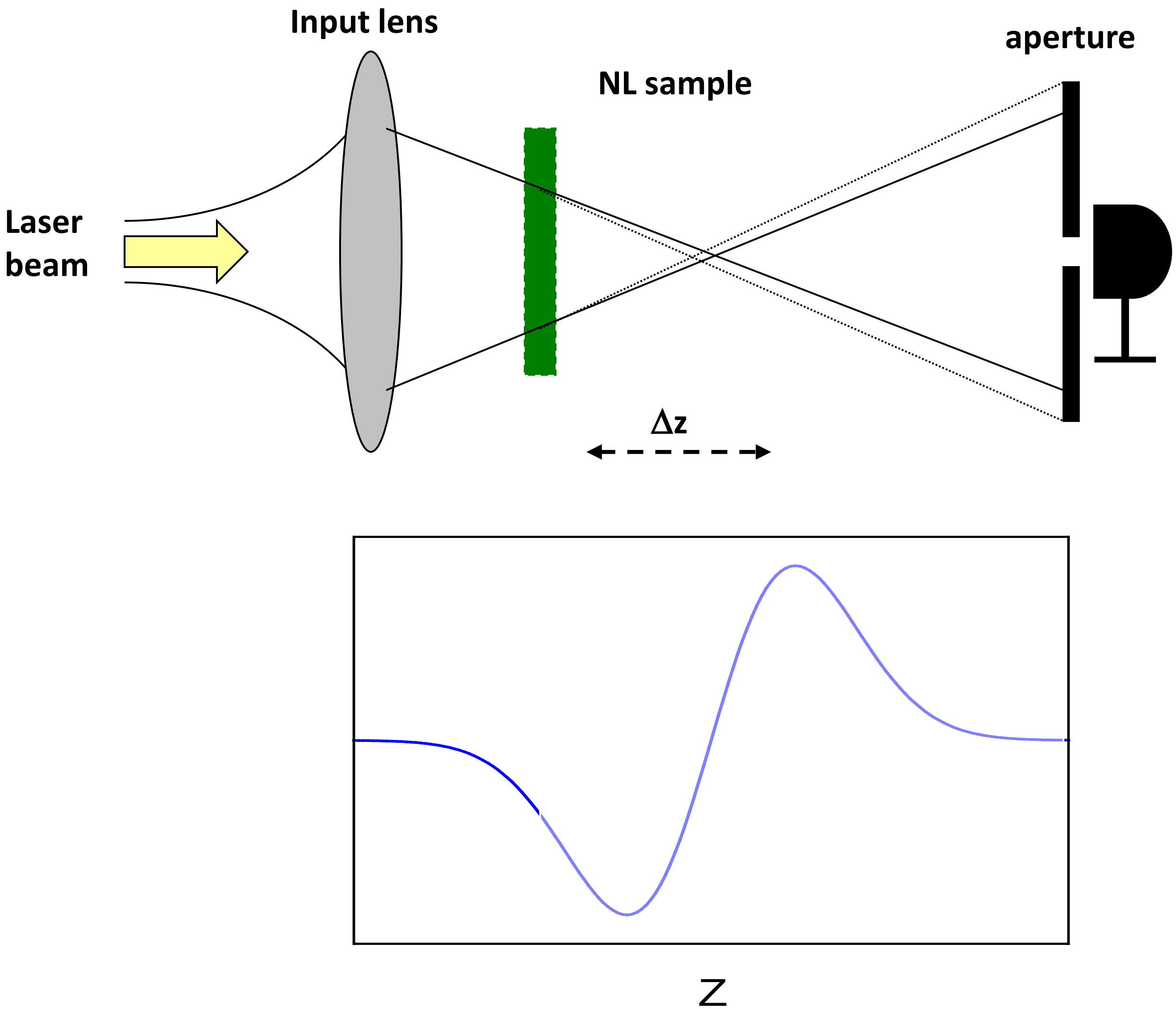

Self-focusing

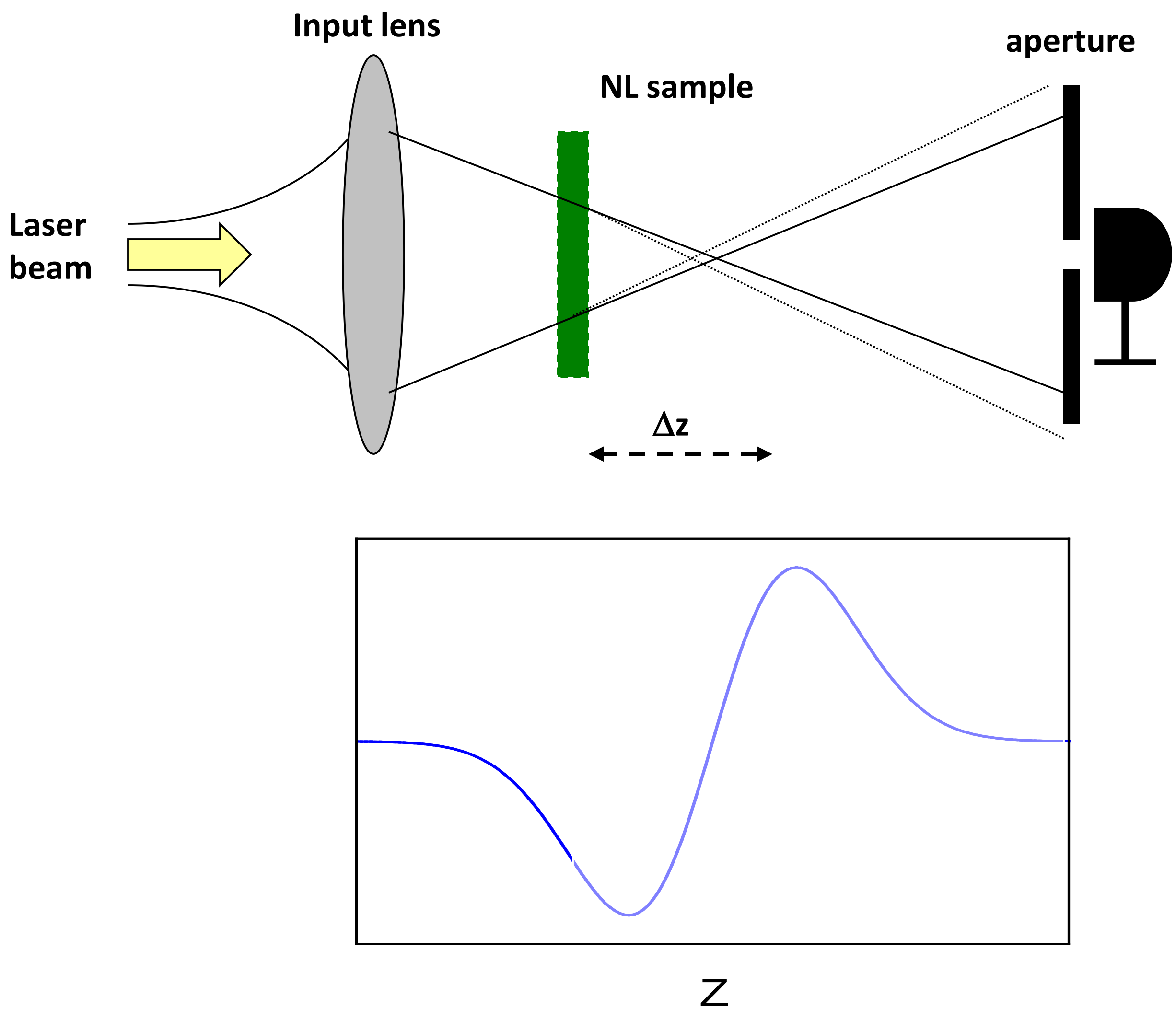


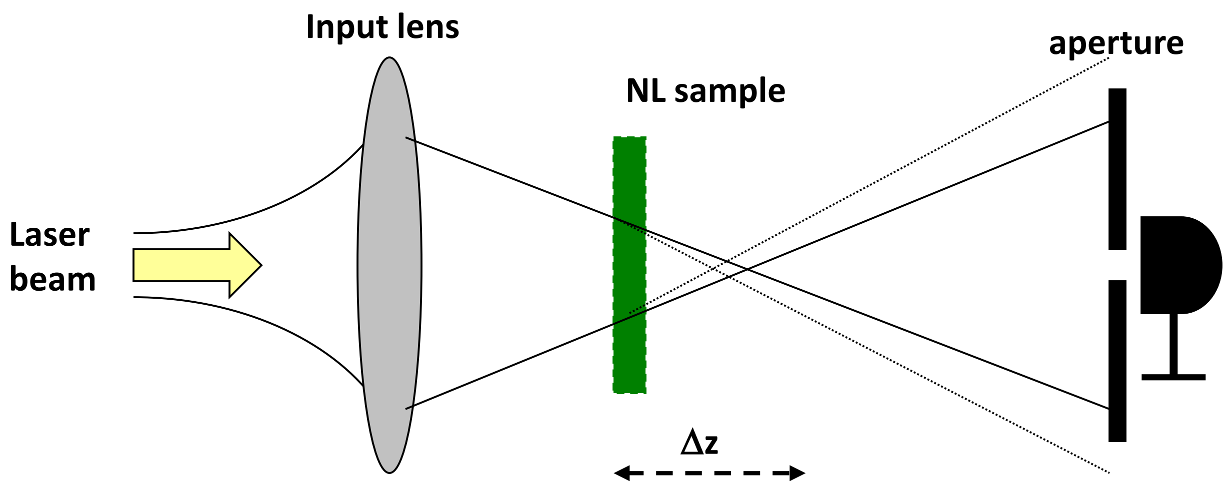

Opt. Lett. 14, 955-957 (1989).

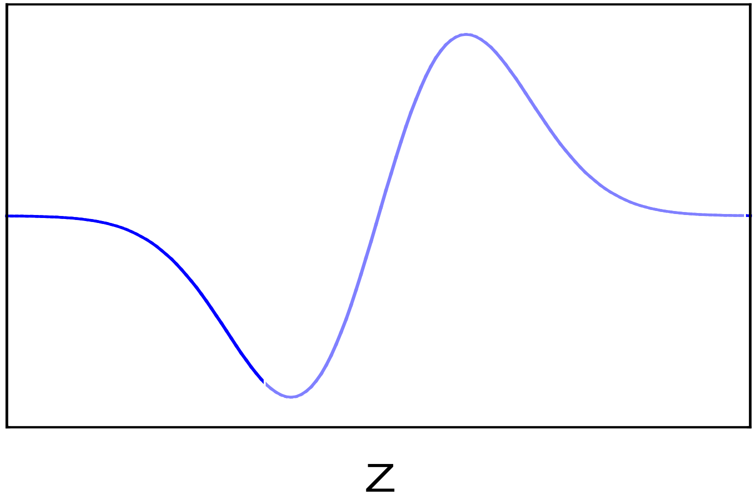

Input lens
aperture
NL sample
Laser
beam
Δz

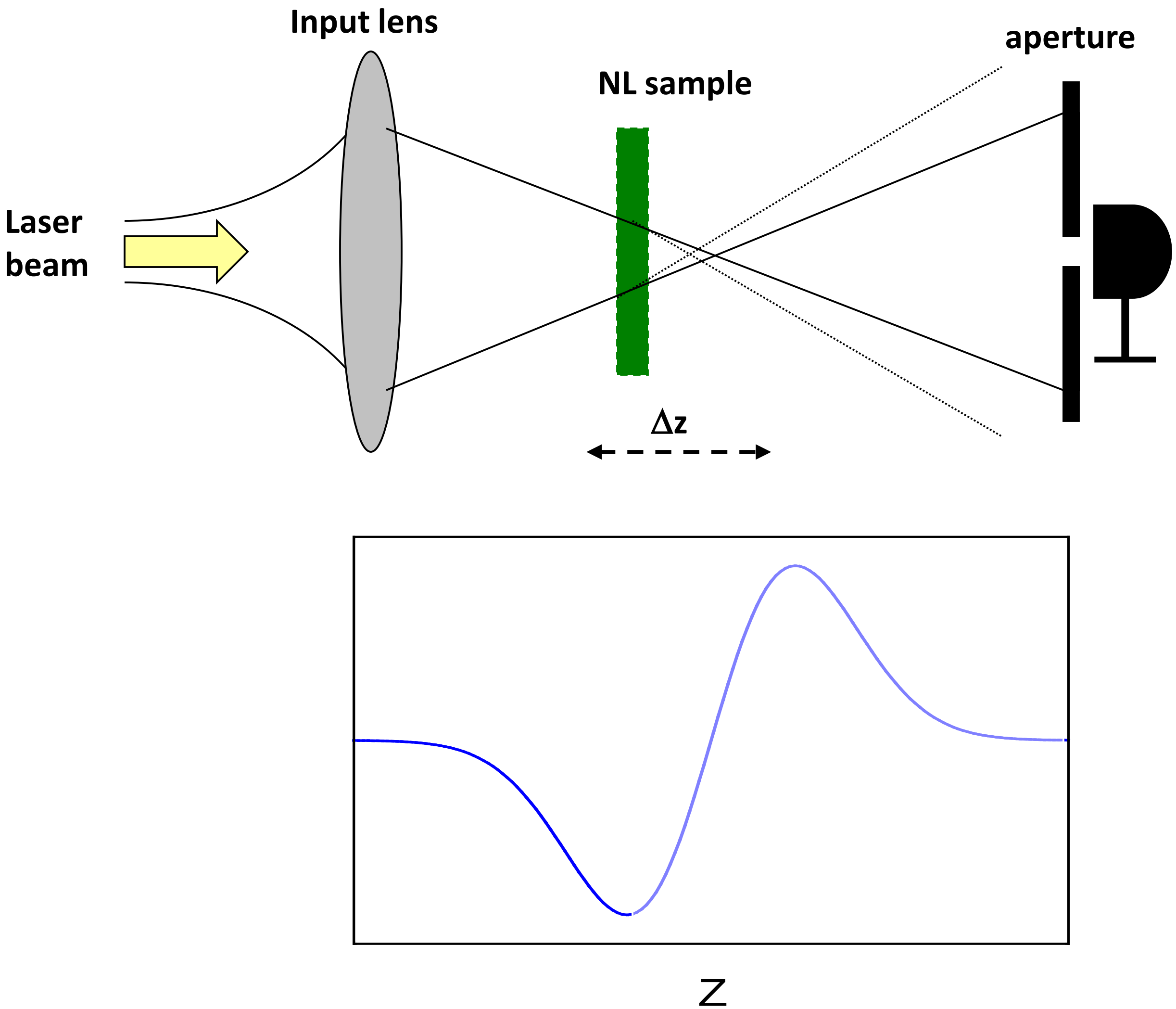

Z

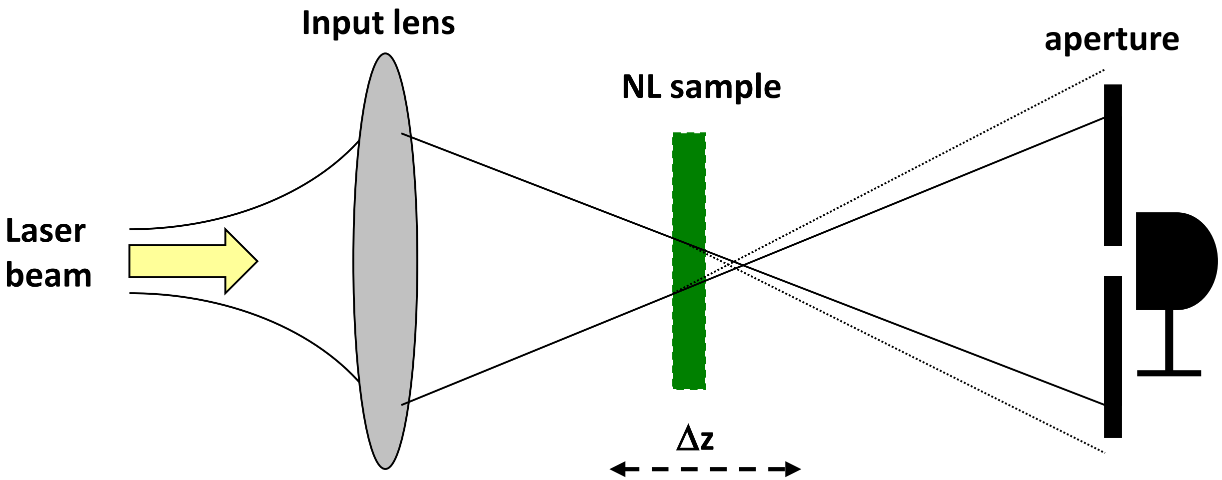

Input lens
aperture
NL sample
Laser
beam
Δz
Z

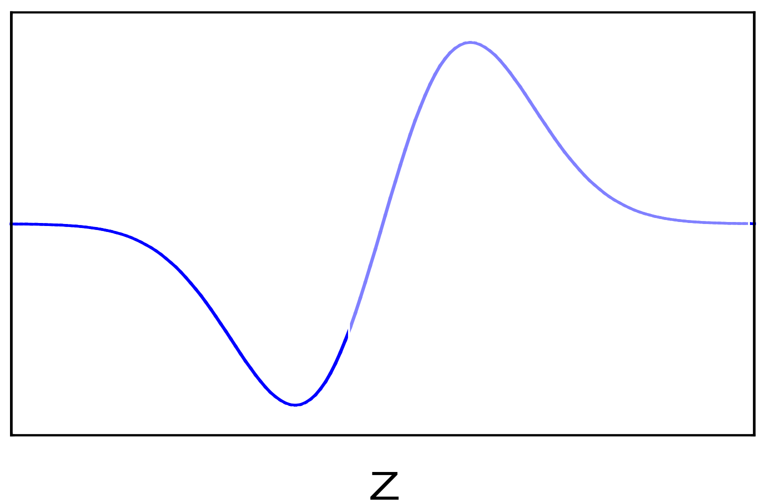

Input lens
aperture
NL sample
Laser
beam
Δz
Z

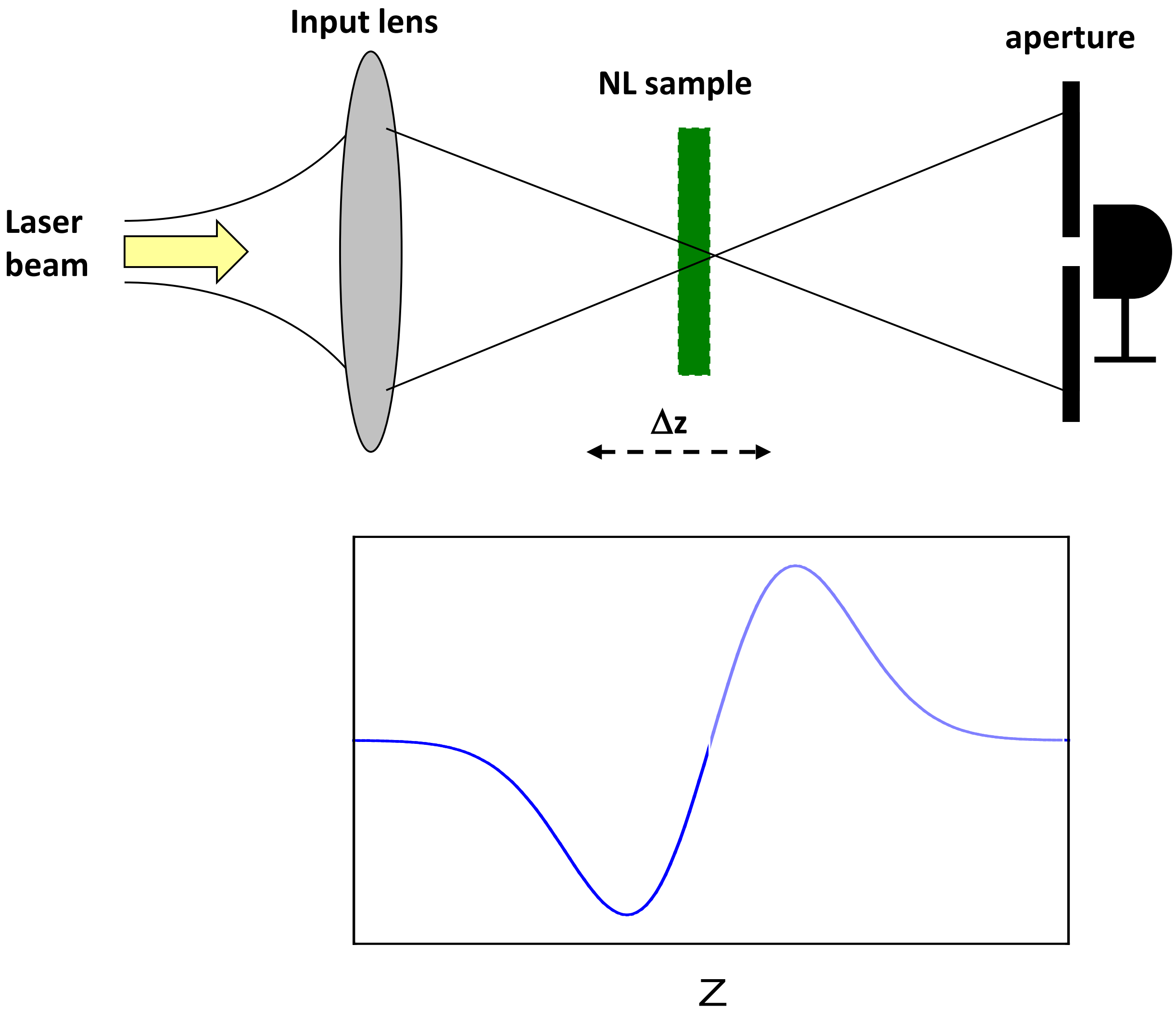

Input lens
aperture
NL sample
Laser
beam
Δz

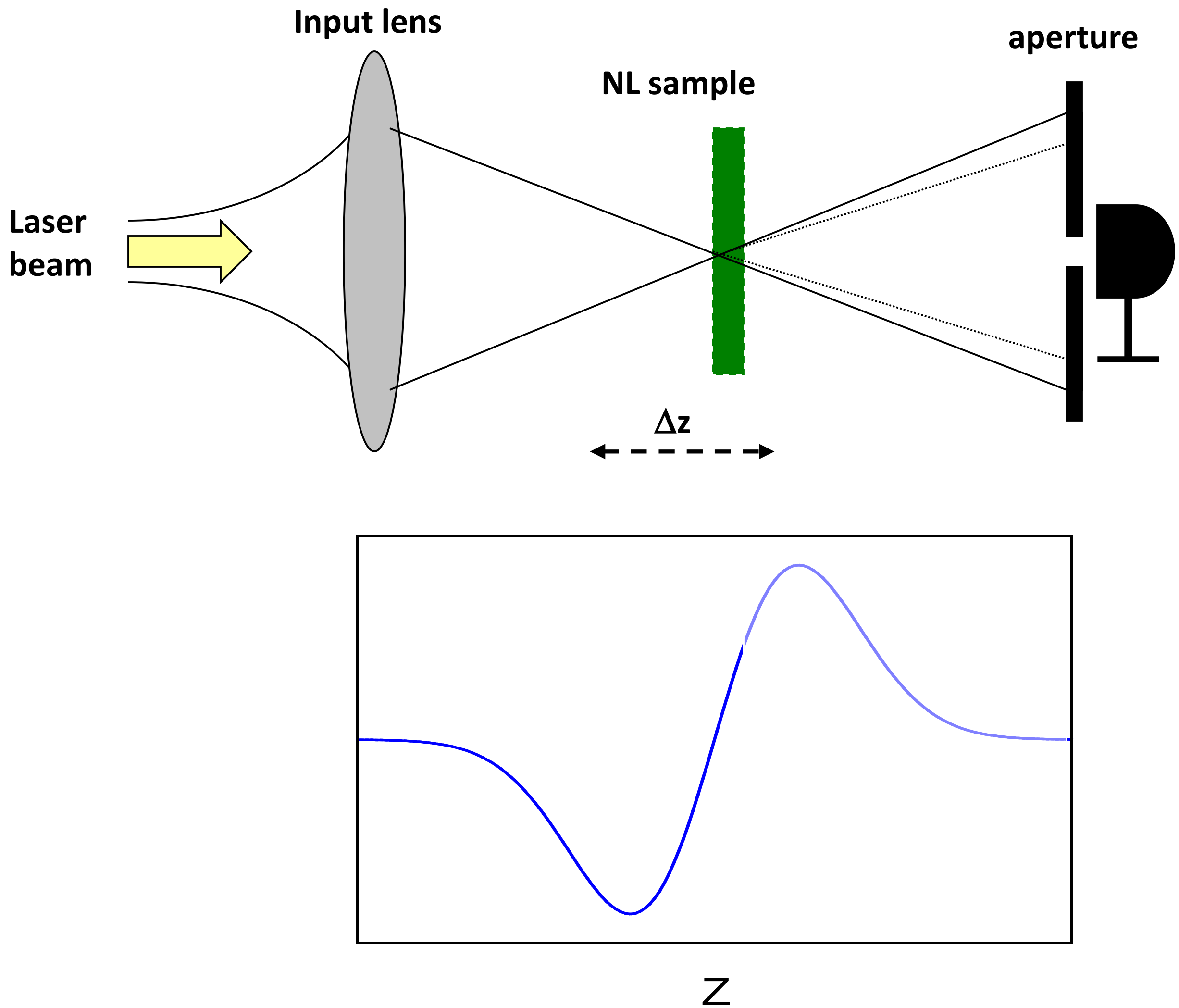

Z

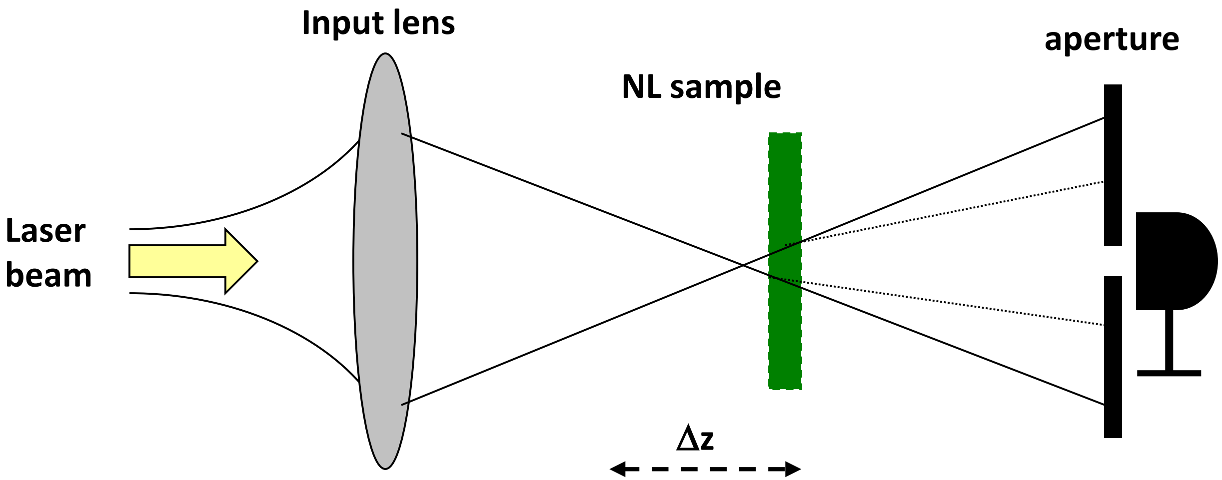

Input lens
aperture
NL sample
Laser
beam
Δz
Z

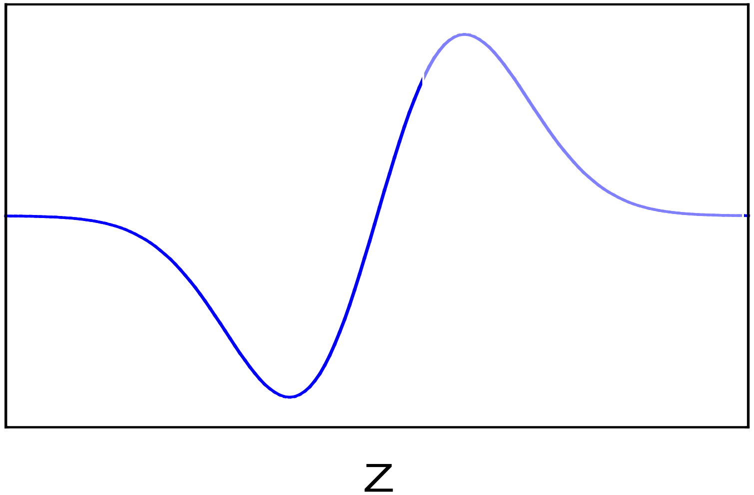

Input lens
aperture
NL sample
Laser
beam
Δz

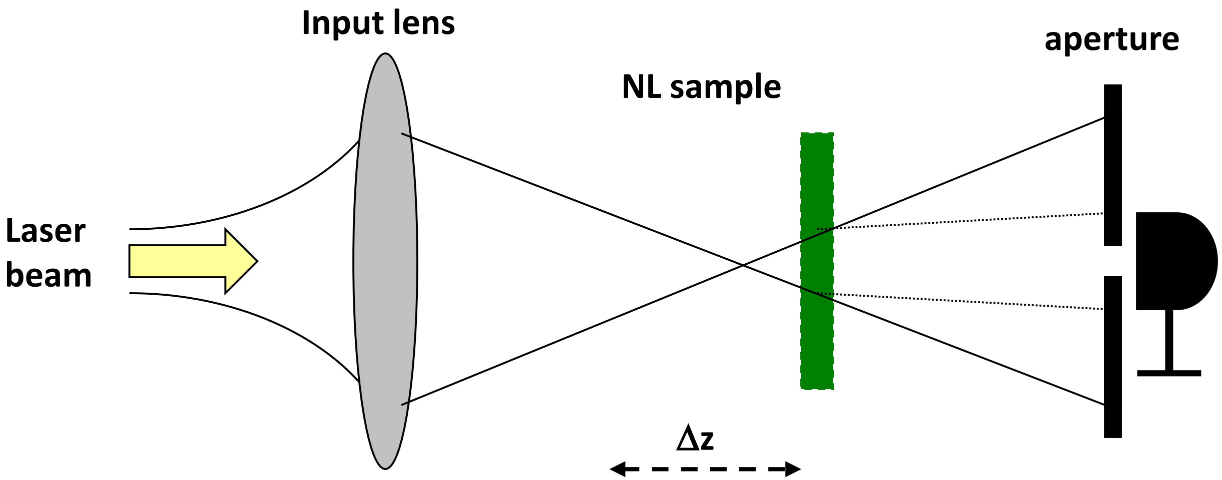

Z

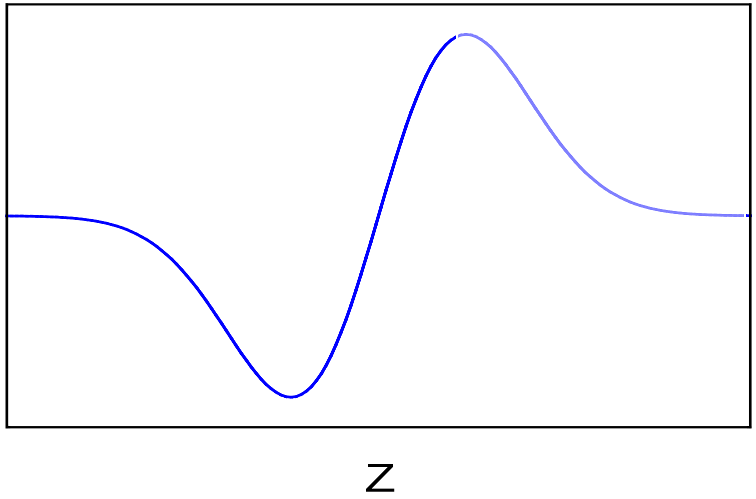

Input lens
aperture
NL sample
Laser
beam
Δz
Z

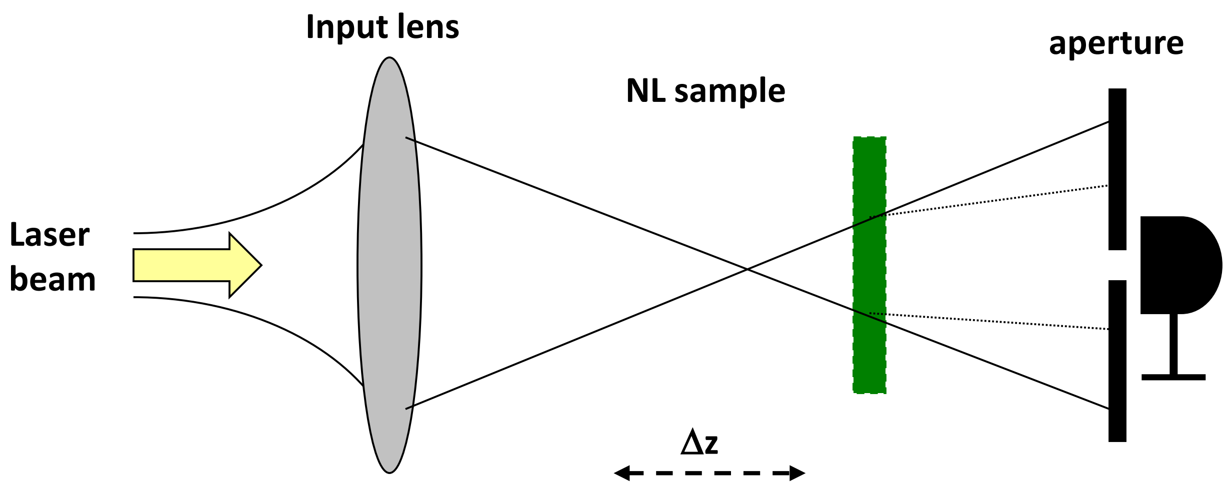

Input lens
aperture
NL sample
Laser
beam
Δz
Z

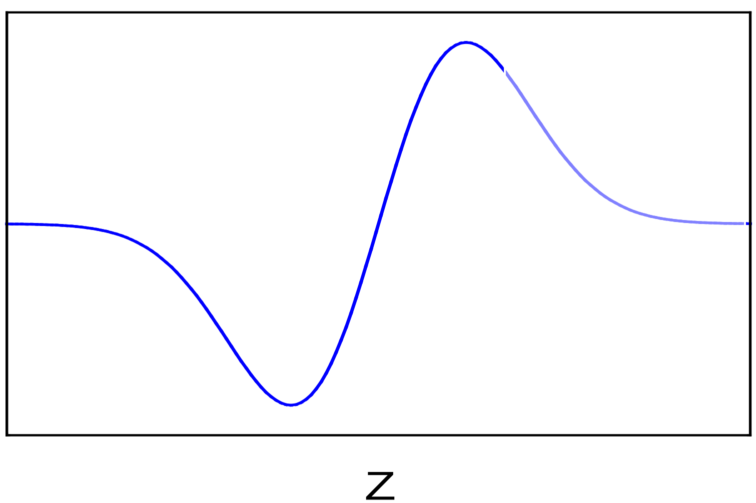

Input lens
aperture
NL sample
Laser
beam
Δz

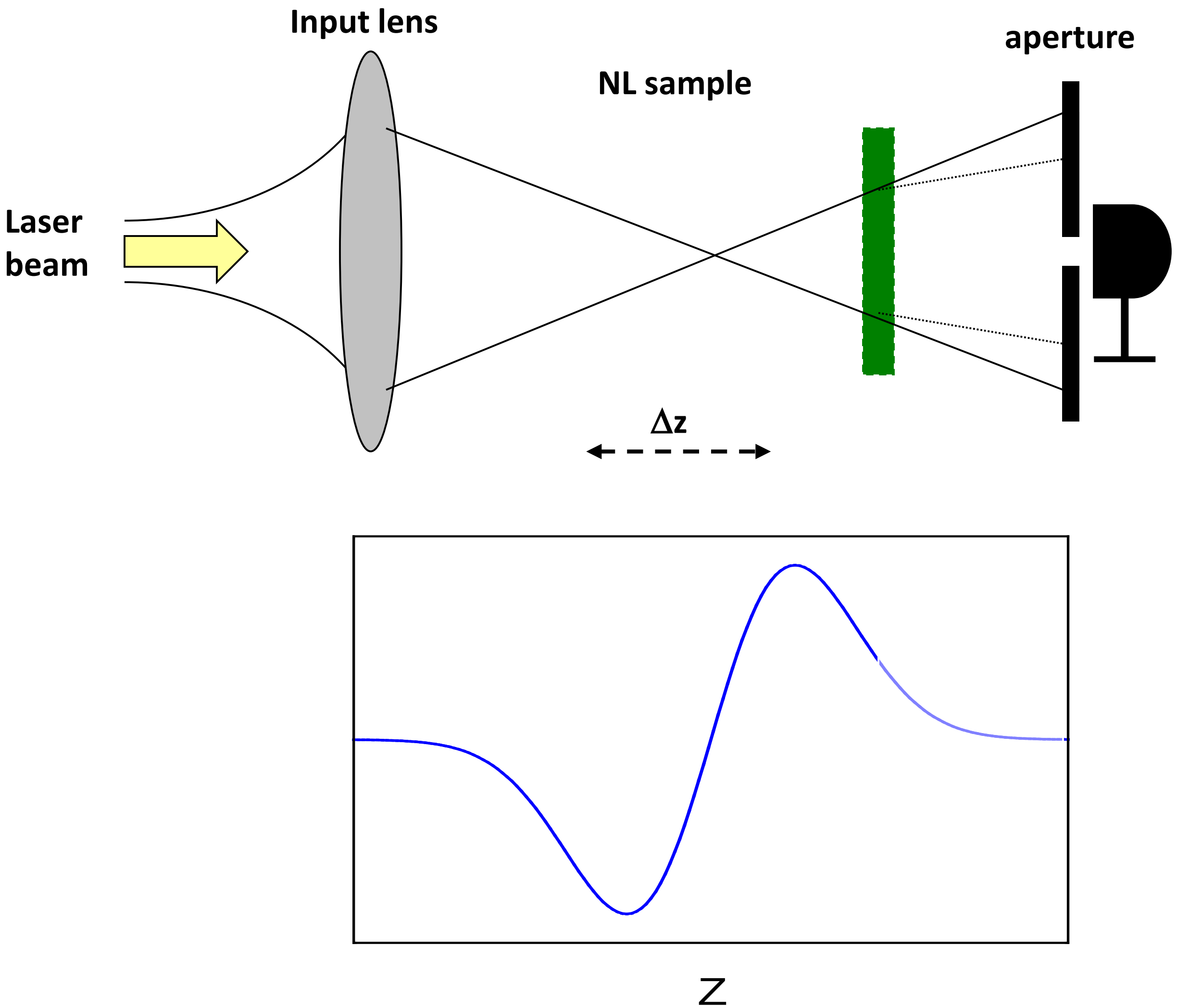

z

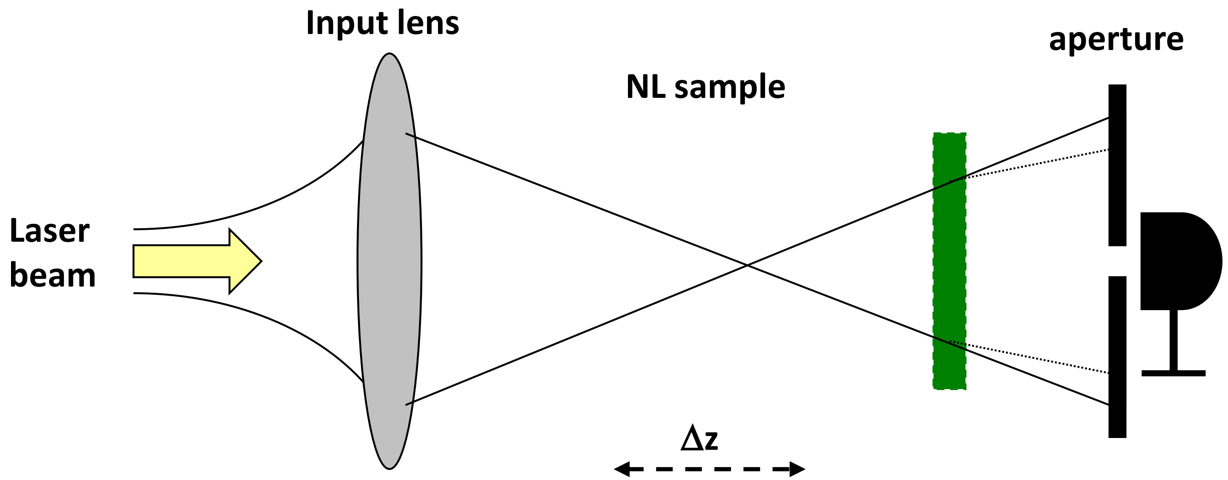

Input lens
aperture
NL sample
Laser
beam
Δz

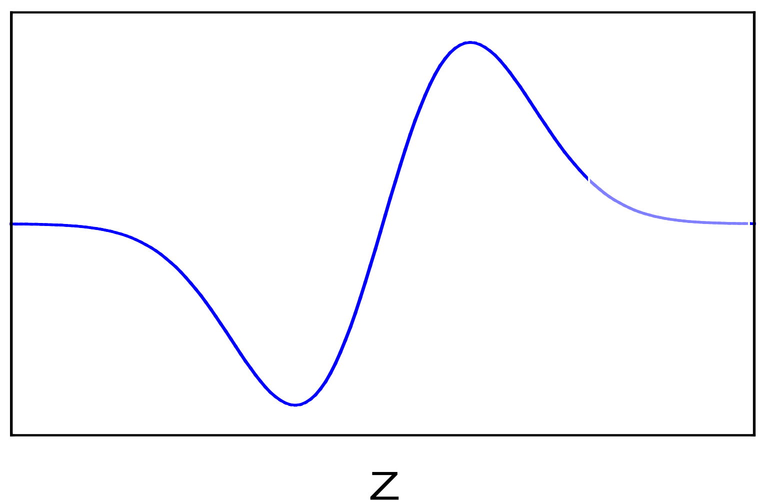

Z

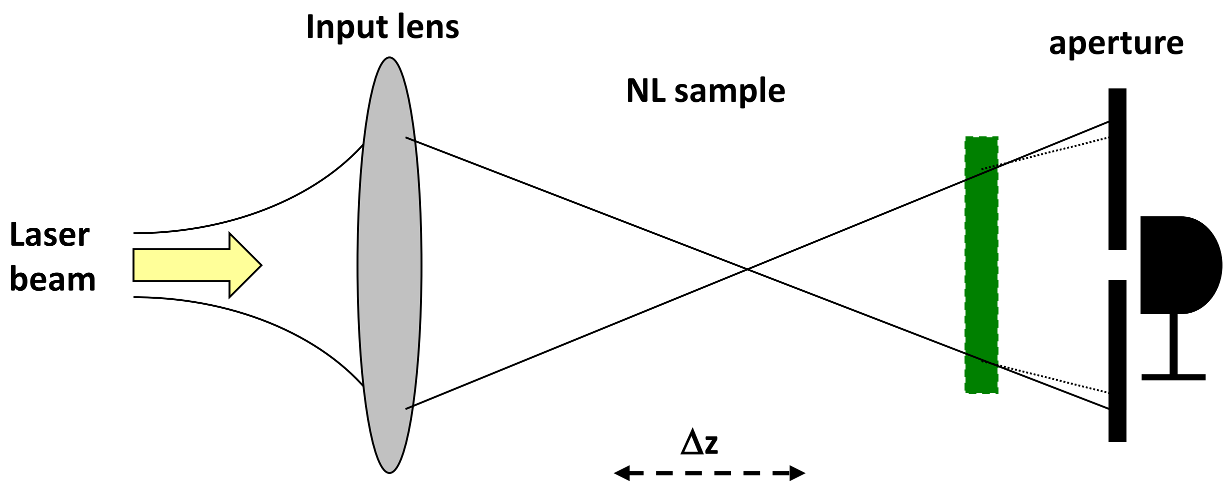

Input lens
aperture
NL sample
Laser
beam
Δz

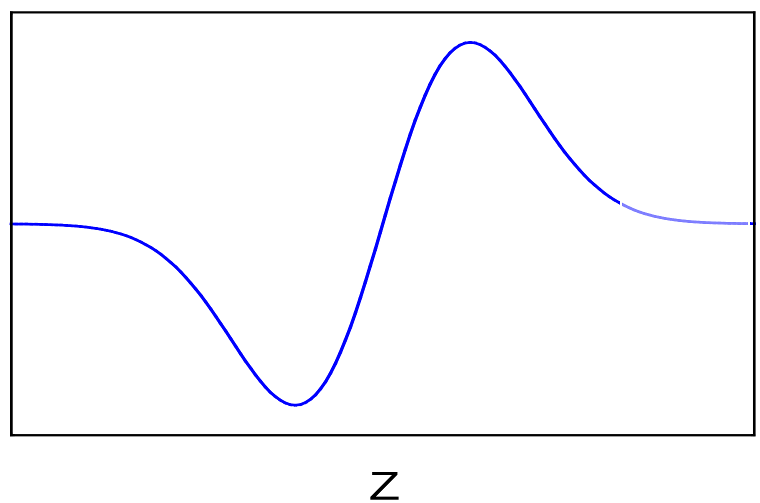

z

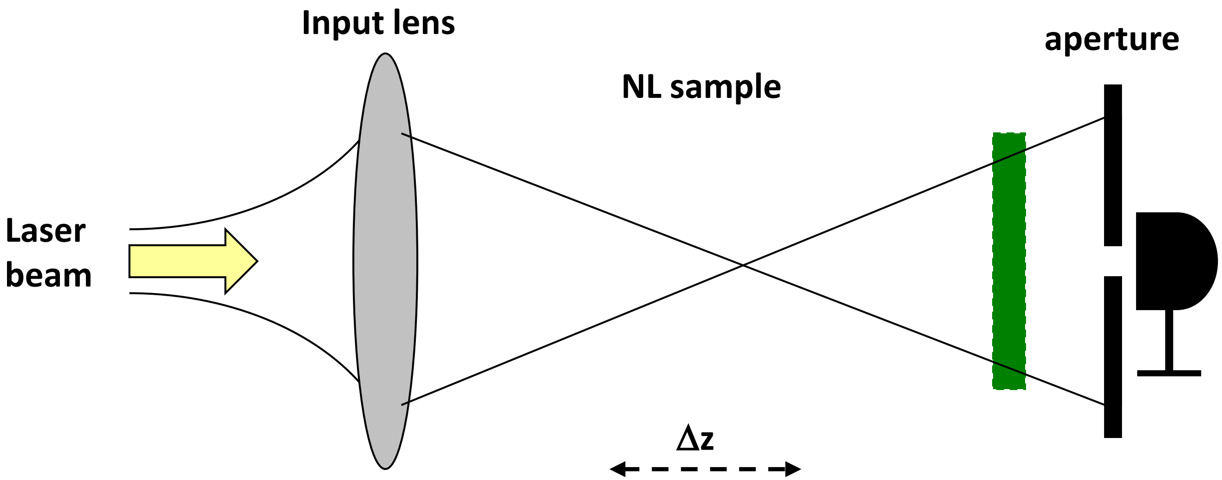

Input lens
aperture
NL sample
Laser
beam
Δz
z

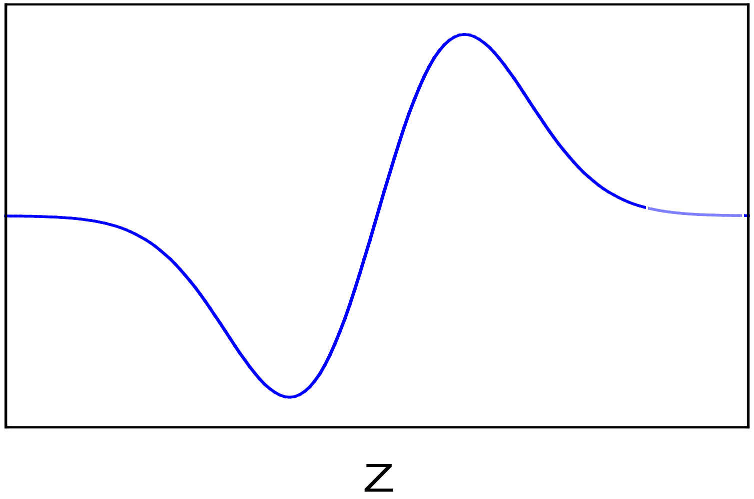

Input lens
aperture
NL sample
Laser
beam
Δz


Z


Input lens
aperture
NL sample
Laser
beam
Δz

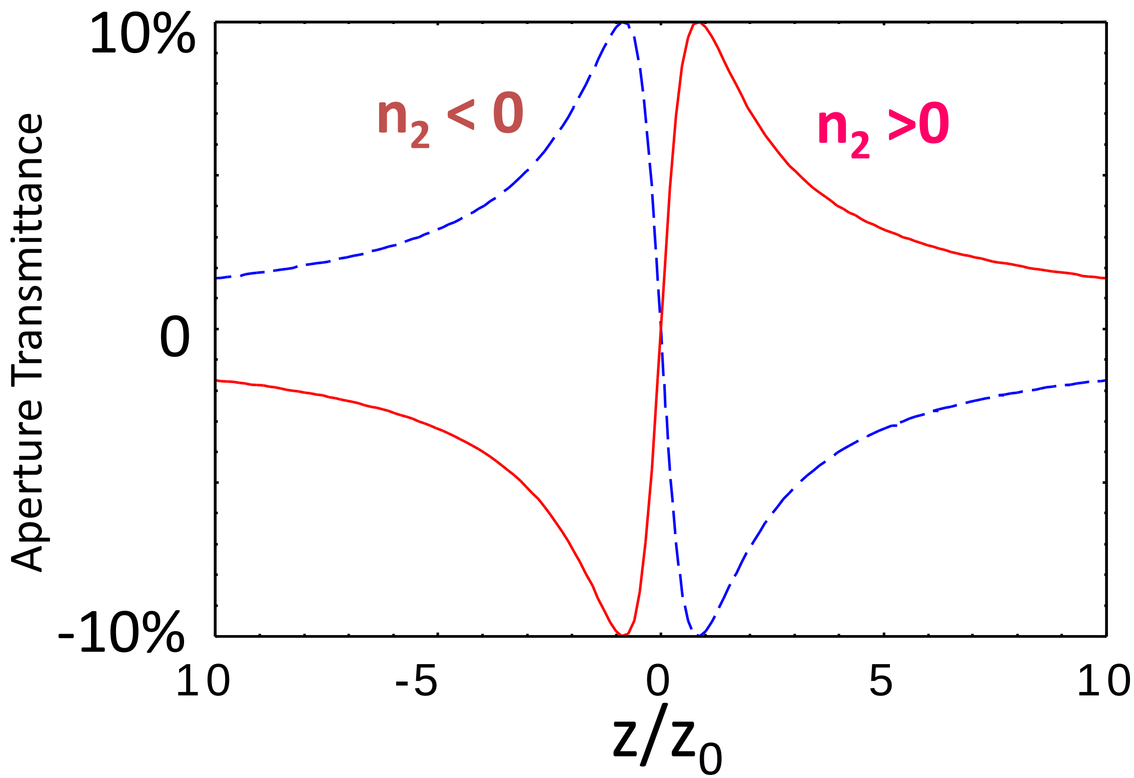

Z


Input lens
aperture
NL sample
Laser beam
Δz


Z

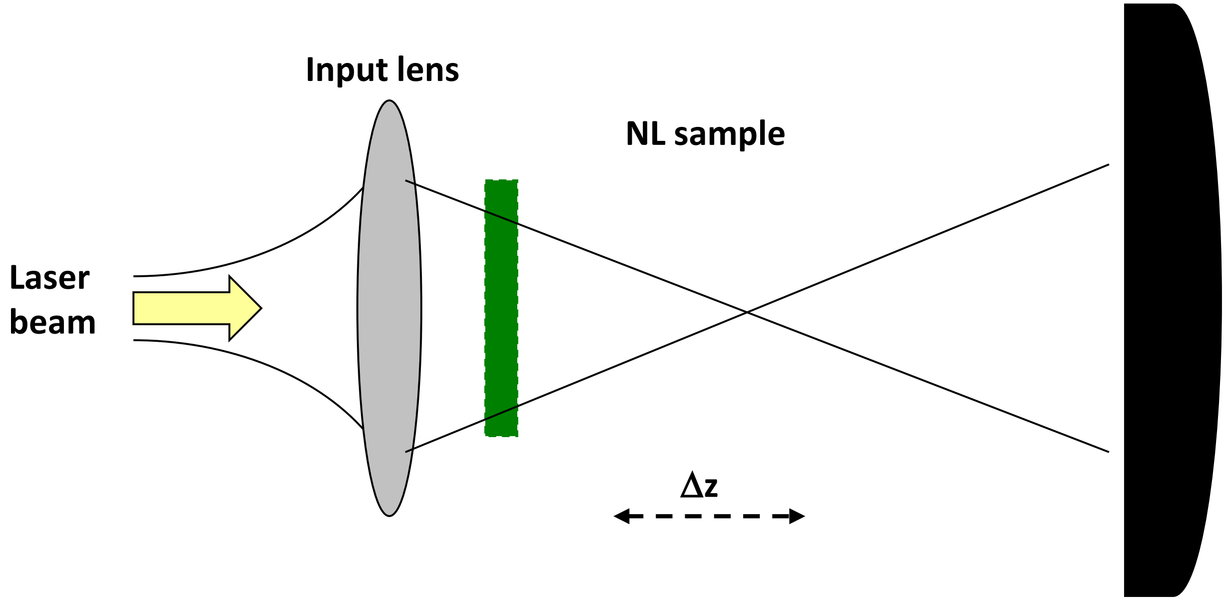
# Z-scan measurement technique

The aperture transmittance can be plotted as a function of Z:

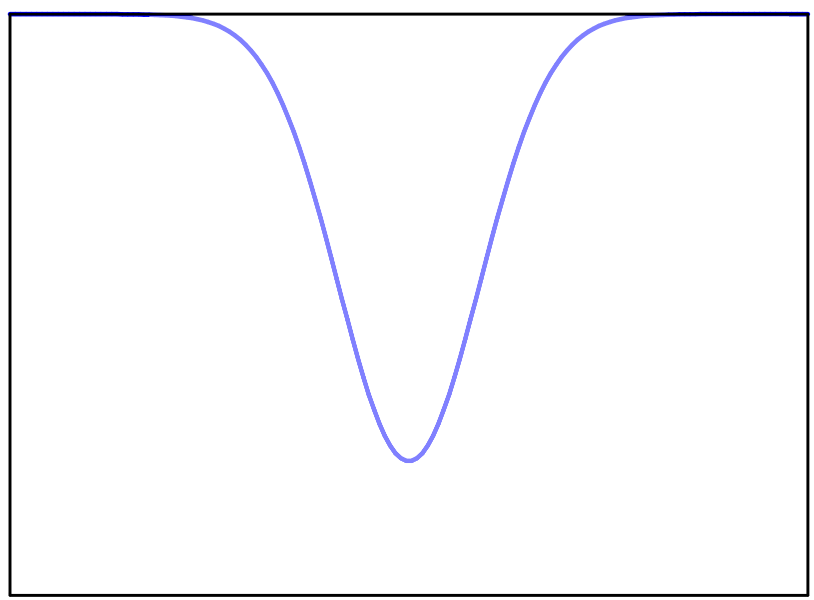


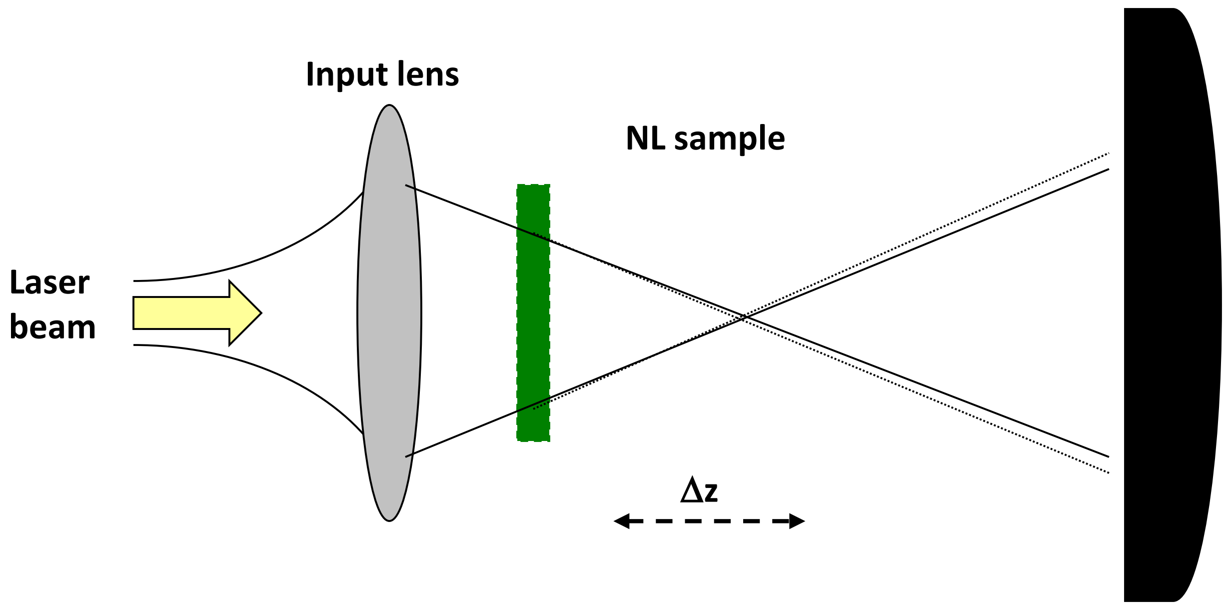

$\Delta T_{p-\mathrm{v}} \propto |\Delta\phi_0|$ where $\Delta\phi_0$ is peak phase shift giving $n_2$

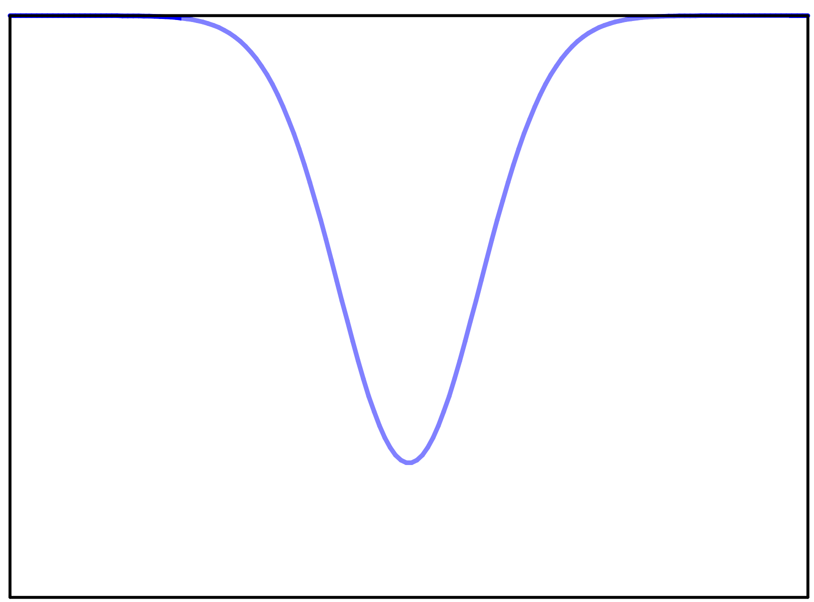
# OPEN APERTURE Z-SCAN

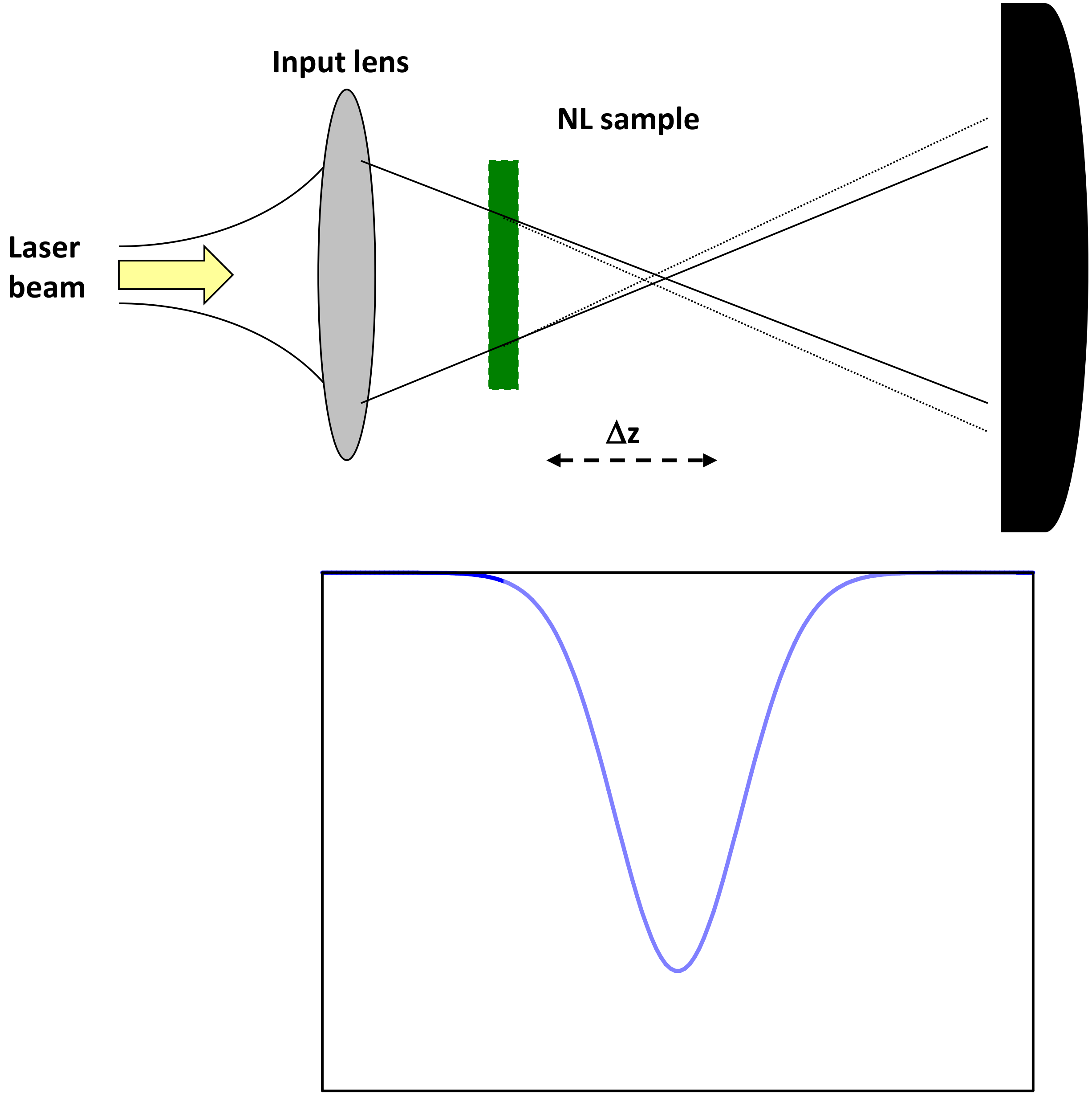


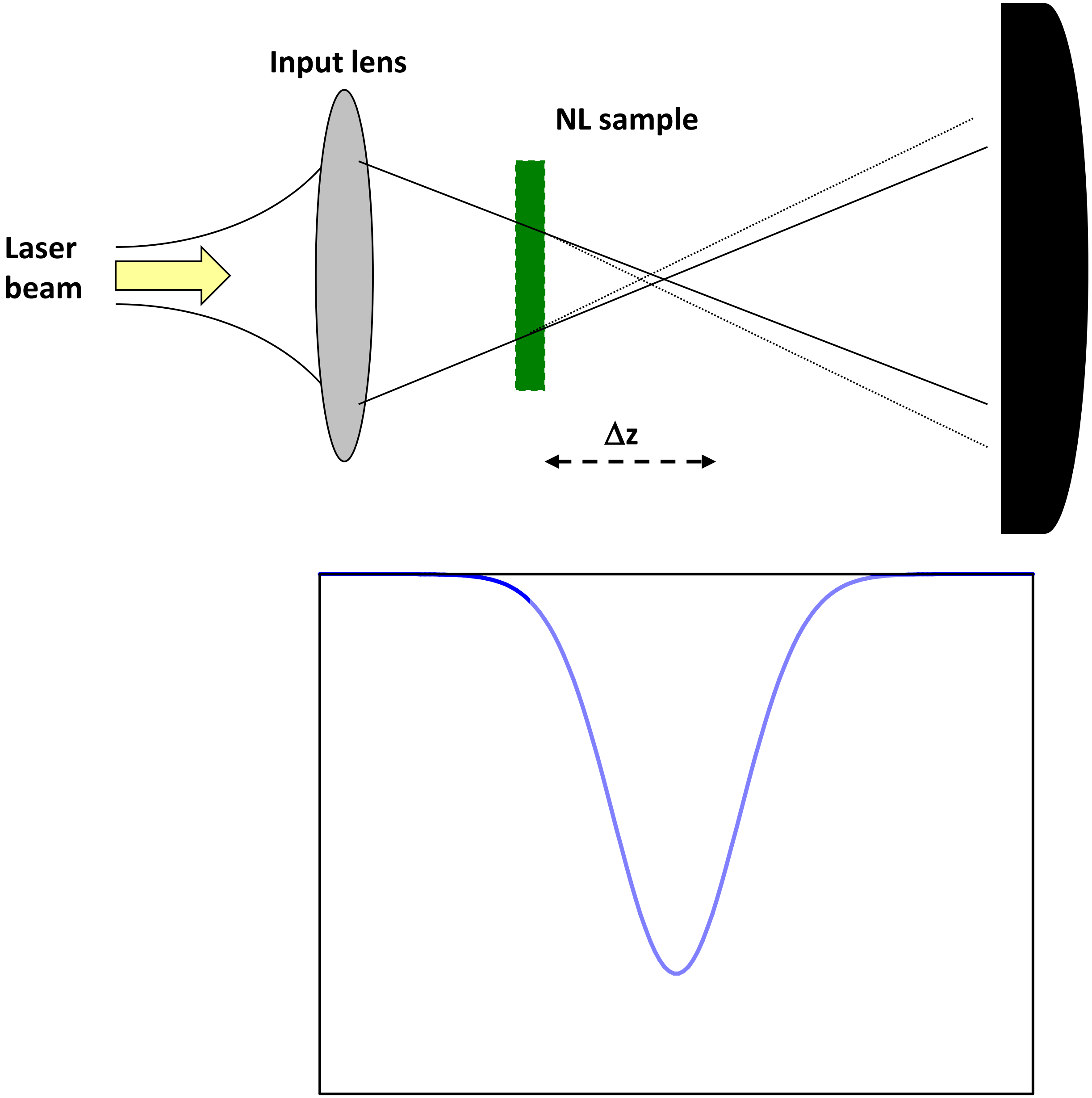

Self-focusing

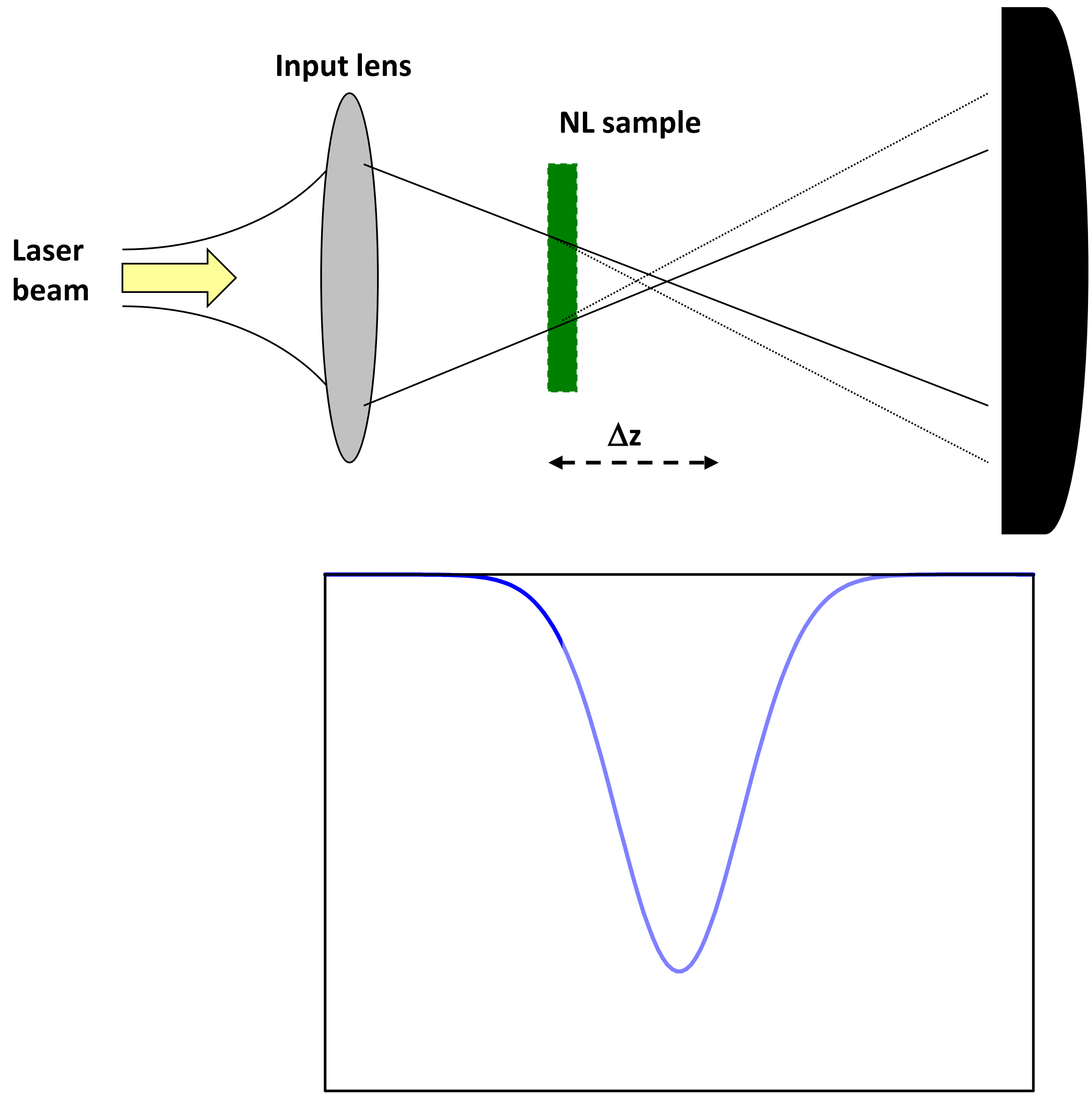


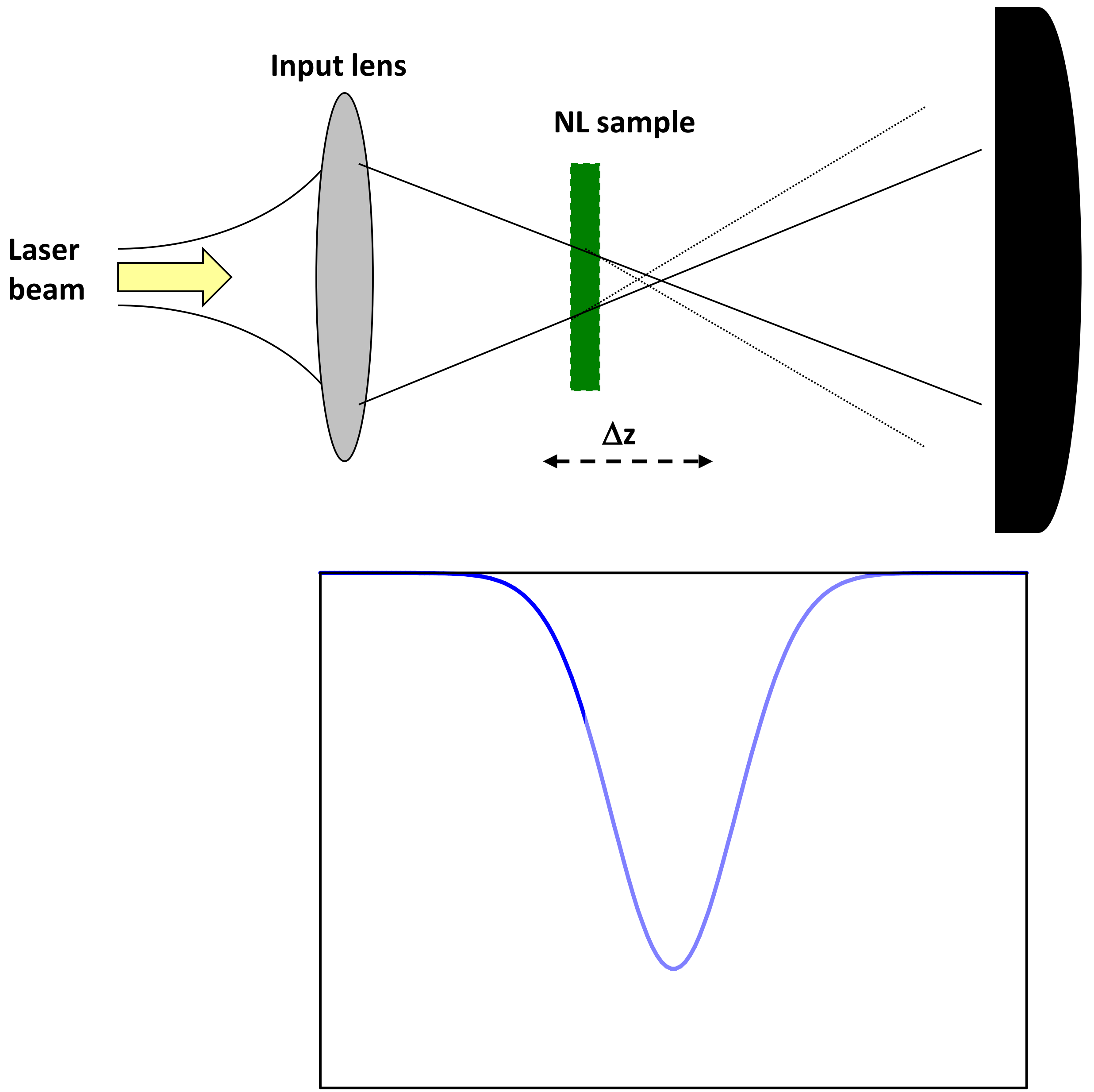

Input lens
NL sample
Laser
beam
Δz

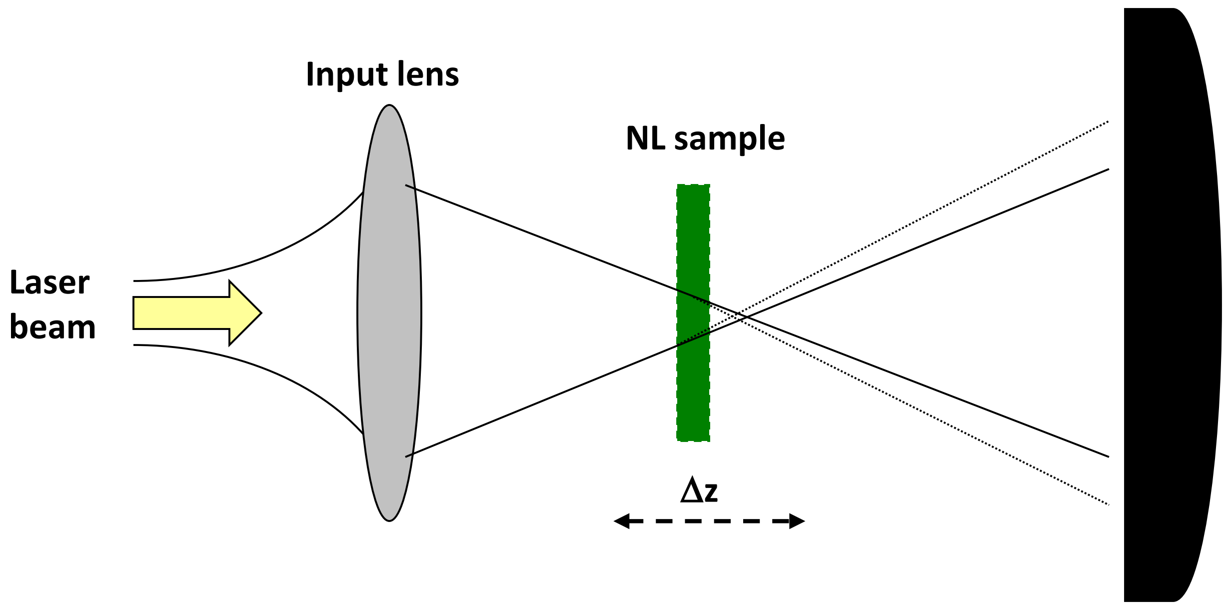


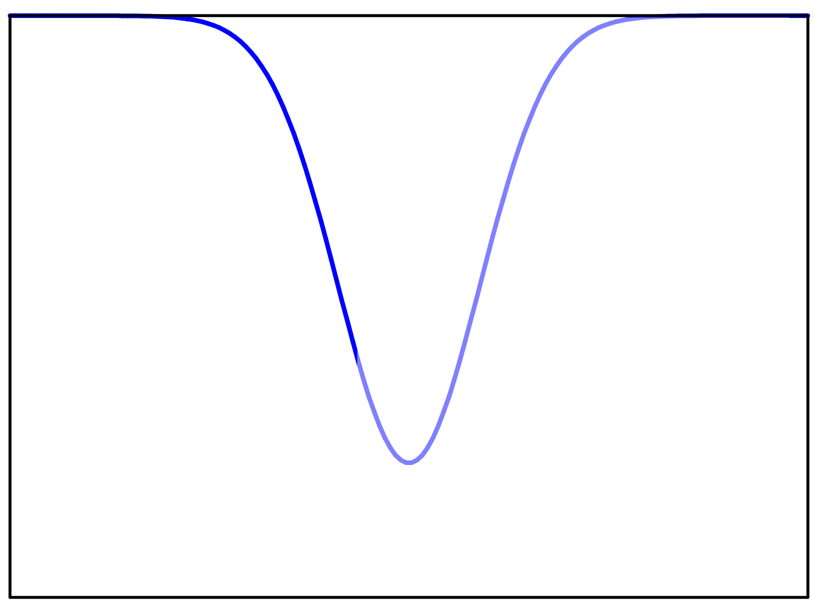

Input lens
NL sample
Laser
beam
Δz

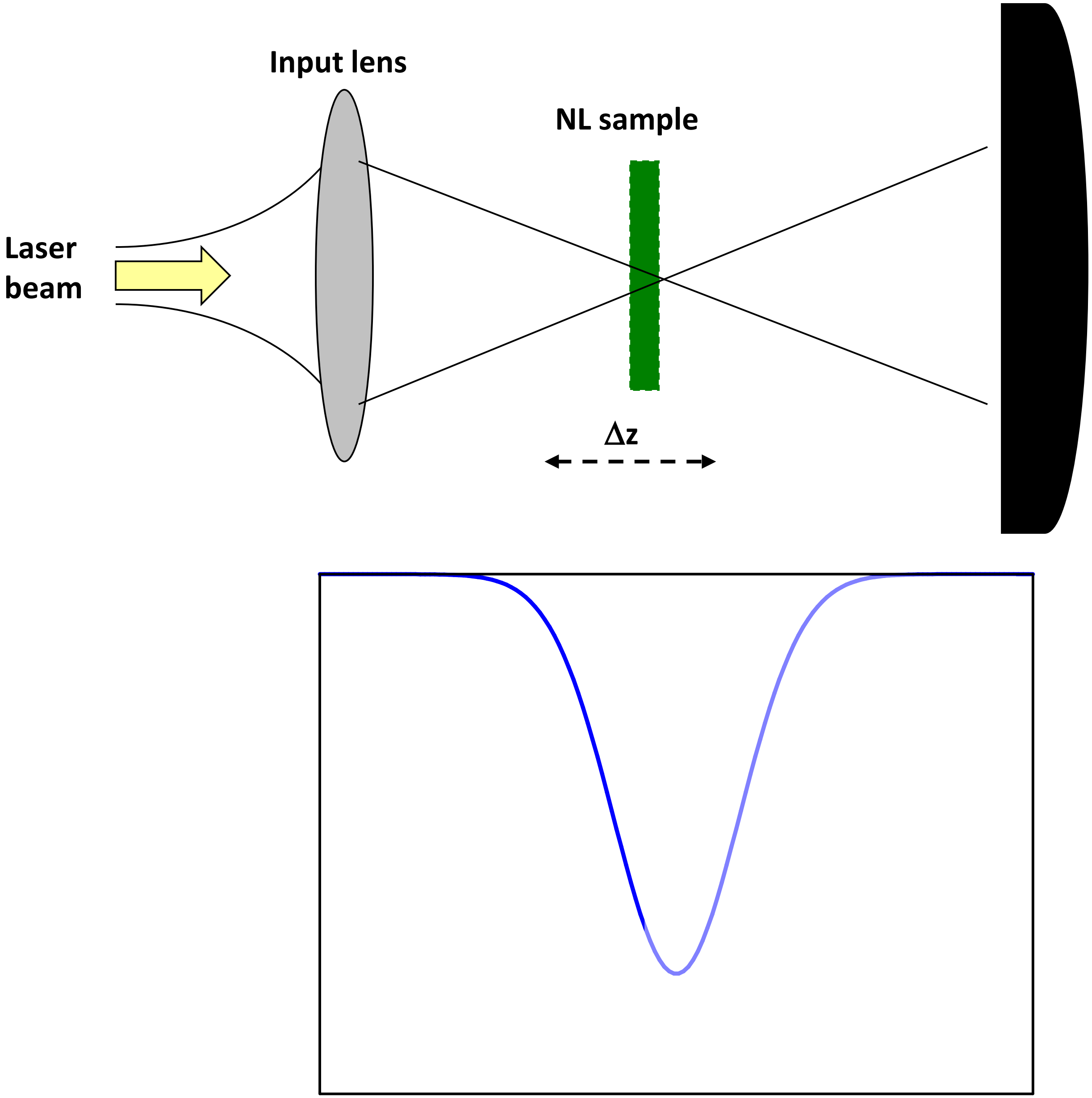

Input lens
NL sample
Laser
beam
Δz

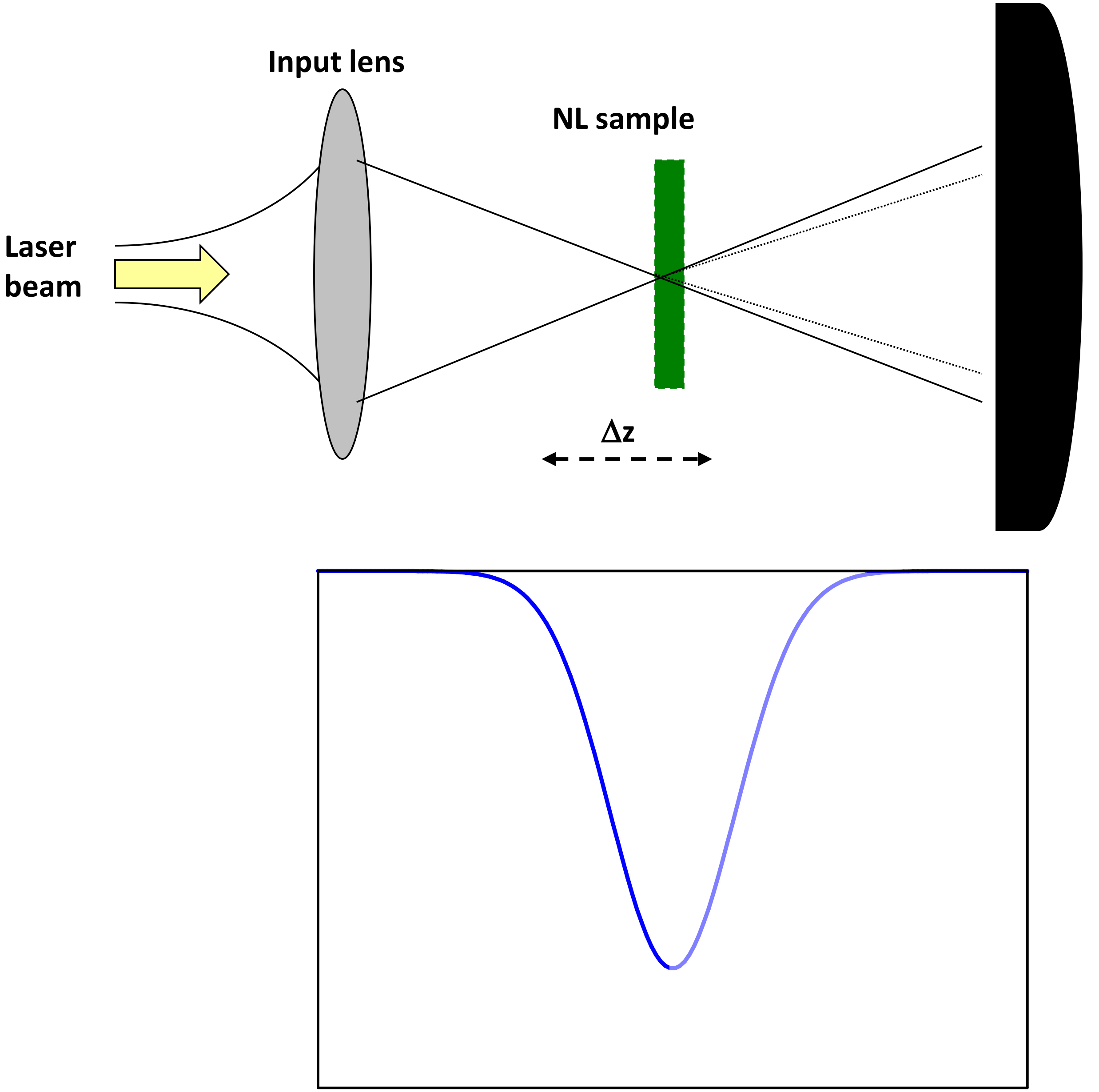

Input lens
NL sample
Laser
beam
Δz

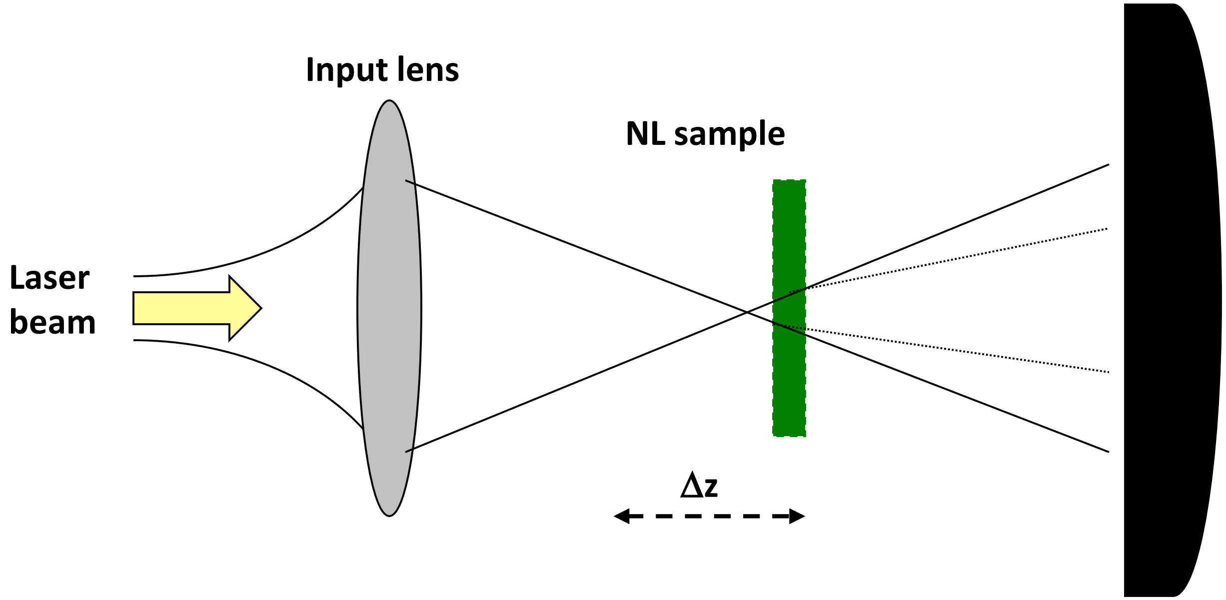

Input lens
NL sample
Laser
beam
Δz

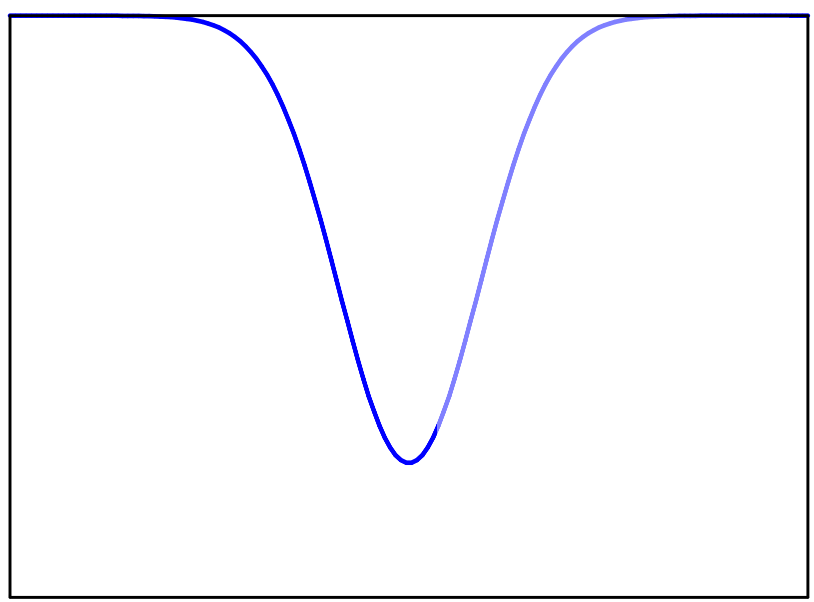

Input lens
NL sample
Laser
beam
Δz

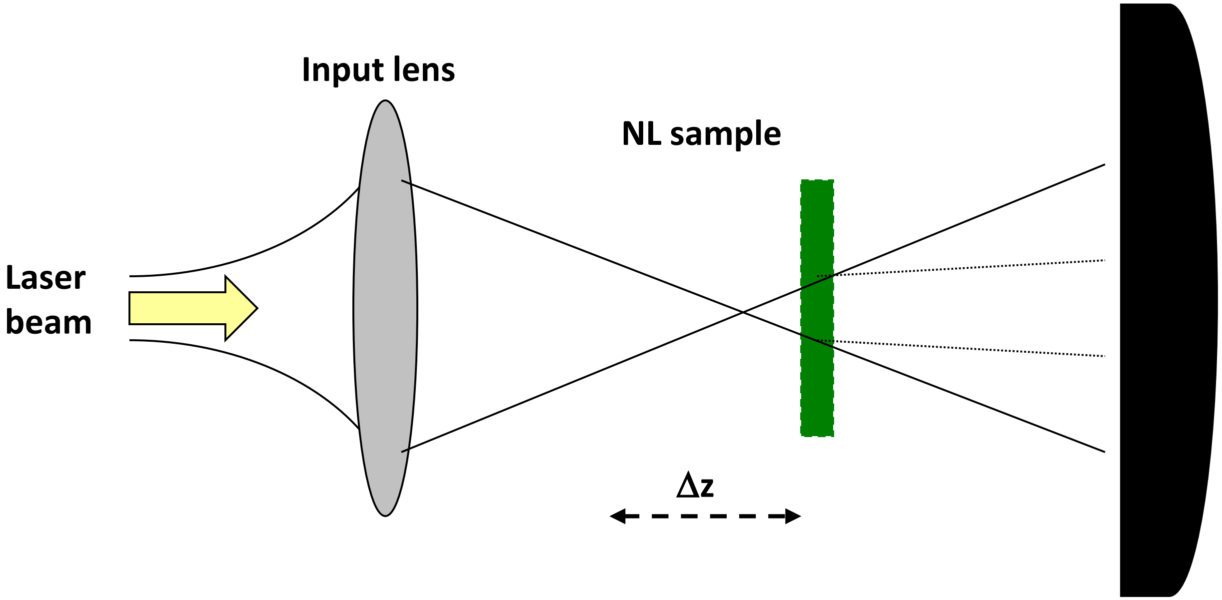


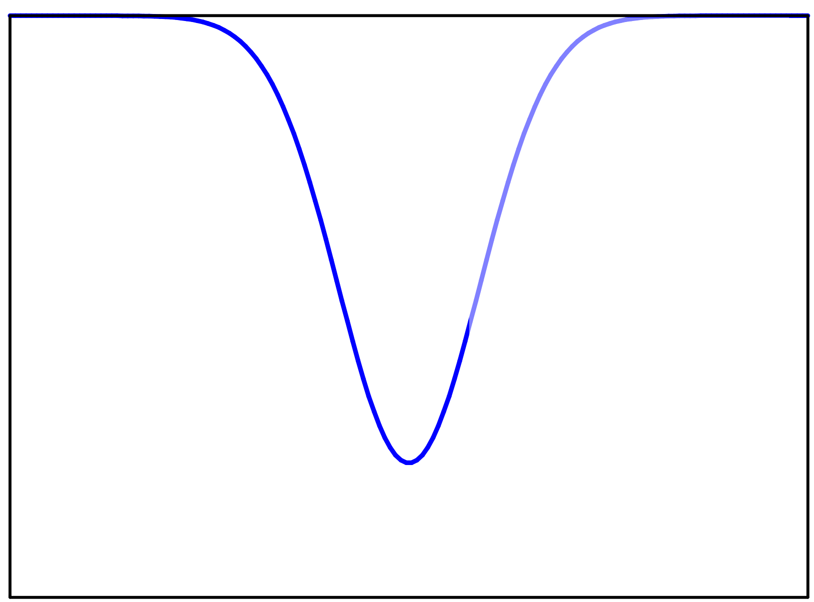

Input lens
NL sample
Laser
beam
Δz

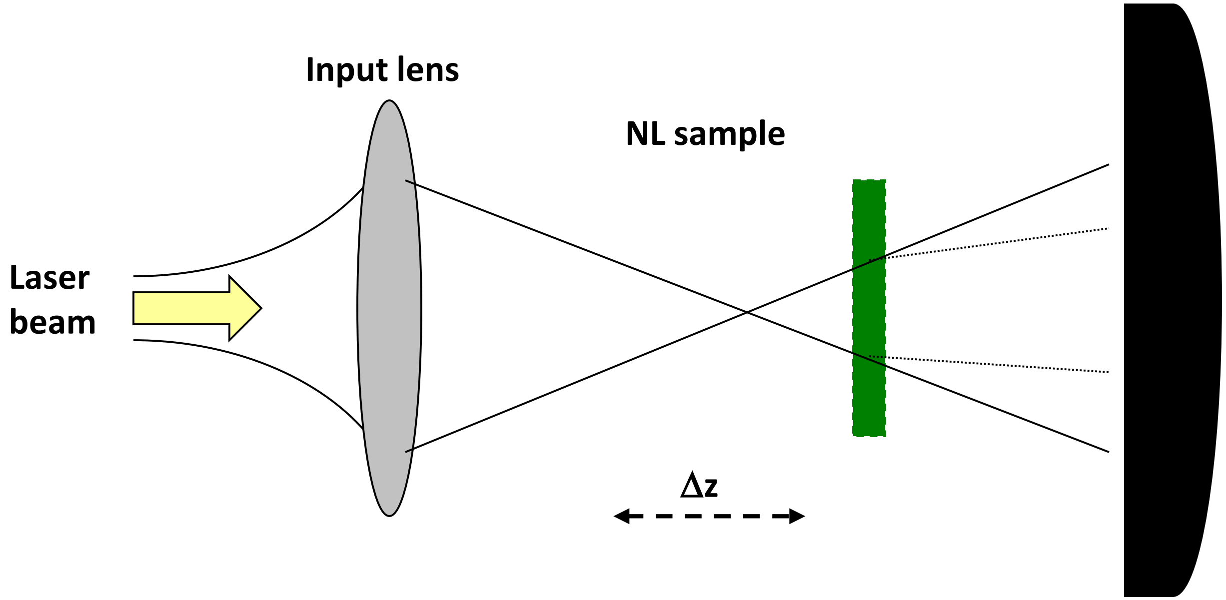

Input lens
NL sample
Laser
beam
Δz

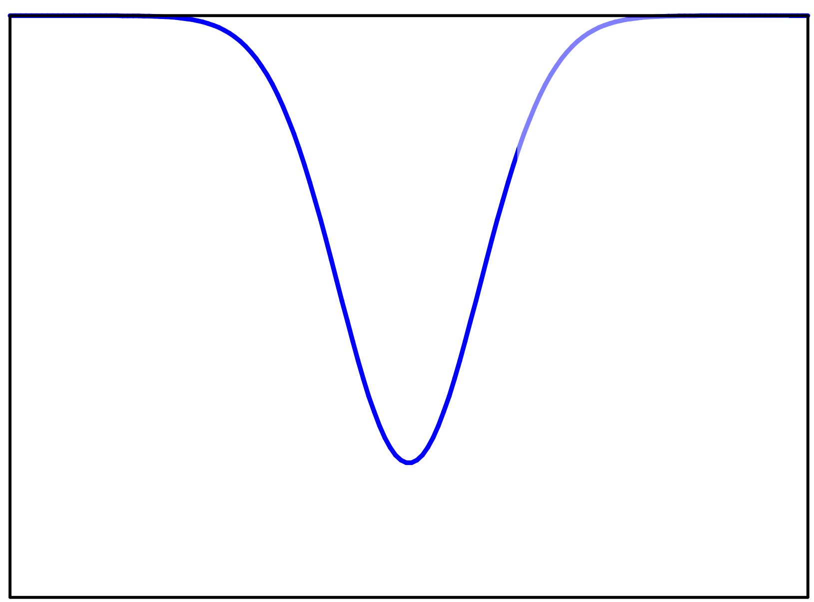

Input lens
NL sample
Laser
beam
Δz

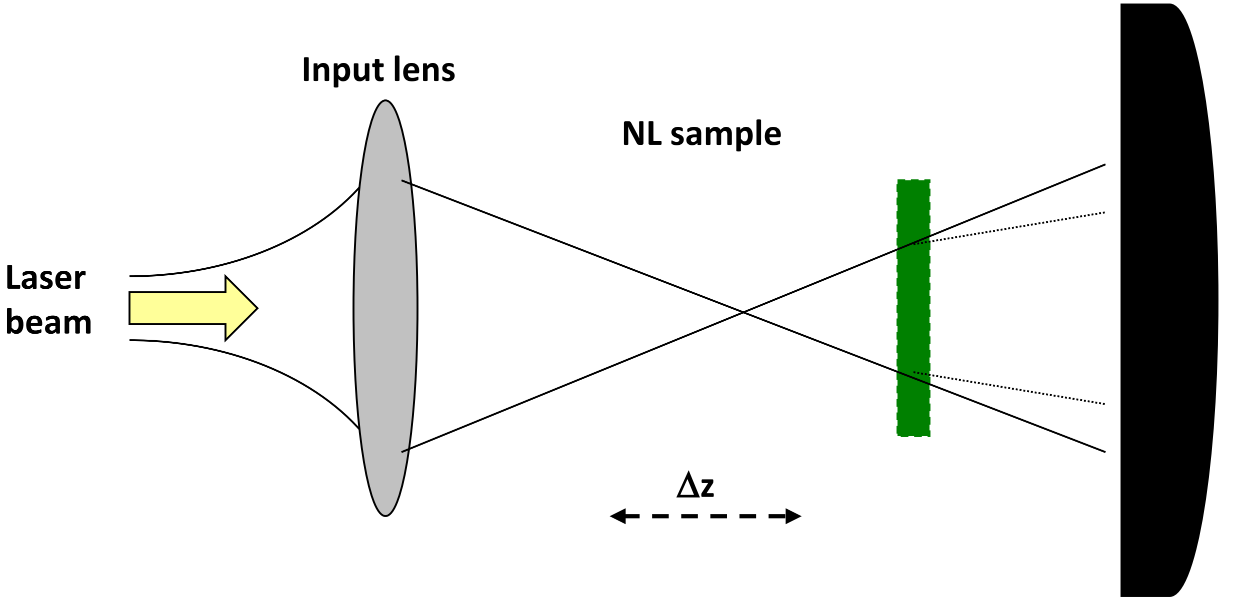


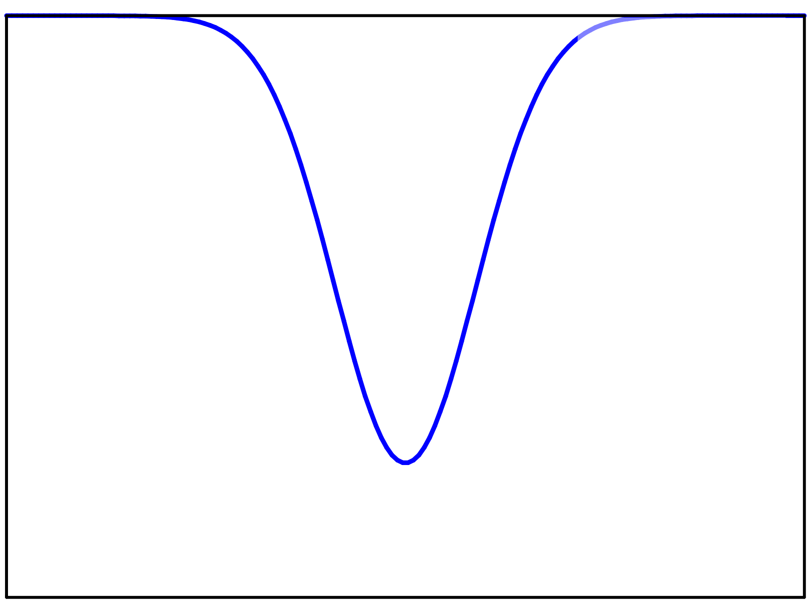

Input lens
NL sample
Laser
beam
Δz

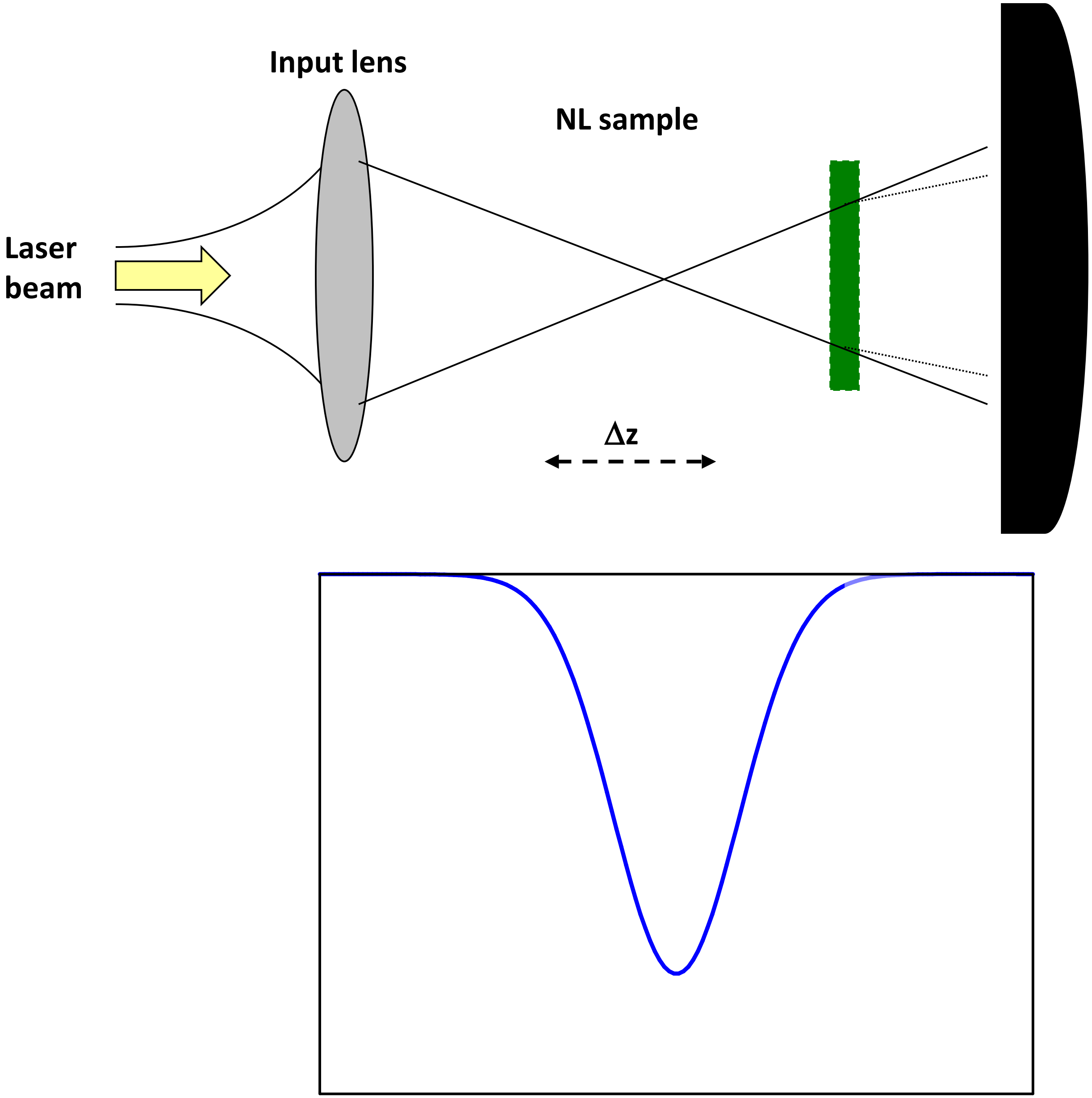


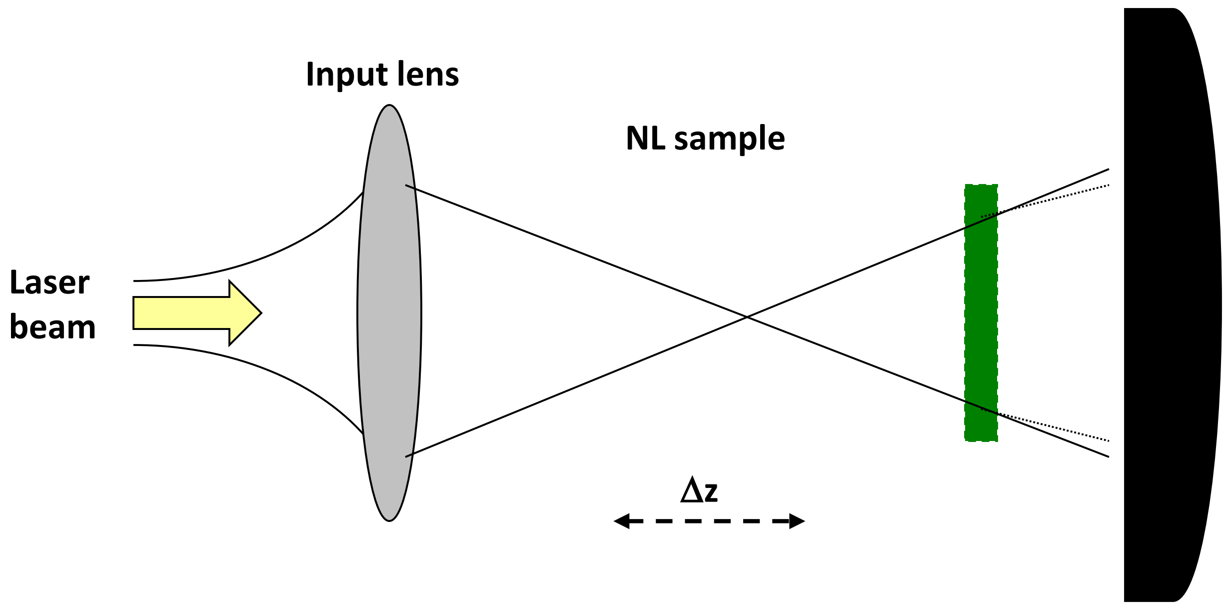

Input lens
NL sample
Laser
beam
Δz

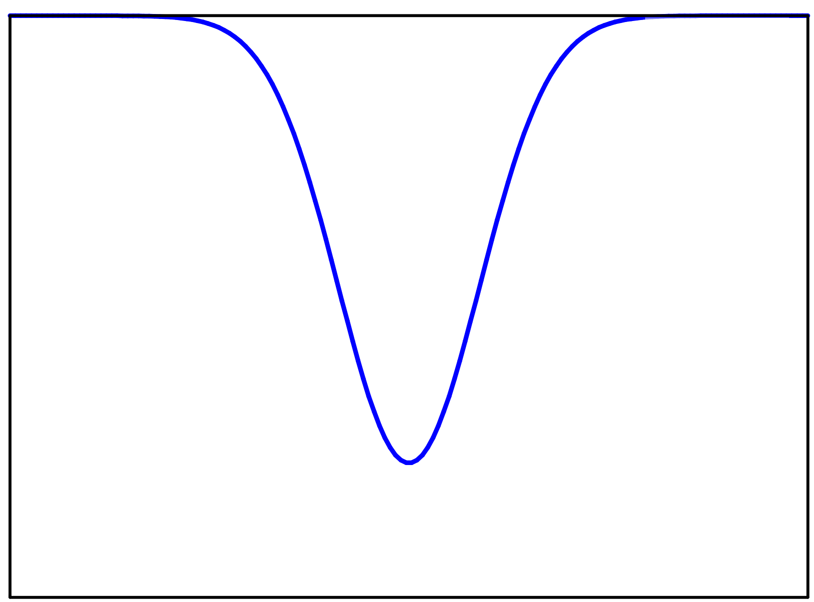


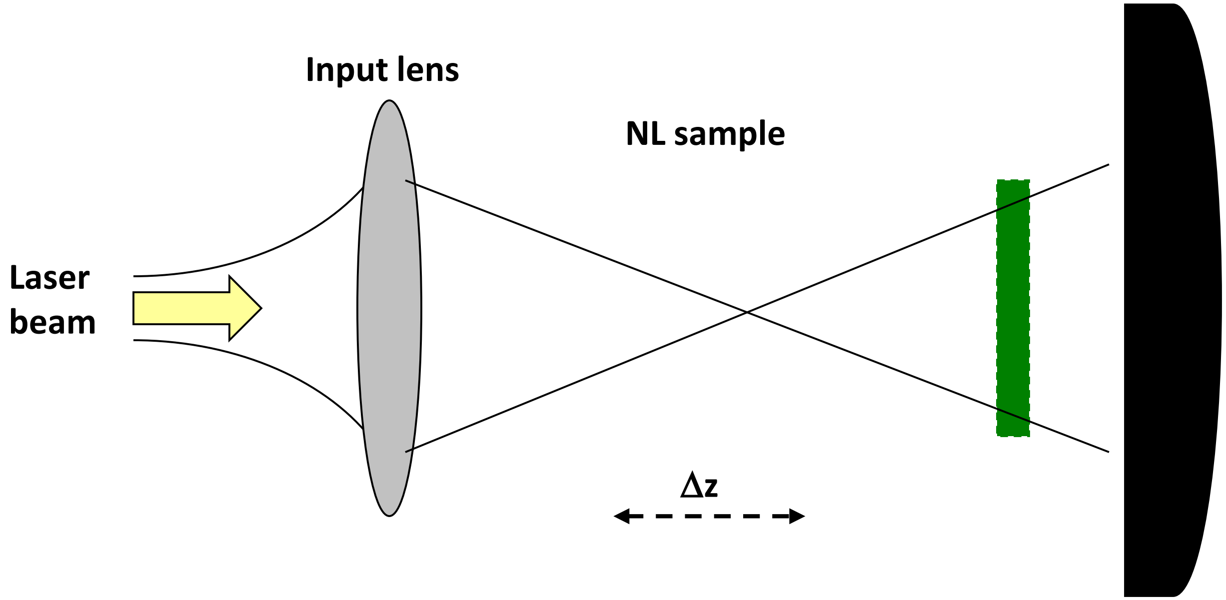

Input lens
NL sample
Laser
beam
Δz

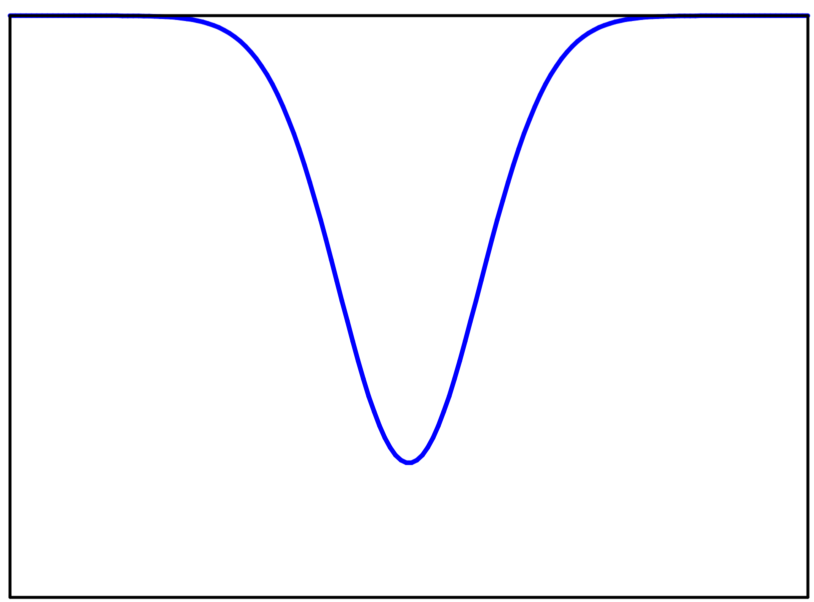



Input lens
NL sample
Laser
beam
Δz

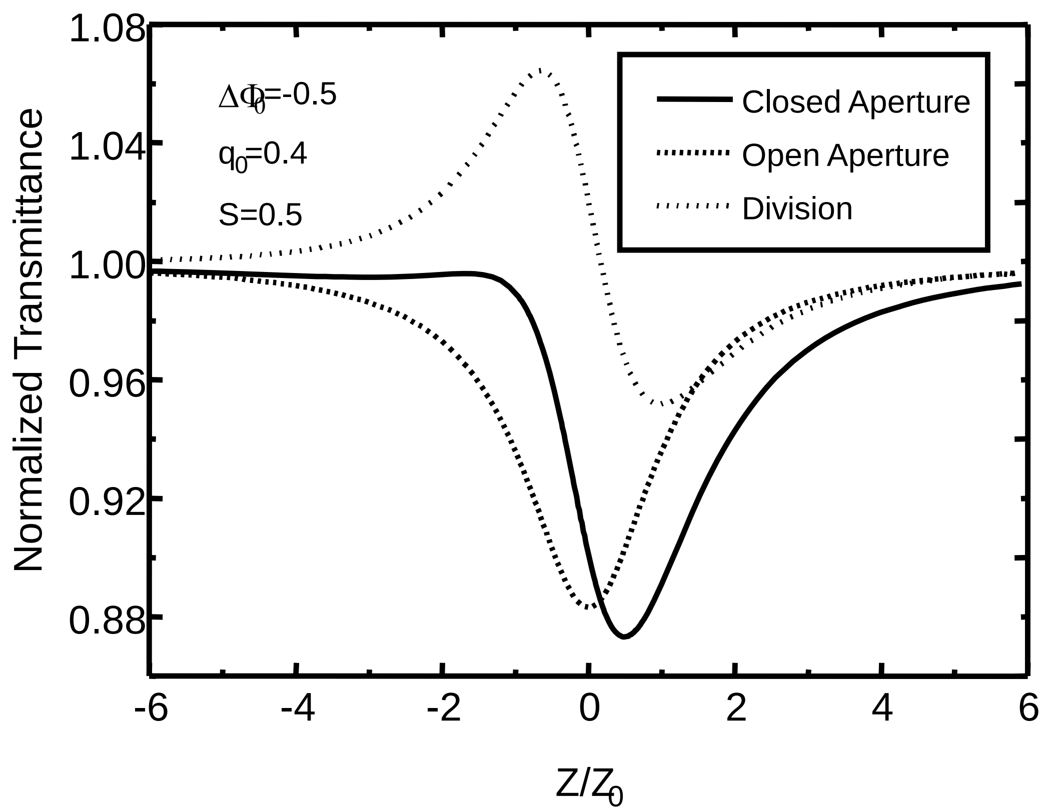

Input lens
NL sample
Laser
beam
Δz




Input lens
NL sample
Laser
beam
Δz



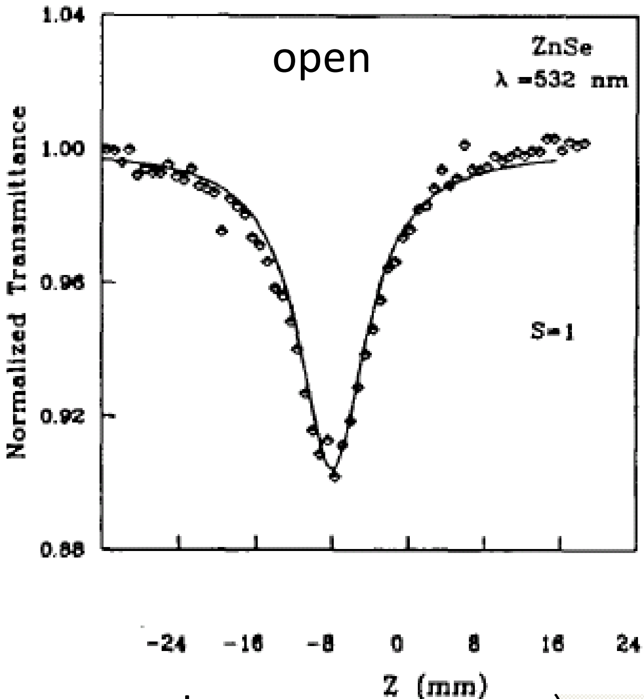
# Separation of NLAbsorption and NLRefraction

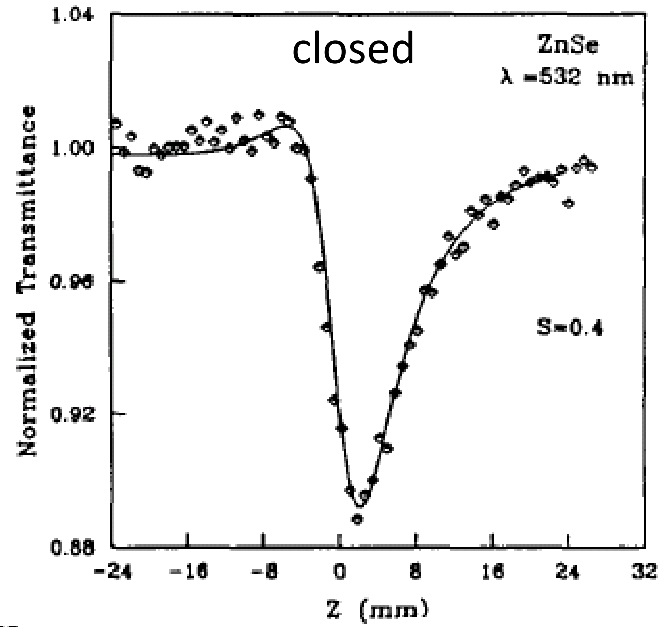



But – this doesn't give the physical mechanism(s)

Life isn't so simple. This assumes $\chi^{(3)}$.

# Semiconductors



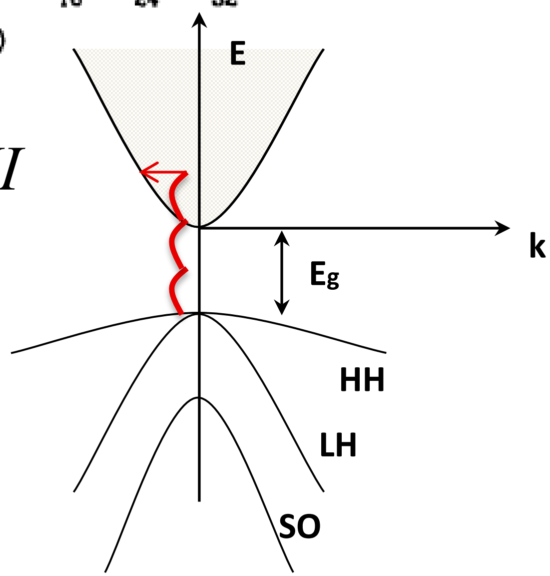



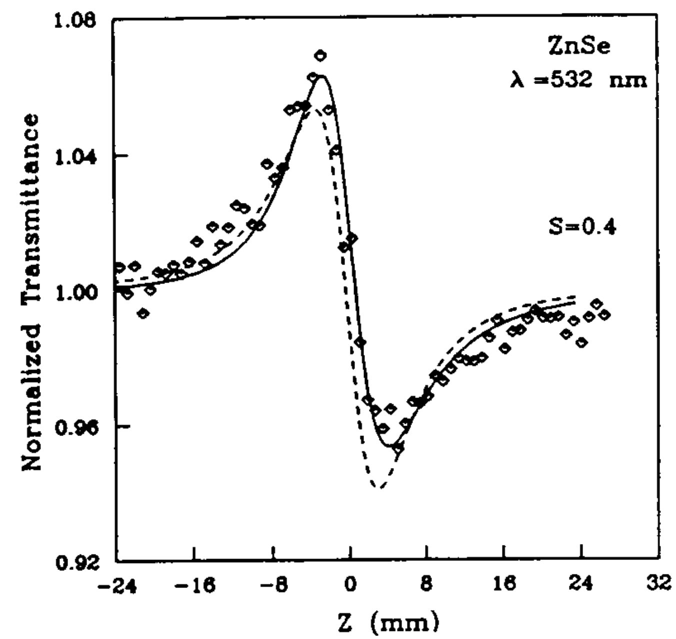

psec pulses

$$\frac{dI}{dz} = -\alpha_2 I^2 - \sigma_{FCA} N I$$

$$\frac{dN}{dt} = \frac{\alpha_2 I^2}{2\hbar w}$$

$$\frac{d\varphi}{dz} = k_0 n_2 I + \sigma_{FCR} N$$



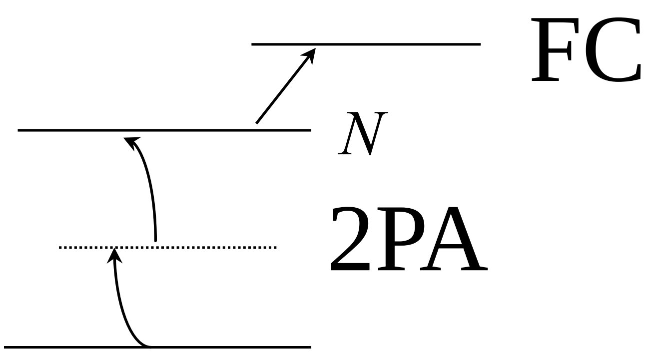



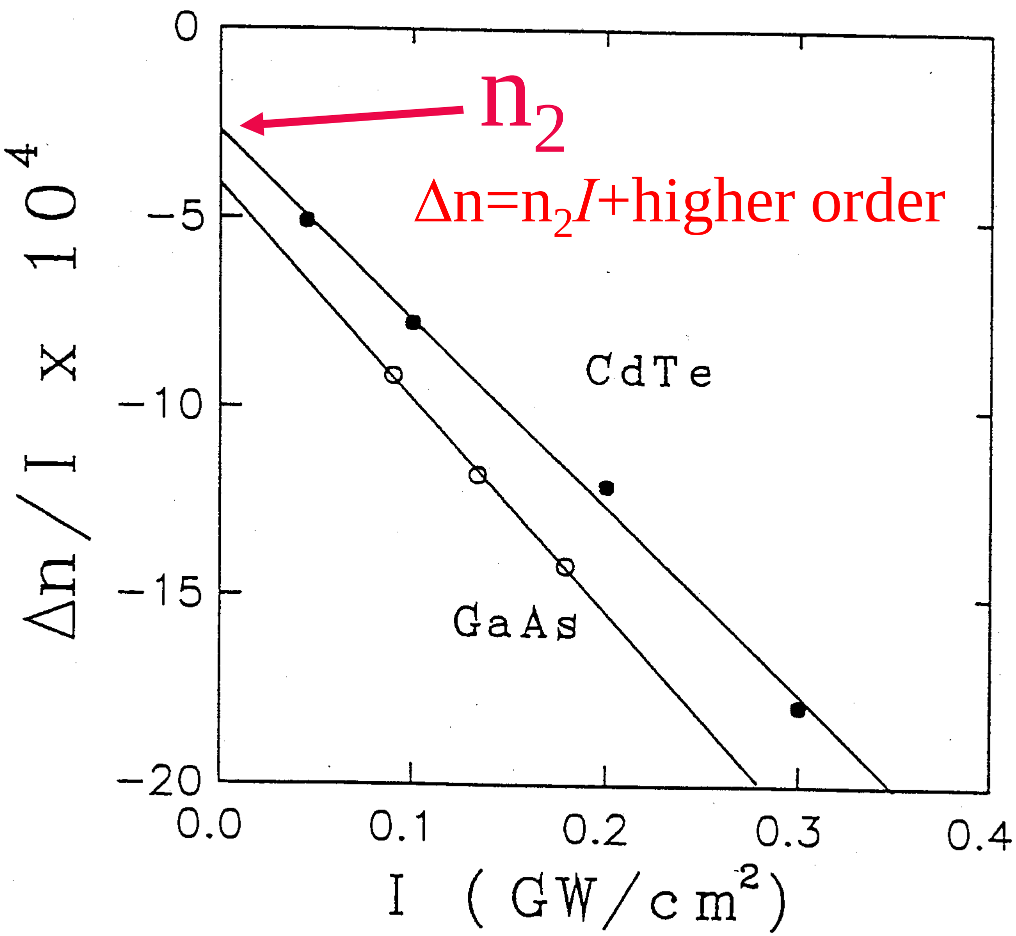
# Information from Z-scan at different I's

$$\frac{dI}{dz} = -\alpha_2 I^2 - \sigma_{FCA} N I$$

$$\frac{dN}{dt} = \frac{\alpha_2 I^2}{2\hbar w}$$

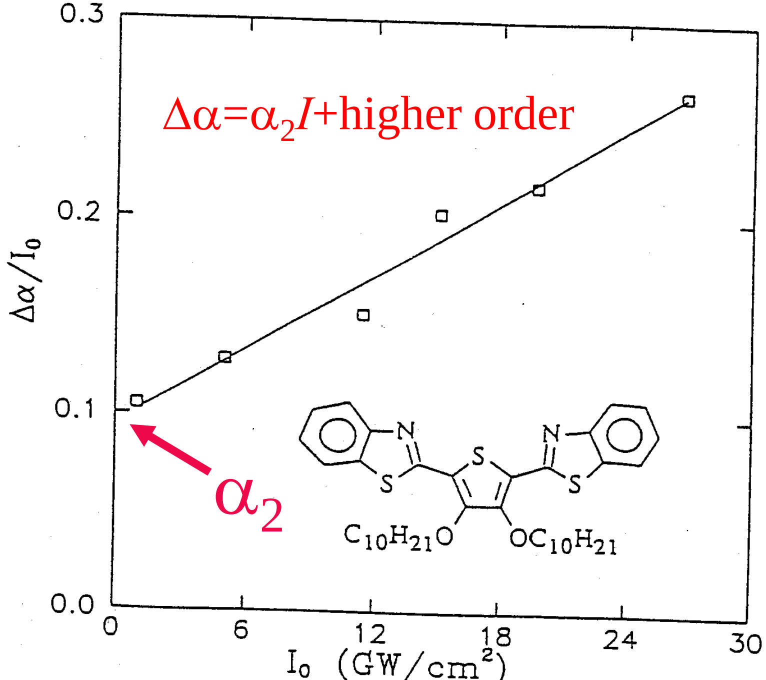
$$\frac{d\varphi}{dz} = k_0 n_2 I + \sigma_{FCR} N$$

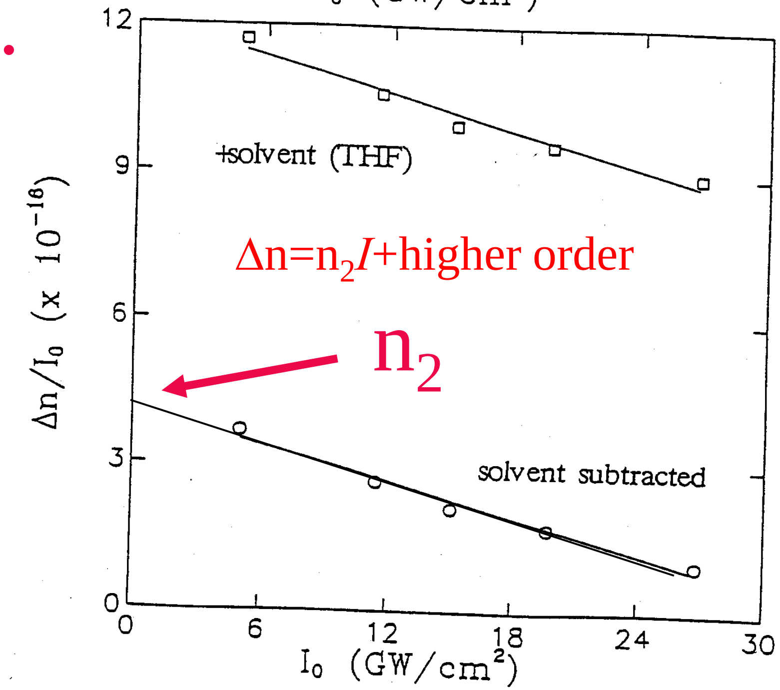


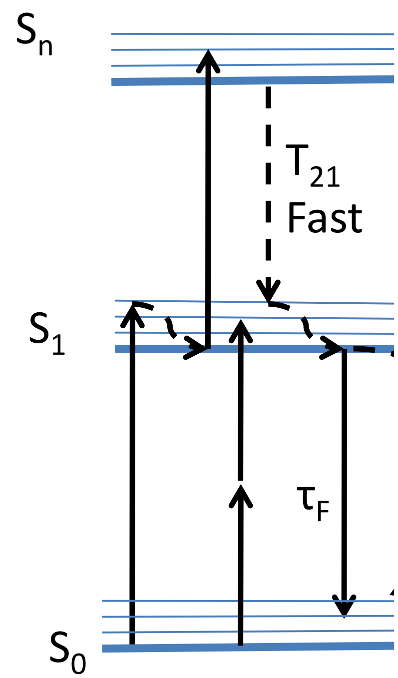




This shows the $n_2$ along with the 5th-order NLR from excited carriers

# See same effects in organic materials.



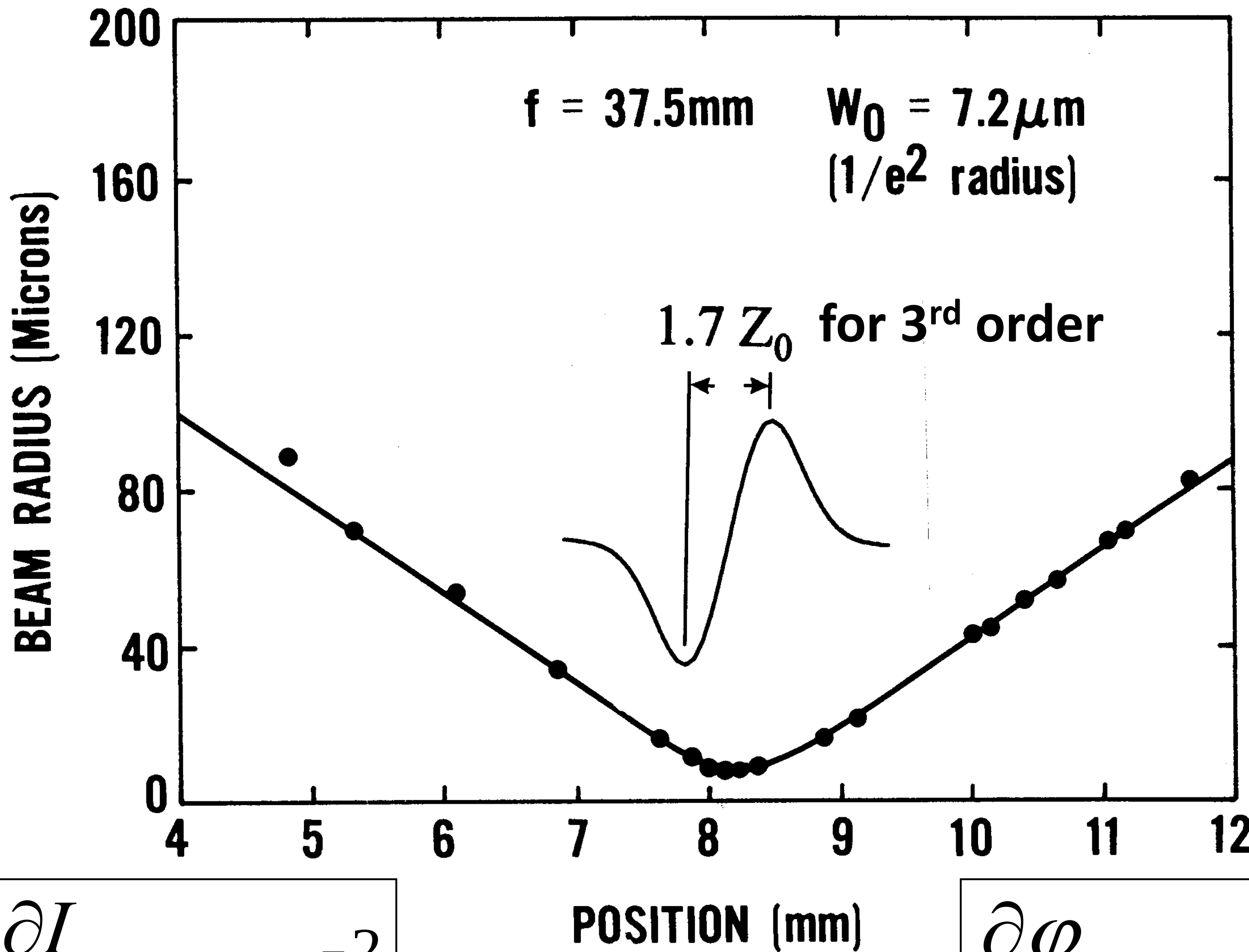

$$\frac{dI}{dz} = -\alpha_2 I^2 - \sigma_{ESA} N I$$

$$\frac{dN}{dt} = \frac{\alpha_2 I^2}{2\hbar w}$$

$$\frac{d\varphi}{dz} = k_0 n_2 I + \sigma_{ESR} N$$

# Thin-sample approximation
# External self action (Alex Kaplan)

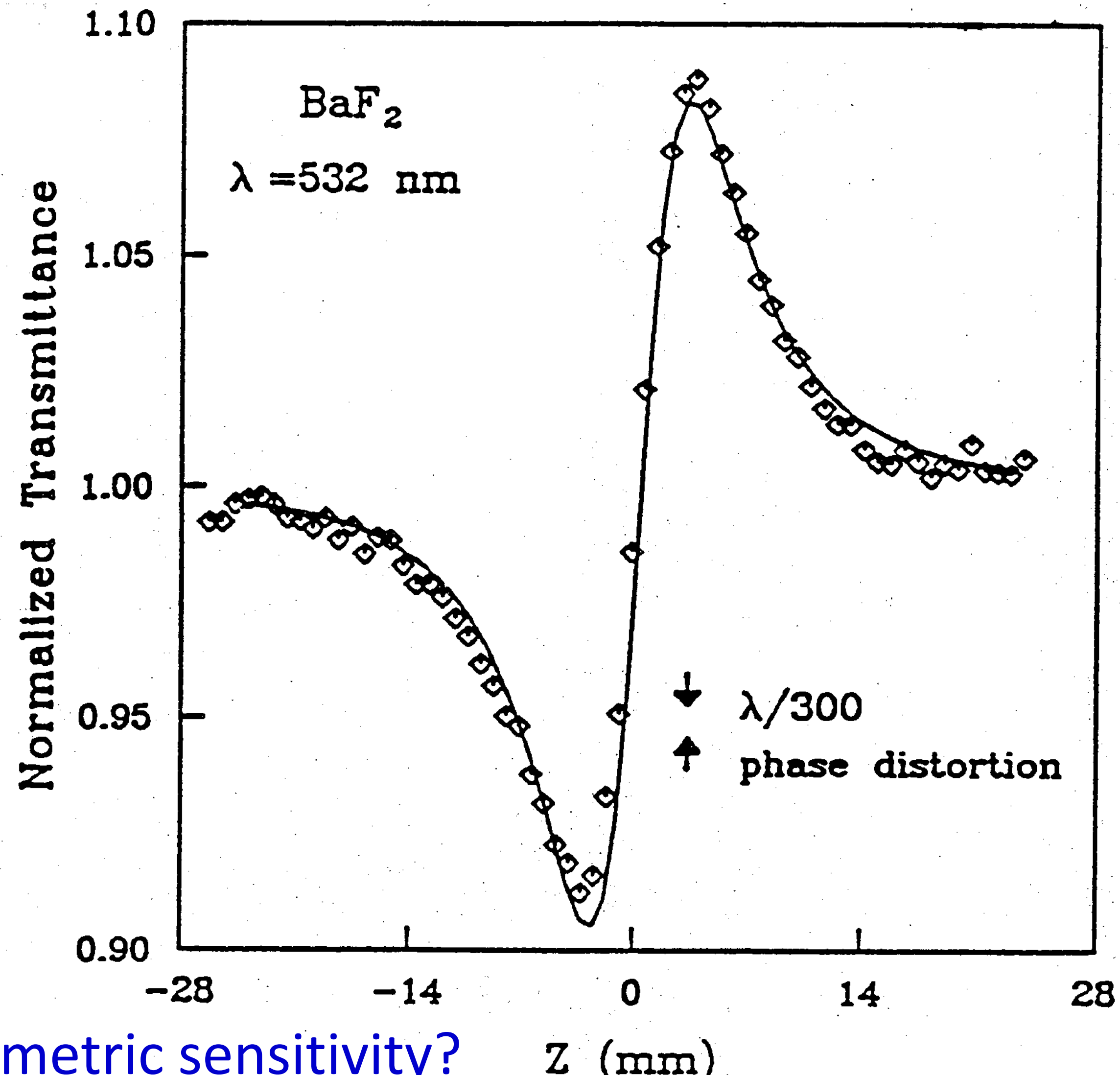
$L<Z_0$ and $L\Delta\varphi<Z_0$




$$\frac{\partial I}{\partial z}=-\alpha_2 I^2$$

$$\frac{\partial \varphi}{\partial z}=k_0 n_2 I$$

# Sensitivity



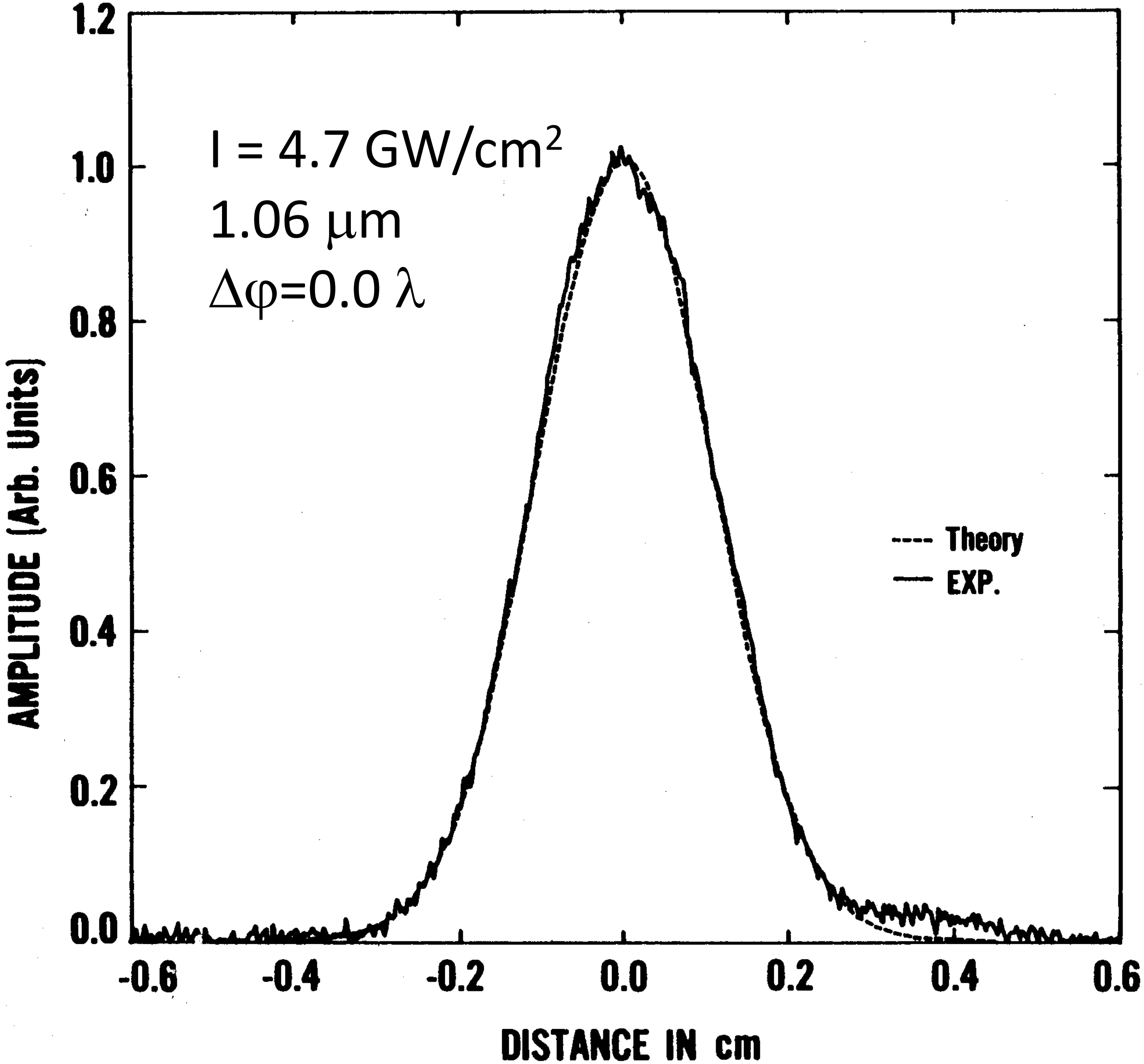

Only $n_2$ at 532nm

Why interferometric sensitivity?

M. Sheik-Bahae et al, JQE QE-26, 760-769 (1989).

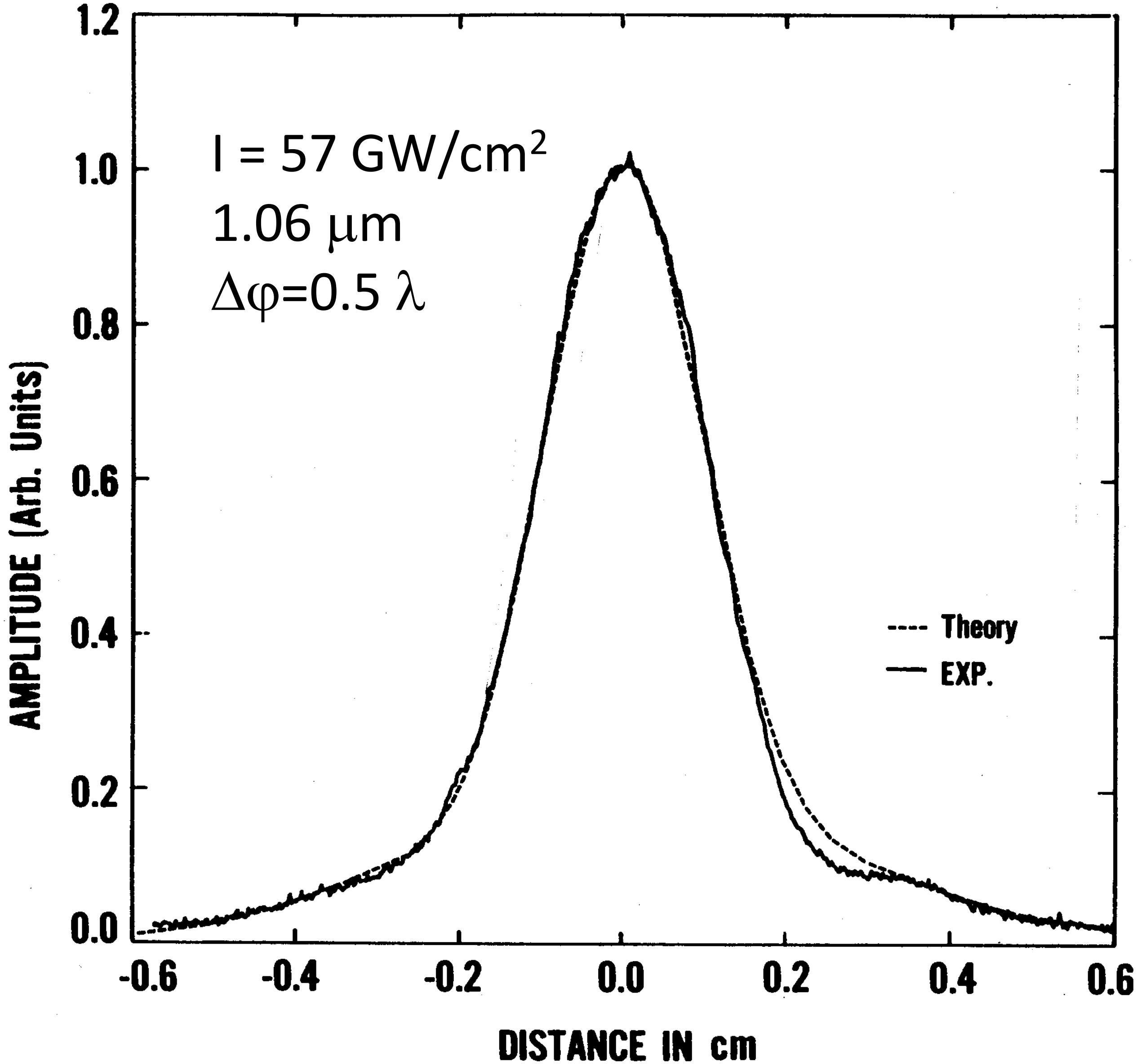
# NaCl

Far field

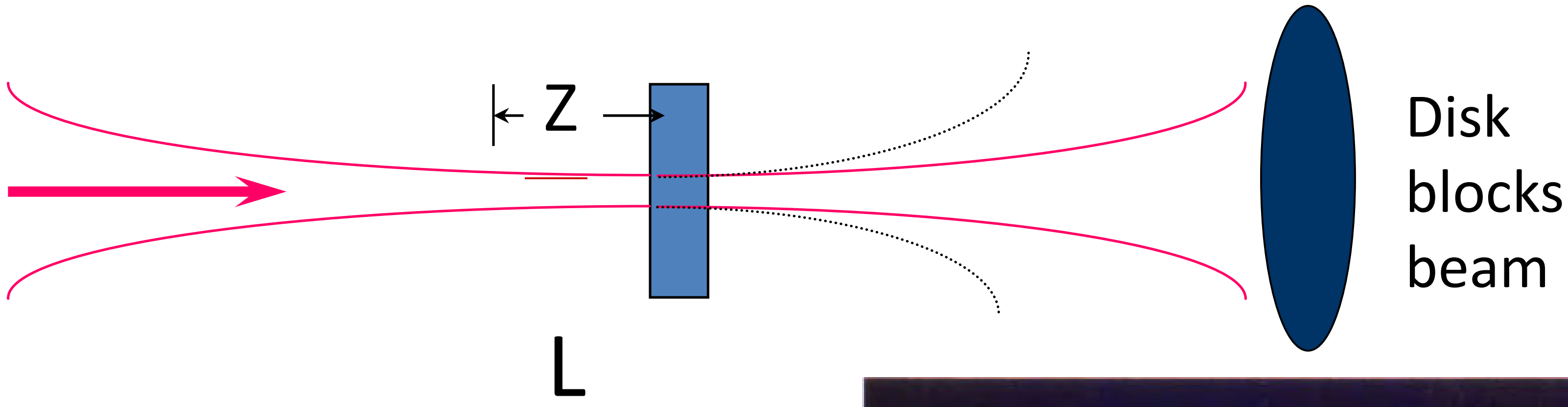


# NaCl

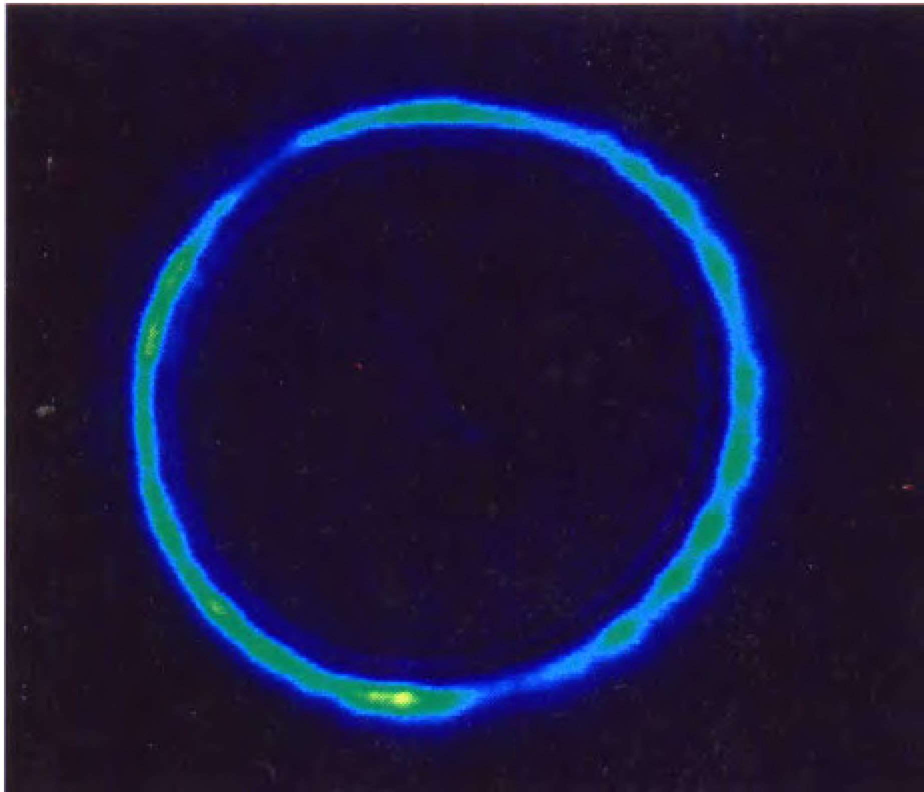
Far field



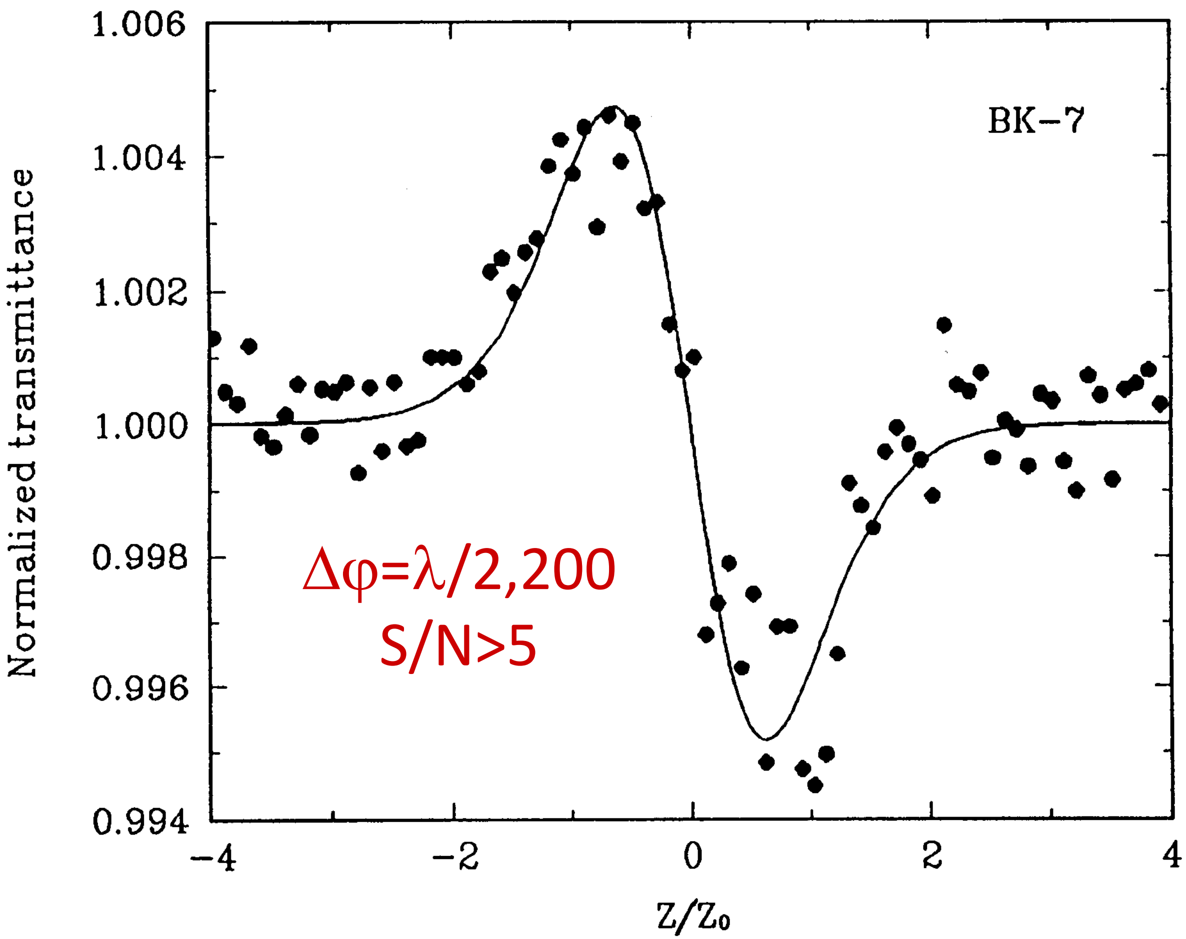
# EZ-Scan or Eclipsing Z-scan




can greatly increase sensitivity, but more difficult (not EZ)



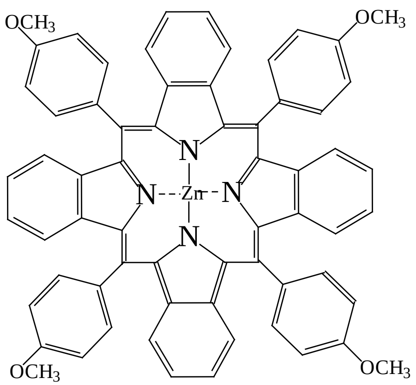
# EZ-Scan of BK-7 Glass (low I)



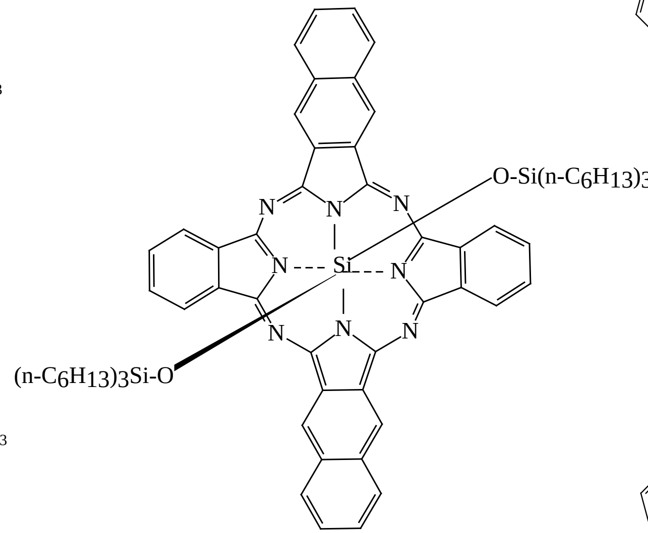

Why interferometric sensitivity?

# Resonant 2PA = ESA

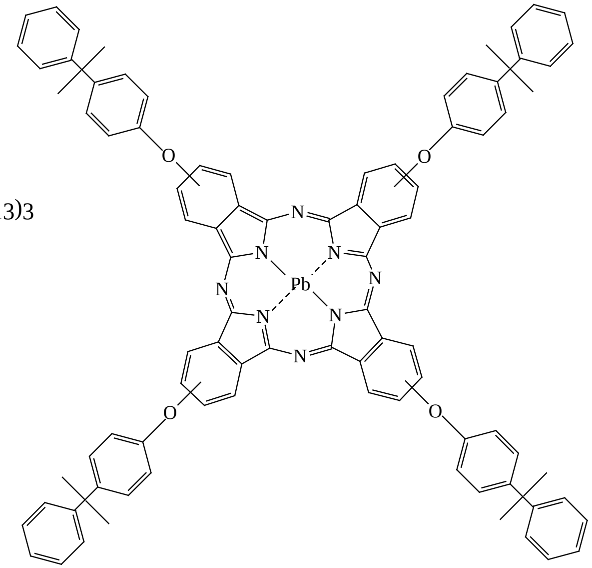
## (excited-state absorption)




ZincTetra(p-methoxyphenyl) tetrabenzporphyrin (Zn:TMOTBP)




Silicon Naphthalocyanine (SiNc)




Lead tetrakis (β-cumylphenoxy) phthalocyanine (PbPc)

Just make the intermediate state truly resonant: i.e. a “real” state

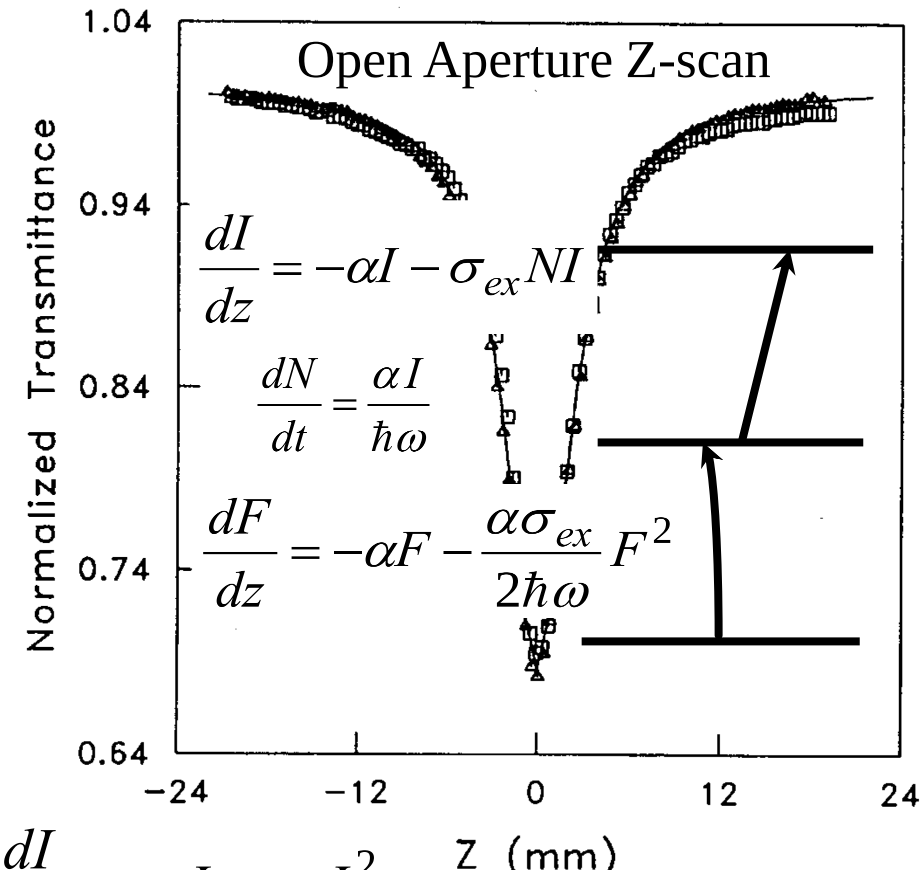
# Chloro-Aluminum Phthalocyanine

## 532 nm, two sets of data in each Z-scan

ENERGY FIXED!

△ 30 ps pulse (FWHM)

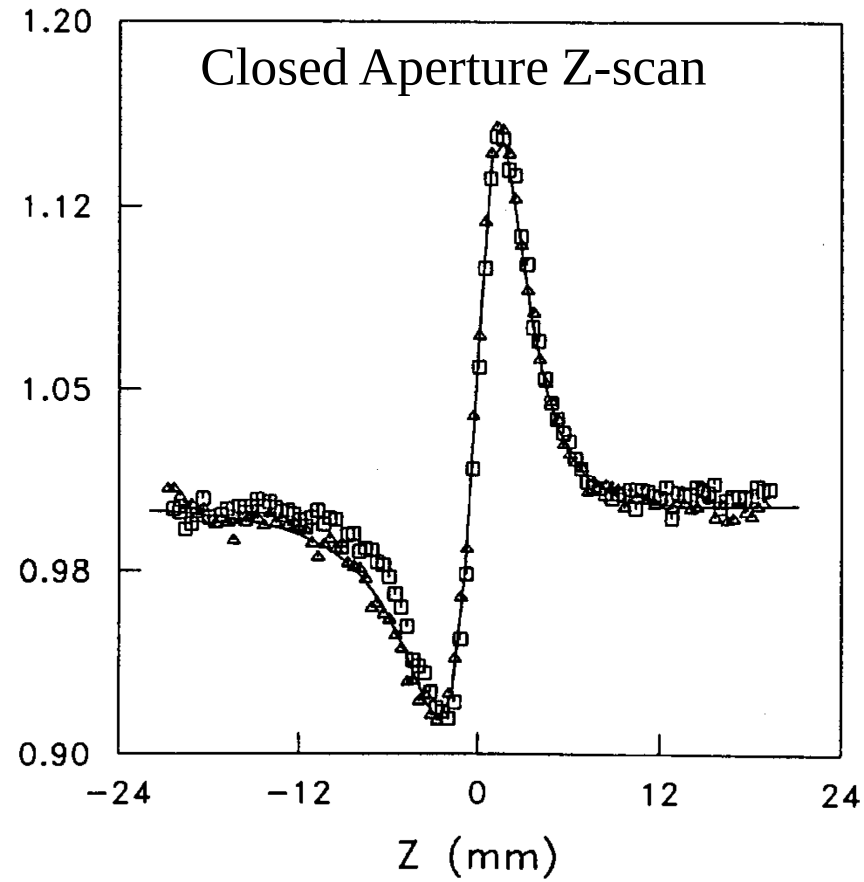
□ 62 ps pulse (FWHM)




$$\frac{dI}{dz} = -\alpha I - \sigma_{ex} N I$$

$$\frac{dN}{dt} = \frac{\alpha I}{\hbar\omega}$$

$$\frac{dF}{dz} = -\alpha F - \frac{\alpha \sigma_{ex}}{2\hbar\omega} F^2$$



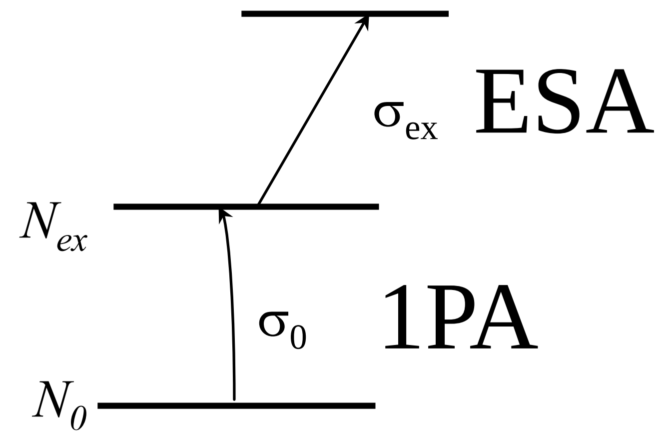

$$\frac{dI}{dz} = -\alpha I - \alpha_2 I^2$$

with Joe Perry, JPL (now GeorgiaTech), Applied Physics, B54, 46-51 (1992) 

# Excited-State Nonlinearities

$$\frac{dI}{dz} = -\sigma_0 N_0 I - \sigma_{ex} N_{ex} I$$

with $$\frac{dN_{ex}}{dt} = \frac{\sigma_0 N_0 I}{\hbar\omega}$$




integrate over t

$$\frac{dF}{dz} = -\sigma_0 N_0 F - \frac{\sigma_0 \sigma_{ex}}{2\hbar\omega} N_0 F^2$$

$$\frac{dI}{dz} = -\alpha I - \alpha_2 I^2$$

Looks like 2PA

How to go from 2PA to RSA?

If you don't assume $\sigma_{ex} >> \sigma_g$

$$\frac{dI}{dz} = -\alpha I - \sigma_{ex} N I \qquad \frac{dN}{dt} = \frac{\alpha I}{\hbar\omega} \qquad \sigma_g N_g = \alpha$$

$$\frac{dF}{dz} = -\sigma_{ge} N_g F - \sigma_{ge} N_g \frac{(\sigma_{eu} - \sigma_{ge})}{2\hbar\omega} F^2 \qquad F = \int_{-\infty}^{\infty} I(t)dt$$

For phase

$$\frac{d\phi(z,t)}{dz} = kn_2 I(z,t) + (\sigma_{euR} + \sigma_{geR}) N_e(z,t)$$

$$\left.\frac{d\langle\phi(z,t)\rangle_t}{dz}\right|_{ESR} = (\sigma_{geR} + \sigma_{exR}) \frac{\alpha}{\hbar\omega} \frac{\int_{-\infty}^{\infty} dt\, I(z,t) \int_{-\infty}^{t} dt' I(z,t')}{\int_{-\infty}^{\infty} dt\, I(z,t)} = \frac{1}{2}(\sigma_{geR} + \sigma_{exR}) \frac{\alpha}{\hbar\omega} F$$

Slow response in time

$$\left.\frac{d\langle\phi(z,t)\rangle_t}{dz}\right|_{n_2} = kn_2 \frac{\int_{-\infty}^{\infty} dt\, I^2(z,t)}{\int_{-\infty}^{\infty} dt\, I(z,t)} = \frac{kn_2}{\sqrt{2}} F$$

Assuming Gaussian and ultrafast response

## 2PA induced ESA

$$\frac{dI(z,t)}{dz} = -\alpha_2 I^2(z,t) - \sigma_{ex} N_e I \qquad \frac{dN_e}{dt} = \frac{\alpha_2 I^2}{2\hbar\omega}$$

Looks like 3PA

$$\frac{dF}{dz} = -\alpha F - \frac{N_g \sigma_g \sigma_{ex}}{2\hbar\omega} F^2$$

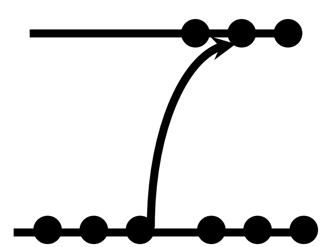
Here the effective $\chi^{(3)}$ looks just like 2PA and it can be difficult to tell the difference, e.g. a Z-scan looks the same unless you hit it hard (then saturation of the linear absorption occurs).

$$\frac{dI}{dz} = -\alpha I - \alpha_2 I^2$$

Looks just like eq. for 2PA, but a $\chi^{(1)}:\chi^{(1)}$ nonlinearity

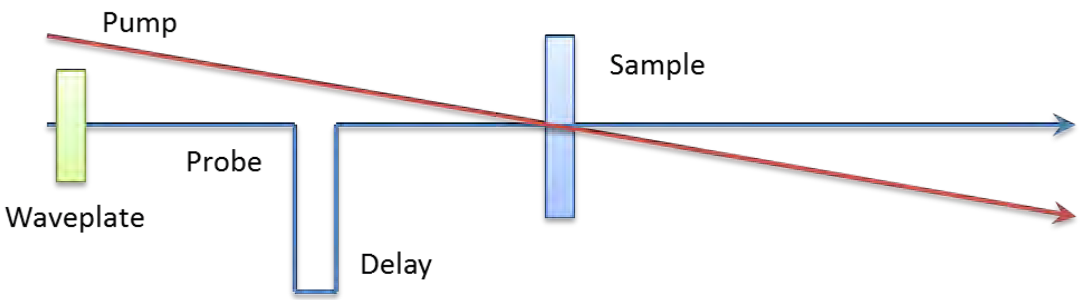
Now look at saturation. Use rate equations to obtain:

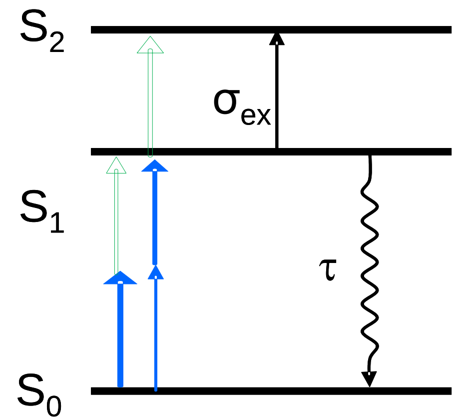
$$\frac{dI}{dz} = -\frac{\alpha_0}{1+\frac{I}{I_{Sat}}} I \cong -\alpha_0 I\left(1 - \frac{I}{I_{Sat}}\right) = -\alpha_0 I + \frac{\alpha_0}{I_{Sat}} I^2$$



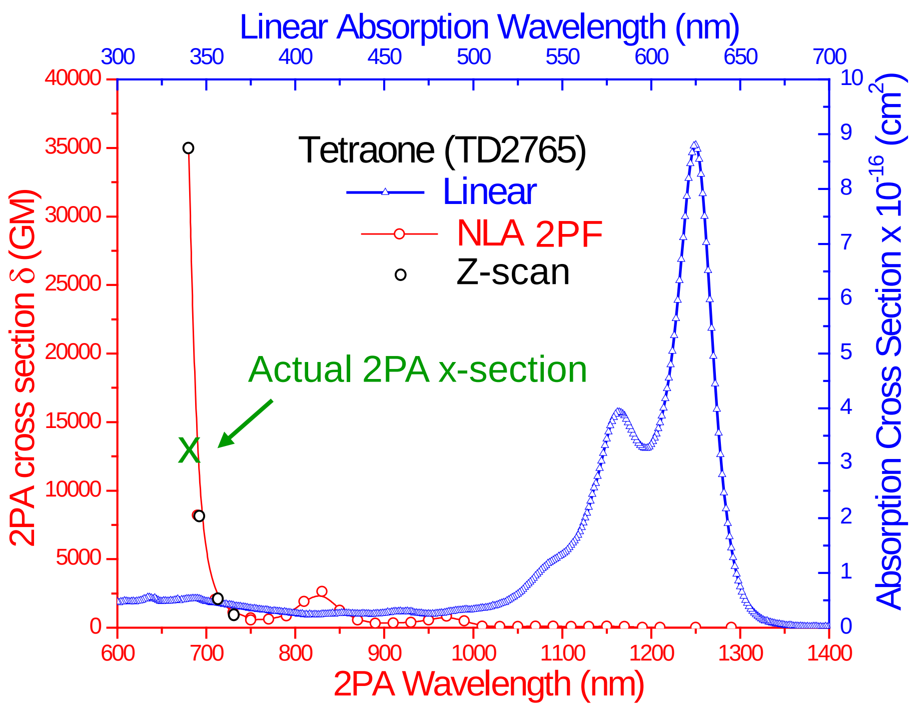
~~“negative 2PA”~~

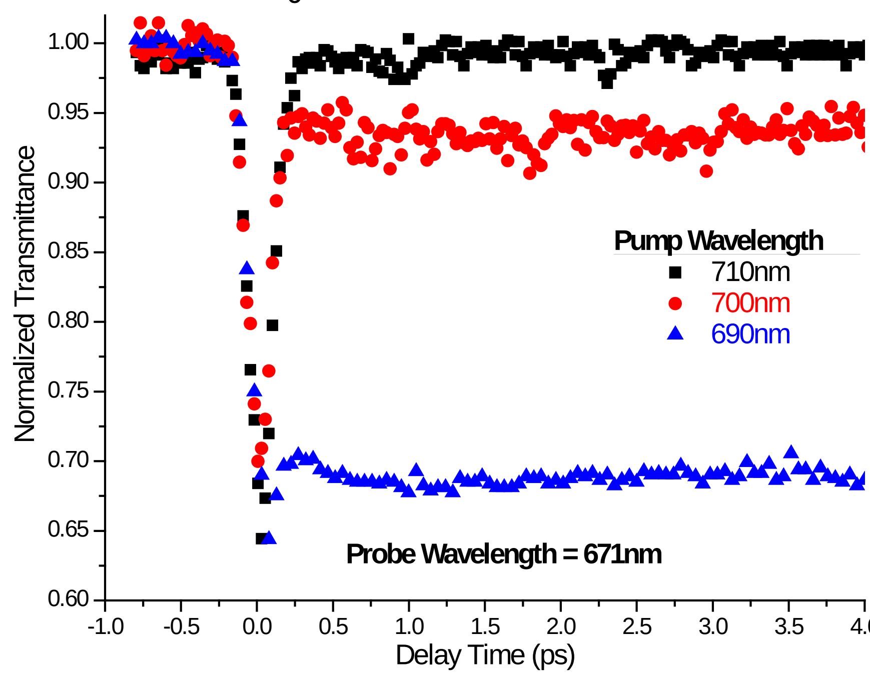
# Distinguishing ESA from 2PA




## A more complicated system – 2PA followed by ESA



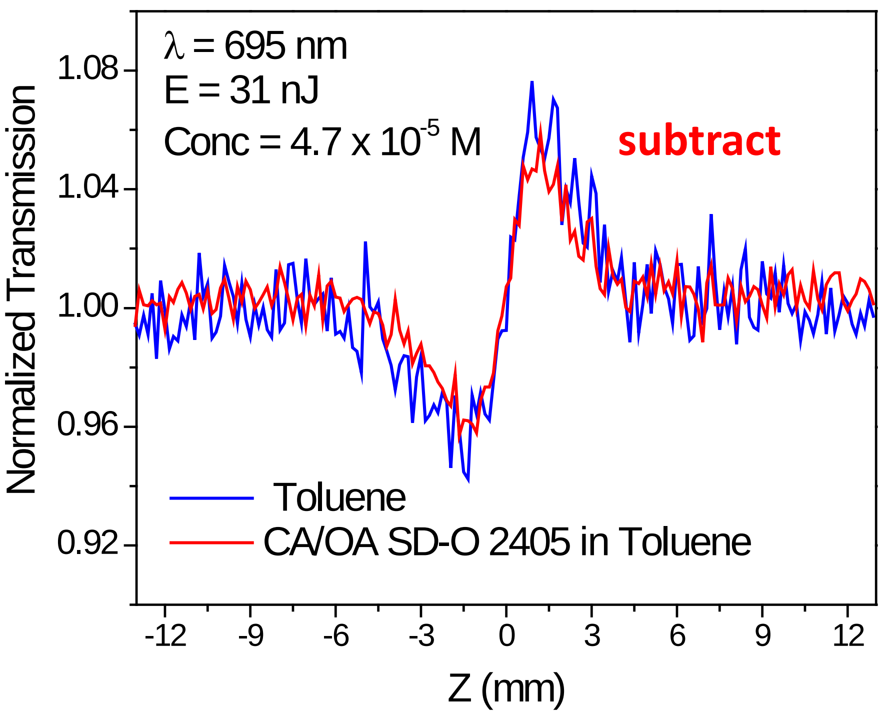



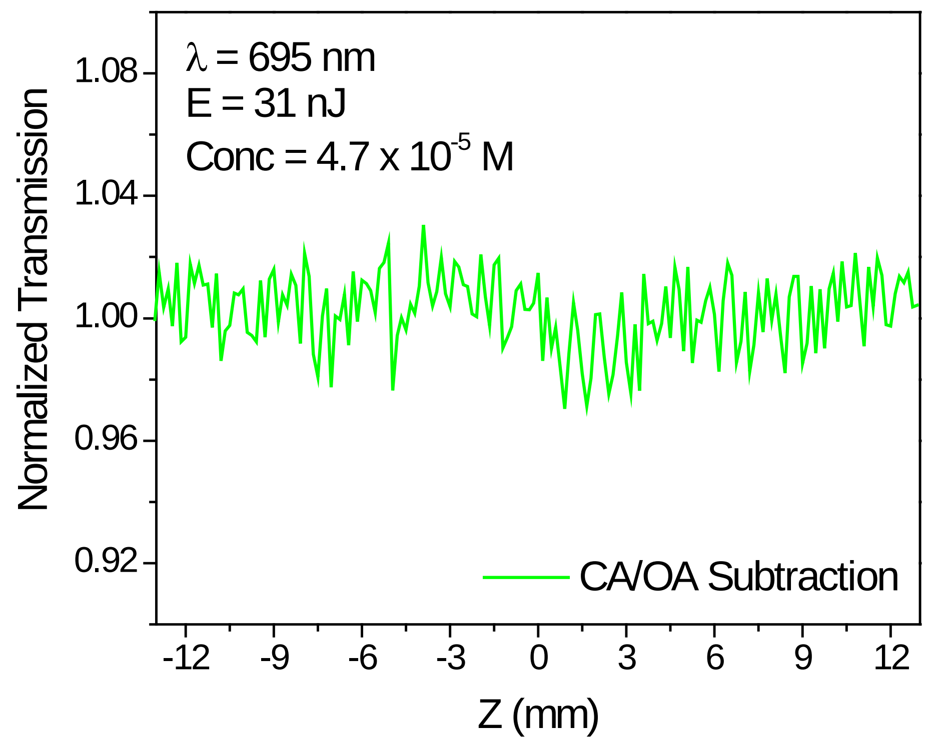

**Pump Probe was used to determine pure maximum 2PA of 8000 – 12000 GM**

# Limitation of Z-Scan for solutions

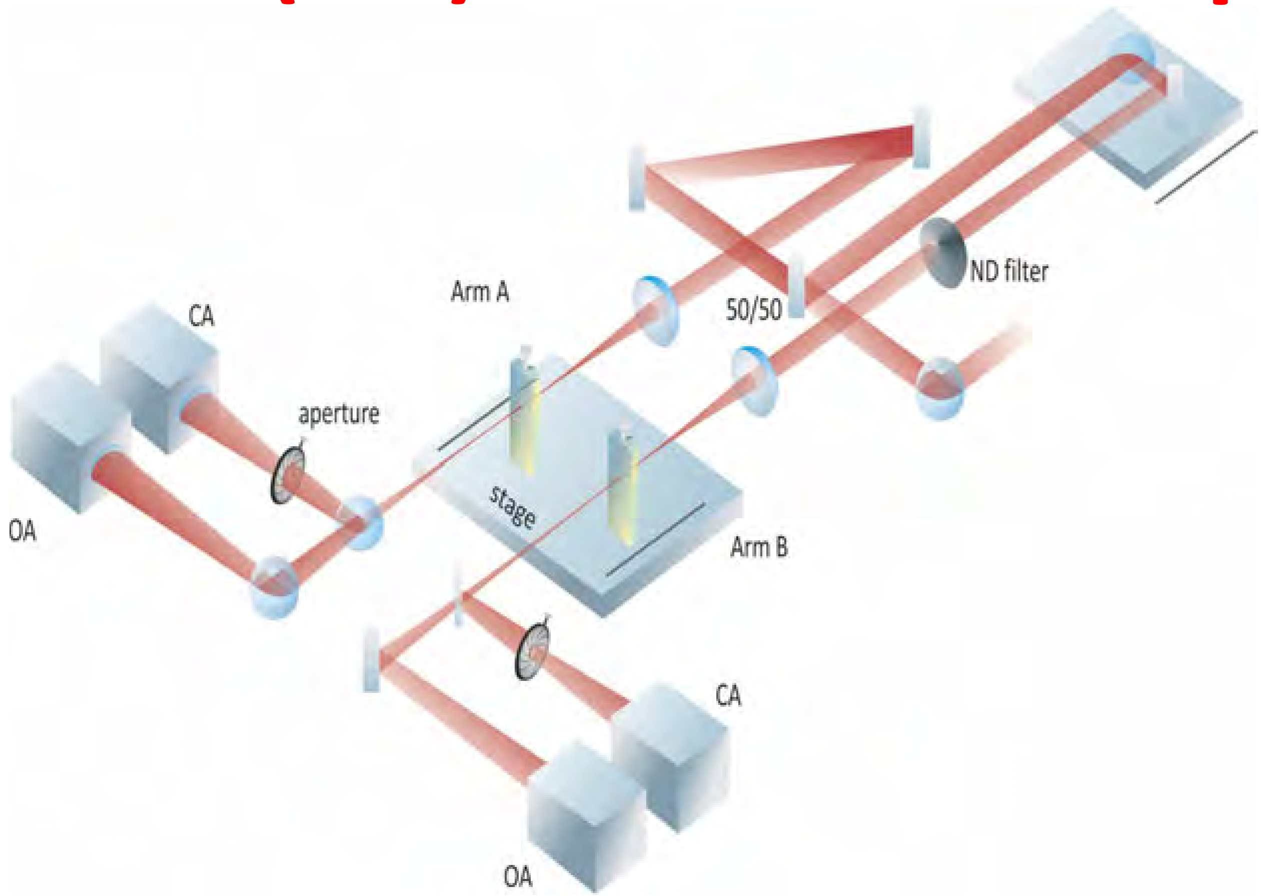
Solute NLR can be buried in noise:

- For low solubility
- Spectral regions where sign of $n_2$ changes

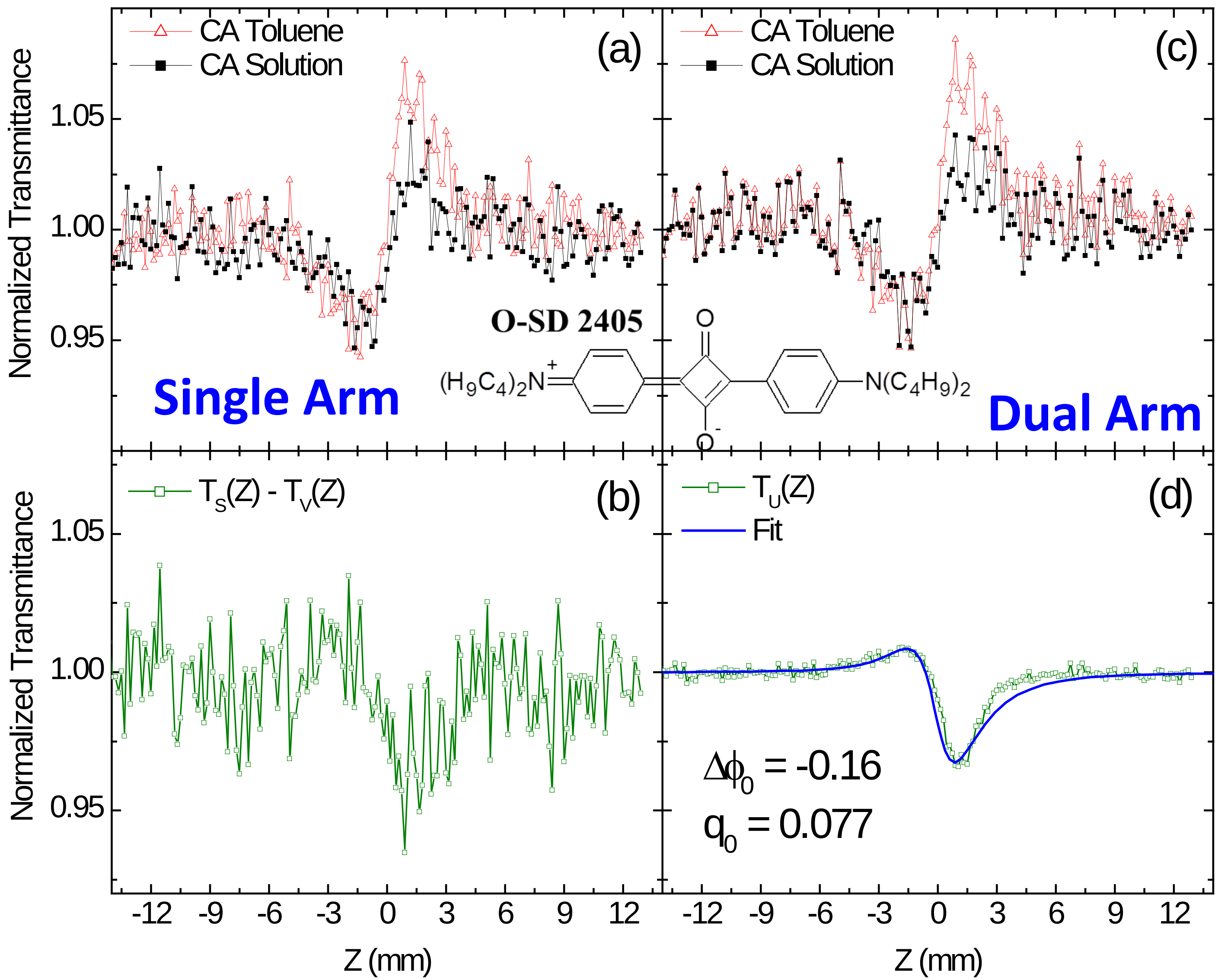


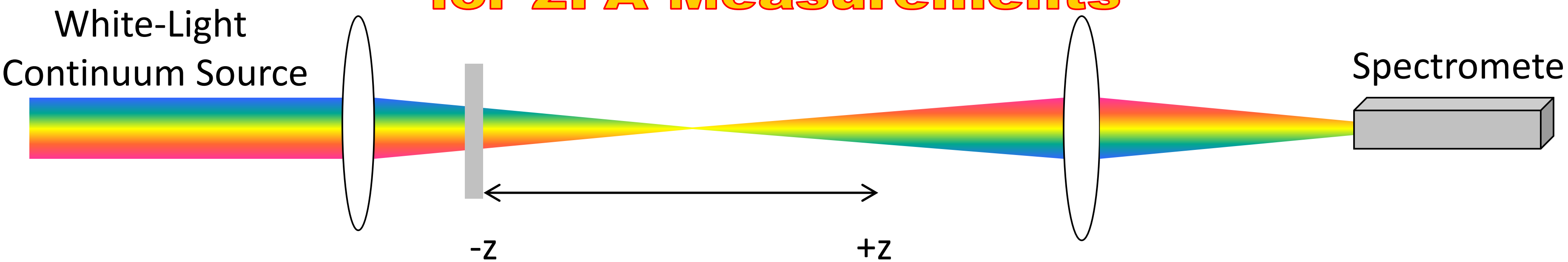
# Dual-arm (DA) Z-scan Technique

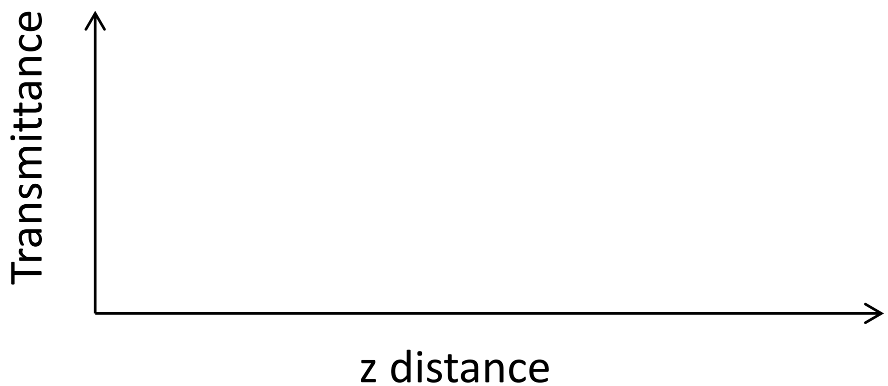



- Identical irradiance distribution in each arm
- Noise correlated (e.g. beam pointing, beam shape, energy, etc.)
- Increases signal-to-noise (SNR) ratio


CA Toluene
CA Solution
(a)
(c)
Normalized Transmittance
1.05
1.00
0.95
O-SD 2405
Single Arm
Dual Arm
$(H_9C_4)_2N^+$
$N(C_4H_9)_2$
O
$O^-$
$T_S(Z) - T_V(Z)$
(b)
$T_U(Z)$
Fit
(d)
$\Delta\phi_0 = -0.16$
$q_0 = 0.077$
-12 -9 -6 -3 0 3 6 9 12
Z (mm)

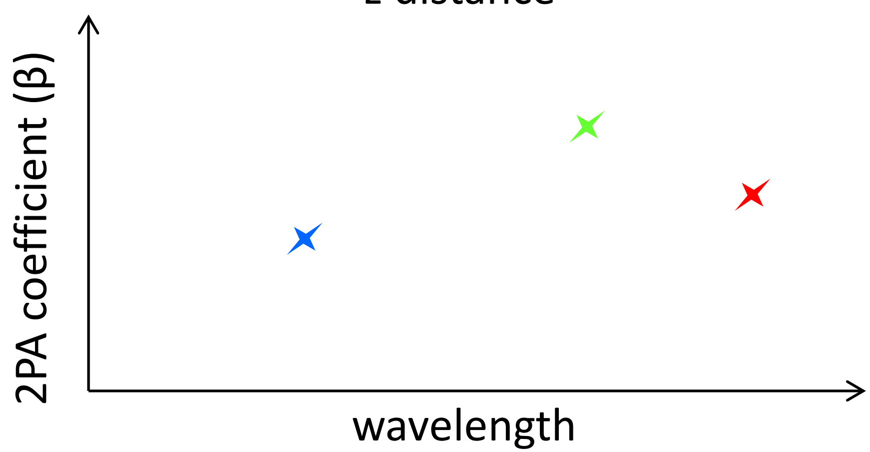
# White-Light Continuum (WLC) Z-scan Technique for 2PA Measurements



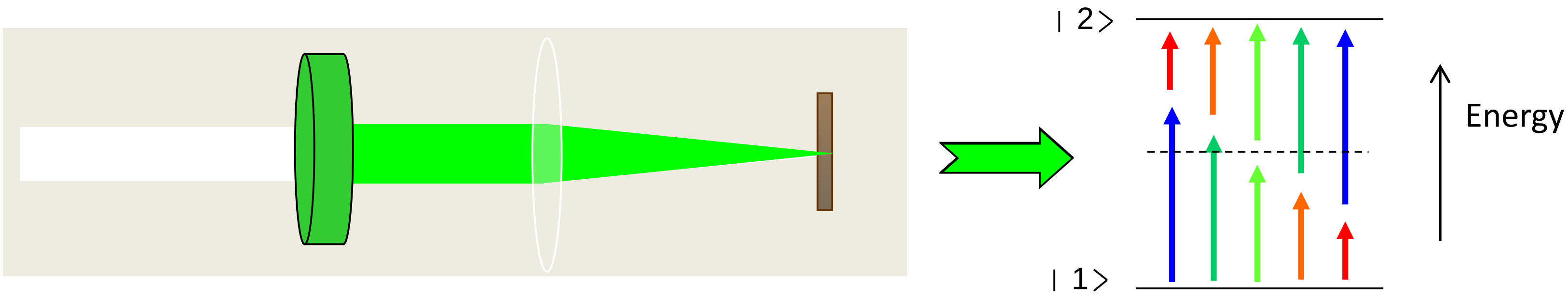

## Problem!

Lots of wavelengths present in sample simultaneously.

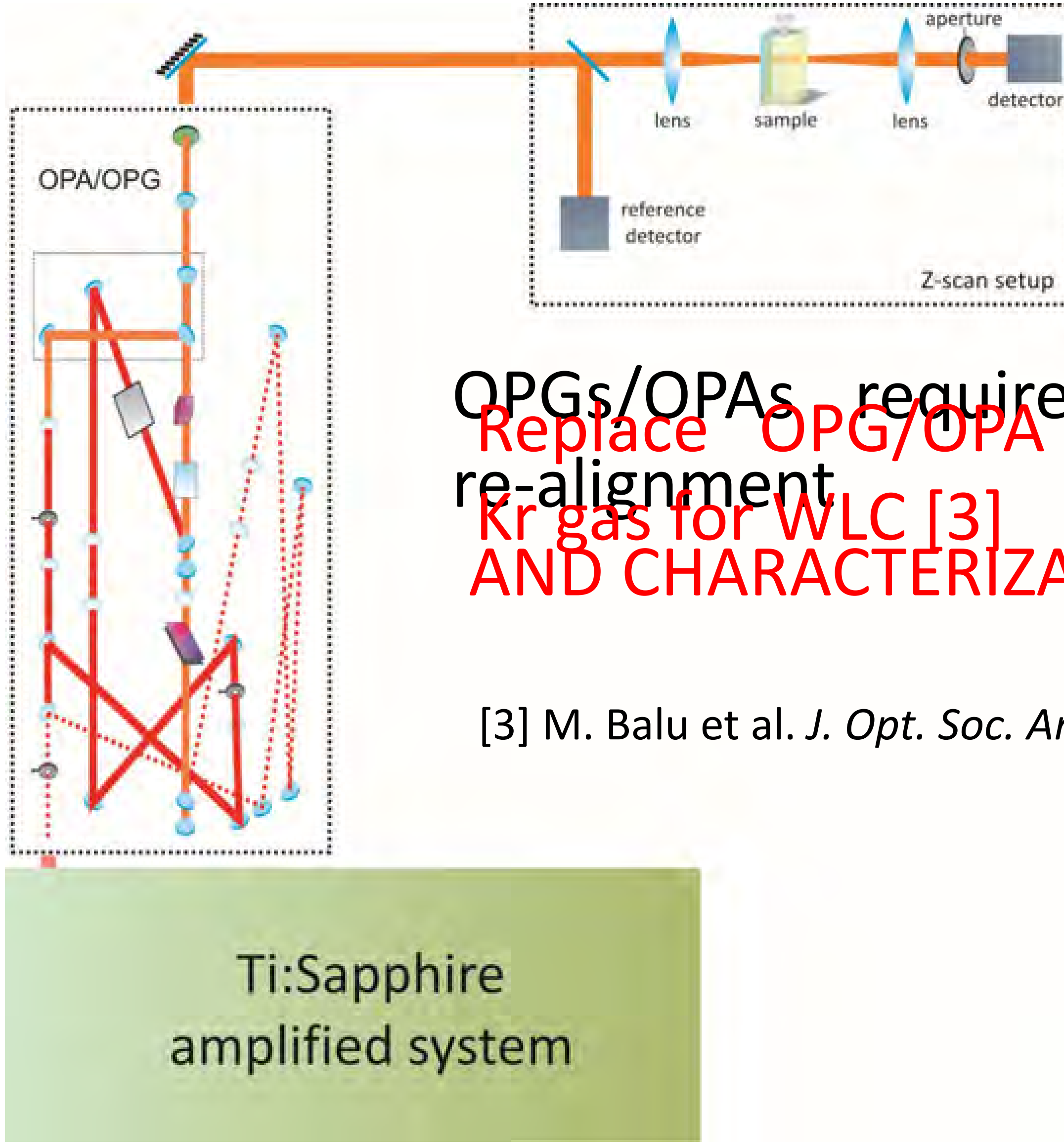


# WLC Z-scan

For degenerate nonlinearities it is necessary to select a narrow band of the WLC for each scan



# Nonlinear Spectroscopy Techniques



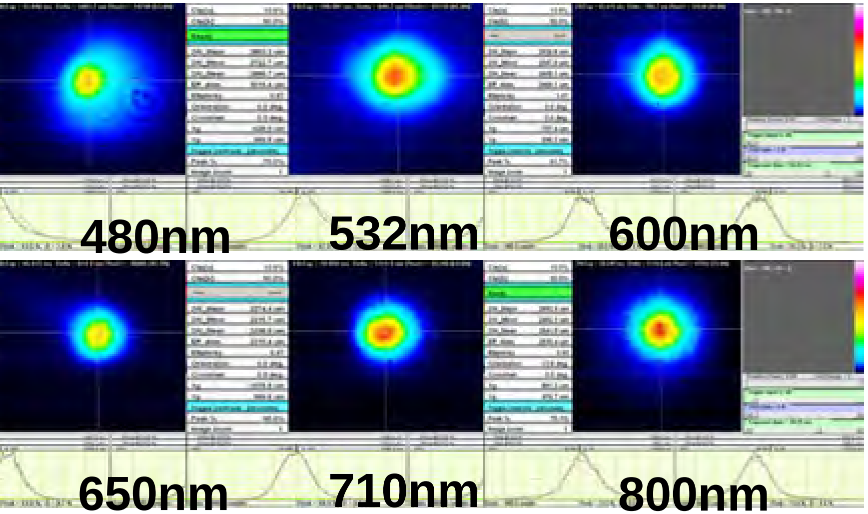

OPGs/OPAs require constant re-alignment

Replace OPG/OPA with Kr gas for WLC [3]

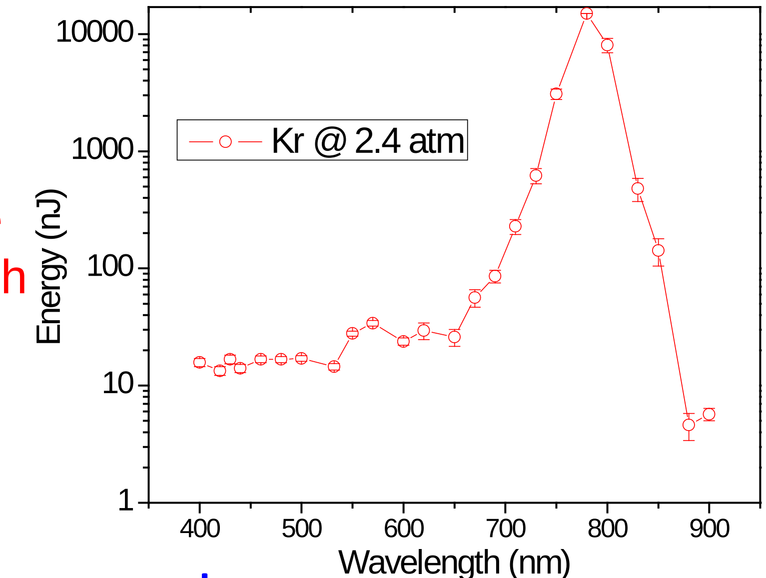
AND CHARACTERIZATION

[3] M. Balu et al. *J. Opt. Soc. Am. B* **25**, 159 (2008)

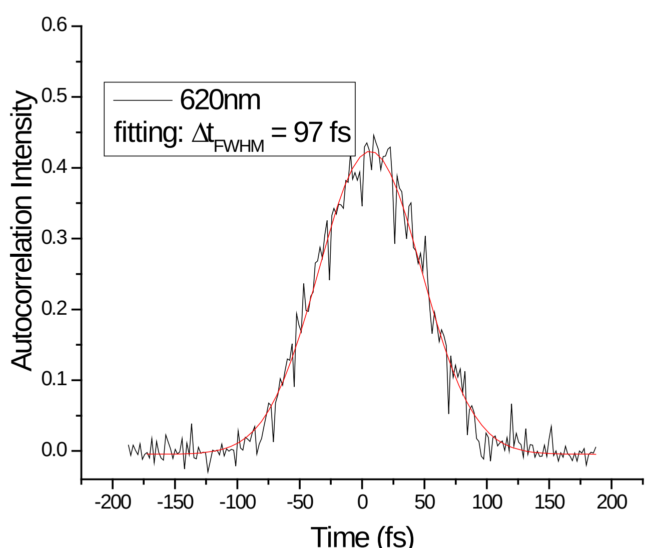
# Beam Profiles

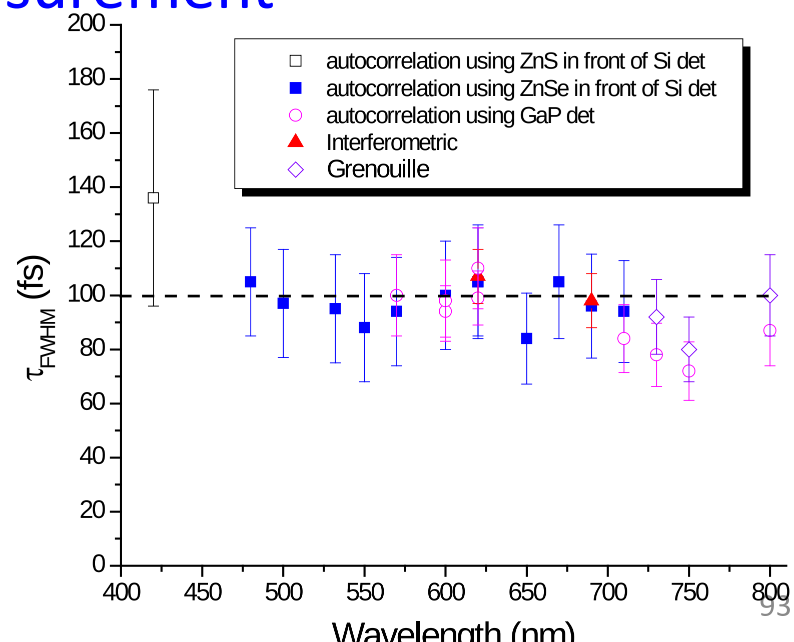



Energy available after each filter



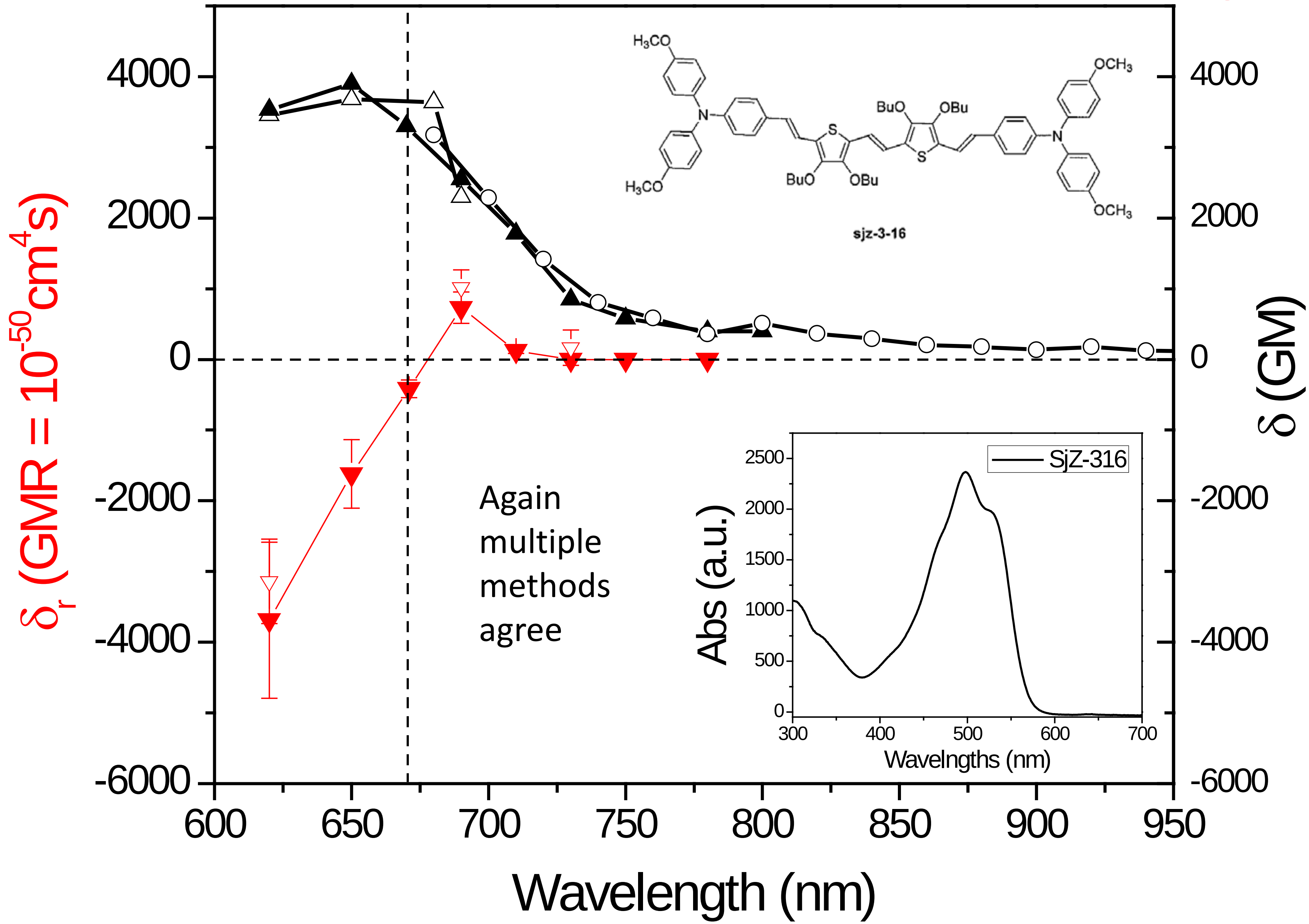

## Pulse Width Measurement




Mihaela Balu

# Molecule from Marder group

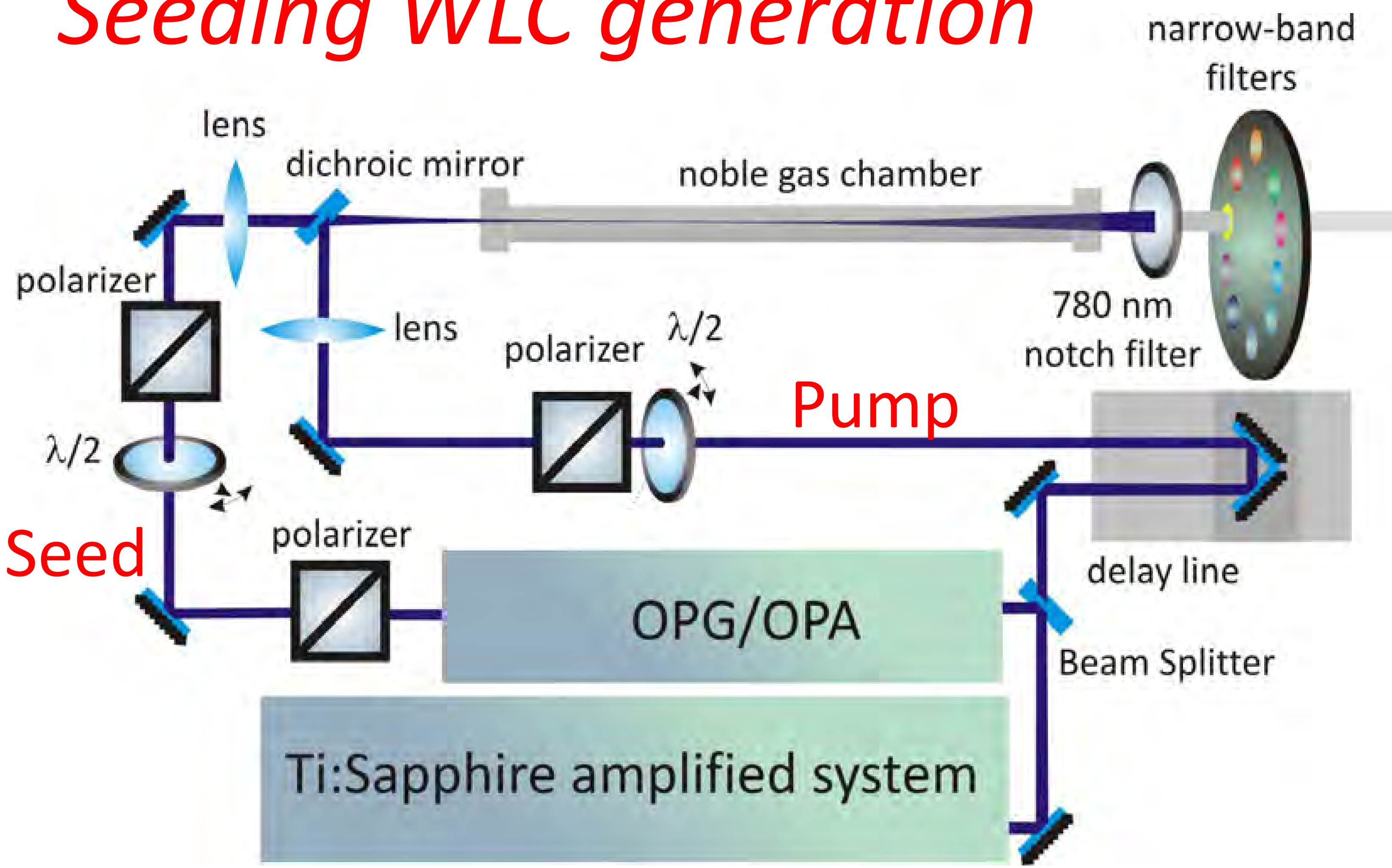


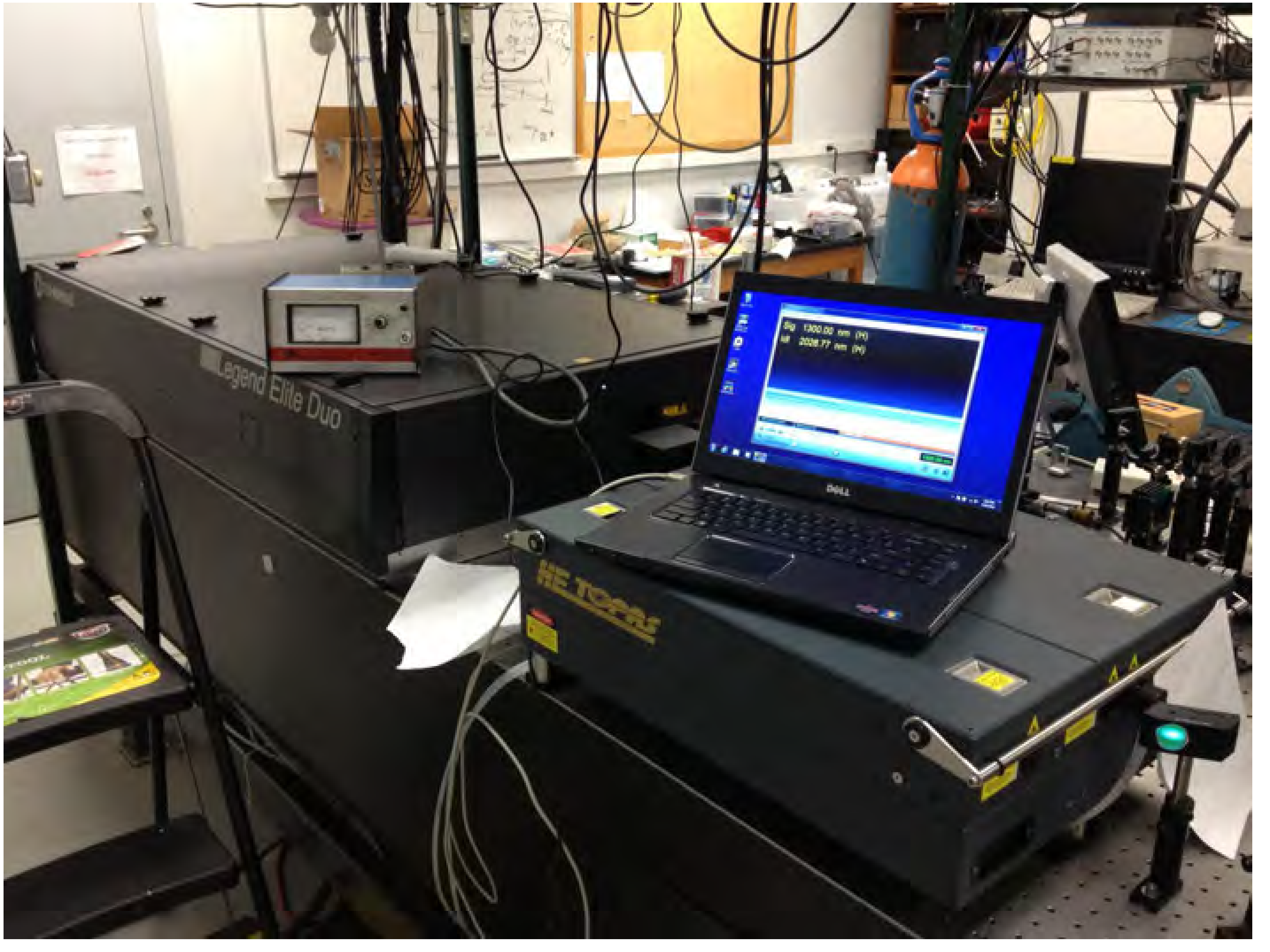
# OUTPUT STAYS THE SAME

# But want more energy, more λ's

# How to get more energy?

## *Seeding WLC generation*

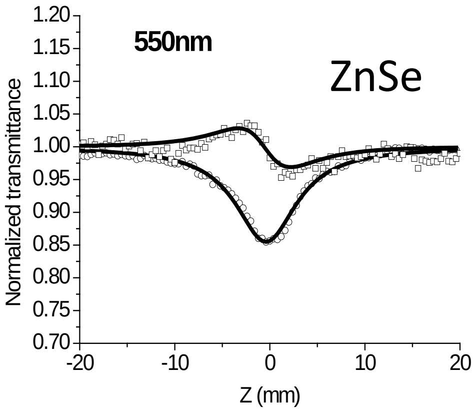


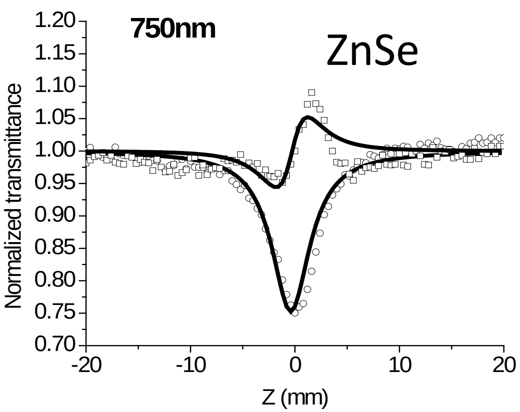


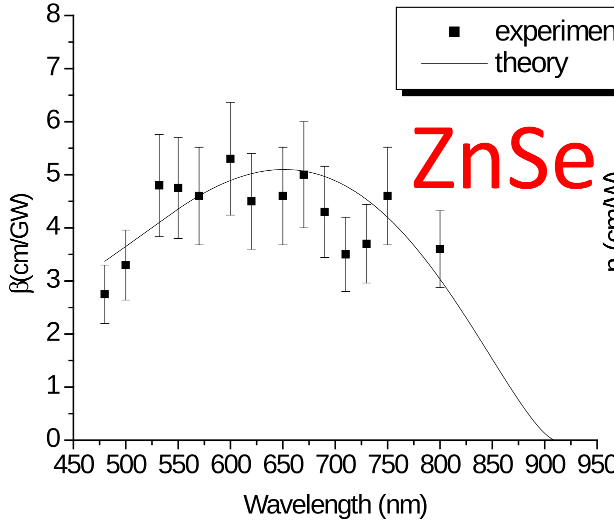

Facilities –12mJ, 1kHz, 40fs!

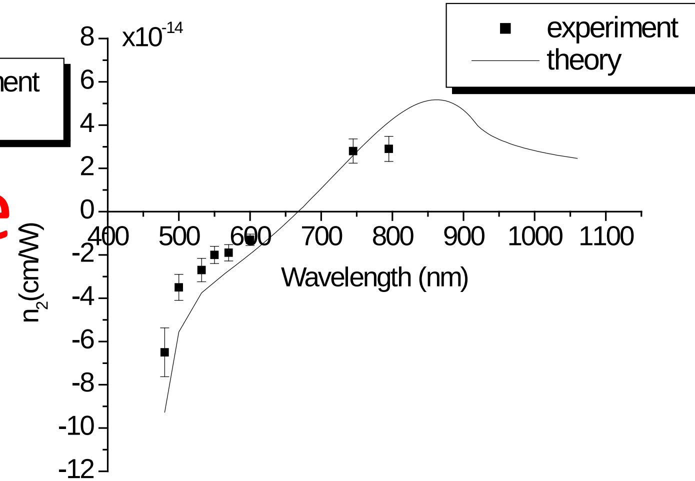
>1mJ @ 2 μm!

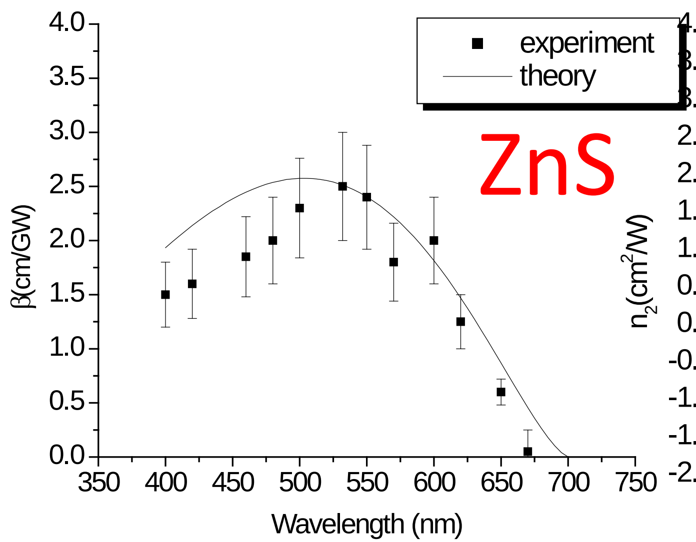
# Spectra and Dispersion (fs) WLC Z-scan

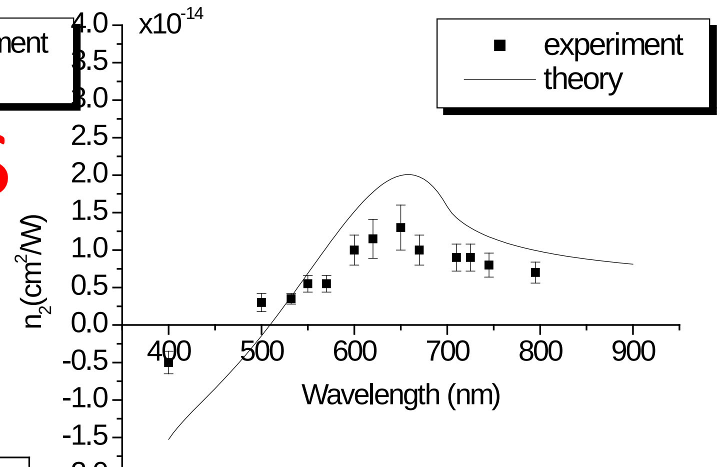


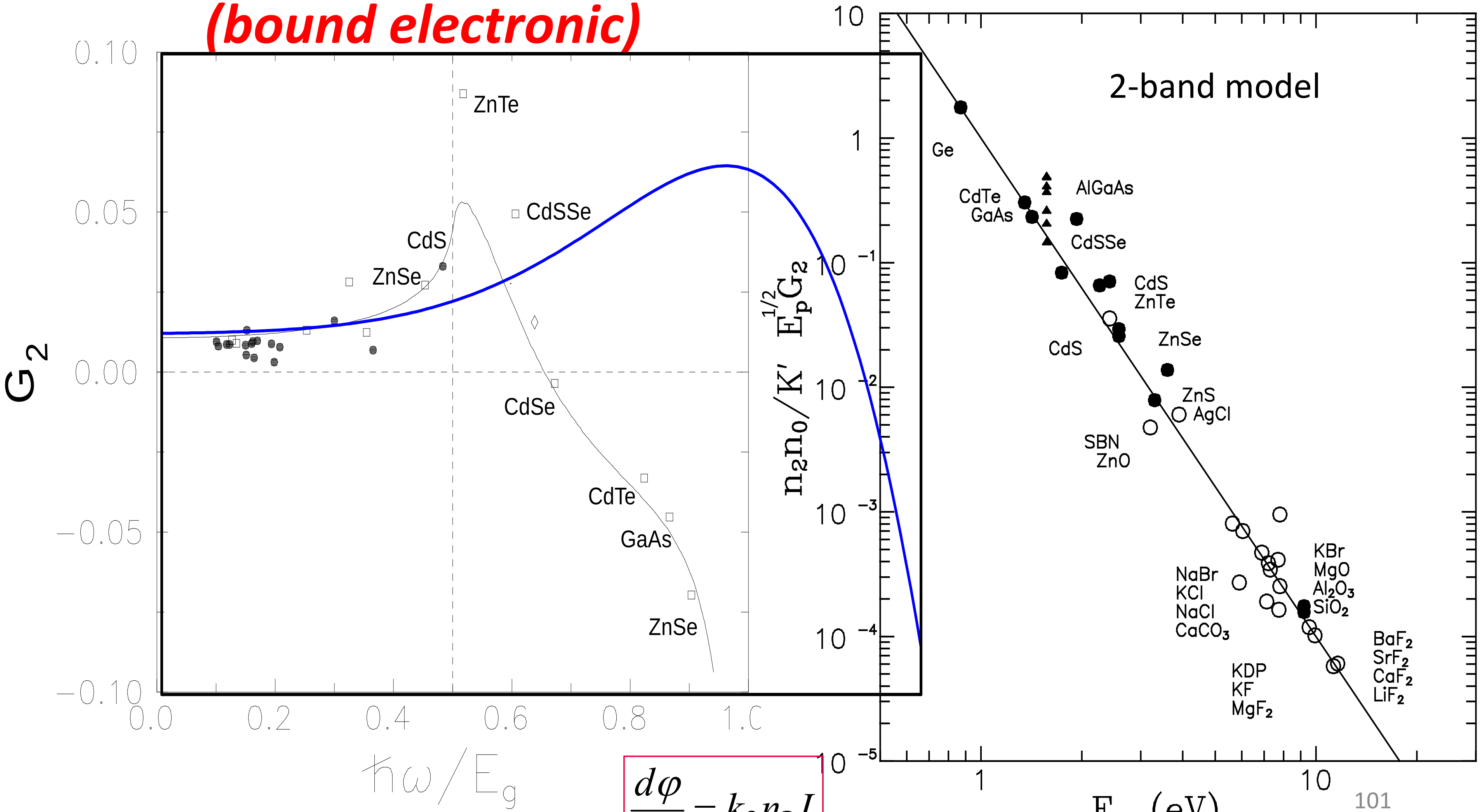




Note sign change of $n_2$

JOSA B, Vol. 25 Issue 2, pp.159-165 (2008)

# Nonlinear Refraction In semiconductors (bound electronic)

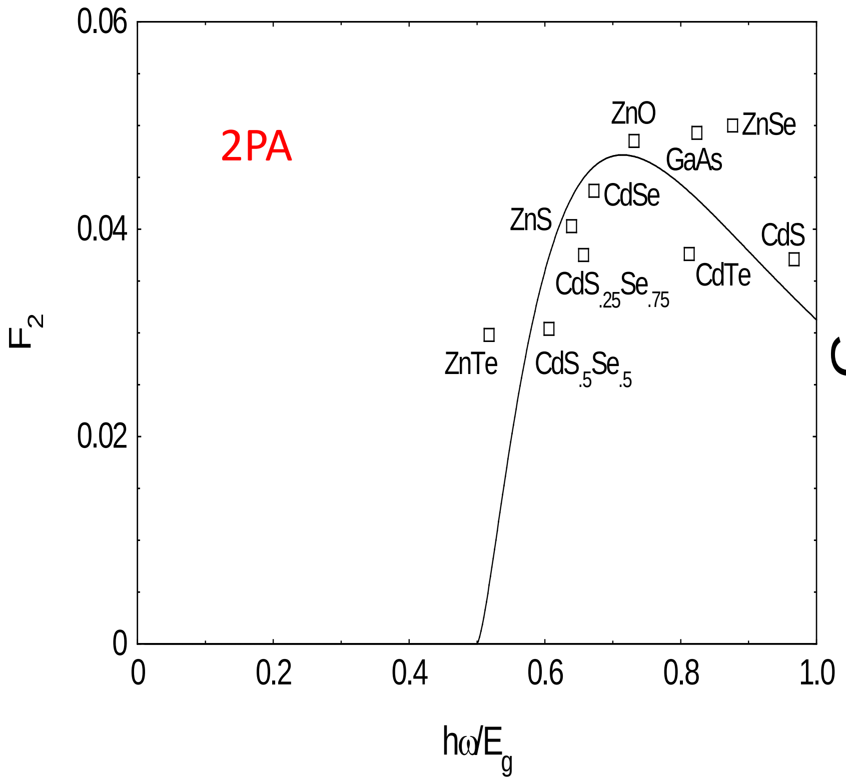
$$n_2 = K \cdot G_2(\hbar\omega / E_g) / E_g^4$$

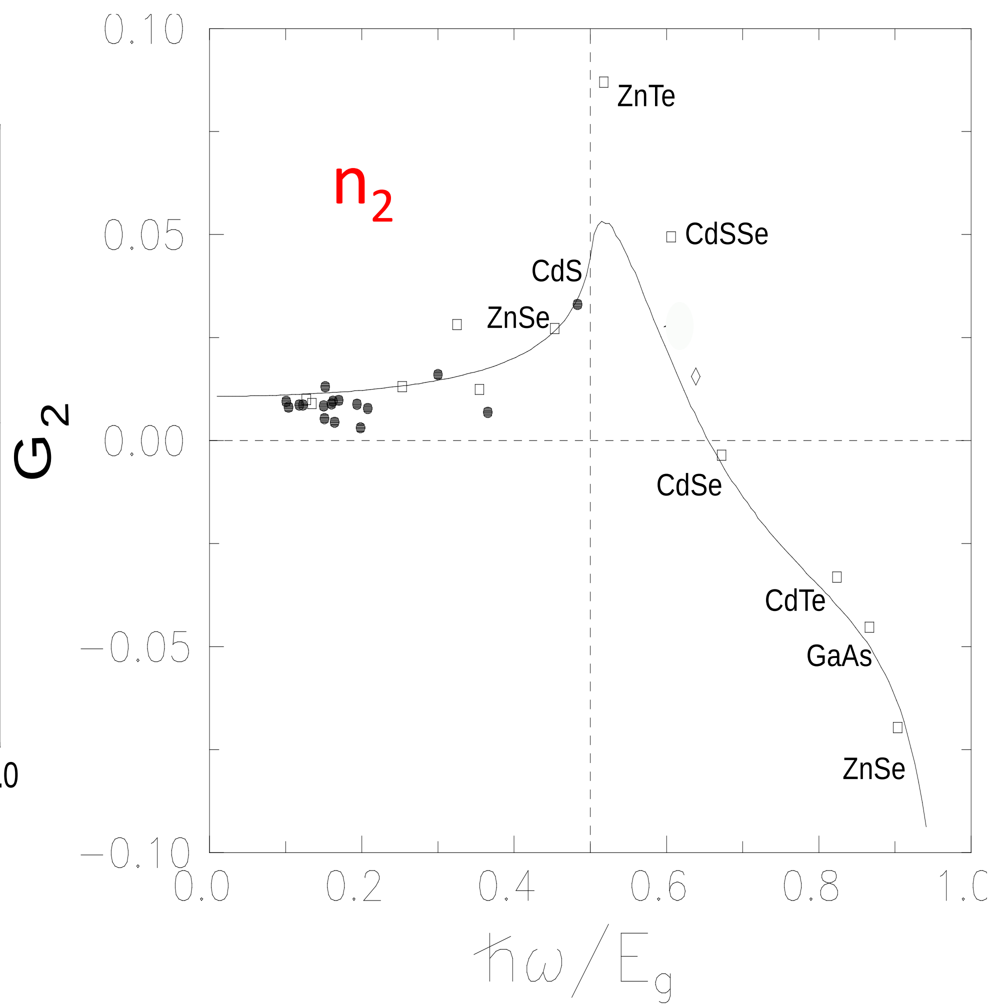



Phys. Rev. Lett., 65, 96-99 (1989)

$$\frac{d\varphi}{dz} = k_0 n_2 I$$

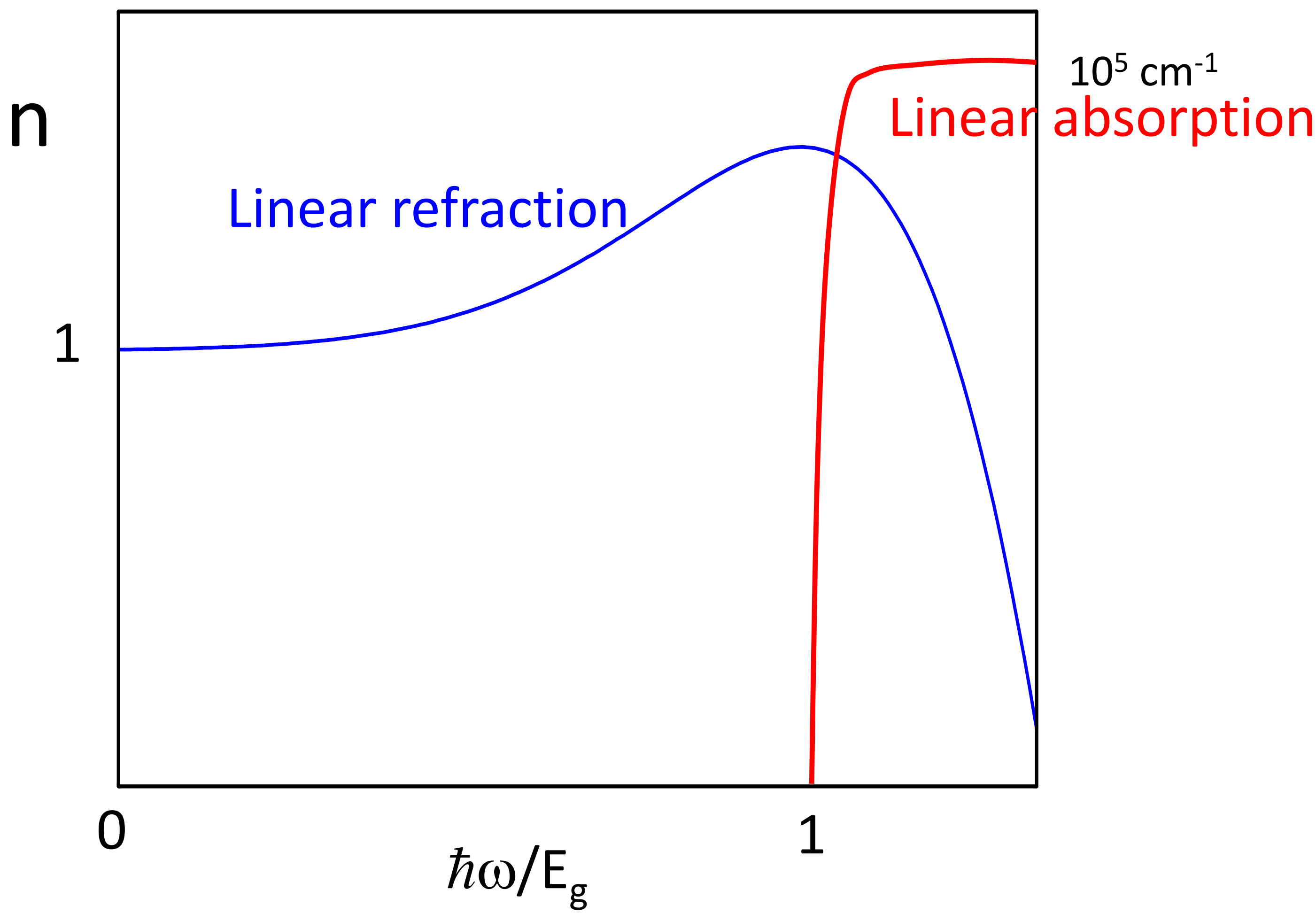
# These quantities are related, but strictly only in their nondegenerate form.



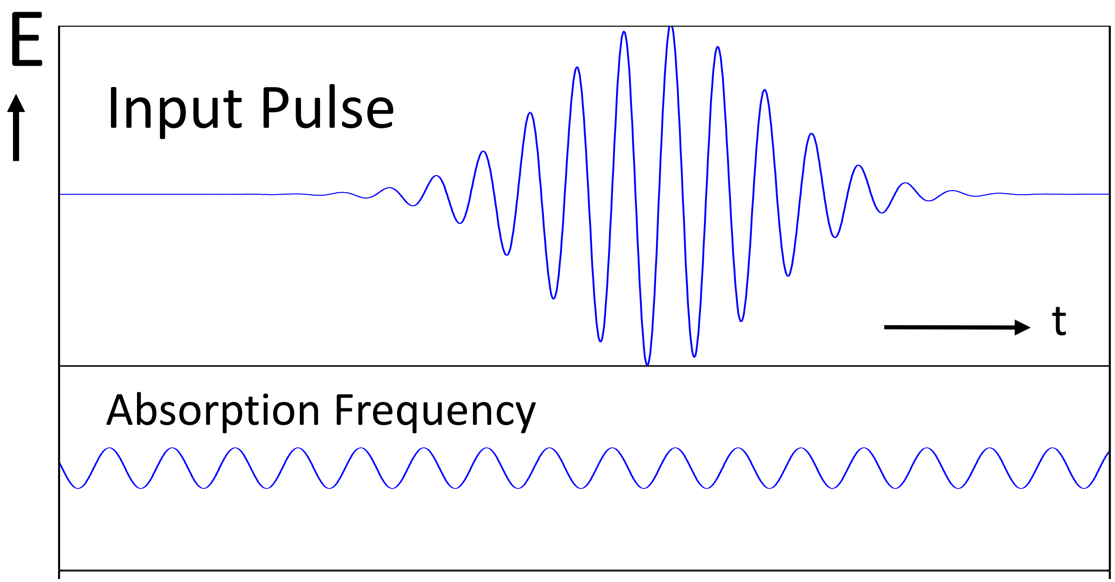



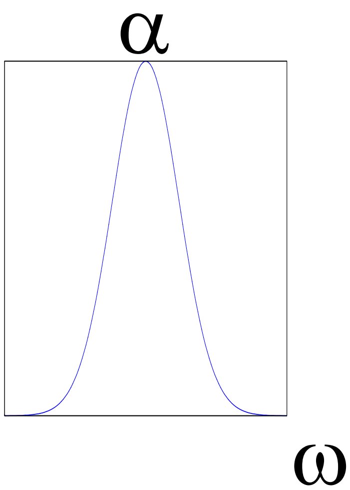

JQE, QE-27, 1296-1309 (1991)

# Linear Absorption- refraction

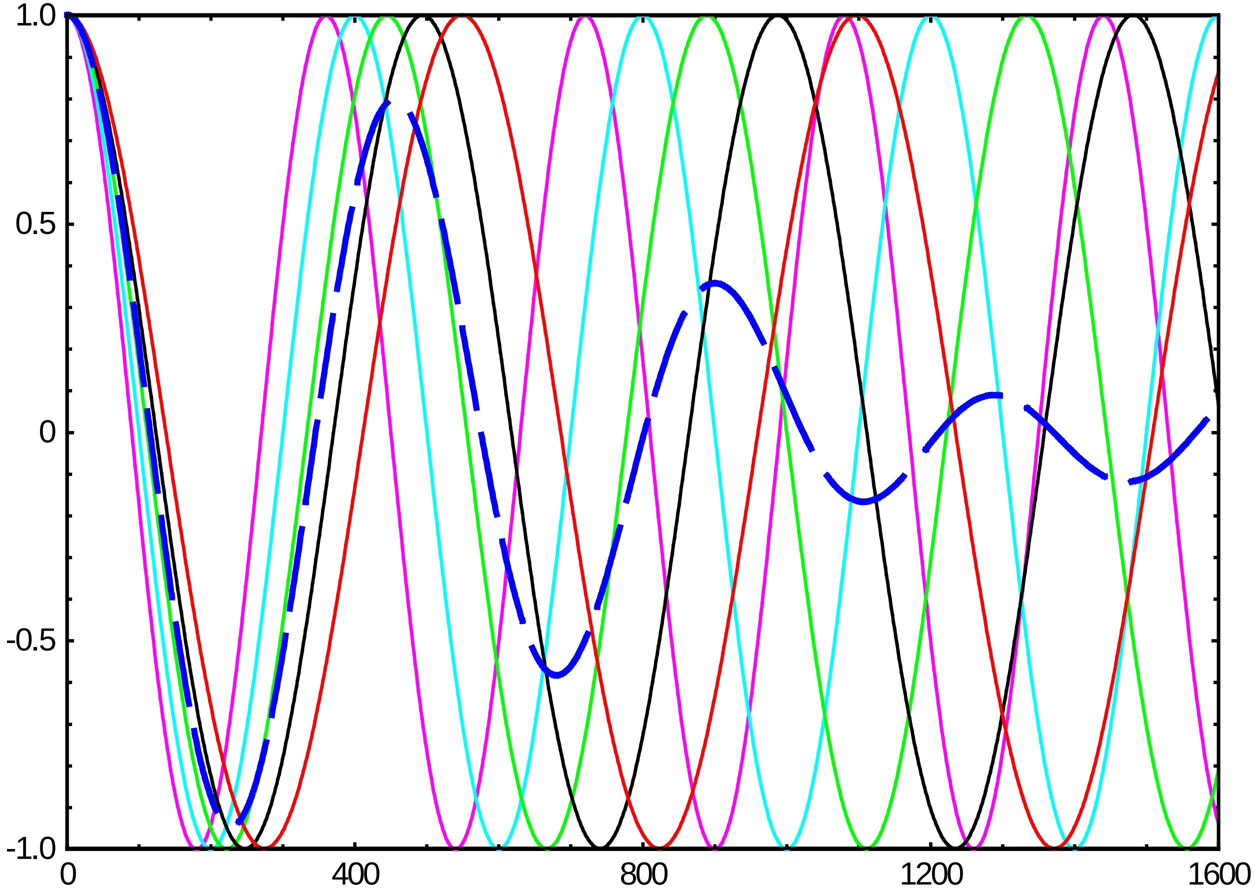


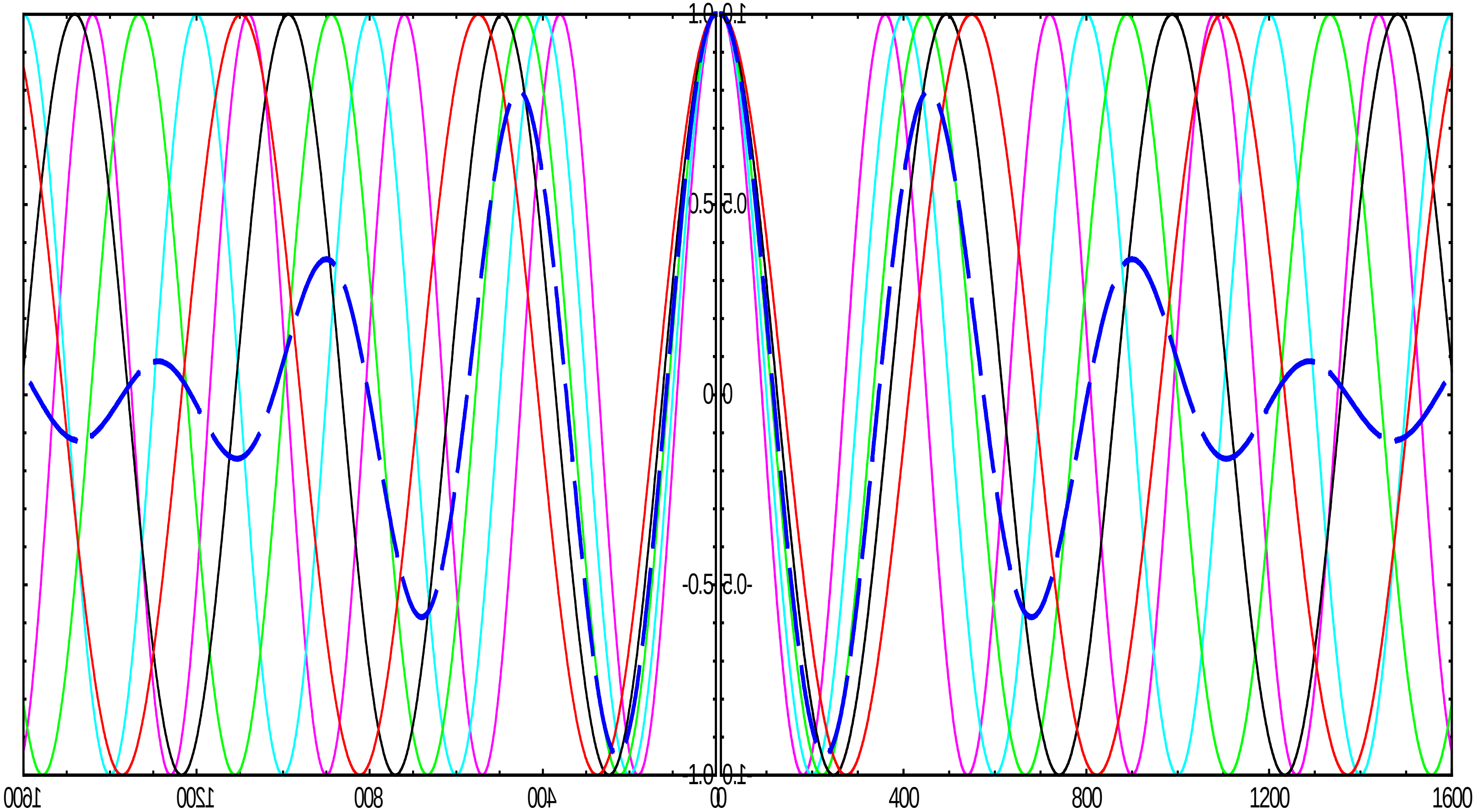
# Causality & Kramer-Kronig Relations



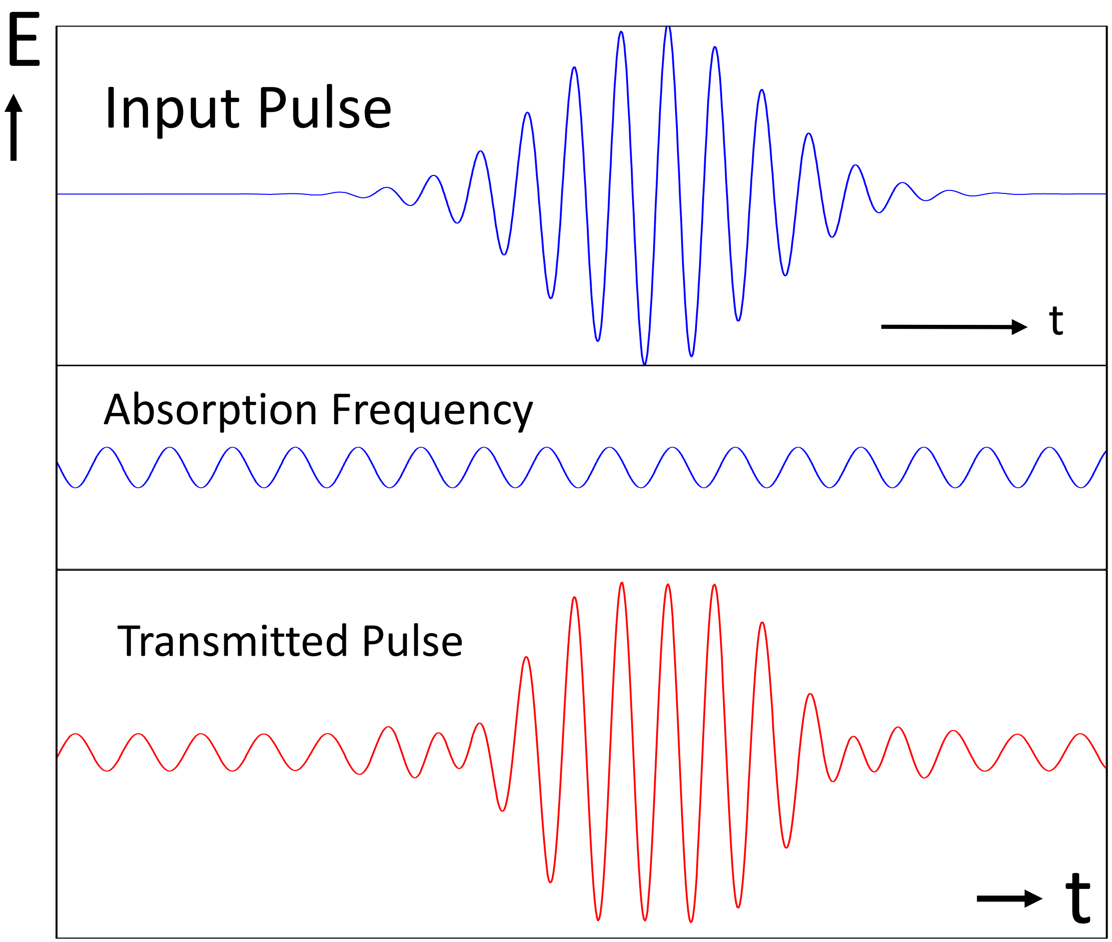



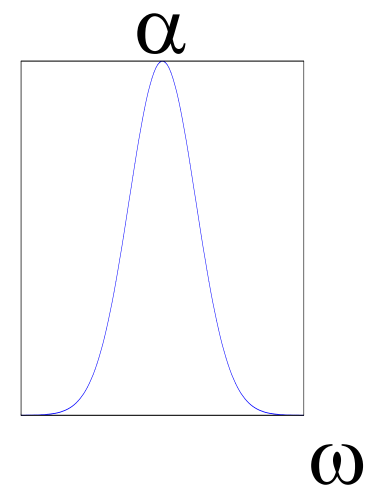

John Toll 1956

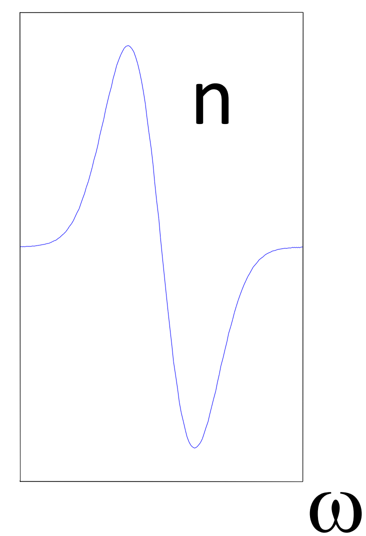

1.0
0.5
0
-0.5
-1.0
0
400
800
1200
1600


1.0
0.5
0
-0.5
-1.0
0
400
800
1200
1600

# Causality & Kramer-Kronig Relations




John Toll 1956

# Kramers-Kronig

$$P(t) = \varepsilon_0 \int_{-\infty}^{\infty} \chi^{(1)}(t - t_1) E(t_1) dt_1$$

**Statement of causality in time domain**

$$\chi(t) = \chi(t)\theta(t)$$

**Fourier Transform**

$$\chi(\omega) = \int_{-\infty}^{\infty} \chi(t) e^{-i\omega t} dt$$

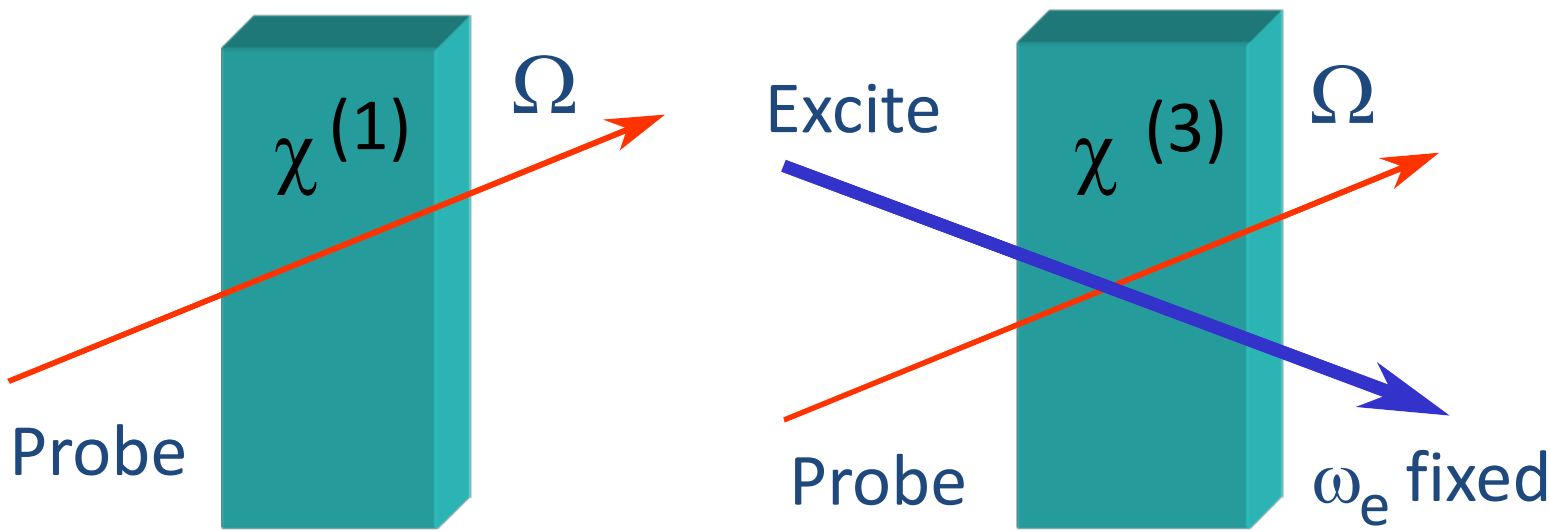
$$\chi'(\omega) = \frac{1}{\pi} \wp \int_{-\infty}^{\infty} \frac{\chi''(\Omega)}{\Omega - \omega} d\Omega \qquad n(\omega) - 1 = \frac{c}{2\pi} \wp \int_{-\infty}^{\infty} \frac{\alpha(\Omega)}{\Omega - \omega} \frac{d\Omega}{\Omega}$$

**Can do same thing for:**

$$\chi^{(3)}(\tau_1, \tau_2, \tau_3) = \chi^{(3)}(\tau_1, \tau_2, \tau_3)\theta(\tau_1)\cancel{\theta(\tau_2)}\cancel{\theta(\tau_3)}$$

# Kramers-Kronig

$P=\varepsilon_0\chi E= \varepsilon_0(\chi^1 + \chi^3 E^2 + \chi^5 E^4 + \ldots)E$




$$n(\omega)-1=\frac{c}{2\pi}\wp\int_{-\infty}^{\infty}\frac{\alpha(\Omega)}{\Omega-\omega}\frac{d\Omega}{\Omega}$$

$$[n(\omega,\omega_e)-1]-[n(\omega)-1]$$

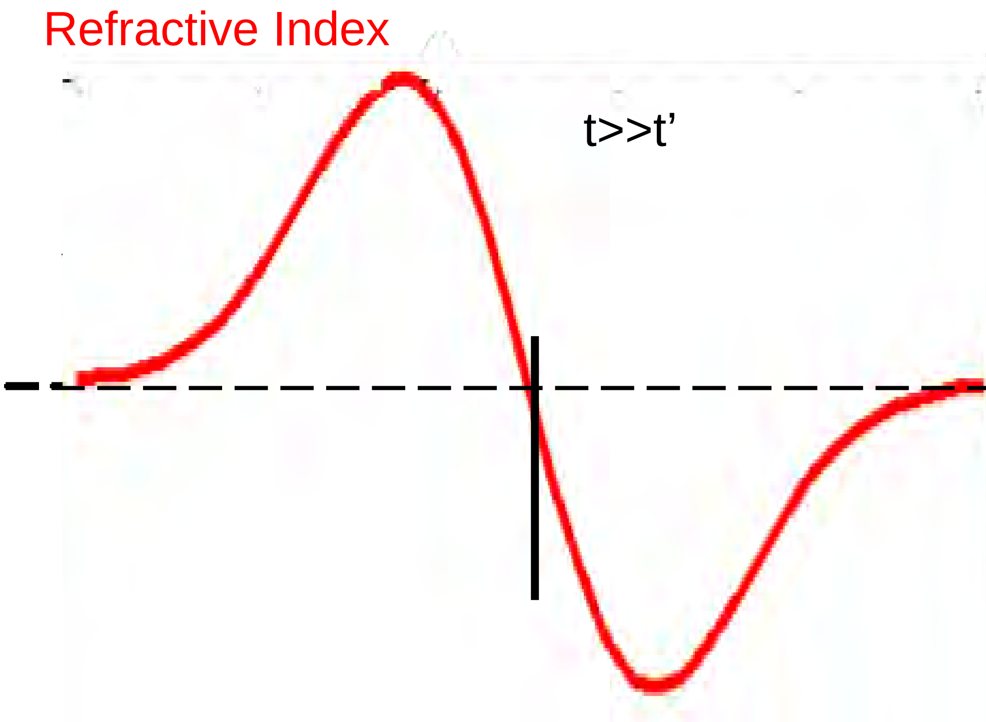
$$=\Delta n(\omega,\omega_e)=\frac{c}{2\pi}\wp\int_{-\infty}^{\infty}\frac{\Delta\alpha(\Omega,\omega_e)}{\Omega-\omega}\frac{d\Omega}{\Omega}$$

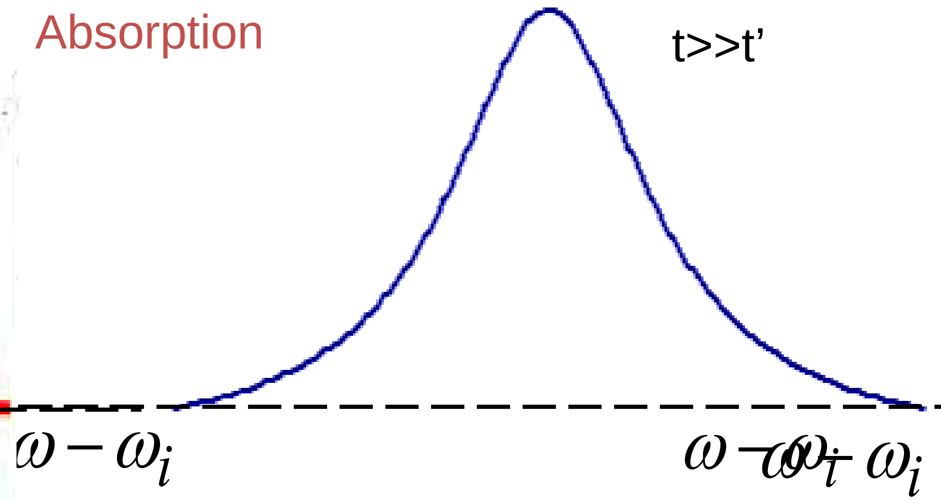
$$\frac{dI_p(\omega)}{dz}=-[\alpha_2(\omega;\omega_e)I_e(\omega_e)]I_p(\omega)$$

[ ] is a 'linear' absorption coefficient

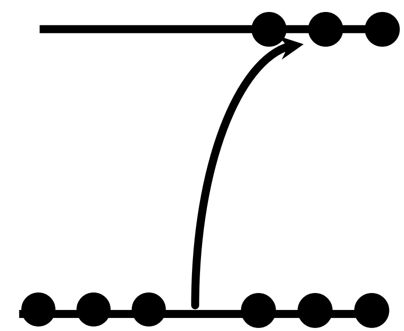
Hutchings et al, Optical and Quantum Electronics, 24, 1-30 (1992).

# Saturation

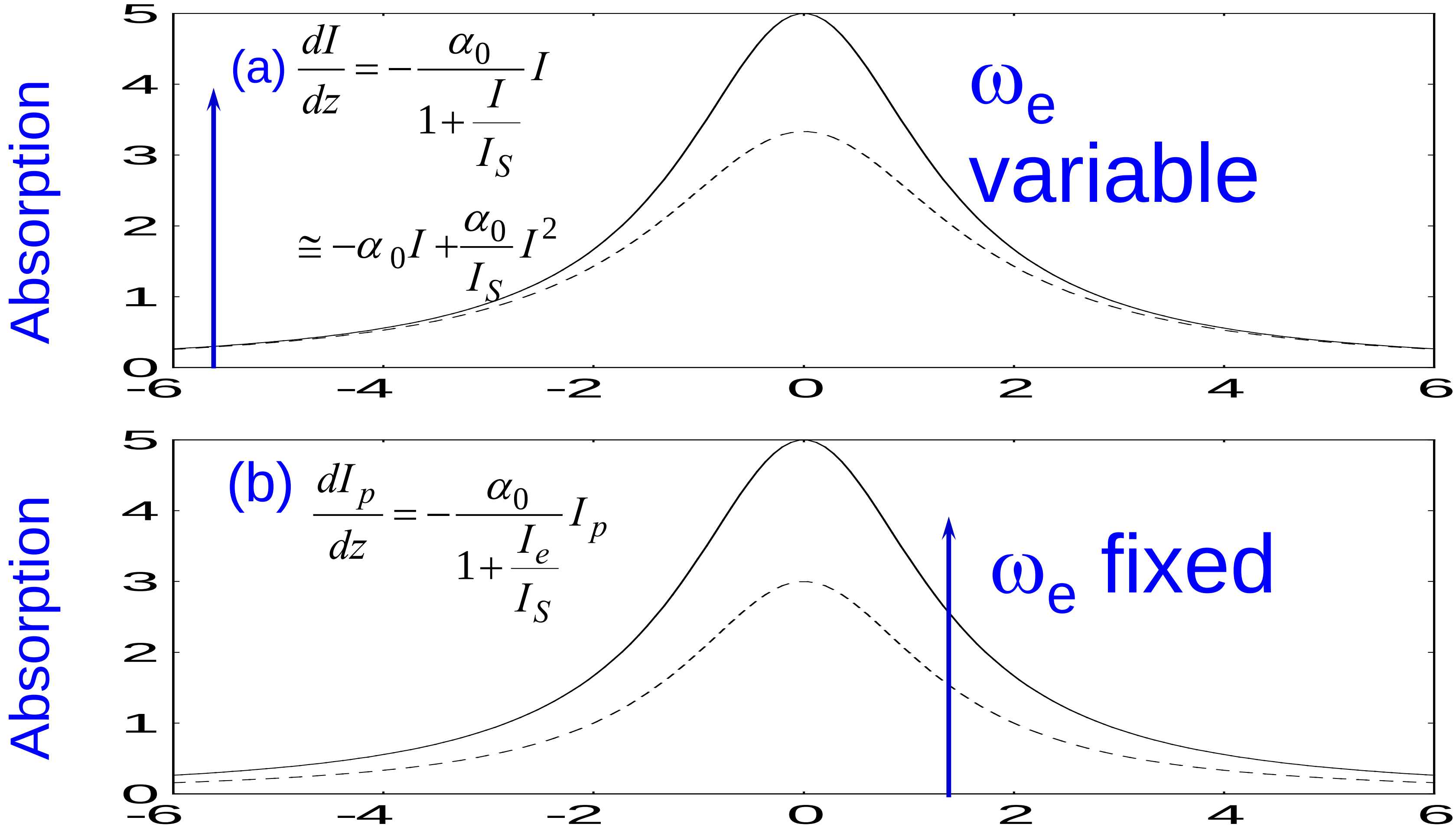



$$\frac{dI}{dz} = -\frac{\alpha_0}{1+\frac{I}{I_{Sat}}} I \cong -\alpha_0 I\left(1-\frac{I}{I_{Sat}}\right) = -\alpha_0 I + \frac{\alpha_0}{I_{Sat}} I^2$$



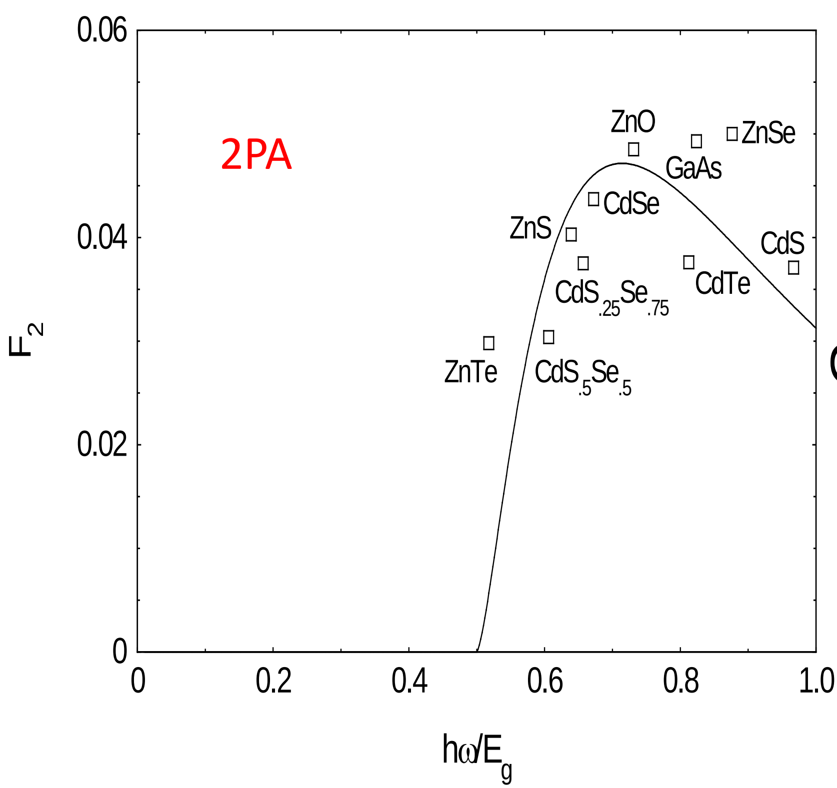
# 2-level atom saturation

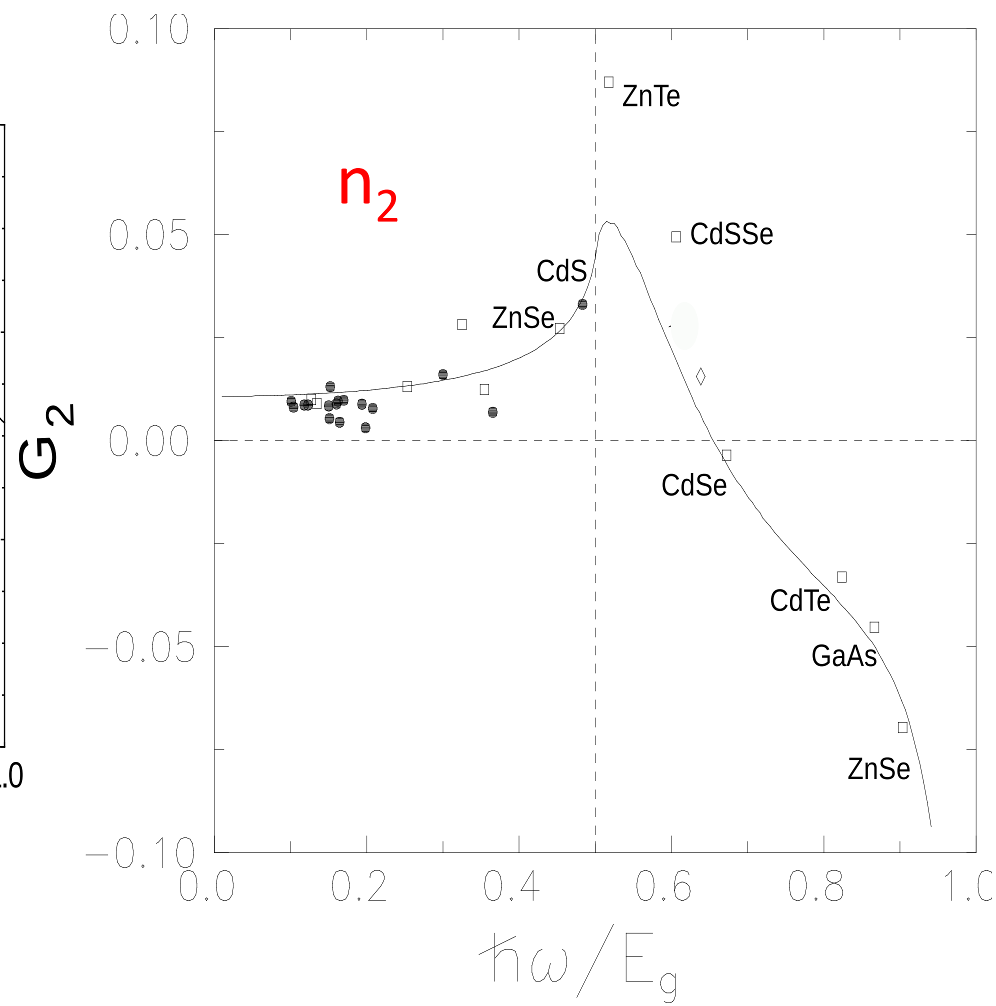



Kramers-Kronig works in the nondegenerate case

# Semiconductor 2PA & $n_2$

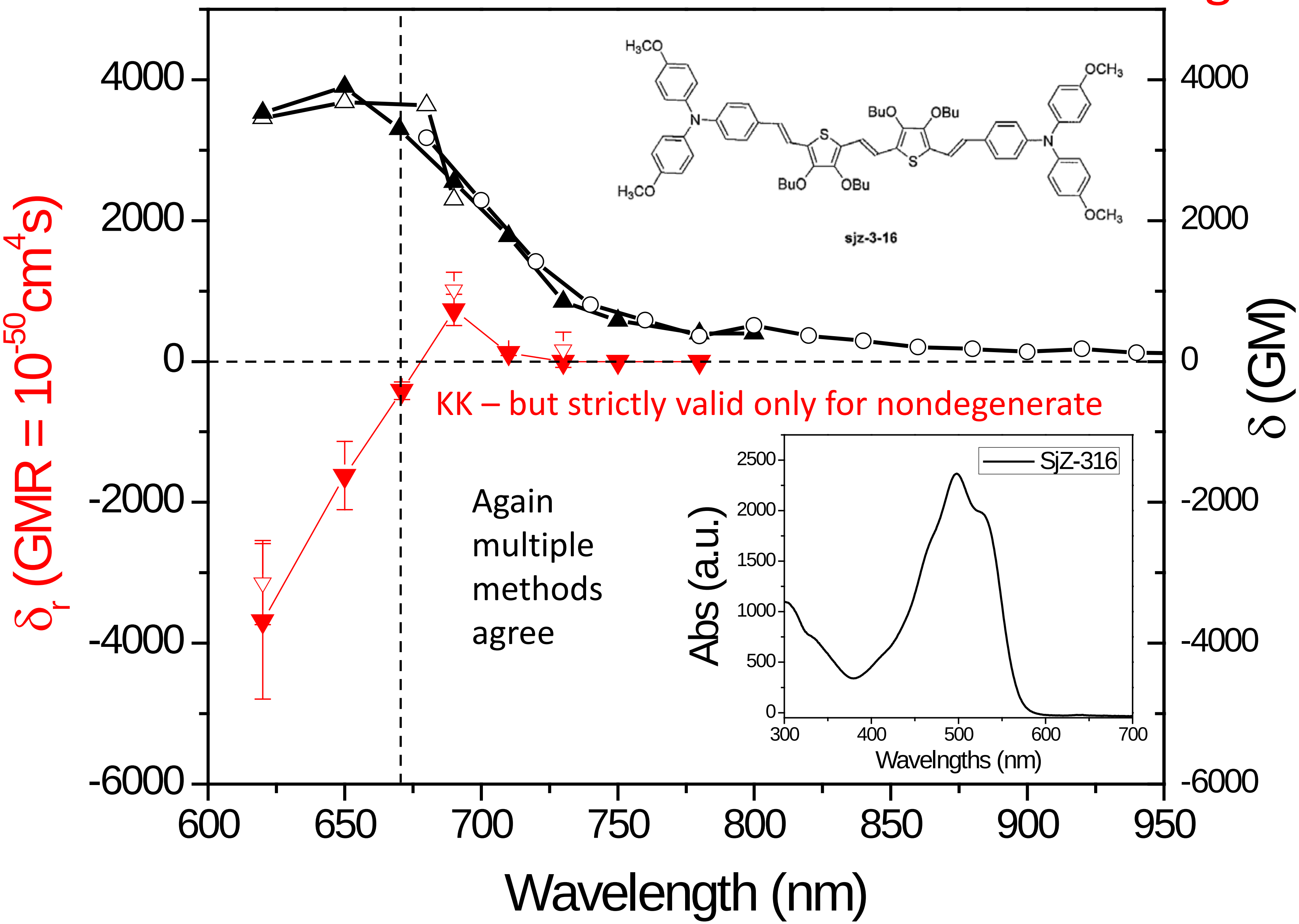
These quantities are related, but strictly only in their nondegenerate form.



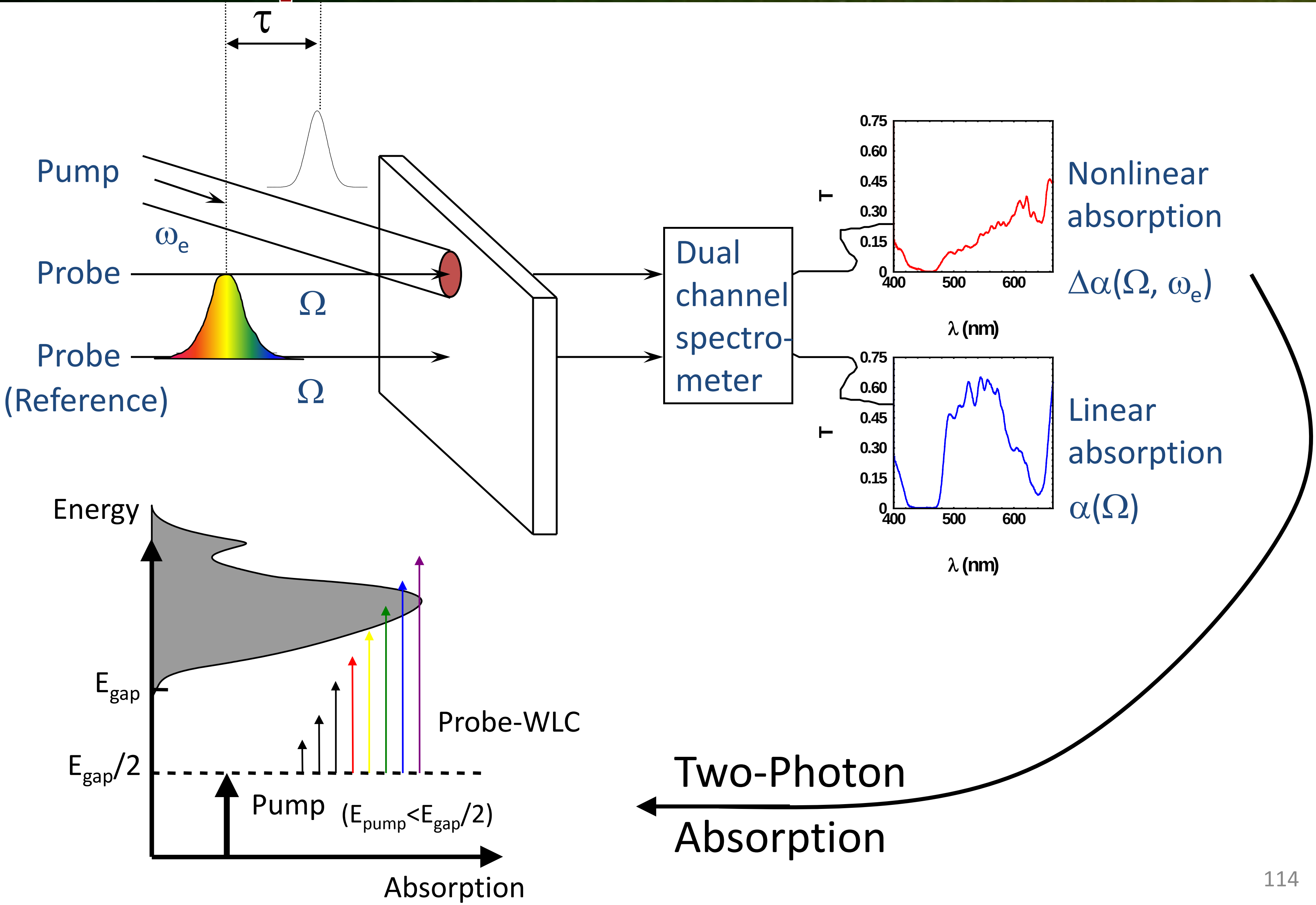




JQE, QE-27, 1296-1309 (1991)

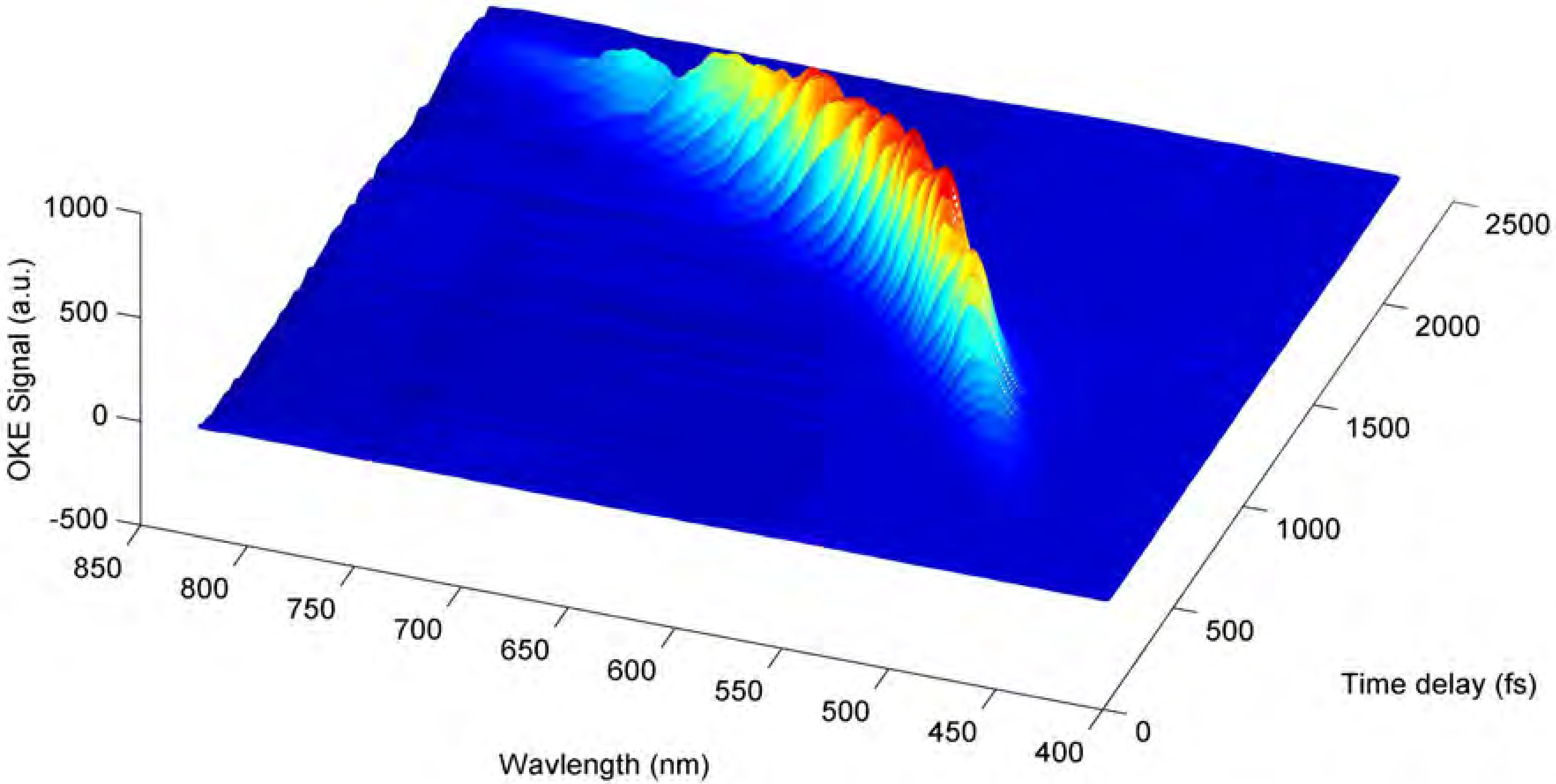
# Molecule from Marder group



# NLO Spectrometer

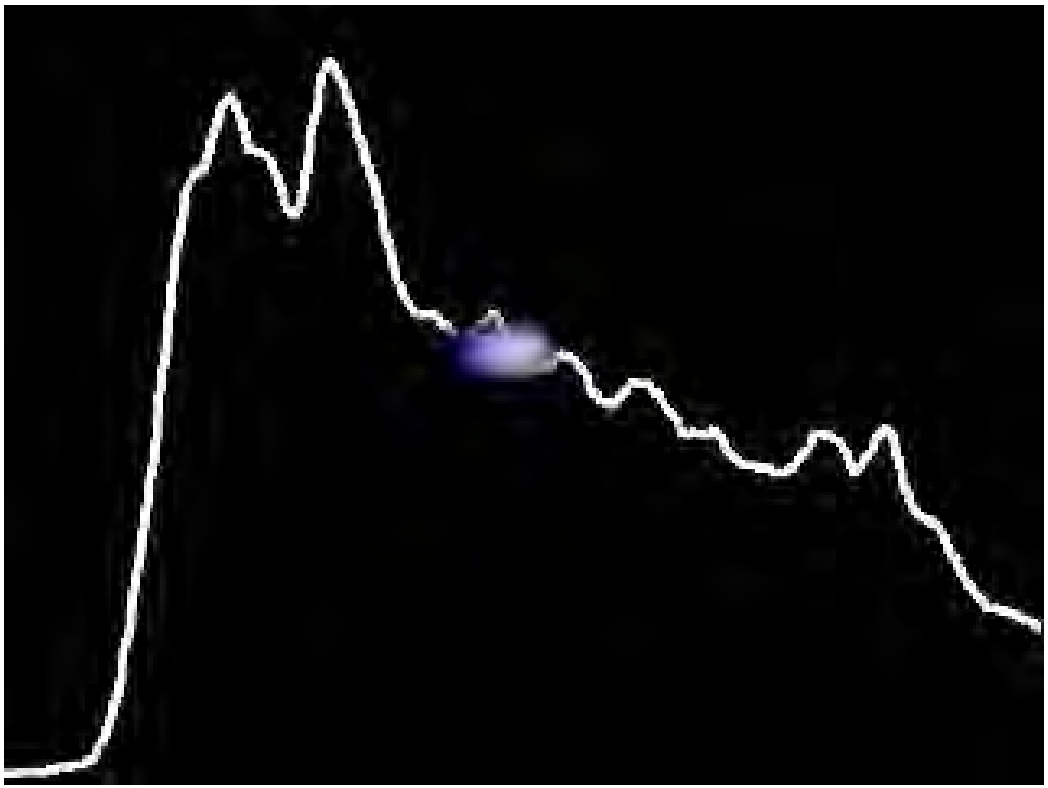


# White-Light Continuum Spectrum vs. Time as Determined by the Optical Kerr Effect

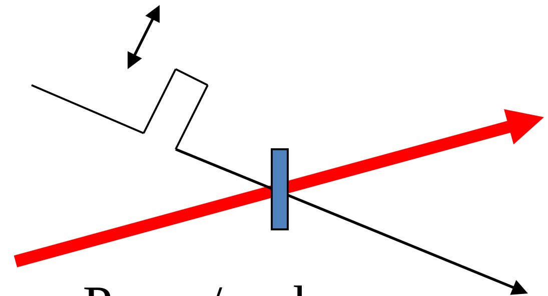


# Nondegenerate 2PA Data

T



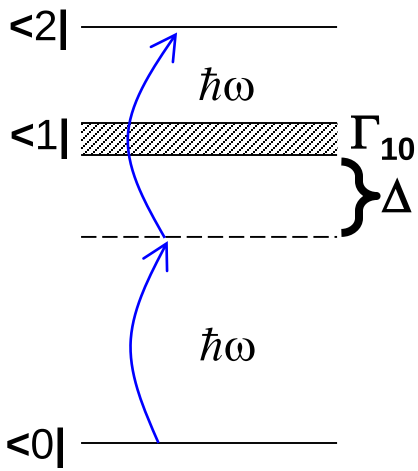
Wavelength



# 2PA and ISRE

(Intermediate State Resonance Enhancement)

**Degenerate 2PA**




"Virtual" State

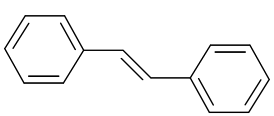
$\Delta = |E_{10} - \hbar\omega| >> \Gamma_{10}$

Lifetime

$\Delta t_1 \sim 2\pi \hbar / \Delta$

**As Δ ↓, 2PA probability ↑ !**

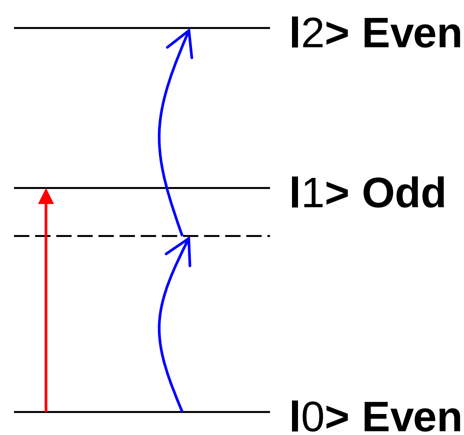
**Symmetric**



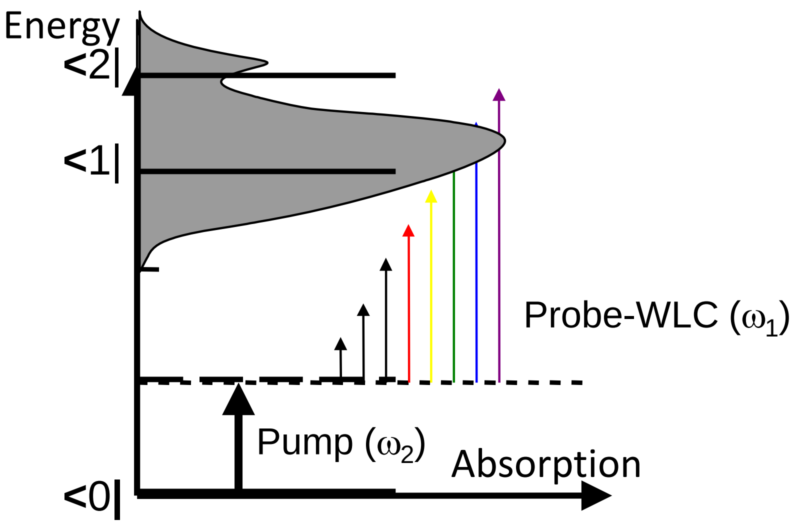
**Selection Rules**

**1PA** – Odd Parity Allowed

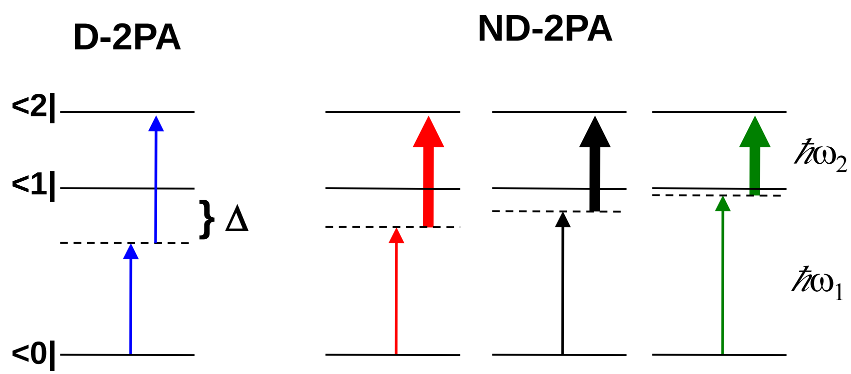
**2PA** – Even Parity Allowed

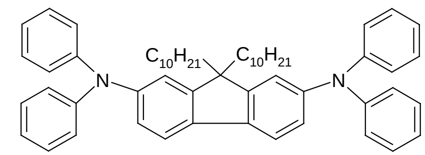


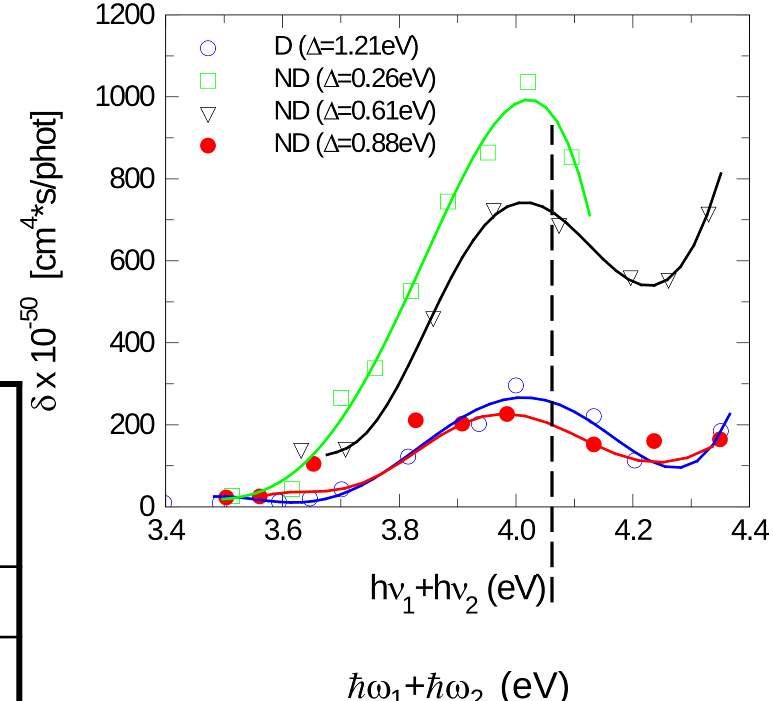
# Nondegenerate 2PA Spectroscopy



# 3-Level SOS Approximation (ISRE)



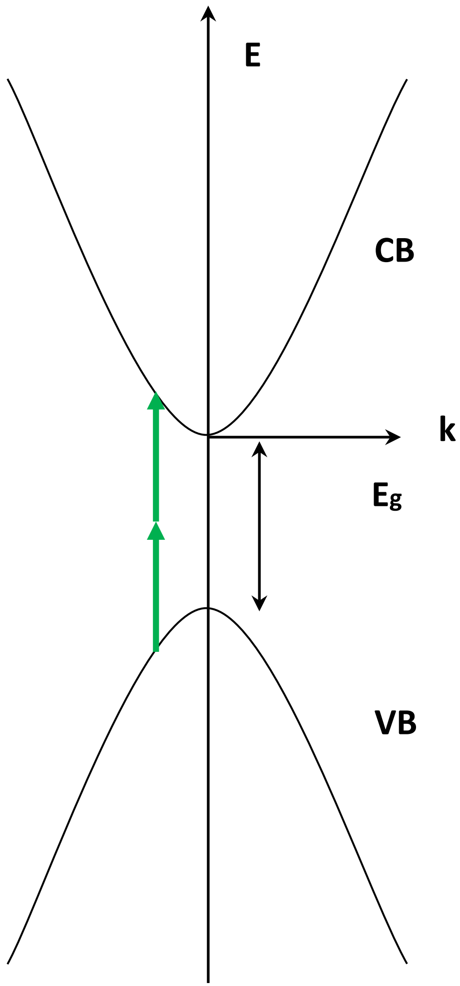




| Δ (eV) | δ (GM) | $\frac{\delta_{ND}}{\delta_D}\,\mathrm{exp}$ | $\frac{\delta_{ND}}{\delta_D}\,3level$ | $\frac{\delta_{ND}}{\delta_D}\,SOS$ |
|---|---|---|---|---|
| **1.21** | 253 | 1.00 | 1.00 | 1.0 |
| **0.88** | 237 | 0.94 | 1.14 | 1.32 |
| **0.61** | 708 | 2.79 | 1.63 | 1.85 |
| **0.26** | 1036 | 4.10 | 4.26 | 3.91 |

*Journal of Chemical Physics* **2004**, *121 (7)*, 3152-3160.

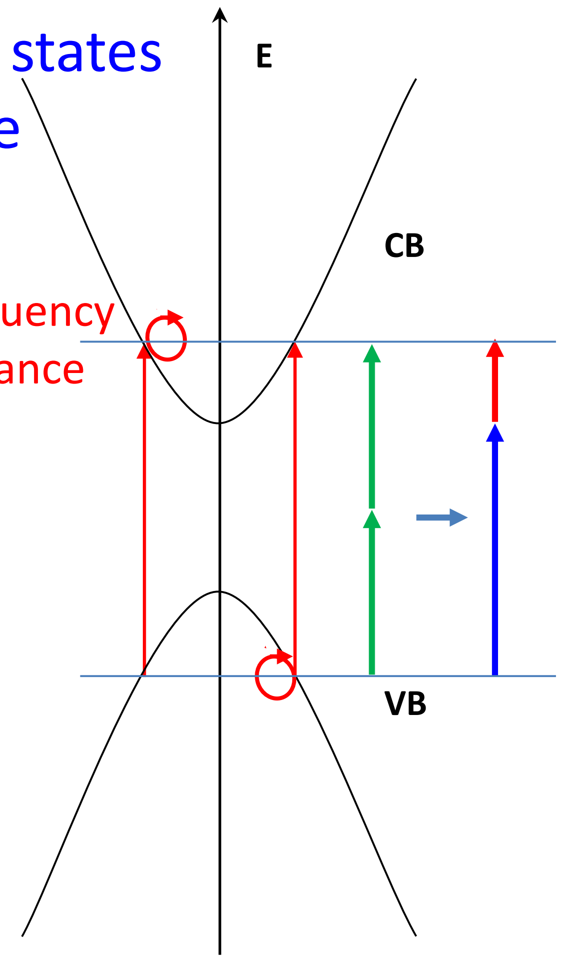
# Now look at enhancement in semiconductors

## Calculating 2PA in semiconductors




**Perturbative approach**

1 and 2 PA states degenerate




B.S. Wherrett, JOSA B **1**, 67 (1984)

# 2PA and scaling laws

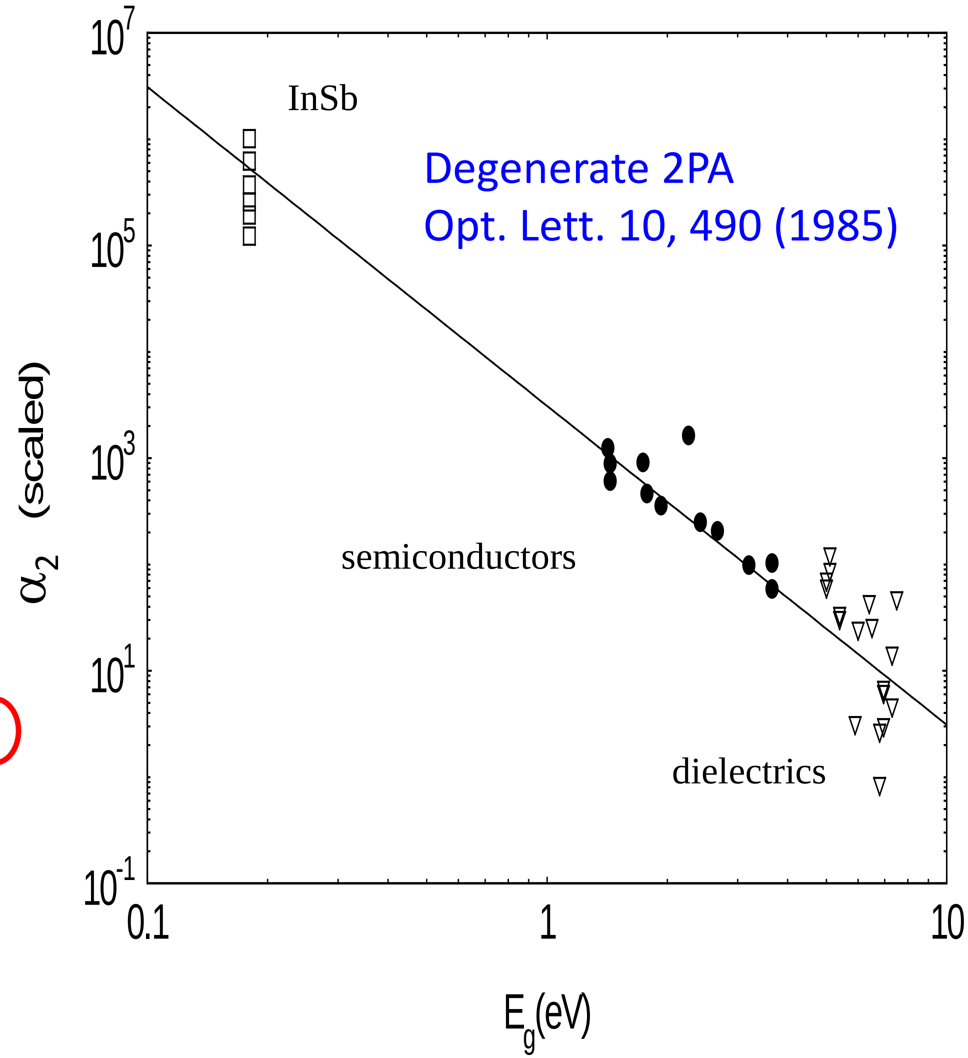
## Degenerate

$$\alpha_2(\omega) = K_2 \frac{\sqrt{E_p}}{n_0^2 E_g^3} \frac{(2\hbar\omega / E_g - 1)^{3/2}}{(2\hbar\omega / E_g)^5}$$

## Non-Degenerate

$$\alpha_2(\omega_1;\omega_2) = K \frac{\sqrt{E_p}}{n_1 n_2 E_g{}^3} F_2\left(\frac{\hbar\omega_1}{E_g};\frac{\hbar\omega_2}{E_g}\right)$$

$$F_2{}^{2PA}(x_1;x_2) = \frac{(x_1 + x_2 - 1)^{3/2}}{2^7 x_1 x_2{}^2}\left(\frac{1}{x_1} + \frac{1}{x_2}\right)^2$$

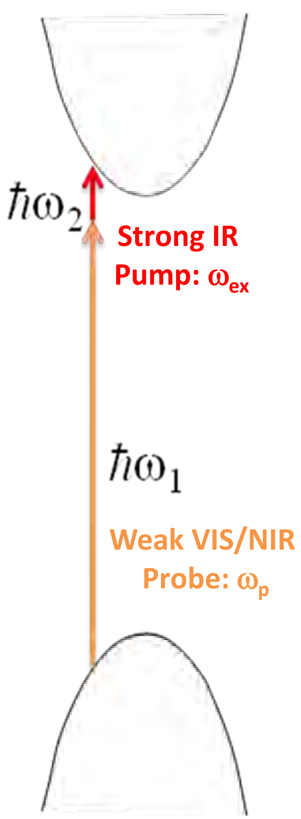


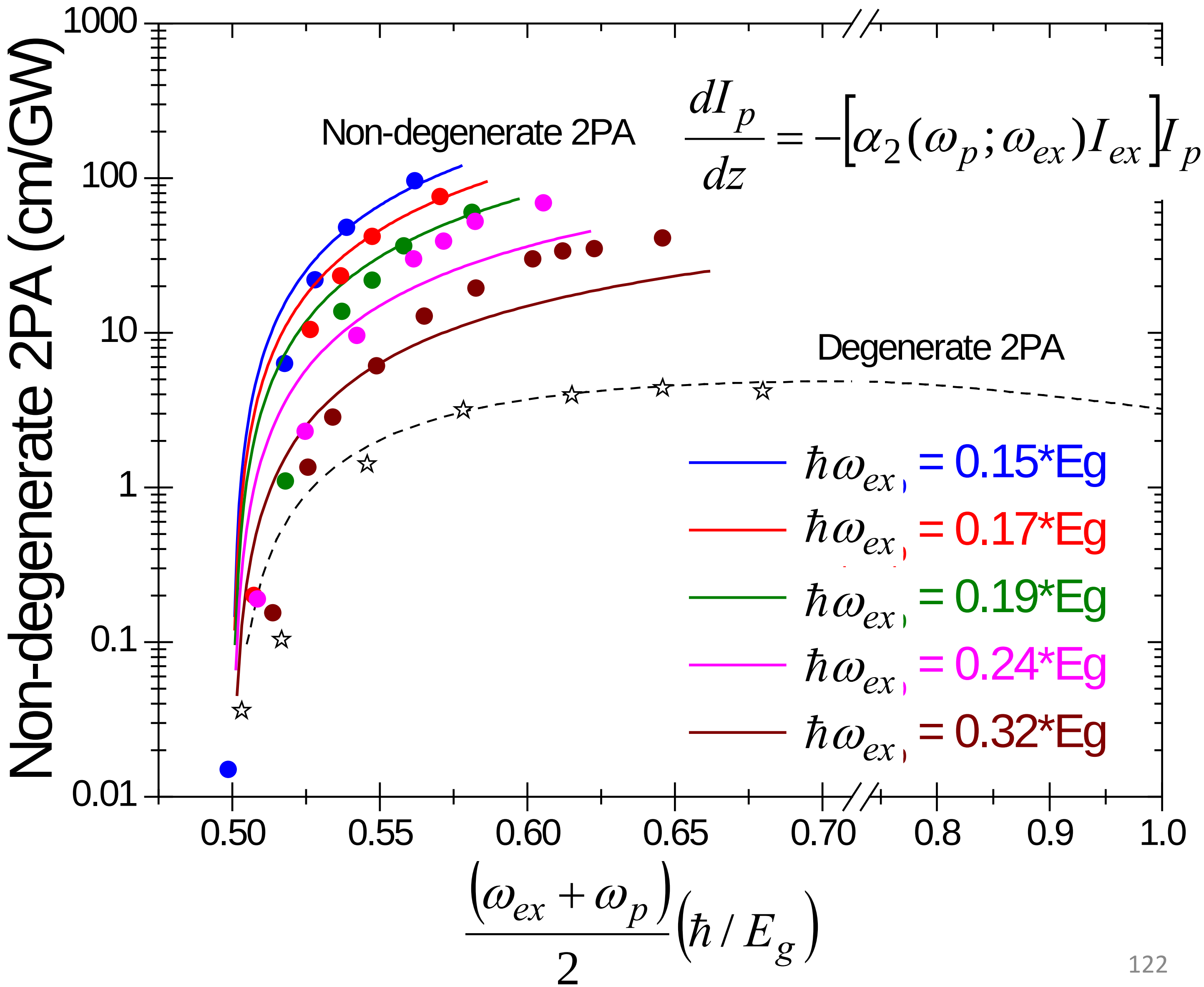



Phys. Rev. Lett., 65, 96-99 (1989)

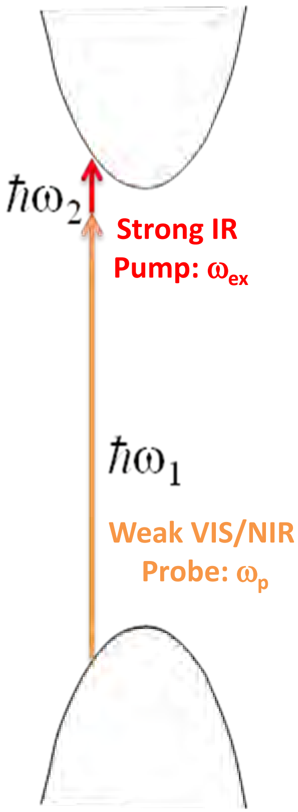
# END-2PA: Enhancement Depends on Pump Frequency

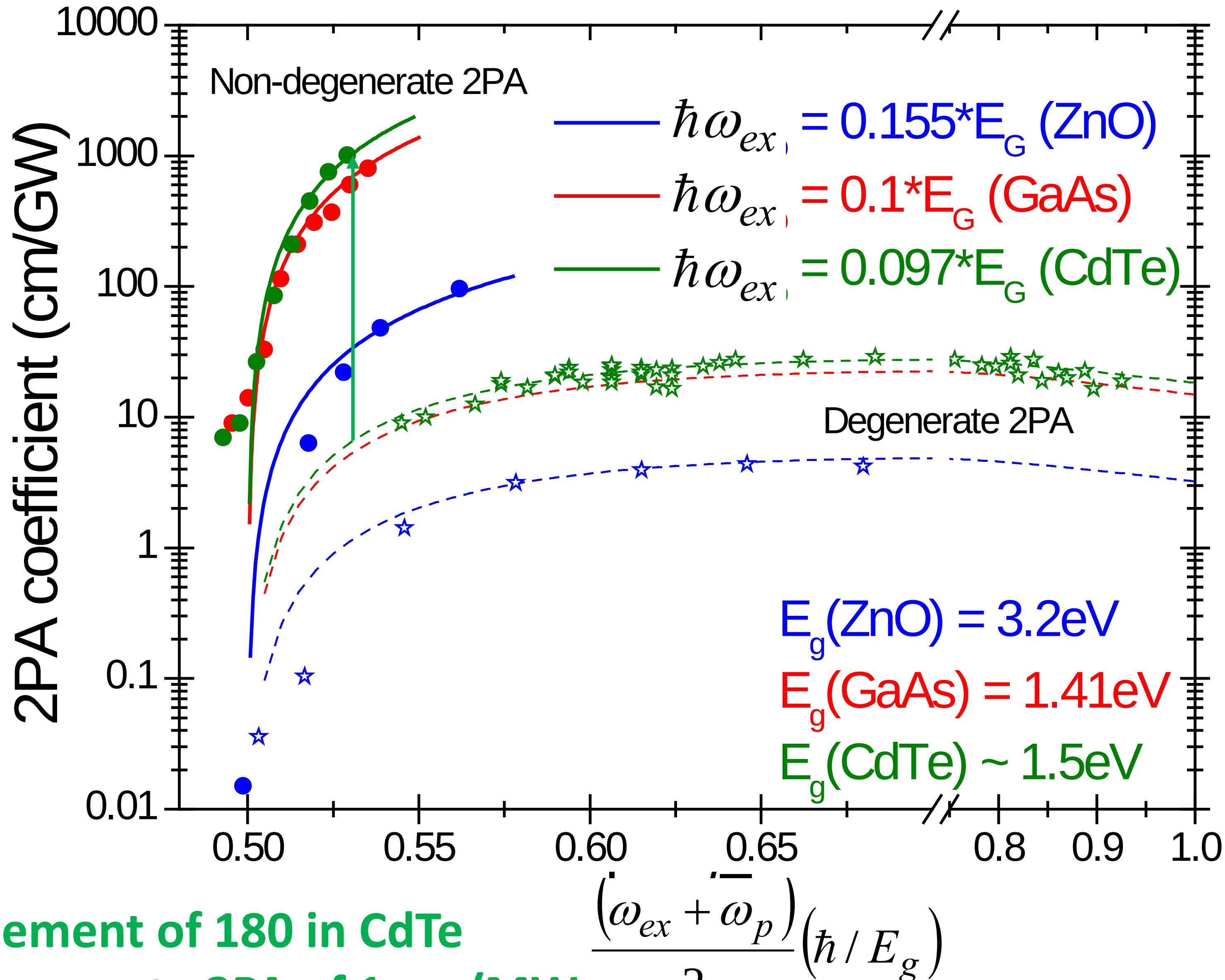
ZnO



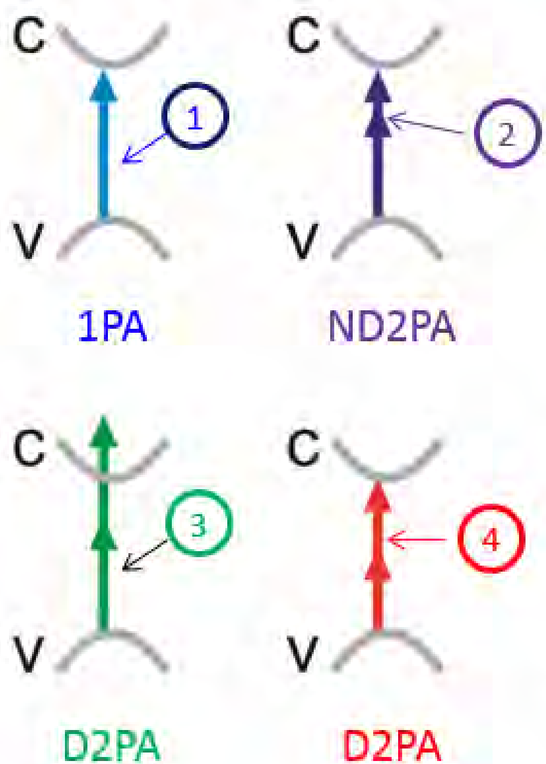
# ND 2PA

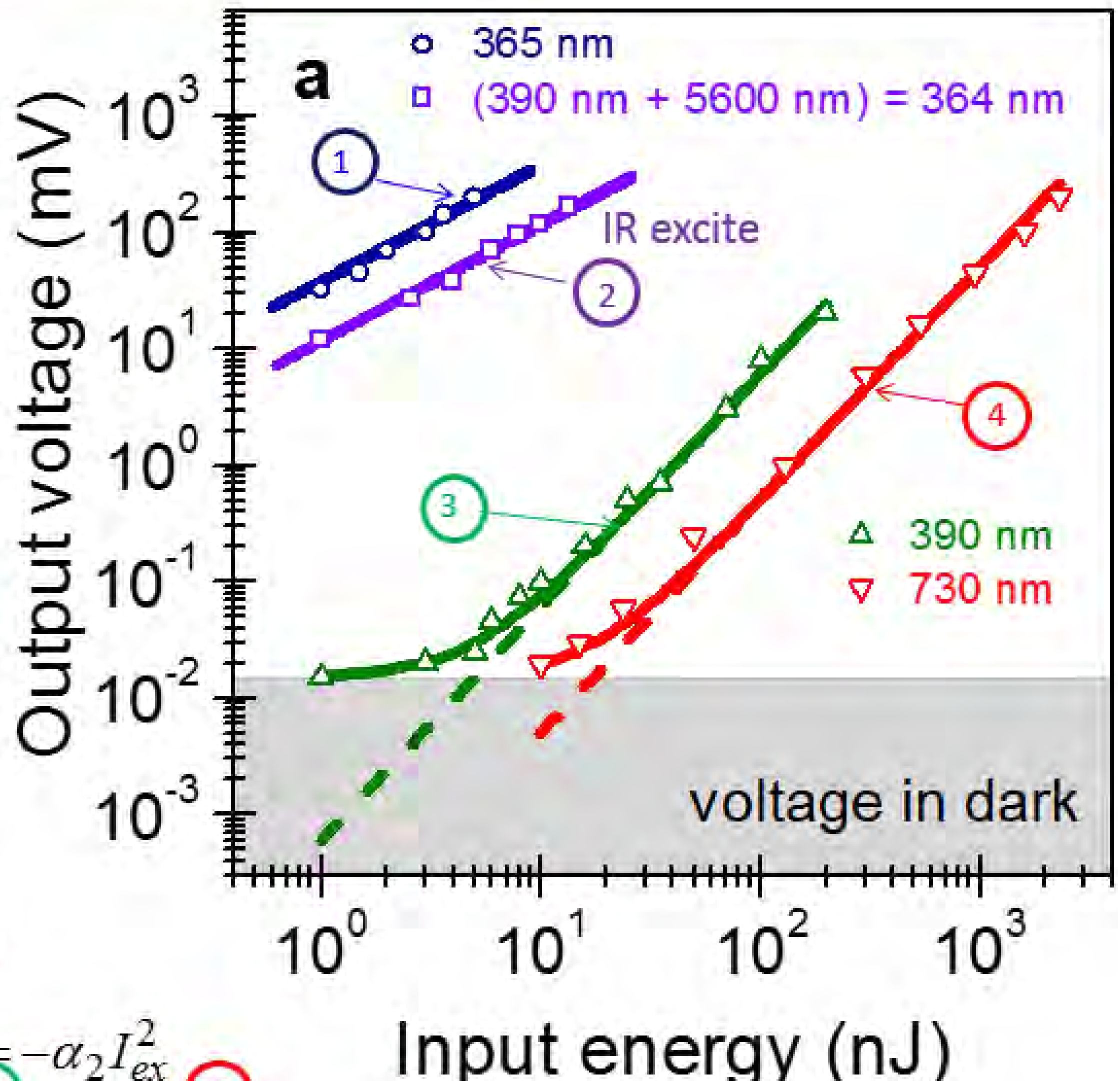



- **Enhancement of 180 in CdTe**
- **non-degenerate 2PA of 1 cm/MW**

# GaN detector response for different processes




$$\frac{dI_p}{dz} = -\alpha_2(\omega_p;\omega_{ex}) I_{ex} I_p$$ (2)

$$\frac{dI_{ex}}{dz} = -\alpha_2 I_{ex}^2$$ (3) (4)

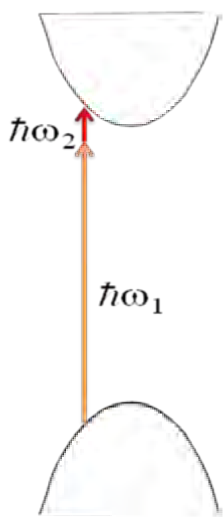
# IR Detection - Linear Power dependence

D 2PA

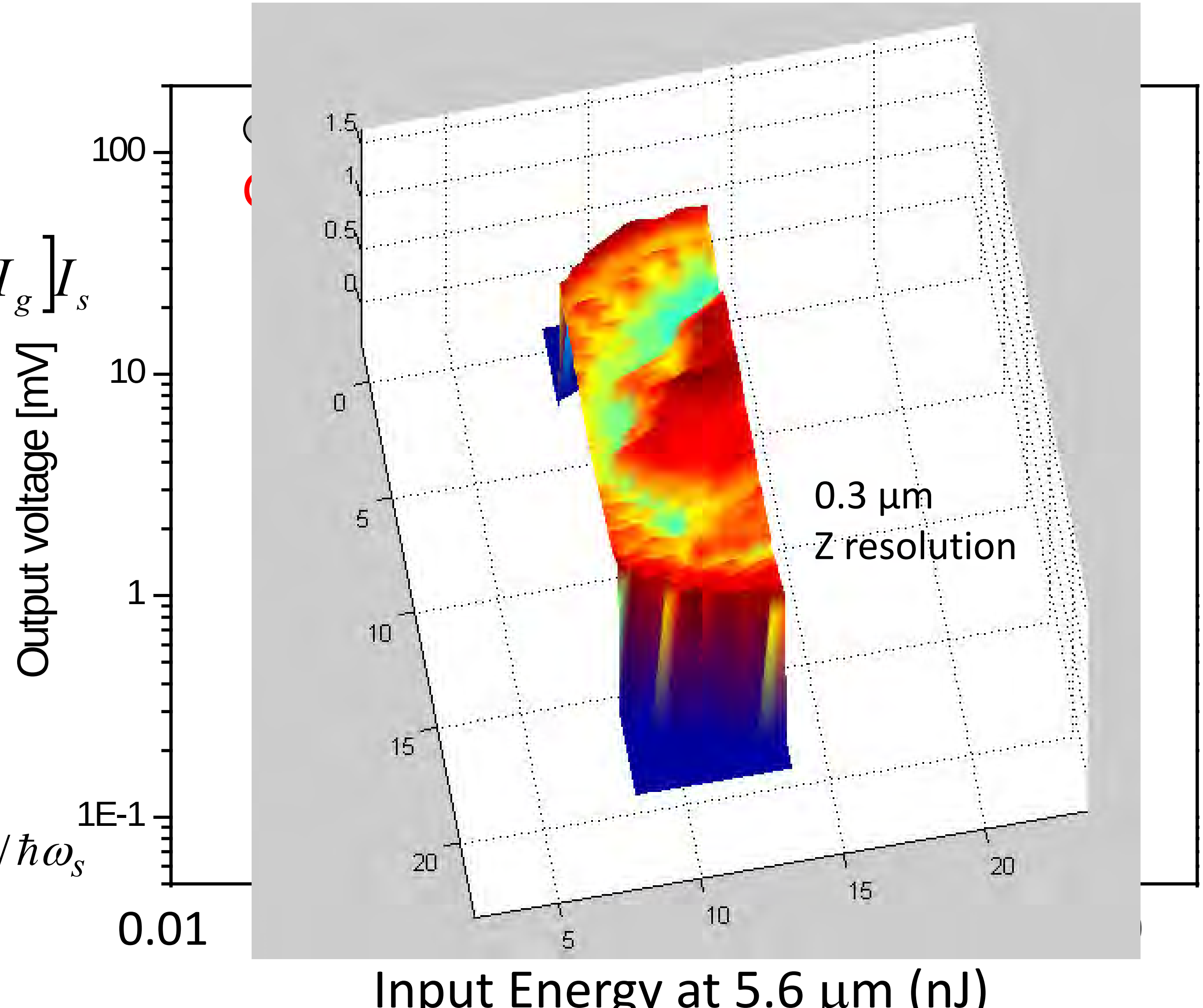
$$\frac{dI}{dz} = -\alpha_2(\omega;\omega)I^2$$

ND 2PA

$$\frac{dI_s}{dz} = -\left[2\alpha_2(\omega_s;\omega_g)I_g\right]I_s$$

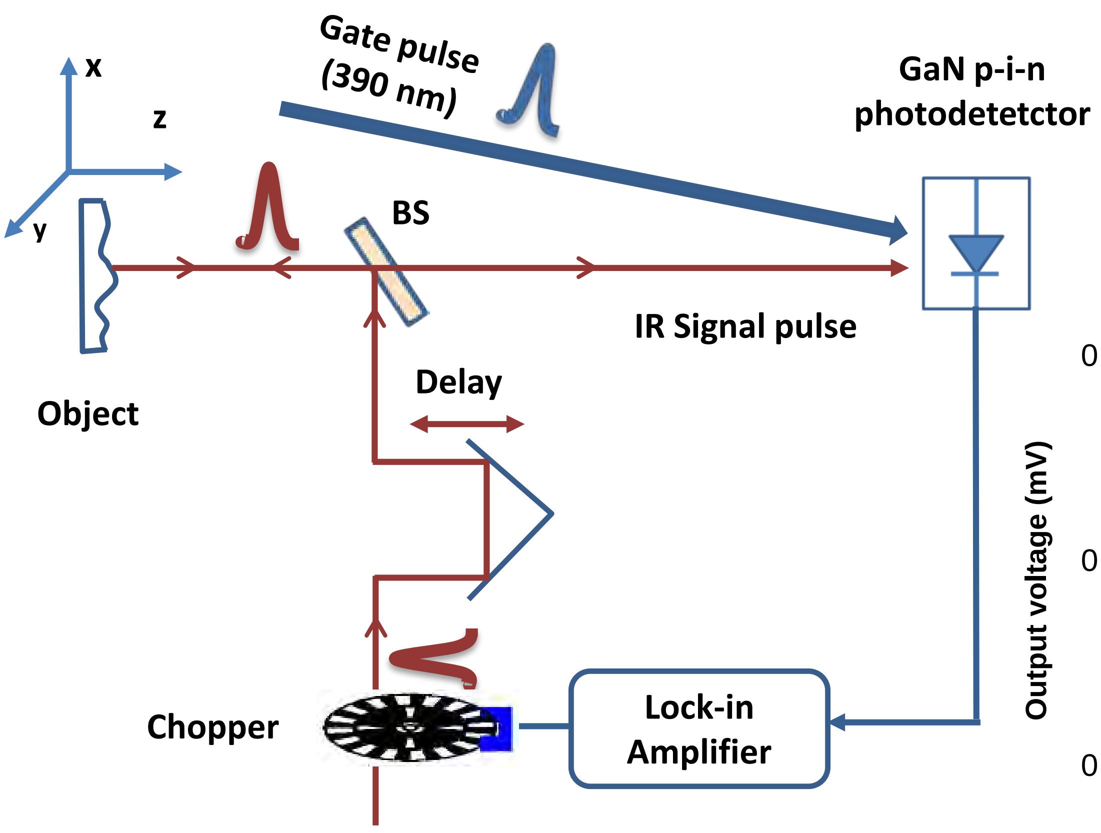



$$\frac{dN}{dt} = 2\alpha_2(\omega_s;\omega_g)I_g I_s / \hbar\omega_s$$

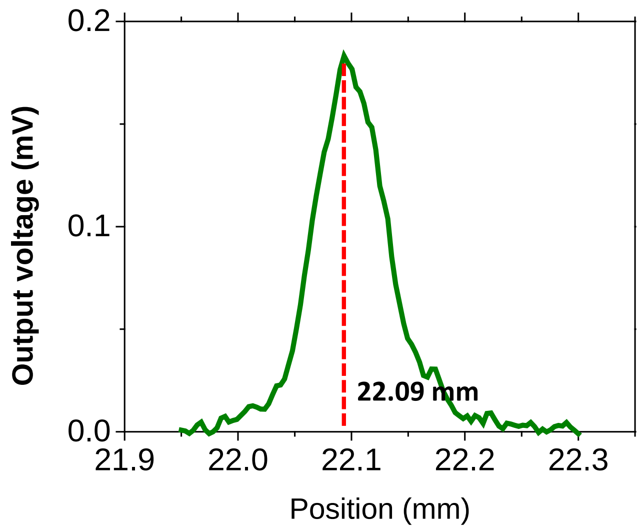



Nature Photonics 5, 561-565, (2011)

# 3-D IR imaging via ND-2PA with short pulses

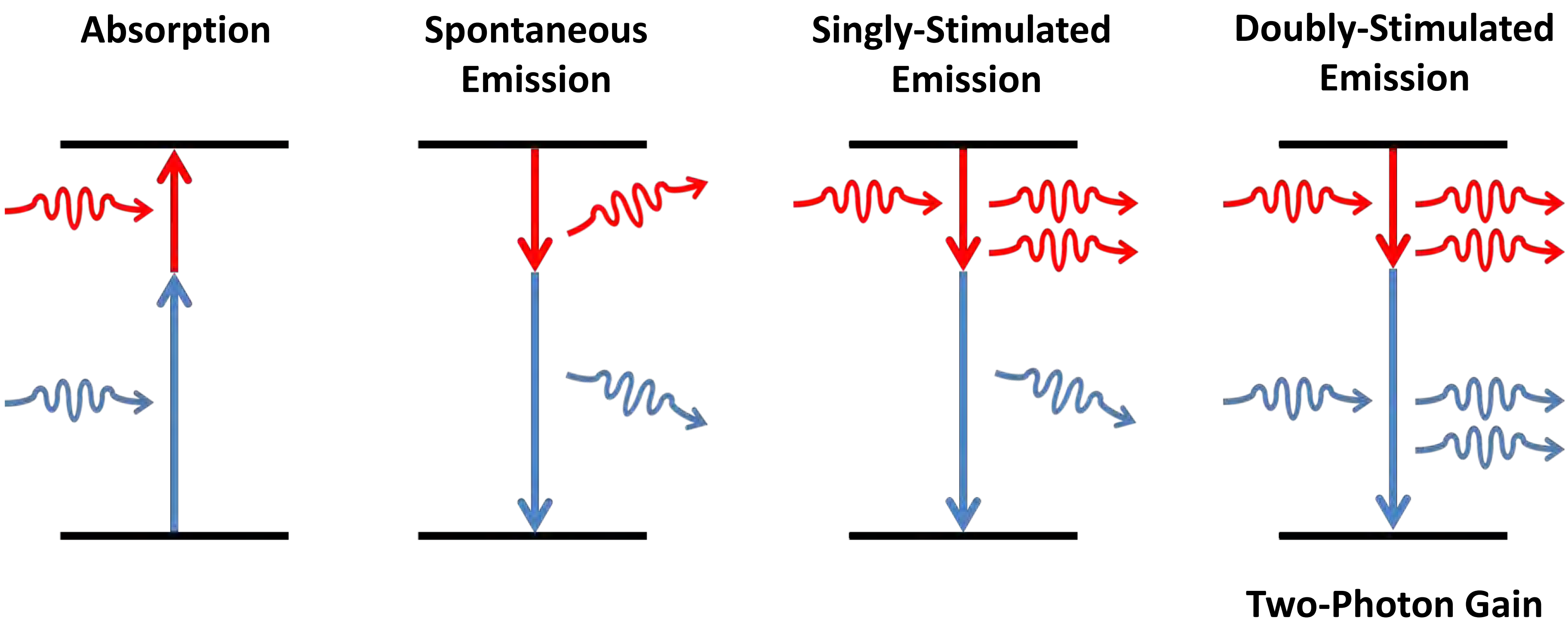



**Cross-correlations of IR and the gate pulses**



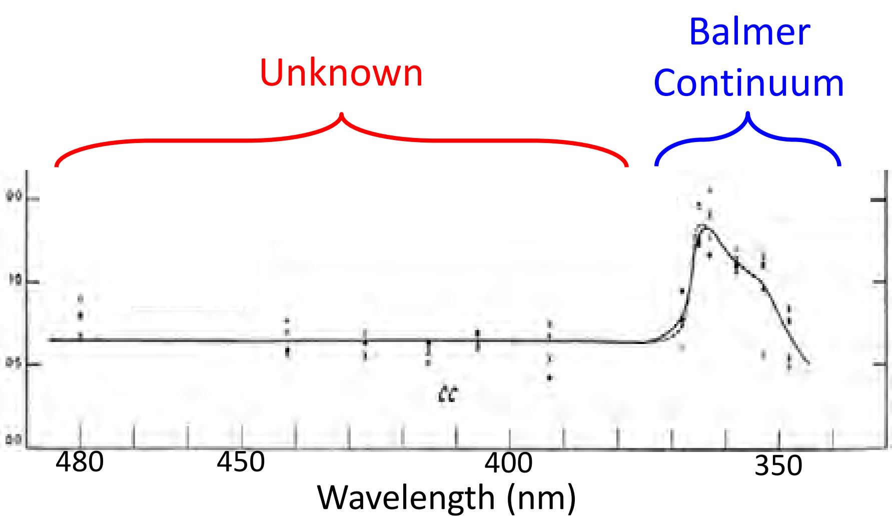

BS: Beam splitter

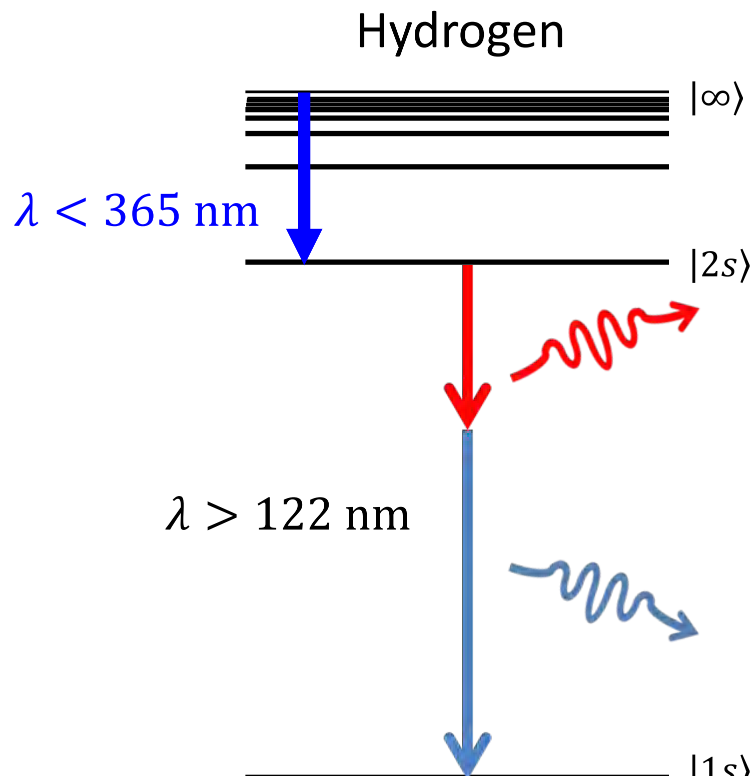
# Two-Photon Transitions




M. Göppert-Mayer, Ann. Physik, **9**, 273, (1931).
D. J. Gauthier, Progress in Optics, **45**, 205-272 (2003).

# Spontaneous 2PE


$$\langle 1s|\hat{\boldsymbol{\mu}}|2s\rangle = 0$$

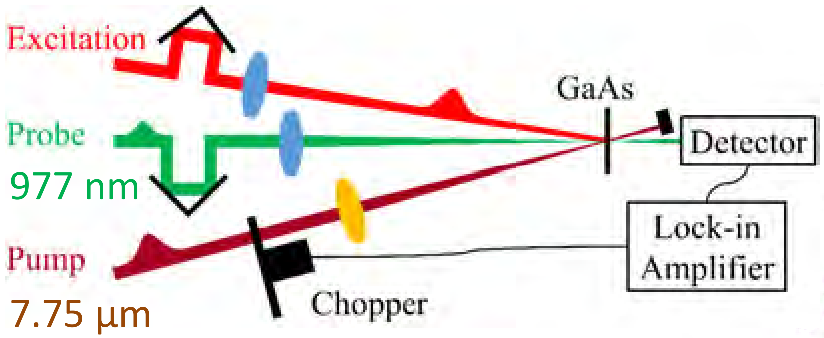
$$\langle 1s|\hat{\boldsymbol{\mu}}|j\rangle\langle j|\hat{\boldsymbol{\mu}}|2s\rangle \neq 0$$

$$6.5\ \mathrm{s}^{-1} < W_{1s,2s}^{(2sp)} < 8.7\ \mathrm{s}^{-1}$$

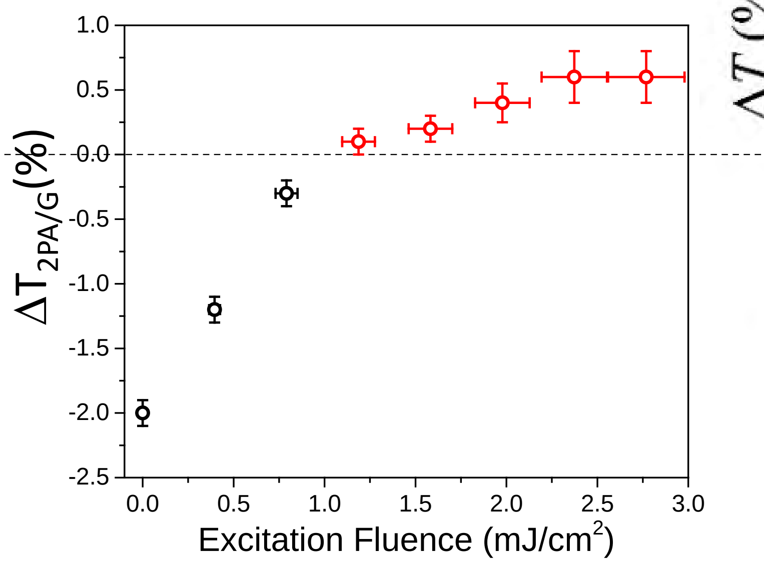
T. L. Page, Mon. Not. R. Astron. Soc., **96**, 604 (1936).
G. Breit and H. Teller, Astrophys. J., **91**, 215, (1940)
M. Landherr, NASA, http://www.spacetelescope.org/projects/fits_liberator/fitsimages/mike_landherr_1/

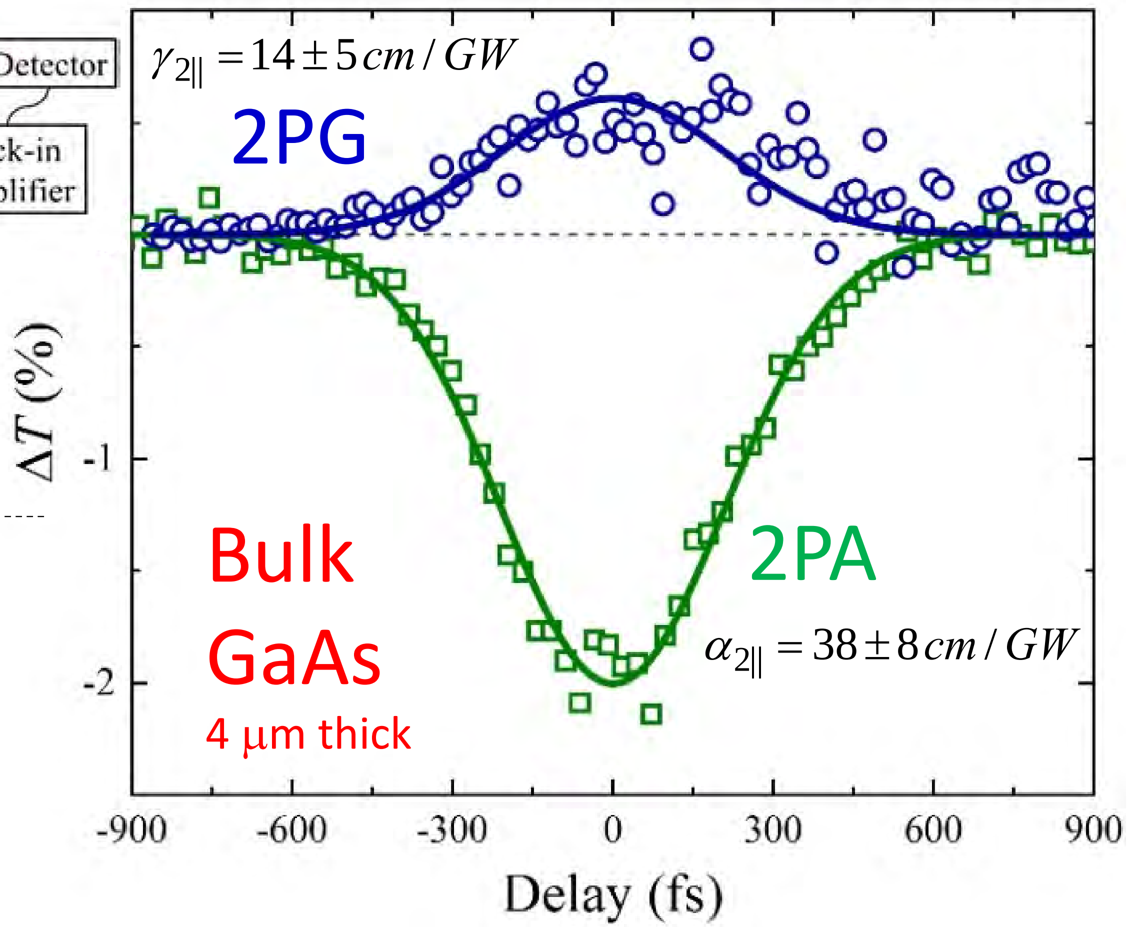
# 2-photon gain, 2PG

## Pump-probe with and without excitation




$\hbar\omega_a/\hbar\omega_b = 7.9$




No net gain - yet

# Two-photon laser?

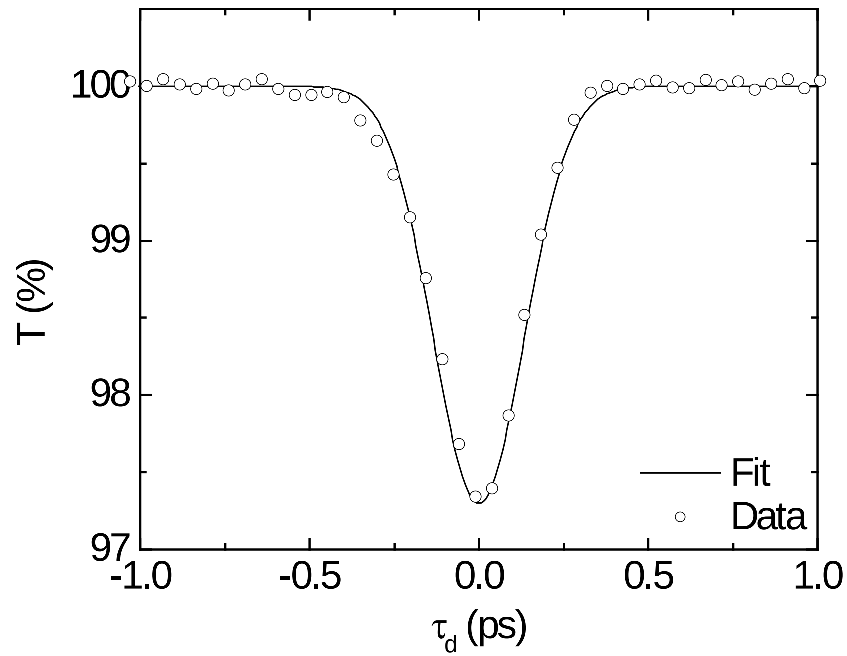
- 2-photon gain is the inverse process of 2PA
- Theory of 2PA enhancement in QW's shows another order of magnitude increase in 2PA
- This is above the 2-3 orders of magnitude enhancement of END 2PA
- Competing processes are 3PA, FCA, Urbach tail

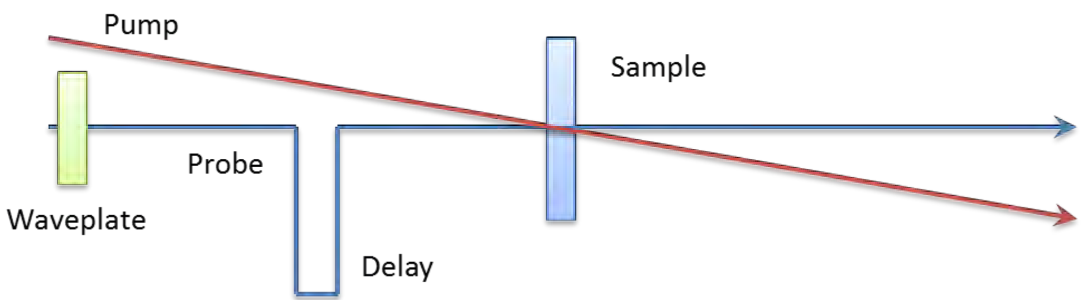
3PA

- Experiments soon in waveguide geometry

# Measuring Time Resolved NLA

- Excite-probe is a simple method for measuring Nonlinear Absorption (NLA)
  - Magnitude
  - Time dynamics
  - Polarization dependence
- Limited to NLA



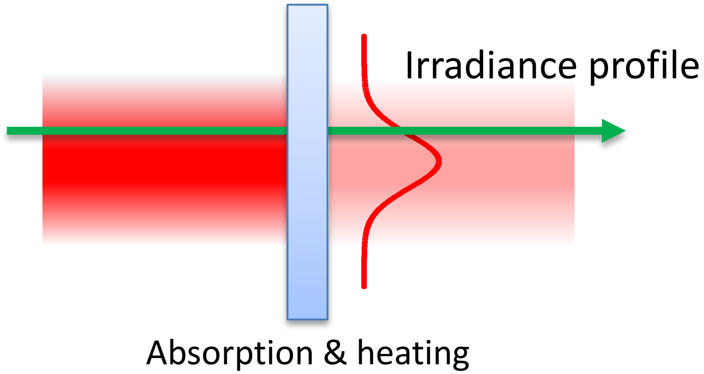




Excite-probe of ZnO

**Would like an equally simple and flexible method for NLR**

# learn from the Photothermal Beam Deflection

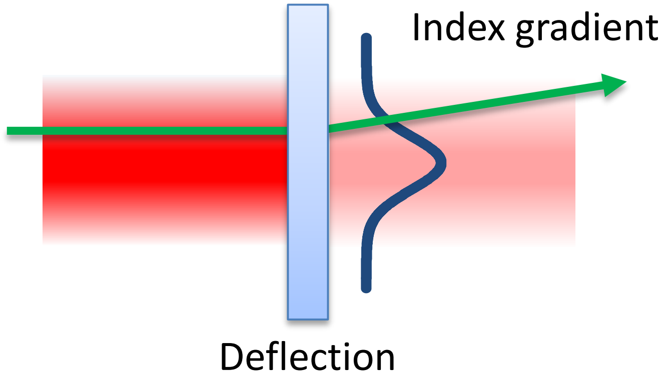
- Use to measure very small absorption signals.
- Excitation beam is absorbed by sample.
- Small probe is displaced.




1) Spear, J. D. and R. E. Russo (1991). Journal of Applied Physics **70**(2): 580-586.
2) Jackson, W. B., et al. (1981). Appl. Opt. **20**(8): 1333-1344.
3) Sell, A., et al. (1990). J. Appl. Phys. **69**(3): 1330-1336.

# Photothermal Beam Deflection

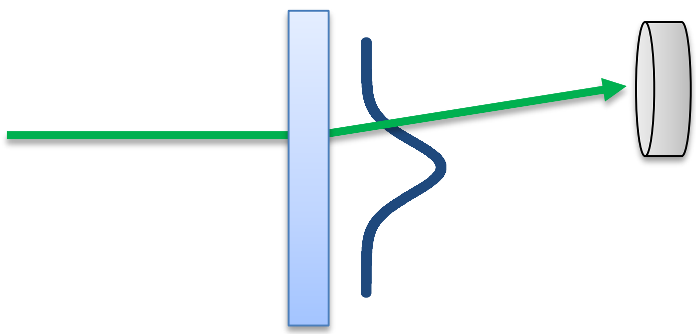
- Absorption of excitation beam induces thermo-optic index gradient.
- Probe beam deflected by index gradient




1) Spear, J. D. and R. E. Russo (1991). Journal of Applied Physics **70**(2): 580-586.
2) Jackson, W. B., et al. (1981). Appl. Opt. **20**(8): 1333-1344.
3) Sell, A., et al. (1990). J. Appl. Phys. **69**(3): 1330-1336.

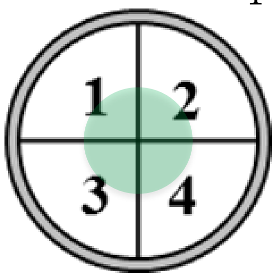
# Photothermal Beam Deflection

- Absorption of excitation beam induces thermo-optic index gradient.
- Probe beam deflected by index gradient.
- Detected by quad cell detector.



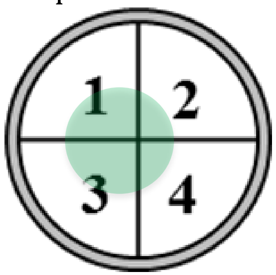
Detection

- Measured by quad cell detector
  - $\frac{\Delta E}{E} = \frac{(E_1+E_3)-(E_2+E_4)}{E_1+E_3+E_2+E_4}$




No deflection

$$\frac{\Delta E}{E} = 0$$




Deflected beam

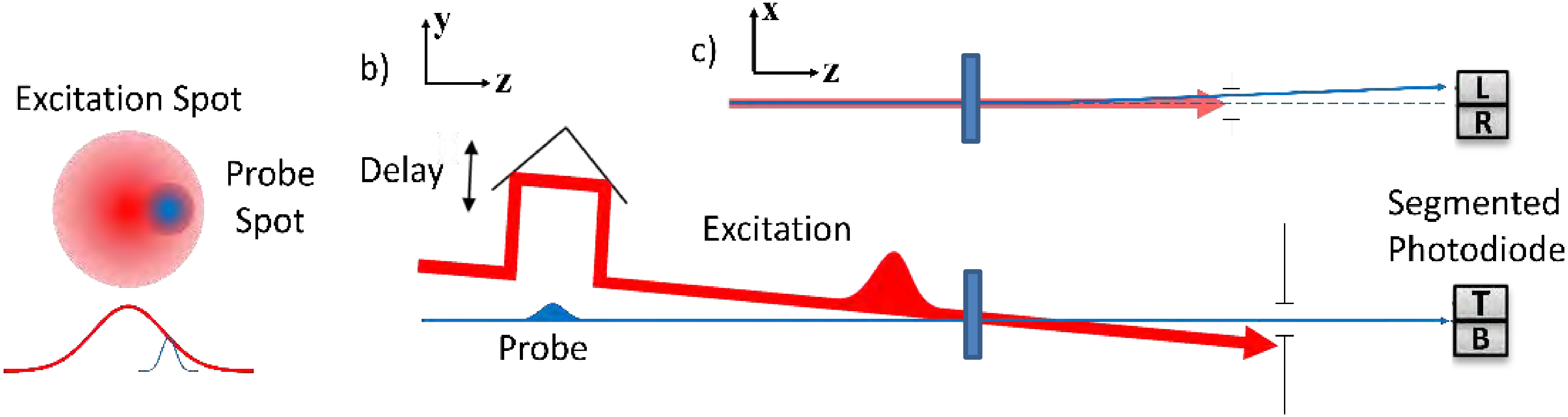
$$\frac{\Delta E}{E} \succ 0$$

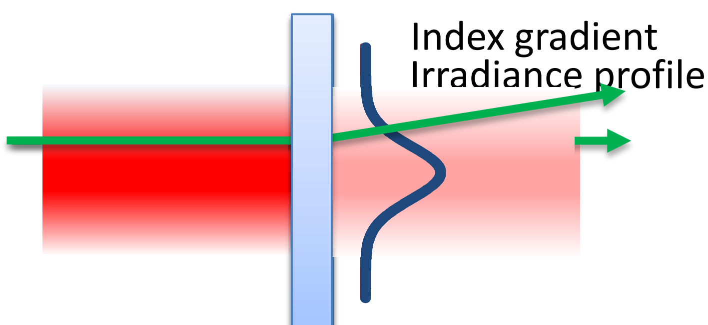
  - Deflection proportional to signal difference $\Delta x \propto \Delta E/E$ (for small $\Delta x$).

**Change from CW to pulsed to measure ultrafast nonlinearities.**

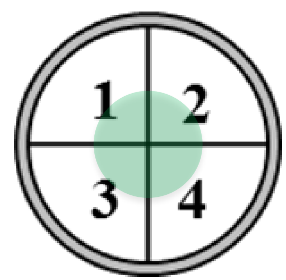
1) Spear, J. D. and R. E. Russo (1991). Journal of Applied Physics **70**(2): 580-586.
2) Jackson, W. B., et al. (1981). Appl. Opt. **20**(8): 1333-1344.
3) Sell, A., et al. (1990). J. Appl. Phys. **69**(3): 1330-1336.

# Beam Deflection




Deflection



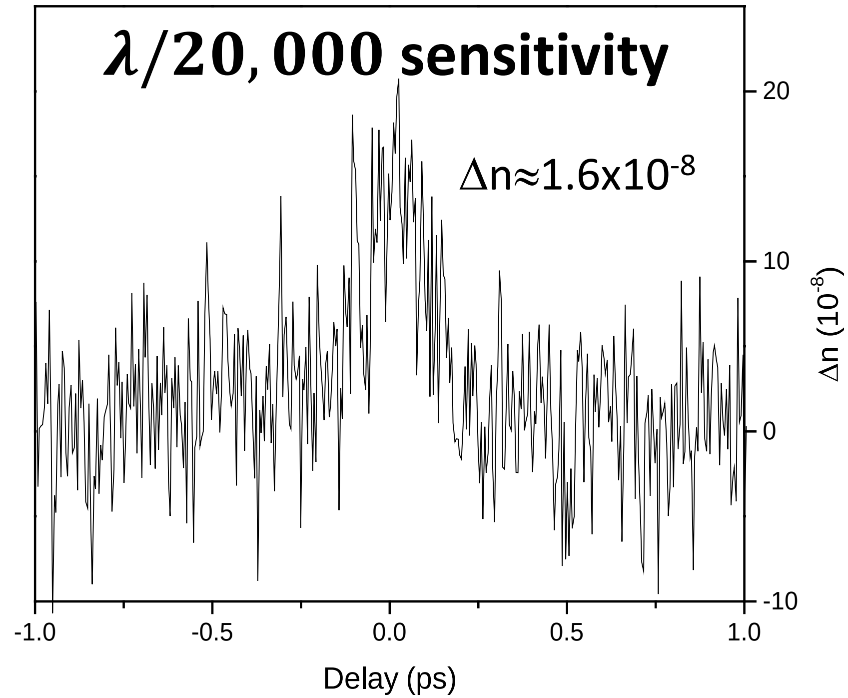

No deflection

$$\frac{\Delta E}{E} = 0$$

1) Spear, J. D. and R. E. Russo (1991). Journal of Applied Physics **70**(2): 580-586.
2) Jackson, W. B., et al. (1981). Appl. Opt. **20**(8): 1333-1344.
3) Sell, A., et al. (1990). J. Appl. Phys. **69**(3): 1330-1336.

# Example - Fused Silica

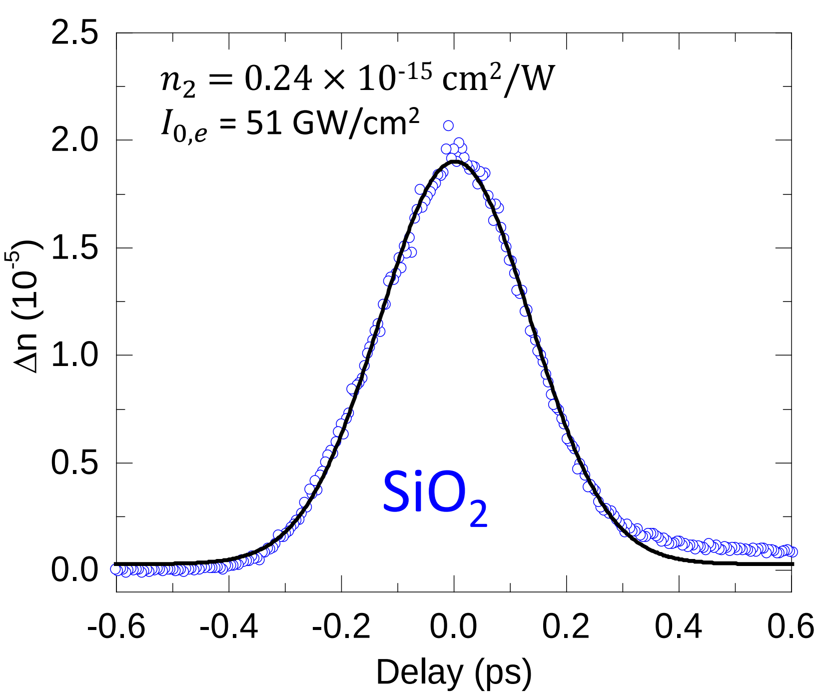
- $\Delta n$ follows cross-correlation indicates electronic nonlinearity
- NLR coefficient $n_2$
  - Literature: $0.25 \times 10^{-15}$ W/cm²
  - Measured: $0.24 \times 10^{-15}$ W/cm²
- Ratio of $\Delta n_{\parallel}/\Delta n_{\perp}$
  - Expected: 3
  - Measured: 3.1
- Turn down irradiance to find max sensitivity of $\lambda/20,000$

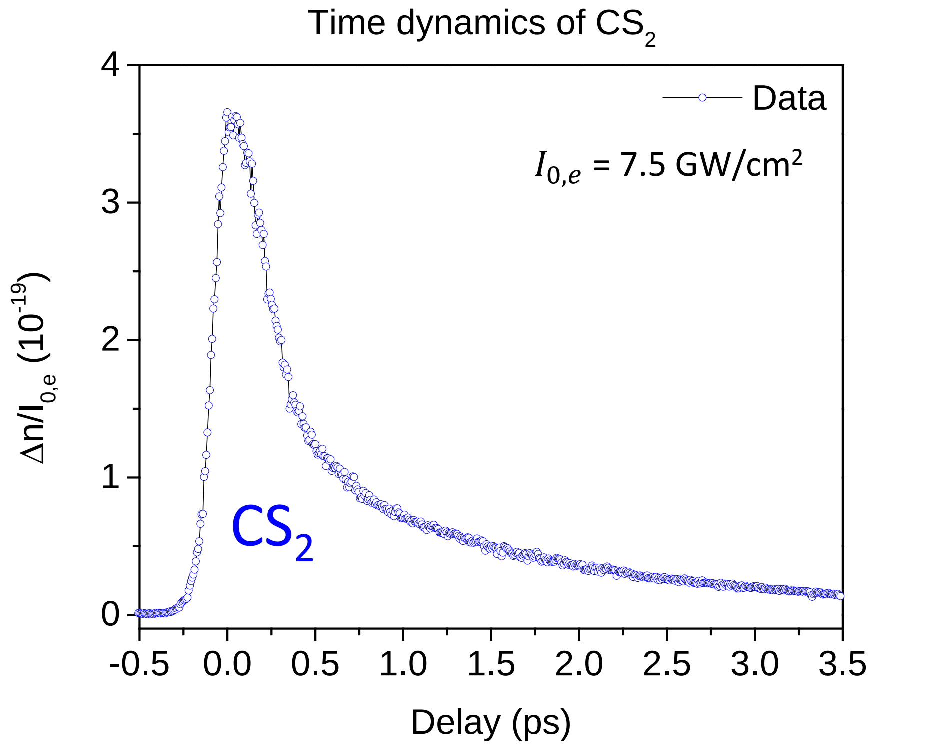



1) Milam, D. (1998). Appl. Opt. **37**(3): 546-550.

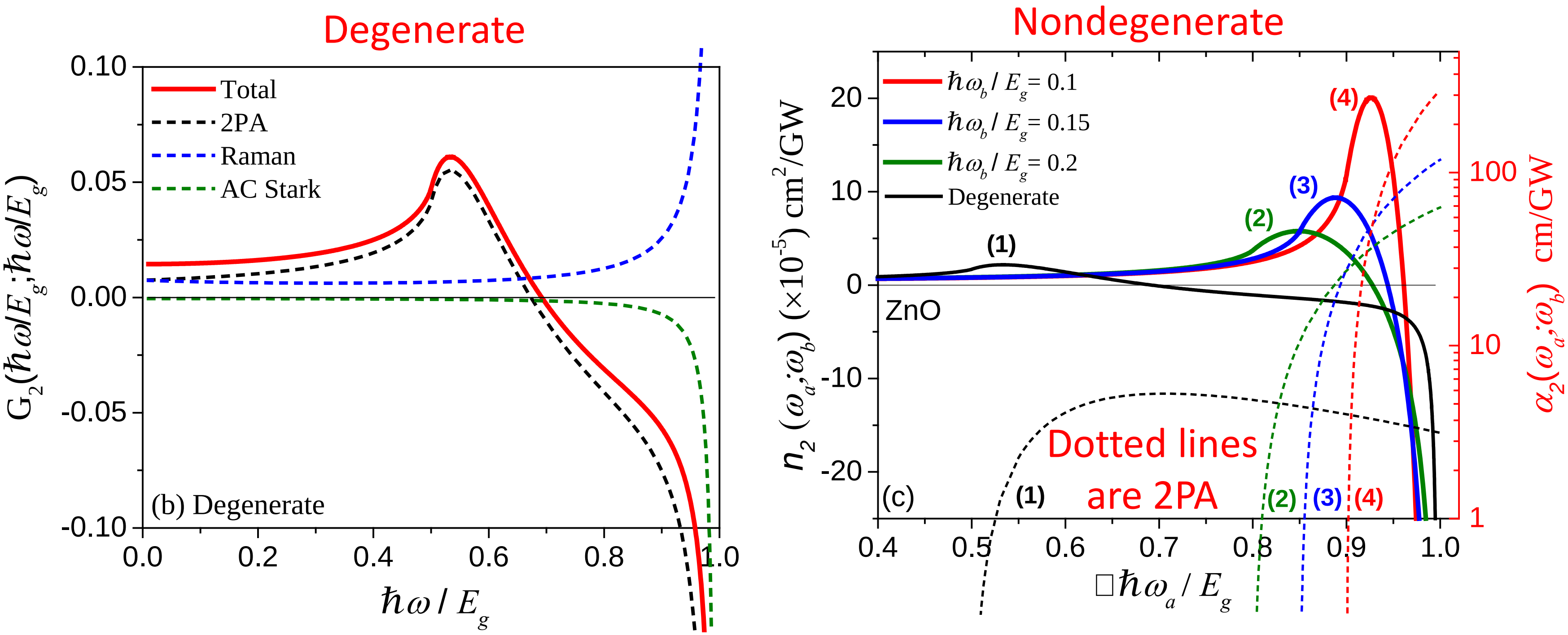
# Analysis of Beam Deflection

- Signal proportional to average index change: $\Delta E/E = k_{p,0} L \sqrt{\frac{2}{e}} \frac{w_{p0}}{w'_e} \langle \Delta n_p(\tau_d) \rangle$
- Instantaneous response follows cross-correlation of excitation and probe.
- Sensitive to sign of NLR.
- Non-instantaneous response can be time-resolved.



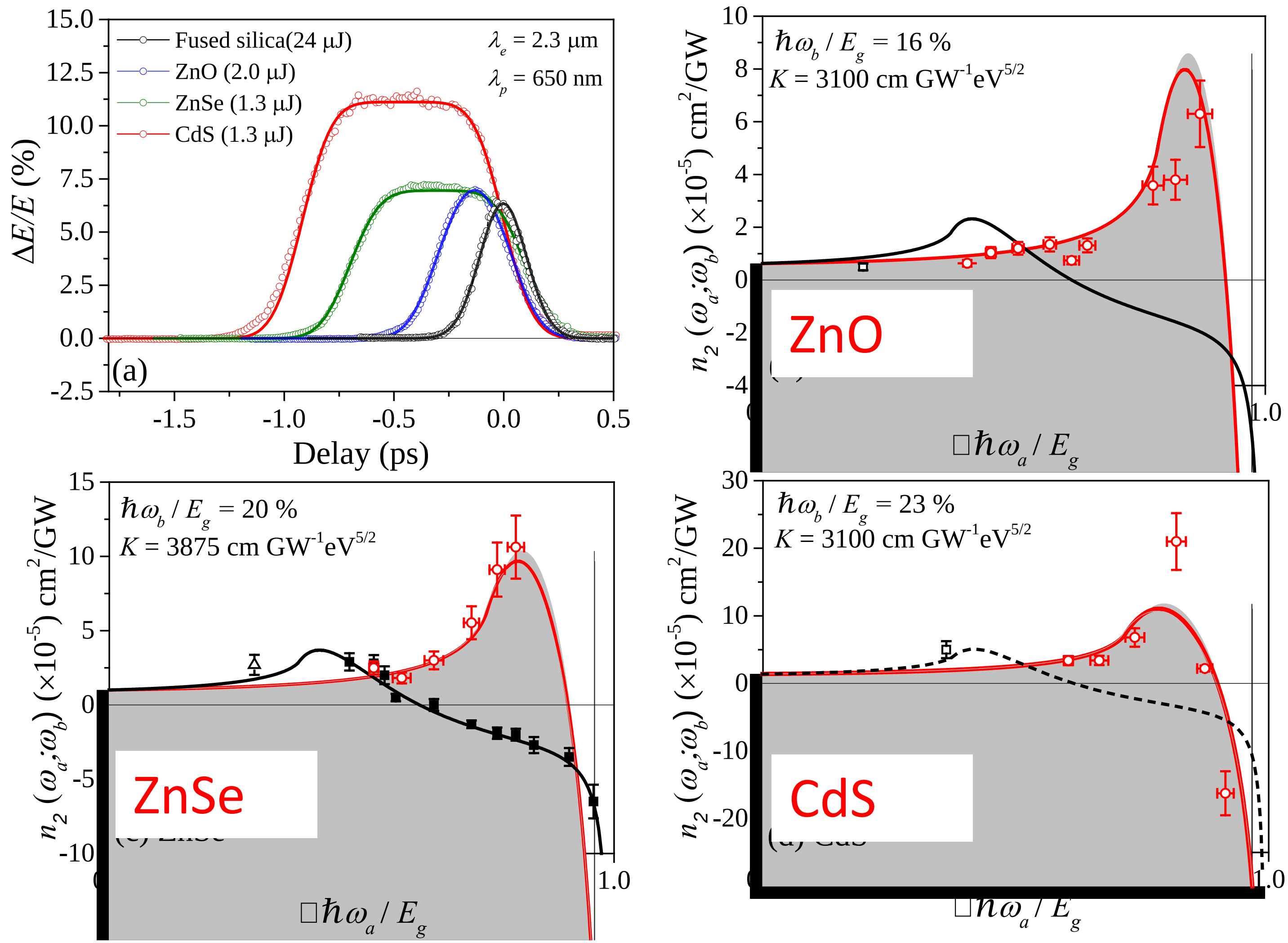



# Nondegenerate Nonlinear Refraction



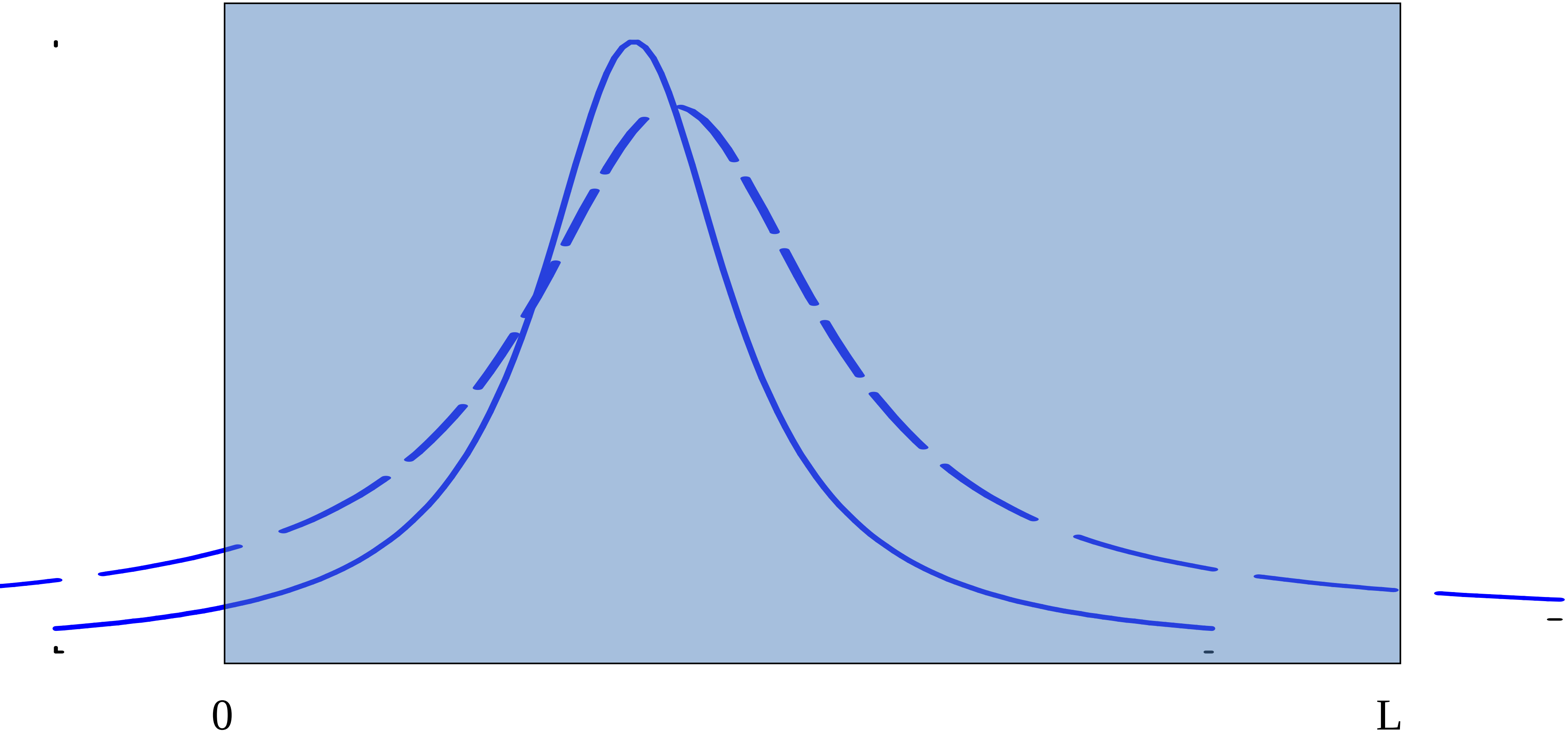

These calculations come from the Kramers-Kronig integral of the Nonlinear Absorption spectrum for a fixed excitation wavelength.

# Beam Deflection Measurements of NLR

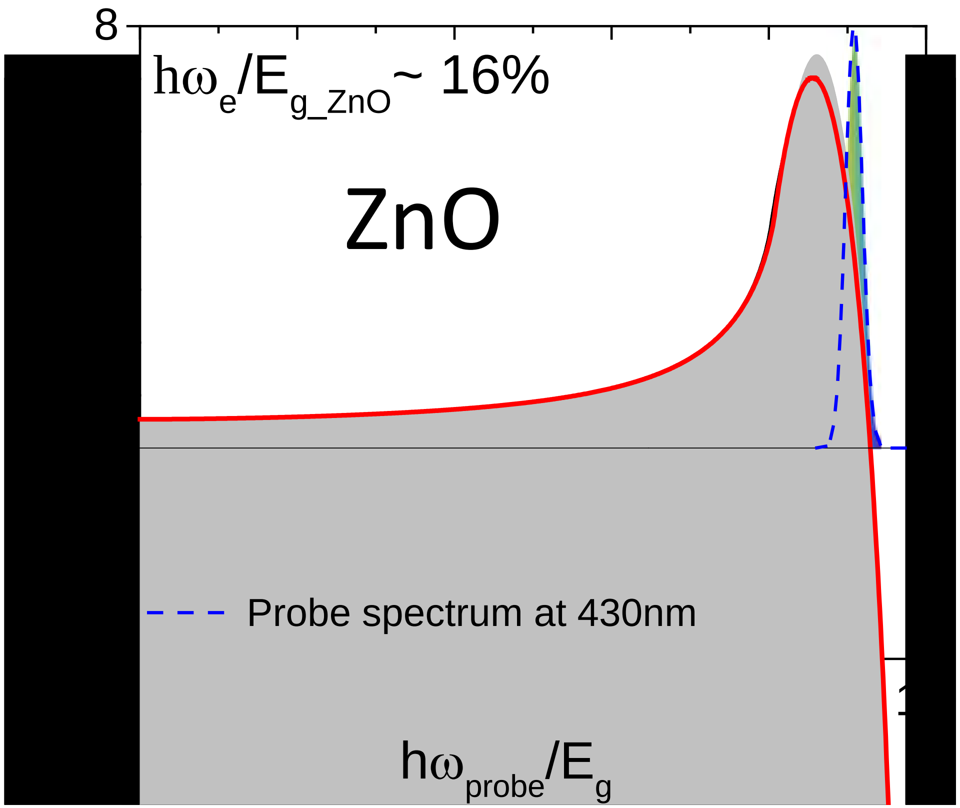


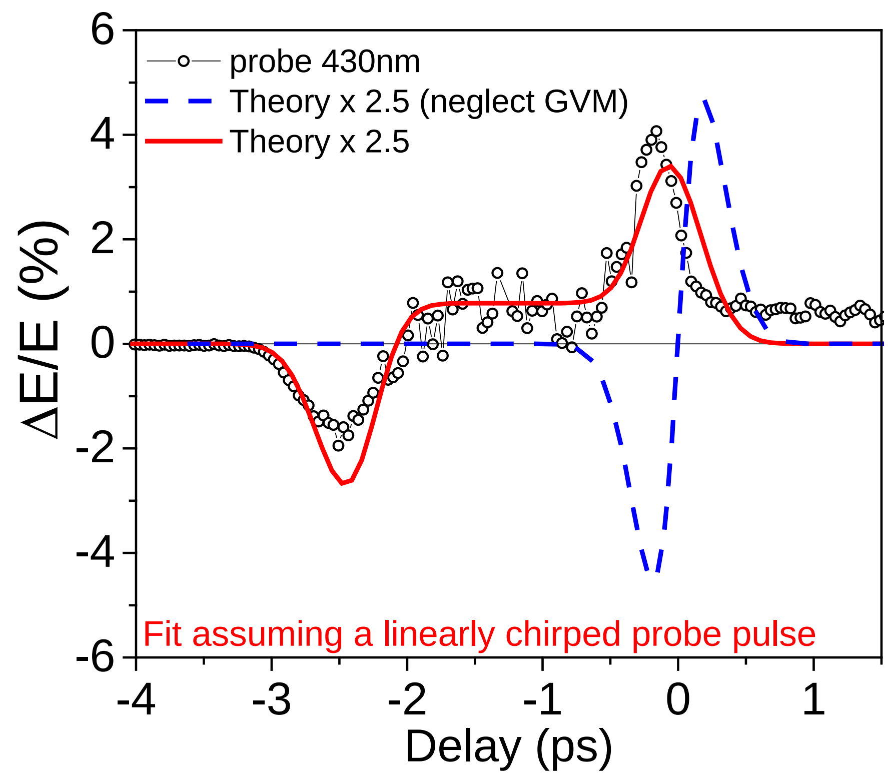
# Temporal Walkoff of Nondegenerate Pump and Probe

(GVM – group velocity mismatch)



# Beam Deflection Measurements of NLR

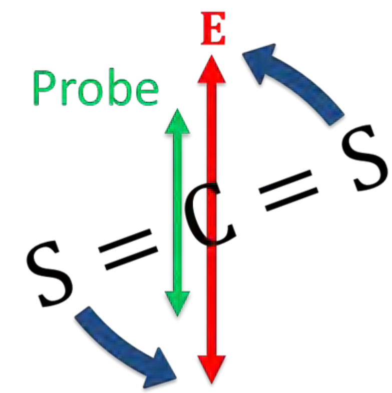


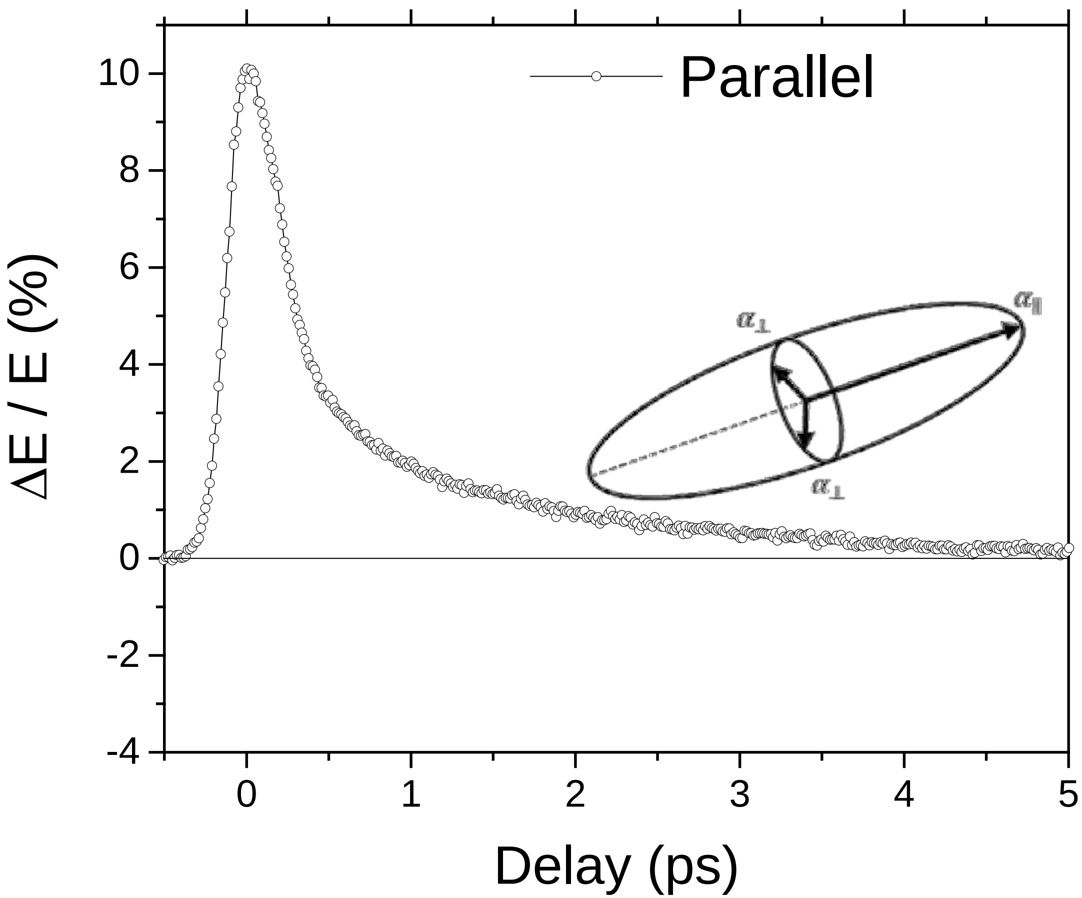



# Transient Nonlinear Refraction of $CS_2$

$$\Delta n_p(t) = 2n_2 I_e(t) + \int_{-\infty}^{t} R(t-t') I_e(t') dt'$$

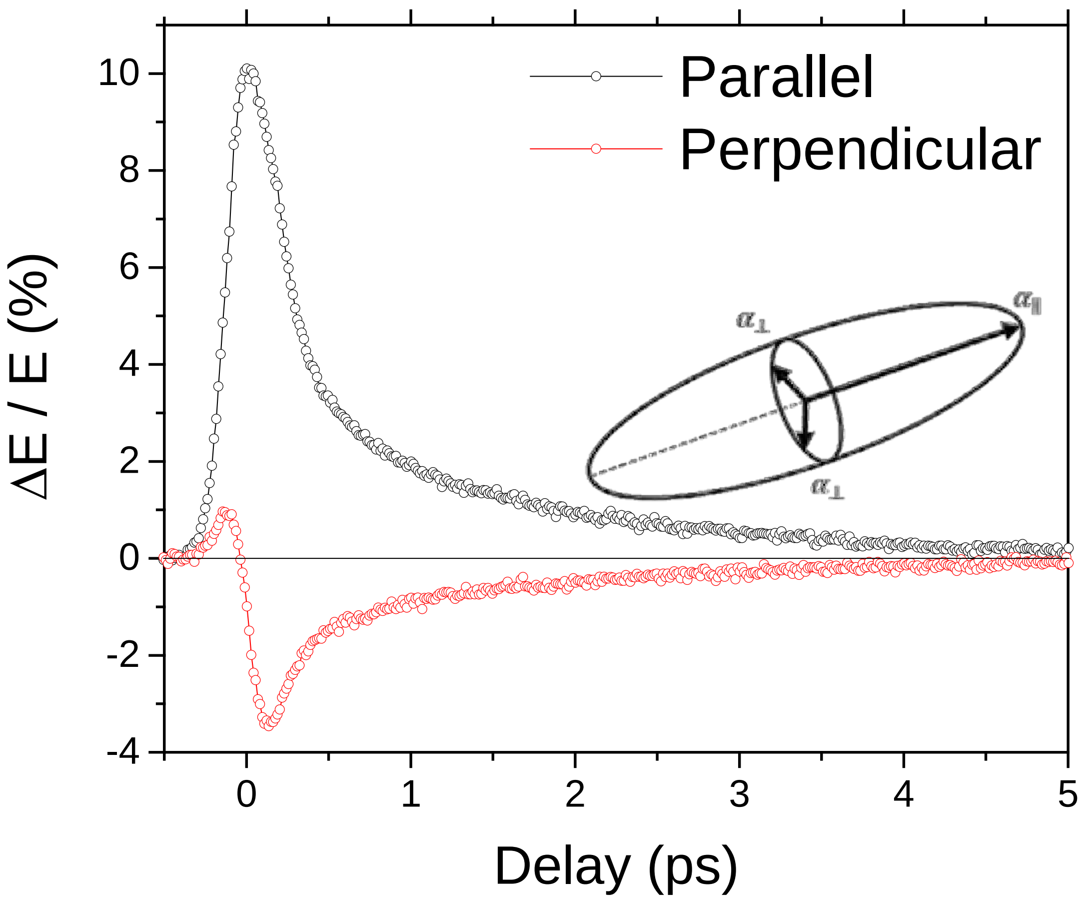
Parallel $\Delta n_{\parallel} > 0$

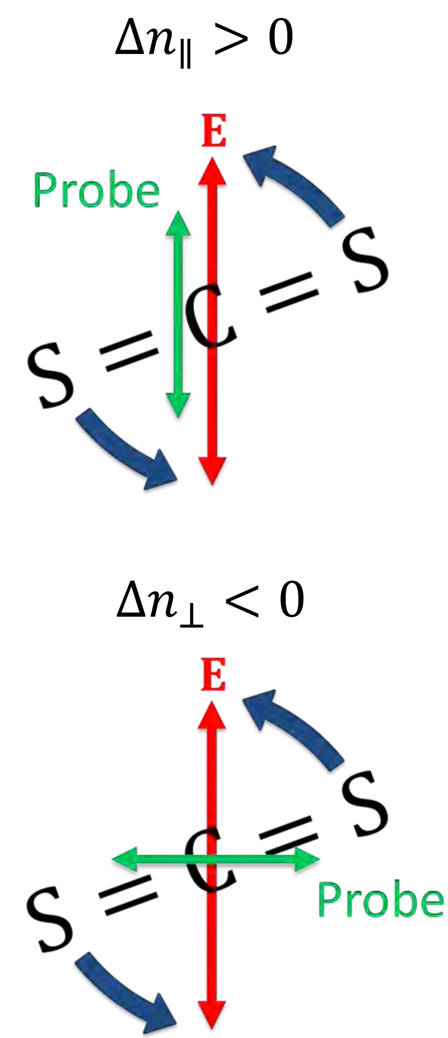


# Transient Nonlinear Refraction of $CS_2$

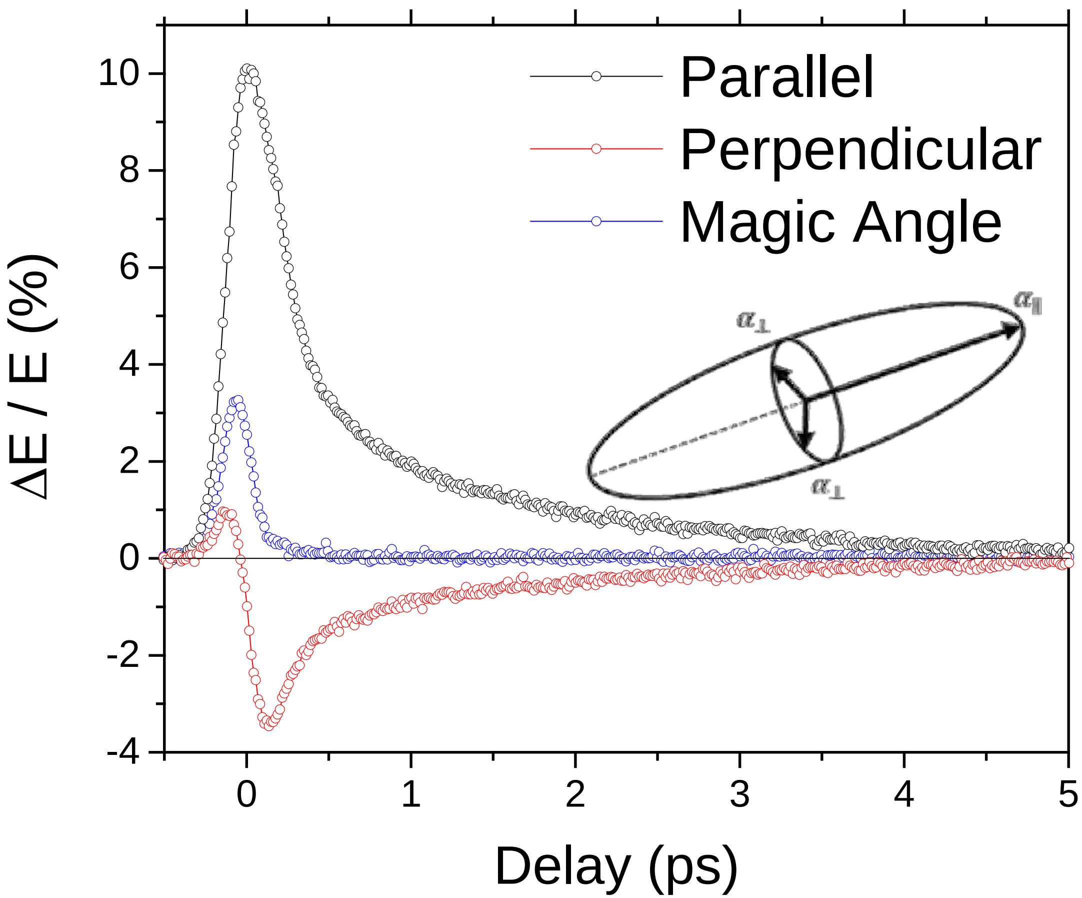
$$\Delta n_p(t) = 2n_2 I_e(t) + \int_{-\infty}^{t} R(t-t')I_e(t')dt'$$



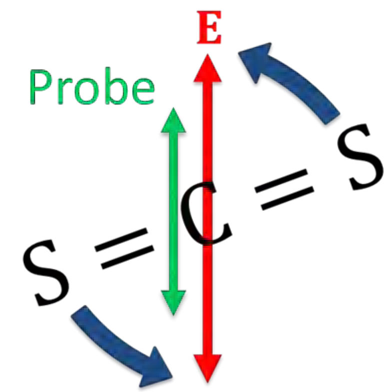



# Transient Nonlinear Refraction of $CS_2$

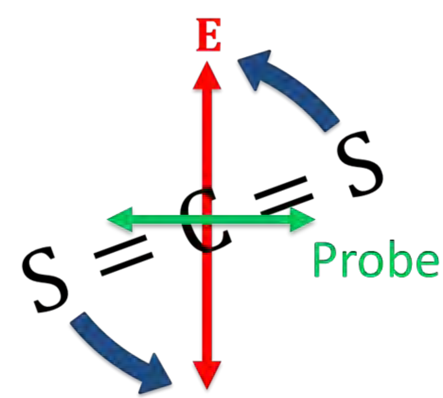
$$\Delta n_p(t) = 2n_2 I_e(t) + \int_{-\infty}^{t} R(t-t')I_e(t')dt'$$




$\Delta n_{\parallel} > 0$

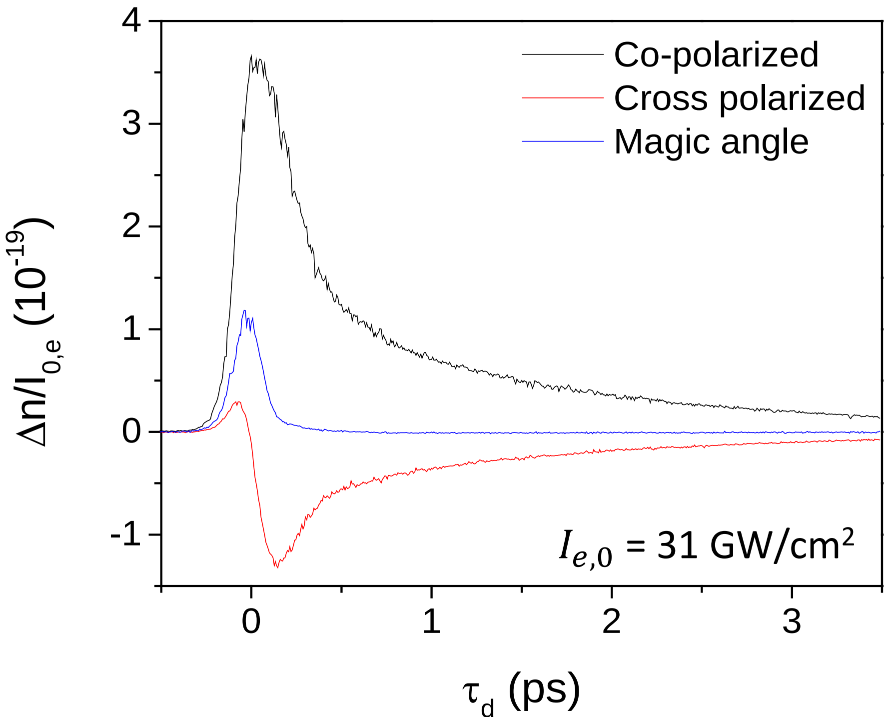


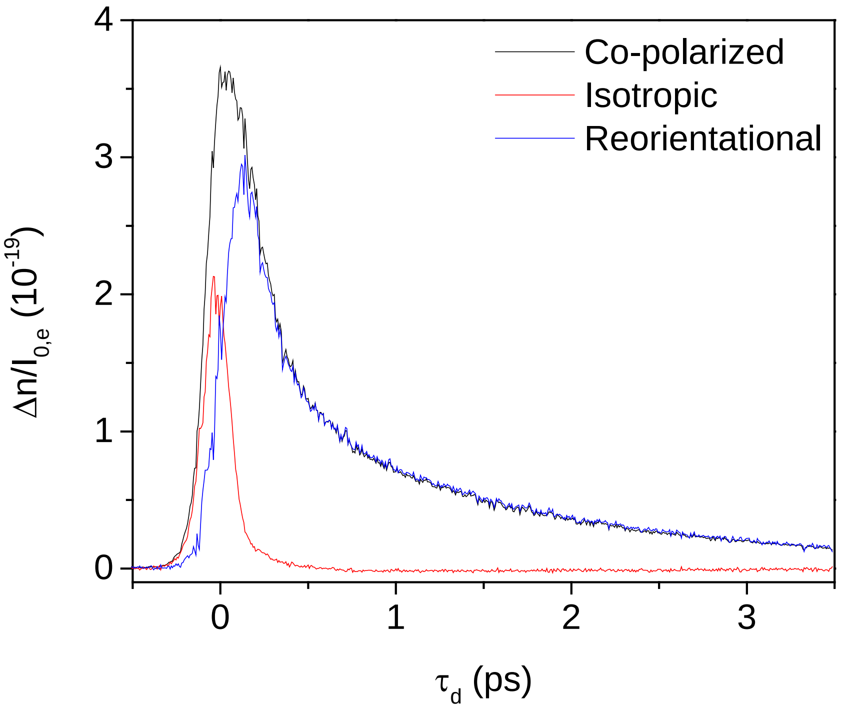

$\Delta n_{\perp} < 0$



# Beam deflection from $CS_2$

- Measured $CS_2$ at three polarizations
  - Co-polarized ($\Delta n_{tot}(0°)$)
  - Cross polarized ($\Delta n_{tot}(90°)$)
  - "Magic" angle ($\Delta n_{tot}(54.7°)$)
- Scale magic angle by 9/5 to get isotropic component.
- Subtract isotropic from co-polarized to get reorientational component.

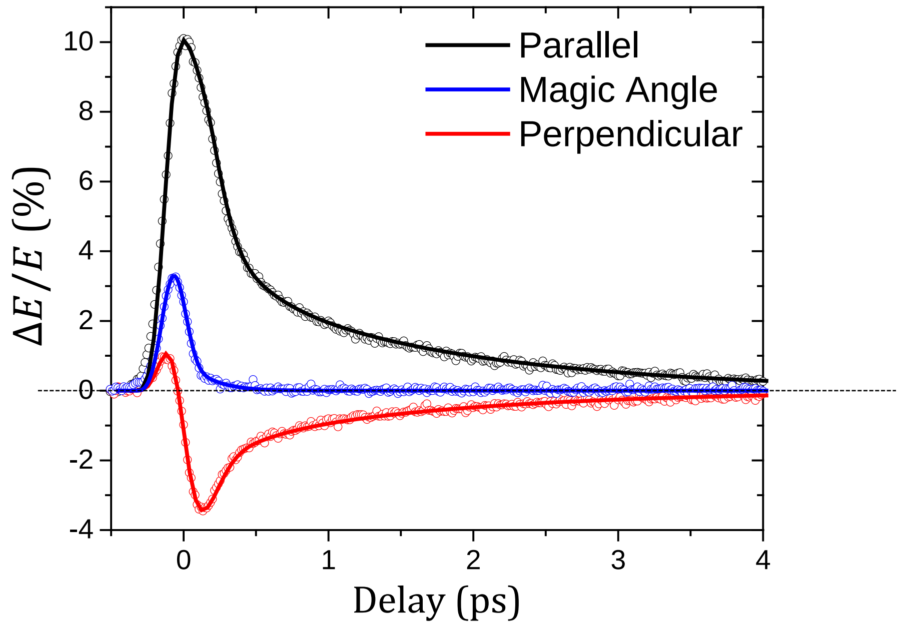


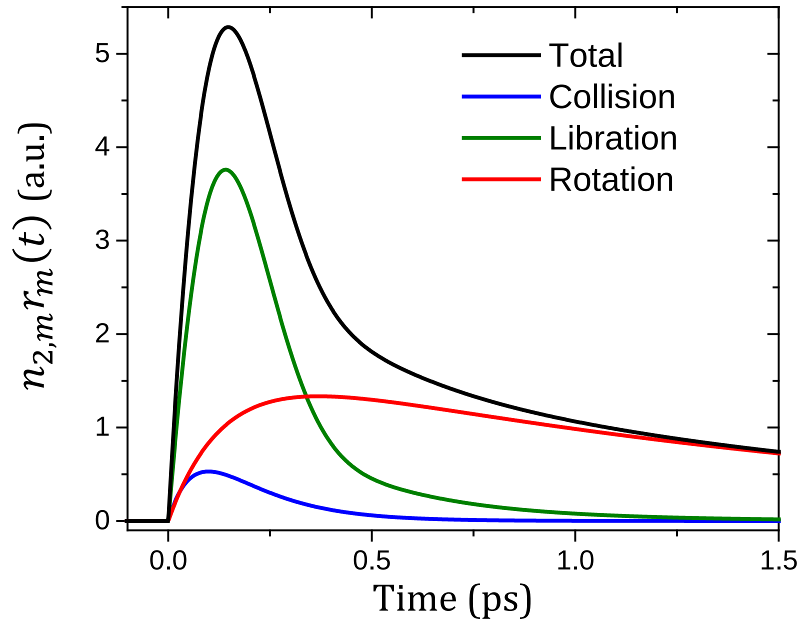



# Response Function of $CS_2$

$$\Delta n(t) = 2n_{2,el}I_e(t) + \int_{-\infty}^{t} R(t-t')I_e(t')dt'$$

$$R(t) = \sum_m n_{2,m} r_m(t)$$



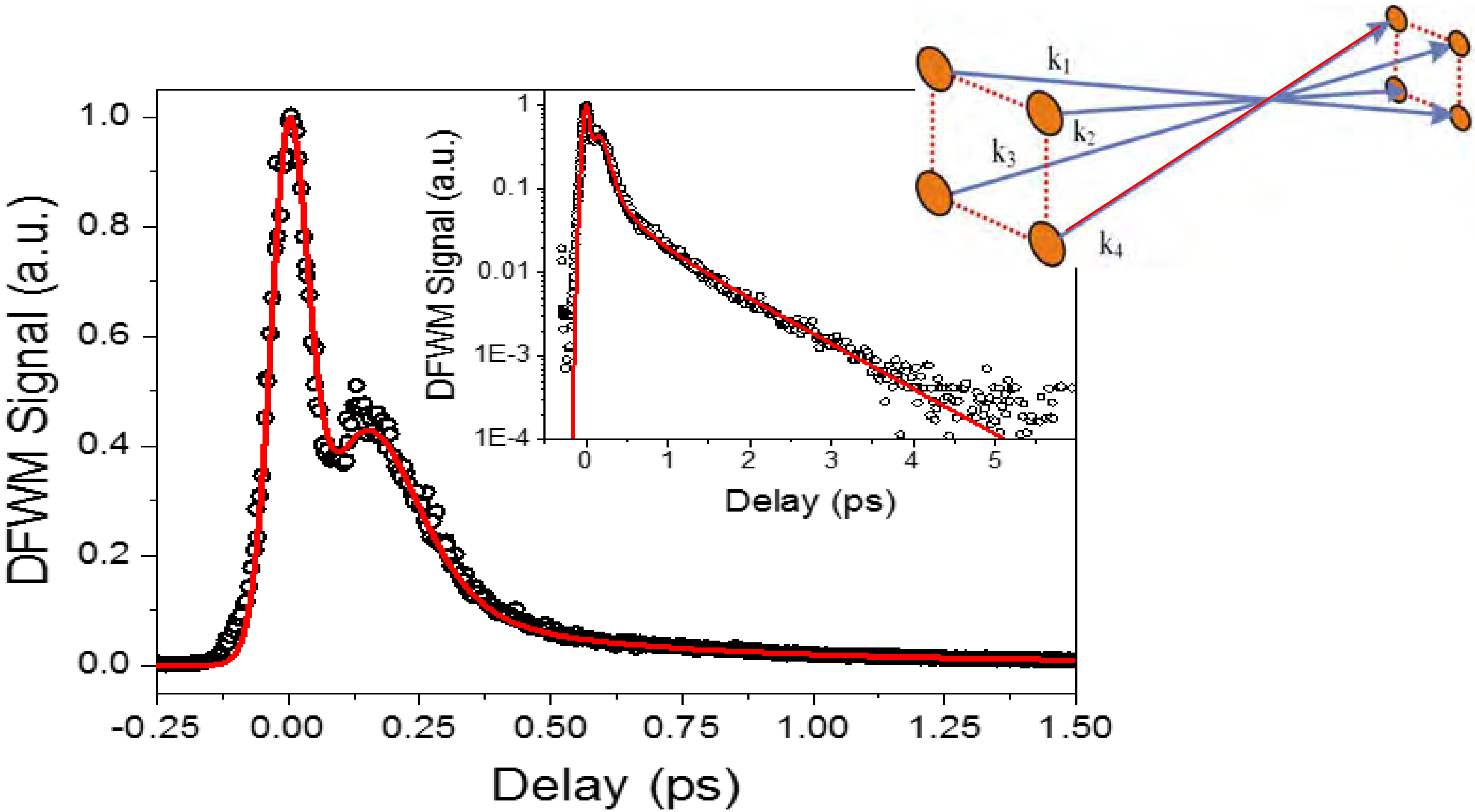




| Mechanism | $n_{2,m}$ | $\tau_{r,m}$ (fs) | $\tau_{f,m}$ (fs) | Symmetry |
|---|---|---|---|---|
| Electronic | 1.5 ± 0.4 | Instantaneous | | $iso$ |
| Collision | 1.0 ± 0.2 | 150 ± 50 | 140 ± 50 | $iso$ |
| Libration | 7.6 ± 1.5 | * | 450 ± 100 | $re$ |
| Diffusive | 18 ± 3 | 150 ± 50 | 1610 ± 50 | $re$ |

*$\omega_0$ = 8.5 ± 1.0 $ps^{-1}$ , $\sigma$ = 5 ± 1 $ps^{-1}$

Reichert et al. Optica, **1**(6), 436, (2014).

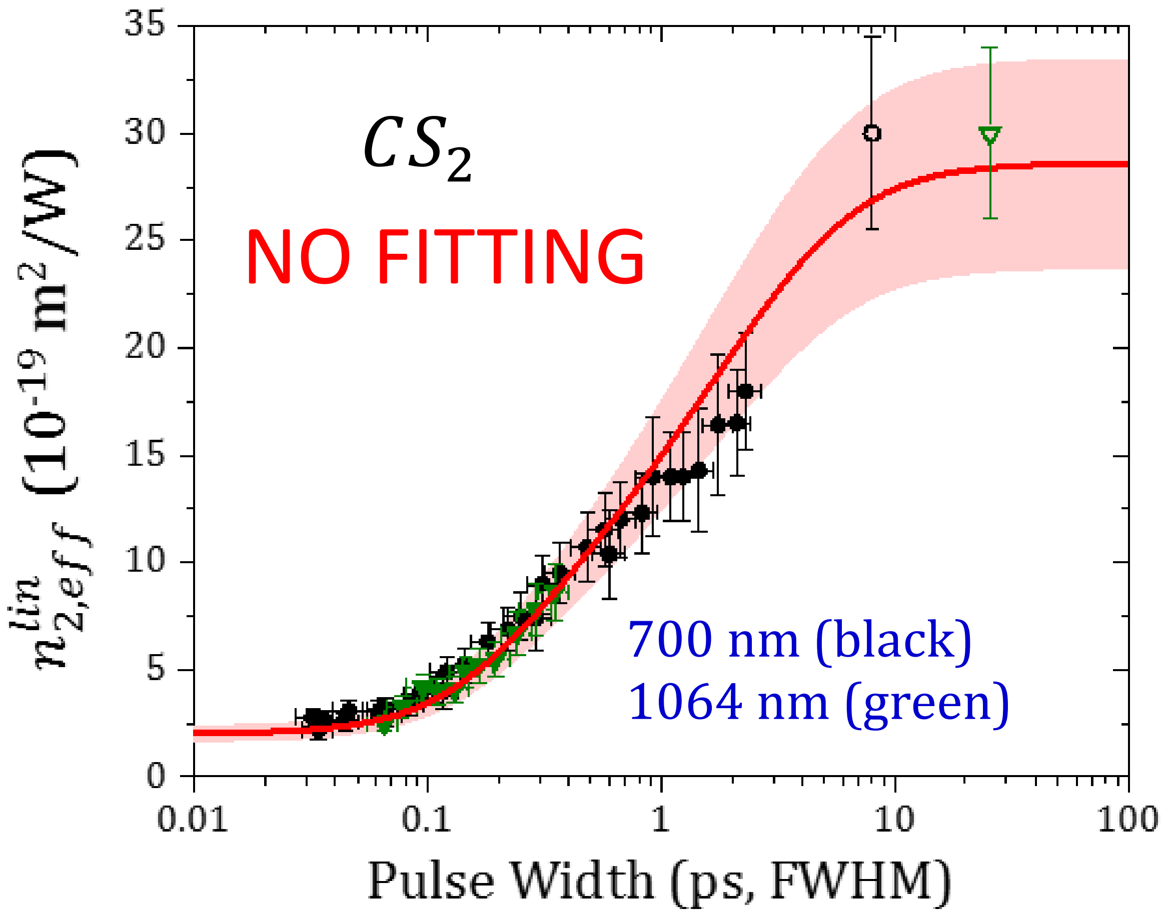
# DFWM in $CS_2$




DFWM signal (black circles) and calculation (red curve) using the response function model values of Table 1. Inset shows semi-logarithmic plot out to 6 ps delay.

# Comparison with Z-scan

$$n_{2,\mathrm{eff}} = n_2 + \frac{\int I(t)\left[\int_{-\infty}^{t} R(t-t')I_e(t')dt'\right]dt}{\int I^2(t)dt}$$

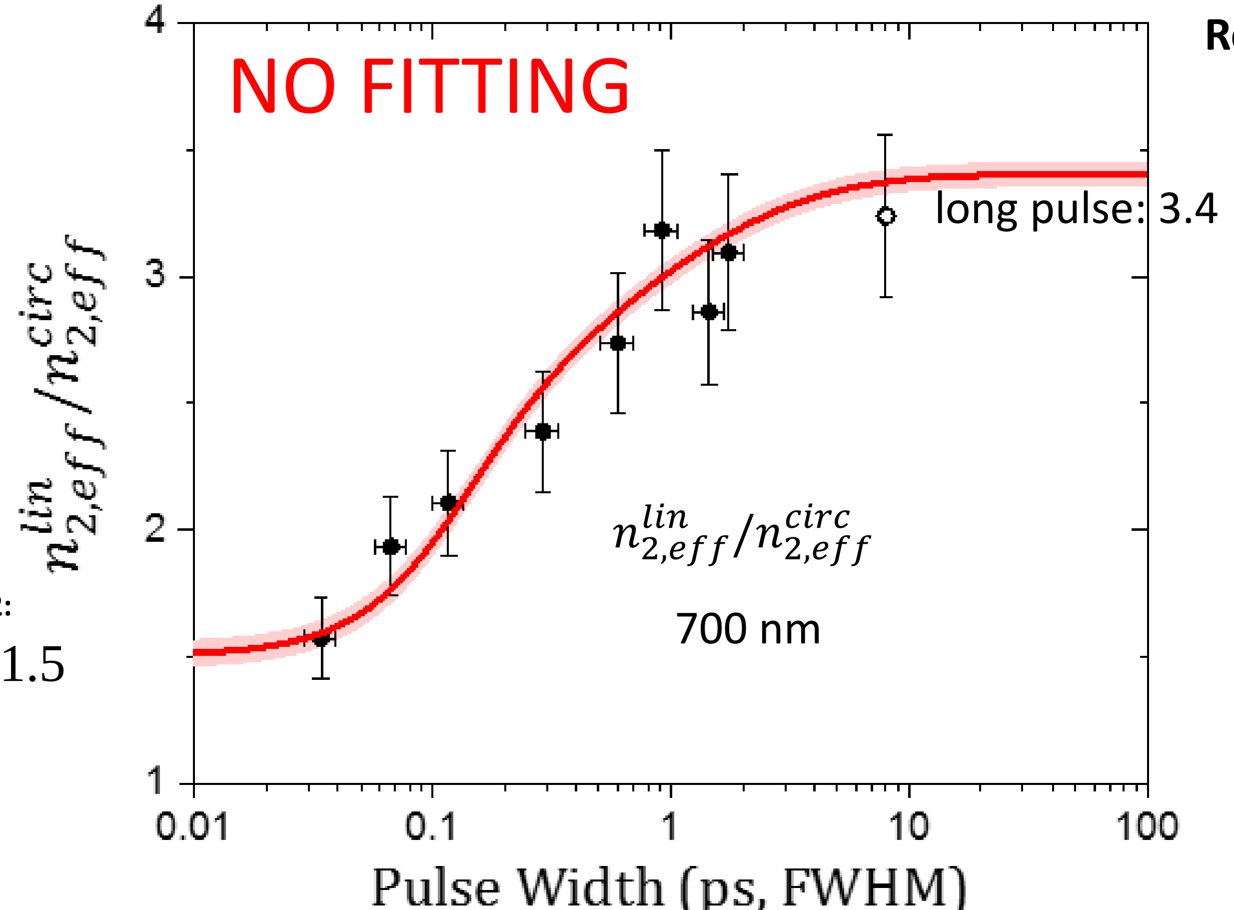



Z-scans taken over large pulse width range.

Solid line is not a fit, but is the $n_{2,eff}$ found from beam deflection data.

# Z-scan

## Polarization dependence shows symmetry




**Re-orientational $n_2$:**

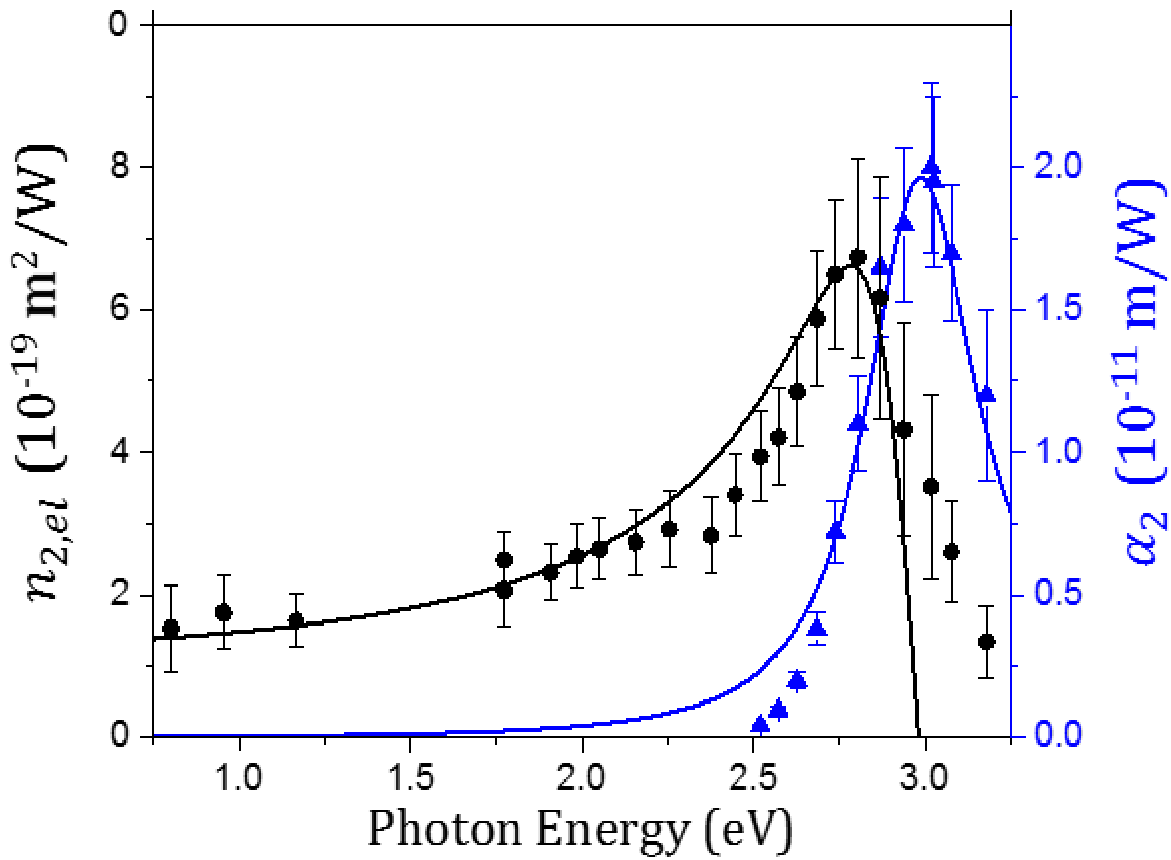
$$\frac{n_{2\_linear}}{n_{2\_circular}} = 4$$

**Electronic $n_2$:**

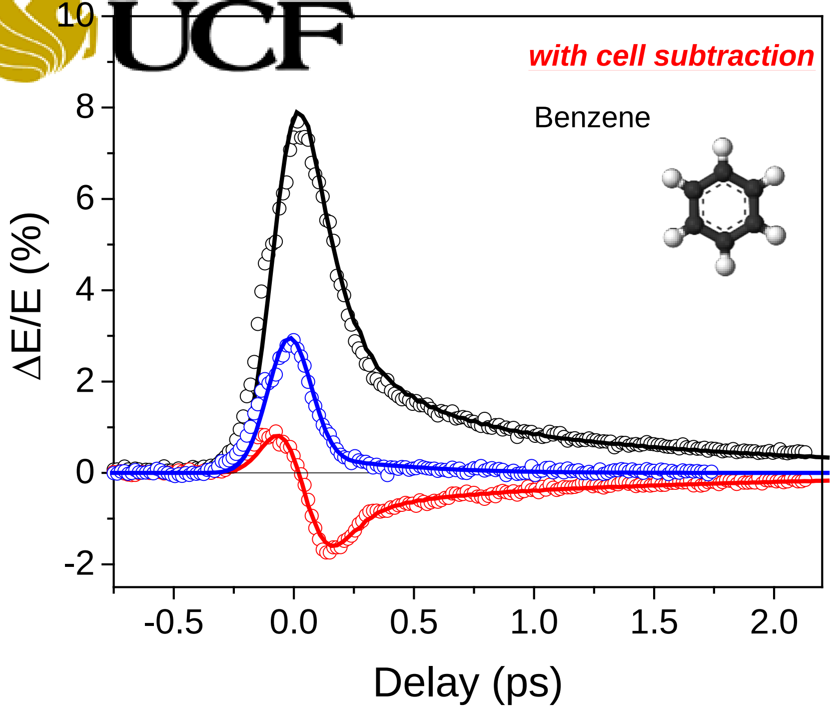
$$\frac{n_{2\_linear}}{n_{2\_circular}} = 1.5$$

$$\left.\frac{n_{2,eff}^{lin}}{n_{2,eff}^{circ}}\right|_{long} = \frac{n_{2,eff}^{lin}|_{long}}{\frac{(n_{2,el}+n_{2,c})}{1.5} + \frac{(n_{2,l}+n_{2,d})}{4}}$$

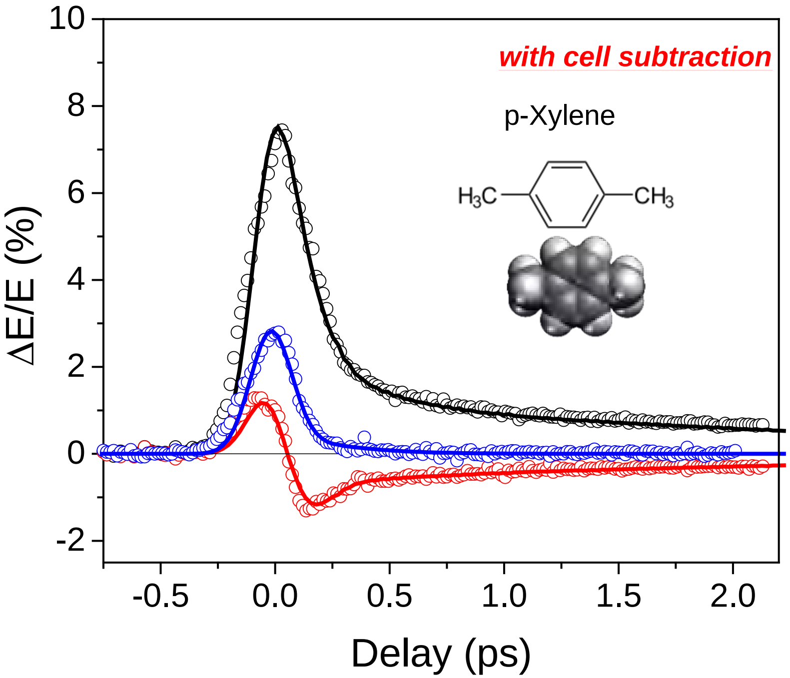
# Dispersion of $n_2, \alpha_2$ in $CS_2$




Z-scan measurements of NLR (black circles) for fs pulses with non-instantaneous component subtracted, and 2PA (blue triangles). Curves represent the SOS model (3 levels) fit for 2PA (blue) and NLR (black). NLRx2.

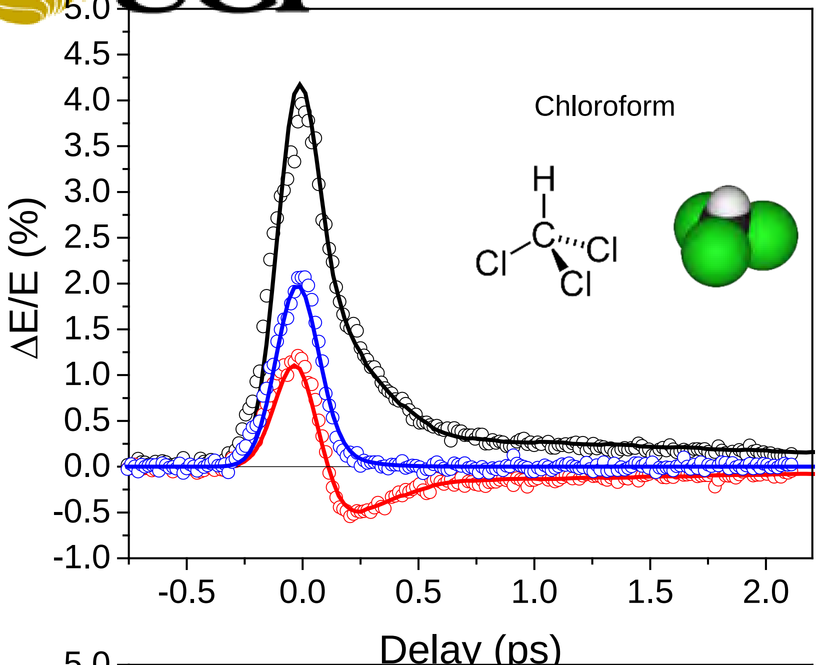



| $n_{2,el}$ | $n_{2,c}$ | $\tau_{r,c}$ | $\tau_{f,c}$ | $n_{2,l}$ | $\omega_0$ | $\sigma$ | $\tau_{f,l}$ | $n_{2,d}$ | $\tau_{r,d}$ | $\tau_{f,d}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.57 | 0.25 | 200±50 | 300±50 | 1.15 | 12±2 | 8±2 | 350±50 | 2.8 | 100±50 | 1500±100 |



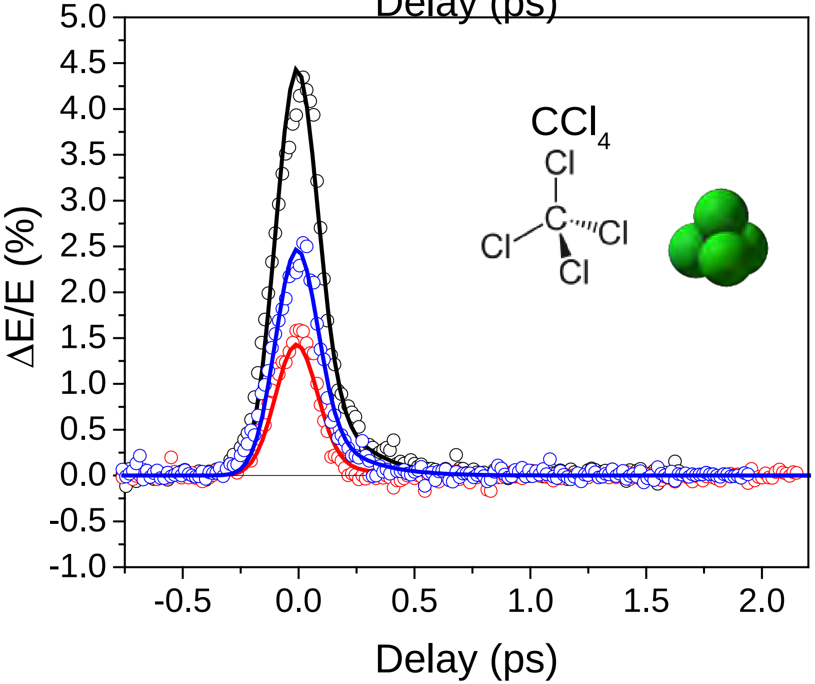

| $n_{2,el}$ | $n_{2,c}$ | $\tau_{r,c}$ | $\tau_{f,c}$ | $n_{2,l}$ | $\omega_0$ | $\sigma$ | $\tau_{f,l}$ | $n_{2,d}$ | $\tau_{r,d}$ | $\tau_{f,d}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.6 | 0.2 | 200±50 | 200±50 | 0.85 | 12±2 | 6±2 | 350±50 | 3.1 | 100±50 | 2500±100 |

- n dispersion is using Toluene

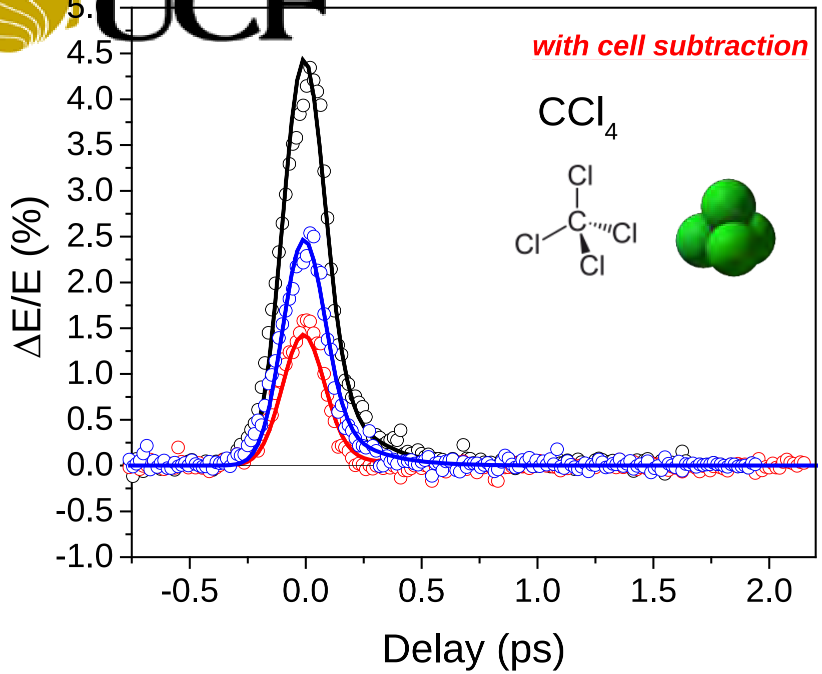



| $n_{2,el}$ | $n_{2,c}$ | $\tau_{r,c}$ | $\tau_{f,c}$ | $n_{2,l}$ | $\omega_0$ | $\sigma$ | $\tau_{f,l}$ | $n_{2,d}$ | $\tau_{r,d}$ | $\tau_{f,d}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.41 | 0.08 | 100±50 | 100±50 | 0.4 | 5±2 | 2±1 | 250±50 | 0.75 | 500±50 | 1800±300 |

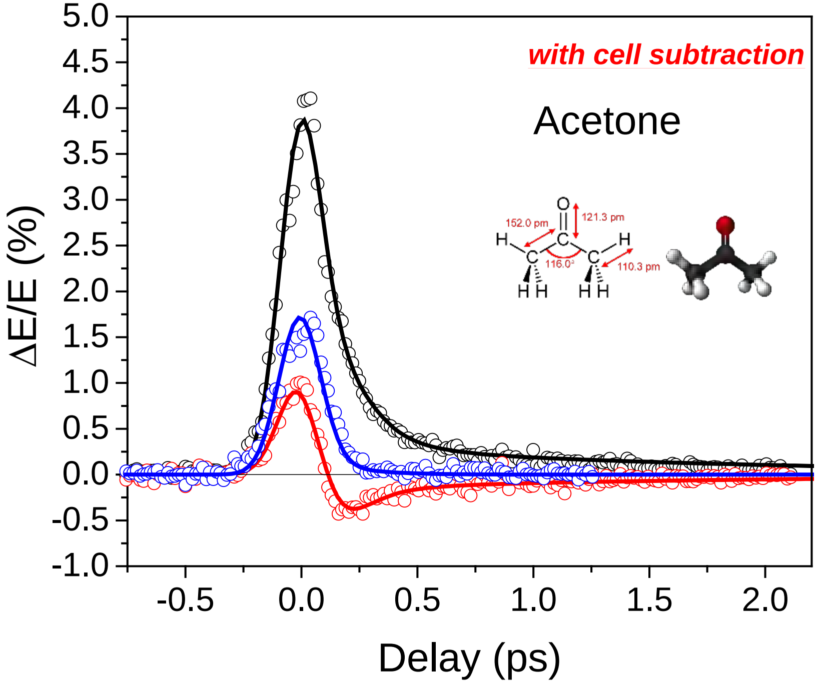
Peng Zhao




| $n_{2,el}$ | $n_{2,c}$ | $\tau_{r,c}$ | $\tau_{f,c}$ | $n_{2,l}$ | $\omega_0$ | $\sigma$ | $\tau_{f,l}$ | $n_{2,d}$ | $\tau_{r,d}$ | $\tau_{f,d}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.46 | 0.2 | 100±50 | 150±50 | 0 | NA | NA | NA | 0 | NA | NA |




<table>
<tr><th rowspan="2">$n_{2,el}$</th><th rowspan="2">$n_{2,c}$</th><th>$\tau_{r,c}$</th><th rowspan="2">$n_{2,l}$</th><th>$\omega_0$<br>$\sigma$<br>$\tau_{f,l}$</th><th rowspan="2">$n_{2,d}$</th><th>$\tau_{r,d}$</th></tr>
<tr><th>$\tau_{f,c}$</th><th></th><th>$\tau_{f,d}$</th></tr>
<tr><td rowspan="2">0.46</td><td rowspan="2">0.2</td><td>100±50</td><td rowspan="2">0</td><td>NA<br>NA</td><td rowspan="2">0</td><td>NA</td></tr>
<tr><td>150±50</td><td>NA</td><td>NA</td></tr>
</table>

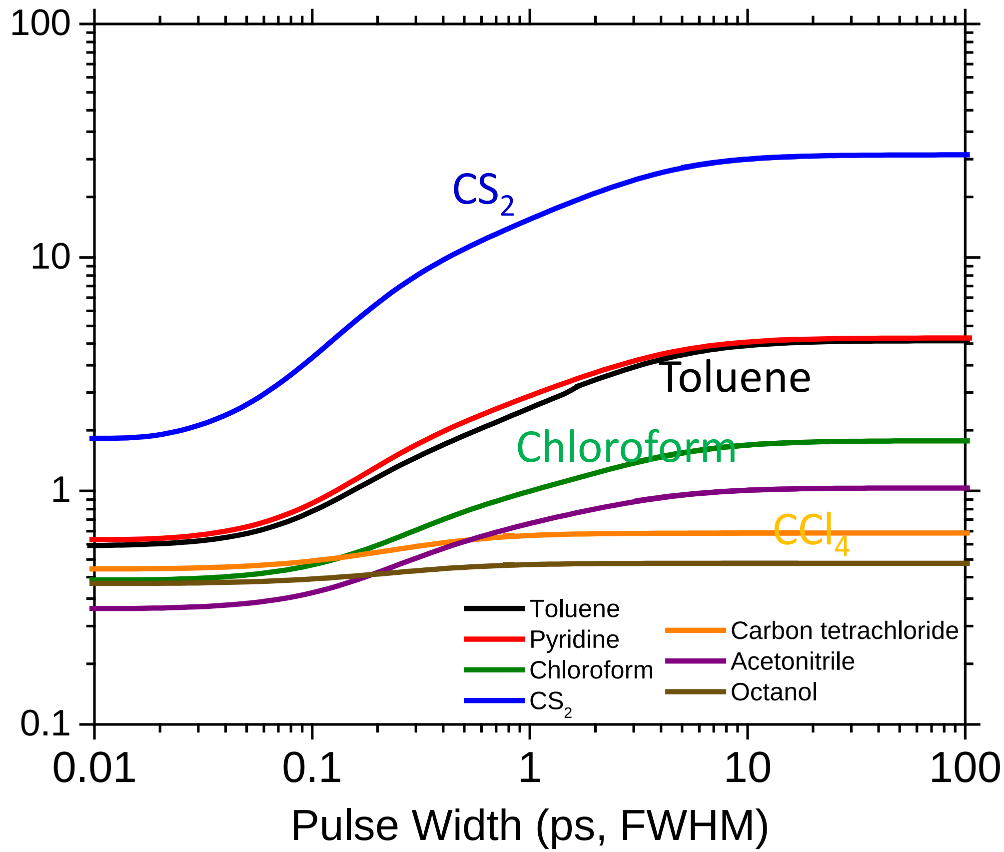



<table>
<tr><th rowspan="2">$n_{2,el}$</th><th rowspan="2">$n_{2,c}$</th><th>$\tau_{r,c}$</th><th rowspan="2">$n_{2,l}$</th><th>$\omega_0$<br>$\sigma$<br>$\tau_{f,l}$</th><th rowspan="2">$n_{2,d}$</th><th>$\tau_{r,d}$</th></tr>
<tr><th>$\tau_{f,c}$</th><th></th><th>$\tau_{f,d}$</th></tr>
<tr><td rowspan="2">0.35</td><td rowspan="2">0.05</td><td>100±50</td><td rowspan="2">0.26</td><td>5±2<br>6±2</td><td rowspan="2">0.5</td><td>100±50</td></tr>
<tr><td>150±50</td><td>200±50</td><td>1800±300</td></tr>
</table>

# Calculation of effective $n_2$

$$n_{2,\text{eff}} = n_{2,\text{el}} + \frac{\int I(t)\left[\int_{-\infty}^{t} R(t-t')I_e(t')dt'\right]dt}{\int I^2(t)dt}$$

24 solvents studied to obtain response functions



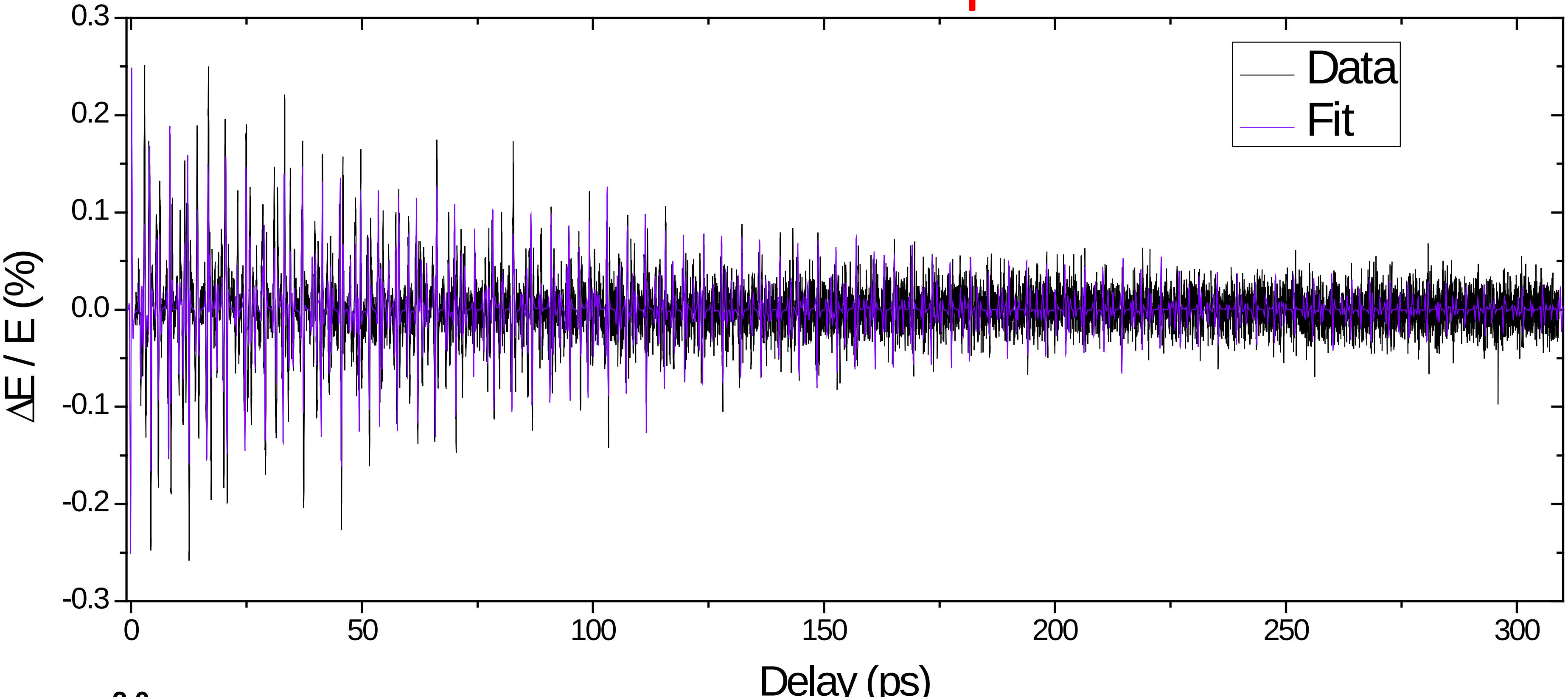

## Anisotropic Polarizability Tensor *

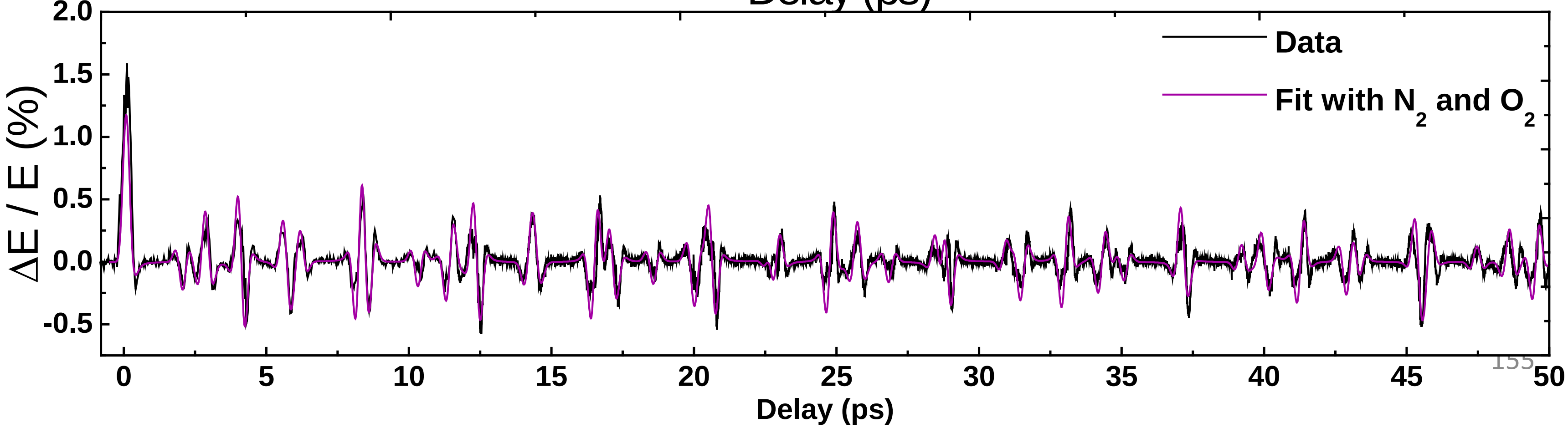
ratio of the maximum and minimum components
2.75 for $CS_2$,
2.3 for nitrobenzene,
2.1 for Toluene,
1.64 for DCM,
1.29 for cyclohexane,
1.26 for ethanol and
1.34 for methanol

Consistent

* **Kenneth J. Miller, *J. Am. Chem. Soc.* 1990, *112*, 8543-8551**

# Remove the sample in BD

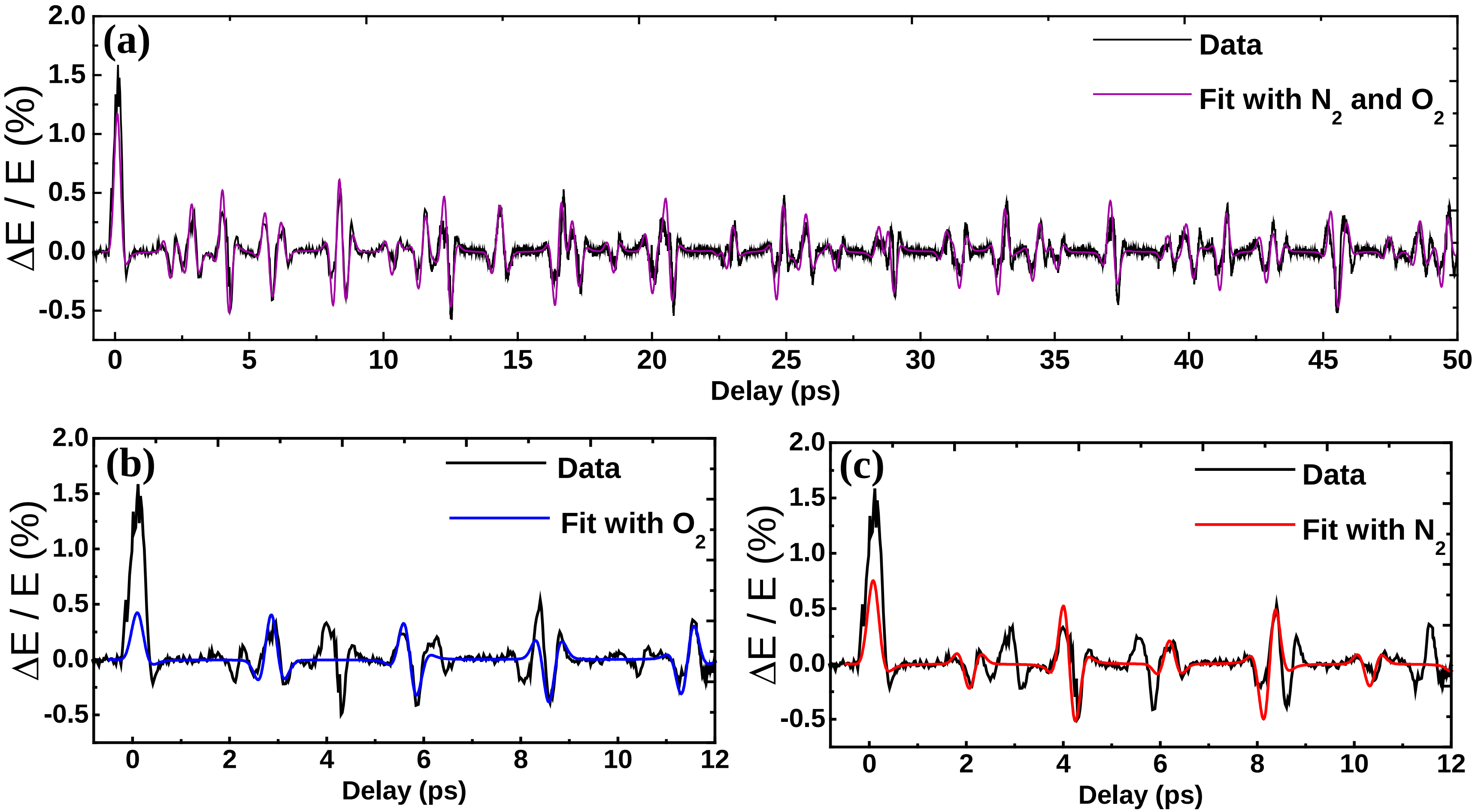


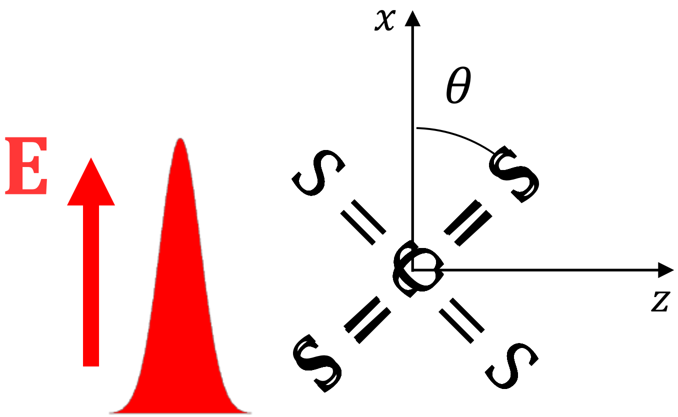
# Nonlinearity of Air

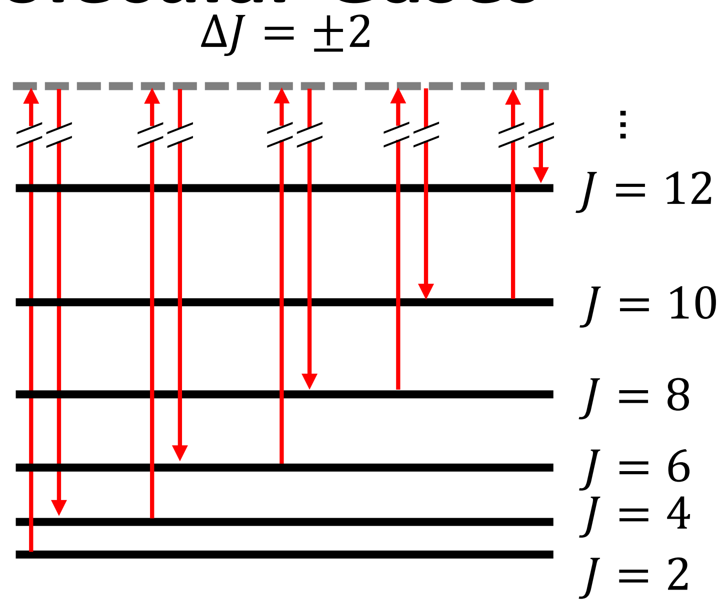
$$\Delta n(t) = \frac{N\Delta\alpha}{2\varepsilon_0 n_0}\left(\langle\cos^2\theta\rangle_t - \frac{1}{3}\right)$$

$$T = (2cB)^{-1}$$
$$B(O_2) = 1.46\ \text{cm}^{-1} = 181\ \mu\text{eV}$$
$$B(N_2) = 2.02\ \text{cm}^{-1} = 250\ \mu\text{eV}$$



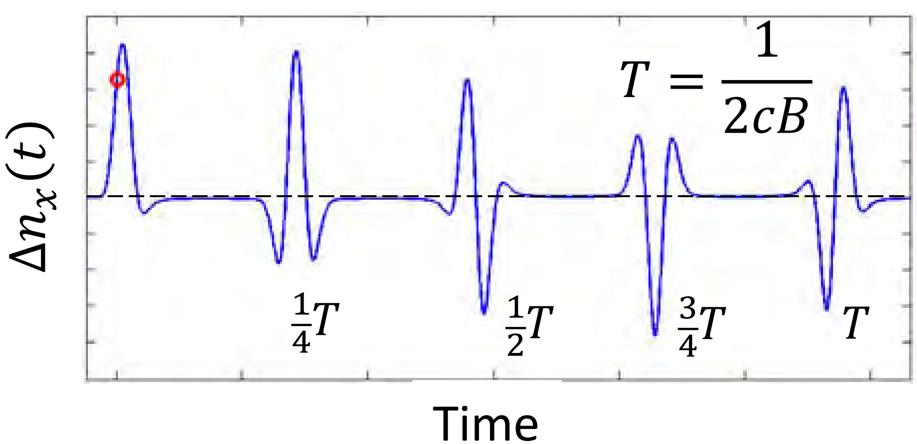
# Response of Dilute Molecular Gases

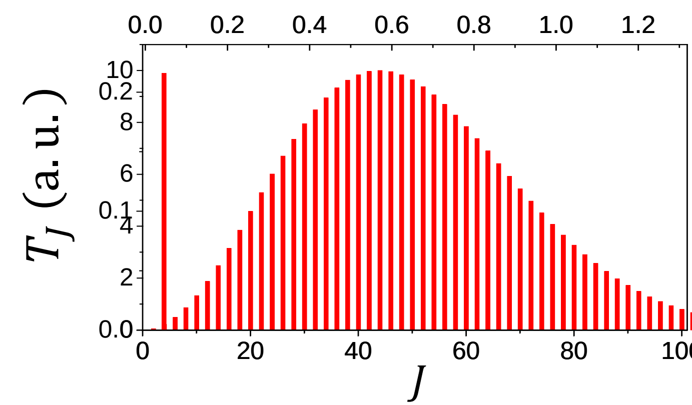


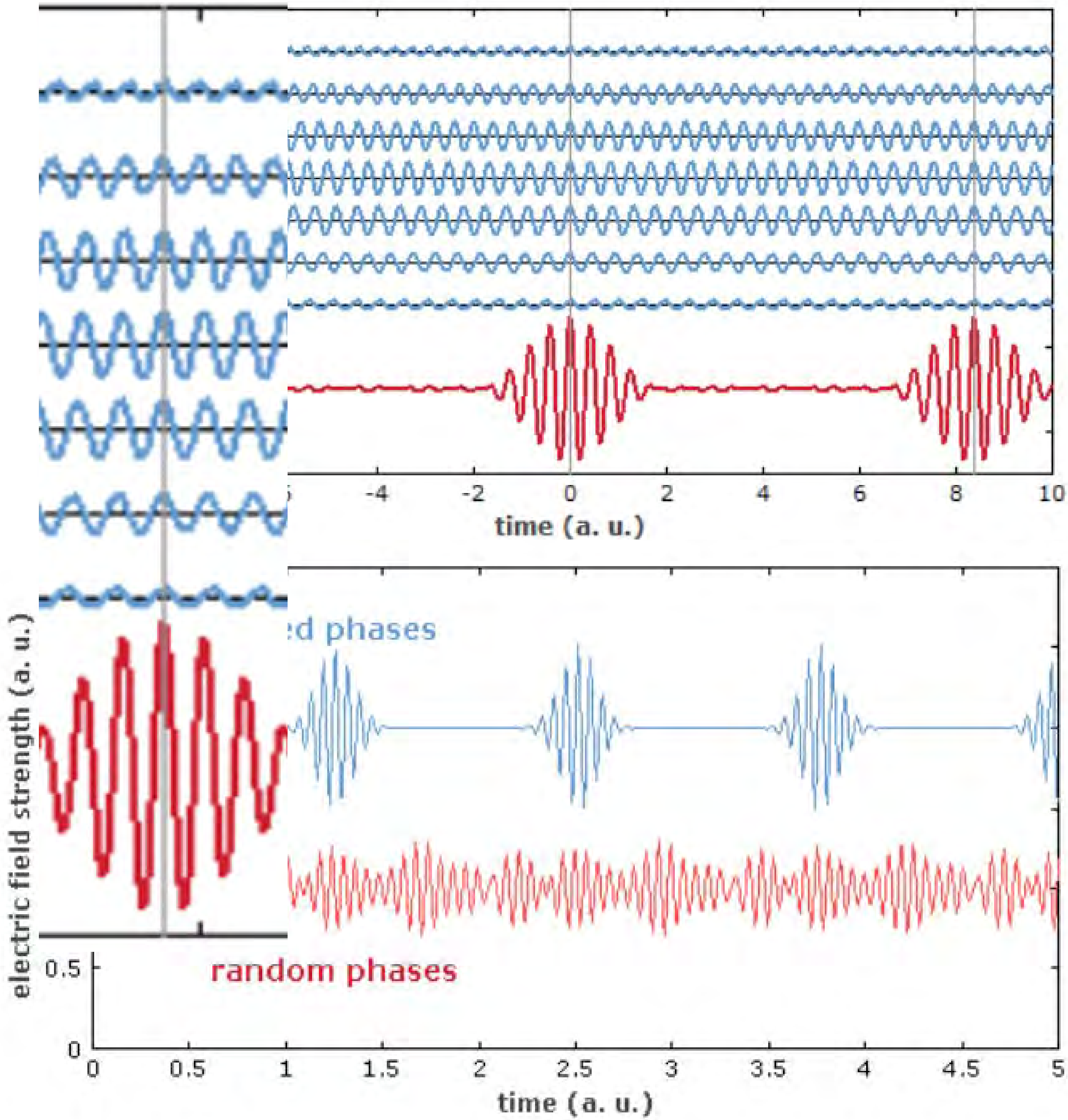




$$\Delta n(t) \propto \left( \langle \cos^2 \theta(t) \rangle - \frac{1}{3} \right)$$

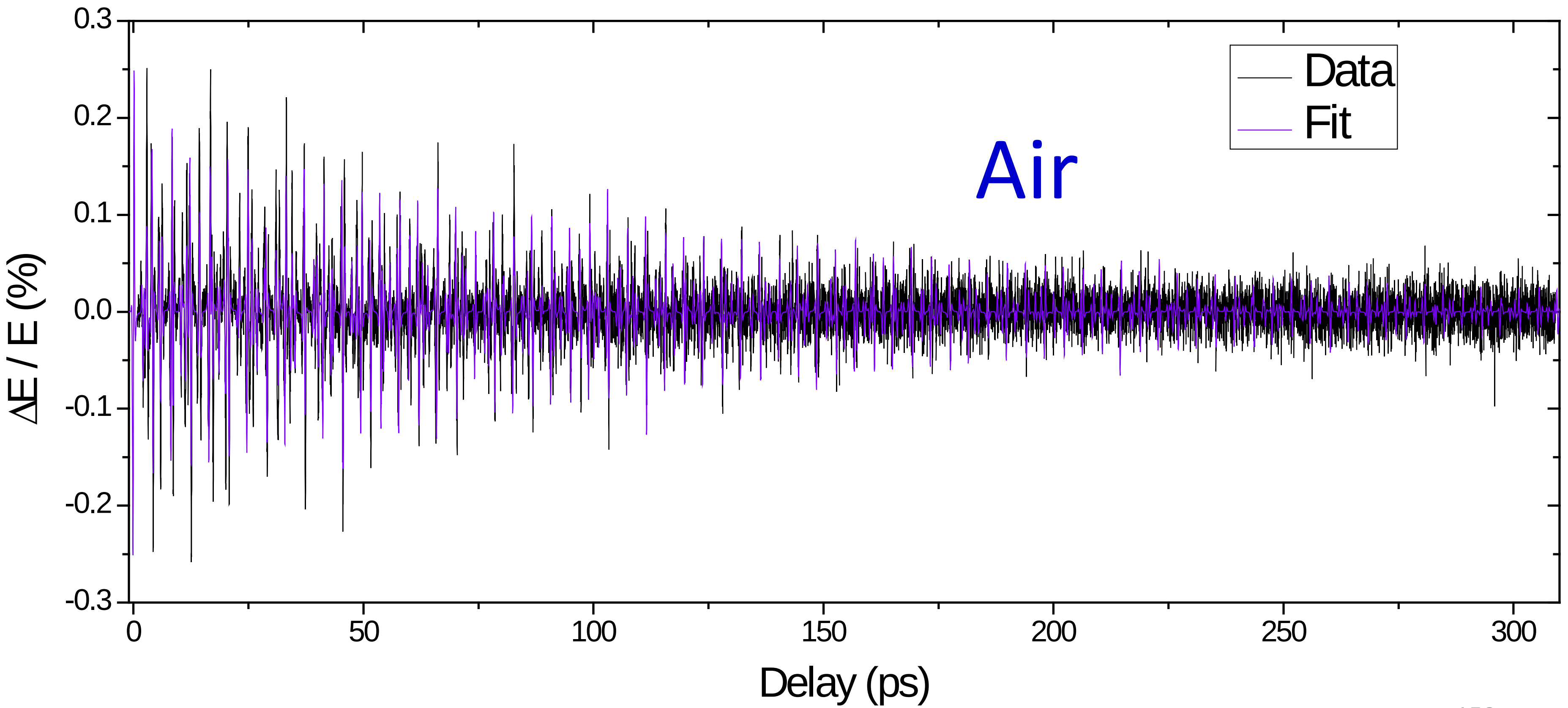
$$\nu_{J,J-2}\ (\mathrm{THz}) = 2cB \cdot (2J - 1)$$



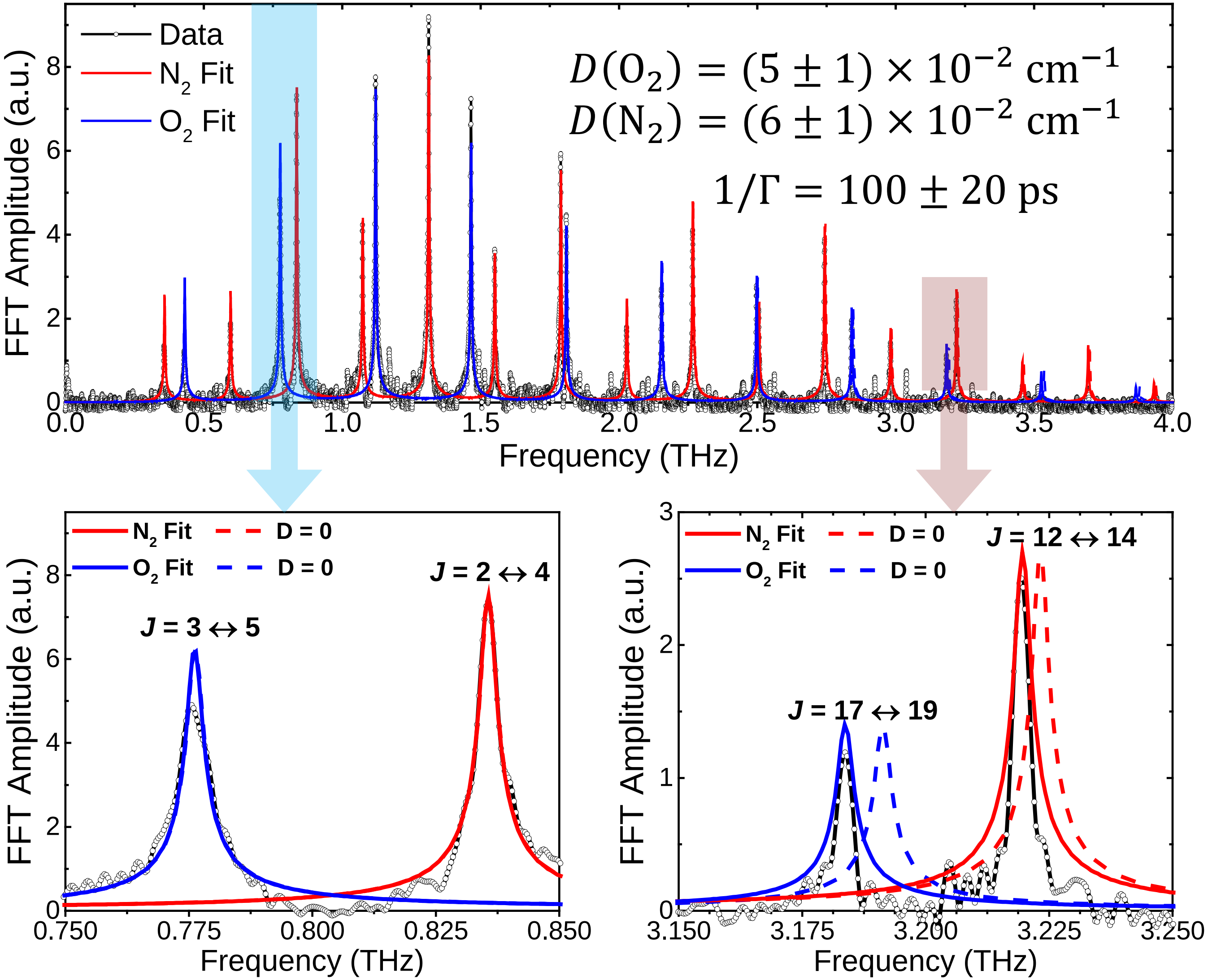




-4
-2
0
2
4
6
8
10
time (a. u.)
ed phases
random phases
electric field strength (a. u.)
0.5
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
time (a. u.)

# Take Fourier transform

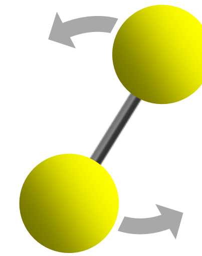


# Rotational Raman Spectrum



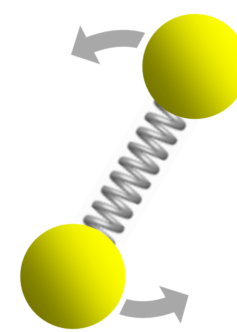

Rigid rotor

$$\nu_J = cB \cdot J(J+1)$$

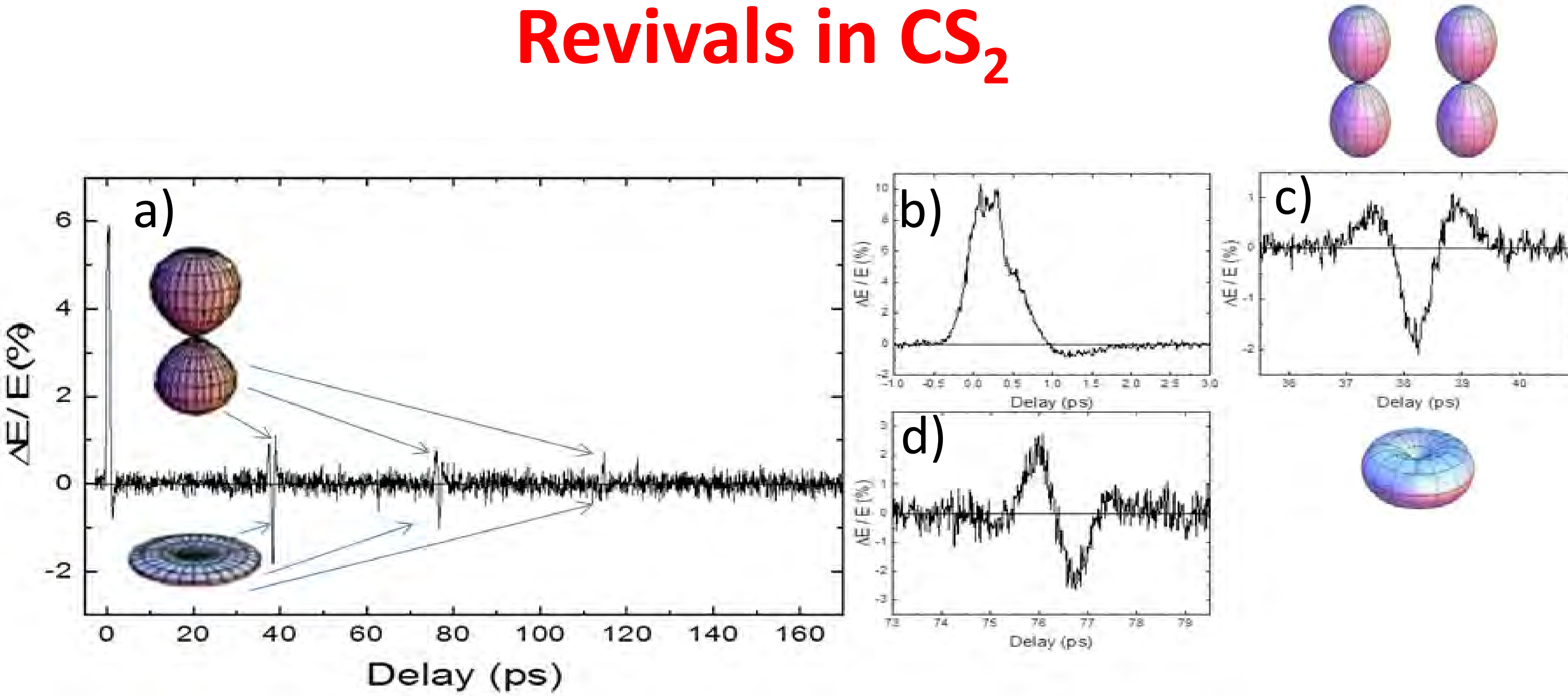


Centrifugal stretching

$$\nu_J = cB \cdot J(J+1) - cD \cdot J^2(J+1)^2$$



# Revivals in $CS_2$



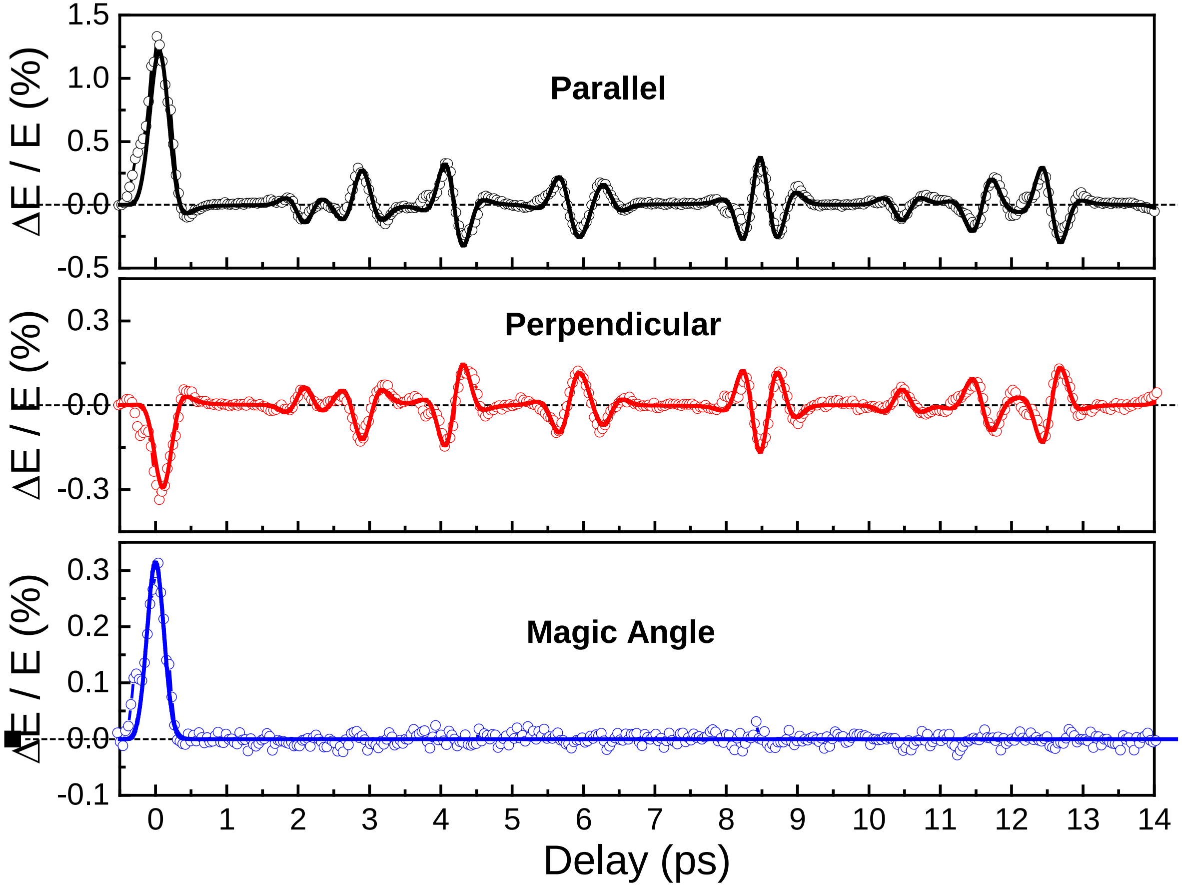

(a) beam deflection signal from $CS_2$.
(b) zero delay
(c) ¼ revival
(d) ½ revival

$E_e = 92\ \mu J$
$\lambda_e = 800\ nm$
$\lambda_p = 650\ nm$

# Eliminating Rotational Nonlinearity

$$\Delta n(t) = \underbrace{2n_2 I_e(t)}_{\text{Electronic}} + \underbrace{\Delta n_r(t)}_{\text{Rotational}}$$

$$\frac{\Delta n_e}{\Delta n_r} \propto \frac{n_2}{(\Delta\alpha)^2}$$




$$\Delta\alpha(\mathrm{N_2}) = 0.69\ \text{Å}^3$$
$$\Delta\alpha(\mathrm{O_2}) = 1.09\ \text{Å}^3$$

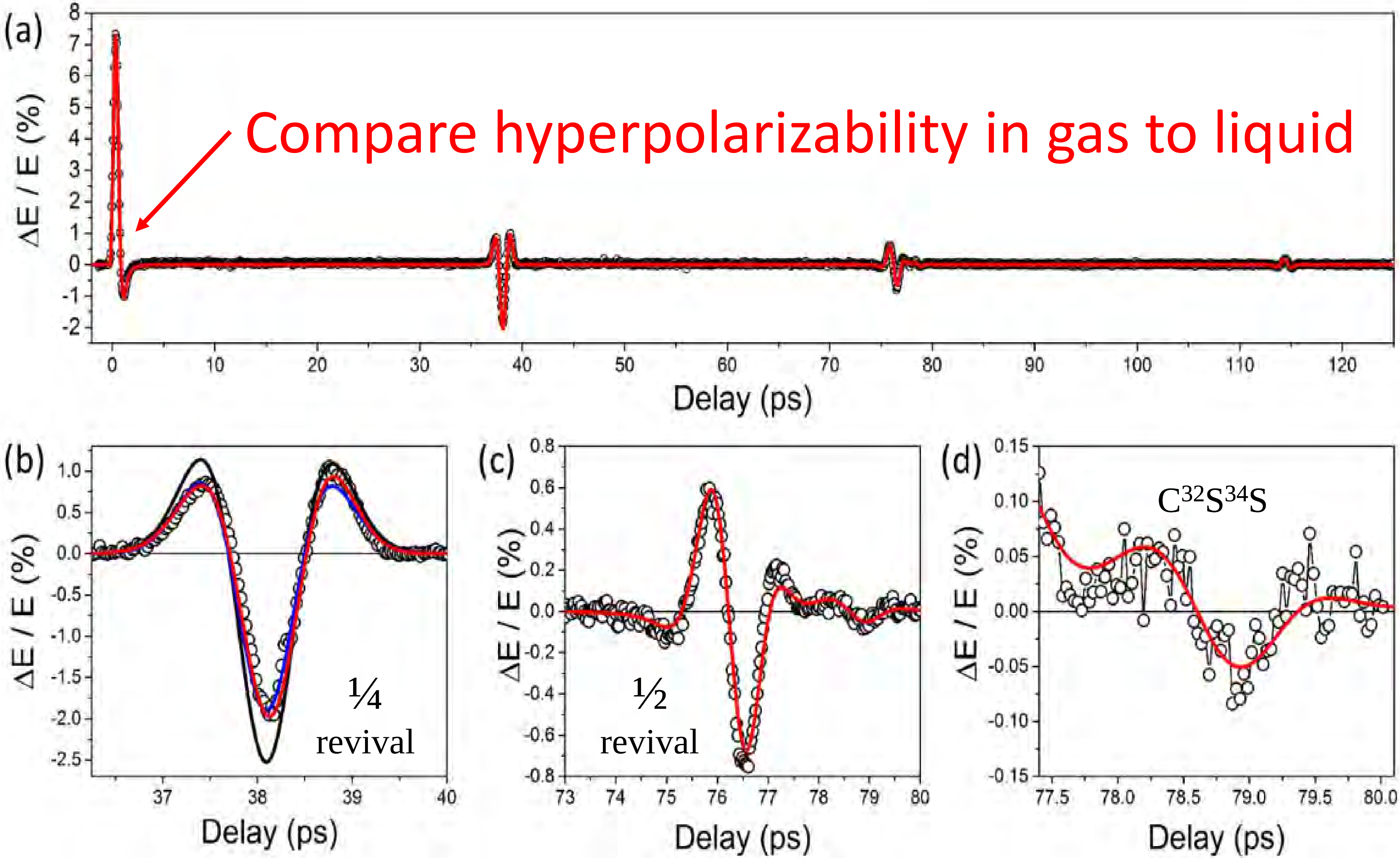
- Can unambiguously measure $n_2$

$$n_{2,el} = 1.0 \times 10^{-23}\ \mathrm{m^2/W}$$

- Agrees well with literature*

Bridge, et al., Proc. R. Soc. A, **295**, 334 (1966).
*Wahlstrand, et al., PRA, **85**, 043820 (2012).
*Liu and Chin, Opt. Express, **13**, 5750, (2005).

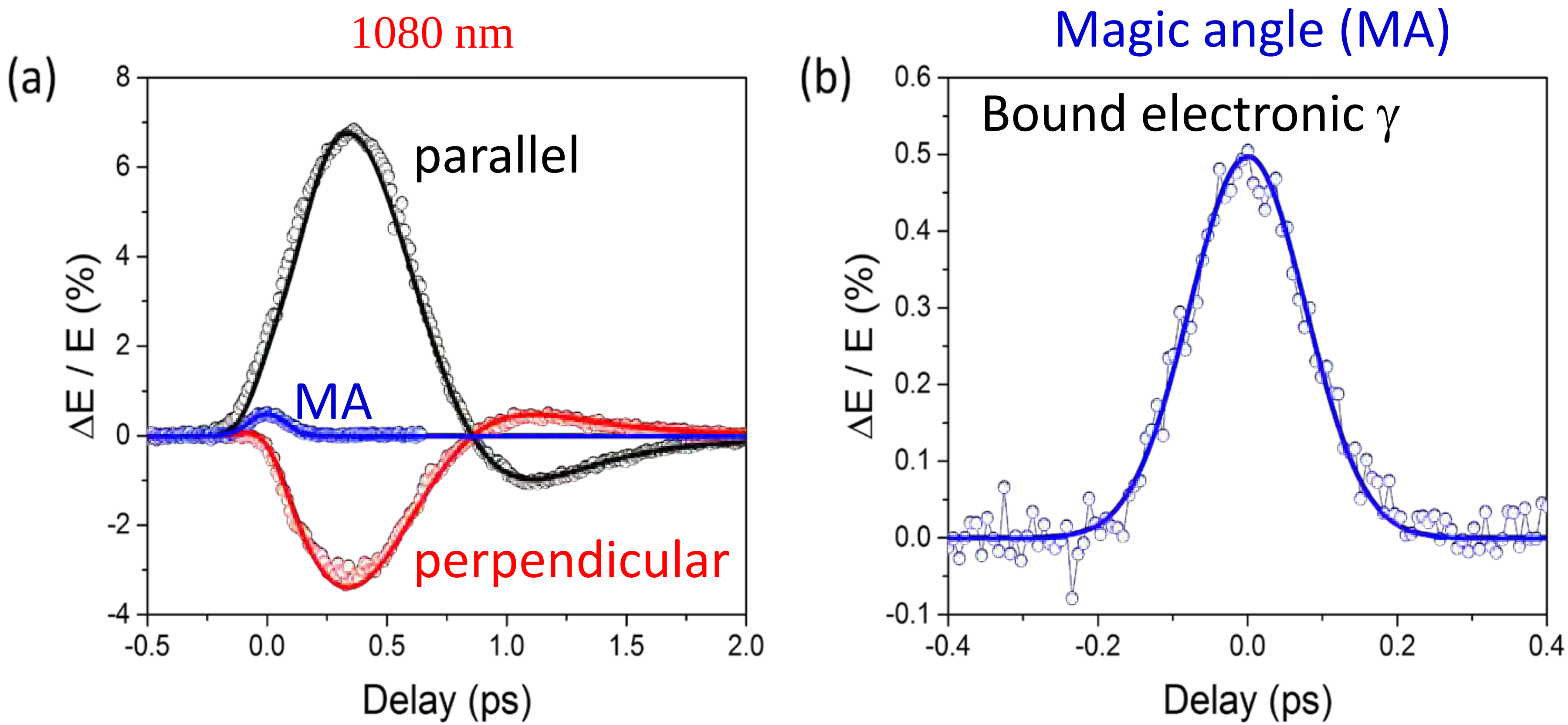
# $CS_2$ gas




black curve includes only the vibrational ground state of $C^{32}S_2$

blue curve includes the 1st excited vibrational state and isotopoloque $C^{32}S^{34}S$

# BD of $CS_2$ gas near 0 delay



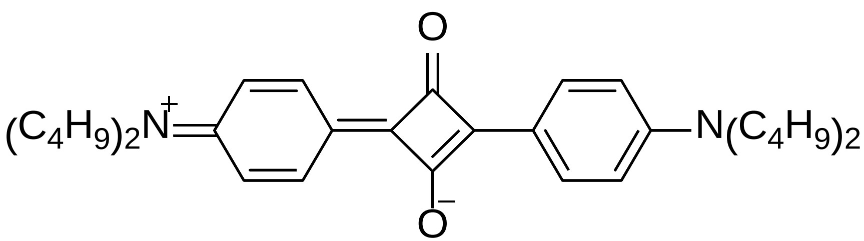

$\gamma$ ($CS_2$ gas) = $(1.9 \pm 0.4) \times 10^{-61}$ $C^4m^4/J^3$ ($(1.5 \pm 0.4) \times 10^{-36}$ esu).

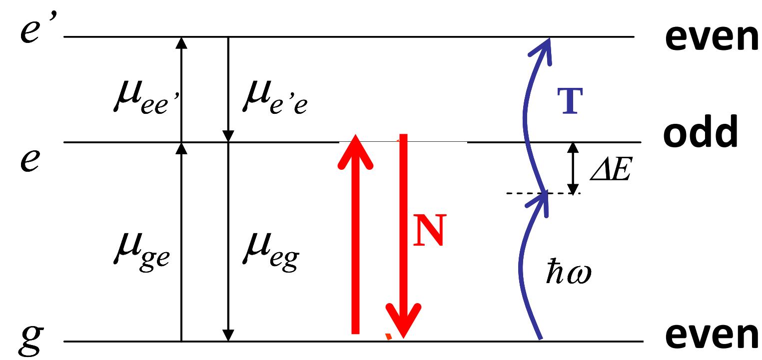
In liquid phase $f^{(3)} = 5.35$

$\gamma$ ($CS_2$ liquid) = $(1.9 \pm 0.5) \times 10^{-61}$ $C^4m^4/J^3$ ($(1.8 \pm 0.4) \times 10^{-36}$ esu).

To Simplify the SOS model

$\Delta\mu=0$




$$\chi^{(3)}_{xxxx} = \frac{N}{3\varepsilon_0}\left\{ \frac{\mu^x_{ge}\bar{\mu}^x_{ee'}\bar{\mu}^x_{e'e}\mu^x_{eg}}{(\Omega_{eg}-\hbar\omega)(\Omega_{e'g}-2\hbar\omega)(\Omega_{eg}-\hbar\omega)} + \frac{\mu^x_{ge}\bar{\mu}^x_{ee'}\bar{\mu}^x_{e'e}\mu^x_{eg}}{(\Omega^*_{eg}-\hbar\omega)(\Omega_{e'g}-2\hbar\omega)(\Omega_{eg}-\hbar\omega)} - \frac{\mu^x_{ge}\mu^x_{eg}\mu^x_{ge}\mu^x_{eg}}{(\Omega_{eg}-\hbar\omega)(\Omega_{eg}-\hbar\omega)(\Omega_{eg}-\hbar\omega)} - \frac{\mu^x_{ge}\mu^x_{eg}\mu^x_{ge}\mu^x_{eg}}{(\Omega_{eg}-\hbar\omega)(\Omega^*_{eg}-\hbar\omega)(\Omega_{eg}-\hbar\omega)} \right\}$$

T-Terms (first two terms)

N-Terms (last two terms)

## Essential State Model

- Ground state, 1PA state, and 2PA Final States.
- $\mu_{ge}$ and $\mu_{ee'}$ allowed, $\mu_{ge'}=0$

**Two-Photon (T) Terms *v.s.* Negative (N) Term.**

**Kuzyk, M. G.; Dirk, C. W. *Phys. Rev. A* 1990, *41*, 5098.**

# Cascaded Second-Order Nonlinearities

## Second-Harmonic Generation, SHG

Ignore the SH and just look at the fundamental.

SHG now looks like loss - 2 photons of the fundamental make 1 photon of the SH.

In 2PA, 2 photons of the fundamental makes heat.

It's difficult to tell the difference for low conversion efficiency.

Autocorrelation function the same

And, by causality there must be an associated phase change.

# Cascaded Second Order nonlinearity

$$\frac{\partial E}{\partial z} = i\frac{\mu_0 c\omega}{2n}\mathcal{P}^{NL} e^{i(k'-k)z}$$

SHG

$$\frac{\partial \mathcal{E}_2}{\partial z} = i\frac{\omega}{n_2 c} d_{eff}\mathcal{E}_1^2 e^{i\Delta kz}$$

$$\frac{\partial \mathcal{E}_1}{\partial z} = i\frac{\omega}{n_1 c} d_{eff}\mathcal{E}_1^* \mathcal{E}_2 e^{-i\Delta kz}$$

On phase match – low depletion

$$\mathcal{E}_2 = i\frac{\omega}{n_2 c} d_{eff}\mathcal{E}_1^2 z$$

For $\chi^{(3)}$

$$\frac{\partial \mathcal{E}_\omega}{\partial z} = i\frac{\omega}{2n_0 c}\chi^{(3)}\mathcal{E}_\omega \left|\mathcal{E}_\omega\right|^2$$

$$\frac{\partial \mathcal{E}_1}{\partial z} = i\frac{\omega}{n_1 c} d_{eff}\mathcal{E}_1^*\left(i\frac{\omega}{n_2 c} d_{eff}\mathcal{E}_1^2 z\right) \Rightarrow \frac{\partial \mathcal{E}_1}{\partial z} = -\frac{\omega^2}{n_1 n_2 c^2}\left(d_{eff}\right)\mathcal{E}_1^*\mathcal{E}_1^2 z$$

# Now include off phase match

SHG Equations

A) $$\frac{dE_{2\omega}}{dz} = i\frac{\omega}{n_{2\omega}c} d_{eff} E_\omega^2 e^{-i\Delta kz}$$

B) $$\frac{dE_\omega}{dz} = i\frac{\omega}{n_\omega c} d_{eff} E_{2\omega} E_\omega^* e^{i\Delta kz}$$

For $\chi^{(3)}$

$$\frac{\partial \mathcal{E}_\omega}{\partial z} = i\frac{\omega}{2n_0 c}\chi^{(3)} \mathcal{E}_\omega \left|\mathcal{E}_\omega\right|^2$$

in the small depletion limit

$$E_{2\omega}(z) = i\frac{\omega}{n_{2\omega}c} d_{eff} e^{-i\Delta kz/2} \mathrm{sinc}(\Delta kz/2)\, z\, E_\omega^2$$

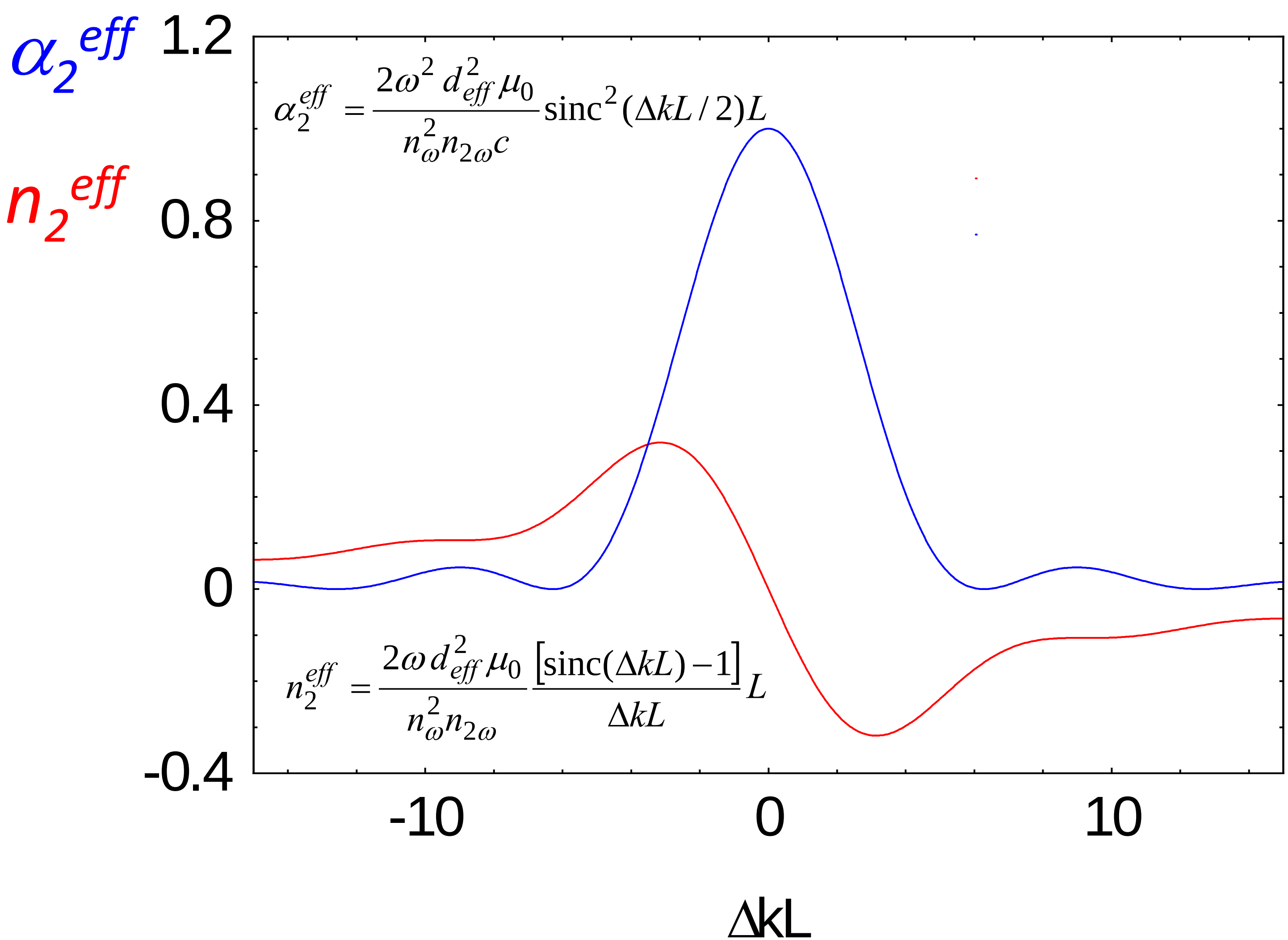
plugging this into B) gives

$$\frac{dE_\omega}{dz} = -\frac{\omega^2 d_{eff}^2}{n_\omega n_{2\omega} c^2} e^{i\Delta kz/2} \mathrm{sinc}(\Delta kz/2)\, z \left|E_\omega\right|^2 E_\omega$$

$$\frac{dE_\omega}{dz} = i\frac{\omega^2 d_{eff}^2}{n_\omega n_{2\omega} c^2} \mathrm{sinc}(\Delta kz/2)\left[-\sin(\Delta kz/2) + i\cos(\Delta kz/2)\right] z \left|E_\omega\right|^2 E_\omega$$

# Effective 2PA Coefficient and Phase Shift

$\chi^2 : \chi^2$




Note what appears like Kramers-Kronig relations

# Cascading in KTP

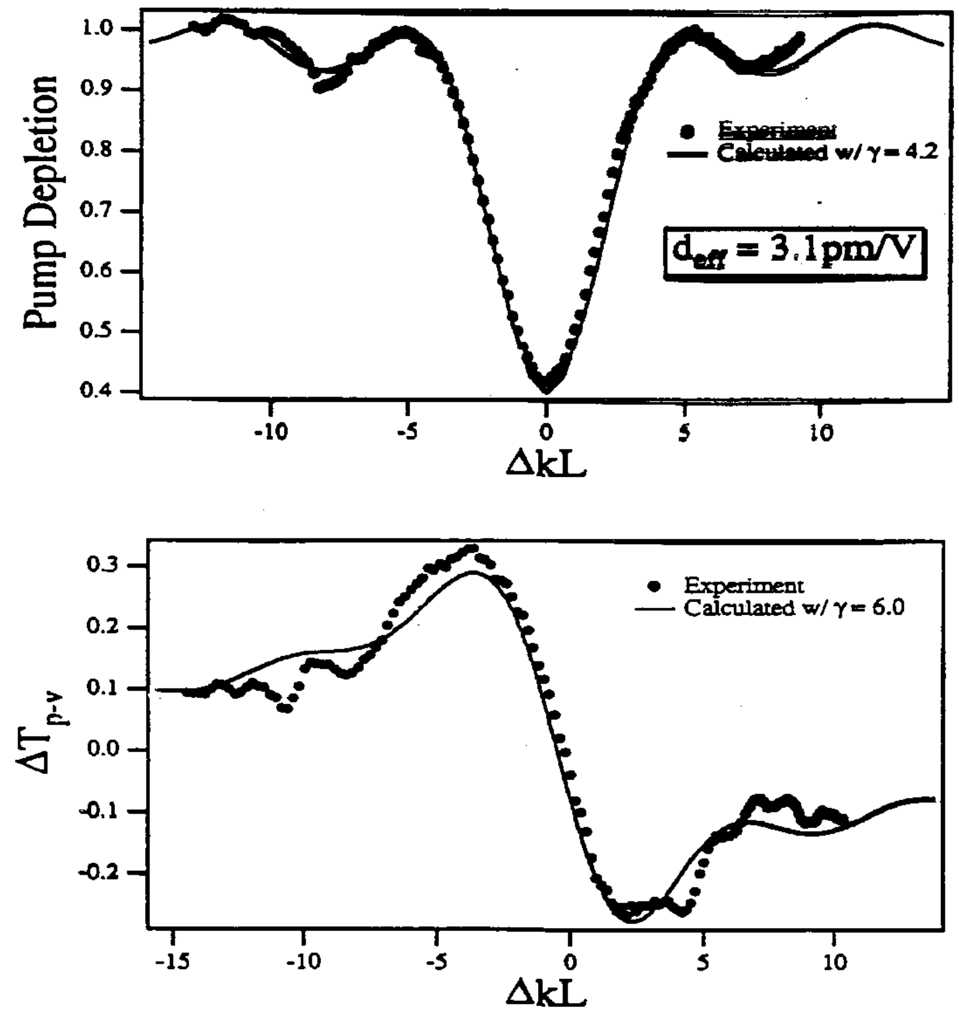
Gives a measure of $d_{eff}$

Also note the relation between the phase shift from $\Delta T_{p\text{-}v}$ and the loss.

"Self-Focusing and Defocusing by Cascaded Second Order Effects in KTP", R.J. DeSalvo, D.J. Hagan, M. Sheik-Bahae, G. Stegeman, H. Vanherzeele and E.W. Van Stryland, Opt. Lett. 17, 28 (1991).

## KTP

$\lambda = 1064\text{nm},\ \tau_p = 30\text{psec},\ L = 1\text{ mm}$




at $\Delta kL = +/-3$; $n_2 = -/+2 \times 10^{-14}\ \text{cm}^2/\text{W}$

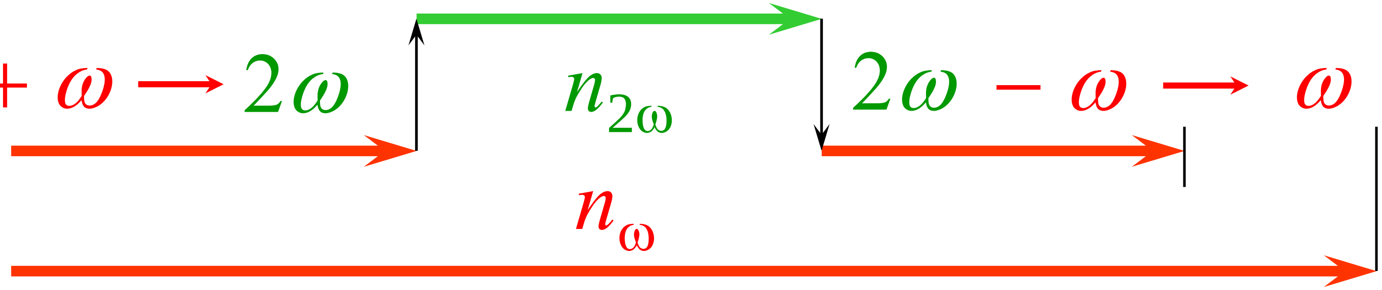
# Cascading Processes

Up-Conversion

Down-Conversion

$\omega + \omega \rightarrow 2\omega$

$2\omega - \omega \rightarrow \omega$




$$n_{2\omega} > n_{\omega}$$

Effects: $[\chi^{(2)}]^2$

Symbol: $\chi^{(2)}:\chi^{(2)}$

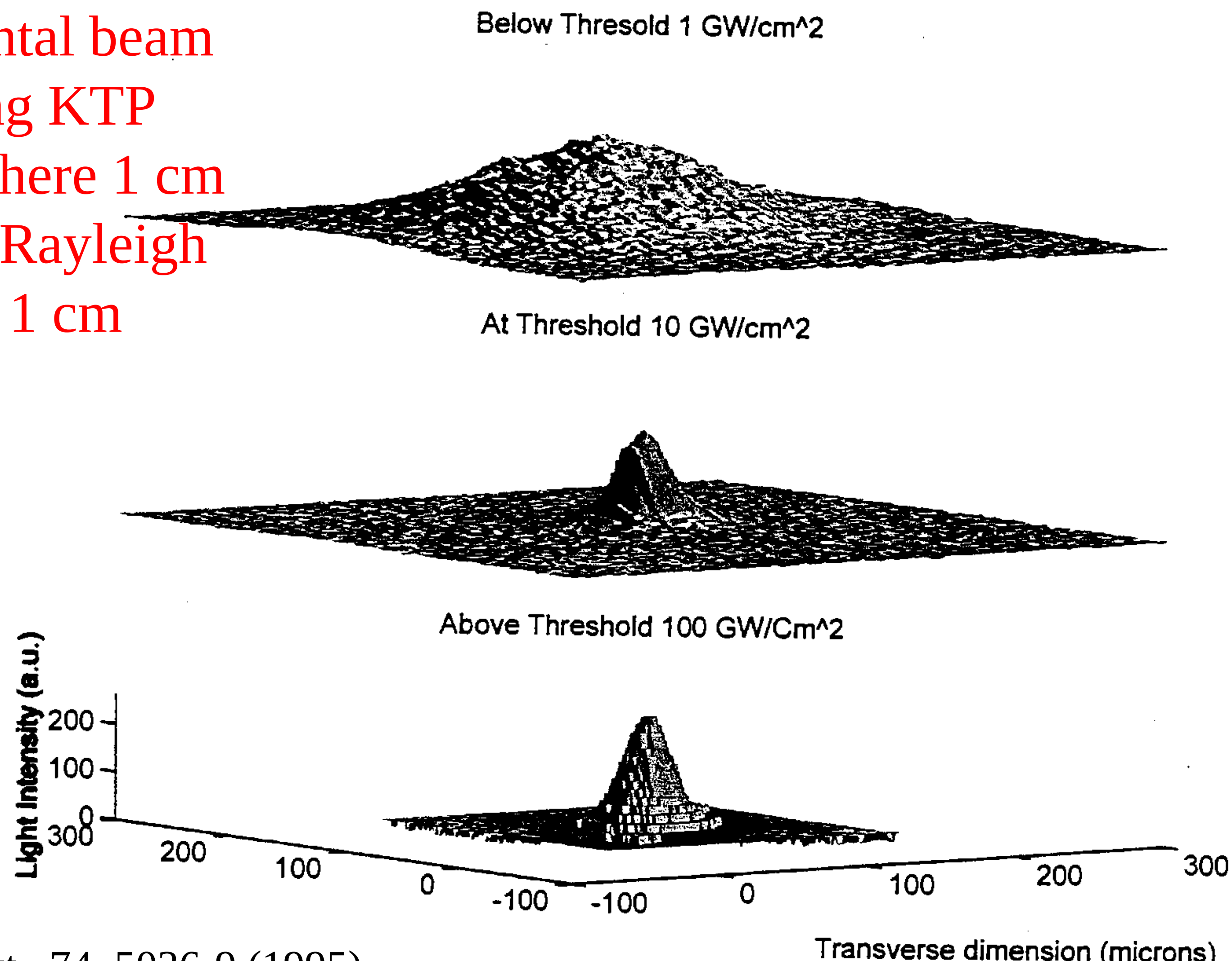
# "Index of Refraction" Changes

Here this is no "real" index of refraction change, but there is a phase shift, i.e. another beam is unaffected in amplitude or phase unless coupled by $\chi^{(2)}$ and energy transfer occurs.

d Photonics

# Spatial Solitary Waves

Simply shine a bright fundamental beam into a long KTP crystal – here 1 cm With the Rayleigh range << 1 cm




Phy. Rev. Lett., 74, 5036-9 (1995)
"Observation of Two-Dimensional Spatial Solitary Waves in a Quadratic Medium", W.E. Torruellas, Z. Wang, D.J. Hagan, E.W. Van Stryland, G.I. Stegeman, L. Torner and C. Menyuk

# Third-order nonlinearities

$\chi^{(1)}:\chi^{(1)}$ ESA

$\chi^{(1)}:\chi^{(1)}$ Saturation

"$\chi^{(1)}:\chi^{(1)}$ reorientation"

$\chi^{(2)}:\chi^{(2)}$ Cascading

$\chi^{(3)}$ 2PA

All give third-order (effective $\chi^{(3)}$) nonlinear responses

# Different nonlinearities mimic each other

$$\frac{dI}{dz} = -\alpha I - \sigma_a N I \qquad \frac{dN}{dt} = \frac{\alpha I}{\hbar\omega}$$

$$\frac{dF}{dz} = -\alpha F - \frac{N_g \sigma_g \sigma_{ex}}{2\hbar\omega} F^2$$ i.e. $\chi^{(1)}:\chi^{(1)}$

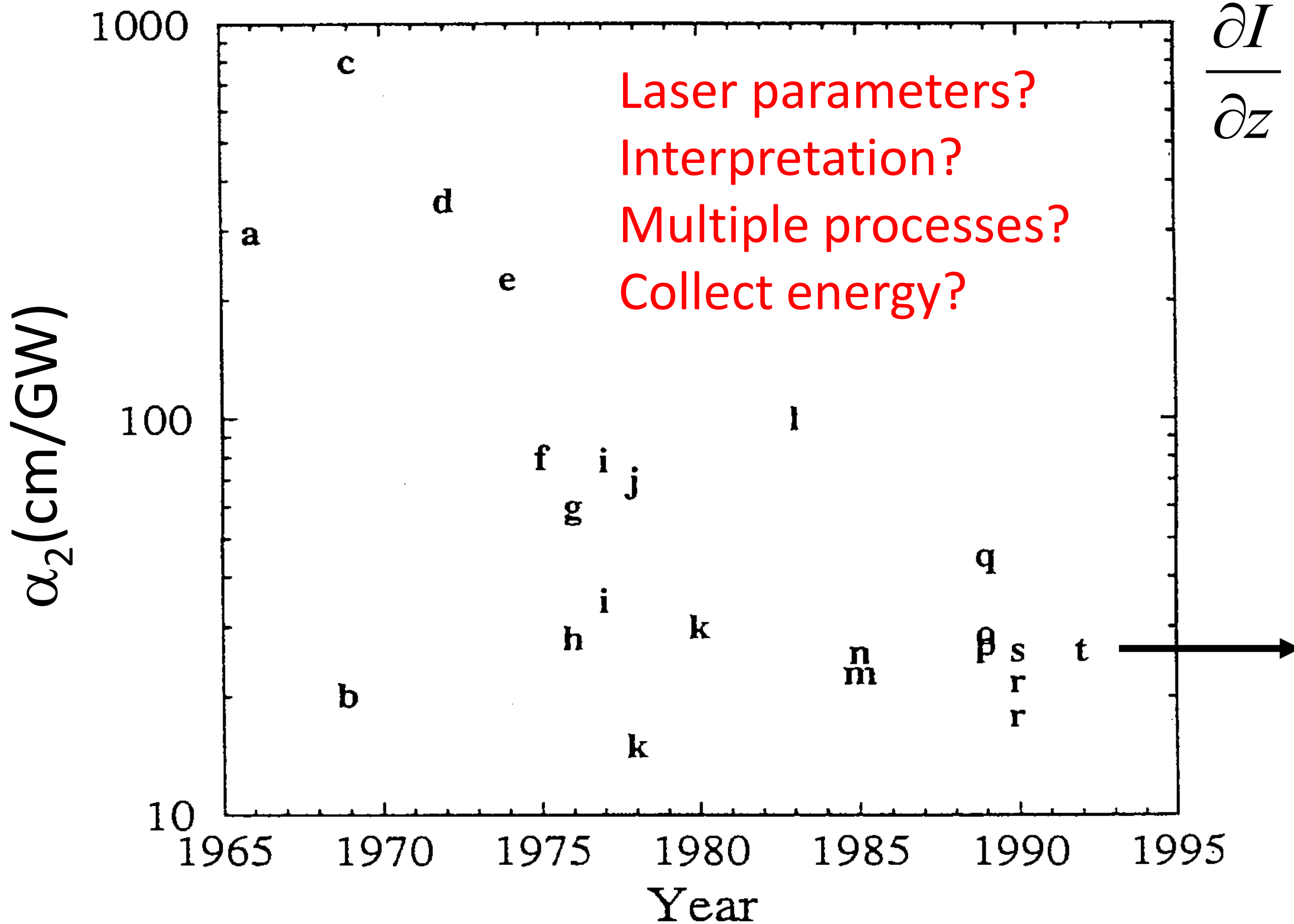
2PA $$\frac{dI}{dz} = -\alpha I - \beta I^2$$ i.e. $\chi^{(3)}$

2PA ESA $$\frac{dI}{dz} = -\beta I^2 - \sigma N I$$ i.e. $\chi^{(3)}:\chi^{(1)}$

And cascaded $\chi^{(2)}:\chi^{(2)}$ often looks like $\chi^{(3)}$

# Materials Characterization

## Reported value of 2PA coefficient of GaAs at 1μm vs. year



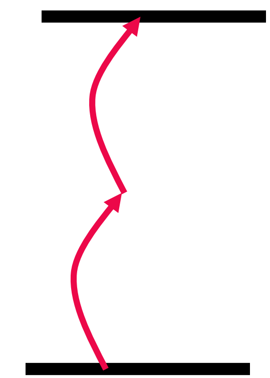

Laser parameters?

Interpretation?

Multiple processes?

Collect energy?

$$\frac{\partial I}{\partial z} = -\alpha_2 I^2$$



Opt. Lett. 10, 490 (1985)

# $\chi^{(3)}$ susceptibility

Wouldn't it be nice if nonlinear materials parameters were material constants?

It should be a material constant like n, dn/dT or $C_p$.

If $\chi^{(3)}$ is used for cumulative nonlinearities, its value depends on the pulsewidth, e.g. even for $CS_2$ $n_2$ depends on pulsewidth.

I conclude that $\chi^{(3)}$ is overused and can often be replaced by more physical quantities that are material constants, e.g. use $\chi^{(1)}:\chi^{(1)}$ etc.

# Conclusion

Nonlinear Spectroscopy Comes of Age

NLO Spectrometer nearly here

# Thank you

ewvs@creol.ucf.edu

**Acknowledgements:**

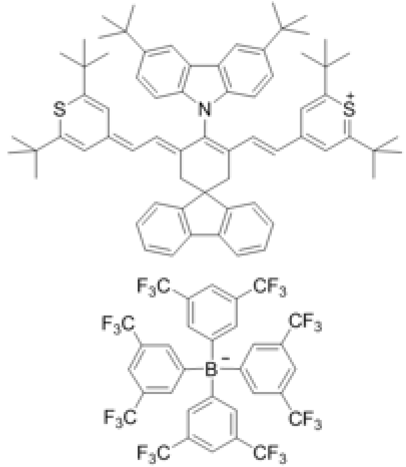
Collaborators:

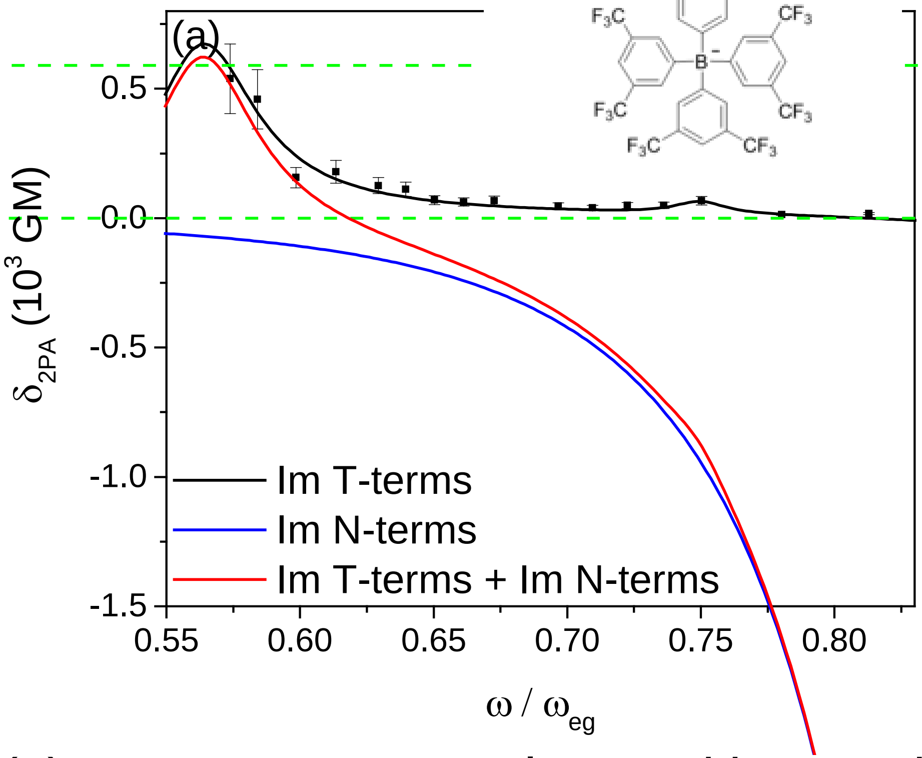
- Groups of Marder, Perry and Bredas (Georgia Tech)
- Olga Przhonska (National Acad. of Sciences, Ukraine)
- Group of Alex Jen (U. of Washington)

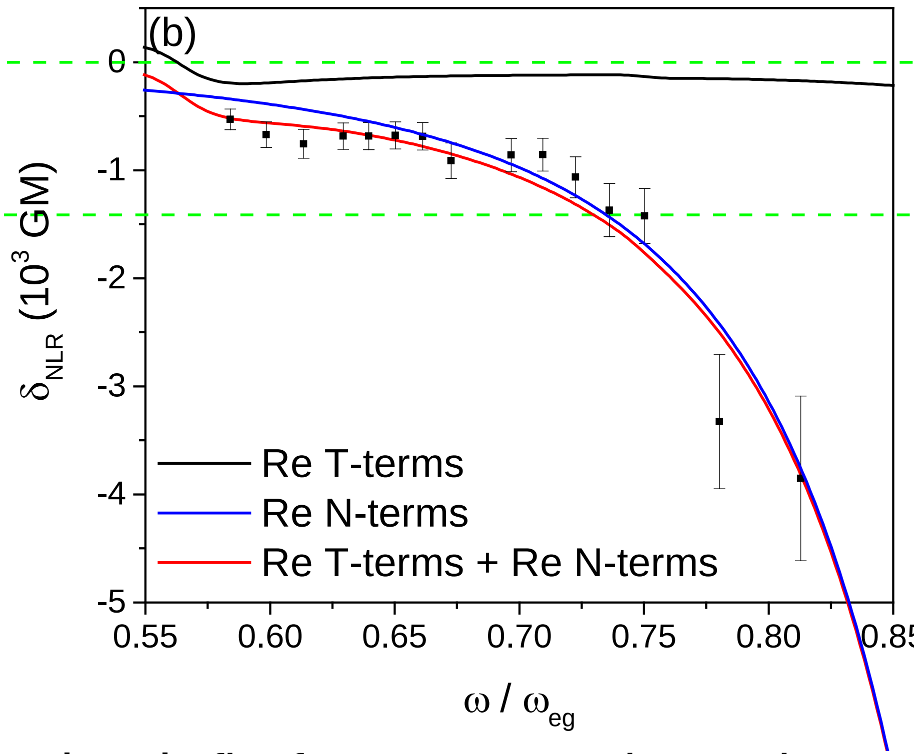
Funding: NSF, AFOSR – COMAS MURI, ARL

**www.creol.ucf.edu**

# YZ-V-69 Marder group




(a) 2PA spectrum along with quasi 3-level fit for YZ-V-69 in carbon tetrachloride.

*(b)* $n_2$ spectrum and fits.

solid black line, blue line, and red line are T-terms, N-terms, and their sum