

been carried out, in part to illustrate the relative sensitivity of these quantities to chemical sequence distribution. These results indicate that $\langle \mu^2 \rangle / x$ is generally much more sensitive to both chemical composition and chemical sequence distribution than is $\langle r^2 \rangle_0 / nl^2$, a result of some importance with regard to the possible characterization of such distributions by measurements of configuration-dependent properties. This enhanced sensitivity in the case of $\langle \mu^2 \rangle / x$ is obviously due to the fact that in the calculation of $\langle r^2 \rangle_0 / nl^2$ chemically different units differ in conformational energy but have essentially identical values of the quantity being averaged, the skeletal bond vector, as expressed in the skeletal bond coordinate system. On the other hand, in the calculation of $\langle \mu^2 \rangle / x$, both the conformational energy and the group dipole moment depend on the chemical nature of the comonomeric unit. Similarly calculated results²¹ for ethylene-vinyl chloride chains confirm this enhanced sensitivity of the mean-square dipole moment to chemical composition and chemical sequence distribution.

Summary

It has been demonstrated clearly that analysis of the dipole moments of randomly coiled chain molecules by means of rotational isomeric state theory can provide very valuable information on the conformational energies and spatial configurations of such molecules. The main advantages of this approach are the possibility of extending measurements into the region of very short chain length and the absence of any effect of excluded volume on the dipole moments of most chain molecules. In addition, there is usually a very rapid convergence of the mean-square dipole moment per bond to its limiting value for infinite chain length and a marked sensitivity of the dipole moment to both the stereochemical and chemical structure of the chain.

It is a pleasure to acknowledge that much of the work carried out by the author on the dipole moments of chain molecules has been supported by the National Science Foundation. The author also wishes to thank the members of the Stanford University Department of Chemistry for their hospitality during his 1973-1974 sabbatical year there, when this manuscript was written.

Laser Measurement of Optical Absorption in Liquids

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When a laser beam passes through a material with finite optical absorption, the heat generated increases temperature, which changes the index of refraction, which in turn affects the optical beam. The results include a defocusing¹⁻⁴ or focusing^{5,6} of the beam (depending upon the sign of the index change with temperature), a change in phase delay as index changes,⁷ and a smearing of the beam due to free convection effects if the material is fluid.^{8,9} Certain of the effects are observable for beams in the power range of only milliwatts to watts in materials normally thought to be "transparent" (absorption coefficients of 10^{-4} cm^{-1} or lower), and are thus useful for the measurement of low optical absorption coefficients with relatively simple experimental arrangements.¹⁰⁻¹² The methods give true absorption, as calorimetric methods do, not absorption plus scattering, as in transmission methods. The methods have been applied primarily to the measurement of

absorption in samples to be used for optical experiments, or for the study of materials considered for optical transmission. They should also play an important role in absorption spectroscopy.

Although we stress in this Account the aspects that are important for absorption measurements, there are also undesirable consequences of index changes from thermal absorption. For high average powers, the spreading or "thermal blooming" in passing through solid windows or fluid cells may be significant even when these materials are relatively transparent. High power beams in the atmosphere may suffer a thermal blooming and a distortion from

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(10) R. C. Leite, R. S. Moore, and J. R. Whinnery, *Appl. Phys. Lett.*, **5**, 141 (1964).

(11) D. Solimini, *J. Appl. Phys.*, **37**, 3314 (1966).

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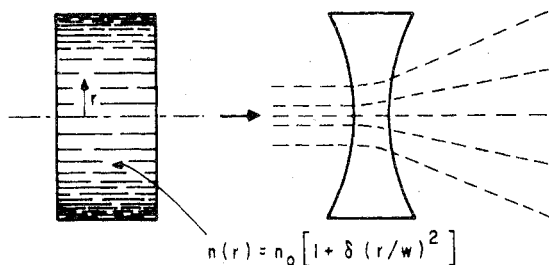


Figure 1. A cell with quadratic variation of index near the axis and its equivalent diverging lens representation.

free convection.¹³⁻¹⁵ The phase change caused by the thermal change in the index may also be important in phase-modulated or phase-locked systems. If dn/dT , the change of refractive index with temperature, is positive, as it is for certain semiconductors and lead glasses, there may be a self-focusing effect.^{5,6} This can increase intensity appreciably and may be either desirable or undesirable, depending upon the application. Many of these effects will also be of importance to chemists.

Porto first observed the thermal lens effect when he placed samples of organic liquids within the resonator of a helium-neon laser to study their Raman spectra.¹⁶ A series of transients was observed following insertion of the samples, with time constants of the order of seconds. Following decay of the transients, final beam size was increased over that prior to insertion of the sample. The time constant of the effects strongly suggested that these were thermal effects, but there was some worry about this hypothesis because of the low absorption coefficients of the liquids used. A careful analysis of the effect¹ revealed that it would be observable for absorption coefficients as low as 10^{-4} cm^{-1} with his configuration and power level, and the method was used for the measurement of the absorption in purified samples of five materials, carbon disulfide, benzene, nitrobenzene, toluene, and carbon tetrachloride.¹⁰ To check the method, following a suggestion of Townes, a dye solution of copper sulfate in water (0.1 M and 0.01 M) was measured by standard photometric techniques, then diluted to 10^{-3} M and checked by the thermal lens method. Agreement was within 10%, which was the approximate accuracy of measurement of spot size.

The nature of the lens is easy to see. If a beam of gaussian intensity distribution with radius enters a material with optical absorption, temperature increase will be greatest along the axis. If dn/dT is negative, as it is for most materials, the index will be lower on the axis than on the edges of the beam and the lens effect will be a diverging one leading to the thermal spread or blooming mentioned. Figure 1 shows this effect with the analogy to a simple diverging lens. The quadratic terms in the expansion for $n(r)$ will be dominant, and for a thin region of length l the focal length, f_{∞} , of the equivalent lens in a steady state determined by radial heat conduction is

$$f_{\infty} = \frac{\pi J k w^2}{P \alpha l (dn/dT)} \text{ cm} \quad (1)$$

with n the index of refraction, k the thermal conductivity (cal/(cm sec °C)), P the power in the laser beam (watts), l the sample length (cm), α the absorption coefficient (cm^{-1}), w the "beam radius" (cm), defined as the radius for which field amplitude in the gaussian beam has fallen to e^{-1} of its axial value, and $J = 4.184 \text{ J/cal}$. The derivation is given in the following section. If the beam is suddenly turned on at time $t = 0$, the lens effect builds up with time so that focal length follows the relation

$$f(t) = f_{\infty} [1 + t_c/2t] \quad (2)$$

where t_c is a characteristic thermal time constant given by

$$t_c = \frac{w^2}{4D} \text{ sec} \quad (3)$$

with thermal diffusivity $D = k/\rho c_p$ and $\rho =$ density (g/cm^3), c_p the specific heat (cal/g °C), and k the thermal conductivity. For typical materials the thermal time constant t_c is of the order of seconds for w in the range of a millimeter, although it may be fractions of a millisecond in tightly focused beams.¹⁷

Measurement of the focal length, either in the transient condition or in steady state, then permits determination of α , provided other quantities in eq 1 are known. This review presents an analysis of the thermal lens effect and then a description of two methods used to determine focal length, including a simple and sensitive one which we now use in the majority of cases. The phase changes may also be measured by interferometry, and we describe very precise measurements by Stone¹⁸ using such interferometric techniques. Still other thermal lens methods, and related methods used for gases and solids, are also briefly described.

Before going to the details, we might note the several phenomena which may cause a change of refractive index with temperature. The most common is thermal expansion, which leads to a decrease in density (except in anomalous regions) and a negative contribution to dn/dT . Molecular polarizability may, however, also be a function of temperature and in certain materials may lead to a net positive dn/dT . In liquid crystals, the order parameter is a function of temperature, leading to a positive dn/dT for the ordinary ray and a negative dn/dT for the extraordinary ray in these anisotropic materials. The variation of the band gap energy with temperature is an important factor in dn/dT for semiconductors.

Analysis

The analysis to be given is that of Gordon, *et al.*,¹ corrected by two factors pointed out in later work.^{12,18} The model is that of a gaussian beam passing through an elemental length of an absorbing sample in which heat flow is radial and convection effects are negligible. The beam is turned on at $t = 0$ and the transient effects are developed.

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(17) F. W. Dabby, R. W. Boyko, C. V. Shank, and J. R. Whinnery, *IEEE J. Quantum Electron.*, **5**, 516 (1969).

(18) J. Stone, *J. Opt. Soc. Amer.*, **62**, 327 (1972).

The intensity distribution of the laser beam for the fundamental gaussian mode is

$$S(r) = (2P/\pi w^2) \exp(-2r^2/w^2) \quad (4)$$

where r is radius from the axis and w is the "beam radius," defined following eq 1. P is total power in the beam. The heat generated per unit length and unit time between r and $r + dr$, in a medium with absorption coefficient α , is then

$$Q(r)dr = \alpha S(r)2\pi r dr / J = [2\alpha P / (J\pi w^2)] \exp(-2r^2/w^2)2\pi r dr \quad (5)$$

where J is Joule's coefficient, 4.184 J/cal, if Q is in cal/(sec cm²) and P is in watts.¹⁹

Carslaw and Jaeger²⁰ give Green's function for the problem, yielding temperature at radius r and time t for a unit line heat source at r' and time zero, in an infinite medium

$$G(r, r', t) = \frac{1}{4\pi kt} \exp\left[-\frac{(r^2 + r'^2)}{4Dt}\right] I_0\left(\frac{rr'}{2Dt}\right) \quad (6)$$

where I_0 is the modified Bessel function of first kind, order zero, and D is diffusivity, defined following eq 3. Thus if the beam is turned on at $t = 0$, the temperature rise is

$$\Delta T(r, t) = \int_0^\infty \int_0^t Q(r') G(r, r', t') dt' dr' \quad (7)$$

After substitution of eq 5 and 6, the radial integration may be evaluated through use of eq 13.3(1) of Watson,²¹ interpreted for the modified Bessel function as

$$\int_0^\infty I_0(br') e^{-p^2 r'^2} r' dr' = (1/2p^2) \exp(b^2/4p^2) \quad (8)$$

The remaining integral is simplified by the transformation $y = (w^2 + 8Dt')^{-1}$, giving

$$\Delta T(r, t) = -\frac{\alpha P}{J\pi\rho c} \frac{1}{4D} \int_{w^{-2}}^{(w^2+8Dt)^{-1}} e^{-2r^2 y} \frac{dy}{y} \quad (9)$$

This function has solutions in terms of exponential integrals²²

$$\Delta T(r, t) = \frac{\alpha P}{4J\pi k} \left[Ei\left(-\frac{2r^2}{w^2}\right) - Ei\left(-\frac{2r^2}{8Dt + w^2}\right) \right] \quad (10)$$

Curves for ΔT as a function of radius are plotted for several values of t/t_c , with t_c defined by eq 3, in Figure 2. Near the axis the curves are parabolic and may be approximated by expanding (10) in a power series,^{22, 23} to terms in r^2

$$\Delta T(r, t) \approx \frac{\alpha P}{4J\pi k} \left[\ln\left(1 + \frac{2t}{t_c}\right) - \frac{2(r^2/w^2)}{1 + t_c/2t} \right] \quad (11)$$

(19) If it is preferred to express heat energy in joules also, with k in joules/(sec cm °C) and c_p in joules/(g °C) J is simply replaced by unity in all expressions.

(20) H. S. Carslaw and J. C. Jaeger, "Operational Methods in Applied Mathematics," 2nd ed, Dover, Publications, New York, N. Y., 1948, p 343.

(21) G. N. Watson, "Bessel Functions," 2nd ed, Macmillan, New York, N. Y., 1948, p 393.

(22) E. Jahneke and F. Emde, "Tables of Functions," Teubner, Berlin, 1938, pp 1-8.

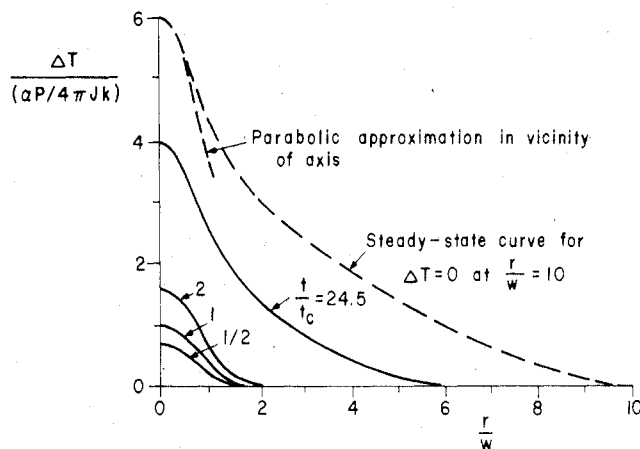


Figure 2. Radial temperature distribution for a gaussian beam in infinite medium. Also steady-state distribution for finite boundary condition. Parameters defined in the text (from ref 1).

The first term represents a logarithmic rise with time of temperature throughout the region and never reaches equilibrium in the infinite medium. However, this term does not become important until time is very large, and then any boundaries will limit the temperature increase. Reference 1 also derives the steady-state solution in a cylinder for which $\Delta T = 0$ at $r = a$, and this is plotted for $a/w = 10$ in Figure 2, with its quadratic approximation near the axis. The latter is a good approximation up to $r/w = 1$, and the quadratic approximation, eq 11 to eq 10, should be similarly good within this range; 87% of the beam energy is included within this range.

The variation of refractive index with radius is proportional to ΔT for small temperature variations, so, using eq 11

$$n(r, t) \approx n_0 + \frac{dn}{dT} \frac{\alpha P}{4J\pi k} \left[\ln\left(1 + \frac{2t}{t_c}\right) - \frac{2(r^2/w^2)}{1 + (t_c/2t)} \right] \quad (12)$$

Since dn/dT is small, the first term in the brackets contributes only a small part to the r -independent index up to times for which the finite boundaries limit temperature, so this term is dropped. The remaining quadratic expression can be written

$$n(r, t) \approx n_0 [1 + \delta(r/w)^2] \quad (13)$$

where

$$\delta = -2 \frac{dn}{dT} \frac{\alpha P}{4J\pi k n_0 [1 + (t_c/2t)]} \quad (14)$$

A short length l of a region with quadratic index variation is known to act as a thin lens with focal length given by^{1, 24}

$$f = -\frac{w^2}{2\delta l n_0} = \frac{\pi J k w^2}{P \alpha l (dn/dT)} \left[1 + \frac{t_c}{2t} \right] \quad (15)$$

which gives eq 1 and 2.

(23) As pointed out by Stone,¹⁸ a factor of π was missing in eq A13 and A14 of ref 1, but this was a typographical omission not affecting the equations used in the body of that paper.

(24) This includes a factor $(1/n_0)$ to account for refraction of rays coming out of the sample into air at a small angle. Equation 3 and subsequent results of ref 1 omit this factor, which is appropriate for application to an element of a continuous medium, but not for a sample imbedded in air.

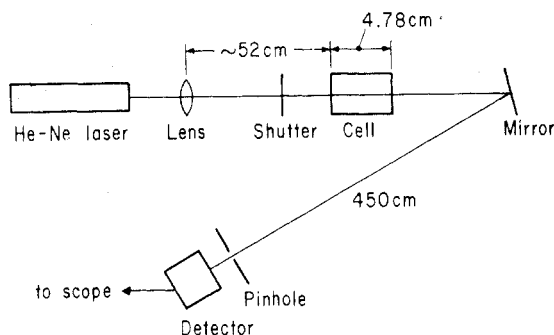


Figure 3. Arrangement of the experiment for ref 12.

The length l is restricted to be small by three considerations. (1) w is assumed constant so that the beam should not diffract appreciably over the length of the cell, requiring $l \ll \pi w^2/\lambda$. (2) $l \ll f$ so that the thin lens development above applies. (3) Power is considered constant over the length of the cell, implying that absorption and scattering losses are negligible in reducing P . The last restriction is easiest to remove provided attenuation may be considered as in a plane wave, $\exp(-\alpha - \alpha_s)z$, where α_s is scattering decay constant. Integration over the length of the cell then gives absorbed power, which replaces Pal in eq 15, by

$$P_{\text{abs}} = \frac{P\alpha}{(\alpha + \alpha_s)} [1 - e^{-(\alpha + \alpha_s)l}] \quad (16)$$

The other two restrictions may also be eliminated by integrating defocusing effects over the expanding beam, but generally require numerical integration because of the nonlinear nature of the interactions.

In the series approximation, more terms may be taken in the expansion of (10), leading to spherical aberrations in the lens; interference effects from these are frequently observed.^{8,9}

Methods Using Direct Measurement of Thermal Lens Strength

In the measurements of Gordon, *et al.*,¹ and Leite, *et al.*,¹⁰ the sample was placed within the laser resonator in order to increase the power P . The beam was scanned by an aperture just outside one laser mirror, moved across the beam by a motor-driven micropositioner, to determine beam radius. Solimini studied the sources of error in this technique and attempted to optimize cavity design for best sensitivity.²⁵ He then measured the absorption coefficients of some 27 organic liquids by the method.¹¹ Since later techniques are simpler, or more accurate, or both, we will not give more details of this arrangement, but do note that beam scanning is done more conveniently by using a rotating mirror to sweep the beam across a fixed aperture, with the detected output displayed on a scope.

It is simpler to place the sample outside the laser cavity, and for most commercial lasers it is essential. Power is lower outside than inside, but Hu recognized that one could still obtain good sensitivity by placing the cell at the position of minimum radius of curvature of the beam wave front and sampling by placing an aperture on the axis and noting the tran-

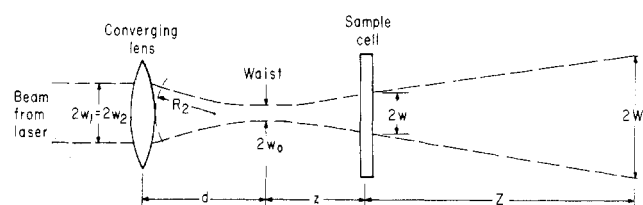


Figure 4. Definition of gaussian beam quantities for the method of ref 12.

sient changes in intensity after turning on the beam. Analysis and experiment showed that with these choices the method is simple and gives good sensitivity and accuracy.¹²

The experimental arrangement for this second method is shown in Figure 3. The converging lens placed outside the laser focuses the beam to a minimum radius w_0 and the sample cell is placed a distance z beyond this minimum or "waist." A detector with an aperture is placed on the axis some distance away, although it is convenient to use a mirror, as shown, to keep the arrangement on one bench. By tilting the mirror until detector output is maximum, the pinhole is conveniently aligned to beam center. The shutter is best placed at the beam waist for sharp chopping.

A gaussian beam is completely specified by its beam radius w at a given position and the radius of curvature R of its wave front at that or another known position.²⁶ Then, referring to Figure 4, if radius is w , a wave front radius of curvature is R_1 at the front of the thin lens L , with focal length f_1 , the beam radius is the same coming out of the lens, but wave front radius of curvature R_2 (defined negative if the wave is converging) is

$$\frac{1}{R_2} = \frac{1}{R_1} - \frac{1}{f_1} \quad (17)$$

Gaussian beam theory²⁶ then shows that the waist with minimum radius w_0 occurs at a distance d away with

$$w_0 = w_2 [1 + (\pi w_2^2 / R_2 \lambda)^2]^{-1/2} \quad (18)$$

$$d = -R_2 [1 + (R_2 \lambda / \pi w_2^2)^2]^{-1} \quad (19)$$

Reference 12 shows that a maximum sensitivity to the thermal lens occurs if the sample is placed a "confocal distance" $z = \pi w_0^2/\lambda$ to the right. Then, assuming the cell appreciably shorter than this z ($z = 20$ cm for $w_0 = 0.2$ mm and $\lambda = 6328$ Å) and the distance Z to the detector large enough so that $Z^2 \gg z^2$, the intensity at the detector (assumed at beam-center bc) builds up with time after turning on the laser beam as

$$\frac{I_{bc}(0)}{I_{bc}(t)} = 1 - \frac{\Theta}{(1 + t_c/2t)} + \frac{\Theta^2}{(1 + t_c/2t)^2} \quad (20)$$

where

$$\Theta = \frac{P_{\text{abs}}}{J\lambda k} \left(\frac{dn}{dT} \right) \quad (21)$$

and P_{abs} is given by eq 16.

(26) See, for example, A. E. Siegman, "An Introduction to Lasers and Masers," McGraw-Hill, New York, N. Y., 1971, Chapter 8.

(25) D. Solimini, *Appl. Opt.*, 5, 1931 (1966).

Table I^a
Experimental Results of Absorptivity α and Published Data^b of Scattering Loss α_s

	Density, g/cm ³	Specific heat, cal/g °C	Refractive index	$-dn/dT$, 10 ⁴ °C ⁻¹	α , 10 ⁴ cm ⁻¹	α_s , 10 ⁴ cm ⁻¹ , at 6328 Å	$\alpha + \alpha_s$, 10 ⁴ cm ⁻¹
Carbon tetrachloride	1.575	0.206	1.4601	5.7	<0.1	0.5	<0.6
Chloroform	1.480	0.230	1.446	5.8	0.17	0.5	0.67
Bromobenzene	1.495	0.254	1.560	5.36 ^c	0.19		
Benzene	0.875	0.413	1.501	5.45 ^c	0.21	1.5	1.71
Chlorobenzene	1.106	0.310	1.524	5.53	0.23	2.0	2.23
Trichloroethylene	1.462	0.220	1.478	5 ^c	0.41		
Heavy water	1.10	1.00	1.328	1.04 ^c	<0.47	0.1	<0.57
Carbon disulfide	1.26	0.25	1.62	7.9	1.4	4.6	6.0
Toluene	0.87	0.40	1.50	5.8	3.3	1.1	4.4
Cyclohexane ^d	0.66	0.59	1.38	5.2	7.6	0.25	7.8
Ethanol	0.79	0.57	1.36	3.6	15.5	0.25	15.8
Water	1.00	1.00	1.33	1.04	29	0.10	29
Nitrobenzene	1.20	0.33	1.55	4.6	58	4.6	62.6

^a From ref 18. ^b Specific references given in ref 18. ^c Data not available; estimated from similar liquids. ^d All liquids purified by Widmer-type distillation apparatus except these.

Figure 5 shows oscilloscope traces measured with an ethanol sample and a calculated, normalized curve of eq 20 showing that observed buildup curves closely resemble the theoretical forms. For $\theta \ll 1$, the squared term in eq 20 may be dropped and the absorption coefficient related directly to the initial and final intensities at the detector. Assuming $\alpha l \ll 1$

$$\alpha = -\frac{[I_{bc}(0) - I_{bc}(\infty)]}{I_{bc}(\infty)} \frac{J\lambda k}{Pl(dn/dT)} \quad (22)$$

For a numerical example, let us use Figure 5a for ethanol. $I_{bc}(0) - I_{bc}(\infty)$ would be estimated as about a half unit from the figure, but expansion of the oscilloscope scale at the time of the measurement gave 0.67, with $I_{bc}(\infty)$ as 3.5. Then using $J = 4.184$ J/cal, $k = 4.23 \times 10^{-4}$ cal/(cm sec °C),²⁷ $\lambda = 0.633 \times 10^{-4}$ cm, $P = 9.4 \times 10^{-3}$ W, $l = 4.78$ cm, and $dn/dT = -3.6 \times 10^{-4}$ (from Table I); α is calculated as 1.33×10^{-3} cm⁻¹, about 15% below Stone's value (Table I). Values of k and dn/dT differ from table to table for a given material, so these need to be obtained precisely if high accuracy in α is required.

In applying the technique, the position of the waist and the beam radius need not be calculated but can be determined by focusing on a card. Measurement error is only a few per cent if the sample is within a region approximately $\pi\omega_0^2/\lambda$ about the exact position. The size of the detector aperture is not critical as long as it is small compared with beam radius at the detector. Sensitivity of the method is limited by short-term fluctuation of laser intensity, which is typically 0.5%, which permits measurement of absorption coefficients in the range 10^{-5} cm⁻¹. We now use this as the most common method of measuring optical absorption of samples to be used in our laboratory. Some unconventional applications have included the measurement of cooling from anti-Stokes fluorescence^{28a} and the measurement of thermal absorption in nematic liquid crystals.^{28b} Absorption coefficients for ordinary and ex-

(27) From "Handbook of Chemistry and Physics," 36th ed, Chemical Rubber Co., Cleveland, Ohio, 1955.

(28) (a) R. K. Jain, C. Hu, T. K. Gustafson, S. S. Elliot, and M. S. Chang, *J. Appl. Phys.*, 44, 3157 (1973); (b) Chenming Hu, Ph.D. Thesis, University of California, Berkeley, 1973.

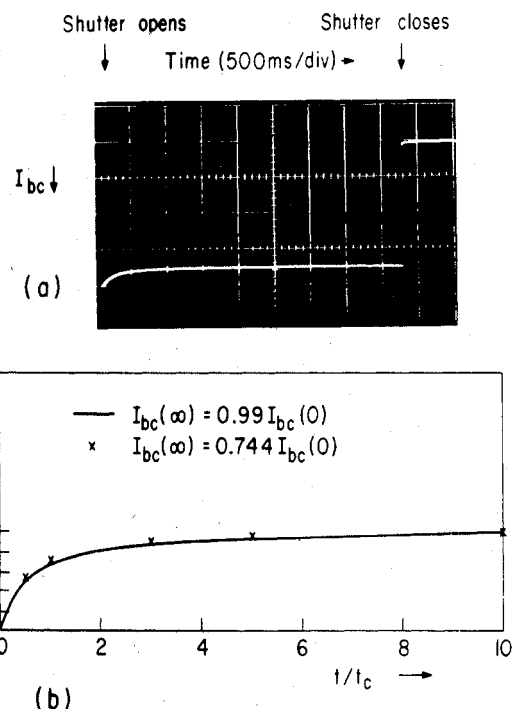


Figure 5. Oscilloscope trace of I_{bc} (inverted) vs. time after the shutter opens. Horizontal scale is 500 msec/div. Laser power is 9.4 mW. (a) Cell filled with ethanol; (b) $I_{bc}(t)$ calculated for $\theta = -0.01$ (line) and -0.3 (crosses) (from ref 12).

traordinary rays are different in these crystals because of the anisotropy.

Interferometer Measurement of the Lens Effect

The lens effect described arises because of differences in phase delays for rays on the axis and off-axis. Interferometric techniques are accurate for measurement of phase delays and have been employed in very precise work by Stone.¹⁸ His arrangement, using a He-Ne laser at 6328 Å, is shown in Figure 6. The water cell, about 1 cm long, is for absorption of radiation at 3.39 μ m, since heating from such radiation would markedly affect results. The interferometer, to quote Stone, "consists of two uncoated Homosil fused-quartz parallel flats 25.4 mm in diameter and 6 mm thick. The beam marked S (for strong) passes directly through plate 1 and the beam marked W (for weak) is first reflected twice

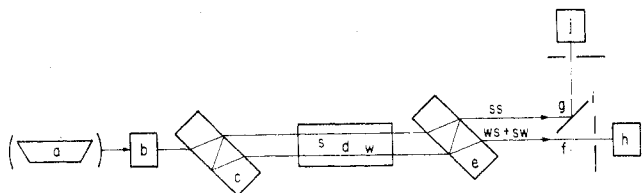


Figure 6. Optical arrangement for loss measurement by interferometry: (a) He-Ne laser, 6328 Å, (b) water cell, (c) plate 1, (d) sample cell, (e) plate 2, (f) interferometer beam, (g) reference beam, (h) signal detector, (i) mirror, (j) reference detector (from ref 18).

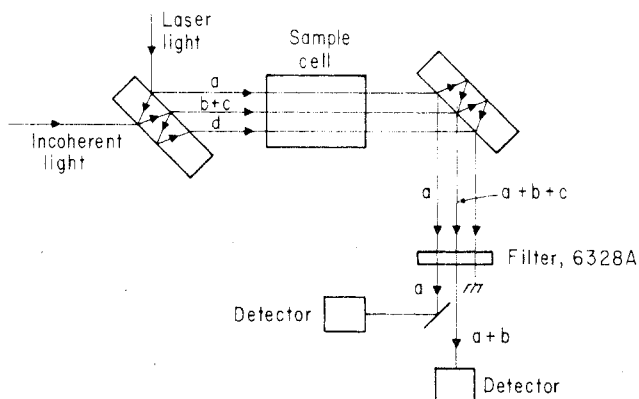


Figure 7. Optical arrangement to measure absorptivity spectrum using an incoherent source; a and b are laser beams; c and d are incoherent light beams (from ref 29).

from plate 1. The beam marked SS is the result of beam S passing through plate 2, and the beam marked WS + SW consists of a super-position of beam W passing through plate 2 and beam S after being reflected twice in plate 2. The latter pair is combined interferometrically, whereas beam SS is the reference beam for the divider. . . . Although beams WS and SW have equal irradiance upon emerging from the interferometer, in passing through the cell one has a much higher irradiance than the other. Thus the heating of the liquid by the strong beam is large, whereas that by the weak beam is almost negligible. The optical-path change is then equivalent to that caused by heating by a single beam whose irradiance is the difference between that of beam S and beam W." The beam SS of the figure was used as a reference and the interference signal in detector h divided by this reference electrically in order to reduce the effect of fluctuations in laser output.

ΔT is given by eq 10. In the example Stone cites, with $P = 10$ mW, $\alpha = 10^{-4}$ cm $^{-1}$, $w = 1$ mm, $k = 2.5 \times 10^{-4}$ cal/(cm sec °C), $\rho = 1.6$ g/cm 3 , $c_p = 0.2$ cal/(g °C), $\Delta T = 7 \times 10^{-5}$ °C after 3.2 sec. The phase change $\Delta\phi = (2\pi l/\lambda)(dn/dT)\Delta T = 0.045$ radian, which is detectable by interferometry.

Table I, selected from Stone's results for 31 liquids, shows absorption coefficients as low as 10^{-5} cm $^{-1}$. For materials with absorption coefficients of 10^{-4} cm $^{-1}$ or greater, results are in good agreement with those of Solimini¹¹ using the thermal lens method described earlier with the sample in the laser cavity. For materials which we have checked by the method with sample outside the cavity¹² agreement is still better. Since this is a single-wavelength measurement, it does not reveal much about the absorp-

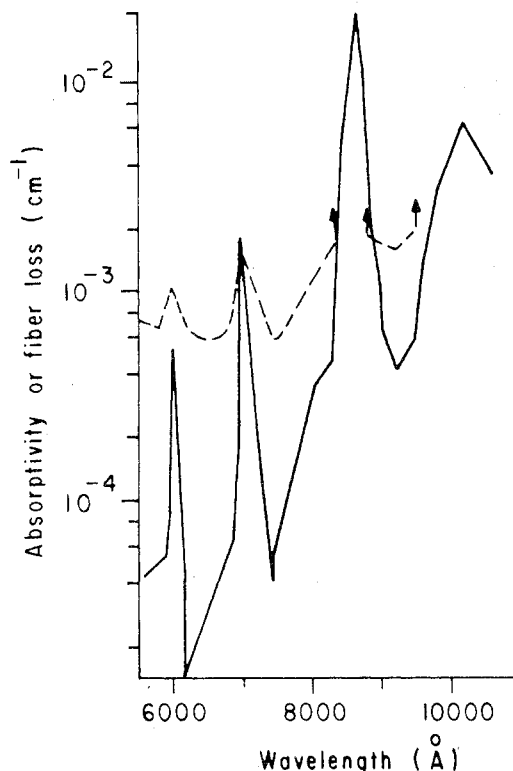


Figure 8. Absorptivity spectrum of chlorobenzene (solid line) and transmission loss spectrum of a glass fiber filled with bromobenzene (broken line), measured by the method of Figure 7 (from ref 29).

tion mechanisms, but the tail of the uv peaks is believed to be the mechanism for the low-loss liquids. The difference between water and heavy water shows that isotopic shift of the absorption minimum is possible.

Stone recently made an important extension²⁹ in which the thermal lens is formed by incoherent light, although the interferometry is done with laser light. In this way the absorption spectrum can be measured over a range of wavelengths without requiring a tunable or multifrequency laser. Figure 7 shows the arrangement. The incoherent light was from a high-pressure xenon arc lamp with collimating optics and one of a set of interference filters of 100 Å band width centered at 200-Å spacings between 5600 and 10,600 Å. The beam b + c in the cell has the incoherent light c to form the thermal lens and the laser light b to probe it. Interference is produced between the two laser beams a + b in the detector, with a ratio again taken to the reference laser beam a in the other detector. The beam shape is not completely controllable for the incoherent beam, but scanning of the profile showed that it was a reasonable approximation to a gaussian over all the wavelengths used. Figure 8 shows the measured absorptivity spectrum of chlorobenzene and the transmission loss spectrum of a glass fiber filled with bromobenzene, taken in this way. With about 2-3 mW of power in the heating beam, absorptivities as low as 2×10^{-5} cm $^{-1}$ were measured by this method. The absorption peaks of the two materials of Figure 8 occur at the same wavelengths and were identified by Stone as overtones of the fundamental C-H vibration at 3.3 μ m.

(29) J. Stone, *Appl. Opt.*, 12, 1828 (1973).

Additional Thermo-optical Methods and Other Applications

At least two additional methods closely related to those described above have been utilized. Kohanzadeh and Auston³⁰ utilized the beat frequency between the fundamental TEM₀₀ and the first transverse mode, TEM₀₁, since frequency of the latter is influenced by any lens within the laser cavity.²⁶ The comparisons of ref 12 show it potentially to be the most sensitive method, but it has the disadvantage of the first method described—that the sample must be placed within the laser cavity. The cavity must also be maintained very free from vibration for the beat frequency to be a “clean” one.

Another method utilizes the change in phase with time after turn-on of the beam. In the first instant (for $t \ll t_c$) the phase delay changes linearly with time, which amounts to a sudden frequency shift, $\Delta\omega = d(\Delta\phi)/dT$. The interference between rays on the axis (where phase shift is maximum) and a reference beam, or with rays from the outer part of the beam where phase shift approaches zero, then yields a beat frequency proportional to the thermal lens effects.^{7,31} Although a simple and interesting effect, ref 12 estimates this as the least sensitive of the methods so far discussed.

The thermal lens methods work for solids and gases also, but many solids have low values of dn/dT , at least in the visible range. Rich and Pinnow³² described a very sensitive calorimetric technique for solids which permits measurement of absorption coefficients as low as $5 \times 10^{-6} \text{ cm}^{-1}$. In this method the cooling rates of suspended samples are measured after being heated to equilibrium by laser beams of known power. For gases, Kreuzer³³ has shown that

(30) Y. Kohanzadeh and D. H. Auston, *IEEE J. Quantum Electron.*, **6**, 475 (1970).

(31) Y. Kohanzadeh, K. W. Ma, and J. R. Whinnery, *Appl. Opt.*, **12**, 1584 (1973).

(32) T. C. Rich and D. A. Pinnow, *Appl. Phys. Lett.*, **20**, 264 (1972).

the optoacoustic effect, whereby the thermal effects from the absorbed energy generate pressure acoustic waves, is a very sensitive one. He and coworkers³⁴ have applied the technique to measure several common pollutants in air at concentrations of a few parts per billion, using intense sources. This effect can be used for liquids also, but is not very sensitive at low laser intensities³⁵ and is difficult to interpret at intensities high enough to produce vaporization or boiling.³⁶

Conclusion

The thermal energy absorbed from a laser beam passing through a nearly transparent material permits absorption coefficient measurements with sensitivities to 10^{-5} cm^{-1} or less by a variety of techniques. The ones stressed in this article utilize the phase changes arising from changes in index of refraction, either to measure the amount of defocusing or the phase changes by interferometry, and are generally called the “thermal lens effects.” To apply to a wide range of frequencies, tunable laser (or parametric oscillator) sources are desirable, and many of these are now available. However, the method utilized by Stone of forming the lens with filtered incoherent radiation and probing it with a coherent source is an important alternative.

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(36) G. S. Bushanam, Ph.D. Thesis, University of Colorado, 1973.