# Molecular Size and Mass Sensitive Femtosecond Thermal Spectrometer

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## Abstract

Though a single ultrashort pulse has inconceivable thermal effect, highly repetitive femtosecond lasers often result in some heating effects. Instead of fretting over the thermal effect, we have used this to develop the time-resolved photothermal lens spectroscopy for molecular sensitivity.

## 1. Introduction

Thermal Spectroscopic techniques are typically insensitive to molecular parameters, such as, molecular mass, and their specific structures. Typical thermal processes are developed using the conduction model wherein the systems' overall physical characters suffice and no molecular level sensitivity is necessary. However, over the recent past, we have furthered the Thermal spectroscopic techniques to a level where we have developed thermal approaches that depend on the specific molecular level characteristics, including their structure and mass.
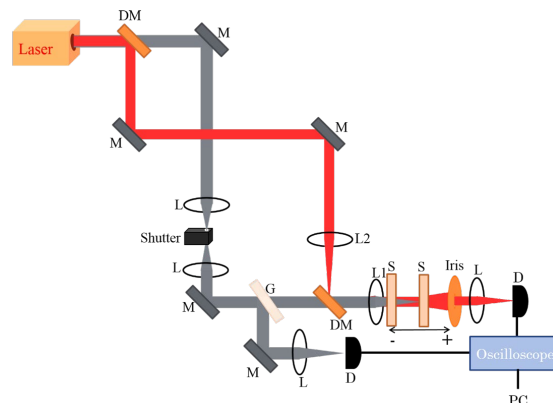
## 2. Principle

Thermal Lens (TL) spectrometry is a well-established, highly sensitive photothermal technique that can be utilized for the thermal, optical, and chemical analysis of solids, liquids, and gases. We demonstrate the great advantage of using ultrashort infra-red laser pulses to induce the photothermal effect in place of the traditional continuous lasers. Under such conditions, thermal processes can be preferentially induced before any material damage even when the excitation wavelength is resonant to the sample absorption wavelengths. However, the thermal dissipation of the heat generated under such conditions can no longer be explained by the simple conduction only model, which does not require any molecular characteristics. As soon as convective mode of heat transfer gets included, the molecular properties of the system play a major role in the process, in turn, the TL spectrometry under this condition becomes molecule sensitive, thus providing us with the ultrasensitive Thermal Spectrometer with Molecular Size and Mass Sensitivity.

A laser beam diverges after passing through a nearly transparent solvent. This divergent of the laser beam could only be explained if there is a decrease in the refractive index of the sample due to heat deposition in the system.

This observation has led to the TL spectroscopy using a single laser beam. To enhance the sensitivity of the TL spectroscopy, the dual beam TL technique has been developed. The dual beam TL technique is more sensitive as compared to the single beam TL technique as in the dual beam case, one beam creates the TL signal while the second beam measures this TL signal. A more accurate signal measurement can be done in this case as compared to the single beam TL technique. This dual beam TL technique has two types of experimental setups, namely, the mode-matched and the mode-mismatched depending on the beam waist parameters of the pump and the probe beams. The mode-mismatched TL technique is more sensitive as compared to mode-matched TL technique and is used widely for photochemical study and hydrodynamic relaxation. Continuous wave (cw) lasers are typically used in TL study but recently, femtosecond high repetition rate (HRR) lasers are also being used for TL study. Each femtosecond pulse deposits a small amount of energy to the sample and, in case of the HRR laser, this small amount of energy accumulates to result in a long time TL signal. The HRR laser provides better signal to noise ratio as compared to the cw laser. Our specific experimental approach is detailed in the next section.

## 3. Experimental Details

The experimental set-up used to study the molecular effect on the thermal phenomenon is a two-color-pump-probe mode-mismatched TL technique as shown in **Figure 1**.



**Figure 1.** Schematic diagram of experimental set-up: (DM)-Dichroic mirror; (M)-Mirror; (L)-Lens; (G)-Glass plate; (S)-sample; (D)-Detector; (PC)-Personal Computer.

We use a mode-locked Er-doped femtosecond fiber laser (Femtolite Mira Inc) that produces laser pulses of two colors centered at 1560 nm and 780 nm with a repetition rate of 50 MHz. The laser pulses centered at 1560 nm has the pulse width of ~300 fs with an average power of 12 mW at the sample, while the laser beam of pulses centered at 780 nm has the pulse-width of ~100 fs with an average power of 6 mW at the sample. The laser beam of pulses centered at 1560 nm acts as the pump pulse and is focused on the sample. The laser beam of pulses centered at 780 nm acts as the probe beam and is collimated through the sample with the telescopic arrangement of two lens (**Figure 1**). To measure the position dependent TL signal, a motorized translational stage (Newport: M-6 UTM150CC.1) is used to scan the sample across the focal point of the pump beam. The sample cell used has a width of 1 mm. The strength of the TL signal is measured by measuring the transmittance of the probe beam through a 60% closed aperture situated in the far field. The intensity of the probe beam is measured with the help of an amplified silicon photo-detector (Thorlabs: PDA 100A-EC) with 200 MHz oscilloscope (Tektronix TDS 224). A National Instruments GPIB card is used to interface the oscilloscope to the computer and data acquisition is achieved through LabVIEW programs. An InGaAs photodiode (Acton Research) (**Figure 1**) is used to measure the absorption of the pump beam by the sample. The same photodiode also used to analyze the fluctuation in the pump beam. The maximum TL signal is found at the focal point of the pump beam. For analysis of hydrodynamics relaxation, a shutter is used in the pump beam and the sample is placed at the focal point of the pump beam. A telescopic arrangement is used to reduce the activation time of the shutter (**Figure 1**).
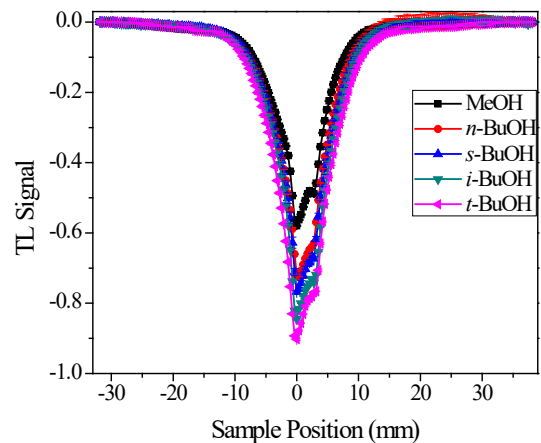
## 4. Results

The alcohols have strong absorption in the communication band due to hydroxyl group (OH). This absorbed energy is transformed to heat via non-radiative relaxation. This heat generated in the sample results in a TL. The strength of the TL signal is measured by observing the change in the probe beam divergence. The change in probe beam intensity through a closed aperture located in the far field is an indirect way of measuring the probe beam divergence. The magnitude of stationary TL signal at different sample positions with respect to the focal point of the pump beam is measured by the relation [1]:

$$S(z, t_\infty) = \frac{I(z, t_\infty) - I_0}{I_0} \qquad (1)$$

where, $S(z, t_\infty)$, is the strength of stationary TL signal at each Z-position of the pure samples (figure 2). $I(z, t_\infty)$ and $I_0$ are the probe beam transmittance through the aperture in the presence pump beam after a sufficiently long time and in the absence of the pump beam, respectively. The maximum TL signal is observed at the focal point of the pump beam through the pump-probe mode-mismatched TL technique. This can be seen in **Figure 2**.

Despite the fact that methanol (MeOH) has a strong absorption of the pump beam, it has a small TL signal in comparison to the isomers of butanol. The magnitude of TL signal for pure samples, in case of strongly absorbing sample, depends on a number of factors. We have uncovered the unexplored combined effect of the conduction and convection for absorbing samples to show that the molecular nature of the thermal character essentially arises on inclusion of both the thermal dissipation process unlike the traditional approach of neglecting the convection contributions.



**Figure 2**. TL signals for pure samples, namely, MeOH, *n*-BuOH, *s*-BuOH, *i*-BuOH, *t*-BuOH, with respect to Z-position of the sample.

This new approach of correctly considering the combined effect of convection in addition to conduction for heat dissipation in fluids has provided us the requisite sensitivity to justify the molecular structure and size effect [2]. Thus, the experimental data can be appropriately fitted as per the observed molecular distinction: **Figure 2** shows distinction between the isomers of butanol (BuOH) with respect to MeOH as reference.

## 5. Conclusion

Typical thermal spectroscopic techniques are insensitive to molecular parameters: e.g., molecular mass and structures. Thus, typical thermal processes use conduction model where the systems' overall physical characters suffice and no molecular sensitivity is needed. We have advanced the TL Spectroscopy to the molecular level and demonstrated how it depends on the specific molecular characteristics, including their structure and mass.

## 6. Acknowledgements

## 7. References

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