Exploring Thermal Lens Spectrometry as an Analytical Tool

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Abstract

A thermal lens is created when the energy from a traversing laser deposits into a solution. This summer we explored different setups for a thermal lens experiment and tested them for analytical purposes. Absorbance detection in a one-color, single-beam experiment proved to be ten times more sensitive than a commercial UV-vis spectrometer. In addition to absorbance, fluorescence quantum yields can also be measured with this apparatus. The two-color, dual-beam experiment was configured in two ways—mode-matched and mode-mismatched. In the latter configuration, the limit of detection was improved a hundredfold. Trace chemical analysis is made possible with detection on the order of parts per million. The two-color setup was also used to investigate dynamics of the photobleaching of methylene blue. In the photobleaching of methylene blue, the preliminary results showed that thermal lens signals behaved in accordance with the expected kinetics of this photochemical reaction.

Experimental Setup

One-Color, Single Beam Setup
### Two-Color, Dual Beam Coaxial Setup
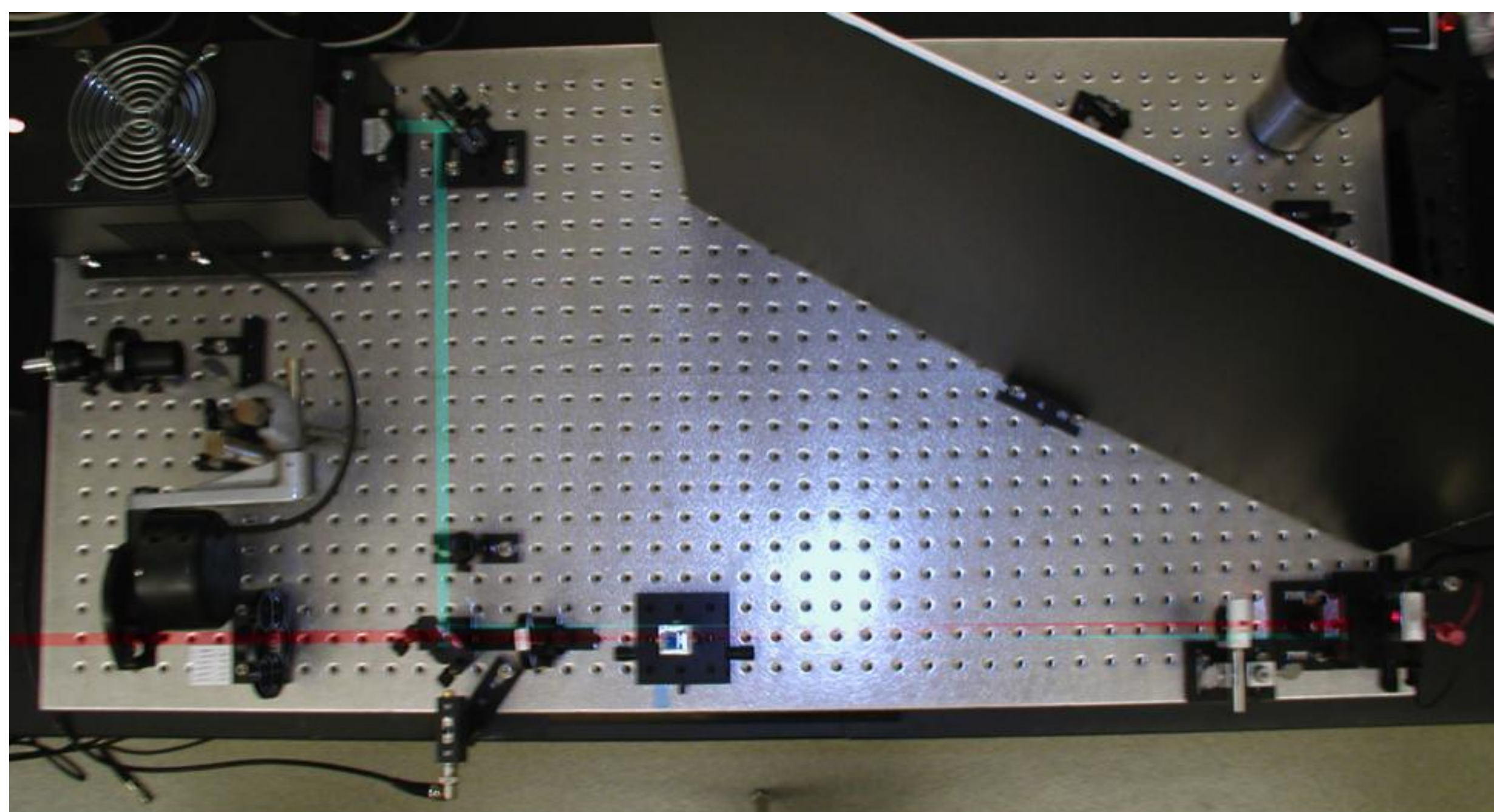
### Two-Color, Dual Beam Mode-Mismatch Setup

In the two color dual beam coaxial setup, both the excitation beam and the probe beam are focused through the same lens into a single spot. The sample cell is placed at a confocal distance from the focal point so that the phase front curvature of the probe beam is minimized and the largest fractional change (where the thermal lens signal change comes from) is achieved. However, at the confocal position, the power density of the excitation beam is reduced by a factor of two relative to the power density at the focal point. Since the strength of the thermal lens depends on the energy deposited into the sample, we want to maximize the power density of the excitation beam in the sample cell. To do this, the excitation beam is focused through another shorter lens, and the focal point is centered within the sample cell. In this case, the radii of probe beam and the pump beam are different in this case, so the configuration is called mode-mismatched. Another advantage of the mode-mismatched configuration is that it is much easier to align the probe beam and the excitation beam.
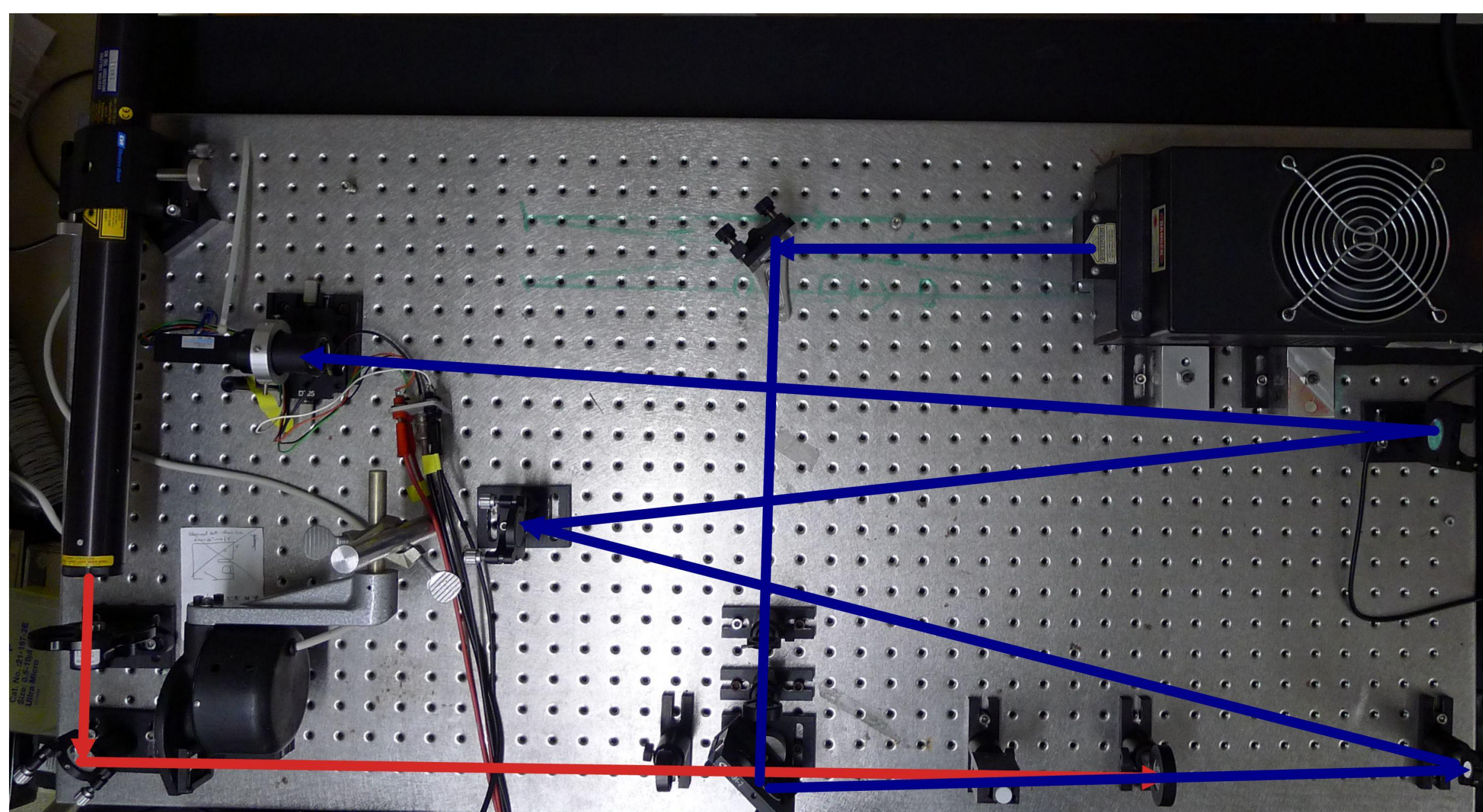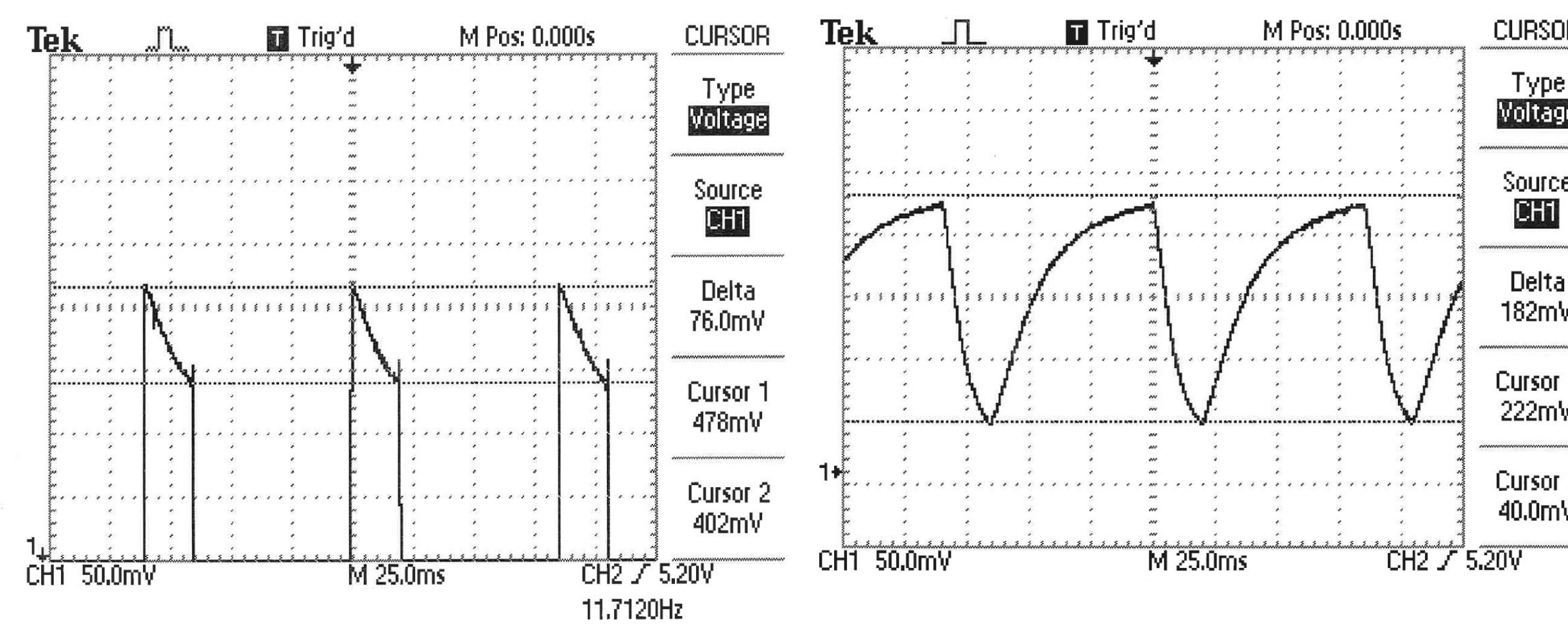

Mode-mismatched Beam Scheme
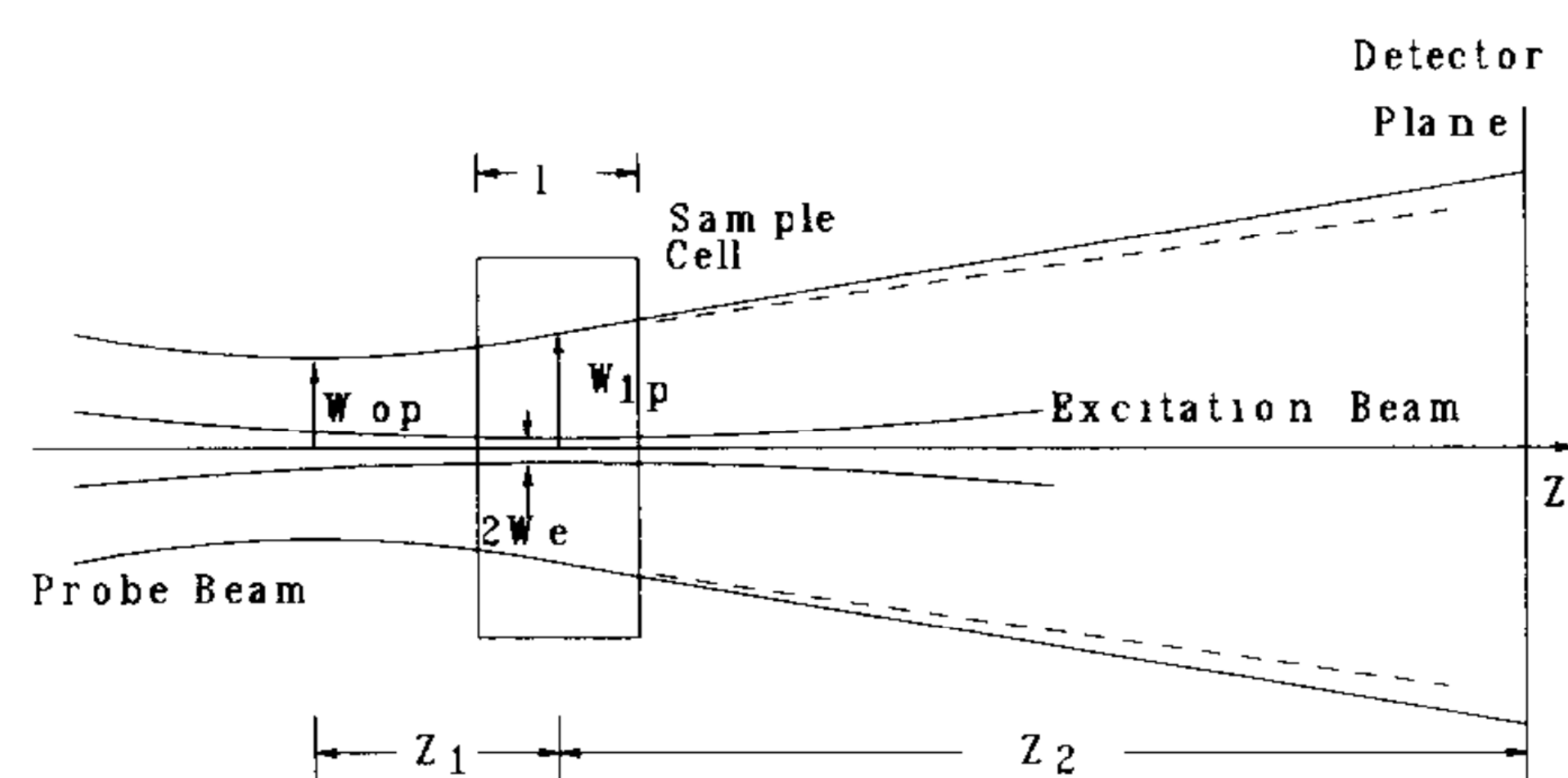
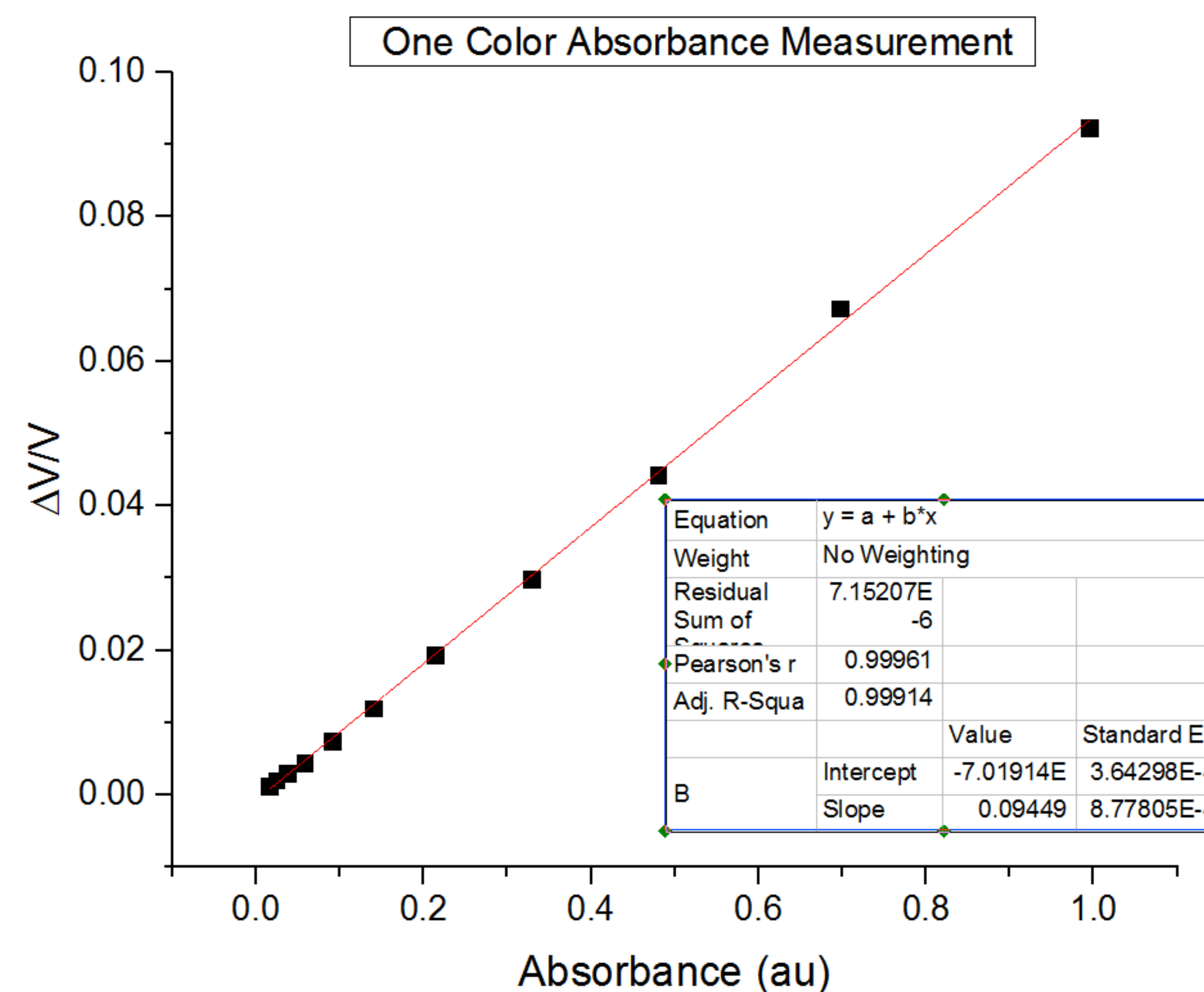## Thermal Lens Effects
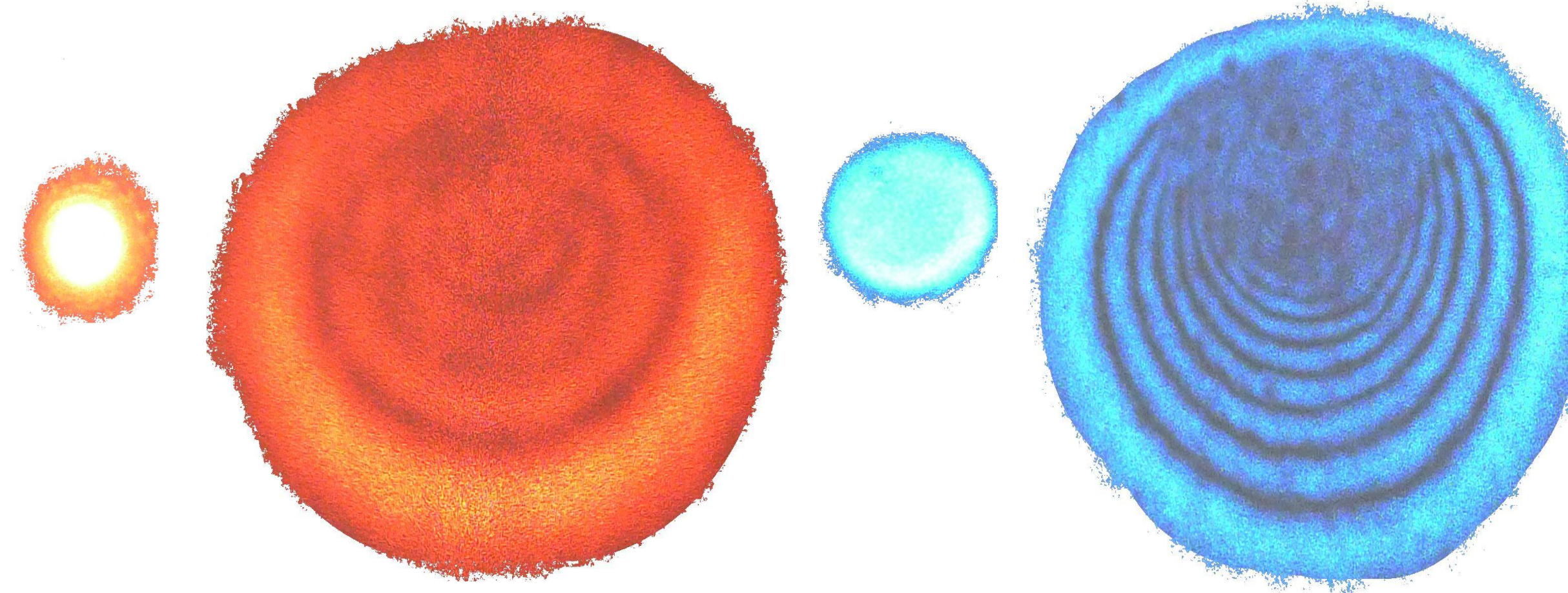
Oscilloscope Trace of Thermal Lens Signals

Application

Trace Detection

Apparatus	Limit of detection (au)
UV-Sis Spectrometer	0.01
One Color Setup	0.01
Two Color Mode-Matched Setup	0.001
Two Color Mode-Mismatched Setup	0.00001

Absorbance Measurement with One-Color, Single-Beam Application

One Color Absorbance Measurement

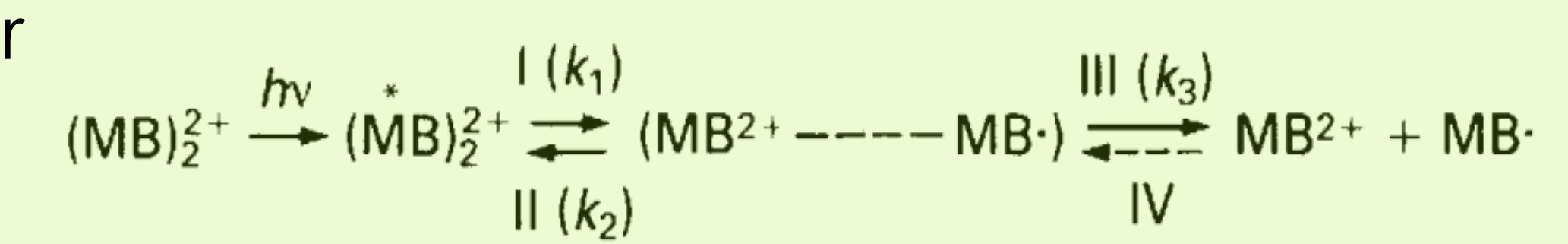| Equation	y = a + b*x	
Weight	No Weighting	
Residual Sum of Squares	7.15207E-6	
Pearson's r	0.99961	
Adj. R-Squa	0.99914	
	Value	Standard Err
B Intercept	-7.01914E	3.64298E-4
Slope	0.09449	8.77805E-4

Photobleaching of Methylene Blue

We chose Methylene Blue as our candidate in developing thermal lens as an analytical tool for kinetics problems. A Methylene Blue solution contains both monomer species and an appreciable amount of dimer species. With light excitation, Methylene Blue undergoes photobleaching and becomes colorless. Previous studies show that the bleaching processes are different for the monomer species and the dimer species, whose reaction schemes are shown below. We tried to reproduce the results using thermal lens spectrometry and attempted to determine the kinetic constants in both reactions.

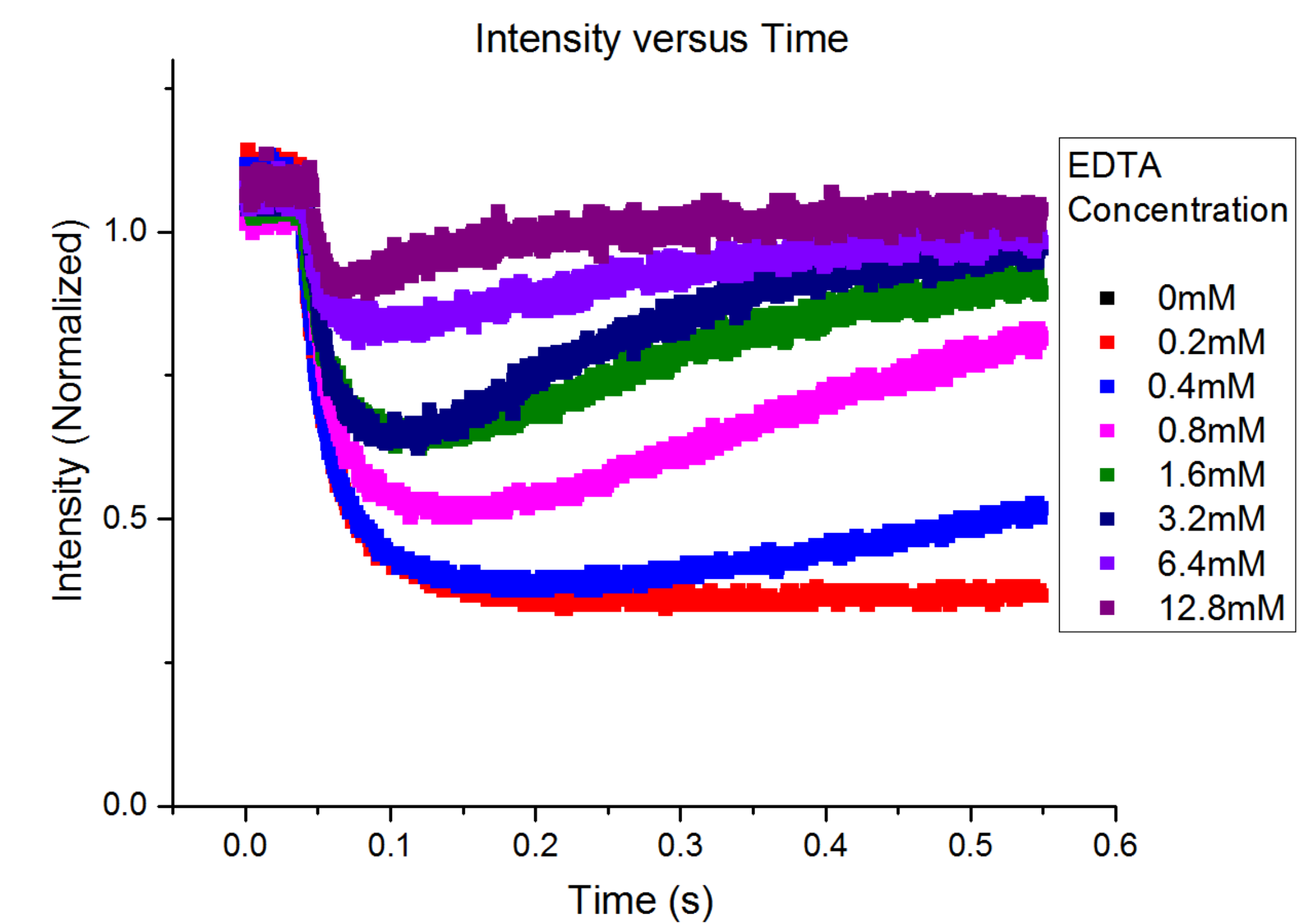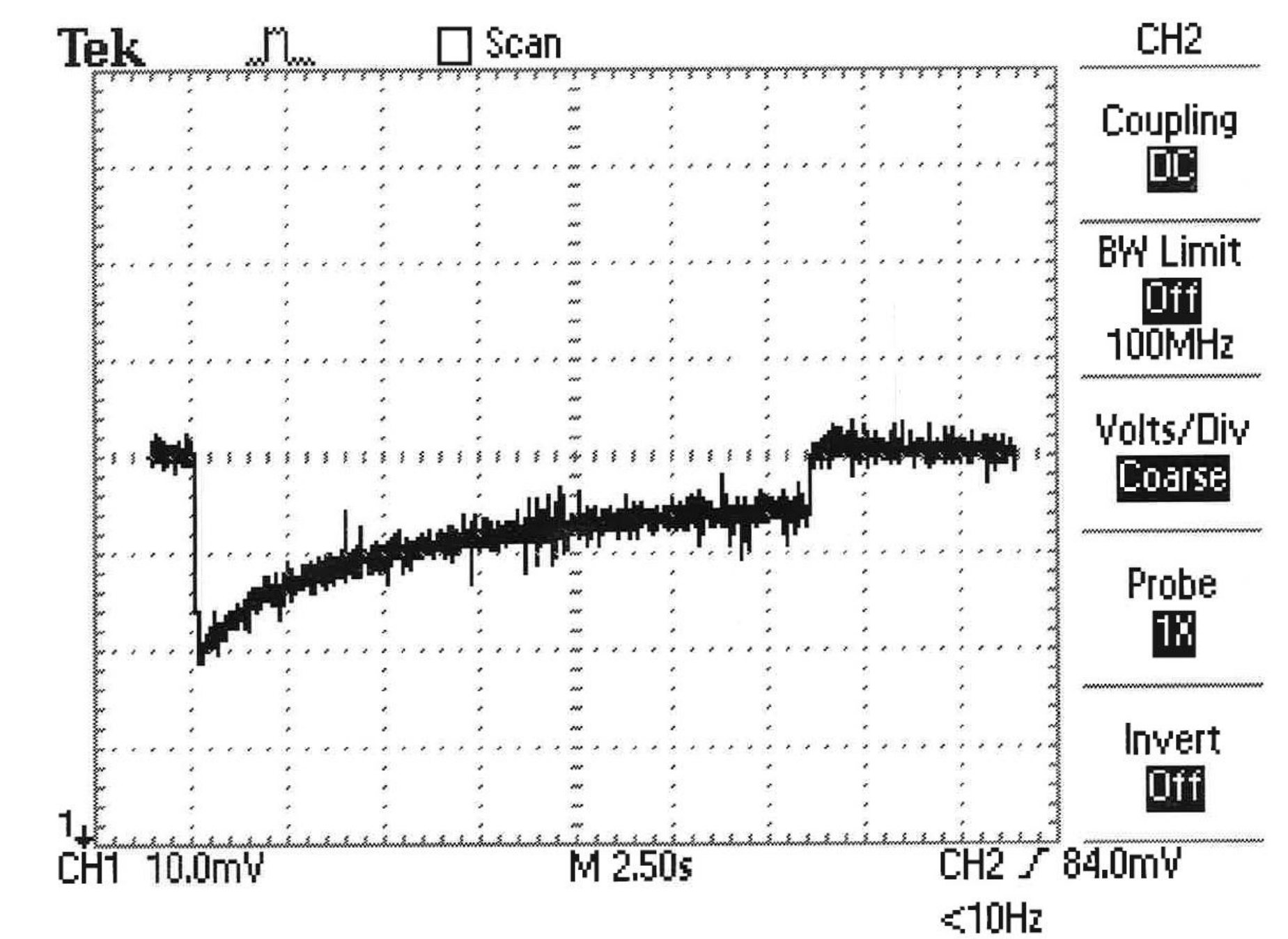## Reaction Schemes of Photobleaching of Methylene Blue

Monomer

$$MB^+ \xrightarrow{h\nu} {}^*MB^+ \xrightarrow[EDTA]{k} MB\cdot$$

Dimer

$$(MB)_2^{2+} \xrightarrow{h\nu} {}^*(MB)_2^{2+} \underset{II\,(k_2)}{\overset{I\,(k_1)}{\rightleftharpoons}} (MB^{2+} ---- MB\cdot) \underset{IV}{\overset{III\,(k_3)}{\rightleftharpoons}} MB^{2+} + MB\cdot$$

Photobleaching of MB in the presence of EDTA

Photobleaching of MB in Sodium Sulfate

Future Work

The preliminary results show that the thermal lens behaviors are consistent with expectations: the photobleaching of the monomer species is diffusion controlled and the dimer species contribute mostly to the photobleaching of methylene blue in an arduous solution. We want to determine the kinetic constants from thermal lens signals and see whether they match with literature values. To do this, we write down the two first order differential equations for the change of absorbance with respect to time A(t) in the reaction, and then from the differential equations we find an algebraic solution to A(t). Using this algebraic solution and the Thermal Lens model developed by Lowe and Snook, we fit the experimental data and extract the kinetic constants from the fits. We were able to obtain the numbers but they were not quite in the expected range. One possible reason is that the parameters we chose for the model are not accurate enough. Our next step is to adjust our parameters according the thermal lens behavior of a non-bleached sample.

References

1. Shen, Lowe and Snook, Chemical Physics 165 (1992) 385-396
2. Lowe Snook Analyst, 1993,118, 613-616
3. Junqueira, Severino, Dias, Gugliottia and Baptista, Phys. Chem. Chem. Phys., 2002, (4), 2320-2328

Acknowledgements