Determination of photochemical reaction rates using thermal lens spectrometry

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Abstract. Considering the time dependence of the absorption coefficient due to the photo-induced chemical reaction (PCR) and species diffusion, we calculate the temperature rise in the thermal lens (TL) effect and the TL signal at the detector plane. This theoretical approach removes the restriction that the PCR time constant is much greater than the characteristic TL time constant, which was assumed in a previously published model. Aqueous Cr(VI)-diphenylcarbazide solution is investigated, and quantitative experimental results for the thermal, optical and PCR properties of the sample are obtained. The relative difference between the parameters extracted from the same experimental data of the Cr(VI) solution using the previous and present models is found to be less than 5%, showing the present model can be used to study the PCR. Moreover the present model is more general than the previous one.

1. Introduction
Thermal lens (TL) spectrometry has been explored as a highly sensitive photothermal technique with attractive characteristics such as its remote and nondestructive nature, and can be used for the thermal, optical and chemical analysis of solids, liquids, and gases [1]-[7]. The TL effect is based on the temperature rise produced by a non-radiative decay process following absorption of optical energy by the sample. The generated transverse temperature gradient induces a refractive index gradient that behaves like an optical lens and can be probed by another laser beam, providing quantitative information on the physical properties of the sample.

To study chemical kinetics, a non-equilibrium process was introduced into the TL theoretical model to investigate the photo-induced chemical reaction (PCR) in liquids [7]-[11]. During the laser excitation, the PCR effect changes the concentration of absorbing species in the excited volume, generating a gradient from the outside to inside this volume; mass diffusion may then compensate for part of the consumed species [12]. After prolonged excitation, the amplitude of the TL signal reaches a steady state, reflecting an equilibrium in the concentration of the absorbing species. Under the assumption that the PCR time constant is much greater than the characteristic TL time constant, Pedreira and co-authors [10] modified the final expression for TL intensity I(t) by considering the
temporal dependence of the optical absorption coefficient $A_e(t) = C(t)\varepsilon$, where $\varepsilon$ is the molar optical absorption coefficient of the sample, and $C(t) = (C_0 - C_{eq})\exp(-k_T t) + C_{eq}$ expresses the time dependence of the species concentration. $C_0$ denotes the initial concentration, while $C_{eq}$ is the equilibrium concentration in the illuminated area and $k_T$ is the total reaction rate constant ($s^{-1}$). The final expression proposed in [10] agreed quantitatively with the experimental results for aqueous Cr(VI)-diphenylcarbazide solutions. However, other materials may yield much smaller PCR time constants as compared to the chromium solutions, and the assumption restricts the applicability of the model. Therefore, it is desirable to have a complete theoretical description of this phenomenon. In this work, the time dependence of the optical absorption coefficient and mass diffusion of species due to the PCR are taken into account. We completely solve the heat conduction equation for the TL effect and calculate the TL signal. A comparison between the fitted parameters for the Cr(VI) sample with the present model and the previous one [10] is presented.

2. Theory
In a mode-mismatched TL experiment [4]-[6], a cw TEM$_{00}$ Gaussian beam (excitation laser) excites a weakly absorbing sample of thickness $l$, producing a TL. A weak TEM$_{00}$ Gaussian beam, collinear with the excitation beam, probes the TL. The radii of the excitation and probe beams in the sample are $\omega_{0e}$ and $\omega_{1p}$, respectively, as depicted in Fig. 1(a). The probe beam propagates in the z-direction, and the sample is located at $z = 0$. The distance between the sample and the detector plane is $Z_2$, while the distance between the sample and the probe beam waist (radius $\omega_{0p}$) is $Z_1$. The sample dimensions are large compared with the excitation beam radius, thereby avoiding edge effects. The excitation laser energy absorbed by the sample is sufficiently low that it can be considered uniform along the propagation direction.

$$Q(r,t)/\rho c = Q_0\phi\left[\left(1-C_{eq}'\right)\exp(-k_T t) + C_{eq}'\right]\exp\left(-\frac{2r^2}{\omega_{0e}^2}\right),$$

(1)

where $Q_0 = 2P_e\phi/(\rho c \pi \omega_{0e}^2)$. $P_e$ is the excitation power, and $C_{eq}' = C_{eq}/C_0$; $\phi = C_0\varepsilon$. $\phi$ is the fraction of the absorbed energy available for conversion to fluorescence. $c$ and $\rho$ are specific heat and mass density of the sample, respectively. The solution of the heat conduction equation, using the boundary condition as in Ref. [13], is

$$\frac{T(r,t)}{Q_0\varepsilon'} = C_{eq}'\left(\frac{1}{1+2t'/t_e}\right)\exp\left(-\frac{2r^2/\omega_{0e}^2}{1+2t'/t_e}\right)dt' + \left(\frac{1-C_{eq}'}{\exp(k_T t')}\right)\left(\frac{1}{1+2t'/t_e}\right)\exp\left(-\frac{2r^2/\omega_{0e}^2}{1+2t'/t_e}\right)dt',$$

(2)

Figure 1. (a) Scheme of the geometric positions of the beams in a mode-mismatched TL experiment, (b) a schematic diagram of the time-resolved TL experimental apparatus: $M_i$, $L_i$, and $P_i$ denote mirrors, lenses, and photodiodes, respectively.
with the characteristic TL time constant $t_c = \omega_0^2 / 4D$, and the thermal diffusivity of the sample is $D = k / \rho c$. $k$ is the thermal conductivity of the sample.

The temporal and radial distributions of the temperature rise inside the sample induce a refractive index gradient that acts as an optical element, introducing a phase shift $\Phi$ in the probe beam $\Phi = (2\pi / \lambda_P) l (d\theta / dt) [T(r,t) - T(0,t)]$ [4]. $d\theta / dt$ is the temperature coefficient of the refractive index at the probe beam wavelength $\lambda_P$. $\Phi$ describes the distortion of the probe beam caused by the temperature change in the medium. Using Eqs. (1) and (2),

$$\Phi = \int_0^{t_c} \left[ \frac{\theta_{eq}}{1 + 2t' / t_c} \right] - \exp \left( \frac{-2mg}{1 + 2t' / t_c} \right) dt' + \int_0^{t_c} \exp \left( k_r t_c \right) \left[ 1 - \exp \left( \frac{-2mg}{1 + 2t' / t_c} \right) \right] dt' \quad (3)$$

In Eq. (3), $\theta_{eq} = \theta_1 C' e^{\phi e}$ and $\theta_m = \theta_0 e^{\phi e}$ with $\theta_1 = P_e (d\theta / dt) \phi / \omega_0 e^2$. $m = \omega_1 e^{2} / \omega_0 e^2$ quantifies the degree of the mode mismatch of the probe and excitation beams. The intensity $I(t)$ of the probe beam, with the phase shift $\Phi$, at the detector plane can be calculated using Fresnel diffraction theory as described in Ref. [4].

3. Results and discussions

We use both previous and present models to evaluate the thermo-optical and PCR properties of an aqueous Cr(VI)-diphenylcarbazide solution. Figure 1(b) shows a schematic illustration of the experimental apparatus used in this work. A diode-pumped solid-state laser at 532.0 nm and a very weak 543.5 nm He-Ne laser provided the Gaussian TEM$_{00}$ excitation and probe beams, respectively. The liquid sample was contained in a $l = 0.5$ cm quartz cuvette. More details about the experimental setup can be found in Refs. [10] and [14]. The values of $\omega_0 e^2$, $m$ and $V = Z_1 / Z_c$ were 72$\mu$m, 45.25 and 8.3, respectively. The sample was prepared as described in Ref. [10] at the Cr(VI) concentration of 40ppb. Measurements were performed at 30ºC by recording TL transients at different time scales and excitation beam power levels.

![Figure 2](image-url)

**Figure 2.** (a) Normalized TL signals $I(t)/I(0)$ for the 40ppb Cr(VI) sample. Solid lines: least-square curve fitting using the present model. (b) Relation between $\theta$ and pump power with the solid lines representing the best linear fits.

Figure 2(a) presents normalized TL signals for different excitation powers. At the very beginning ($t < 200$ ms), one can see that the probe beam intensity decreases due to the TL effect. Thereafter, the reduction of the absorbing species concentration due to the PCR diminishes this effect, and the probe beam intensity increases. The induced gradient of absorbing species in the excited region eventually approaches the equilibrium concentration due to mass diffusion, and the probe beam intensity is
affected analogously. The solid lines display the least-square curve-fitting results using the present model. The fitted parameters are indicated in Fig. 2(b) and Table 1 for different excitation power levels.

These results can be compared with those obtained using the previous model, as shown in Table 1. As expected, the two models are in good agreement with a small relative difference (less than 5%) in terms of the fitted parameters. The experimental results thus demonstrate that both models can be used to study samples with long PCR time constants. However, the present model may be applied to study materials with different PCR time constants, while the previous model is only suitable for the samples having long PCR time constants.

| Fitted parameters | Present model | Previous model |
|-------------------|--------------|---------------|
|                  | Eq. (3)      | Eq. (11) of Ref. [10] |
| \(D\) (cm\(^2\)s\(^{-1}\)) | 1.40±0.05 | 1.50±0.09 |
| \(1^l\theta_{eq}/dP_e\) (W\(^{cm^{-1}}\)) | 18.1±0.2 | 18.5±0.6 |
| \(1^l\theta_{st}/dP_e\) (W\(^{cm^{-1}}\)) | 30.7±0.6 | 31.3±0.9 |
| \(C'_{eq}/C_0\) | 0.59±0.02 | 0.57±0.03 |
| \(k_T\) (s\(^{-1}\)) | 2.0±0.1 | 1.9±0.1 |

Table 1: Experimental results obtained using the present model, Eq. (3), and the previous one.

4. Conclusions

In conclusion, this paper reports the theoretical model of the time-resolved mode-mismatched TL for studying photo-induced chemical reactions (PCR) in liquids. Aqueous Cr(VI)-diphenylcarbazide was investigated, and quantitative results were obtained for the thermal and optical properties. Comparison between the PCR time constants extracted from the same experimental data using both models revealed a small relative difference of less than 5%, showing that both models can be used for PCR with long reaction time constants. Unlike the previous model, the present model has no restrictions with regard to PCR time constants; the present model can be used to study the PCR effect irrespective of short or long PCR times. The previous model is actually a special case of the present one.

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References
[1] Bialkowski S E 1996 Photothermal Spectroscopy Methods for Chemical Analysis (Wiley, New York)
[2] Snook R D and Lowe R D 1995 Analyst 120 2051
[3] Marcano A, Loper C, and Melikechi N 2001 Appl. Phys. Lett. 78 3415
[4] Shen J, Lowe R D and Snook R D 1992 Chem. Phys. 165 385
[5] Baesso M L, Shen J, and Snook R D 1994 J. Appl. Phys. 75 3732
[6] Astrath N G C, Rohling J H, Medina A N, Bento A C, Baesso M L, Jacinto C, Catunda T, Lima S M, Gandra F G, Bell MJV, Anjos V 2005 Phys. Rev. B 71 214202/1
[7] Franko M and Tran C D 1991 Rev. Sci. Instrum. 62 2430
[8] Arnaud N and Georges J 2001 Anal. Chim. Acta 445 239
[9] Albuquerque T A S, Pedreira P R B, Medina A N, Pereira J R D, Bento A C, and Baesso M L 2003 Rev. Sci. Instrum. 74 694
[10] Pedreira P R B, Hirsch L R, Pereira J R D, Medina A N, Bento A C, Baesso M L, Rollemborg M C, Franko M, and Shen J 2006 J. Appl. Phys. 100 044906
[11] Braslavsky S E and Heibel G E 1992 Chem. Rev. 92 1381
[12] Levine N 1995 Physical Chemistry (McGraw-Hill, New York)
[13] Carslaw H S and Jaeger J C 1959 Conduction of heat in solids (Clarendon Press, Oxford)
[14] Astrath N G C, Astrath F B G, Shen J, Zhou J, Michaelian K H, Fairbridge C, Malacarne L C, Pedreira P R B, Medina A N, Baesso M L 2009 Opt. Lett. 34 3460