A New Approach for a Pump-Probe Photothermal Experiment

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Calculations of the signal, observed in a pump-probe photo-thermal experiment, are performed using a close field nonlinear geometrical optics approximation. Dependence of the thermo-optical signal from the position of the detector and magnitude of the beams spots size is studied. It is shown that the possibilities of the thermo-optical experiment, as a highly sensitive technique for light detection, can be substantially improved by increasing the probe beam spot size and varying the position of the detector in the vicinity of the sampl: cell. Prelirninary experimental results are shown for the situation of weak absorbing liquid:;. A good qualitative agreement between theory and experiments is obtained.

I. Introduction

When a beam of light with a transversal Gaussian profile of intensities propagates in an absorbing liquid, a similar spatial d stribution of temperatures, and consequently of the refraction index, is induced. This effect is called therinal lens effect and it is well known since the first days of nonlinear optics when studies on intracavity spectrcscopy were performed.[1-2] Currently there is a renewed nterest in the thermal lens effect due to its potential applications as a highly sensitive optical detector.[3-5] In this detector the lens is generated by a pump field of high intensity or with high absorption in the medium. The generated thermal lens is tested by a probe beam, which is not absorbed in the medium, so it does not form any thermal lens. If the pump field is chopped, defocusing of the probe beam is detected in phase with the pump beam modulation function. In the usual theoretical interpretation of this experimental arrangement, the thermal lens is considered a defocusing one, having one virtual focus (parabolic approximation). This interpretation is true when the probe beam diameter is much smaller than the pump field one. On the other liand, it has been shown experimentally that a good thermo-optical signal is obtained in the opposite situation, when the aberrant effects of the thermal lens become dominant.[6-7] Diffraction theories have been develope1, which allow to estimate the magnitude of the signal in this situation but using a far field approximation.[7-8] Recently, it has been shown that important features of the therrnal lens phenomenum develops in the vicinity of the sample cell.[9] A close field approximation which is valid for any magnitude of the bearns' diameters, has been developed.[10-11] In this work we use this theory to study the possibilities of the thermo-optical method. The magnitude of the signal is calculated as a function of the position of the detector and the magnitude of the beams' diameters. It is shown that there is a position of the detector in the vicinity of the sample cell where the photo-thermal signal reaches its maximum value. Experimental evidence of this effect is shown for water solution of copper hexamine complex ($(Cu(NH_4)_6)^{+2}$) and ethanol solution of iodine. A good qualitative agreement between theory and experiment is observed.

II. Theory

The fundamental equations of the thermai lens effect were obtained in the early seventies using the quasi-optical and nonlinear geometrical optics approximation.[10] They can be rewritten in the following compact way,[11]

$$\frac{dP}{dz} = -\alpha P, \tag{1}$$

$$\frac{dr}{dz} = \theta, \tag{2}$$

$$\frac{d\theta}{dz} = \frac{\beta P}{r}, \tag{3}$$

where, r and z are the transversal and longitudinal coordinates, respectively; a is the absorption coefficient;

P is the power contained in a ray tube of radius r, which is given by

$$P(r,z) = 2\pi \int_0^r I(r',z)r'dr', \qquad (4)$$

$I(r,z)$ is the light intensity; $\theta = \theta(r,z)$ is the inclination to the beam axis of the elementary ray $r = r(z)$; $\beta = \alpha(dn/dT)/(2\pi n_0 \gamma)$; dn/dT is the thermal gradient of the refractive index; n_0 is the unperturbed refractive index and γ is the sample thermal conductivity.

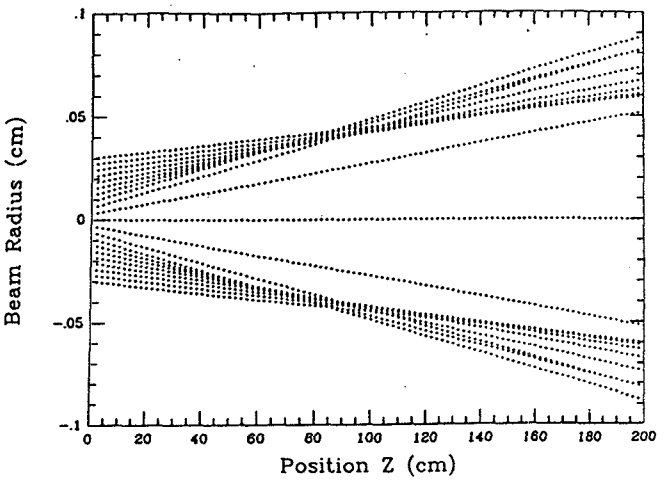

Figure 1.: Defocusing of the probe rays after passing the thermal lens. The position $z = 0$ refers to the rear front of the sample cell. The calculation was performed for a pump field power of 20 mW, and a pump beam radius such that $a_0 = 0.01$ cm, $\alpha = 0.14$ cm^{-1}, and the water thermal parameters $dn/dT = 10^{-4}$ °C^{-1} and $\gamma = 1.3$ 10^{-3} cal/(s cm °C^{-1}).

We consider that the pump field generates the thermal lens, inducing deviations of the probe rays which are given by the function θ. The observed thermo-optical signal P_s is determined by the difference

$$P_s = P_p(d,z) - P_{op}(d,z)\ , \qquad (5)$$

where, $P_p(d,z)$ is the probe field power that propagates through a difragma of radius d located at the position z in the presence of the thermal lens and $P_{op}(d,z)$ is the same magnitude, but measured in the absence of the thermal lens. We assume that the pump field is Gaussian with beam radius a_0.

The pump field power P_0 is calculated integrating Eq. (1). The result is

$$P_0 = \pi I_0 \frac{a_0^2}{2}\left[1 - \exp\left(-\frac{2r_0^2}{a_0^2}\right)\right]\exp(-\alpha_0 z_0), \qquad (6)$$

where I_0 is the pump intensity at the beam center, α_0 is the pump absorption coefficient, z_0 is the length of the

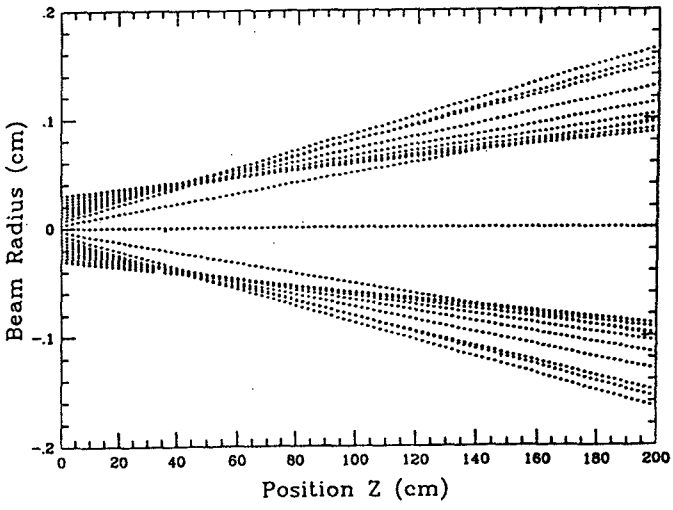

Figure 2.: Defocusing of the probe rays after passing the thermal lens for the same parameters of Figure 1, but for a pump field power of 100 mW.

sample cell and r_0 is the initial radial coordinate. For further calculation we consider that inside the sample cell the beam barely broadens, so we can assume $r = r_0$ in the right hand of Eq. (3) (Thin lens approximation). Taking into account this assumption and inserting Eq. (6) into Eq. (3) we obtain,

$$\theta = \theta_0 + \frac{\sigma}{r_0}\left[1 - \exp\left(-\frac{2r_0^2}{a_0^2}\right)\right], \qquad (7)$$

where $\theta_0 = \theta(z = 0)$ and

$$\sigma = \frac{I_0 a_0^2}{4n_0\gamma}\left(\frac{dn}{dT}\right)(1 - \exp(-\alpha_0 z_0)). \qquad (8)$$

Eq. (7) defines the deviation with respect the initial beam direction of the ray $r(z)$, which has the initial radial coordinate r_0. In other words, θ is a parametric function of r_0. The ray equation $r(z)$ can be obtained inserting Eq. (7) into Eq. (2). After integration we get the straight lines

$$r(z) = r_0 + \theta(r_0)z. \qquad (9)$$

Each ray of light, with initial radial coordinate r_0, is deflected after the thermal lens to an angle given by $\delta = arc\ tan(\theta(r_0))$. In the Figure 1 we have plotted an ensemble of probe field rays deflected by the thermal lens. The parameters used in this calculation are: $dn/dT = 10^{-4}\,°C^{-1}$, $\gamma = 1.2\,10^{-33}$ Cal/(s.cm $°C^{-1}$), $\alpha_0 = 0.14$ cm^{-1}, $a_0 = 0.01$ cm, $I_0 = 300$ W/cm^2, which correspond to the water solution used in the experiments and to a pump power of 30 mW.; the probe beam was considered having a square intensity distribution with a diameter $a_p = 2a_0 = 0.02$ cm. Two

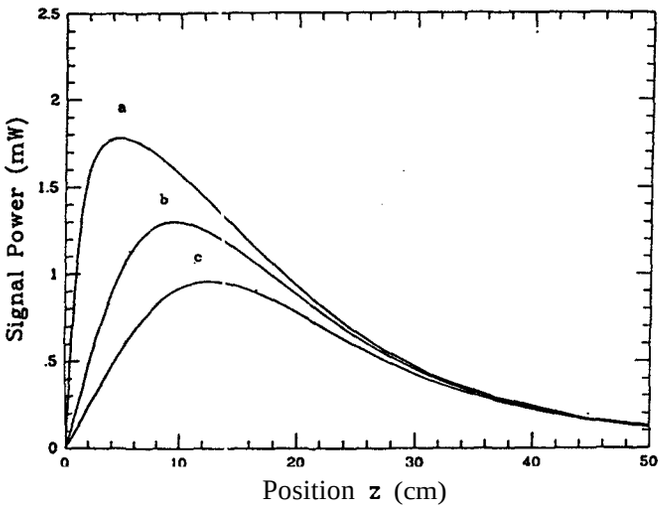

Figure 3.: Photothermal signal as a function of the detector position z for the situation $a_p = 2a_0$ and for different values of the pump field power: 100 mW (line a), 20 mW (line b) and 10 mW (line c). The rest of the parameters are as in Figure 1.

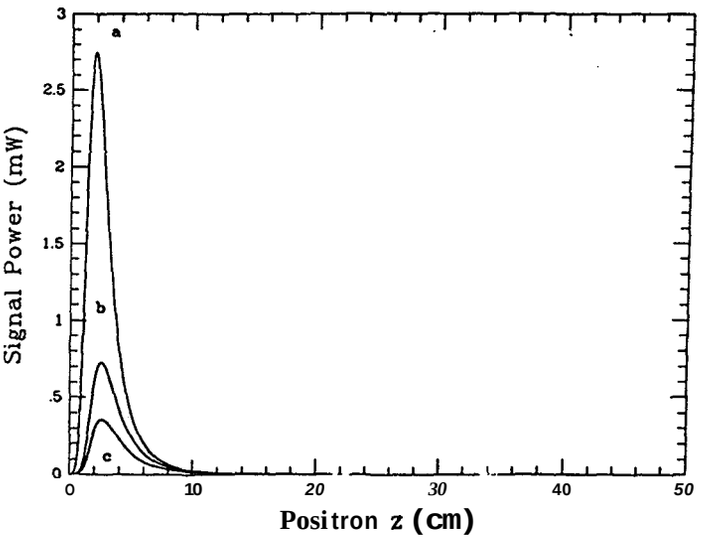

Figure 4.: Photothermal signal as a function of the detector position z for the situation $a_p = a_0/2$ and for different values of the pump field power: 100 mW (line a), 20 mW (line b) and 10 mW (line c). The rest of the pararneters are as in Figure 1.

important features are observed in the probe beam deflection due to the presence of the thermal lens. Firstly, we observe that the beam is strongly deviated to the bearn periphery. A ring shaped structure is generated. This kind of ring shaped structure has been recently reported.[10] Secondly, at a certain distance from the sample cell the probe beam is focused into a ring. The position of the ring of foci depends on the pump field power. In Figure 2 the probe beam rays for the situation of higher piimp power are plotted. As expected, the beam defocusing is substantially increased and the ring of foci is closer to the sample cell. It is obvious that locating the detector in the vicinity of sample cell the photothermal signal reaches its maximum value. As it is shown below, the position z, for which the signal reaches its maximum, is also a function of the pump power. At higher pump power this point is closer to the sample cell.

If we consider that the probe beam is Gaussian with a beam radius a_p, then the probe field power measured by the detector in the presence of the thermal lens is given by

$$P_p = \pi I_{0p} \frac{a_p^2}{2}\left[1 - \exp\left(-\frac{2r_0^2(z)}{a_{pc}^2(z)}\right)\right], \qquad (10)$$

where I_{op} is the probe intensity at the center of the beam. The other parameters are

$$a_{pc}(z) = a_p\sqrt{1+\frac{z^2}{z_c^2}}; \qquad (11)$$

where $z_c = \pi n_0 a_p^2/\lambda$ and λ is the probe wavelenght.

In the calculation of Eq. (10) we have taken into account the usual diffraction effects that take place during the propagation of a Gaussian beam.[12] In Eq. (10) r_0 can be considered a function of z as given by Eq. (9). Therefore, taking into account Eq. (5), the photothermal signal measured at a distance z_c from the sample cell is

$$P_s = \pi I_{op}\frac{a_p^2}{2}\left|\left[1 - \exp\left(-\frac{2r_0^2(z_c)}{a_{pc}^2(z_c)}\right)\right] - \left[1 - \exp\left(-\frac{2d^2}{a_{pc}^2(z_c)}\right)\right]\right|, \qquad (12)$$

where d is the diameter of the diafragma before the detector.

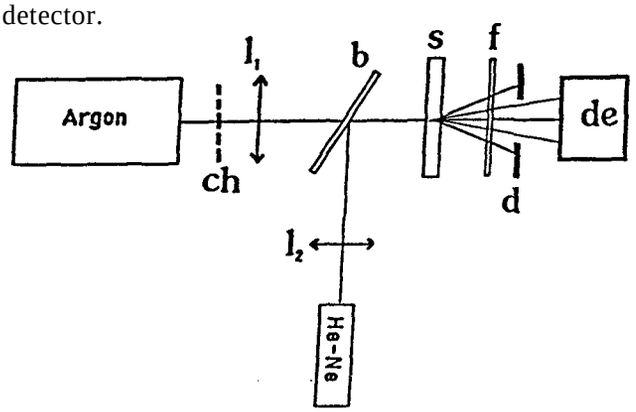

Figure 5.: Experimental set-up of a pump-probe thermal lens experiment consisting in: a pump field (Argon laser), a probe field (He-Ne laser), a chopper (ch), focusing lenses (l_1 and l_2), a beamsplitter (b), a sample cell (s), a filter (f), a diafragma (d) and a detector (de).

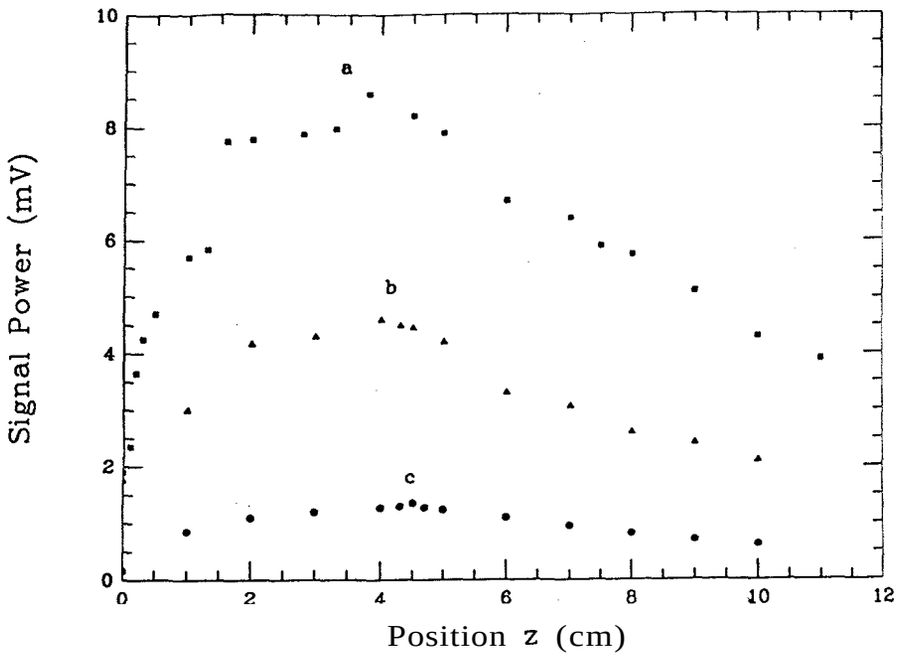

Figure 6.: Photothermal signal as a function of the detector position measured for a 7.5 mMl water solution of $(Cu(NH_4)_6)^{+2}$. The line "a" correspond to a pump field power of 100 mW, the line "b" refers to a pump power of 20 mW and the line "c" to a pump power of 10 mW. The rest of the pararneters are as in Figure 1.

Using Eq. (12) we estimate the photothermal signal as a function of the detector position for different probe beam diameters. In Figure 3 we show the results obtained for different pump field power levels. There is a position of the detector for which the detected signal is maximal. In Figure 4 we have plotted the results for the situation when the probe beam diameter is smaller than the pump field one. The signal in this case is substantially smaller comparing with the previous situation for large z and small power (see lines b and c). Although it is possible to obtain a good signal level in this situation (see line a), the position z for a maximum signal is very close to the cell. Additionally the maximum is very sensitive to small changes of the detector position. These facts make the experiment for measuring the photothermal signal difficult to be performed in this situation. In the next section we show experimental results obtained for a water solution of cupper hexamine complex ($(Cu(NH_4)_6)^{+2}$). A good qualitative agreement between theory and experiments is obtained.

III. Experiment

The set-up used in the pump-probe thermal lens experiment is shown in Figure 5. After passing through the chopper (ch), the ligh from a c.w.Argon laser (λ = 514.5 mm) is focused onto the sample cell using a 20 cm focal length lens l_1. This light generates the thermal lens in the sample cell. After the cell a filter F cancels the pump field. The generated thermal lens is tested by the light of a 1 mW power He-Ne laser (λ = 632 mm), which is focused onto the cell using an independent 20 cm lens l_2 and the beamsplitter (b). This probe light passes through the filter (f), the diafragma (d) and is detected by the detector (de). The samples used were water solution of copper hexamine complex $(Cu(NH_4)_6)^{+2}$ of a concentration of 0.75 mMl. Similar experiment were also performed for a 50 mMl ethanol solution of iodine. The cell was 0.025 cm long. The absorption coefficient in this situation was 14 cm^{-1} approximately. The pump field is chopped at 15 Hz and the signal is detected at the same frequency and amplified using a lock-in amplifier. Moving the detector after the sample cell was possible to measure $P_s(z)$ and changing the position of the lens l_2 was possible to change the probe beam diameter.

We measured the photothermal signal as a function of the position of the detector for different values of the probe beam diameter and different levels of the pump field power. In the Figure 6 the photothermal signal is plotted as a function of the position of the detector for three different values of the pump field power. In this figure it is shown that the signal reaches its maximum value at a given position z. As it is predicted by the theory, the maximum is obtained in the vicinity of the sample cell. The position of this maximum is a function of the pump intensity. For higher pump power this

maximum is closer to the sample cell. This dependence is weak, but it is in a good qualitative agreement with the theoretical predictions (see lines a, b and c in Figure 3).

The photothermal signal was very small when the probe beam spot was smaller than the pump spot. Consequently it was difficult to obtain results similar to the ones presented at Figure 6. From the calculations shown above anc from this experimental result we confirm that for a good photothermal signal it is suggested to use a probe field with a beam radius larger than the pump field one. More experiments are under going in order to have a better comparison between theory and experiment.

IV. Conclusion

The photothermal signal of a pump-probe thermal lens experiment is calculated using the quasi-optical nonlinear geometrical optics approximation. It is shown that the magnitude of the signal is strongly dependent on the pump field power and that there is a position of the detector for which the signal reaches its maximum value. Experiments performed in water solution of the copper hexamine complex and ethanol solution of iodine are in good qualitative agreement with the theoretical predictions.

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