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Thermal Lensing: A New Spectroscopic Tool

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The introduction of lasers into chemical research has been one of the most exciting advances of recent years. Lasers have opened up many new fields of study which were inconceivable in the absence of laser technology. This Account describes one such new field which holds great promise in the study of weak spectral transitions.

When lasers are focused into an absorbing material the refractive index may be affected in such a way that the medium behaves as a lens. This effect has been understood for a number of years. Only in the past few years, however, has this "thermal lens" effect been shown to be a valuable spectroscopic tool. It has been used in the study of weak spectral transitions as well as in studies of quantum yield measurements, of lifetime measurements, of thermal properties of various materials, of analytical chemistry, and of excited-state polarizabilities. Indeed, it holds great promise in many areas where sensitive spectroscopic probes are needed.

The thermal lens effect was first reported in 1964 by Gordon et al.^{1,2} In an attempt to study Raman spectra, they placed cells containing various liquids inside the cavity of a He-Ne laser. Power transients, mode changes, and relaxation-type oscillations with time constants on the order of seconds were observed. These phenomena have been explained in terms of the formation of a thermal lens in the liquids.³

Thermal lens formation results from absorption of the laser light. The absorption, which may be extremely weak, produces excited-state molecules which subsequently decay back to ground states. When the decay involves radiationless processes, localized temperature increases are produced in the sample. Since the refractive index depends on temperature, there is a resulting spatial variation of refractive index which is equivalent to the formation of a lens within the medium. For most liquids, the temperature coefficient of refractive index, dn/dt , is negative. Insertion of the liquid in a Gaussian-shaped beam therefore produces a concave lens and the beam diverges, or "blooms".

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Thus, the thermal lens phenomenon is sometimes referred to as "thermal blooming".

One can observe thermal lensing quite readily. First, a sample is placed in front of or beyond the focal point of a lens which focuses the laser. The resulting thermal lens causes the beam to become more collimated or more divergent after passing through the sample. Next, a pinhole is placed some distance away from the sample and positioned so that the center part of the beam passes through it. When the thermal lens forms, the resulting collimation or divergence causes an increase or decrease, respectively, of the light passing through the pinhole.

The thermal lens phenomenon has been extensively studied since 1965. Much of the early work involved finding ways to avoid the effect, since it can interfere with measurements made in many types of laser spectroscopy. However, thermal lensing had been applied to measurements of weak absorptions of liquids³ (at 632.8 nm), determining thermal properties of liquids,^{4,5} measurements of fluorescence quantum yields,⁶ and investigations of the rate and yield of a photochemical reaction⁷ in the late 1960s and early 1970s.

In 1976, Long, Swofford, and Albrecht demonstrated the usefulness of the thermal lens effect in spectroscopic studies.⁸ Rather than simply observing the lens effect with a single wavelength He-Ne laser, they introduced a second, variable wavelength dye laser into the apparatus. While a dye laser could be used both to create and to probe thermal lens production, it was found that the use of separate heating and probe beams gave better sensitivity. Figure 1A illustrates the experimental arrangement for the two-beam method. Here a continuous wave (CW) dye laser is used as a heating source (HL) to create the lens and a CW He-Cd laser (PL) is used to probe lens production. By chopping the dye

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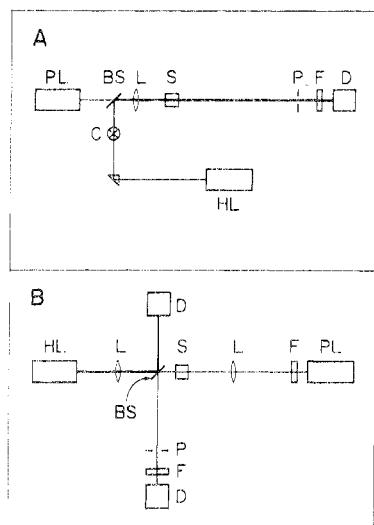


Figure 1. Two possible arrangements for thermal lens apparatus. HL, heating laser (pulsed or CW dye laser); PL, probe laser; L, lens; BS, beam splitter; S, sample; P, pinhole; F, filter; D, detector; C, chopper. In (A) the two laser beams traverse the cell in the same direction and in (B) they traverse the cell in opposite directions. Other, noncollinear arrangements are, of course, also possible.

laser beam and observing changes in the probe beam, one can achieve a high degree of sensitivity. By use of 1-cm cells and 1% of the available dye laser power (about 1 W), a transition in neat liquid benzene was observed with molar extinction coefficient as low as $2 \times 10^{-6} \text{ L mol}^{-1} \text{ cm}^{-1}$. The authors suggested that with full power and 5-cm cells sensitivity better than $10^{-9} \text{ L mol}^{-1} \text{ cm}^{-1}$ might be achievable! To get a feel for this result, consider how one would measure such transitions with conventional spectroscopic techniques. Long, Swofford, and Albrecht obtained the spectrum of the fifth C-H stretching overtone vibration of benzene ($\epsilon_{\text{max}} \approx 2 \times 10^{-5} \text{ L mol}^{-1} \text{ cm}^{-1}$). The same transition had been observed by Ellis in 1928,⁹ but instead of using a 1-cm cell, Ellis used cells up to 7 m long.

The report of such a sensitive measure of weak absorptions led Twarowski and Kliger, in 1976, to consider whether the thermal lens effect might be useful in studying two-photon spectroscopy. The theory of the thermal lens effect had been worked out in detail for CW lasers so it was a straightforward matter to estimate the signal magnitudes for two-photon absorptions. The estimates showed that even with such a sensitive technique the two-photon signals would be too small to observe. This is not too surprising if one considers how much absorption will occur. In an n -photon absorption, the fraction of light absorbed per unit length is

$$\alpha = nN\sigma^{(n)}I^{(n-1)} \quad (1)$$

where n is the number of photons absorbed in each absorption event, N is the number of molecules per cm^3 in the sample, I is the incident photon flux ($\text{photon cm}^{-2} \text{ s}^{-1}$) and $\sigma^{(n)}$ is the cross section for the n -photon absorption process ($\text{cm}^{2n} \text{ s}^{(n-1)} \text{ molecules}^{-1} \text{ photon}^{(1-n)}$). In a one-photon absorption process the fraction of light absorbed is independent of incident intensity. The one-photon absorption process, $\sigma^{(1)}$, is on the order of $10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ for a moderately strong absorption ($\epsilon \sim 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$), on the order of $10^{-26} \text{ cm}^2 \text{ mol}$

ecule^{-1} for the weak benzene transitions seen by Long, Swofford, and Albrecht.

In an absorption process where two or more photons are absorbed simultaneously, the fraction of light absorbed depends on the incident intensity. In a two-photon absorption process, the fraction absorbed increases linearly with incident intensity. Typical, moderately strong transitions have cross sections, $\sigma^{(2)}$, on the order of $10^{-50} \text{ cm}^4 \text{ s molecule}^{-1} \text{ photon}^{-1}$. Thus, even when strong two-photon absorptions are compared to weak one-photon absorptions, there is a difference of 24 orders of magnitude in cross sections. In order to see the two-photon absorptions, then, very intense lasers are necessary (see eq 1). Twarowski and Kliger thus analyzed the thermal lens effect for pulsed lasers¹⁰ since their instantaneous intensities are much larger than available CW lasers. In multiphoton absorption studies two or more photons must be absorbed *simultaneously* for a transition to occur. Thus, power (photons per second) rather than energy (photons) is the important factor since the photons must be delivered at the same instant in time.

The analysis of Twarowski and Kliger showed that pulsed lasers of moderate power (10^{-4} J delivered in 10 ns) could produce easily observable thermal lens signals from two-photon absorption processes. Even three-photon absorptions would be observable with lasers an order of magnitude more intense (typical three-photon cross sections would be $\sigma^{(3)} \approx 10^{-81} \text{ cm}^6 \text{ s}^2 \text{ molecule}^{-1} \text{ photon}^{-2}$). At this point, then, the stage was set to do a variety of spectroscopic studies involving weak one-photon or multiphoton transitions. Whinnery and co-workers had provided detailed analyses of the signals to be expected from thermal lenses produced by CW lasers.^{2,3} Twarowski and Kliger described the thermal lens signals expected from pulsed lasers.¹⁰ Both of these analyses have recently been expanded. Swofford and Morrell recently extended the CW analysis to describe the signals from a chopped, dual beam (using heating and probe lasers) thermal lens spectrometer.¹¹ Friedrich and Klem¹² recently described an extension of the analysis of pulsed thermal lensing so that the time profile of the laser pulse would be taken into consideration whether one used a short pulse (i.e., the time duration of the pulse is short compared to decay of the thermal lens) or any intermediate pulse from an "impulse" source to a CW source.

The Experiment

Before discussing applications of thermal lens spectroscopy, let us look at the experiment itself and the information one obtains from it. Two of the possible arrangements for a dual-beam thermal lens spectrometer are shown in Figure 1. Here the two beams traverse the sample, collinearly propagating in the same or opposite directions. The form of the signal will depend on the position of the sample relative to the focusing lens in Figure 1A or on the relative positions of the sample and the two focusing lenses in Figure 1B.

The signal, in a pulsed experiment, is defined as $S \equiv (I(0) - I(\infty))/I(0)$ where $I(0)$ is the intensity at beam center, i.e., passing through the pinhole in front of the detector, immediately after the lens forms. $I(\infty)$ is the

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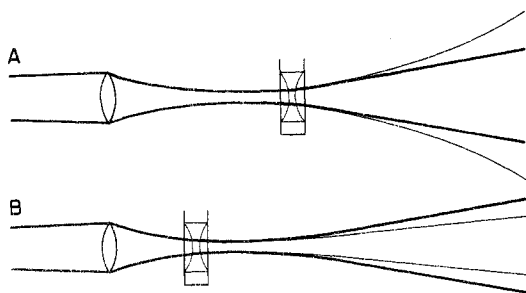


Figure 2. Effect of the thermal lens on probe beam divergence: (A) when sample is placed after the focal point, (B) when sample is placed before the focal point. Heavy line represents beam divergence in the absence of the sample; light line shows effect of the thermal lens.

intensity at a time sufficiently long that the lens has disappeared. The magnitude of this signal is approximately

$$S \approx 2Z/f_0$$

where Z is the distance from the focal point of the heating source lens to the sample and f_0 is the initial focal length of the thermal lens (see Figure 2). f_0 is determined by a variety of factors determined by the thermal characteristics of the sample and optical characteristics of the laser. One can maximize the signal by placing the sample in one of two optimum locations. That location corresponding to negative Z places the thermal lens in front of the focal point of the focusing lens. Since the thermal lens is a divergent lens, such a configuration results in a collimation of the beam when the thermal lens forms, thus increasing the light passing through the pinhole. The location corresponding to positive Z places the sample beyond the fixed lens focal point. Here, the beam diverges more rapidly, resulting in decreased intensity. This characteristic is useful for identifying thermal lens signals. Transient changes upon excitation can be identified as thermal lens transients, as opposed to absorption or emission transients, if the signal changes from increasing intensity to decreasing intensity with changing sample placement.

Signals from CW thermal blooming experiments look different than those described above, though the principles are identical. In pulse experiments the laser excitation deposits energy into the sample quickly. Thus a rapid change in probe laser intensity is observed, followed by decay to the original intensity (see Figure 3). In CW experiments a shutter is opened at some time and energy is then deposited in the sample over some time. The thermal lens thus forms over a period on the order of seconds. The probe intensity passing through the pinhole will then increase or decrease, depending on sample position, to a new steady-state value. The CW experiment is thus characterized by a focal length reached under steady-state conditions, f_∞ , instead of an initial focal length, f_0 , characterizing the pulsed thermal lens. The variation in time of the pulsed signal varies as

$$S_p(t) \propto (1 - 2nt/t_c)^{-2}$$

while that of the CW signal varies as

$$S_{CW}(t) \propto (1 + t_c/2t)^{-1}$$

where n is the number of photons involved in the ab-

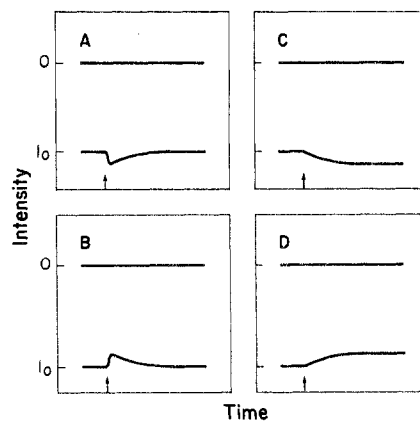


Figure 3. Comparison of signals from pulsed and CW thermal lens experiments. (A and B) Pulsed lens signal with sample placed (A) before or (B) after focal point. (C and D) CW lens signal with sample placed (C) before or (D) after focal point. Arrows indicate time of laser pulse (A, B) or initiation of laser excitation (C, D). Signals are shown larger than normal for purposes of illustration.

sorption process and t_c is a time constant determined by thermal properties of the sample.

For purposes of illustration, the signals shown in Figure 3 are drawn larger than one might expect in a typical experiment. The analyses used to determine absorbance assume small signals so that one generally tries to keep the change in probe intensity down to about 5% or less of the initial probe intensity. Even so, this intensity change can be easily detected as long as the probe laser is sufficiently stable. Thermal lens detection has been carried out directly with oscilloscopes. Signal averaging has also been employed by using data collection with computers, boxcar averagers, and lock-in amplifiers. Interferometry has also been used for detection.^{13,14} With interferometry one does not actually monitor a thermal lens itself. Instead, measurements are made of interference effects produced in a sample when a heating laser causes refractive index changes due to thermal effects.

Though most thermal lens spectroscopy has been carried out in liquid phase, the effect has recently been seen in gas-phase¹⁵ and in solid-phase¹⁶ samples as well. This should further increase the usefulness and versatility of the method.

Vibrational Overtone Spectra

After their initial report of the usefulness of thermal lensing spectroscopy, Albrecht and co-workers used the technique to study vibrational overtone spectroscopy in a variety of molecules.^{8,17-21} This work has brought renewed interest in the local mode model of describing high-frequency vibrational modes.²² It may prove to

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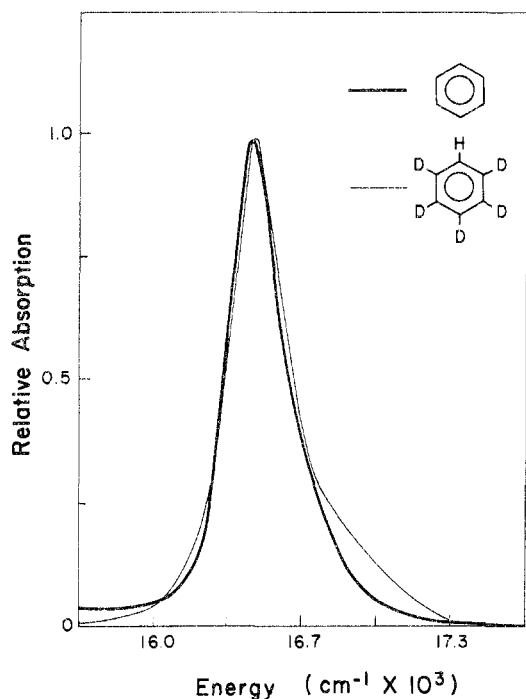


Figure 4. Comparison of benzene and benzene- d_6 absorptions of the sixth C-H stretching overtone vibrational transition. Comparison is facilitated by normalizing peak heights by multiplying the benzene- d_6 peak by a factor close to six and adjusting base-line absorption.

be very important to our understanding of radiationless transitions and energy dissipation in molecules.²¹

Overtone spectra of benzene,^{8,20} substituted benzenes,^{19,20} alcohols,¹⁸ several polyacenes,¹⁷ and several alkanes²⁰ have been studied with thermal lensing spectroscopy. In fact, overtone transitions in the 600–700-nm region have been observed in a wide variety of solvents containing C–H bonds.²³ The benzene overtone transition near 607 nm has received the most study (see Figure 4). In addition to the thermal lens study in liquid phase, it has been studied in both gas²⁴ and liquid²⁵ phase with optoacoustic spectroscopy. A point of some interest is the width of the transition. In liquid phase the transition has a half-width of about 250 cm^{-1} while in gas phase it is about 100 cm^{-1} . The reason for this broadness is an interesting point of controversy which has yet to be satisfactorily resolved. Overtone transitions, though interesting in themselves, can present problems when one is trying to study multiphoton spectra of other molecules in these solvents.

Comparison of the overtone spectra of benzene, pentadeuteriobenzene, and pentafluorobenzene has provided a fine confirmation of the local mode theory.¹⁹ Should there be significant coupling among C–H vibrational modes one might expect significant spectral changes between C_6H_6 , $\text{C}_6\text{D}_5\text{H}$, and $\text{C}_6\text{F}_5\text{H}$. Instead, as one would predict from a local mode model, the spectra are all quite similar (though the $\text{C}_6\text{F}_5\text{H}$ transitions is shifted from 16500 cm^{-1} found in benzene to 16880 cm^{-1}) with the pentasubstituted molecules exhibiting transitions one-sixth as intense as that found in benzene itself (Figure 4).

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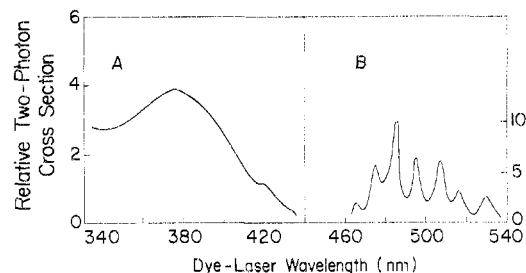


Figure 5. Two-photon spectrum of benzene as determined by the thermal lens method. The transitions to the blue of 430 nm, from ref 32, are transitions to the B_{1u} (~ 420 nm) and E_{1u} (~ 370 nm) states. The transition from 460 nm to 525 nm, from ref 26, is due to a transition to the B_{2u} state. The lowest energy peak, at 532 nm, is due to the seventh C–H stretching overtone.³⁹

Two-Photon Spectra

Thermal lensing was first used to obtain two-photon spectra in 1977 by Twarowski and Kliger. Benzene was the first molecule to be studied²⁶ (see Figure 5B), followed shortly by hexatriene.²⁷ The benzene thermal lensing study demonstrated the usefulness of pulsed lasers for producing both one-photon and two-photon spectra. A structured two-photon absorption was seen from 460 to 540 nm. This is due to the ${}^1\text{B}_{2u} \leftarrow {}^1\text{A}_{1g}$ transition. The ${}^1\text{B}_{1u} \leftarrow {}^1\text{A}_{1g}$ transition was also seen near 425 nm. This was quite significant since the two-photon cross section at this wavelength had been experimentally determined to be less than $10^{-51} \text{ cm}^4 \text{ s molecule}^{-1} \text{ photon}^{-1}$.²⁸ To the blue of these two transitions a two-photon absorption was seen which continuously increased in intensity from 400 nm to 360 nm. Experimental limitations prevented extension of the spectrum beyond 360 nm. From the intensity of the absorption, this absorption was assigned to the ${}^1\text{E}_{2g} \leftarrow {}^1\text{A}_{1g}$ transition. This assignment now seems questionable in light of more recent thermal lensing experiments (vide infra).

The broad transition seen in benzene from 400 to 360 nm is similar to a transition observed in hexatriene in that region.²⁷ Again, a broad transition which peaked to the blue of 360 nm was observed. Liquid-phase butadiene showed a similar feature.²⁹

Colson and co-workers have observed the two-photon thermal lens spectrum of butadiene in both gas and liquid phase.^{15,29} Their results lead them to raise an interesting warning. They suggest that the transient lens may not be entirely due to thermal effects. Rather, effects resulting from the creation of electronically excited states (vide infra) and from microscopic plasmas due to ionization may also contribute. They suggest, in fact, that thermal lensing spectroscopy may be useful in studying ionic plasmas. If the ionic effects are important, however, the lensing signal could not quantitatively be analyzed in terms of two-photon absorption alone.

Vaida, Robin, and Kuebler recently expanded on the suggestion that ionization phenomena may be responsible for some thermal lens spectra.³⁰ They point out that thermal lens spectra in the 360–400-nm region of

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liquid benzene,²⁶ hexatriene,²⁷ and butadiene¹⁵ are quite broad. In all cases, in fact, the spectra seemed to exhibit no spectral maxima in the observed region; instead, they seemed to reach a plateau. These workers suggest that the plateau may be due to ionization phenomena. In the liquid phase the ionization potentials of these molecules would be significantly lower than in the gas phase. They thus suggest that the observed transition might be due to ionization to a liquid-phase conduction band rather than to single molecule effects.

While such liquid ionization phenomena have been observed, recent results of Twarowski, Scott, and Albrecht³¹ and of Ziegler and Hudson³² argue against this explanation. Twarowski et al. studied multiphoton ionization in liquid benzene and found that at 355 nm the ionization signal depended on the cube of the incident laser intensity. They found that the ionization mechanism in liquid benzene involves a two-photon absorption followed by relaxation to a longer-lived transient species, possibly the $^1B_{1g}$ excimer state, out of which ionization occurs upon absorption of the third photon.

Ziegler and Hudson³² extended the benzene two-photon spectrum further into the UV (to 334 nm) than had previously been possible (see Figure 5A). They found a band peaking at 370 nm which closely resembles the one-photon transition to the $^1E_{1u}$ state. They also studied the polarization dependence of the spectrum. Their measured polarization ratio matched closely that measured by Twarowski et al.³¹ for the two-photon step in the ionization mechanism. With these two recent studies, it seems clear that the signals seen in benzene are indeed due to thermal lenses and that they are the result of molecular processes. The earlier assignment²⁷ of the 370-nm benzene band to an $^1E_{2g}$ state is, however, questionable, and a vibrationally induced $^1E_{1u} \leftarrow ^1A_{1g}$ assignment seems more likely. This assignment is based on polarization data, the fact that the intensity of the 370-nm band is comparable to intensities of the 425- and 500-nm vibronic bands, and the fact that the 370-nm band resembles the one-photon $^1E_{1u} \leftarrow ^1A_{1g}$ transition.

Analytical Chemistry

Since the thermal lens effect can be used to measure very weak spectroscopic transitions, it would seem to be a valuable tool for analytical chemistry. Indeed, Dovichi and Harris have begun to explore analytical uses of the thermal lens effect most effectively. They have shown that thermal lens spectroscopy has great potential for analytical chemistry due to its simplicity as well as sensitivity. In the determination of Cu(II) with EDTA, concentrations of copper as low as 1 $\mu\text{g/mL}$ were detected by using a 4-mW He-Ne laser.³³ The authors suggest that with the use of a 1-W laser, detection limits for Cu(II) would be 10^{-10} M or about 10^{-16} mol of Cu(II) in the probe volume.

While the extrapolated detection limits for Cu(II) are impressive, a practical problem with reaching this limit must be considered. That is, background absorption of the solvent could overwhelm absorption from the

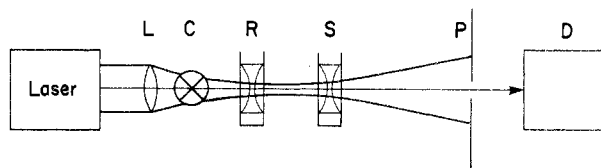


Figure 6. Thermal lens scheme to detect signals from very dilute solute absorptions by subtracting solvent absorptions from sample absorptions. R, reference cell; S, sample cell. All other symbols as in Figure 1.

species being studied. To avoid this problem, Dovichi and Harris have developed a very clever way of eliminating solvent background absorptions.³⁴ The procedure is based on the fact that a sample placed in front of the focal point of the focusing lens in a thermal lens apparatus will tend to collimate the beam while a sample placed beyond the focal point will cause the beam to diverge (see Figure 2). Dovichi and Harris placed a reference cell, with solvent only, in front of the focal point and a sample cell, with sample containing material to be studied, beyond the focal point. This is shown in Figure 6. With careful positioning of the two cells, solvent absorption signals can be nullified. In effect, then, an optical differential amplifier has been produced. Once the apparatus has been adjusted to give a null signal with solvent alone, any signal observed in the sample is due to the material of interest. With this technique Dovichi and Harris have investigated the detection limits of iron(II) with 1,10-phenanthroline. When a 175-mW argon ion laser (at 514.5 nm) was used, iron concentrations as low as 2.8×10^{-12} g/mL have been detected. This level of sensitivity has been observed before only with fluorescence measurements.

Analytical applications in the gas phase as well as liquid phase should be possible for thermal lens spectroscopy. Colson and co-workers^{15,29} have observed gas-phase thermal lens signals to be quite strong. To observe the $^3B_1 \leftarrow ^1A_1$ transition in SO_2 , for example, they needed less than 1 torr m of gas. With conventional spectroscopic methods 800 torr m is needed to see this transition.

Other Applications

Brannon and Magde have recently developed a method for using the thermal lens effect to determine absolute emission quantum yields.³⁵ The method has been used to measure fluorescence yields of fluorescein³⁵ and of cresyl violet.³⁶ It is difficult to decide how accurate the method is for determining emission quantum yields. Comparison of the results obtained from thermal lens experiments and other experiments, however, seems to indicate that the thermal lens method is at least as accurate as, and significantly easier than, most other methods for obtaining emission quantum yields. Thermistor calorimetry³⁷ seems comparable in ease of operation and in accuracy. Optoacoustic spectroscopy^{38,39} appears to be comparable to the thermal lens method in accuracy, but the equipment

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necessary to do this experiment is not as easily available in most laboratories as that necessary for thermal lens experiments.

The thermal lens technique should also prove to be useful to measure excited-state lifetimes of nonemitting states. Most work in pulsed thermal lens experiments have assumed instantaneous lens buildup followed by a lens decay which is determined by thermal characteristics of the sample. One can, however, monitor the buildup time of the lens. With this information one can find the rate of thermal energy deposition into the sample and thus the excited-state lifetime. Friedrich and Klem¹² have presented an analysis of laser-induced refractive index transients which accounts for lens formation times. Their analysis can be used for thermal lens experiments or experiments which monitor refractive index transients by interferometric techniques. These authors show how these experiments can be used to determine excited triplet-state lifetimes. They also expand on the statement of Colson and co-workers²⁹ that lens effects may result simply from the creation of excited states. Klem and Friedrich show how differences in ground- and excited-state polarizabilities will produce refractive index changes and how this can be

used to determine polarizabilities of excited triplet states.

Conclusion

As the above-mentioned examples show, thermal lens spectroscopy has been an interesting, expanding area of research over the past several years. There is every reason to believe that its use will expand into other areas such as studies of thermal properties of polymers or plasma studies. The effect could even be used in reverse. That is, rather than use thermal changes in samples to deduce spectra, lasers can be tuned to deposit specific amounts of heat into samples. Since one can change temperatures by millidegrees, this could, for example, be useful in studying critical point phase transitions very accurately. While it is difficult to predict the extent to which this thermal lens effect will be used, it is clear that we have only just begun to exploit it as a useful spectroscopic tool.

I thank my co-workers and colleagues without whose assistance over the past several years much of the work described above would have been impossible. I also thank the National Science Foundation and the National Institutes of Health for grants which supported parts of the work.