AFOSR 70-0994 TR

AD704156

NONLINEAR REFRACTIVE INDICES
OF CS_2 - CCL_4 MIXTURES

by

Robert Hellwarth* and Nicholas George

California Institute of Technology
Pasadena, California

September, 1969

Grant Number AF-AFOSR-68-1492, Project Number (9768-02)
Research sponsored in part by Air Force Office of Scientific
Research, Office of Aerospace Research, United States Air Force

---

* Also with Hughes Research Laboratories, Malibu, California

19

Qualified requestors may obtain additional copies from the Defense Documentation Center; all others should apply to the Clearinghouse for Federal Scientific and Technical Information.

Reproduction, translation, publication, use and disposal in whole or in part by or for the United States Government is permitted.

Nonlinear Refractive Indices of CS_2-CCl_4 Mixtures †*

Robert Hellwarth
California Institute of Technology, Pasadena, California
and Hughes Research Laboratories, Malibu, California
and
Nicholas George
California Institute of Technology, Pasadena, California

Abstract

We have determined the two independent "fast" nonlinear refractive indices for liquid mixtures of CS_2 and CCl_4 to within 5 % relatively and 8 % absolutely over their range of more than a decade. These indices describe nonlinear propagation of optical pulses of arbitrary polarization, which are of too short duration to be affected by electrostriction. We report measurements of the static Kerr constants of these mixtures having relative accuracy better than one percent. We combine these results with recent data on Rayleigh wing depolarization ratios for the same mixtures to deduce the desired nonlinear indices with the aid of molecular theory. The nonlinear refractive index for linearly polarized light is shown to be two-thirds (± 5%) of the index difference measured by the Kerr effect, at least for molar concentrations of CS_2 greater than 10%. Our measured relative values of the mixture Kerr constants are predicted to within experimental error if one simply replaces the Lorentz local field factors in the classical theory by their 0.6 powers.

---

† Text of talk given at the Non-Linear Optics Conference, Belfast, Northern Ireland, September 12, 1969.

* Research supported in part by the Air Force Office of Scientific Research.

1. Introduction

As high-power laser pulse technology advances, it becomes possible to make controlled and quantitative experimental studies of nonlinear pulse propagation [1], and to make comparisons between these observations and the results of computer-simulated propagation studies [2-4]. In the picosecond-to-nanosecond pulse range, where technology is most advanced, it is not difficult to find materials of high optical quality whose "fast" nonlinear refractive indices respond essentially instantaneously and quadratically to these propagating pulse fields in a way which has been commonly assumed in theory. Evidently, it would be of aid to propagation studies if a variety of materials were available whose fast nonlinear indices were known from independent measurements not involving pulse propagation. In a transparent non-polar fluid, the two independent nonlinear indices that describe the propagation of pulses of arbitrary polarization can be determined from the Kerr constant and the depolarized and polarized light (Rayleigh) scattering strengths of the fluid [5], within certain limits which we discuss in Section 2. We have measured the Kerr constants of mixtures of CS_2 in $CC\ell_4$ as a function of concentration and have combined these with the Rayleigh scattering measurements of Shapiro and Broida [6] on the same mixtures to determine their nonlinear refractive indices. This makes readily available easily prepared, stable, clear liquids of low conductivity whose fast nonlinear index n_2 (for plane polarized pulses) can be chosen anywhere in a range around 10^{-11} to 10^{-12} esu to within 8% absolute accuracy. The effects of these indices are the dominant nonlinear optical effects, unless and until the beam has focused itself to a small spot from which stimulated Raman, Brillouin, and Rayleigh wing scattering commonly emerge, further affecting the incident beam. Also, from intense enough self-focused regions, saturation of the nonlinear index, and electrical breakdown and other catastrophic nonlinear mechanisms become important. However, there is a wide range of experimental regimes where self-focusing and pulse amplitude and frequency modulations may be studied using a nonlinear change $\delta n_{/\!/}$ in the index of refraction for linearly polarized light of the familiar form

$$\delta n_{/\!/} = n_2 E^2, \tag{1}$$

where E is the rms amplitude of the optical field, averaged over several cycles. This index change is related to the accompanying orthogonal index change $\delta n_{\perp}$ by

$$\delta n_{\perp} = \xi \, \delta n_{/\!/} \,. \tag{2}$$

In Section 2 we argue from existing Rayleigh data and some theoretical considerations that $\xi = 1/2$ to within 15%. Our experimental measurements of Kerr constants reported in Section 3 then complete the determination of n_2.

The Kerr constant B is defined by

$$B \equiv (1 - \xi) \, n_2 / \lambda \tag{3}$$

where λ is the free space wavelength of the light experiencing the index changes. Since in our measurements E is a low-frequency field rather than an optical one, there will be a dispersion correction to our n_2 values. This correction is estimated from the standard theory to be never more than a few percent in our mixtures. Since experimental uncertainties are larger than this at present, we will neglect this correction.

We have found a simple empirical modification of the classical theory of the Kerr constant of mixtures which summarizes all of our Kerr data over the entire range of mixtures to better than one percent. We have tried expressions of the following form for B as a function of the molar concentration m of species 1 (CS_2) in species 2 ($CC\ell_4$):

$$B(m, S) = (L\,L')^{2S}\,[mK_1 + (1 - m)\,K_{\underset{0}{2}}]\;N(m)\,/\,n(m) \qquad (4)$$

where N(m) is the total number of molecules per unit volume, n is the linear refractive index of the mixture, and K_1 and K_2 are the "molecular" Kerr constants of the pure liquids chosen so as to give the observed B values at $m = 0$ and 1. We define the Lorentz local field factors $L = (n^2 + 2)/3$ and $L' = (\epsilon + 2)/3$ so that, with $S = 1$, equation (4) gives the classical theory based on the hypothesis of Lorentz local fields acting on independent molecules [7]. Our results for the relative Kerr constants of CS_2-$CC\ell_4$ mixtures are given to within the experimental errors ($\sim 1/2\%$) by using $S = 0.6$ (instead of unity) and $K_1 = 22.62\ K_0$ in (4). Although the S which gives the best fit is far from unity, one cannot conclude that the Lorentz local field concept fails here. We have discovered from our and others' measurements that, at 23°C, the indices of refraction $n(m)$ for our mixtures are given to the remarkable precision of at least two parts in 10^4 by the Lorentz local field formula [7]

$$(n^2 - 1)/(n^2 + 2) = [4\pi N(m)/3] [m\alpha_1 + (1 - m)\alpha_2] \qquad (5)$$

if we use for the molecular polarizabilities the values $\alpha_1 = 8.434 \times 10^{-24}$ cm^3 and $\alpha_2 = 10.461 \times 10^{-24}$ cm^3, which derive from the observed refractive indices, 1.6231 and 1.4593, of the pure liquids CS_2 and $CC\ell_4$ at 23°C and $\lambda = 633$ mμ. These polarizability values fall within one percent of their values for low-density vapors. The combined experimental uncertainties in our prism refractometer measurements of n and of the tabulated data on $N(m)$ appear to be only slightly less than the accuracy of (5) for our mixtures.

We have also measured the static dielectric constant $\epsilon(m)$ of our mixtures by both standard heterodyne and capacitance bridge techniques, and found our results to be predicted to within experimental error of at most 3×10^{-3} by using the values $\alpha_1' = 8.427 \times 10^{-24}$ cm^3 and $\alpha_2' = 11.134 \times 10^{-24}$ cm^3 in equation (5) (but with ϵ for n^2) which yield the observed dielectric constants 2.6325 and 2.232 of the pure liquids CS_2 and $CC\ell_4$ at 23°C.

It is well known that the classical theory of the Kerr effect is not very accurate at liquid densities, and so it is not surprising that (4) with $S = 1$ does not predict B well. Why such a simple modification as reducing S gives such accurate predictions is not understood. It is interesting that Porto has observed that Raman scattering cross-sections in the same mixtures deviate similarly from what one would expect from the classical Lorentz local field theory [8].

2. The Determination of the Nonlinear Index Ratio from Rayleigh Scattering Data

There is a widely used "linear dipole approximation," or LDA, for describing how molecules in a fluid interact with and scatter electromagnetic fields whose frequencies are all low compared to any frequencies at which the molecules absorb. In the LDA all molecules behave electrically as if they were electric dipoles, induced instantaneously and linearly by the total electric field produced at their own center of mass coordinate by external sources and by the dipole moments of all the other molecules. If the LDA is valid, then one can show, independently of the nature of intermolecular correlations, density, or degree of mixture, that the index ratio ξ is given by [9,10]

$$\xi = 1 - 2r \tag{6}$$

where r is the ratio of the depolarized-to-polarized intensities of light scattered from a beam of frequency $\omega_o = c/(n\lambda)$ to the "Rayleigh wings," that is, to all frequencies shifted beyond Brillouin shifts ($\sim$ sound velocity $\div\ \lambda$) from ω_o. Shapiro and Broida have measured the values $r = 0.7(1)$, 0.76(2), 0.77(6), 0.75(3) for mixtures of 10, 53, 67, and 100 volume percent of CS_2 in $CC\ell_4$, respectively [6]. (A number in parentheses following a measured value indicates the uncertainty in the last digit.) Gabelnik and Strauss have measured r = 0.72(5) for pure CCl_4 [11]. These values are not all independent; r is expected to vary smoothly, if at all, as a function of concentration. We feel, therefore, that r is most probably within a few percent of the value 0.75 (the value expected from classical theory) for all concentrations. Therefore, the LDA implies through (6) that it is probable that ξ falls within 10% of the value -1/2. In confirmation, we note that Pauthenier has measured ξ directly to be -0.50 for pure CS_2, but did not assess his accuracy [12]. We now summarize the evidence that the LDA is accurate for our mixtures.

One test of the LDA is how closely a certain relation holds between the Kerr constant and the absolute strength of the depolarized Rayleigh scattering [9,10]. Existing data show that this relation predicts the Kerr constant from the depolarized scattering to within at least 20% for pure CS_2 and to within at least 60% for CCl_4; inaccuracies in the data prevent saying whether the LDA is more accurate [10]. The agreement between the measured ξ with that predicted from (6) is further evidence of the consistency of the LDA for CS_2. Perhaps the most sensitive test of the LDA is the observed accuracy of the Lorentz-Lorenz relation (5) for all CS_2-CCl_4 mixtures. The LDA expression for the molar polarizability obeys a minimum variational principle, and, when minimized with respect to a parameter which describes the magnitude of the local field, it gives (5) [13]. Theoretical estimates of the result of fully minimizing the LDA expression show that the corrections to (5) are less than a few percent. So, if higher multi-pole interactions or collisioninduced perturbations were significant, (5) could not have the absolute accuracy of greater than a percent that it does. However, even though the LDA may be accurate for treating the linear refractive index and Rayleigh scattering from $CC\ell_4$, its Kerr constant may contain a significant part, conceivably as large as half, that arises from electronic nonlinearity of individual molecules, (i. e., their "hyperpolarizability"). Because of this latter (small) possibility, we have less confidence in our prediction for n_2 when it arises mainly from $CC\ell_4$ molecules, that is, for $m \lesssim 0.1$. Fortunately, over most of its range, n_2 depends mainly on the much more polarizable and anisotropic CS_2 molecules present (which are known not to have significant hyperpolarizability [10]) and is insensitive to the hyperpolarizability of $CC\ell_4$.

From the foregoing independent checks of the LDA we feel safe in assuming that (6) is accurate to within 10% for molar concentrations m of CS_2 in $CC\ell_4$ greater than 0.1. The independent uncertainties in the Rayleigh depolarization ratio r combine in (6) to yield

$$\xi = -0.50(7) \qquad (7)$$

which means we may take $n_2 = 2B\lambda/3 \pm 5\%$ for CS_2-$CC\ell_4$ mixtures for which n_2 lies in the top decade of its range.

3. Kerr Measurements

Our Kerr measurements were made by a two-cell null method that has been described in detail elsewhere [14]. Two Kerr cells of identical construction are placed between crossed polarizers with their Kerr fields mutually perpendicular and at 45° with respect to either polarizer. One cell is filled with the mixture under investigation and the other with CS_2 or CCl_4. The Kerr fields in the two cells are perpendicular to the direction along which the beam of a 6328 Å helium-neon laser propagates through them. The output beam from the final polarizer is detected by an S-20 photomultiplier followed by a narrow band amplifier phase-locked to two 400 Hz high-voltage signals which are applied in a ratio R to the two Kerr cells. This ratio is adjusted until the birefringence in one cell cancels that in the other. A phase difference between the polarizations emerging from the first cell of less than a microradian can be detected. This limitation on sensitivity seems to arise from light scattered by turbulence. The observed ratio of the Kerr constants in the two cells ideally is R^2 whose measured values could be reproduced to one part in 500 from one day to the next with independently mixed samples. Our starting liquids were Baker Analyzed Reagent CS_2 and Matheson, Coleman, and Bell Spectroquality Reagent CCl_4.

The results of these ratio measurements are given in Table I for various volume concentrations C defined as the ratio of the volume of pure CS_2 to the total volume of liquid before mixing. At $23^{\circ}C$ to which all our measurements are adjusted,

$$C^{-1} = 1 + 1.5993\,(1 - m)/m. \qquad (8)$$

For our numerical comparisons with (4) we have developed an empirical formula for the total number density N as a function of C that gives the tabulated results for the mixture densities [15] adjusted to 23°C to better than one part in 10^4:

$$N(C)/N(0) \cong (1 + 0.59932C)\,[1 \overset{-\swarrow}{+} 0.0156C(1 - C)]\,, \tag{9}$$

where $N(0) = 6.242 \times 10^{21}\ \text{cm}^{-3}$. The first factor on the RHS would result alone if every molecule occupied the same volume in the mixture as in the pure liquid.

In Fig. 1 we compare our data of Table I with values calculated from (4): first, with the classical value $S = 0$ which gives poor agreement and with the value $S = 0.6$ which gives agreement to within 1/2% everywhere, which is about our relative experimental error. Also in Fig. 1 we compare similarly some very much less accurate data reported in 1932 by Briegleb [16]: first, with $S = 1$, and then with $S = 0.4$ which seemed to give the best agreement, although the scatter in this data made comparisons uncertain in any case.

The Kerr constant for pure CS_2 may be obtained from the three sources quoted in the Landolt-Bornstein tables [17] and an independent measurement of Briegleb [16] which give for $10^9 \times B$ esu the values 346, 355, 360, and 323, respectively, normalized to $\lambda = 546$ mμ and 23°C. From these and its measured λ dependence [17], $B(CS_2) = 341 \pm 18 \times 10^{-9}$ esu at 546 mμ and $277 \pm 15 \times 10^{-9}$ esu at 633 mμ. Therefore, at 23°C and 546 mμ

$$n_2\,(CS_2) = 1\ \ 24(\ 9) \times 10^{-11}\ \text{esu}, \qquad (10)$$

and at 633 mμ it is 6 ± 1% less. Both B and n_2 decrease by around 1/4% per degree at 20°C [14].

These values, used with Table I or equation (4) with (7), give our results for the two nonlinear indices of CS_2-CCl_4 mixtures. Considerable improvement in accuracy for relative indices at different concentrations would result from more accurate measurements of the Rayleigh wing ratio r. Existing experimental uncertainties in the absolute value of the Kerr constant of pure CS_2 (~ 5%) limit our knowledge of the absolute values of the indices further.

TABLE I

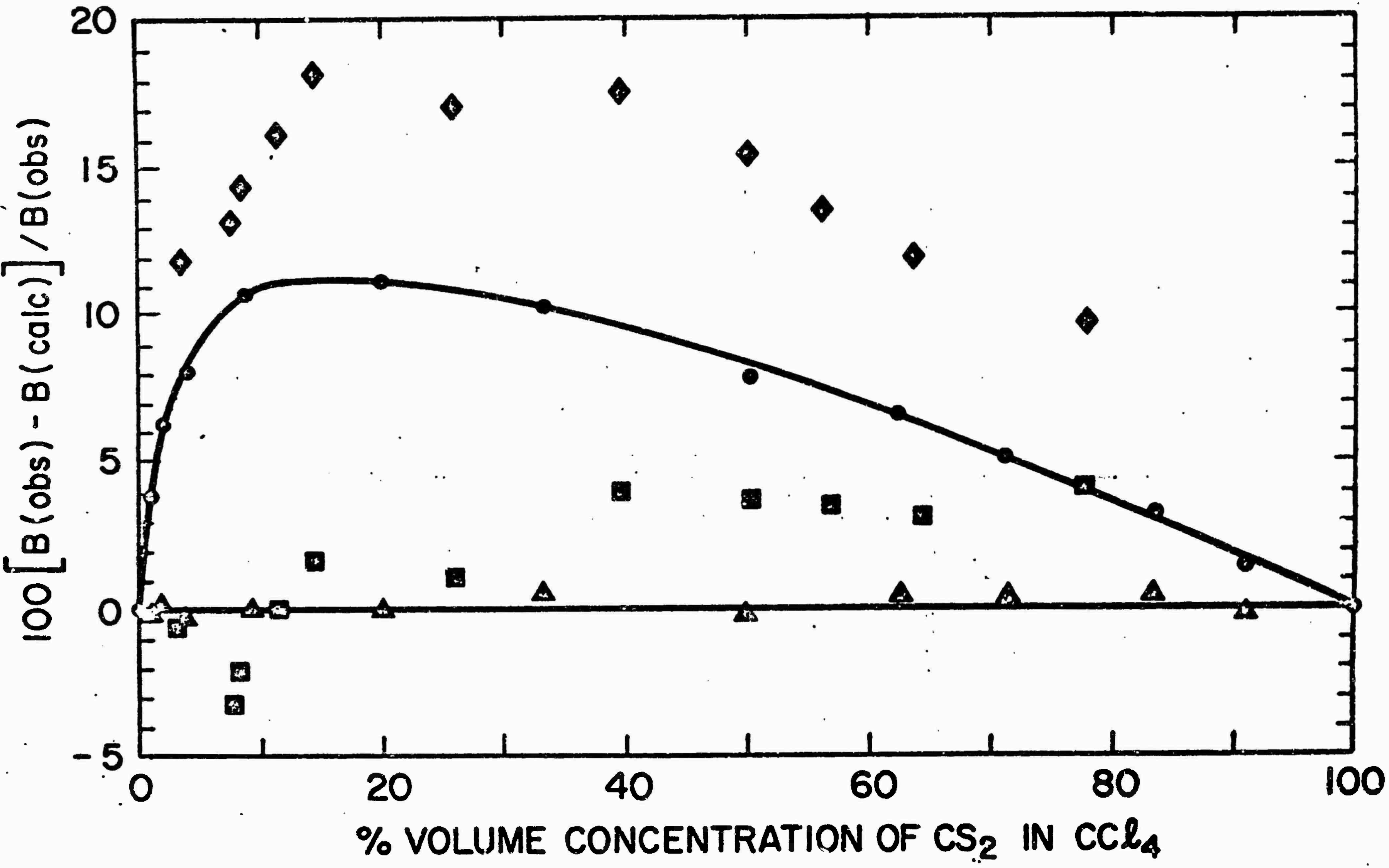
100XC (% Volume Concentration of CS_2 in CCl_4)	Measured $\frac{B\ (\text{mixture})}{B\ (CCl_4)}$
0.990	1.347
1.961	1.696
3.845	2.354
9.091	4.239
20.00	8.219
33.33	13.28
50.00	19.71
62.50	24.97
71.42	28.72
83.33	33.98
90.91	37.27
100.00	41.64

References

1. G. McAllister, J. H. Marburger, and L. G. DeShazer, *Phys. Rev. Letters* *21*, 1648 (1968).
2. J. H. Marburger and W. G. Wagner, *IEEE J. Quantum Electronics* *QE-3*, 415 (1967).
3. F. DiMartini, C. H. Townes, T. K. Gustafson, and P. L. Kelley, *Phys. Rev.* *164*, 312 (1967).
4. E. L. Dawes and J. H. Marburger, *Phys. Rev.* *179*, 862 (1969).
5. The "depolarized" scattered light is that which is linearly polarized perpendicular to the direction of linear polarization of the incident beam; the "polarized" scattered light is that which is polarized perpendicular to the depolarized scattering.
6. S. L. Shapiro and H. P. Broida, *Phys. Rev.* *154*, 129 (1967).
7. M. Born, *Optik* (Springer-Verlag, Berlin, 1965).
8. S. P. S. Porto (private communication).
9. S. Kielich, *Chem. Phys. Letters* *2*, 112 (1968).
10. R. Hellwarth (to be published, *J. Chem. Phys.*).
11. H. S. Gabelnick and H. L. Strauss, *J. Chem. Phys.* *49*, 2334 (1968).
12. M. Pauthenier, *Journal de Physique* *2*, 183 (1921).
13. R. Hellwarth, *Phys. Rev.* *152*, 156 (1966).
14. N. George, R. W. Hellwarth, and C. R. Cooke, *Proceedings of the Conference on Laser Measurements, URSI Committee 1*, (Warsaw, Poland, September 1968), edited by L. Essen.
15. H. Dunken, *Z. Physik Chem. (B)* (Leipzig) *53*, 264 (1943).
16. G. Briegleb, *Z. Physik Chem.* *16*, 249 (1932).
17. Landolt-Bornstein, *Zahlenwerte und Functionen I/3* (Springer-Verlag, Berlin, 1962), p. 509.

Figure Caption

Figure 1. Observed Kerr constant B(obs) compared with the constant B(calc) calculated from (4). Our observations compared: ○ with S = 1, △ with S = 0.6. Briegleb's observations compared: ◇ with S = 1, ▣ with S = 0.4.


100[B(obs) - B(calc)]/B(obs)
20
15
10
5
0
-5
0
20
40
60
80
100
% VOLUME CONCENTRATION OF CS_2 IN CCl_4

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Engineering and Applied Science Division California Institute of Technology Pasadena, California 91109	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

NONLINEAR REFRACTIVE INDICES OF CS_2 - CCL_4 MIXTURES

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Scientific Interim

5. AUTHOR(S) *(First name, middle initial, last name)*
Robert Hellwarth
Nicholas George

6. REPORT DATE September 1969	7a. TOTAL NO. OF PAGES 15	7b. NO. OF REFS 17

8a. CONTRACT OR GRANT NO. AF-AFOSR-68-1492 b. PROJECT NO. 9768-02 c. 6144501F d. 681305	9a. ORIGINATOR'S REPORT NUMBER(S) 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

1. This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES TECH, OTHER	12. SPONSORING MILITARY ACTIVITY AF Office of Scientific Research (SREE) 1400 Wilson Boulevard Arlington, Virginia 22209

13. ABSTRACT

We have determined the two independent "fast" nonlinear refractive indices for liquid mixtures of CS_2 and $CC\ell_4$ to within 5% relatively and 8% absolutely over their range of more than a decade. These indices describe nonlinear propagation of optical pulses of arbitrary polarization, which are of too short duration to be affected by electrostriction. We report measurements of the static Kerr constants of these mixtures having relative accuracy better than one percent. We combine these results with recent data on Rayleigh wing depolarization ratios for the same mixtures to deduce the desired nonlinear indices with the aid of molecular theory. The nonlinear refractive index for linearly polarized light is shown to be two-thirds (±5%) of the index difference measured by the Kerr effect, at least for molar concentrations of CS_2 greater than 10%. Our measured relative values of the mixture Kerr constants are predicted to within experimental error if one simply replaces the Lorentz local field factors in the classical theory by their 0.6 powers.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Nonlinear Refractive Index						
Kerr Constant						
Rayleight Wing Scattering						
Light Scattering						
Liquids						