Photothermal Spectroscopy
Lecture 1 - Principles

Aristides Marcano Olaizola (PhD)
Research Professor
Department of Physics and Engineering
Delaware State University, US

Outlook

1. Photothermal effects: thermal lens and thermal mirror.
2. Sensitivity of the photothermal methods.
3. Photothermal characterization of materials.
4. Photothermal spectroscopy – a new kind of spectroscopy

Photothermal are those effects that occur in matter due to the generation of heat that follows the absorption of energy from electromagnetic waves.

Photoelastic – changes in density due to temperature

$$\Delta V = \alpha_T \cdot V \cdot \Delta T$$

Photorefractive – change of the refraction index due to temperature

$$\Delta n = \frac{\partial n}{\partial T} \cdot \Delta T$$

There are two major characteristics of the photothermal effects:

- **Universality**
- **Sensitivity**

In any interaction of light and matter there is always a release of heat

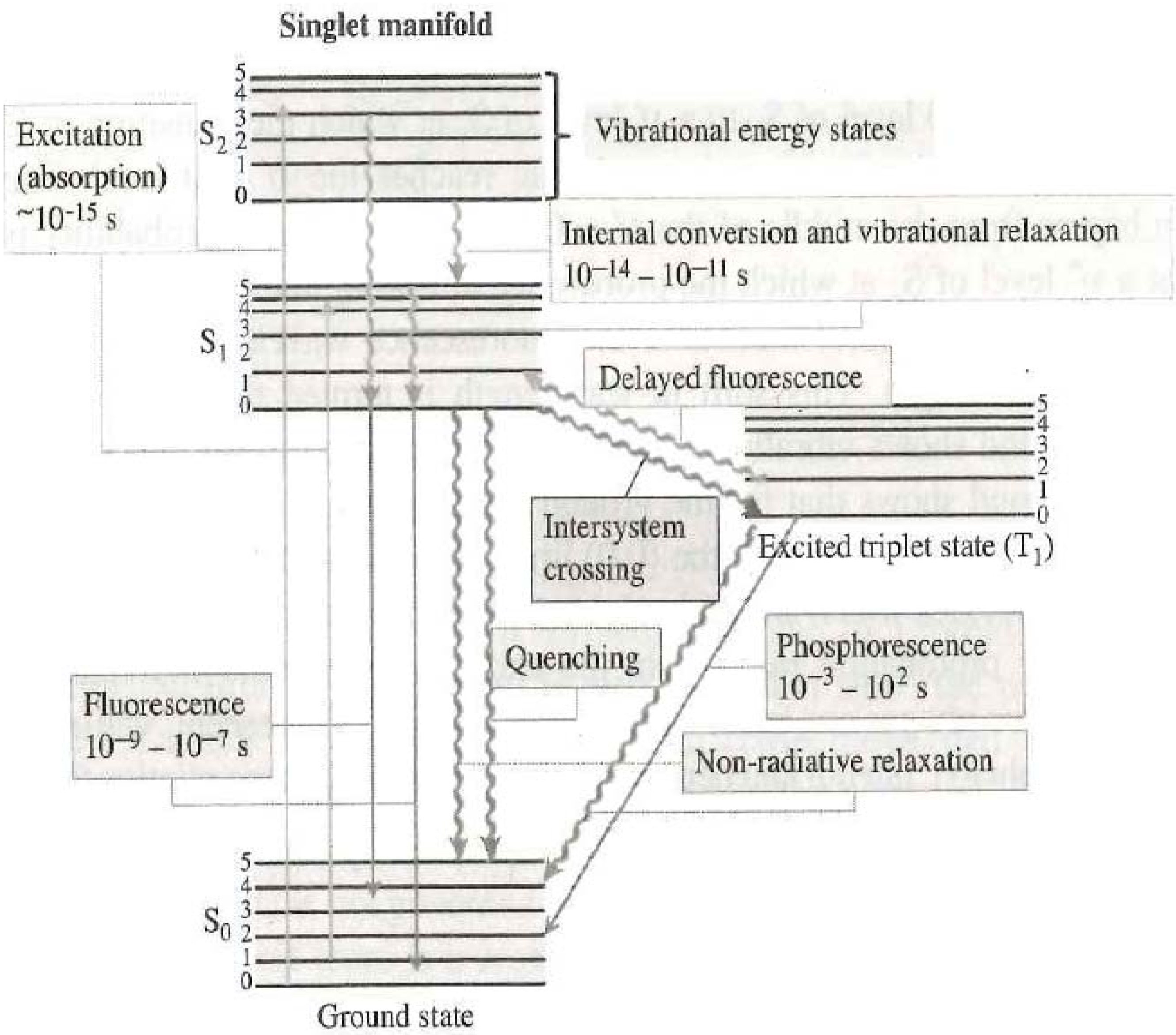
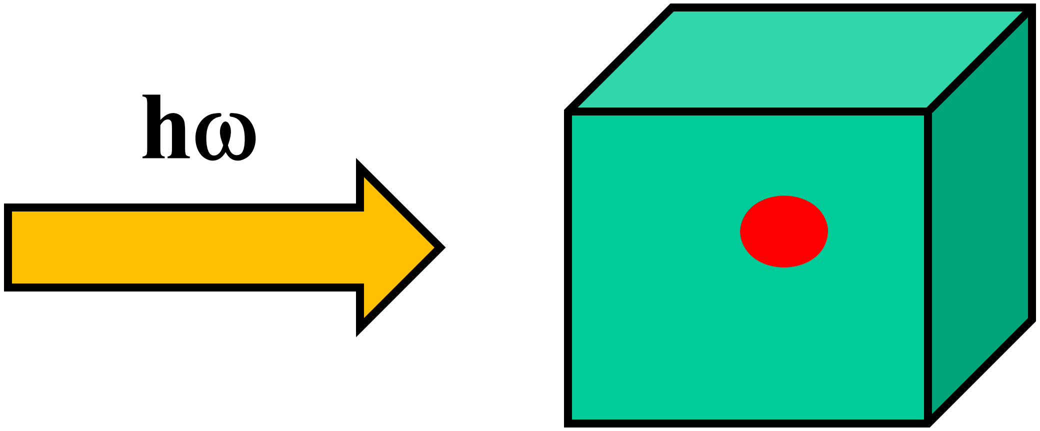


Figure 9.17. Jablonski diagram, showing electronic and vibrational energy levels

Consider one absorbing atom contained in 1 μL of water



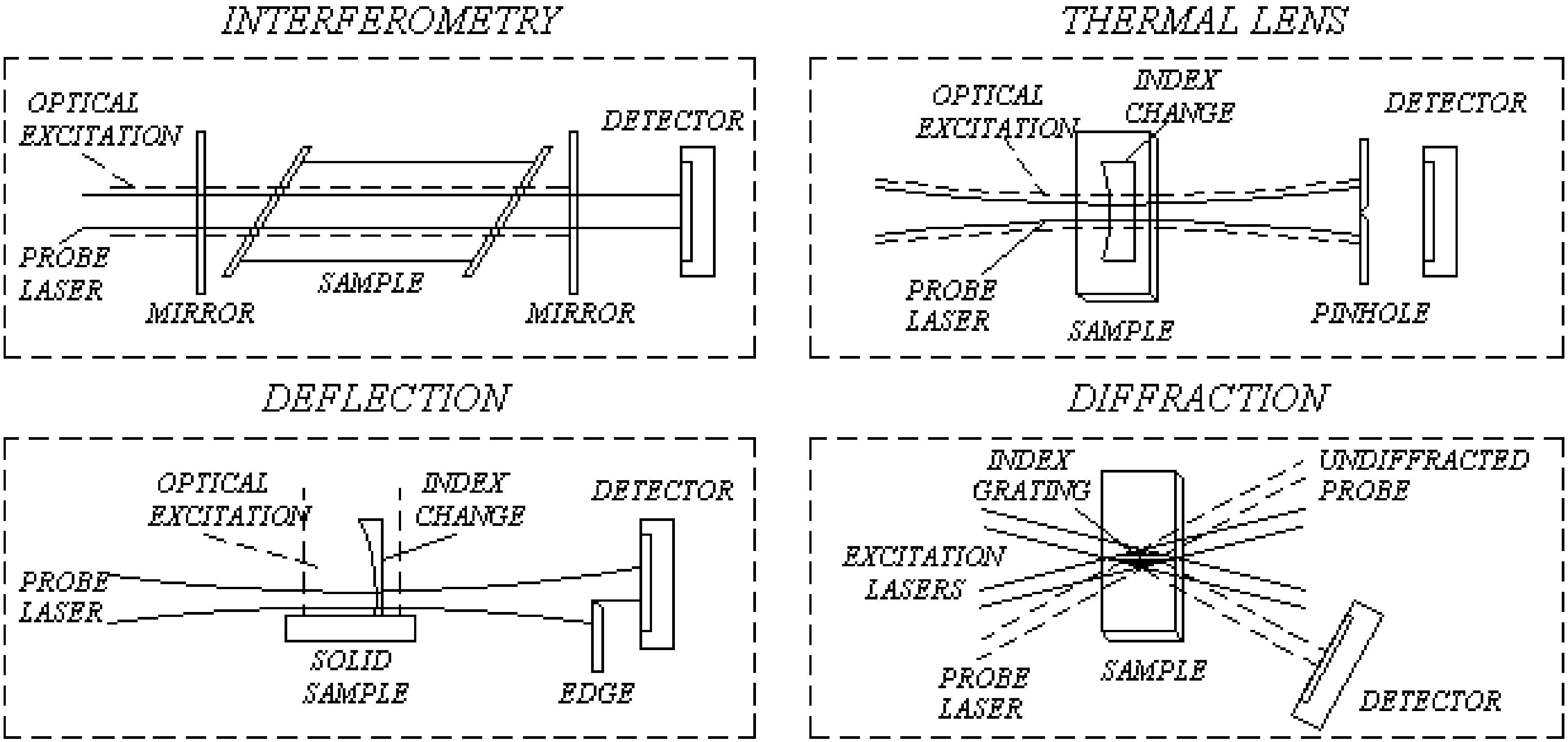
Consider also that a beam of light illuminates the sample continuously. The atom will absorb one photon and will release the energy of this photon toward the surrounding water molecules (heating) in 10^{-10}- 10^{-13} s.

Thermal diffusion will remove the generated heat. However, this effect is slow. It will take between tens of ms to seconds to equilibrate the temperatures. During this time the atom will accumulate the energy of 10^{8}-10^{13} photons. This can raise the temperature an average of 10^{-3} ^{o}C.

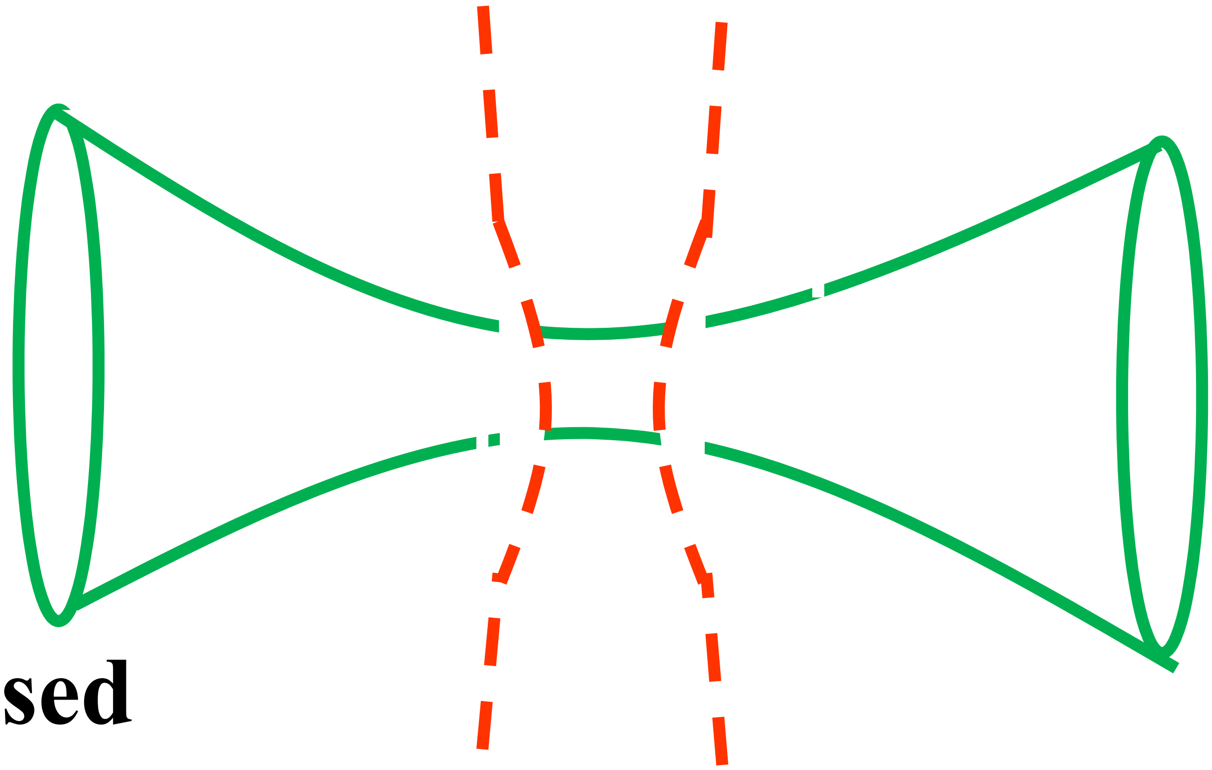
Photothermal method has a phase character. The signal is in most of the cases proportional to the change of phase

$$\Phi = 2\pi \frac{L}{\lambda} \left(\frac{\partial n}{\partial T} \right) \Delta T$$

Photothermal Effects



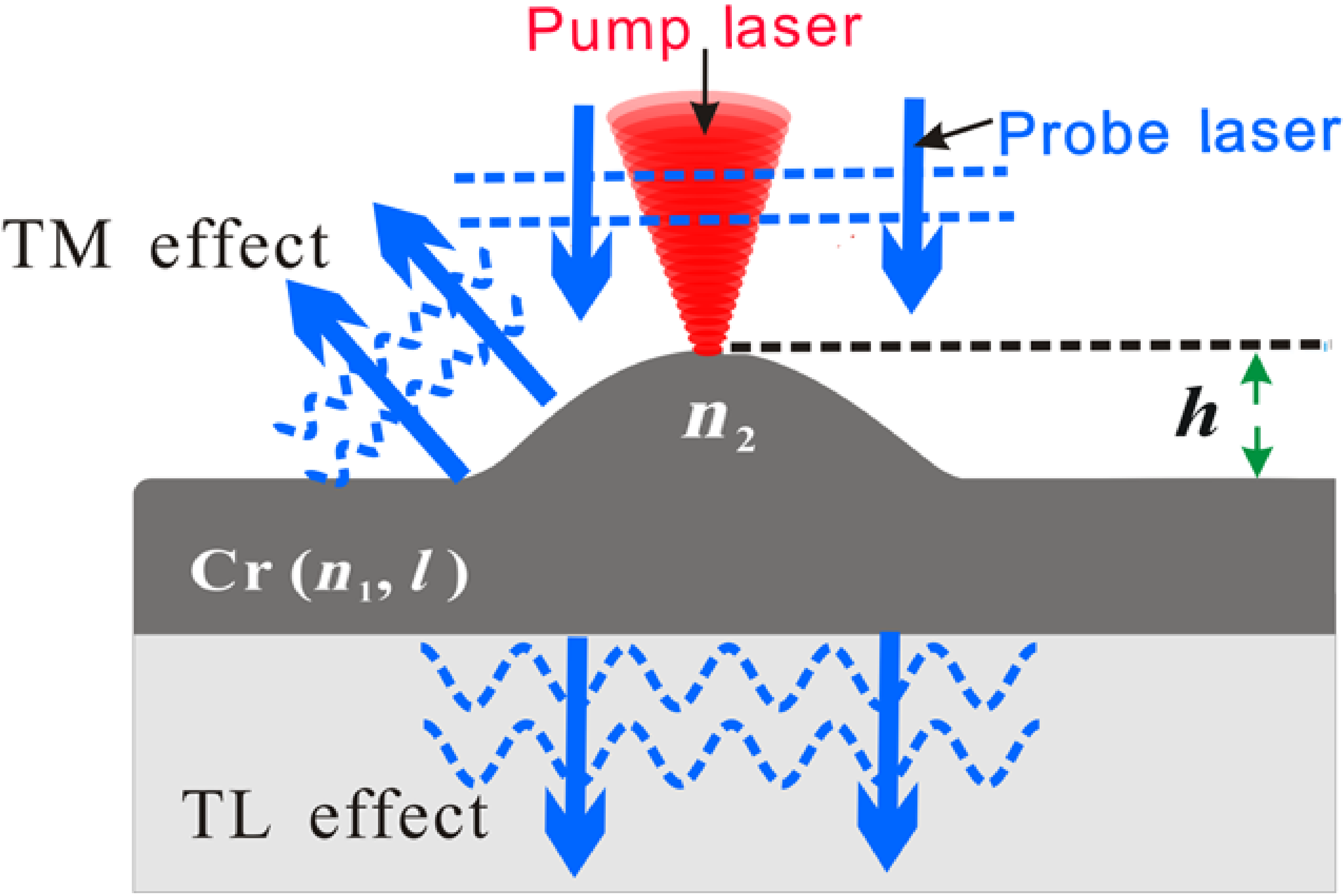
S. E. Bialkowski. “Photothermal Spectroscopy Methods for Chemical Analysis”. New York: Wiley, 1996.



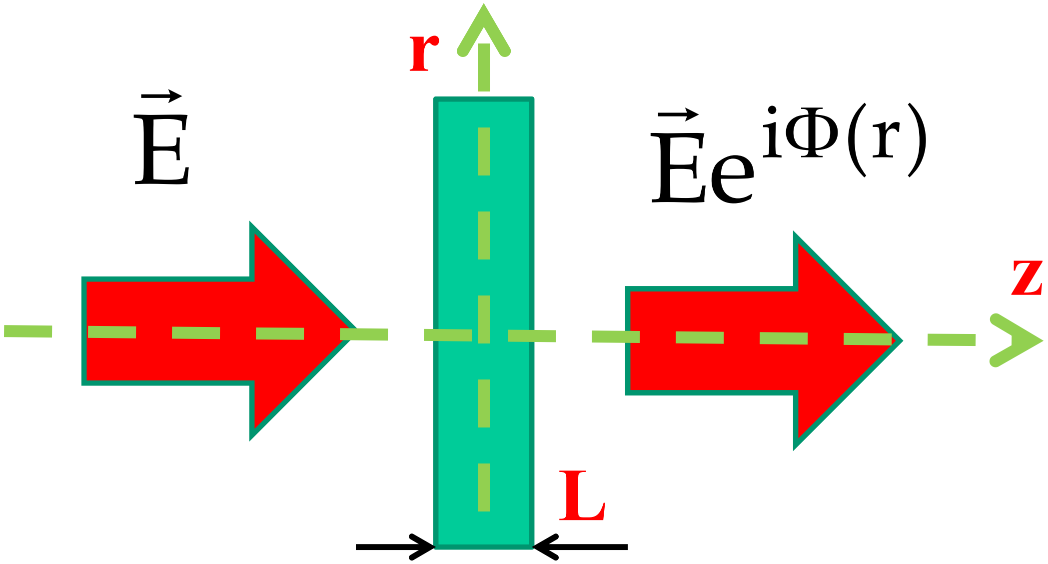
Thermal lens

Focused beam

Photothermal Mirror Effect



Thermal lens act like a phase plate

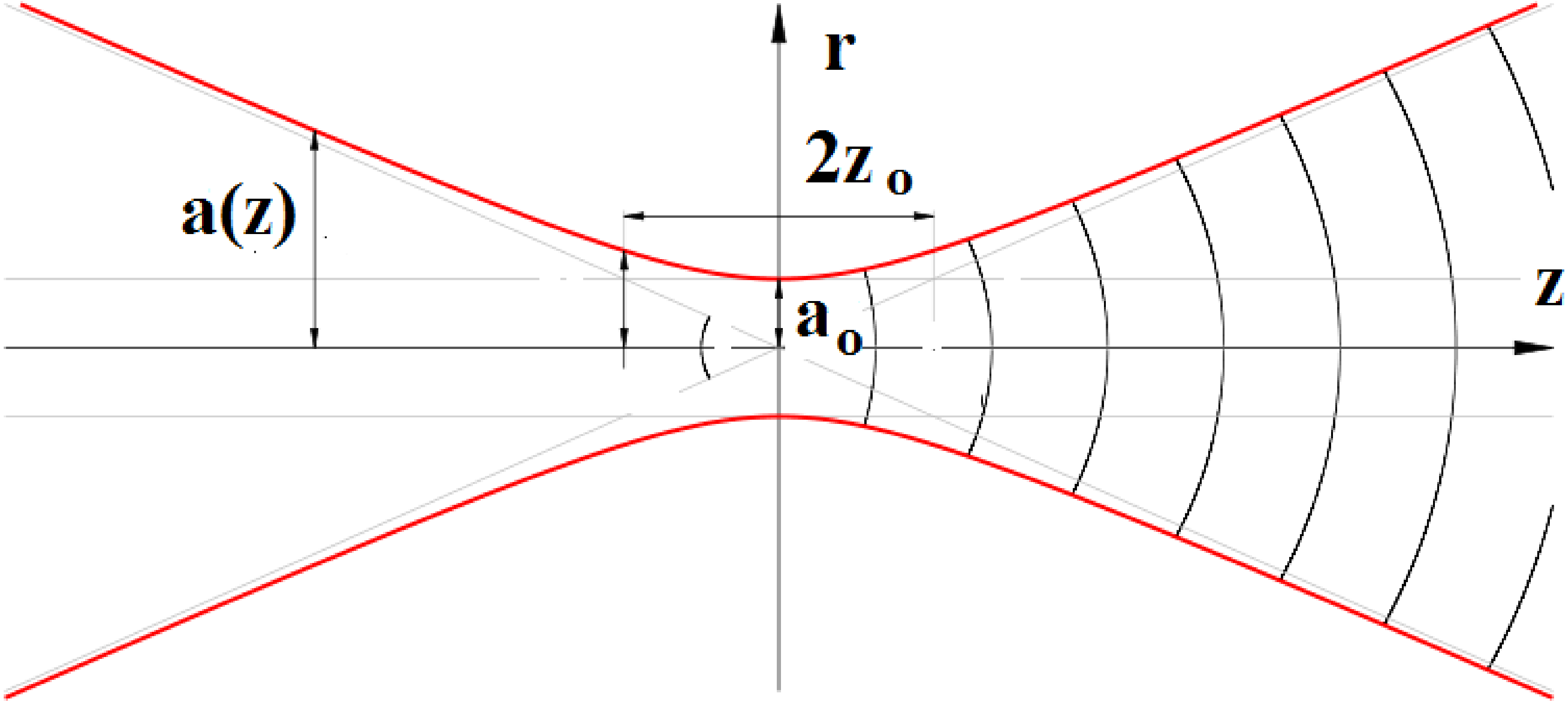


$$\Phi(r) = \frac{2\pi}{\lambda} L\Delta n(r) \qquad \Delta n(r) = \frac{\partial n}{\partial T} T(r)$$

The change in temperature T is proportional to absorption α

To calculate the induced phase we calculate first the distribution of temperature generated thanks to the absorption of a Gaussian beam in the sample.

Excitation Gaussian Beam Intensity



Gaussian Beam Amplitude

$$E(z,r,t)=\frac{E_o(t)}{a(z)/a_o}\cdot\exp\left[-\frac{r^2}{a^2(z)}-\frac{i\cdot k\cdot r^2}{2\cdot R(z)}-i\cdot artg\left(\frac{z}{z_o}\right)\right]$$

$a(z)=a_o\sqrt{1+z^2/z_o^2}$ **beam spot radius**

$R(z)=\left(z^2+z_o^2\right)/z$ **curvature radius**

$z_o=\pi a_o^2/2$ **Rayleigh range**

z **sample's position**

For a given sample's position z and for continuous excitation (CW) the intensity of the excitation beam is

$$W(r,t) = \frac{2P_o}{\pi a^2} \cdot \exp\left[-\frac{2r^2}{a^2} \right]$$

where P_o is the total light power

This function has axial symmetry. It is convenient to solve the Laplace equation in cylindrical coordinates.

Thermal diffusivity equation –Laplace Equation

We write the Laplace equation considering axial symmetry

$$\frac{\partial T}{\partial t} - D \cdot \nabla^2 T = \frac{\alpha \cdot W(r,t)}{C_p \cdot \rho}$$

D	**thermal diffusivity coefficient**
α	**absorption coefficient**
C_p	**heat capacity**
ρ	**density**

In cylindrical coordinates with axial symmetry

$$\nabla^2 = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{\partial^2}{\partial z^2}$$

We will also neglect the dependence on z (thin lens approximation)

The solution of this equation was first obtained by Whinnery in 1973 (add ref here)

$$T(r,t)=\frac{\alpha}{C_p\rho}\int_0^t\int_0^\infty W(\xi,t)\cdot G(r,\xi,t,\tau)\cdot\xi\cdot d\xi\cdot d\tau$$

$$G(r,\xi,t)=\frac{I_o\left(r\xi/2D(t-\tau)\right)}{2D(t-\tau)}\exp\left(-\frac{r^2+\xi^2}{4D(t-\tau)}\right)$$

I_o is the modified Bessel function of zeroth order

Using the table integral

$$\int_0^\infty I_o(b\xi)\cdot\exp\left(-p^2\xi^2\right)\cdot\xi\cdot d\xi = \frac{\exp\left(b^2/4p^2\right)}{2p^2}$$

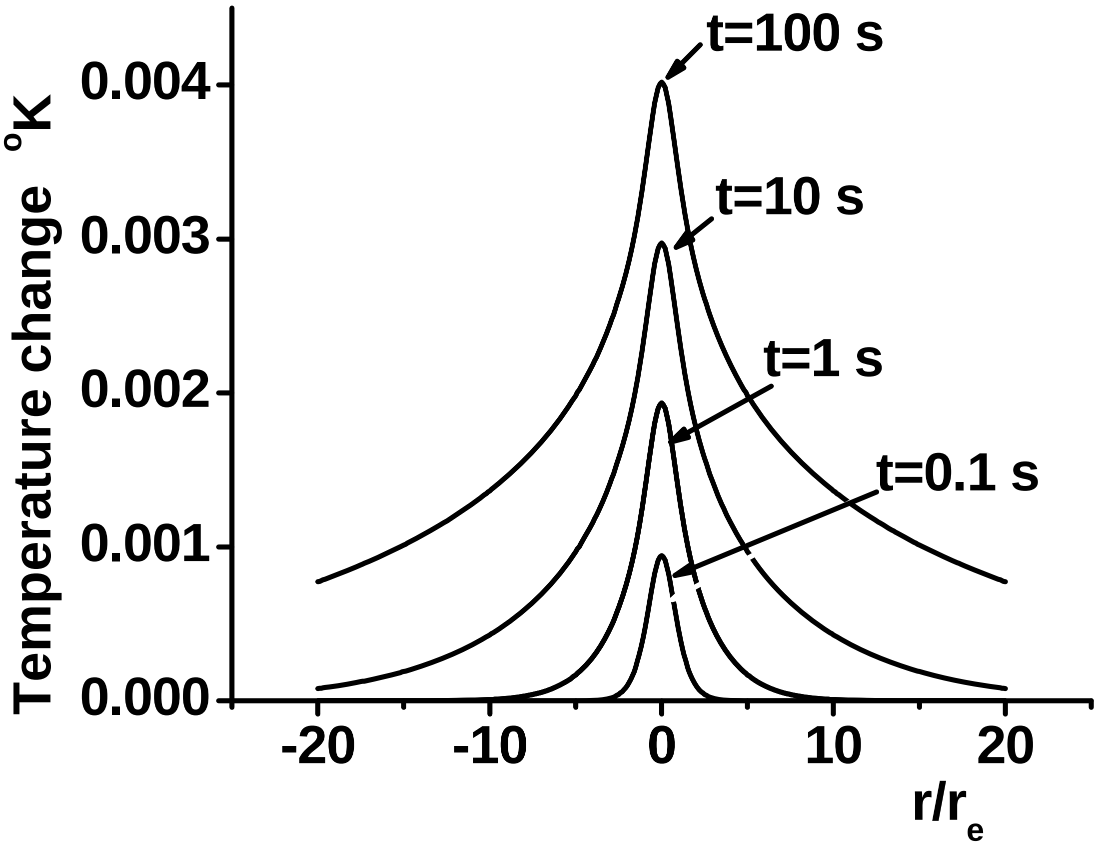
We obtain

$$T(r,t) = T_o \int_1^{1/(1+2t/t_c)} (1/\eta)\cdot\exp\left(-2r^2\eta/a^2\right)\cdot d\eta$$

where $T_o = \alpha P_o / 4\pi\kappa$ $\quad t_c = a^2/4D$

and κ is the thermal conductivity coefficient

Field of Temperatures generated by the absorption of a beam of light



For water using a 30 mW of 532 nm light

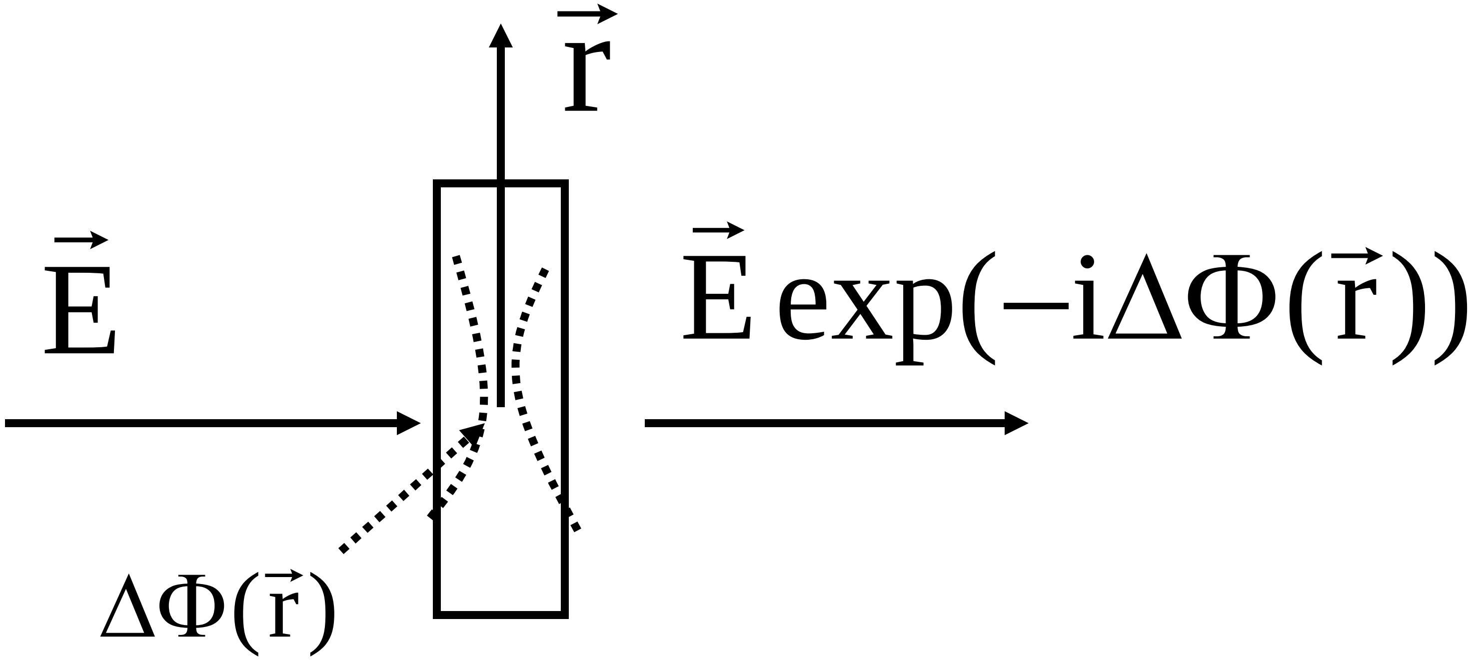
Refraction index depends on temperature

$$n(T) = n_o + \left(\frac{\partial n}{\partial T}\right) \cdot \Delta T + \left(\frac{\partial^2 n}{\partial T^2}\right) \Delta T^2 + \cdots$$

For most of the solvents first order is enough. For example for ethanol

$$n(T) = 1.3 + 4 \cdot 10^{-4}\,{}^{o}C^{-1} \cdot \Delta T$$

Thermal lens works as a phase plate (thin lens approximation)



$$\Delta\Phi(\vec{r}) = \frac{2\pi}{\lambda_p} \cdot L \cdot \frac{\partial n}{\partial T} \cdot T(\vec{r})$$

The solid samples the thermoelastic effects add an additional term

$$\Delta\Phi(\vec{r}) = \frac{2\pi}{\lambda_p} \cdot \left(L \cdot \frac{\partial n}{\partial T} + \alpha_T n \right) \cdot T(\vec{r})$$

Where α_T is the linear thermo-elastic coefficient

CW excitaion

The phase difference with respect to the center of the beam is

$$\Phi(\mathrm{r},\mathrm{z},\mathrm{t}) = (2\pi/\lambda_{\mathrm{p}})[\mathrm{n}(\mathrm{r},\mathrm{z},\mathrm{t}) - \mathrm{n}(0,\mathrm{z},\mathrm{t})]$$

Using the results obtained for the temperature

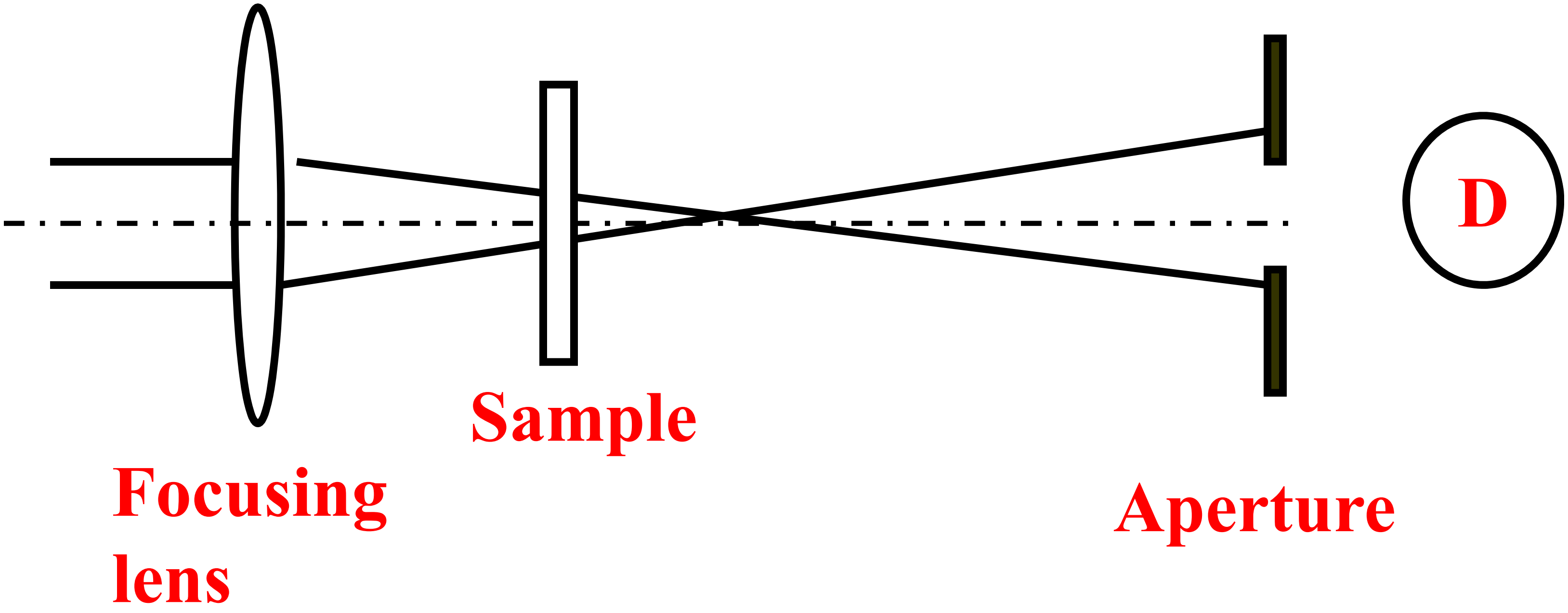
$$\Phi(g,z,t) = -\Phi_o \int_{1/(1+2t/t_C(z))}^{1} \frac{[1-\exp(-2m(z)g\tau)]}{\tau} d\tau$$

where

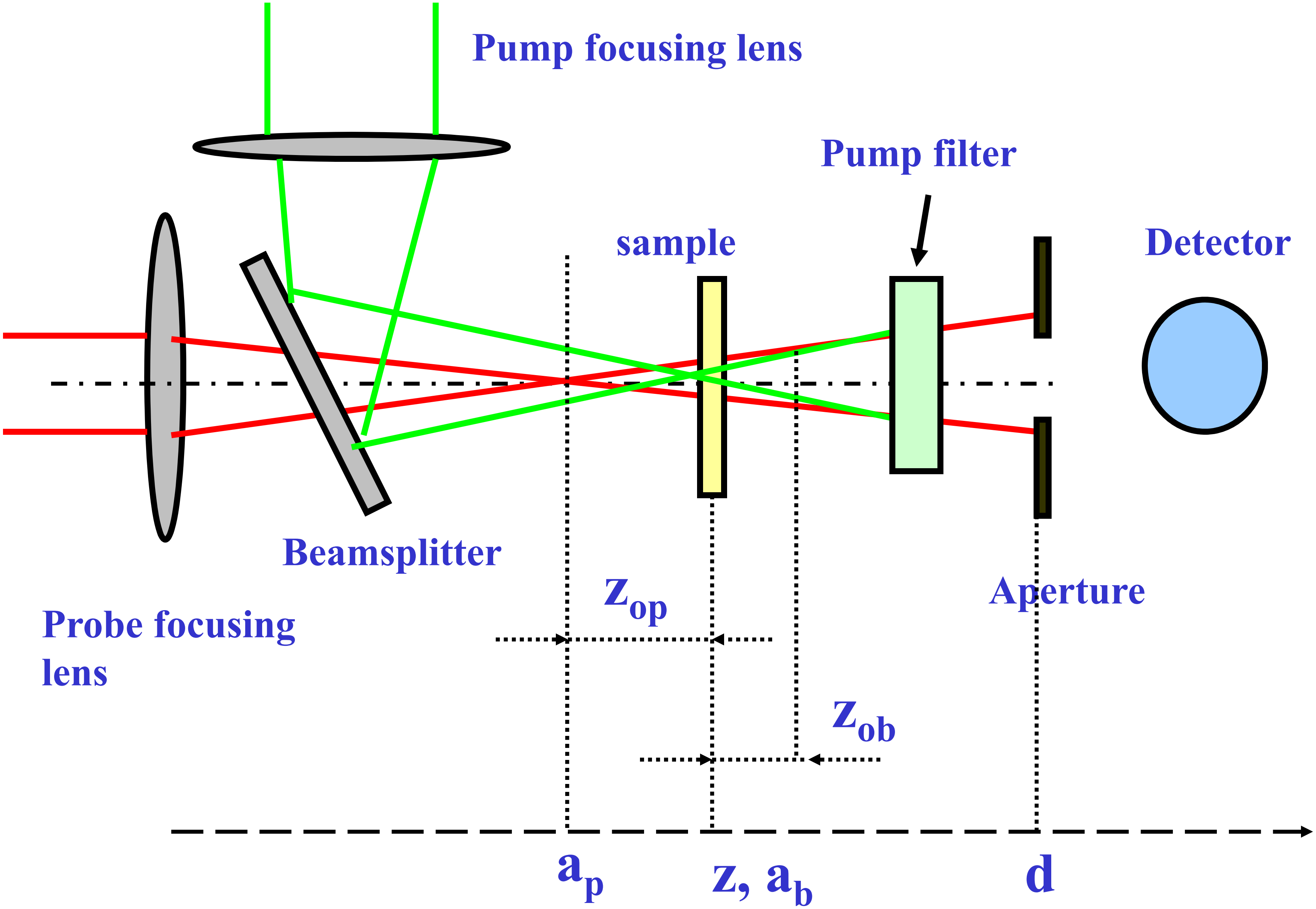
$$m(z) = a_p^2(z)/a^2(z)$$ **Mode matching coefficient**

$$\Phi_o = P_e \alpha L (dn/dT)/(2\kappa\lambda_p)$$

Single beam photothermal lens (PTL) experiment



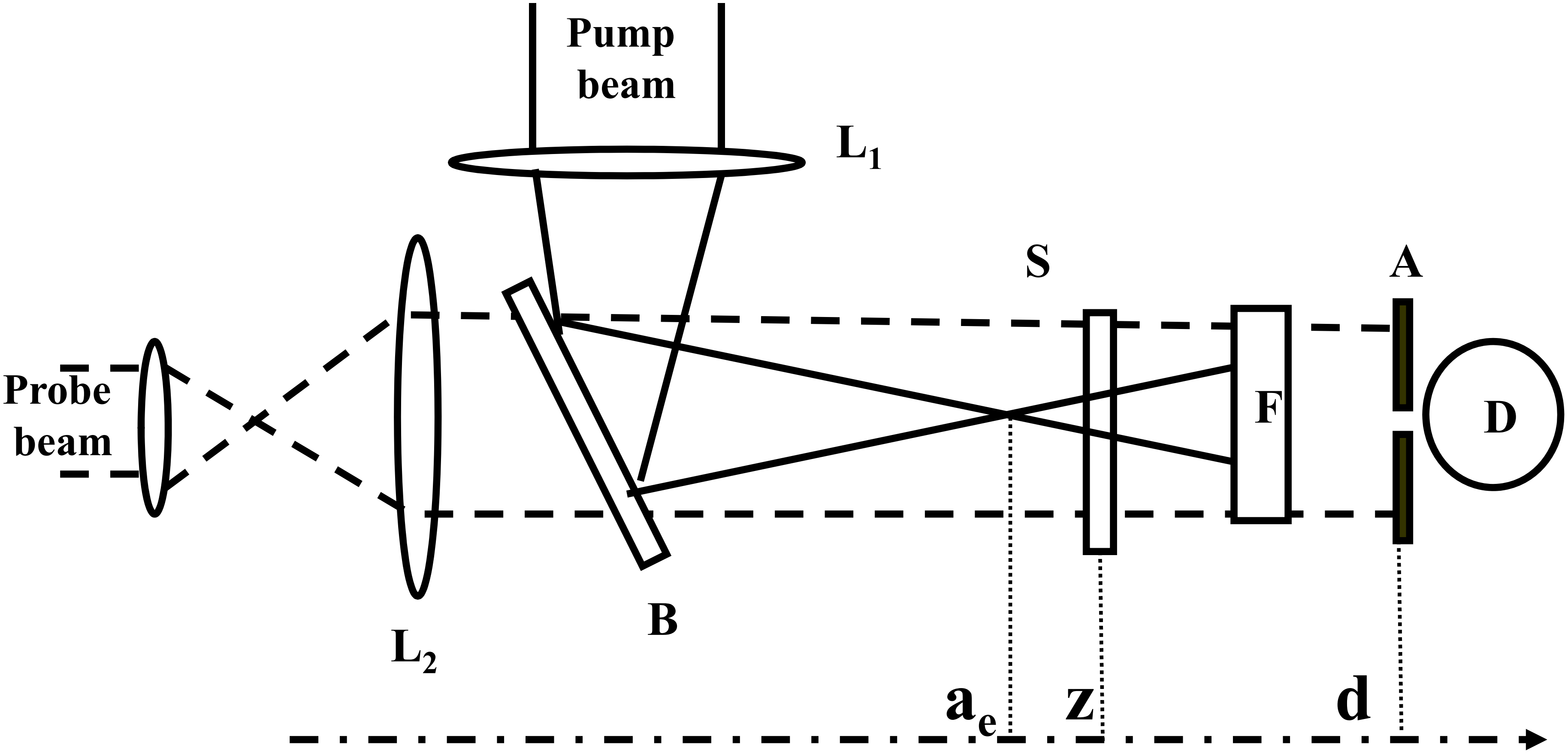
Pump-probe experiment (m>1)



Advantages of the pump-probe experiment

1. Higher sensitivity
2. Time dependence experiments possible
3. Spectroscopy possible by using tunable pump sources.
4. Detection technology in the visible. No need of UV or IR detectors.
5. Different experimental configurations possible.

Pump-probe optimized mode-mismatched experiment (m>>1)



We define the PTL signal as

$$S(z,t) = \frac{W_p(t,z,\Phi) - W_p(z,t,0)}{W_p(z,t,0)}$$

$$W_p(z,t,\Phi) = \int_0^b \left| E_p(z,t,r,\Phi \right|^2 \cdot 2\pi r dr$$

where z is the sample position, b is the aperture radius.

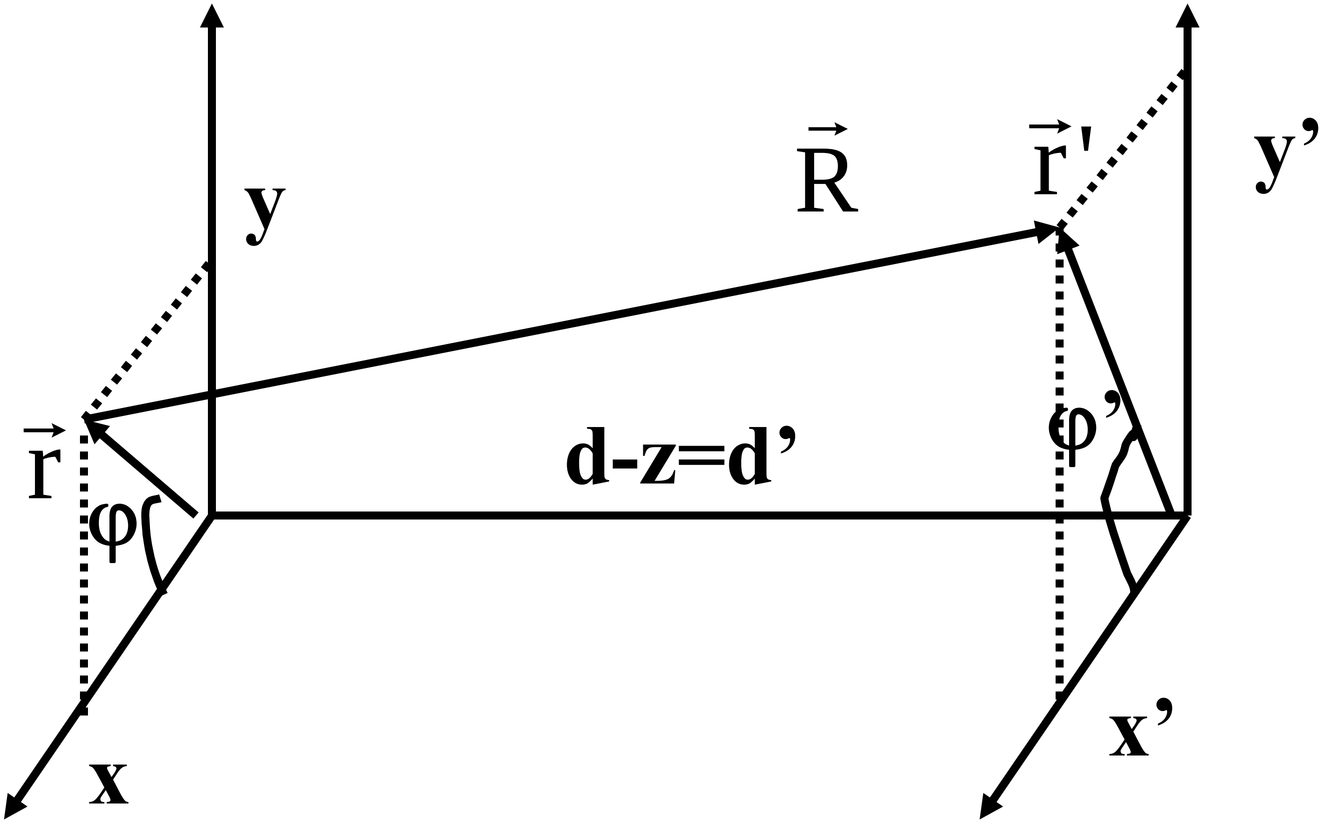
For the sake of simplicity we can consider the radius of the aperture small (b→0). Then the signal can be calculated as

$$S(z,t)=\frac{\left|E_p(z,t,0,\Delta\Phi)\right|^2-\left|E_p(z,t,0,0)\right|^2}{\left|E_p(z,t,0,0)\right|^2}$$

We calculate the probe amplitude at the far field using the Fresnel approximation

Plane of the sample

Detection plane



We suppose r, r’ << (d-z)

Using a Fresnel diffraction approximation we obtain*

$$E_p(z,t,0,\Phi) = \int_0^{\infty} \exp(-(1+iV)g - i\Phi(g,t))dg$$

$$V = z_p / z_{op} + z_{op}[(z_p / z_{op})^2 + 1] / d$$

z_{op} is the Rayleigh range of the probe field, z_p is the probe beam waist position, d is the detector position

$$\Phi(g,z,t) = -\Phi_o \int_{1/(1+2t/t_C(z))}^{1} \frac{[1-\exp(-2m(z)g\tau)]}{\tau} d\tau$$

*** Shen J, LoweRD, Snook RD (1992) Chem Phys165: 385-396. DOI:10.1016/0301-0104(92)87053-C.**

For small phases we can also obtain*

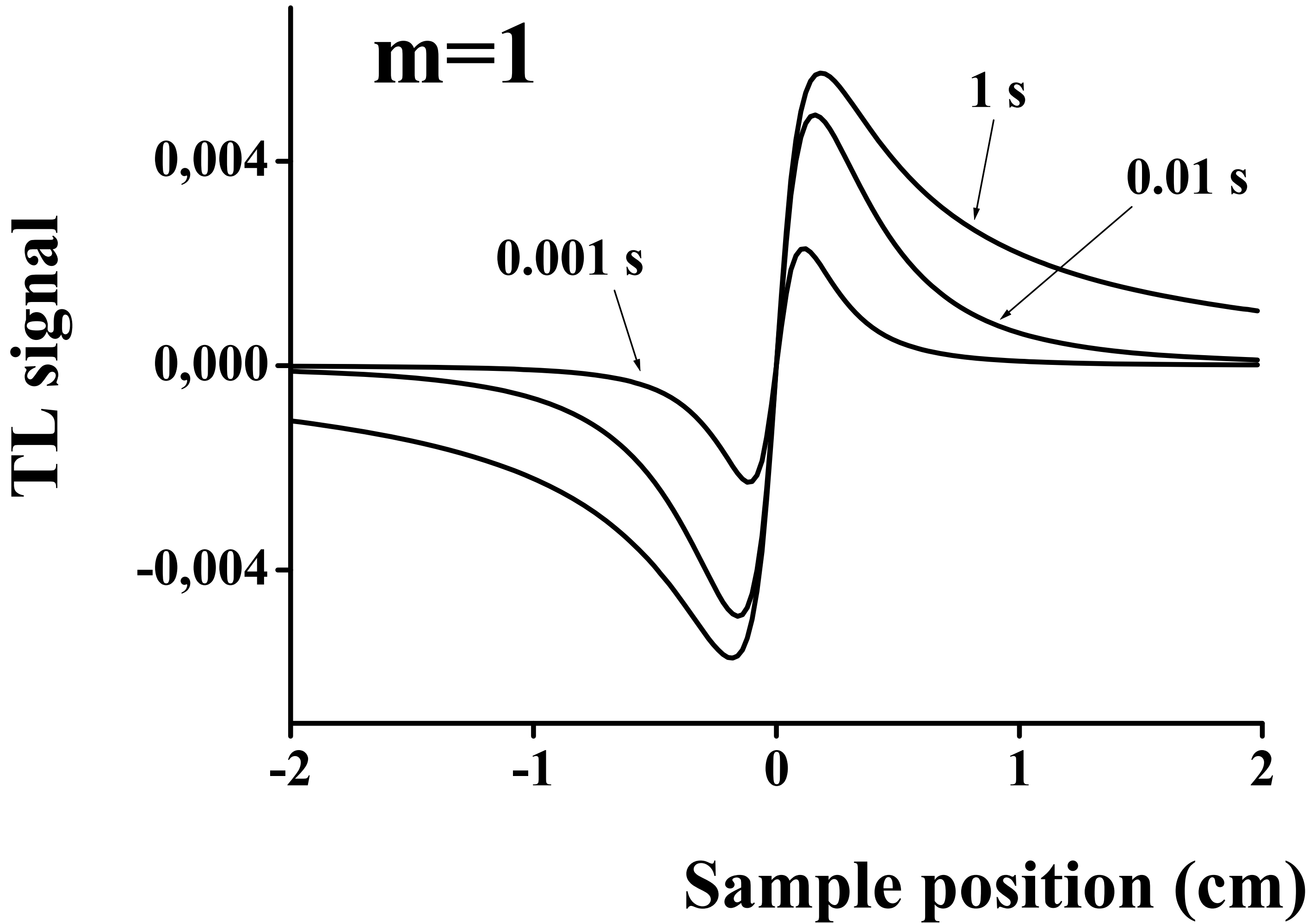
$$S(z,t) = \Phi_o \tan^{-1}\left\{ \frac{4mVt/t_c}{V^2 + [1+2m]^2 + [1+2m+V^2]2t/t_c} \right\}$$

$$\Phi_o = P_e \alpha l \, (dn/dT)/(\kappa\lambda_p)$$

$$m(z) = a_p^2(z)/a^2(z)$$

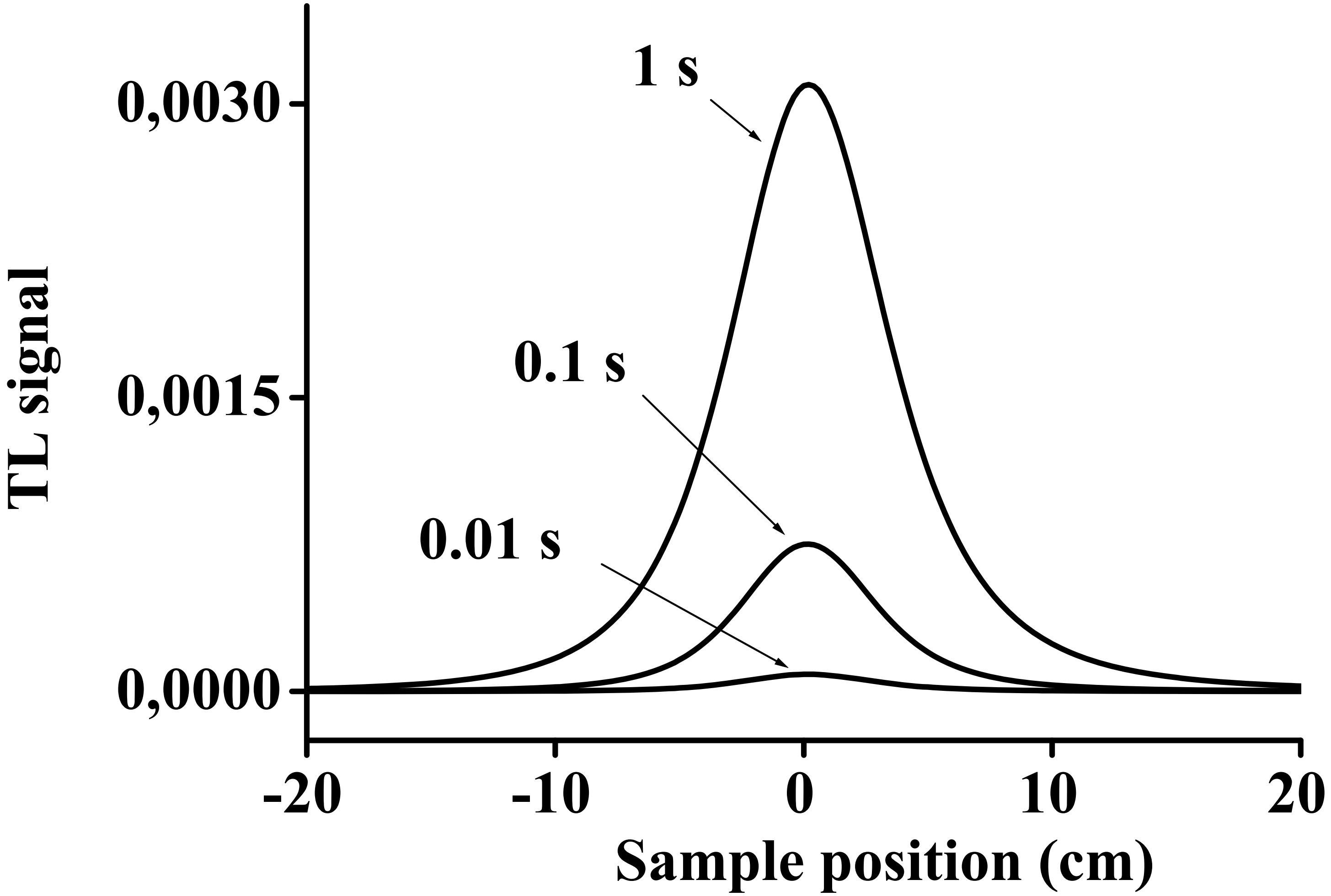
$$t_c(z) = a^2(z)/4D$$

* Marcano A, Loper C, Melikechi N (2002) Pump probe mode mismatched Z-scan, J OptSoc Am B 19: 119-124.



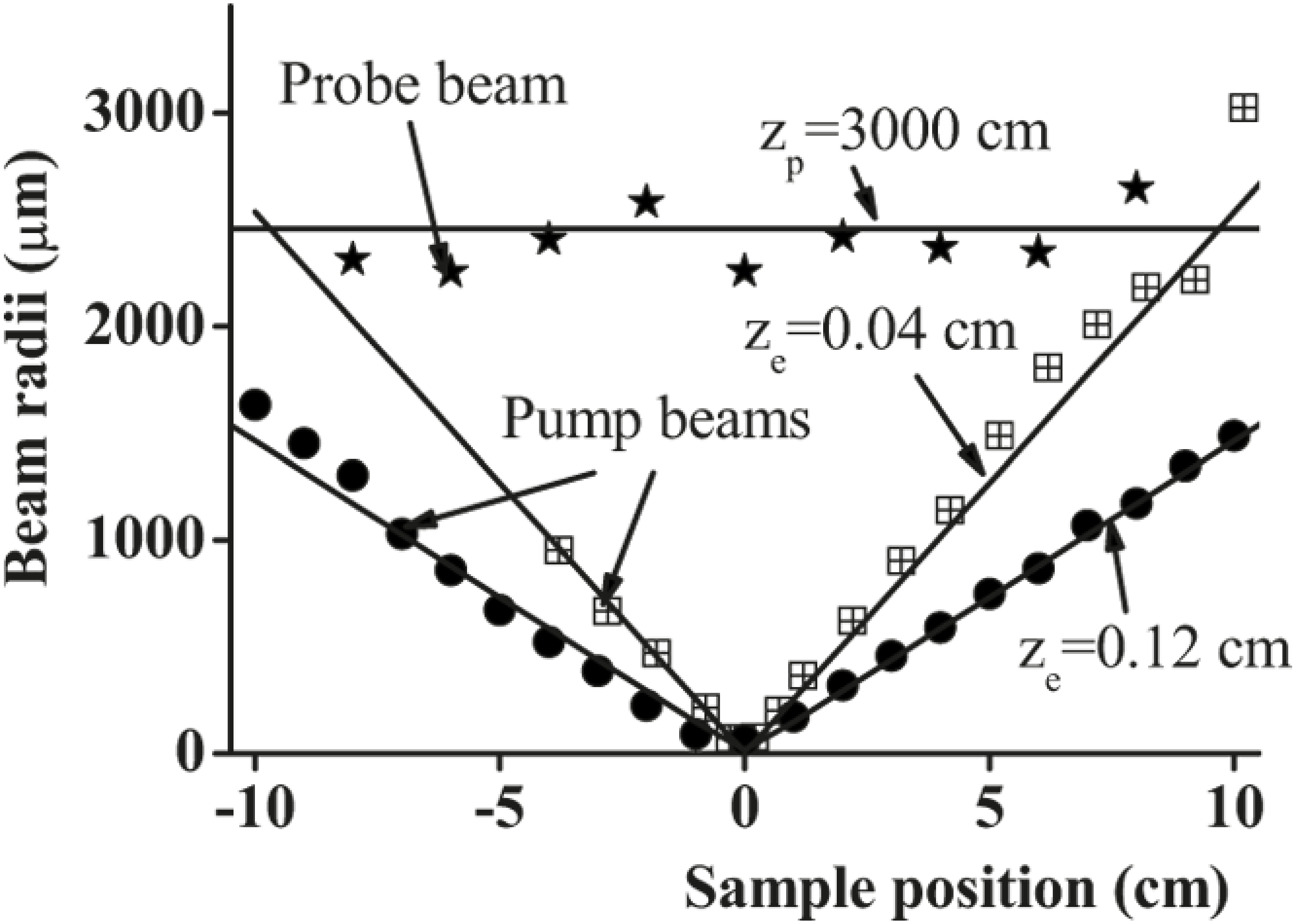
The TL signals were calculated using the following parameters: Φ_o=0.01, λ_p=632 nm, λ_e=532 nm, z_{op}=0.1 cm, z_e=0.1 cm, d=200 cm, D=0.891 10^{-3} cm^2/s and different time values as indicated.

Optimized mode mis-match experiment

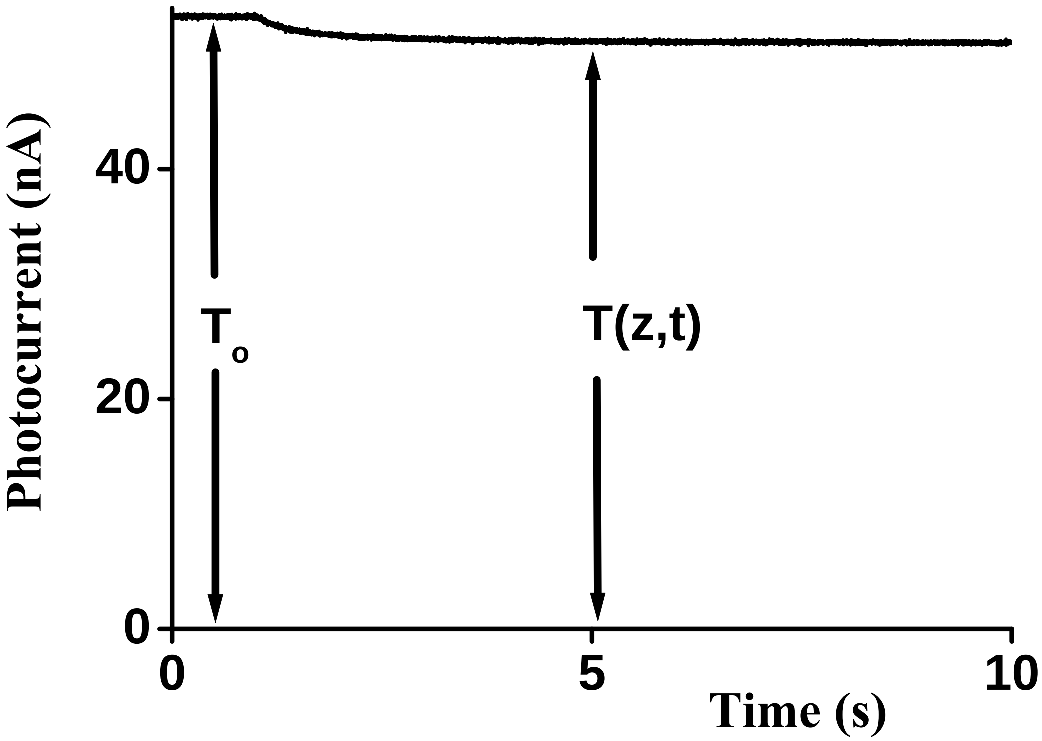


The TL signals were calculated using the following parameters: Φ_o=0.01, λ_p=632 nm, λ_e=532 nm, z_p=100 cm, z_e=0.1 cm, L=200 cm, a_e=0 and D=0.891 10^{-3} cm^2/s and different time values as indicated

Mode-mismatched scheme

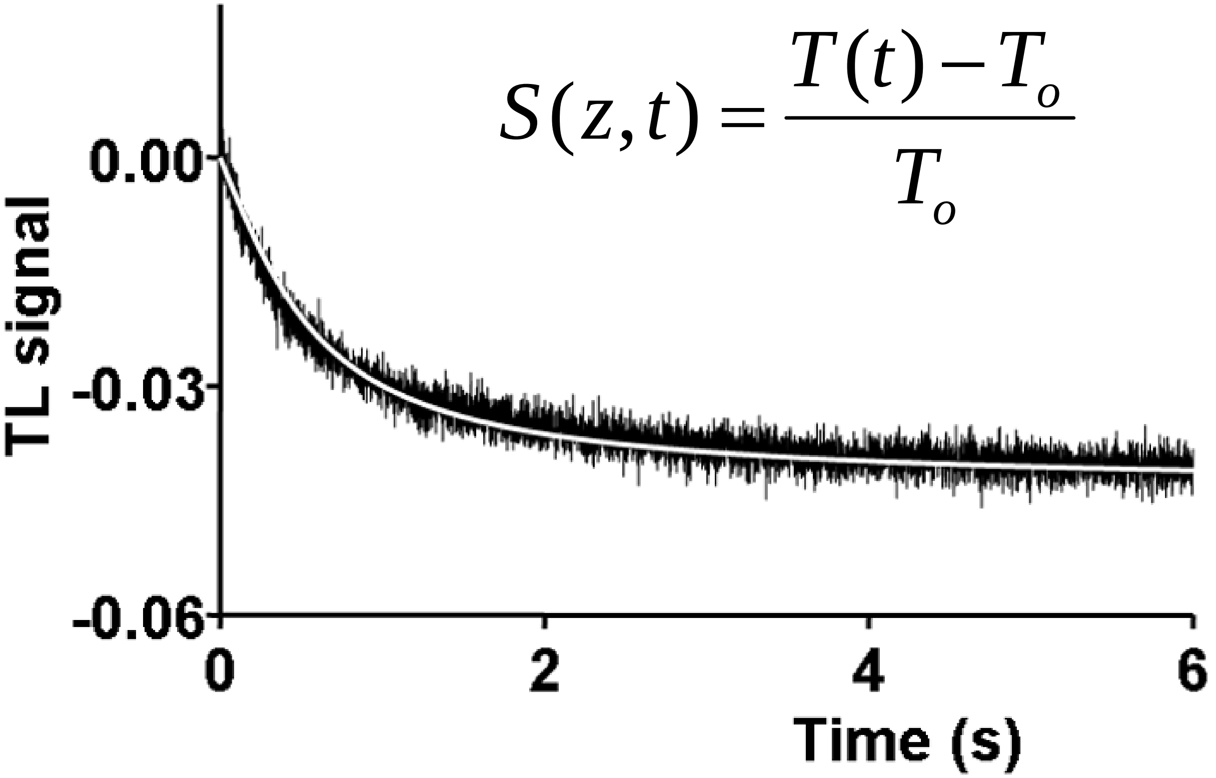


Probe transmission through the aperture



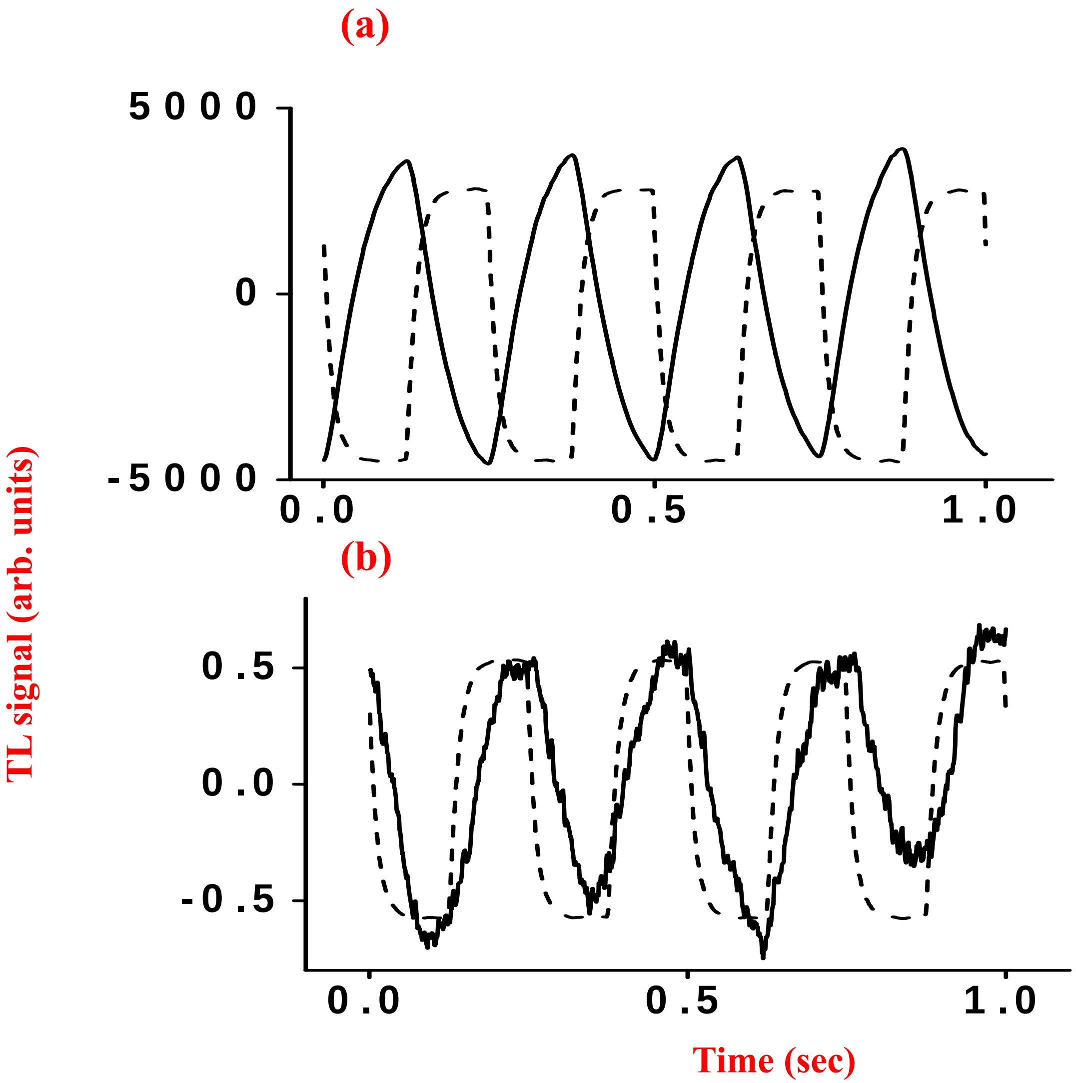
Transmitted through the aperture probe light (632 nm) using 250 mW of 532 nm excitation beam of light . The sample is a 2-mm column of water

Experimental PTL signal



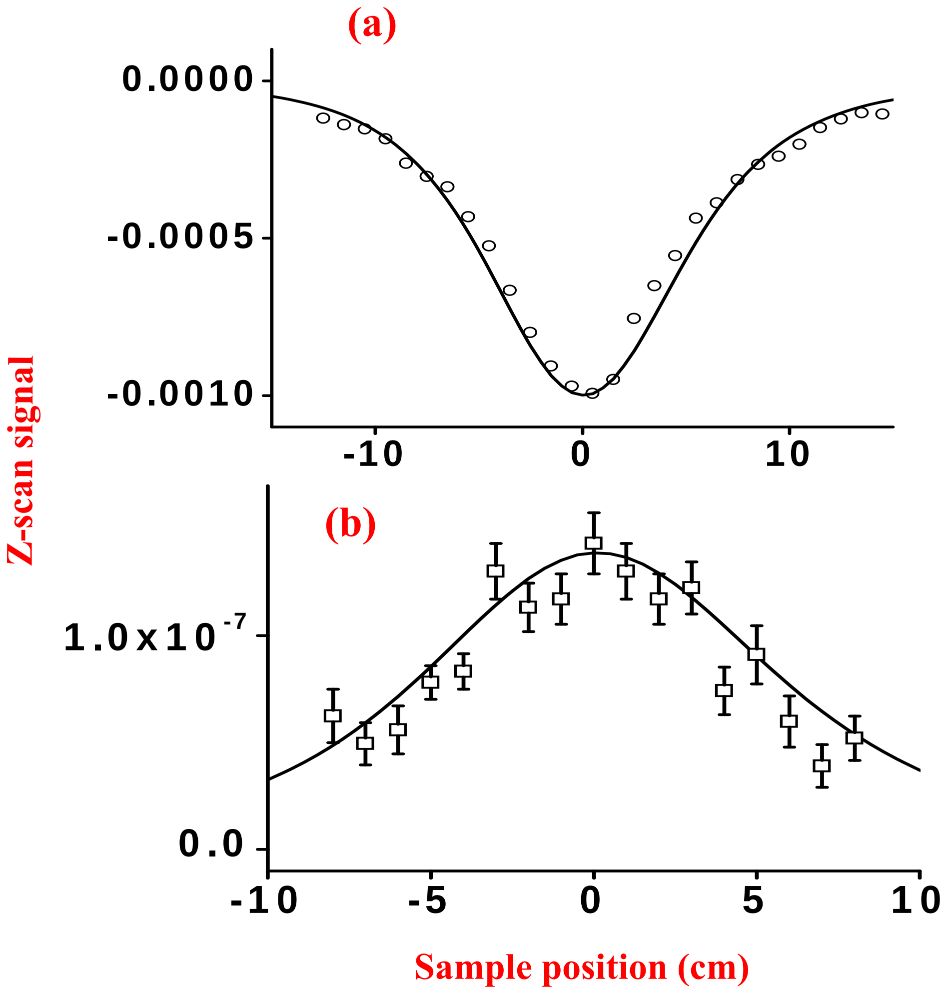
$$S(z,t) = \frac{T(t) - T_o}{T_o}$$

PTL signal calculated using the data of previous slide. The solid line is the theoretical fitting of the data.

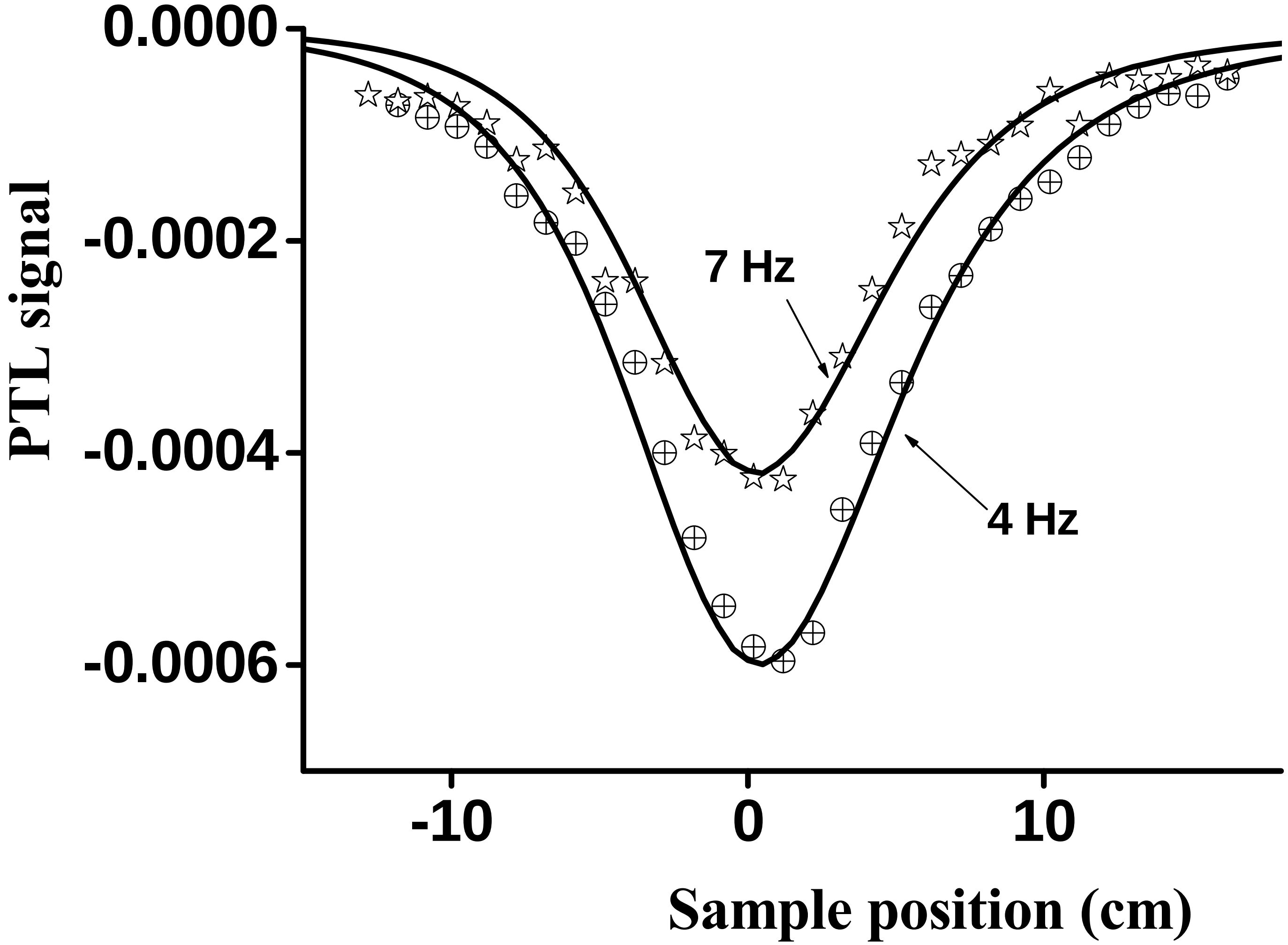


PTL signal as a function of time from the distilled water sample (a) and BK7 optical glass slab (b). The doted line is the pump field time dependence. The signal-to-noise ratio for the PTL is 10 and 75000 for BK7 glass and water, respectively.

Z-scan signal for the distilled water sample (a) and the BK7 optical glass slab (b).

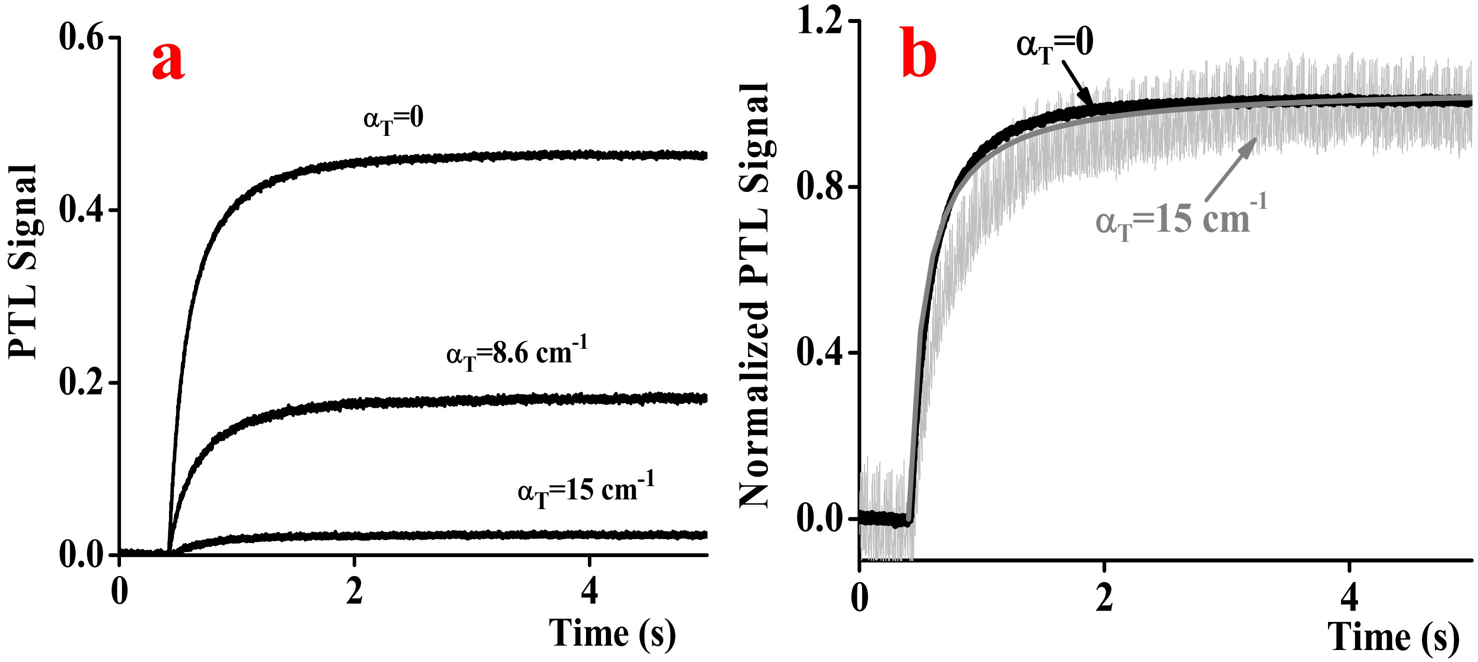


Marcano A. , C. Loper and N. Melikechi, Appl. Phys. Lett., 78, 3415-3417 (2001).

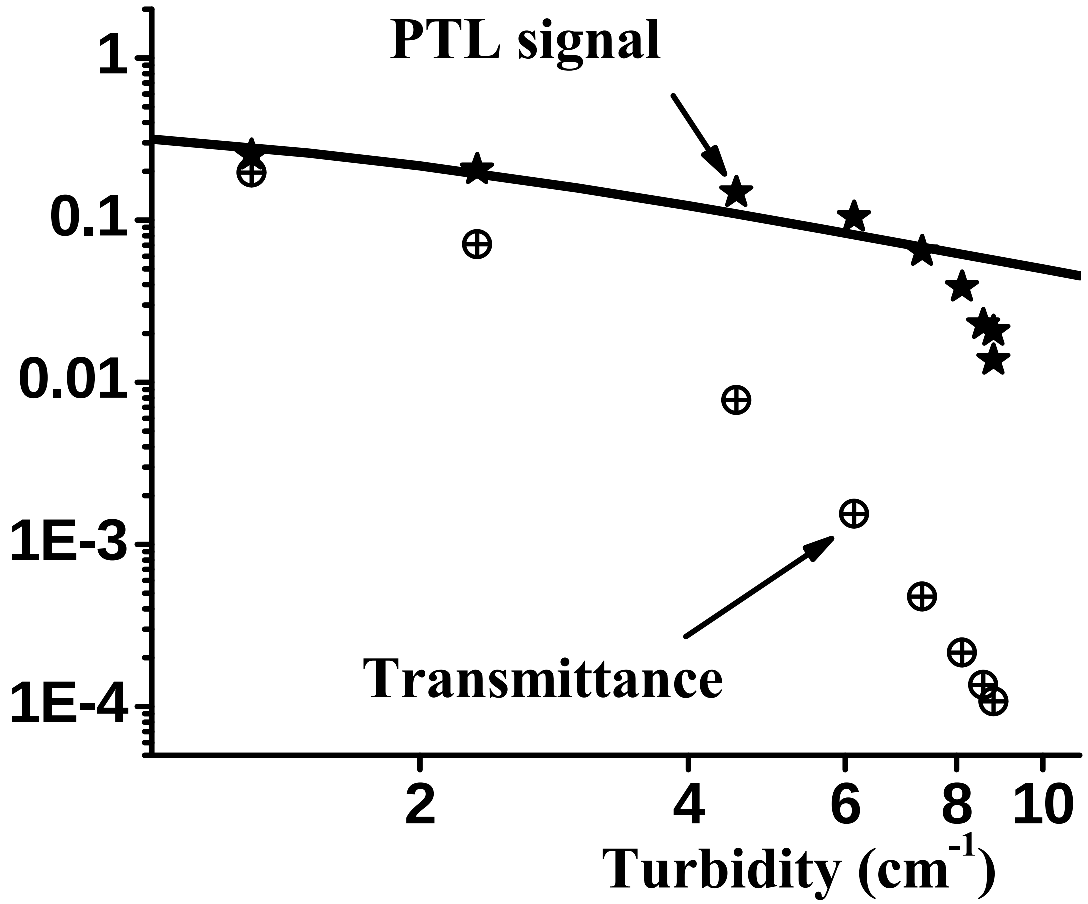


PTL signal from water for two different chopping frequencies : 4 y 7 Hz.

PTL signal is nearly scattering free

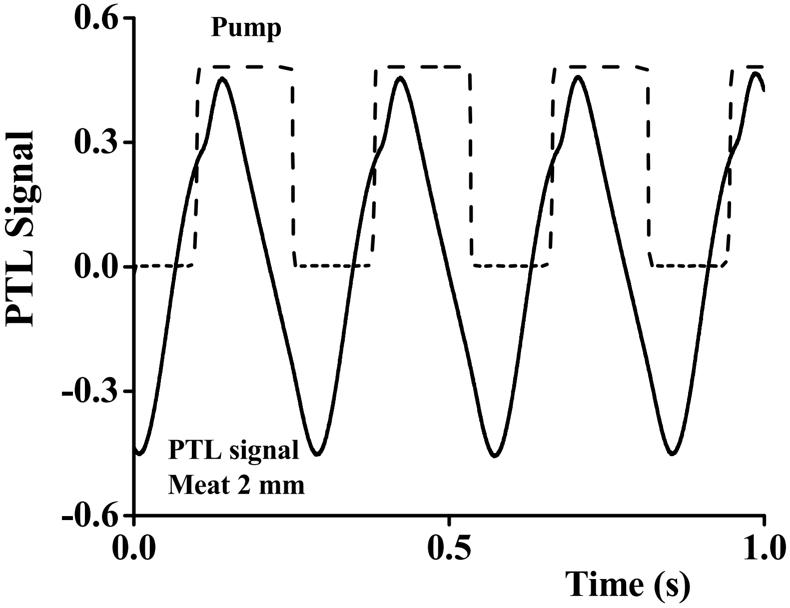


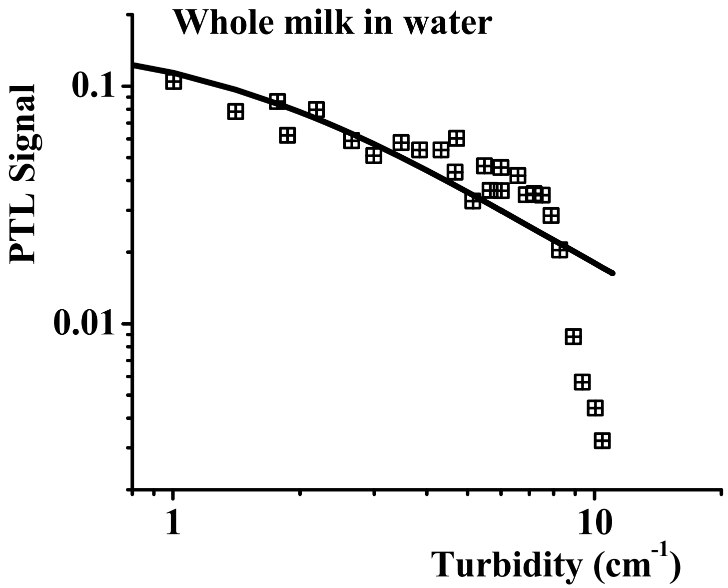
a- PTL signal as a function of time for samples (water with latex microspheres) with turbidities of 0, 8.6 and 15 cm^{-1} obtained using 80 mW of 532 nm CW light from the DPSS Nd-YAG laser,b- Normalized PTL signal for α_T=0 (black) and α_T=15 cm^{-1} (light grey) over the stationary values showing the different signal-to-noise ratios.



PTL signal as a function of turbidity The solid line is the model prediction. The dependence of transmittance is also plotted for comparison

The signal can be detected in highly turbid samples

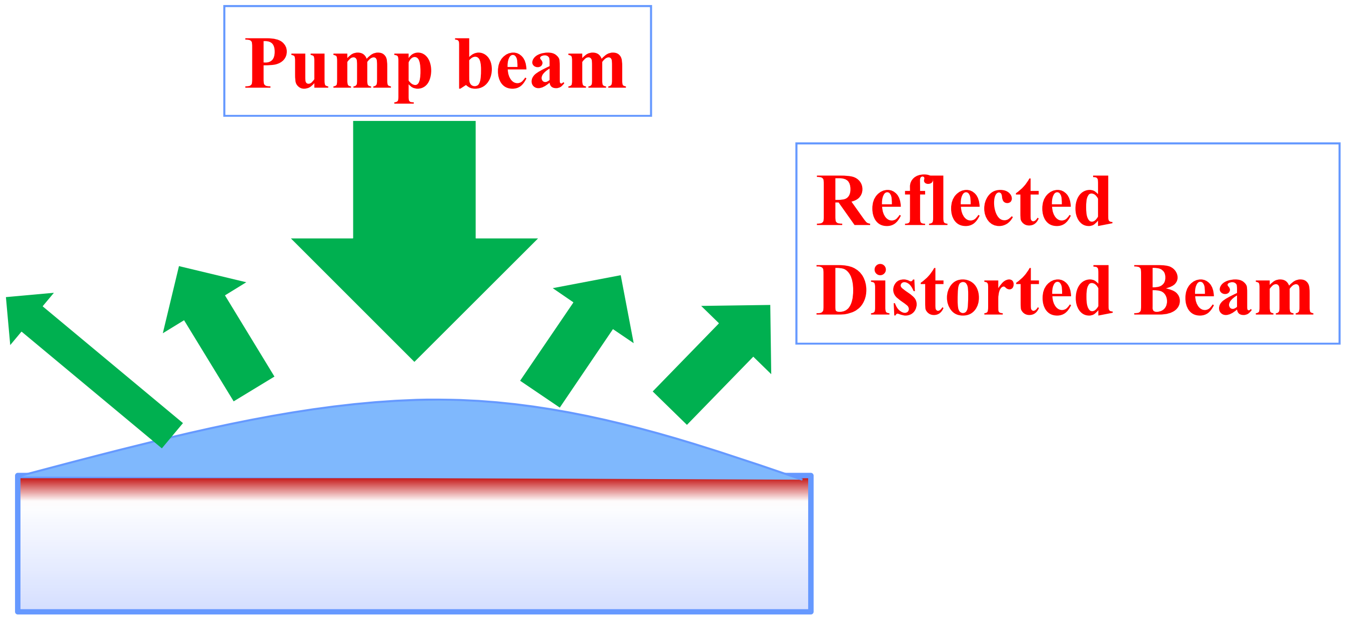




Marcano A., Isaac Basaldua, Aaron Villette, Raymond Edziah, Jinjie Liu, Omar Ziane, and Noureddine Melikechi, “Photothermal lens spectrometry measurements in highly turbid media”, Appl. Spectros. 67 (9), 1013-1018, 2013 (DOI: 10.1366/12-06970).

Photothermal Mirror Method

This method involves the detection of the distortion of a probe beam whose reflection profile is affected by the photo-elastic deformation of a polished material surface induced by the absorption of a focused pump field



Pump beam

Reflected Distorted Beam

Photothermal Micromirror

The theoretical model used to explain the PTM method is based on the simultaneous resolution of the thermo-elastic equation for the surface deformations and the heat conduction equation.

$$\frac{\partial}{\partial t}T - D\nabla^2 T = \frac{\alpha I(r,t)}{C_p \rho}$$

$$(1-2\nu)\nabla^2 \vec{u} + \nabla \cdot \left(\nabla \cdot \vec{u}\right) = 2(1+\nu)\alpha_T \nabla T$$

where ν is the Poisson ratio, α_T is the thermo-elastic

Boundary conditions

$$T(\infty, z, t) = 0$$

$$\sigma_{rz}\big|_{z=0} = \sigma_{zz}\big|_{z=0} = 0$$

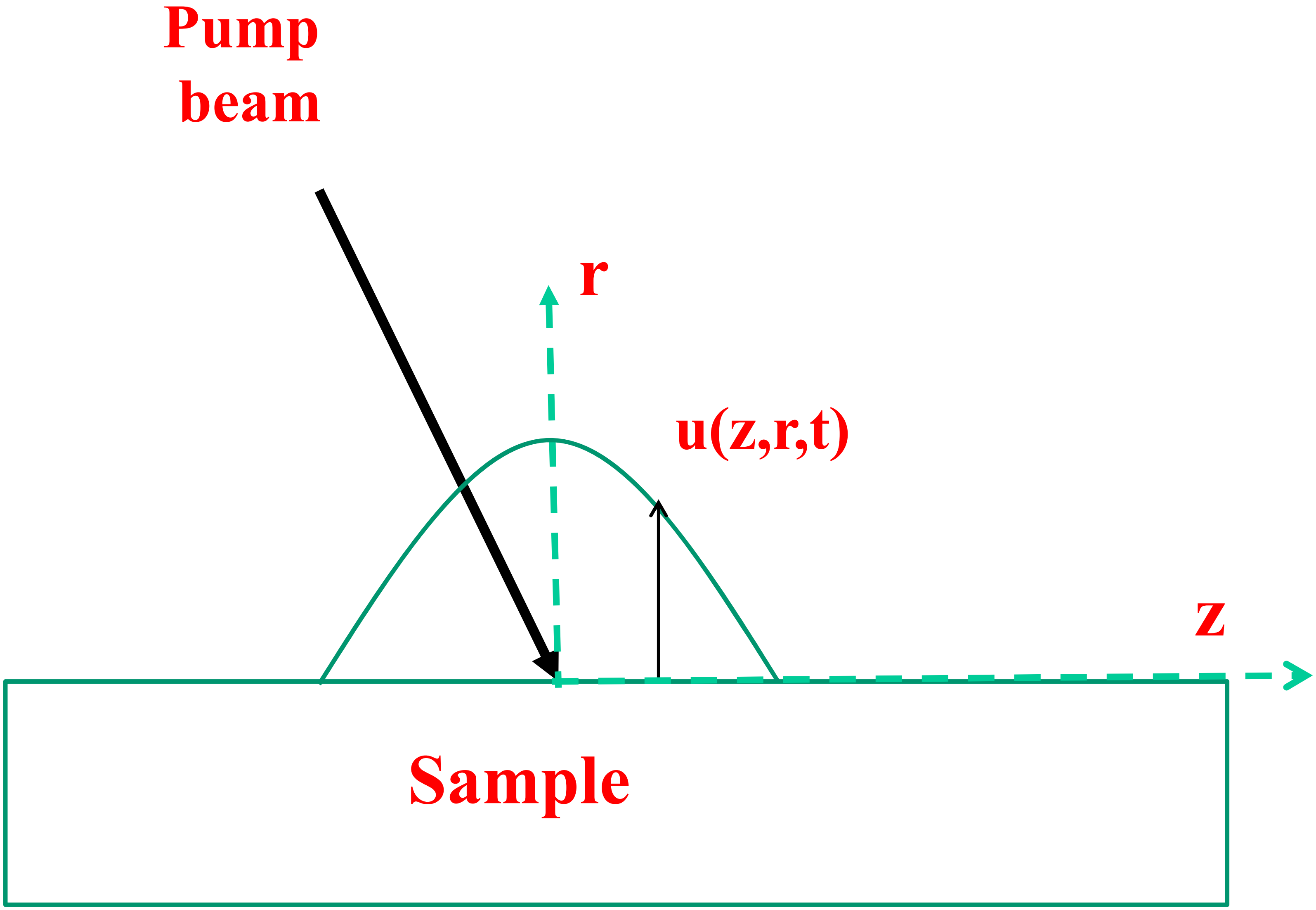
Normal stress components

Initial condition $T(r, z, 0) = 0$

The phase difference will be

$$\Delta\Phi = \frac{2\pi}{\lambda_p}\left[\left(u_z(r,0,t) - u_z(0,0,t)\right)\right]$$

Scheme of the PTM experiment



References for PTM theory

- L. Malacarne, F. Sato, P. R. B. Pedreira, A. C. Bello, R. S. Mendes, M. L. Baesso, N. G. C. Astrath and J. Shen, “Nanoscale surface displacement detection in high absorbing solids by time-resolved thermal mirror”, *Appl. Phys. Lett.*92(13), 131903/3 (2008). DOI: 10.1063/1.2905261.
- F. Sato, L. C. Malacarne, P. R. B. Pedreira, M. P. Belancon, R. S. Mendes, M. L. Baesso, N. G. Astrath and J. Shen, “Time-resolved thermal mirror method: A theoretical study”, *J. Appl. Phys*.104(5), 053520/9 (2008). DOI: 10.1063/1.2975997.
- L. C. Malacarne, N. G. C. Astrath, G. V.B.Lukasievicz, E. K. Lenzi, M. S. Baesso and S. Bialkowski, “Time-resolved thermal lens and thermal mirror spectroscopy with sample-fluid heat coupling: A complete model for material characterization’, *Appl. Spectros*.65(1), 99-104 (2011). DOI: 10.1366/10-06096.
- V. S. Zanuto, L. S. Herculano, M. S. Baesso, G.V.B. Lukazievicz, C. Jacinto, L. C. Malacarne and N.G.C. Astrath, “Thermal mirror spectrometry: an experimental investigation of optical glasses”, *Opt. Mat.*35(5), 1129–1133 (2013).DOI: 10.1016/j.optmat.2013.01.003.
- N. G. C. Astrath, L. C. Malacarne, V. S. Zanuto, M. P. Belancon, R. S. Mendes, M. L. Baesso and C. Jacinto, “Finite size effect on the surface deformation thermal mirror method”, *J. Opt. Soc. Am. B*28(7), 1735-1739 (2011). DOI:10.1364/JOSAB.28.001735.

For opaque materials

$$\Delta\Phi(g,t)=\Phi_o\int_0^\infty \exp\left(-\eta^2/8\right)f(\eta,t)J_o\left(\eta\sqrt{gm}\right)d\eta$$

$$f(\eta,\tau)=(\eta\tau)Erfc\left(\frac{\eta\sqrt{\tau}}{2}\right)-2\sqrt{\frac{\tau}{\pi}}\exp\left(-\frac{\eta^2\tau}{4}\right)+\frac{2}{\eta}Erf\left(\frac{\eta\sqrt{\tau}}{2}\right)$$

where

$$\tau=t/t_c \quad ; \quad g=r/a$$

***Erf(x)* is the error function and *Erfc(x)* is the complementary error function.**

A. Marcano, G. Gwanmesia, M. King and D. Caballero, Opt. Eng., 53(12), 127101 (2014). DOI:10.1117/1.OE.53.12.127101.

$$\Phi_o = -P\psi\alpha_T(1+\nu)(\lambda_p\kappa)^{-1}$$

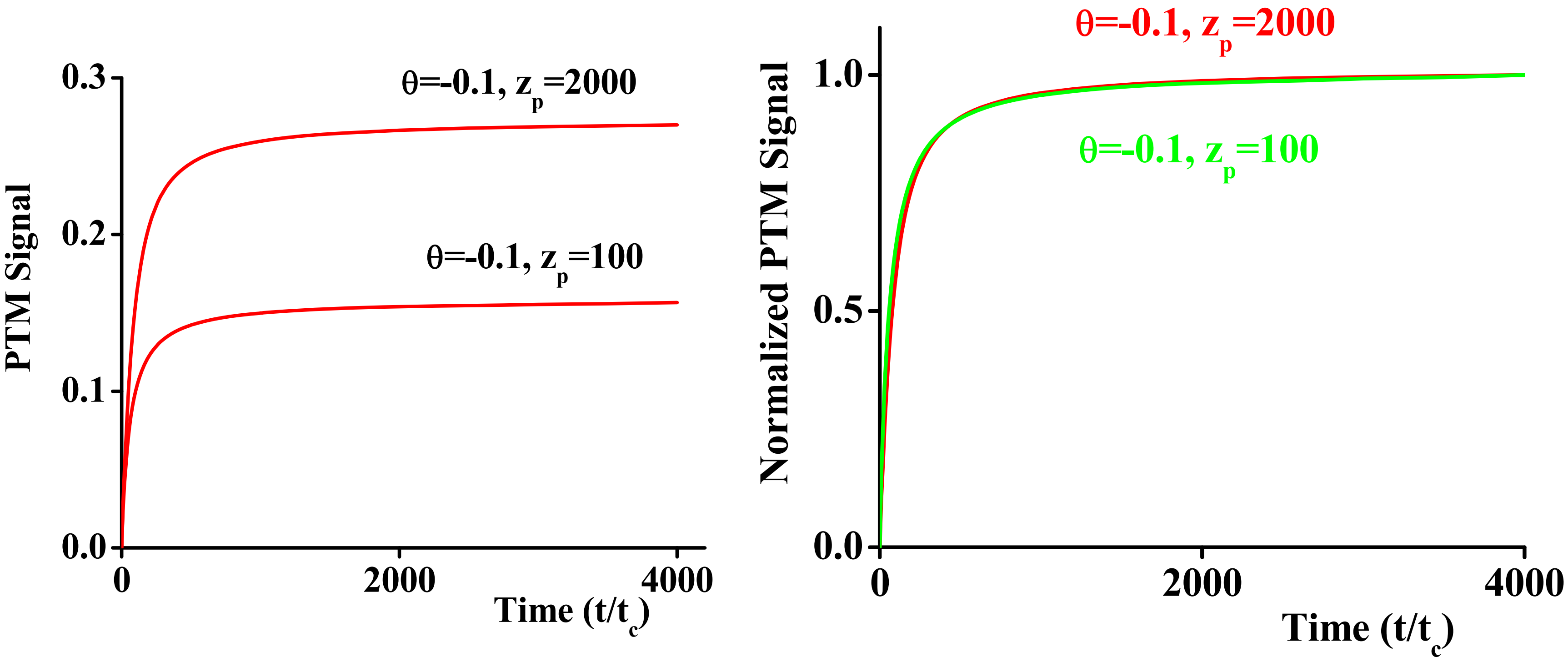
ψ is thermal quantum yield
κ is the thermal conductivity
P is the pump power

$$t_c = \frac{a^2}{4D}$$ PTM time build-up

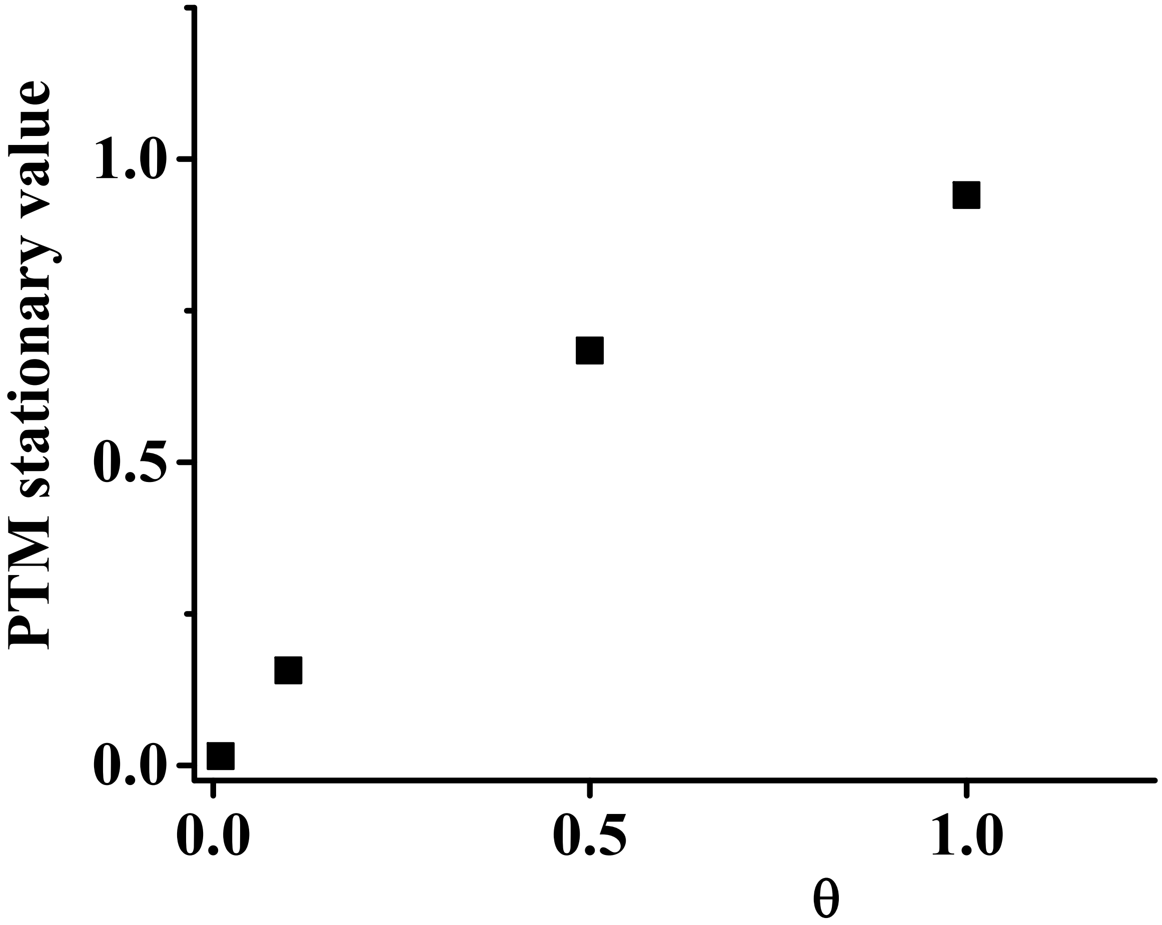
Diffraction theory provides the value of the field amplitude of the center of the probe beam at the detection plane in a similar way it does for the PTL case

$$E_p(t,\Phi) = \int_0^\infty \exp(-(1+iV)g - i\Phi(g,t))dg$$

$$S_{PTM}(t) = \frac{\left|E_p(t,\Delta\Phi)\right|^2 - \left|E_p(t,0)\right|^2}{\left|E_p(t,0)\right|^2}$$

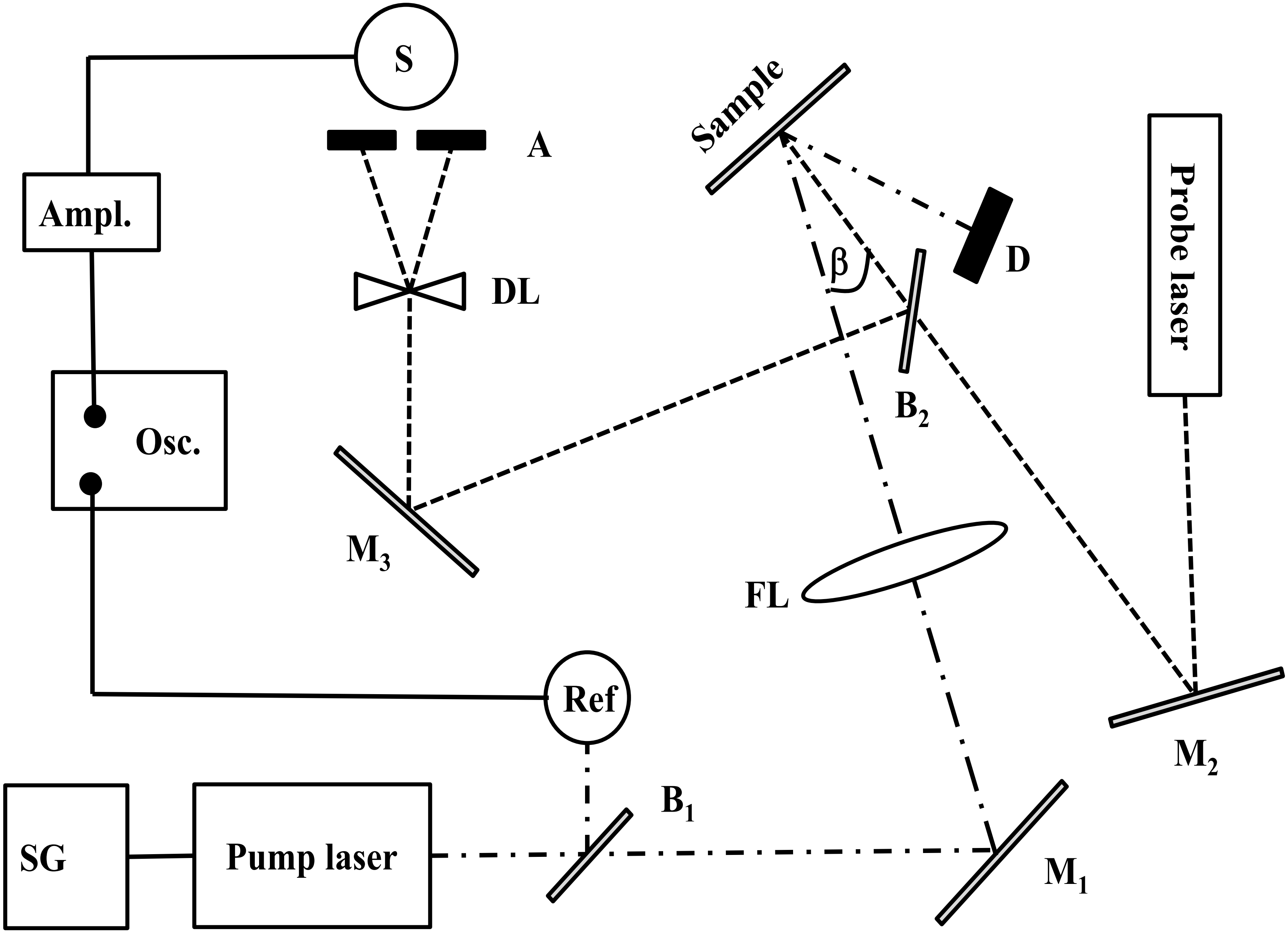


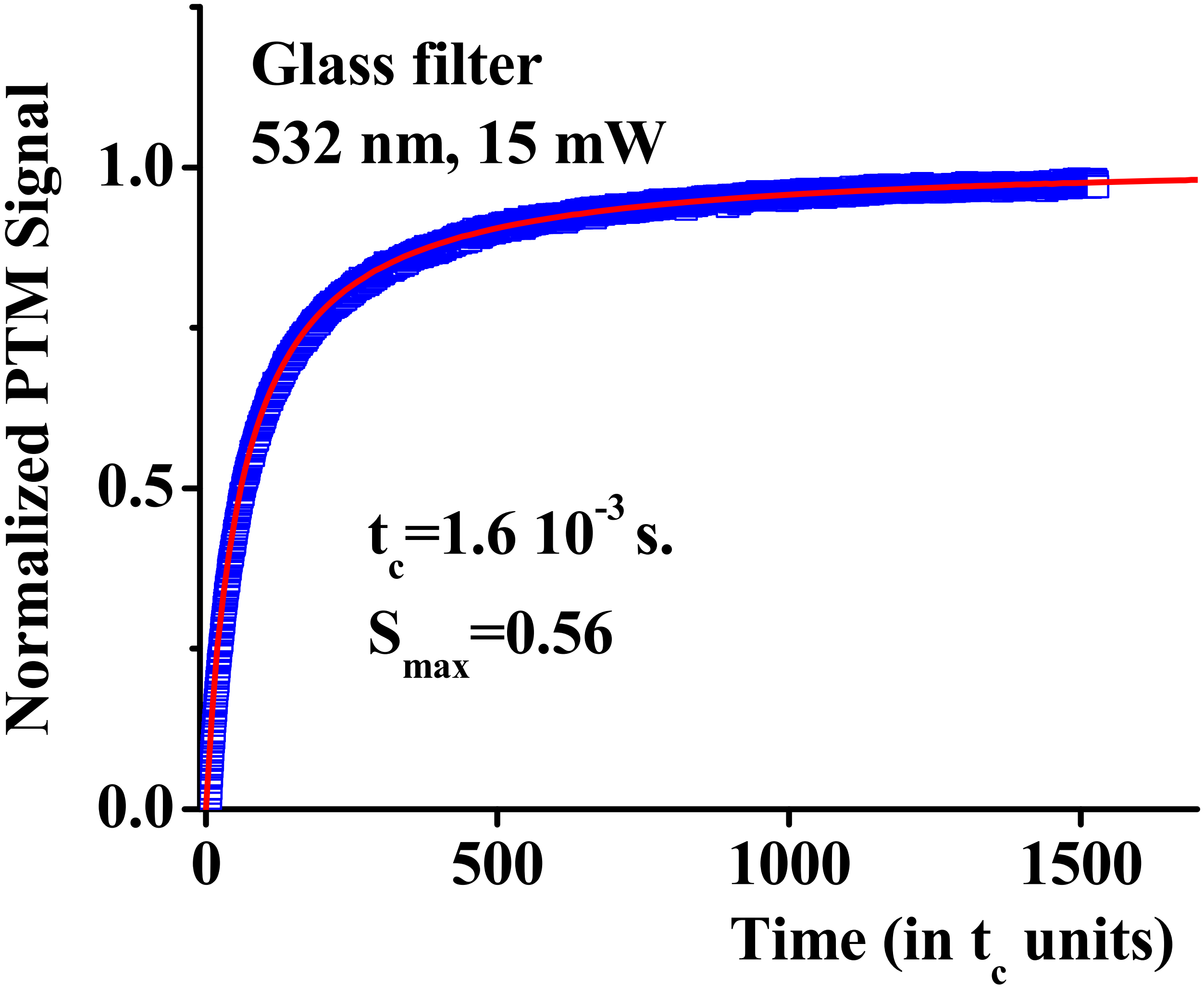
PTM signal for different probe beam Rayleigh ranges

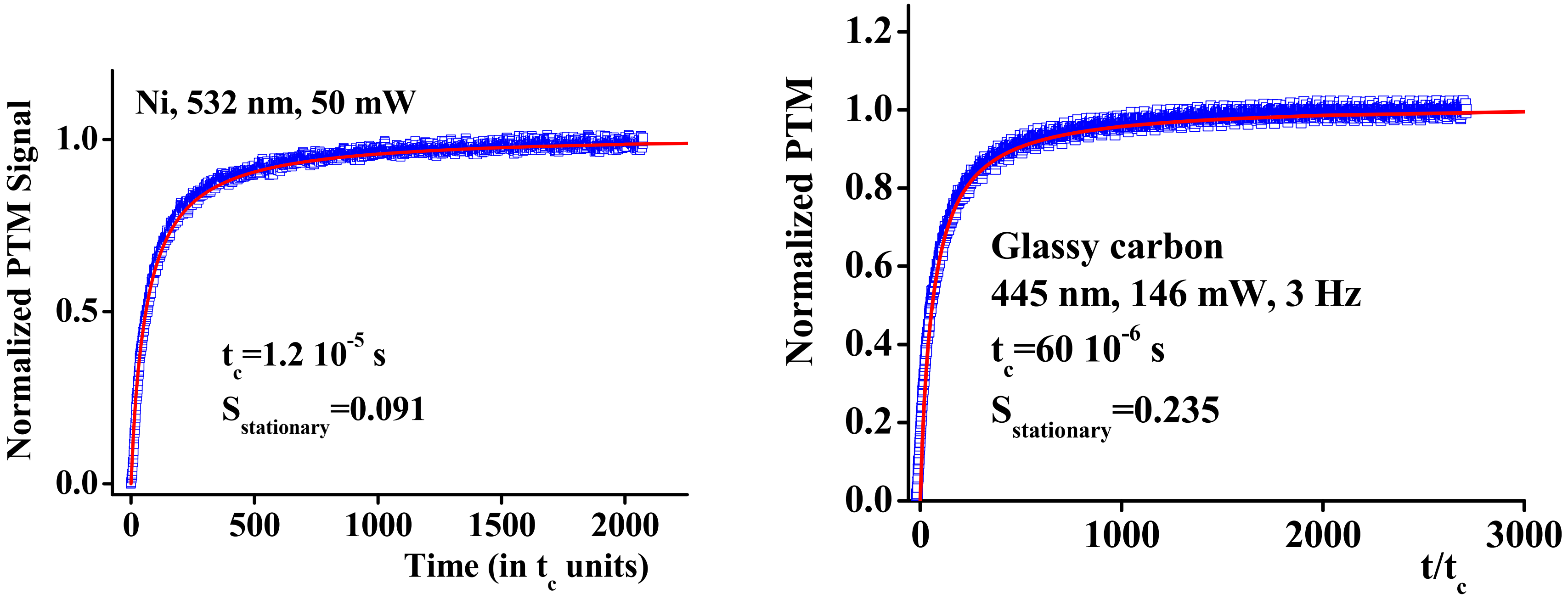


PTM signal as a function of PTM phase amplitude

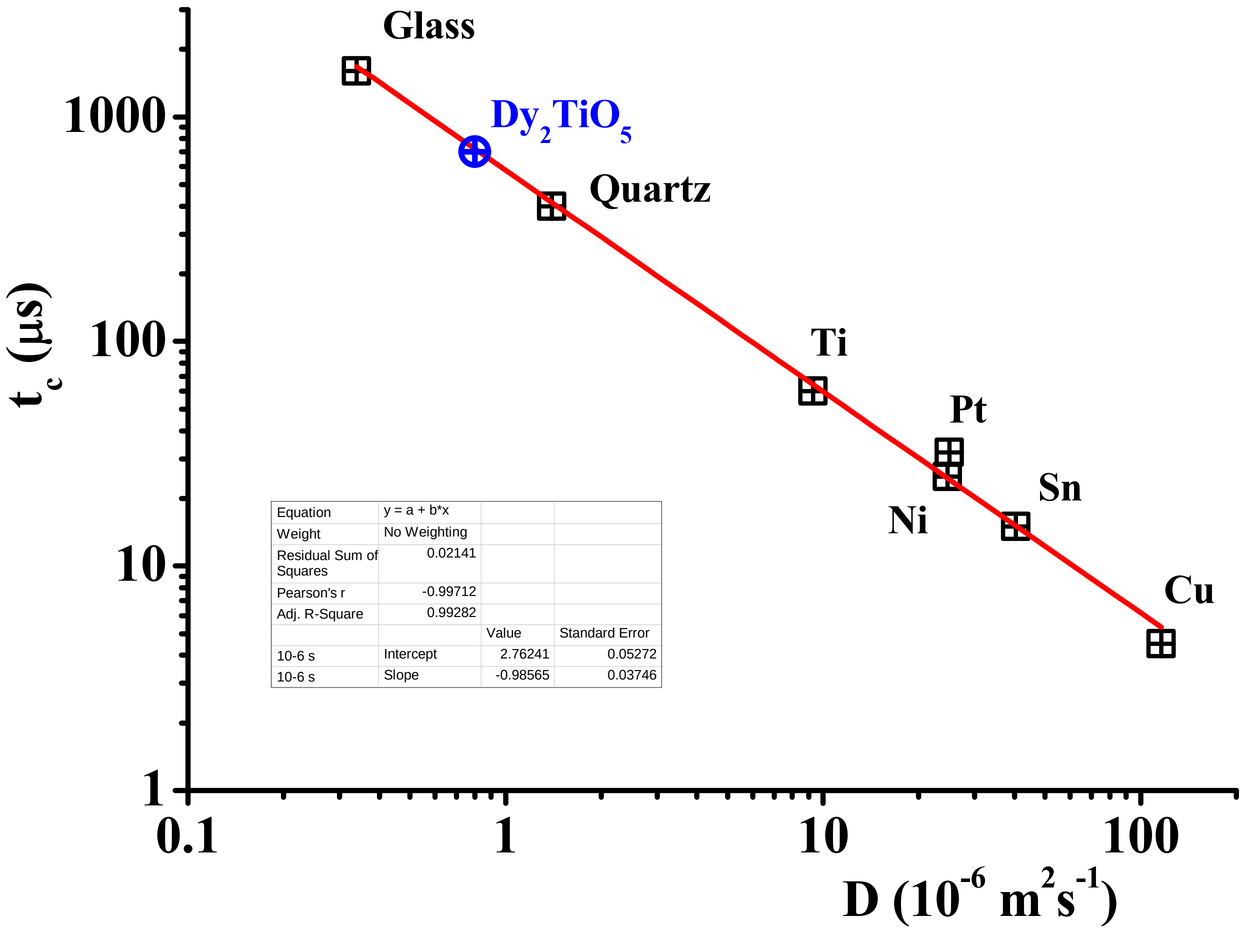
PTM mode-mismatch set-up




Glass filter
532 nm, 15 mW
t_c=1.6 10^{-3} s.
S_{max}=0.56
Normalized PTM Signal
0.0
0.5
1.0
0
500
1000
1500
Time (in t_c units)



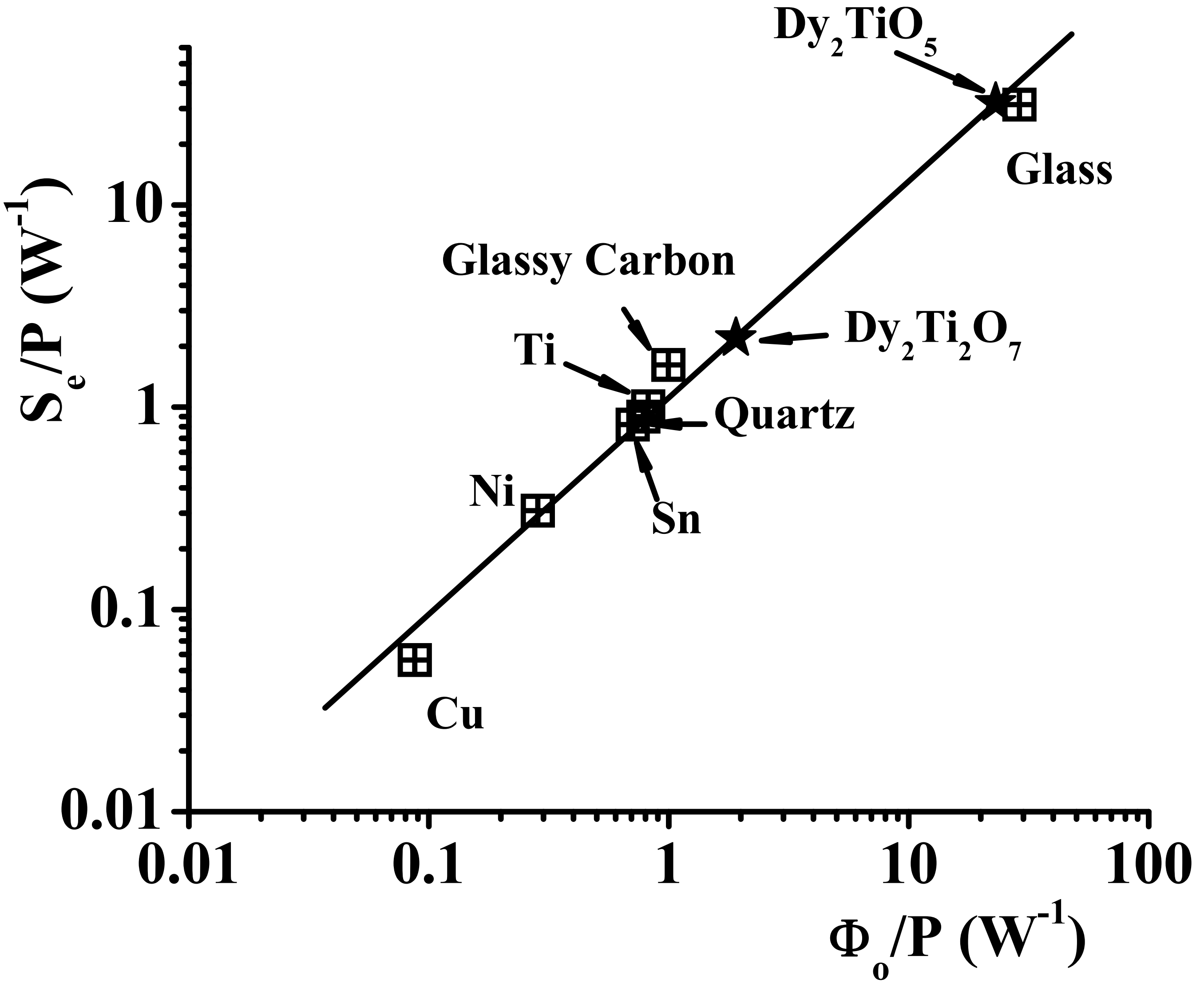
PTM signal from Ni and glassy carbon samples using 532 nm and 445 nm diode lasers



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.02141		
Pearson's r	-0.99712		
Adj. R-Square	0.99282		
		Value	Standard Error
10-6 s	Intercept	2.76241	0.05272
10-6 s	Slope	-0.98565	0.03746

Values of t_c versus D

Stationary value versus PTM phase



Conclusions

PTL and PTM are versatile and sensitive technique to determine the absorption and photothermal properties of matters.

The use of pump-probe configuration allows the implementation of PTL an PTM spectroscopy as new method of analysis.