January 1, 1985

Photothermal Lens Aberration Effects in Two Laser Thermal Lens Spectrometry

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A comparison of theories describing two laser photothermal lens signals is given. The aberrant nature of this lens is accounted for in a theory which treats the propagation of a monitor laser in terms of a phase shift in this laser beam wave front. The difference between theories are discussed in terms of the predicted signal strengths and temporal behavior. The aberrant theory results in smaller theoretical signal strengths and different functional relationships between signal and analyte level.

One of the issues that many have addressed through both experimental and theoretical investigation is that of the beam overlap in two laser photothermal lens spectrophotometry (TLS). The problem is difficult to address because of the many degrees of freedom in these experiments.[1] In two laser TLS, the monitor laser beam is characterized by a beam waist and a radius of curvature of the wave front at the photothermal lens. This photothermal lens is formed by absorption of radiation from a pump laser beam. Although the pump laser induced photothermal lens is of a Gaussian profile, its effect on the propagation characteristics of the monitor beam is generally assumed to be due to propagation through a parabolic medium. The latter parabolic lens medium approximation greatly simplifies calculations. For short optical path lengths, the parabolic medium is a simple lens defined by only a focal length.

To address the fact that there are several degrees of freedom in these experiments, many researchers have assumed that a maximum TLS signal will occur when the beam waist of the monitor laser is equal to that of the pump laser.[1–4] Furthermore, since the maximum TLS signal will be obtained when the beam waist of the pump laser is a minimum, i.e., focused into the absorbing medium, this places further constraints on the adjustable experimental parameters, allowing the monitor laser beam characteristics (focus position and minimum spot size) to be varied over a relatively small range of values.[1,5]

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Received 3 April 1985.
0003-6935/85/172792-05$02.00/0.

It is the purpose of this paper to address the first assumption. The questions that are posed here are: How accurate are the parabolic lens approximation equations when the beam waists are matched? If this is not a good approximation, what are the optimum beam characteristics of the monitor laser in these two laser TLS experiments?

Formation of the photothermal lens by a pump laser propagating in the fundamental TEM_{00} mode has been addressed by Twarowski and Kliger[2] and others. The results have been keenly summarized by Fang and Swofford.[1] Basically, for pulsed laser excitation, the pump laser produces a time-dependent refractive-index perturbation given by

$$n(r,t) = n_0 + \left(\frac{dn}{dT}\right) \frac{2\ln 10 AEp}{\pi\omega_p^2(1 + 2t/t_c)\varphi Cp} \exp\left[\frac{-2r^2}{\omega_p^2(1 + 2t/t_c)}\right], \quad (1)$$

where A is the sample absorbance, Ep is the pump laser energy in joules, ω_p is the pump laser beam waist electric field radius, t_c is the characteristic time constant equal to $\omega_p^2/4K$, K being the thermal diffusivity of the sample, and the product φC_p is the density-dependent heat capacity. In the parabolic lens approximation, the time-dependent focal length of the thermal lens $f(t)$ is determined from the curvature of the refractive index at zero radius and integrated over the path length of the sample medium[6]:

$$\frac{1}{f(t)} = \frac{1}{n_0}\frac{dn}{dT}\frac{8\ln 10 AEp}{\pi\varphi C_p}[\omega_p^2(1 + 2t/t_c)]^{-2}. \quad (2)$$

The TLS signal is due to the change in monitor laser beam intensity passing through a pinhole placed some distance d from the sample. Twarowski and Kliger have shown that for a monitor laser beam focused at a distance z in front of the sample, the on-axis ($r = 0$) signal is given by

$$\frac{I(t)-I(\infty)}{I(t)} = 2\frac{d}{f(t)}\left[\frac{zd+(z^2+z_R^2)}{z_R^2+(d+z)^2}\right] - \left(\frac{d}{f(t)}\right)^2\left[\frac{z_R^2+z^2}{z_R^2+(d+z)^2}\right], \quad (3)$$

where z_R is the Rayleigh range of the monitor laser.

Several assumptions were made in deriving Eq. (3). Most important are that the fraction of pump laser energy absorbed by the sample is small and that the length of the sample is short. Together, these assumptions insure that the amount of energy deposited in the sample is a constant over the length of this sample and that the radial dependence of the deposited energy is also independent of distance through the sample.

Although the latter theory yields an analytical result which defines the TLS signal as a function of sample absorbance, it is intuitively incorrect since it does not account for the real profile of the photothermal lens, which is not parabolic, nor does it account for monitor laser beam waist variations other than through the wave front curvature implicitly defined in the Rayleigh range and focus spot distance. An alternative to the parabolic lens approximation has more recently been described by Weaire *et al.* in their studies of nonlinear refraction in InSb.[7]

In the latter theory of the laser intensity change at the detector, the effect of the nonlinear refractive index is treated in terms of a radially dependent phase shift in the light propagation equation. Calculation of the signal for a two laser TLS experiment can be performed in a similar fashion. The phase shift of a ray of wavelength λ propagating through a length l of medium that has undergone a small temperature change of dT is

$$\Delta\phi = \frac{-2\pi l}{n_0}\left(\frac{dn}{dT}\right)dT. \quad (4)$$

Similarly, for an equivalent on-axis temperature change, the parabolic TLS focal length at $t = 0$ is

$$\frac{1}{f_0} = \frac{4l}{n_0\omega_p^2}\left(\frac{dn}{dT}\right)dT, \quad (5)$$

and the phase shift is related to the parabolic TLS focal length by

$$\Delta\phi = \frac{-\pi\omega_p^2}{2\lambda}\left(\frac{1}{f_0}\right), \quad (6)$$

which can be used to compare directly the result of the two theories. A typical TLS focal length is -10^3 m, and for $\omega_p^2 = 7.3 \times 10^{-7}$ m^2 and $\lambda = 632.8$ nm, which is typical in our experiments,[5] the maximum on-axis phase shift is ~0.002 rad. Conversely, for a phase shift of $\Delta\phi = 1$, the focal length is -1.8 m, which is about the minimum focal length we have observed. With such small phase shifts the theory described by Weaire *et al.* is certainly valid.

For simplicity, it is assumed that the monitor laser is focused with a minimum beam waist ω_0 in the sample and that the optical path length of the sample medium is less than the Rayleigh range. The radially dependent phase shift can be calculated from Eq. (1) as

$$\Delta\phi/(r,t) = \frac{2\pi l}{\lambda}[n_0 - n(r,t)]. \quad (7)$$

The electric field of the monitor laser as it emerges from the sample at $z = 0$ is

$$E(r,o) = E(o,o)\exp\left[\frac{-r^2}{\omega_0^2} + i\Delta\phi(r,t)\right]. \quad (8)$$

Expanding the Gaussian radially dependent portion of this complex phase shift results in the series

$$E(r,o) = E(o,o)\sum_{m=0}^{\infty}\frac{[i\Delta\phi(o,t)]^m}{m!}\exp\left(\frac{-r^2}{\omega_m^2}\right), \quad (9)$$

where $\omega_m^2 = [2m\omega_0^2 + \omega_p^2(t)]/\omega_0^2\omega_p^2(t)$; $\omega_p^2(t) = \omega_p^2(1 + 2t/t_c)$ and $\Delta\phi\,(o,t) = -4l\ln(10)AEp(dn/dT)/\omega_p^2(t)\varphi C_p$ or can be related to the parabolic focal length through Eqs. (2) and (6). The calculation of the electric field at a distance d from the sample is reduced to the calculation for that of a series of TEM_{00} beams.

$$E(r,d) = E(o,o)\sum_{m=0}^{\infty}\frac{[i\Delta\phi(o,t)]^m}{m!}\left(1+\frac{d^2}{z_m^2}\right)^{-1/2} \times \exp\left\{-r^2\left[\frac{1}{\omega_m^2(d)} + \frac{ik}{2Rm(d)}\right] + iP_m(d)\right\}, \quad (10)$$

where $\omega_m(d) = \omega_m(0)(1 + d^2/z_m^2)^{,1/2}$ $R_m(d) = d(1 + z_m^2/d^2)$, $P_m(d) = \tan^{-1}(d/z_m)$, $z_m = \omega_m^2(0)/\pi\lambda$, $\omega_m^2(0) = \omega_0^2\omega_p^2(t)/[\omega_0^2 + \omega_p^2(t)]$, and $k = 2\pi/\lambda$. Finally, the $r = 0$ electric field is

$$E(o,d) = E(o,o)\sum_{m=0}^{\infty}\frac{[i\Delta\phi(o,t)]^m}{m!}(1 + d^2/z_m^2)^{-1/2}\exp[iP_m(d)], \quad (11)$$

which can be used to calculate the TLS signal since $I \propto E*(o,d)E(o,d)$ at the detector.

Although this result is not analytical and thus less appealing than that of Eq. 3, the theory does incorporate the effect of a finite monitor beam waist and the aberrant nature of the photothermal lens. The calculations are not as formidable as they first appear. Even with large on-axis phase shifts on the order of unity, the series converges rapidly, and calculations of the TLS signals take well under 1 sec on a DEC VAX computer. It may also be noticed that the first term in the series is that of the propagation of the monitor laser in the absence of any phase shift. This fact shortens the calculation time requirements for the TLS signal as defined by the intensity dependence in Eq. (3).

The restriction that the monitor laser be focused into the sample is not necessary but is imposed only to simplify the calculated signal. The effect of this condition on the resulting TLS signals has been tested in accordance with the theory of Twarowski and Kliger. A program was written which scanned the focus position of the monitor laser relative to the photothermal lens under the constraint that the spot size of the pump and monitor laser be equal at the sample. This constraint limited the range over which the distance could be varied. For each monitor laser focus to photothermal lens distance, a new detector position was calculated for the maximum TLS signal.[5] It was found that the TLS signal does not vary with the monitor laser focus position at the optimum detector distance. Thus the results presented below may be taken as being generally valid for all pump–monitor laser optical geometries.

To address the questions pertaining to the validity of matching beam waists, a set of conditions similar to those of our previous experiments was chosen.[5] In particular, the pump laser beam waist electric field radius was 0.8 mm; a He–Ne laser (λ = 632.8 nm) was used as the monitor; and an optimum detector distance of 3.61 m, as determined by the procedure prescribed above, was used in the calculations. Figure 1 illustrates the effect of the probe laser beam waist radius on the calculated TLS signal. The upper line is that for the parabolic lens approximation, and the lower line was calculated using the phase shift method with matched beam waists. Both calculated TLS signals demonstrate nonlinearities due to the large phase shift and correspondingly small focal length. Although it is not apparent from this figure, both lines show similar curvature when plotted on a relative scale so that the maximum values of each line are equal. They are, however, not identical. A comparison of the TLS signal theories for a monitor laser beam waist which is much smaller than that of the pump laser is shown in Fig. 2. In this case, the differences between the two theoretical descriptions are aparently insignificant.

Another critical point to address in comparing the two theories is that of the temporal behavior of the TLS signal. Figure 3 illustrates the temporal behavior of both theories for a small phase shift. Again the beam waists are matched in the sample. Data of this type, e.g., time resolved, have been used to determine thermal conductivities of the sample medium.[8–10] It is clear from this figure that different values of t_c would be derived from the two curves. However, both theoretical curves result in a straight line when the inverse square root is plotted relative to time. Thus the calibration procedure used by Bailey *et al.*[9] is no doubt an important experimental procedure and should insure accurate thermal conductivity determinations. As may be gleaned from Fig. 2, the temporal behavior of the TLS signal is not dependent on the particular theory when the monitor laser beam waist is very small compared with that of the pump. Subsequently, thermal conductivities may be able to be determined without apparatus calibration if this condition is met.

The ratio of the TLS signals calculated using both methods is illustrated in Fig. 4 as a function of the beam waist ratio ω_0/ω_p. The phase shift TLS signal is equal to that of the parabolic lens in the limit as ω_0 approaches zero. This is not surprising given the fact that the focal length of the parabolic lens is calculated from the curvature of the refractive-index profile at zero radius. To address the question of the maximum TLS signal, the theoretical phase shift TLS signal has been calculated as a function of the beam waist ratio. A typical result of these calculations is shown in Fig. 5. These data are of a small 0.001 phase shift and again are for conditions of previous experiments. The fact that the relative TLS signal increases with the monitor to pump beam waist ratio is surprising. The curvature of a Gaussian shaped refractive-index profile decreases as the radius increases. Since for most materials (dn/dT) is negative, the photothermal lens has a negative on-axis focal

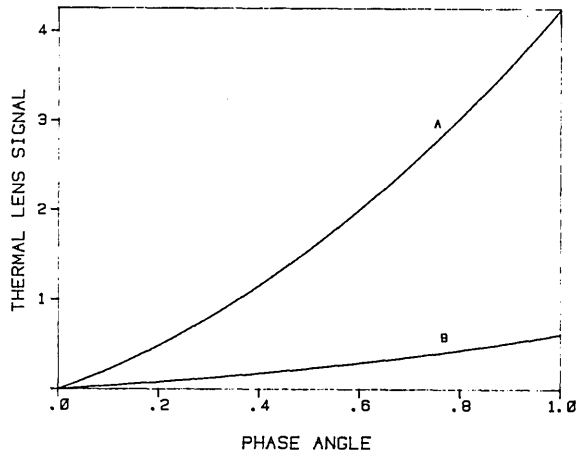

Fig. 1. Comparison of the parabolic lens theory A to the phase shift theory B for ω_p = 0.8 mm, ω_0 = 0.8 mm, d = 3.61 m.

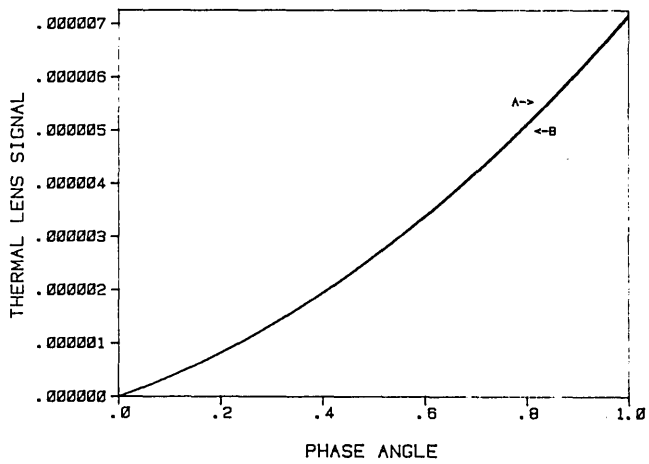

Fig. 2. Comparison of the parabolic lens theory A to that of the phase shift B for ω_p = 0.8 mm, ω_0 = 0.025 mm, d = 3.61 m.

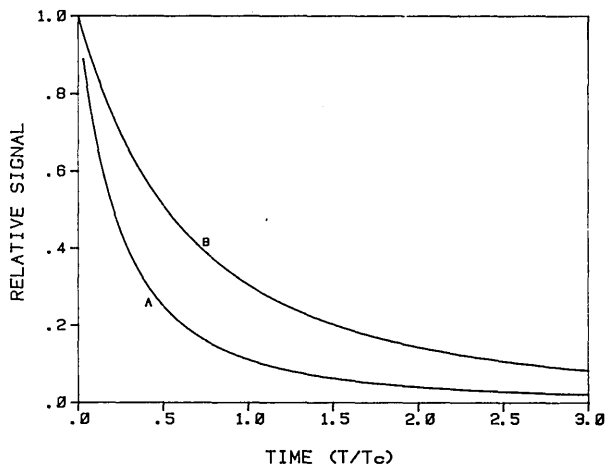

Fig. 3. Relative temporal TLS signals for the parabolic lens theory A and phase shift theory B for $\Delta\phi$ = 0.001, ω_p = 0.8 mm, ω_0 = 0.8 mm, d = 3.61 m. The magnitude of B is a factor of 6 less than that of A on an absolute basis.

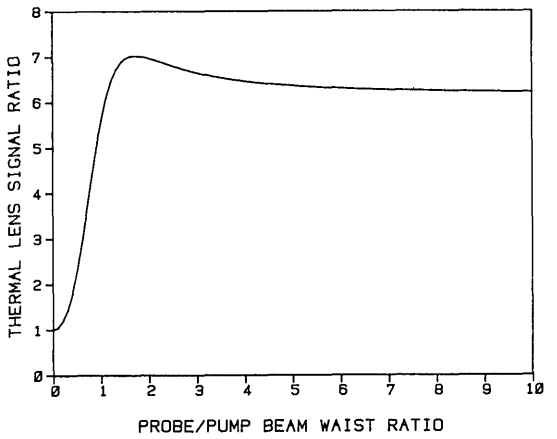

Fig. 4. Ratio of the parabolic lens TLS signal to that of the phase shift for conditions as in Fig. 3.

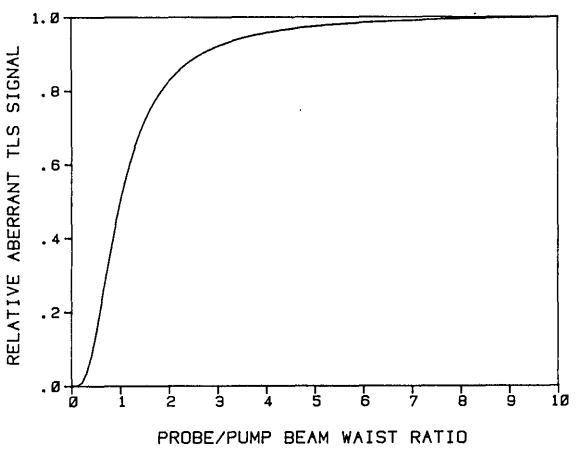

Fig. 5. Phase shift TLS signal as a function of monitor beam waist. Conditions are those of Fig. 3.

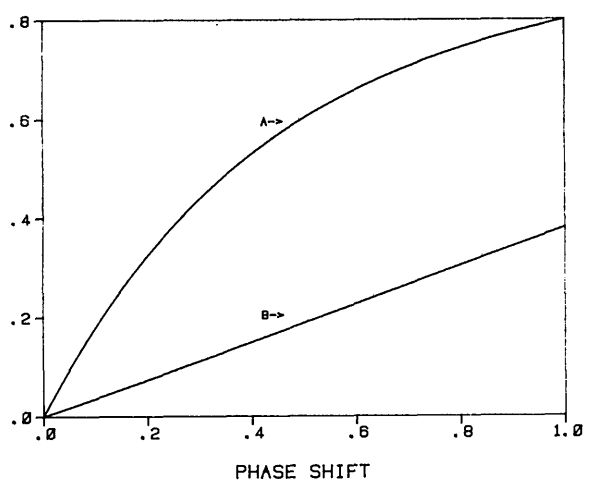

Fig. 6. Comparison of parabolic lens A to phase shift B for conditions identical to that of Fig. 1 but with a different signal definition.

length; that is, the on-axis portion of the monitor laser will diverge. At larger radii, the photothermal lens has a positive focal length due to the positive curvature of the Gaussian refractive-index profile. In fact,

$$\frac{1}{f(r)} = K \exp(-2r^2/\omega_p^2) \left\{\frac{4r^2}{\omega_p^2} - 1\right\}, \tag{12}$$

where the constant K is dependent on the magnitude of the phase shift. Thus one would expect the TLS signal to decrease with increasing monitor laser beam waist, since that portion of the monitor laser beam profile at radii $>\omega_p/2$ will be focused toward the detector, while the on-axis portion will be defocused.

This apparent discrepancy is in part due to the definition of the TLS signal [Eq. (3)] where the change in intensity is divided by the intensity during the time that the photothermal lens is present. This signal definition was chosen because it is proportional to the on-axis temperature change (neglecting the second-order inverse focal length term) and subsequently proportional to the absorbance. In the parabolic lens approximation, this linear dependence is important in analytical applications such as spectroscopy and quantitative spectrophotometry. Another reason for the TLS signal increase with increasing monitor laser beam waist radius is that the strength of the photothermal lens in Eq. (12) decreases in an exponential fashion with squared radius. This Gaussian dependence will result in smaller positive focal lengths for off-axis rays than the negative on-axis focal length.

The signal defined in Eq. (3) may result in a maximum linear range in the parabolic lens approximation but does not necessarily result in a maximum linear range in the phase shift theory. A comparison of the parabolic lens theory with that of the phase shift for a signal definition of $[I(oo) - I(t)]/I(oo)$ is illustrated in Fig. 6. Other than this difference in signal definition, the parameters are the same as those used to calculate the results in Fig. 1. This signal definition results in a linear signal with respect to phase change for the phase shift theory. Compared to Fig. 1, this latter data suggest that this is a better way to define the signal for analytical applications. However, although the phase shift theory yields a signal, as defined here, which exhibits a linear relationship to the phase shift at this particular detector distance, it has been found that at distances other than this optimum, the signal is not linear. The reason for this fact is not clear at this point but nonetheless suggests an empirical method for maximizing the linear range. That is, (1) the best detector distance is calculated from the parabolic lens theory for the particular optical geometry[5]; (2) the signal is defined as $[I(oo) - I(t)]/I(oo)$. An exact derivation of the optimum distance for signal linearity may be obtained from the phase shift theory intensity equations. To perform this calculation, the zero root of the second derivation with respect to detector distance may be found. It appears that this differential must be evaluated numerically.

To summarize: it has been shown that the parabolic lens approximation is accurate only in the limit of a

small monitor beam waist relative to that of the pump. However, this should not be taken as an invalidation of data interpreted in terms of the latter approximate theory. Quantitative data on thermal conductivities, analyte concentrations, etc. may still be obtained, but these data cannot be obtained directly from the TLS signal. Working curves or calibrations must be obtained and the resulting TLS signals interpreted relative to these results. The monitor beam waist dependence on the TLS signal has also been more accurately described using the phase shift theory. The conclusion to be gleaned from Fig. 5 is that the greater the monitor beam waist the greater the TLS signal. This result may prove useful for future optimization of experiment design for quantitative measures of trace analytes.[5] Although the theory developed here was for a pulsed pump laser created thermal lens, this theory will work equally well for cw laser excitation. Treatment of the latter TLS signals will vary only in the form of the refractive index [Eq. (1)].

This research was supported in part by BRSG S07 RR07093-17 awarded by the Biomedical Research Support Grant Program, Division of Research Resources, National Institutes of Health.

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PHYSICS

MEASUREMENTS REDUCE LIMIT FOR ANISOTROPY OF SPACE

Is there a preferred reference frame in space? According to Einstein's Theory of General Relativity, the answer is "no," and physicists at NBS have confirmed this with an experiment based on atomic clocks that is 300 times more sensitive than any previous measurement. In a test of spatial anisotropy, NBS scientists made comparisons between a hydrogen maser atomic clock and a clock based on laser-cooled beryllium ions stored in a magnetic trap. If there were a preferred direction in space, the hydrogen maser would be relatively unaffected while the rate of the ion-based clock would be dependent on its orientation in space. The experiments, conducted by John Prestage, John Bollinger, Wayne Itano, and Dave Wineland, showed no dependence, within 100 microhertz, of the relative clock rates on their orientation with respect to the sun or fixed stars. This represents about a 300-fold improvement over the 1961 Hughes et al./Drever experiments based on careful nuclear magnetic resonance measurements.