Winter 2008 Qualifying Examination
Physical Chemistry II Exam
Chemistry Department
Evans

Based on "Determination of Subyoctomole Amounts of Nonfluorescent Molecules Using a Thermal Lens Microscope" *Analytical Chemistry* **2001**, 73, 2112-2116.

1.   In thermal lens microscopy what is actually being measured and how does it relate to the processes of absorption of laser light by molecules and the subsequent relaxation from the excited electronic states?

2.   The authors claim subyocomole detection limits? The calibration line corresponded to 0.42 to 3.38 molecules detected. How can the authors detect fractions of molecules? What does this mean in a physical sense?
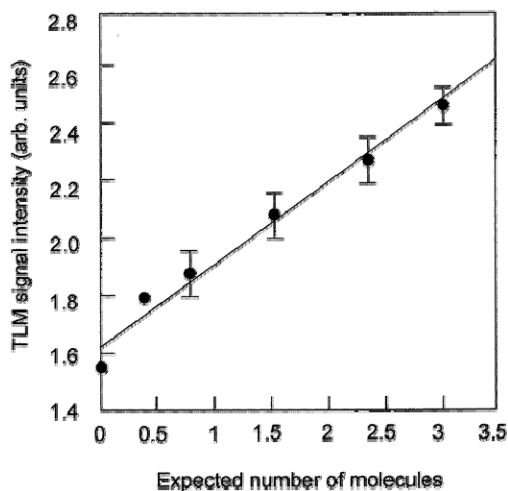
3.   UV-visible absorption measurements of organic molecules produce broad, non-descript spectra, which is why UV-visible absorption techniques lack selectivity.   Evaluate the thermal lens microscopy (TLM) technique in terms of selectivity. Compare the selectivity of TLM with that of Laser-induced Fluorescence.

4.   The TLE signal results from temperature changes of what magnitude? Show how the authors arrived at this number given the following data.
   ▪   Total heat generated by an average of 1.0 molecule in the probing volume $= 3.7 \cdot 10^{-17}$ J (from paper)
   ▪   Density of benzene $= 0.877$ g/mL
   ▪   molar heat capacity of benzene $= 135$ J/mol·K

5.   Discuss in some detail how each of the lasers, the solute, and the solvent contribute to the sensitivity of the TLE measurement given the following expression for the thermal lens signal (S_{TL}):

$$S_{TL} = (P_e \cdot dn/dT \cdot A) / (\lambda_p \cdot \kappa)$$

where P_e is the power of the excitation laser, dn/dT is the refractive index temperature coefficient, A is the absorbance given by εbc (Beer's Law), λ_p is the wavelength of the probe laser, and κ is the thermal conductivity of the solvent.

Benzene has a relatively small thermal conductivity and a relatively large refractive index temperature coefficient. Do these properties support the authors' suggestion that the use of benzene as the solvent is advantageous to the TML measurement?

6.   The authors suggest that one of the possible applications of the thermal lens technique is to use it as a detector for electrophoretic separations on a microchip. One of the challenges in separation science is that miniaturization of our separation devices will require techniques that can detect very small quantities of materials. One of the major problems with electrophoretic separations on a microchip is very poor sensitivity with most detection schemes. Discuss how the marriage of TLM and electrophoretic separations on a microchip could help to overcome the selectivity issue with TLM and the sensitivity issue inherent with the use of microchips.