Appl. Phys. B 54, 538–543 (1992)

Applied Physics B Photophysics and Laser Chemistry

Sensitivity Enhancement in Thermal Lens Laser Spectrometry

J. Slaby* **and F. Träger****

Physikalisches Institut der Universität Heidelberg, Philosophenweg 12, W-6900 Heidelberg, Fed. Rep. Germany

Received 1 November 1991/Accepted 20 February 1992

Abstract. A novel experimental configuration for thermal lens detection is described. The method makes use of optical filtering of the probe beam by means of a circular aperture. This considerably reduces noise associated with intensity fluctuations of the probe beam. The technique provides an enhancement of the signal-to-noise ratio by almost one order of magnitude as compared to other thermal lens laser spectrometers. A theoretical calculation of the signal enhancement associated with optical filtering of the probe beam is presented. Furthermore, experiments on methyl blue dissolved in ethylalcohol are described which verify the theoretical predictions.

PACS: 07.65.–b, 78.20.Nv, 66.60+a

Photothermal and photoacoustic spectroscopies are based on the absorption of light in a sample followed by radiationless deexcitation and local heating. The detection of such processes makes possible extremely sensitive absorption measurements, particularly for species that do not emit fluorescence but convert the electronic or vibrational excitation energy into heat. Applications include areas like analytical chemistry or trace analysis in environmental research, to mention only two examples. For solid samples, detection most commonly relies on the photoacoustic effect [1], the *gas-coupling* version of which was investigated theoretically by Rosencwaig and Gersho [2]. For liquids, a very sensitive method to detect heating by absorption of electromagnetic radiation and eventually determine the absorbance, is to record variations of the index of refraction caused by a local rise of the sample temperature. An important technique for such measurements is based on the observation of a thermal lens in the sample [3]. It gives rise to a change of the spatial divergence of a probe laser beam which causes a variation of the light intensity at a photodetector in the beam path. The general configuration of a thermal lens spectrometer was suggested and analyzed by Hu and Whinnery [4]. Two types of such instruments can be distinguished. In a single beam arrangement the same laser beam serves both for heating of the sample and detection of the generated thermal lens. In a dual beam set-up an intense laser heats the sample dual-beam for generation of the thermal lens and the index of refraction is probed with an additional low intensity light beam.

The main advantage of a thermal lens absorption spectrometer is a much higher sensitivity as compared to a measurement of the intensity attenuation of a light beam transmitted through the sample. This can be described by an enhancement factor E [5]. In a standard absorption measurement the intensity I of the transmitted beam can frequently be described by Beer's law $I = I_o e^{-A}$, with I_o the intensity at the first surface and A the absorption. For weak absorption, it follows that $\Delta I = I_o A$ and the relative change of the signal is $s_A = \Delta I/I_o = A$. In a thermal lens spectrometer, on the other hand, a time dependent signal $I(t) = I_o[1 + s_{TL}/(1 + t_c/t)]$ is generated, where t_c is the characteristic time for formation of the thermal lens. The relative change of the signal measured at $t = 0$ and $t \gg t_c$ is $s_{TL} = \Delta I/I_o = EA$. The enhancement factor E can be expressed as $E = (dn/dT) \cdot P/(\lambda k)$, where dn/dT is the derivative of the index of refraction with respect to temperature, k stands for the thermal conductivity of the liquid, and λ is the wavelength of light. E is linearly proportional to the light power P. It depends, however, in a nontrivial way on the optical and thermal properties of the liquid under investigation. To make the enhancement factor E as large as possible, organic solvents with large values of dn/dT and low thermal conductivity k are most appropriate. Carbon tetrachloride, for example, gives a sensitivity enhancement 20 times larger than water. It should be mentioned, that E also depends on the geometry of the experimental arrangement.

* Permanent address: Institute of Experimental Physics, Warsaw University, Hoza 69, PL-00-681 Warsaw, Poland

** Present address: Fachbereich Physik der Universität Kassel, Heinrich-Plett-Strasse 40, W-3500 Kassel, Fed. Rep. Germany

For the generally accepted model of an aberrant thermal lens [6] the optimum configuration for a single beam spectrometer is found if the sample is placed at a distance of $\sqrt{3}z_c$ from the beam waist, where $z_c = \pi w_o^2/\lambda$ is the confocal distance of the beam and w_o is the beam radius.

If the signal enhancement factor is known, the minimum detectable absorption can be determined. The fundamental detection limit results from statistical variations of the photon flux recorded by the detector. Let $N \sim I$ be the total number of photons and $\Delta N \sim \Delta I$ the difference of the photon numbers counted with and without a thermal lens in a time interval T_C. In order to obtain a signal-to-noise ratio of at least unity, ΔN must be equal or larger than the statistical fluctuations of the photon number ΔN_n. Assuming Poisson statistics we can write $\Delta N_n = \langle N \rangle T_C$, where $\langle N \rangle$ is the average number of detected photons per unit time [7]. Since $s_{TL} = \Delta N/N = EA$, one finally obtains for the minimum detectable absorption $A_{min} \approx (\langle N \rangle T_C E)^{1/2}$.

The signal generated with the thermal lens technique is proportional to the power P of the heating beam. Therefore, it might seem at a first glance that smaller and smaller absorbances can be detected by simply increasing P further and further. In practice, however, excessive heating can stimulate convective flow in the liquid by which the thermal lens is destroyed. Therefore, the power of the heating beam should be kept at a moderate level.

Another problem is, that the ultimate sensitivity as discussed above is difficult to achieve experimentally since the photodetector records the probe beam intensity even in the absence of absorption; in other words, the thermal lens technique is inherently associated with a certain background. Intensity fluctuations of the probe beam usually impose a considerably higher detection limit than expected theoretically.

1 Noise Suppression in Thermal Lens Laser Spectrometers

In view of these limitations, various methods have been developed to suppress noise in thermal lens spectrometers and enhance the sensitivity of absorption measurements. The different techniques can be grouped into two categories. In the first one, improvements are realized by processing the signal of the photodetector. Averaging of analog signals and digital filtering have been applied. Significant progress, for example, was made by Swofford and Morell [8] who introduced the repetitively pulsed dual-beam thermo-optical spectrometer. Digital methods for signal processing proved to be particularly efficient in the case of pulsed laser excitation, for example in the work by Bialkowski [9]. The problem of beam deflection was solved by optical processing in the work by Janssen and Harris [10].

The second category of experimental improvements applies modifications of the optical arrangement of a thermal lens spectrometer. Dorion et al. [11], for example, extracted information on the sample absorbance from the spatial Fourier spectrum of a thermal lens. For this purpose an annular aperture located in the back focal plane of a Fourier transforming objective was used and a detector measured the integral intensity behind the aperture. The Fourier transform of the input light distribution is obtained either at infinite distance from the sample or, with the transformation scaled accordingly, in the focal plane of a lens [12]. Therefore, filtering of the spatial Fourier spectrum can be considered as a special case of detection far away from the thermal lens. Spatial filtering has also been accomplished close to the thermal lens by means of a circular mask inserted behind the sample [13]. This method reduces noise by blocking that part of the probe beam which carries no information on the absorption and which reaches the detector even if no thermal lens is generated. A disadvantage of this technique, however, is that the mask must be positioned close to the focal point of the light beam. In a single beam arrangement with an intense light beam (that must predominantly accomplish heating) this can introduce considerable heating of the mask which is associated with additional sources of experimental error.

In the present paper a novel experimental arrangement for high sensitivity thermal lens spectrometry is presented. It makes use of a circular aperture to obtain a considerable enhancement of the signal-to-noise ratio. It has been known for more than three decades that circular apertures can be applied to guide electromagnetic radiation or even focus a beam without seriously reducing the power. Although first experiments of this kind were performed for microwaves, application to visible light has also been demonstrated [14]. It has been shown by recent work [15] that the transmitted beam is only slightly diffracted if the radius of the circular aperture is chosen slightly smaller than twice the spot size of the incident light beam. Even though the power blocked by the aperture is negligible, the light field is noticeably disturbed. Particularly pronounced is a change of the angular divergence of the diffracted field [15]. This effect seems to be very promising for thermal lens detection because the intensity can be expected to remain essentially constant during manipulation of the beam divergence by the aperture. If the photon flux is constant and the enhancement factor E increases one should get an improvement of the signal-to-noise ratio S/N or, equivalently, a lower detection limit. A problem arises, however, if the variation of the angular divergence of the probe beam caused by the thermal lens is amplified in a similar manner behind the aperture. The present paper presents theoretical calculations and an experiment undertaken to solve this problem. Use of a circular lar aperture seems to be a rather simple modification of already existing instruments. The technique, however, requires a careful theoretical analysis in order to find the optimum position of the detector in the beam path and thus obtain maximum signal enhancement. Contrary to the classical detection of a thermal lens far away from the sample, we find that the detector in the new arrangement must be positioned in the near diffraction field behind the aperture. Its position is chosen such that the Fresnel number F of the aperture equals $F = 2$.

2 Theory

The experimental configuration that will be discussed and analyzed theoretically in this section is shown schematically in Fig. 1. The probe with its waist at $z = 0$ travels through

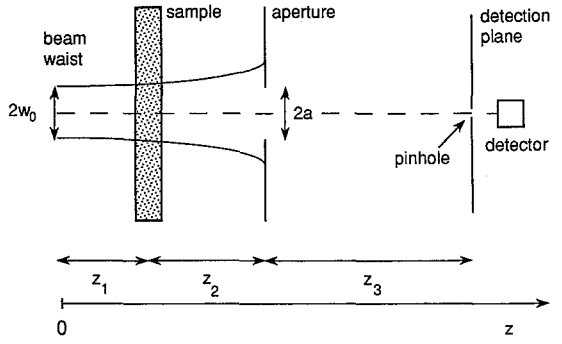

Fig. 1. Schematic representation of a thermal lens spectrometer with an aperture in the light path of the probe beam

the sample and is filtered by a circular aperture. The intensity on the beam axis is recorded by a detector equipped with a pinhole. The probe beam is considered as a linearly polarized, monochromatic Gaussian wave with a waist radius of $r = w_o$. Furthermore, it is assumed that a thermal lens with focal length f is formed in the sample, i.e., at $z = z_1$. Since the generation of the thermal lens by either the probe beam or an additional pump beam are not explicitly considered, the following analysis holds for single-beam as well as for dual-beam spectrometers.

The focal length of the thermal lens can be expressed as [4]

$$f(t) = \frac{k\pi w_H^2}{\frac{dn}{dT} P_{abs}} \cdot \left(1 + \frac{t_c}{t}\right). \tag{1}$$

P_{abs} denotes the power absorbed by the sample, w_H stands for the radius of the heating beam, and $t_c = w_H^2/4D$ is the time constant for generation of the thermal lens. $D = k/(\varrho c_p)$ denotes the thermal diffusivity of the sample, ϱ being the density and c_p the specific heat.

The amplitude $u(r, z)$ of the probe beam at $z = 0$ can be written as $u(r, z = 0) = [2P/(\pi w_o^2)]^{1/2} \cdot \exp[-(r/w_o)^2]$. Use of a complex beam parameter q is convenient to describe the amplitude of the Gaussian beam during its propagation. If the light propagates over a distance z, q is calculated by $q = q_o + z$, with $q_o = i\pi w_o^2/\lambda$ for $z = 0$. The value of q at the aperture can be determined by the well-known matrix method. One obtains [16]

$$q = \frac{Aq_0 + B}{Cq_0 + D}, \tag{2}$$

where A, B, C and D stand for the matrix elements. In order to calculate the values of the beam transfer matrix for propagation from $z = 0$ to $z = z_1 + z_2$ one has to multiply the matrix for the propagation form $z = 0$ to $z = z_1$ with a matrix describing the ray transformation by a lens of focal length f and finally by a matrix describing the propagation from $z = z_1$ to $z = z_1 + z_2$. The following expressions are found:

$$\begin{aligned} A &= 1 - z_2/f\,, \qquad B = z_1 + z_2 \cdot (1 - z_1/f)\,, \\ C &= -1/f\,, \qquad\quad D = 1 - z_1/f\,. \end{aligned} \tag{3}$$

With these matrix elements, the beam parameter q can be computed. As a second step the amplitude of the light field in the detection plane is determined from the diffraction integral. To simplify the analysis, only the light intensity on the beam axis, i.e., for $r = 0$, will be considered. This does not constitute a serious restriction unless a detector without a pinhole is considered. The amplitude u_a of the light field at the aperture is given by

$$u_a = \sqrt{\frac{2P}{\pi w^2}}\, e^{-\frac{i\pi}{\lambda q} r^2}\,. \tag{4a}$$

The radius w of the beam and the radius of curvature R of the light wave are given by

$$1/w^2 = (i\lambda/\pi)\mathrm{Im}(1/q) \quad \text{and} \quad 1/R = \mathrm{Re}(1/q)\,. \tag{4b}$$

In a cylindrically symmetric arrangement as shown in Fig. 1 one obtains for the light field amplitude u_d at the detector

$$u_d = \frac{2\pi}{\lambda z_3} \int_0^a u_a(r)\, e^{-\frac{i\pi}{\lambda z_3} r^2} dr\,. \tag{5}$$

Finally (4) and (5) are combined and the integral is solved. We find

$$u_d = \frac{2\pi}{\lambda z_3} \sqrt{\frac{2P}{\pi w^2}}\, \frac{1 - e^{-\alpha a^2}}{2\alpha} \tag{6}$$

with $\alpha = i\pi/\lambda \times (1/q + 1/z_3)$.

In the following w', u'_d, α' etc. denote the beam radius at the aperture, the amplitude of the light field at the detector, and α for zero absorption ($A = 0$). Similarly, w'' u''_d, α'' are the values of these parameters for $t \gg t_c$, i.e., for steady state conditions with $A > 0$. As usual, the signal s is defined as the relative change of the light intensity with and without absorption $s = (|u''_d|^2 - |u'_d|^2)/|u'_d|^2$. With (6) one obtains

$$s = \left(\frac{w'}{w''}\right)^2 \left| \frac{\alpha'}{\alpha''} \frac{1 - e^{-\alpha'' a^2}}{1 - e^{-\alpha' a^2}} \right|^2 - 1\,. \tag{7}$$

By variation of the geometrical parameters of the arrangement, the configuration can be found for which maximum signal is obtained. A thermal lens in a sample of negligible thickness predominantly changes the radius of curvature of the probe beam. This change can be computed from $1/R'' = 1/R' + 1/f$, where R' and R'' denote the radius of curvature without and with the thermal lens in the beam path, respectively. If a diverging lens ($f < 0$) is placed in the diverging Gaussian probe beam, the radius of curvature increases ($\delta R < 0$) and the probe beam becomes more divergent. For the more realistic case of a sample of finite thickness, the beam diameter changes also. A more divergent probe beam naturally means $\delta w > 0$. This has simple, intuitively obvious consequences. If the beam in the plane of the circular aperture increases in size, the light intensity incident on the aperture decreases together with the intensity of the diffracted field. For growing w, the probe beam can be approximated by a spherical wave which illuminates the aperture with uniform intensity. On the axis behind the aperture the intensity minima for Fresnel number $F = 2, 4, \ldots$ become deeper. In the limit of an ideal spherical wave the minima would be dark, i.e., the intensity would be zero. This effect is due the presence of the aperture and constitutes an important reason for the signal enhancement.

After these qualitative considerations the influence of the position of the detector on the signal will be discussed quantitatively. With (6) and with the definition of the Fresnel number $F = (a^2/\lambda)(1/R + 1/z_3)$ the intensity at the detector can be written as

$$I = \left(\frac{\pi a^2}{\lambda z_3}\right)^2 \cdot \frac{2P}{\pi\omega^2} \cdot \frac{1 + e^{-2(a/\omega)^2} - 2e^{-(a/\omega)^2}\cos(\pi F)}{(a/\omega)^4 + (\pi F)^2}. \quad (8)$$

The signal of a thermal lens spectrometer is defined as $s_{TL} = \Delta I/I$. The intensity variation ΔI results from changes of w and R due to formation of the thermal lens. ΔI can be expressed as

$$\Delta I = \frac{dI}{dw}\,\delta w + \frac{dI}{dR}\,\delta R$$

dI/dR can be written as

$$\frac{dI}{dR} = \frac{dI}{dF} \cdot \frac{dF}{dR} = -\frac{a^2}{\lambda R^2} \cdot \frac{dI}{dF}.$$

Generation of the thermal lens gives rise to $\delta w > 0$ and $\delta R < 0$. In order to maximize the signal s_{TL} the detector position z_3 (and therefore the Fresnel number F) should be chosen such that dI/dw and dI/dF have the same sign and are maximum (or minimum). In order to find the optimum arrangement the signals $s_{TL} = (1/I)(dI/dw)$, which results from changes of the size of the probe beam and $s_{TL}(R) = (1/I)(dI/dF)$ which is due to variations of the curvature of the probe beam have been calculated as a function of F. The results are shown in Fig. 2a, b for different ratios of a/w. As can be seen from Fig. 2a, $F = 2$ gives maximum signal. Figure 2b indicates an optimum signal $s_{TL}(R)$ at a slightly smaller value of F. The experiments described below show that the main source of the thermal lens signal is the variation of the beam size w making the contribution of $s_{TL}(R)$ to the total recorded signal small as compared to $s_{TL}(w)$. Therefore, $F = 2$ was chosen. As can seen be from Fig. 2 larger values of F also give maxima of $s_{TL}(w)$ and $s_{TL}(R)$. Under such conditions, however, a more complex intensity pattern is produced and the system would be more difficult to adjust.

For further illustration of these considerations, calculations for a single-beam thermal lens spectrometer have been performed. With (3)–(7) and $F = 2$ the signal s_{TL} was computed as a function of sample position z_1 for different ratios of a/w_o and different positions of the aperture. In such calculations it must be considered that the focal length of the thermal lens is dependent on the sample position (because of the dependence on w_H, i.e., the diameter of the heating beam). If f_o is the focal length under steady state conditions for a sample located at $z = 0$, the focal length f for another sample position z_1 can be calculated from

$$f = f_o[1 + (z_1\lambda/\pi w_o^2)^2]. \quad (9)$$

Figure 3 shows the computed signals for an arrangement with a circular aperture ($a/w_o = 0.6,\ 0.8,\ 1.0$) placed at $z_2 = 0$ (dashed lines) and $z_2 = 0.9\,\pi w_o^2/\lambda$ (solid lines). For comparison the signal for a classical spectrometer without aperture is also included (dotted line). For $z = 0$, i.e., for the aperture located at the same position as the sample, a much lower signal as compared to the classical configuration is obtained. Another difference is that no change of sign is

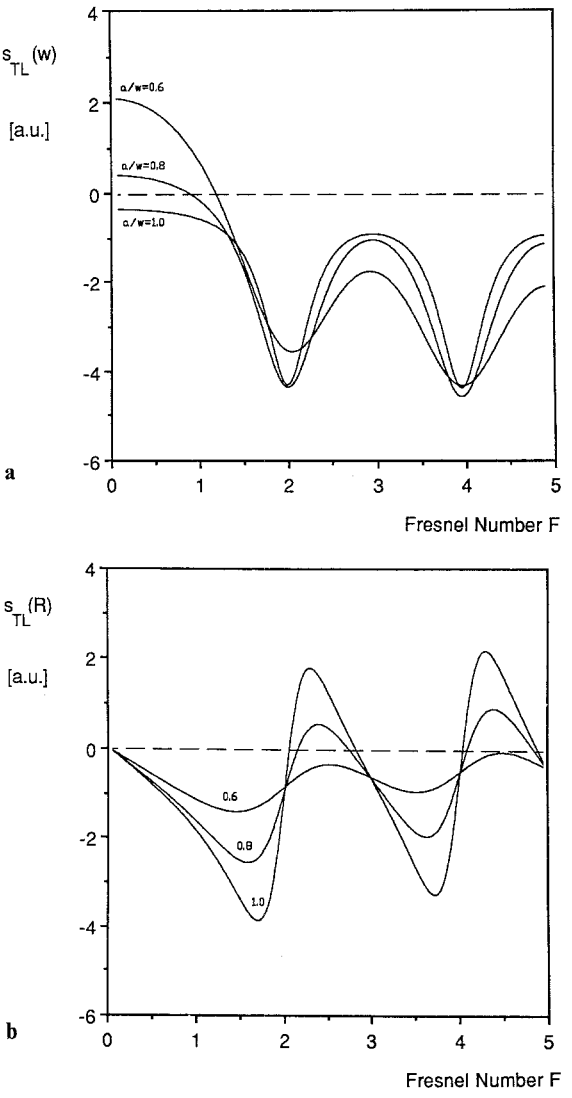

Fig. 2a, b. Thermal lens signal resulting from **(a)** changes of the size $s_{TL}(w)$ and **(b)** variations of the radius of curvature $s_{TL}(R)$ of the probe beam due to formation of a thermal lens. The curves were calculated with (8) and are plotted as a function of the Fresnel number F

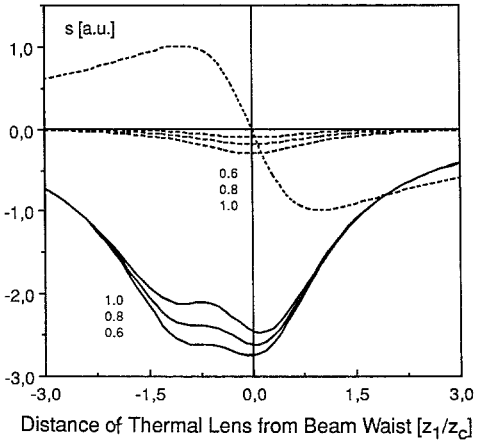

Fig. 3. Thermal lens signal computed for a spectrometer as shown in Fig. 1. The signal is plotted as a function of the position z_1 of the sample and has been calculated for $F = 2$ and values of $a/w_o = 0.6,\ 0.8$, and 1.0. The solid lines (——) refer to $z_2 = 0.8$, the dashed lines (– – –) to $z_2 = 0$, and the dotted line (. . .) represents the signal without aperture, i.e., for a *classical* thermal lens spectrometer

observed if the aperture is translated along the beam axis. If, however, $z_2 = 0.9\pi w_o^2/\lambda$ is chosen, the situation changes significantly and the signal is larger than for a set-up without aperture. Figure 3 shows that the sample and the aperture inserted at the appropriate positions increases the sensitivity by approximately a factor of three.

As outlined above, the new configuration provides maximum signal if the sample is placed in the waist plane of the probe beam. This means that the characteristic time for formation of the thermal lens if four times smaller than for the *classical* arrangement where the sample is placed at a distance from the beam waist of $\sqrt{3}z_c$. For a given time interval of observation, the number of collected data points is also increased by a factor of four and the signal-to-noise ratio is twice as large as for the standard configuration.

In summary, we can conclude that the new optical arrangement should provide a total increase of the signal-to-noise ratio by a factor of 5–10. Experiments with the goal to verify these predictions will be described in the following section.

3 Experiment

In order to test the theoretical predictions described above, a spectrometer with an optical arrangement similar to the one in Fig. 1 was used. The sample consisted of methylblue dissolved in ethylalcohol and contained in a cuvette of 10 mm thickness. In a single beam arrangement, a He–Ne-laser with $\lambda = 6328$ Å and $I = 2$ mW served both for heating of the sample and for probing of the resulting thermal lens. The laser beam was focused to a diameter of $2w_o = 0.12$ mm and the sample was positioned close to the beam waist. The absorption at $\lambda = 6328$ Å was 0.07. The laser beam subsequently passed a circular aperture with a diameter of $2a = 100\,\mu$m. It was mounted 3 mm behind the sample. In order to obtain a magnified image of the near-field diffraction pattern in the detection plane, an additional lens with $f = 10$ mm was used. With the detector positioned 85 cm away from the lens, the magnification amounted to $M = 85$. For detection of the He–Ne laser light, a Si photodiode (Centronic OSD5-O) with a 300 µm pinhole was used. The output of the detector was connected to a FET current-to-voltage converter (4V/1µA) and finally processed by a digital storage oscilloscope (LeCroy 9400). The laser beam was intensity modulated with a mechanical chopper at a frequency of typically 4 Hz.

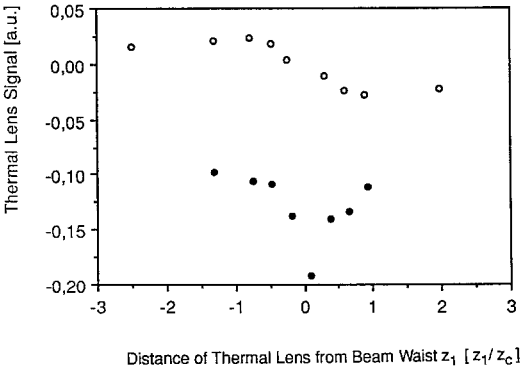

Fig. 4. Dependence of the experimental thermal lens signal on the sample position z_1. The open circles (○) give the signal obtained with a circular aperture and $a/w_o = 0.8$. The full circles (●) represent the signal obtained without the aperture

With the digital storage oscilloscope, the time evolution of the thermal lens signal was recorded. For a single data point typically 20 traces were averaged and stored for further evaluation. The thermal lens signal s_{TL} was computed from $s_{TL} = (U_t - U_o)/U_o$, where U_o is the voltage recorded with the light beam turned off and U_t the voltage measured under steady state conditions with the beam heating the sample. To optimize the signal, the sample and the 100 µm aperture were translated together along the beam axis. Thus, s_{TL} was measured as a function of z_1. For comparison with a *classical* detection system such measurements have also been performed without an aperture behind the sample. The experimental results are shown in Fig. 4.

4 Conclusions

Comparison of the experimental results with the theoretical predictions shows good agreement. This demonstrates an increase of the sensitivity in thermal lens spectrometry by almost one order of magnitude. Clearly, however, no improvement of the ultimate fundamental detection limit arising from photon shot noise can be obtained in this way. We have not observed an improvement of the enhancement factor as compared to the *classical* arrangement with an aperture of twice the probe beam size. With the aperture, however, comparable to the beam diameter and for observation at minimum intensity, i.e., for Fresnel number $F = 2$, the aperture reduces the overall illumination of the detector. Thus, the method is applicable to improve the sensitivity of a thermal lens spectrometer if the main source of noise are fluctuations of the probe beam intensity. The technique introduced here is particularly useful to minimize the influence of such fluctuations in a single-beam arrangement where lock-in detection cannot be applied. The method, however, is also applicable to dual-beam spectrometers. In such an instrument the optical configuration must be chosen such that the focal radii of the heating and the probe beam are of comparable size.

In conclusion we have demonstrated a novel experimental configuration for thermal lens spectrometry with greatly improved sensitivity. The method is simple and can be readily applied to materials that are soluble in liquids with a large temperature coefficient of the index of refraction and with a low thermal diffusivity. This makes possible improved absorption measurements on a great variety of materials in fields like chemistry, physics, biology and many others.

Acknowledgement. One of the authors (J.S.) is very indebted to the Alexander von Humboldt Foundation for a fellowship during his stay at the University of Heidelberg.

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