Winter College on Optics

Photothermal Spectroscopy
Lecture 2 - Applications

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Outlook

1. Optical characterization of matter.
2. The place of photothermal spectroscopy
3. Achromatic character of the mode-mismatched configuration.
4. NIR Photothermal spectroscopy
5. Photothermal-absorbance-fluorescence spectrophotometer.
6. Photothermal spectroscopy of fluorescence and scattering samples.
7. Perspectives.
Material samples exhibit generally more than one type of effect upon interaction with light.

- Incident light
- Reflected light
- Scattered light
- Transmitted light

Additional effects:
- Absorption of light
  - Photoacoustic effects
  - Photothermal effects
  - Photomechanical effects
  - Photochemical effects
  - Luminescence
From the energy conservation law we obtain

\[ P_o(\lambda) = P_T(\lambda) + P_F(\lambda) + P_{Th}(\lambda) + P_s(\lambda) + P_R(\lambda) \]

- \( P_o(\lambda) \) Incident power
- \( P_T(\lambda) \) Transmitted power
- \( P_F(\lambda) \) Power used for fluorescence
- \( P_{Th}(\lambda) \) Power degraded into heat
- \( P_s(\lambda) \) Scattered power
- \( P_R(\lambda) \) Reflected power
\[ T(\lambda) = \frac{P_T(\lambda)}{P_o(\lambda)} \] Transmittance

\[ A(\lambda) = -\log T(\lambda) \] Absorbance

\[ R(\lambda) = \frac{P_R(\lambda)}{P_o(\lambda)} \] Reflectance

\[ F(\lambda) = \frac{P_F(\lambda)}{P_o(\lambda)} \] Fluorescence excitation spectrum

\[ PT(\lambda) = \frac{P_{Th}(\lambda)}{P_o(\lambda)} \] Photothermal spectrum
\[ \Phi_0 = -0.1, \ \lambda_p = 632 \text{ nm}, \ \lambda_e = 750 \text{ nm}, \ L = 200 \text{ cm}, \ D = 0.001491 \text{ cm}^2/\text{s}, \ t = 10 \text{ s}, \ z_p = 0.2 \text{ cm} \text{ for mode-matched scheme and } z_p = 2000 \text{ cm} \text{ for mode-mismatched scheme.} \]
Experimental Z-scan of 1-cm cell containing distilled water measured under the mode-matched (open stars) and mode-mismatched (solid squares) schemes.

\[ \lambda_p = 632 \text{ nm}, \quad \lambda_e = 807 \text{ nm} \]
PTL spectra of distilled water measured using the mode-matched (large open stars) and mode-mismatched (large crossed circles) experimental configurations. Results of previous reports on water absorption of different authors have been included (small symbols).
High precision values of absorption of water in the 300-500 nm spectral region

\[ a \ (m^{-1}) \]

\[ \lambda \ (nm) \]

Comparison of TL spectrum with absorbance spectra of distilled water measured by other authors.

- **TL spectrum**
- Pope and Fry
- Palmer and Williams

**Absorption coefficient (cm\(^{-1}\))**

**Wavelength (nm)**

![Graph showing absorption coefficient vs. wavelength for TL spectra compared to those of Pope and Fry and Palmer and Williams.](image)
NIR spectroscopy of Ethanol

Absorbance

Wavelength (nm)

Ethanol TL

Cary absorbance measurement
NIR of Methanol

PTL Methanol cell 1 mm

Cary absorbance
Laser based PTL, absorbance ,and fluorescence excitation spectrophotometer.

Absorbance (crossed circles), fluorescence excitation (crossed stars) and TL spectra (solid triangles) of a 5 \times 10^{-6} M ethanol solution of Rhodamine 6G. The solid line is the absorbance spectrum of the same sample obtained using a spectrophotometer.
Absorbance (crossed circles), fluorescence excitation (crossed stars) and TL spectra (solid triangles) of the same sample of previous slide after adding of the quencher (KI).
Fluorescence quantum yield spectrum of the $5 \times 10^{-6}$ M ethanol solution of Rhodamine 6G in presence of high fluorescence and in the presence of fluorescence quenching.
White light photothermal lens spectrophotometer
PTL spectrum of 0.125 mM solution of Malachite green in ethanol. There is coincidence with the absorbance spectrum.

PTL and absorbance spectra of a 50 mM solution of R6G in ethanol.

Because of fluorescence both spectra are different. This property of PTL spectroscopy can be used for measuring the quantum yield of fluorescence.
Quantum yield of fluorescence

$$\Omega_F = \left( \frac{\lambda_F}{\lambda} \right) \left( 1 - A_{TL} (\lambda) / (1 - \exp(\alpha(\lambda)L)) \right)$$

**Equation:**
- $A_{TL}(\lambda)$: PTL absorbance
- $\alpha(\lambda)$: absorbance
- $\lambda_F$: Average wavelength of fluorescence
PTL spectroscopy of scattering samples


![Graph a](image1)
![Graph b](image2)

**a**- PTL and extinction spectra of Malachite Green Oxalate with no polystyrene microbeads added; **b**- PTL and extinction spectra of Malachite Green Oxalate containing polystyrene microbeads at concentration of 0.005% by weight. The standard deviation is estimated averaging over 5 different experiments.
a - Normalized PTL spectra of Nile Blue with polystyrene microbeads added at concentration of 0 (crossed circles), 0.0017% (stars) and 0.005% (crossed squares) by weight; b - Normalized extinction spectra of Nile Blue containing polystyrene microbeads at concentration of 0, 0.0017% and 0.005% by weight as indicated. The standard deviation is estimated averaging over 5 different experiments.
a- Scattering quantum yield of the Malachite Green Oxalate sample with added polystyrene microparticles at 0.005 % concentration by weight; b- Scattering quantum yield of the Nyle Blue sample with added polystyrene microparticles at 0.005 % by weight. The standard deviation is estimated averaging over 5 different experiments.
Extinction (solid line) and PTL (crossed circles) spectra of a solution of 50-nm diameter gold nanoparticles at concentration of 1 mg/mL. The standard deviation is estimated averaging over 5 different experiments.
a- Scattering quantum yield of the Malachite Green Oxalate sample with added polystyrene microparticles at 0.005 % concentration by weight; b- Scattering quantum yield of the Nyle Blue sample with added polystyrene microparticles at 0.005 % by weight. The standard deviation is estimated averaging over 5 different experiments.
a- Extinction (solid line) and PTL (crossed circles) spectra of a blood sample; b- Scattering quantum yield of the same blood sample. The standard deviation is estimated averaging over 5 different experiments.
Photothermal mirror effect

Excitation light

Reflected light

Nanometric bump
White-light photothermal mirror spectrophotometer
The signal is defined as

\[ S(\lambda) = \frac{T(\lambda) - T_o}{T_o} \]

\( T(\lambda) \) is the transmission through the aperture of the probe light in the presence of the pump beam.

\( T_o \) is the transmission through the aperture of the probe light in the absence of the pump beam.
A model based on the simultaneous resolution of the thermoelastic deformation of the surface and thermal diffusivity equation predicts that

\[ S(\lambda) = K \cdot P(\lambda) \cdot \Psi(\lambda) \]

\( \Psi(\lambda) \) is the fraction of absorbed energy used to generate heat

\( P(\lambda) \) is the power of the pump light

\( K \) is a proportionality coefficient that does not depend on \( \lambda \)

\( \Psi(\lambda) \) → PTM spectrum
PTM (black crossed squares) and absorbance (red crossed circles) of a glass plate
PTM spectra of a film made using the deposits from a silver nanoparticle solution
PTM spectrum of the dysprosium titanate sample
Conclusions

Photothermal spectroscopy (PT) is a new spectroscopic method that measures the ability of matter to produce heat following the absorption of light.

PT spectra and absorbance spectra coincide for samples with 100 % thermal yield.
Advantages

• High sensitive
• Universality (any sample, any spectral region).
• Scattering and fluorescence free
• Only visible sensor technology required (no IR or UV sensors needed)
• Remote sample analysis possible
• Traditional and modern light source technology can be adapted.
• Low cost.
Light Sources for PT Spectroscopy
Arc lamps

http://zeiss-campus.magnet.fsu.edu/print/light sources/xenonarc-print.htm
High Intensity Tunable Light Source

22K$

www.newport.com
White Leds

10$ on ebay
The Argon laser
NIR lasers (MIRA 900)  
Fs and CW modes  
700-1050 nm

Vantage tunable diode
Laser supercontinuum – good option for photothermal spectroscopy

http://www.nktphototonics.com/