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NONLINEAR OPTICAL PROPERTIES OF MONOLAYER FILMS DEPOSITED ON IR TRANSPARENT SUBSTRATES

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1. Introduction to nonlinear optics
2. Principal effects of nonlinear optics
3. Experimental set-up for realization of nonlinear optics
4. Nonlinear optics of nanomaterials
Introduction to nonlinear optics

Polarization induced by a laser field

\[ P = \varepsilon_0 (\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \cdots) \]

- Linear response
- Nonlinear response

Second harmonic generation

\[ P^{NL} = 2\varepsilon_0 dE^2 \]
The second-harmonic beam was very weak because the process was not phase-matched.
First demonstration of second-harmonic generation

The actual published results...

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.
Introduction to nonlinear optics

Generate field = solution of a wave equation

\[ \nabla^2 E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{1}{\varepsilon c^2} \frac{\partial^2 P^{NL}}{\partial t^2} \]

Fundamental

\[ E_\omega(z, t) = \frac{1}{2} E_1(z, t) e^{i\omega t - ik_\omega z} + cc \]

\[ k_\omega = \frac{n_\omega \omega}{c} \]

Harmonic generation

\[ P_{2\omega}^{NL}(z, t) = \frac{1}{2} P_2(z, t) e^{2i\omega t - 2ik_{2\omega} z} + cc \]

Different phase velocity

2nd harmonic

\[ E_{2\omega}(z, t) = \frac{1}{2} E_2(z, t) e^{2i\omega t - ik_{2\omega} z} + cc \]
Out of phase

\[ e^{2i\omega t - ik_{2\omega}z} \]

\[ e^{2i\omega t - ik_{2\omega}z} \]

Out of phase

\[ L_{coh} \Delta k = \pi \]

\[ L_{coh} = \frac{\lambda}{4\Delta n} \]

Coherence length
The lengths of the problem

\[ \eta \propto L^2 \]

\[ \eta \propto L^2 e^{-L/L_{abs}} \]

\[ \eta \propto \sin^2 \left( \frac{\pi L}{L_{coh}} \right) = L^2 F_q (L) \]
Phase-matching second-harmonic generation

\[ n(2\omega) = n(\omega) \]

Using birefringence

\[ n_o(2\omega) = n_e(\omega) \]
\[ \eta \propto L^2 \]

\[ \eta \propto \sin^2\left(\frac{\pi L}{L_{coh}}\right) \]
Dependence of SHG intensity on length

The SHG intensity is sharply maximized if $\Delta k = 0$. 

Large $\Delta k$  

Small $\Delta k$
Wave vectors

\[ \omega_1 + \omega_2 = \omega_3 \]

\[ \vec{k}_1 + \vec{k}_2 = \vec{k}_3 \]
References

- **Fundamentals of Photonics**
  - Ch. 18 and 19

- **Nonlinear Optics**
  - R. W. Boyd

- **Photonics: Optical Electronics in Modern Communications**
  - A. Yariv and P. Yeh
  - Ch. 8, Ch. 9 and Ch. 14
Atomic origin of optical nonlinearity

Induced dipole moment \( P = N \cdot e \cdot x \) \( D = \varepsilon_0 E + P \)

- Simple harmonic oscillator model (linear)

\[
\frac{d^2x}{dt^2} + 2\gamma \frac{dx}{dt} + \omega_0^2 x = \frac{-eE(t)}{m}
\]

Linear polarization

- Linear polarization: parabolic potential
- 2\(^\text{nd}\) order nonlinearity: Pockels media
- 3\(^\text{rd}\) order nonlinearity: Kerr media

Electronic charge

Restoring force

Atomic nucleus

2\(^\text{nd}\) order nonlinearity is absent in crystals with centro-symmetry!
Nonlinear polarization

- **Linear medium: low field intensity**

  \[ D = \varepsilon_0 E + P \quad P = \varepsilon_0 \chi \cdot E \quad \Rightarrow \quad D = \varepsilon \cdot E = \varepsilon_r \varepsilon_0 E \quad \varepsilon_r = 1 + \chi \]

  Linear polarization

- **Nonlinear medium: high field intensity**

  \[ D = \varepsilon_0 E + P \quad P = \varepsilon_0 \chi \cdot E + \chi^{(2)} \cdot E^2 + \chi^{(3)} \cdot E^3 + ... = P_L + P_{NL} \]

  Nonlinear polarization

  \[ P_i = \varepsilon_0 \chi_{ij} \cdot E_j + 2D_{ijk} \cdot E_j E_k + 4\chi_{ijkl} E_j E_k E_l + ... = P_L + P_{NL} \]

  Linear susceptibility tensor  2nd order nonlinear susceptibility tensor  3rd order nonlinear susceptibility tensor

  **Summation over repeated indices**
Nonlinear optical effects

- **2nd order optical nonlinear effects**
  - Pockels/electro-optic effect
  - Second harmonic generation (SHG)
  - Sum/difference frequency generation (SFG/DFG)
  - Optical parametric amplification/oscillation (OPA/OPO)

- **3rd order optical nonlinear effects**
  - Optical Kerr effect/quadratic Pockels effect
  - Third harmonic generation (THG)
  - Four wave mixing (FWM)
  - Two photon absorption (TPA)
  - Stimulated Raman/Brillion scattering (SRS/SBS)
General methodology for nonlinear optics

- Write the expression of electric field in medium
  - e.g. in an optical waveguide
    \[
    \overline{E} = \text{Re}[E_0 \cdot U(x, y) \exp(ik \cdot z - i\omega \cdot t)] = E_0 \cdot U(x, y) \exp(ik \cdot z - i\omega \cdot t) + c.c.
    \]
  
- Calculate the linear and nonlinear polarization
  \[
  P = \varepsilon_0 \chi \cdot E + \chi^{(2)} \cdot E^2 + \chi^{(3)} \cdot E^3 + \ldots = P_L + P_{NL}
  \]

- Substitute in to the electromagnetic wave equation
  \[
  \nabla^2 \overline{E} = \mu_0 \frac{\partial^2}{\partial t^2} (\varepsilon_0 \overline{E} + \overline{P}) = \mu_0 \varepsilon_0 \frac{\partial^2 \overline{E}}{\partial t^2} + \mu_0 \frac{\partial^2 P_{NL}}{\partial t^2}
  \]

- Focus on the terms with relevant frequencies
  Source term
Pockels effect / Electro-optic (EO) effect

- 2\textsuperscript{nd} order optical nonlinearity
- Externally applied electric field modifies the optical properties of materials
  - Refractive index, birefringence, etc.

Total electric field: \[ \overline{E} = E_{\text{light}} + E_{\text{ex}} = \text{Re}[E_0 \cdot \exp(i \omega \cdot t)] + E_{\text{ex}} \]

\[ P_{NL} = \chi^{(2)} \cdot E^2 = \chi^{(2)} \{ \text{Re}[E_0^2 \cdot \exp(i 2 \omega \cdot t)] + 2E_{\text{ex}} \text{Re}[E_0 \cdot \exp(i \omega \cdot t)] + E_{\text{ex}}^2 + 2E_0 E_0^* \} \]

\[ \sim \chi^{(2)} \{ 2E_{\text{ex}} \cdot \text{Re}[E_0 \exp(i \omega \cdot t)] + E_{\text{ex}}^2 + 2E_0 E_0^* \} \sim 2\chi^{(2)} E_{\text{ex}} E_{\text{light}} \quad (E_0 << E_{\text{ex}}) \]

\[ \varepsilon_r = 1 + \chi + 2\chi^{(2)} E_x \]

Polarization oscillating at the optical frequency  Static polarization  Dielectric constant change due to 2\textsuperscript{nd} order nonlinearity
Second harmonic generation (SHG)

- 2\textsuperscript{nd} order optical nonlinearity
- Use light with wavelength $\lambda = \lambda_0$ to generate light with $\lambda = \lambda_0/2$
  - Frequency doubling $\omega = 2\omega_0$

Total electric field: $\overline{E} = E_{\text{light}} = \text{Re}[E_0 \cdot \exp(i\omega_0 \cdot t)]$

$P_{NL} = \chi^{(2)} \cdot E^2 \sim \chi^{(2)} \cdot \text{Re}[E_0^2 \exp(i2\omega_0 \cdot t)]$

Radiating dipole with a frequency $\omega = 2\omega_0$

Rigorous solution:

$\overline{E}_1 = E_{10} \cdot U_1(x, y) \cdot \exp(ik_1 \cdot z - \omega_1 \cdot t)$

$\overline{E}_2 = E_{20} \cdot U_2(x, y) \cdot \exp(ik_2 \cdot z - \omega_2 \cdot t)$

$\omega_2 = 2\omega_1$

$D = \sum_{ijk} D_{ijk} U_{2i} U_{1j} U_{1k}$

$\frac{d}{dz} E_1 = -i\omega_1 \sqrt{\frac{\mu_0}{\varepsilon_0}} \cdot DE_1^* \cdot \exp[-i(2k_1 - k_2)z]$

$\frac{d}{dz} E_2 = -i\omega_2 \sqrt{\frac{\mu_0}{\varepsilon_0} \frac{1}{2}} \cdot DE_1^2 \cdot \exp[i(2k_1 - k_2)z]$

Energy is conserved.
Phase matching condition

- Only when $2k_1 = k_2$ will SHG be efficient
  - $n(\lambda_1) = n(\lambda_2)$

General rule for parametric processes
- SHG, SFG/DFG, THG, FWM
- momentum conservation

~ 100% SHG conversion efficiency is possible by optimizing phase matching!
Sum frequency generation (SFG)  
Difference frequency generation (DFG)

- 2\textsuperscript{nd} order optical nonlinearity
- Start with two beams $\omega = \omega_1$ and $\omega = \omega_2$
  - SFG: $\omega_3 = \omega_1 + \omega_2$, $k_3 = k_1 + k_2$
  - DFG: $\omega_3 = \omega_1 - \omega_2$, $k_3 = k_1 - k_2$
- SFG/DFG for photodetection
  - Use a 1060 nm laser to convert 10 $\mu$m mid-infrared radiation to 960 nm near-infrared radiation that can be handled by low-cost detectors

Nonlinear optics is a colorful discipline!

---

Image courtesy of Institut für Angewandte Physik
Optical Kerr effect
Third harmonic generation (THG)

- 3rd order optical nonlinear effects
- 3rd order optical nonlinearity is present in all materials

Total electric field: \( \overline{E} = E_{\text{light}} = \text{Re}[E_0 \cdot \exp(i\omega \cdot t)] \)

**Optical Kerr effect: light-induced refractive index change**

\[ P_{NL} = \chi^{(3)} \cdot E^3 \sim \chi^{(3)} \cdot \text{Re}[3E_0^2 E_0^* \cdot \exp(i\omega \cdot t)] \]

Consider only the \( \omega \) terms

\[ I_0 \propto |E_0|^2 = E_0 E_0^* \implies \Delta n = n_2 I_0 \propto I_0 \implies \text{Change of the imaginary part of nonlinear index: two photon absorption} \]

**Third harmonic generation (THG): frequency tripling**

\[ P_{NL} = \chi^{(3)} \cdot E^3 \sim \chi^{(3)} \cdot \text{Re}[E_0^3 \cdot \exp(i3\omega \cdot t)] \]

Consider only the \( 3\omega \) terms
Two photon absorption (TPA)

- Bimolecular process
  - Absorption depends quadratically on light intensity
  - Absorption coefficient $\alpha_{TPA} \propto I_0$
- Resonant enhancement of nonlinear index $n_2$
  - TPA enhanced near $E_{\text{light}} = E_g/2$
- Superior spatial confinement of photo-physical and photo-chemical reactions
  - 3-d patterning using TPA-induced polymerization
Stimulated Raman scattering (SRS)

- 3rd order optical nonlinearity
- Scales with pump light intensity
- Interaction of photons with phonons
  - Photon – phonon = Stokes line
  - Photon + phonon = anti-Stokes line
Stimulated Raman scattering (SRS)

- Amorphous materials typically have broad Raman peaks
  - Phonon energy dispersion
- Heavy atoms $\rightarrow$ low phonon energy $\rightarrow$ small Raman shift
Self-focusing and filamentation

- Higher refractive index at beam center due to the high optical intensity: self-sustained waveguiding
- Stand-off detection
  - Unknown substances are identified at a safe distance
  - Sensing approach: Raman
  - High optical intensity required: pulse-induced filamentation of air
  - Efficient collection of non-coherent light signal?

Femtosecond laser
Si Raman lasers that make the headline

- *First silicon laser pulses with life*

- Gain: Raman amplification
- Loss: free carrier absorption due to TPA
- **Solution 1**: pulsed operation
  - Pulse width $< \tau_{\text{carrier}}$ $< \text{pulse period}$

Si Raman lasers that make the headline

- A continuous-wave Raman silicon laser
- Loss: free carrier absorption due to TPA
- Solution 2: reverse biased p-i-n diode
  - Sweep out free carriers due to TPA

Phenomenology of the non-linear optical effects

\[ \vec{P_i} = \vec{P_i}^L + \vec{P_i}^{NL} = \alpha_{ij} E_j^{(\omega)} + \beta_{ijk} E_j^{(\omega)} E_k^{(\omega)} + \gamma_{ijkl} E_j^{(\omega)} E_k^{(\omega)} E_l^{(\omega)} \]

\[ \vec{P_i}^L = \alpha_{ij} E_j^{(\omega)} \]

\[ \vec{P_i}^{NL} = \beta_{ijk} E_j^{(\omega)} E_k^{(\omega)} + \gamma_{ijkl} E_j^{(\omega)} E_k^{(\omega)} E_l^{(\omega)} \]

where \( \alpha_{ij}, \beta_{ijk}, \gamma_{ijkl} \) are microscopic susceptibilities in microscopic case (hyperpolarizabilities) which are related with macroscopic susceptibility \( \chi_{ijk} \) by equations:

\[ \chi_{ij}^{(\omega)} = L_i^{(\omega)} L_j^{(\omega)} \alpha_{ij} \]

\[ \chi_{ijk}^{(\omega)} = L_i^{(\omega)} L_j^{(\omega)} L_k^{(\omega)} \beta_{ijk} \]

\[ \chi_{ijkl}^{(\omega)} = L_i^{(\omega)} L_j^{(\omega)} L_k^{(\omega)} L_l^{(\omega)} \gamma_{ijkl} \]

where \( i, j, k \) are components of the local Lorenz field, \( L_{i,j,k} \)–Lorenz field factors.
Microscopical aspects of the photoinduced NLO changes

Using the oversimplified expression one can present the microscopic hyperpolarizabilities as:

\[
\alpha_{ij} \equiv \frac{\mu_i \mu_j}{E_g^2} \quad \beta_{ijk} \equiv \frac{\mu_i \mu_j \Delta \mu_k}{E_g^3} \quad \gamma_{ijkl} \equiv \frac{\mu_i \mu_j \Delta \mu_k \Delta \mu_l}{E_g^4}
\]

Here \( \mu_{i,j} \) are transition dipole moments and \( \Delta \mu_{k,l} = \mu_{k,l}^{(ex)} - \mu_{k,l}^{(gr)} \) are differences between excited and ground dipole moments. For the proper EOE all the description will be similar as for the \( \beta_{ijk} \).

The latter term is described by third-order space derivatives of the anharmonic potentials:

\[
\gamma_{ijk} = \frac{\partial^3 U}{\partial x_i \partial x_j \partial x_k}
\]

\[
U = \frac{1}{2!} \alpha_{ij} x^2 - \frac{1}{3!} \beta_{ijk} x^3 - \frac{1}{4!} \gamma_{ijkl} x^4
\]
Orientations of particular glass chromophore

Effective electrooptic or SHG coefficients may be evaluated by estimation of the acentric order parameter \(<\cos^3 \theta\>\) using an expression:

\[
 r_{ijk} = 2\beta_{ijk} N <\cos^3 \theta> L_{ijk} / n^2
\]  

1.5

\[
 <\cos^3 \theta> = \mu E_{\text{eff}} / k_B T
\]  

1.6

where \(N\) is a number of actual LSNC chromophore per volume unit; \(n\) is effective refractive index.

However, at higher concentration intermolecular interactions \(IM\) described by an equation (1.7) may be commensurable with the contribution of the intra-chromophore contribution;

\[
 IM = \mu_{NC} \mu_{pol} / R^3
\]  

1.7

Here \(R\) is a distance between the LSNC possessing state dipole moments \(\mu_{NC}\) and surrounding polymers with dipole moment \(\mu_{pol}\).
Relation between microscopical and macroscopical susceptibilities

The macroscopic second-order non-linear optical susceptibility $\chi_{ijk}$ and microscopic hyperpolarisability $\beta_{ijk}$ are related by expression:

$$\chi_{ijk}(\omega, \omega, \omega) = f_i(\omega) f_j(\omega) f_k(\omega) \beta_{ijk}(\omega, \omega, \omega)$$

where $\chi_{ijk}(\omega, \omega, \omega)$ is a macroscopic second-order optical susceptibility determining the second harmonic generation and Pockels coefficient; $f_{i,j,k}(\omega)$ - are the $i,j,k$ components of the local Lorenz field’s factor.

Using an oversimplified two-band model we can present the microscopic hyperpolarizability as described by an expression:

$$\beta_{ijk}(\omega, \omega, \omega) \approx \frac{\tilde{\mu}_{gr} 2 \Delta \tilde{\mu}_{tr}(j \rightarrow l)}{|E_j - E_l|^4}$$

where $\mu_{gr}$ is a ground state dipole moments; $\Delta \mu_{gr}(j \rightarrow l)$ - transition dipole moments between occupied $j$ and unoccupied $l$ band states.
PRINCIPAL METHODS OF CREATION OF NON-CENTROSYMMETRY

General scheme of the medium polarization for the pure electronic contribution.

Electronic + harmonic electron-phonon contribution.
Electronic + harmonic electron-phonon + anharmonic electron-phonon contribution.
Principal sketch explaining structure of the LSNC.
Principal scheme of creation photo-aligned non-centro symmetry.
Influence of photothermoannealing on the nanocrystallization
Typical pictures of the optical poling in organic chromophore embedded within the PMMA matrix obtained by polarized light at different pump powers:

A) 0.2 GW/cm²;
B) 0.45 GW/cm²;
C) 0.65 GW/cm²;
D) 1.0 GW/cm².
PRINCIPAL SCHEMAT OF OPTICAL POLING

YAG: Nd$^{3+}$

$\lambda = 1.32 \ \mu m$

$\omega$

BS

Sh

$\omega$

P2

L3

S

$2\omega$

F

PM

β-BBO

$\lambda = 0.66 \ \mu m$
IR-TREATMENT OF NANOCOMPOSITES
PRINCIPAL SET-UP FOR PHOTO-INDUCED ELECTRO-OPTIC MEASUREMENT

YAG: Nd

\(\lambda = 1.06 \, \mu m\)

KTP

\(\lambda = 0.53 \, \mu m\)

Sh

P1

\(\lambda = 1.06 \, \mu m\)

M1

M3

M2

M4

He-Ne

\(\lambda = 0.633 \, \mu m\)

BS

P2

S

E

\(\lambda / 4\)

A

PD

PC
Photoinduced optical SHG for the 1540 nm Er-glass lasers after 3-5 min. treated samples in PMMA matrices.
THE EXPERIMENTAL SET-UP FOR THE MEASUREMENT OF INDUCED CHANGES IN THE REFRACTIVE INDEX ($\Delta n$)
Photoinduced beam profile distribution of the photocreated crystalline phase

- microcrystal
- nanocrystal
- metastable crystal
Dependences of the Kerr coefficients in $10^{-12} \text{ m V}^{-2}$ versus temperature
PHOTOINDUCED SURFACE TREATMENT OF THE

AFM images of the organic-inorganic NC
A) before the UV laser treatment,
B) after 500 pulses of the nitrogen 337 nm lasers,
C) after 1500 pulses of the lasers.
PHOTOINDUCED CHANGES OF ELECTROOPTICS
TRANSPARENCY IN CNW

<table>
<thead>
<tr>
<th></th>
<th>Sample</th>
<th>Power Level</th>
<th>Transmission</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>pmm218z1</td>
<td>100 Hz</td>
<td>5.819 %</td>
</tr>
<tr>
<td></td>
<td>before</td>
<td>after</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>pmm260z1</td>
<td>100 Hz</td>
<td>5.032 %</td>
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<tr>
<td></td>
<td>before</td>
<td>after</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>pvk218z2</td>
<td>100 Hz</td>
<td>3.254 %</td>
</tr>
<tr>
<td></td>
<td>before</td>
<td>after</td>
<td></td>
</tr>
</tbody>
</table>

100 MW/cm² | 400 MW/cm²
Laser induced changes of the optical absorption
Set-up
Photoinduced polarimetry
Dye laser
1. For hybrid organic/ionorganic NC principal role for the non-linear optical effects play the charge density gradients of particular structural clusters determining the larger charge transfer and electron-phonon anharmonic interactions;

2. To achieve an enhancement of the nonlinear optical effects it is crucial to have a metastable state of the NC composites near the phase transformation or critical points;

3. The main restraining factor is increasing light scattering of the nano (micro crystallites and their aggregation, and space disordering of the nanoparticles).

4. To achieve the space alignment we need long-range space orientation of the NLO-active chromophore which may be achieved by the thermal poling in the electric field; optical poling by two bicolor coherent beam, single beam induced microcrystallinity due to local thermoheating causing the local additional non-centrosymmetry on the borders nanocrystallite-polymer, electron beam poling.

5. There are two possible regime of the photoinduced changes - in the real time when the pumping and probing beams are temporary synchronised and the second one after the irreversible changes, which remain after the switching off of the external fields. As a consequence occurrence of the grating would play here dominant role.

6. Role of the local overheating, themodiffusion, thermoexpansion etc. and the appeared coherent phonons plays here substantial role.