

## Optical Kerr effect induced by ultrashort laser pulses

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A generalization of the classical molecular-optics theory of the optical Kerr effect (OKE) is presented which permits a study of the effect when induced by ultrashort laser pulses. Explicit relationships between results from this general theory and often-used phenomenological equations governing the temporal behavior of the OKE are established. Numerical results are presented for the liquids carbon disulfide and nitrobenzene, illustrating in detail the temporal nature and intensity of the birefringence induced in these liquids by ultrashort laser pulses. The importance of these results is discussed in connection with a number of self-induced nonlinear phenomena arising from the OKE as well as in conjunction with the OKE shutter switched by an ultrashort laser pulse. In addition, a discussion is given of the nature of the birefringence induced by picosecond laser pulses as well as aspects of the extension of OKE photography to the subpicosecond domain.

### I. INTRODUCTION

The optical Kerr effect (OKE) was first experimentally reported in 1964, independently by Mayer and Gires,<sup>1</sup> and Maker, Terhune, and Savage.<sup>2</sup> However, it was not until the introduction of mode-locked lasers, capable of producing high-intensity coherent-light pulses of picosecond duration, that this effect found wide application to the ultrafast diagnosis of a number of phenomena. These include the measurement of picosecond fluorescent lifetimes and molecular relaxation times,<sup>3-10</sup> the measurement of picosecond pulsewidths,<sup>11-17</sup> optical pulse compression,<sup>18-20, 28</sup> mode locking of lasers,<sup>21-26</sup> nonlinear intensity-dependent discriminators,<sup>17, 27, 28</sup> picosecond time-resolved emission and absorption spectroscopy,<sup>5, 6, 29-31</sup> the temporal measurement of short CO<sub>2</sub> pulses,<sup>32-34</sup> the picosecond framing photography of laser-produced plasmas,<sup>35, 36</sup> and picosecond time-resolved laser emission spectroscopy.<sup>37</sup> In particular, the use of the OKE induced by mode-locked laser pulses in configurations which provide a high-speed optical gate or photographic shutter show considerable promise in extending the range of ultrafast two-dimensional photography.<sup>11, 12, 14, 35-37</sup> For although significant advances have been made in time-resolved one-dimensional photography with the design of image-converter streak cameras<sup>38-41</sup> capable of temporal resolutions ~1 psec,<sup>40, 41</sup> the use of electro-optic techniques appears to be severely limited in permitting two-dimensional photography in this range.

This approach, be it with the aid of Pockels or Kerr cell optical shutters, or with the use of gated-image intensifiers, is primarily limited by the intrinsic response of these devices to fast high-voltage pulses.<sup>42-46</sup> Typically, maximum temporal

resolutions of several hundred psec are recorded. Fortunately, the OKE shutter circumvents these limitations and offers a relatively simple approach to picosecond and subpicosecond two-dimensional photography.

However, in using an OKE shutter for high-speed photographic analysis, particular consideration must be given to its transmission characteristics. These are strongly dependent both on the type of optical configuration used in the photographic system and on the characteristics of the ultrashort optical pulses used to gate the shutter. Before this can be carefully attempted it is necessary to have a thorough knowledge of the response of the Kerr-active medium to the ultrashort pulse.

It is the intent of this paper to analyze in detail the temporal and spatial nature of the birefringence induced in such media by ultrashort laser pulses. This is achieved by a generalization of a classical molecular optics theory of the OKE to determine the response of the birefringence to laser pulses of arbitrary temporal and spatial character. From this analysis, the importance of delineating the relative effects of the molecular orientational and electronic contributions to the induced birefringence is clearly illustrated, and their relative effects for particular pulse characteristics defined. This has led to a firmer understanding of the temporal and spatial nature of the birefringence induced in commonly used liquids (such as carbon disulfide and nitrobenzene), and also to the proposal that under suitable conditions, they may be used in OKE photographic schemes providing temporal resolutions in the subpicosecond range ( $10^{-12}$ – $10^{-14}$  sec). Thus this analysis should aid in understanding the nature and possible limitations peculiar to most applications of the OKE, particularly to its use in ultrafast two-dimension-

al photography; in addition, it should be relevant to the study of many self-induced nonlinear phenomena arising in part or in whole from the OKE.

## II. THEORY OF THE OPTICAL KERR EFFECT INDUCED BY ULTRASHORT LASER PULSES

The most fundamental approach to a study of optically induced birefringence is through the use of classical molecular-optics theory in conjunction with nonequilibrium statistical fluid mechanics. This was first applied to the Kerr and optical Kerr effects by Buckingham,<sup>47-49</sup> who made the first explicit prediction of the optical Kerr effect in 1956,<sup>49</sup> and subsequently by Kielich,<sup>50-55</sup> who enlarged and developed the theory in a number of papers. Both of these authors derived expressions for the various optical Kerr coefficients in terms of liquid and molecular parameters, and found expressions for the induced birefringence in the case of a plane-wave optical field.<sup>49, 50</sup>

In the present paper, this molecular-optics theory of the OKE has been extended to include the more general case of an optical-pulse envelope with an arbitrary spatial and temporal dependence. The mainstay of the method described by Buckingham and Kielich is the adoption of a relaxation-diffusion equation originally proposed by Debye<sup>56</sup> which governs the spatial and temporal behavior of a nonequilibrium molecular distribution function.<sup>50</sup> The form of the induced birefringence is found directly from this distribution function. By selecting a distribution function of known form but with undetermined coefficients, the Debye relaxation-diffusion equation is solved to determine these unknown coefficients and hence find the induced birefringence.

To generalize this approach to include the case

$$n_{\parallel} = n_0 + \delta n_{\parallel}$$

$$= n_0 + \frac{3}{2} n_2^e E_{\omega}^2(\vec{r}, t) + n_2^o \frac{\pi^{1/2}}{3 A_x v \tau_o} \overline{E}_{\omega}^2(\vec{r}, t) \exp\left(A_x^2 (x - vt)^2 + \frac{x - vt}{v \tau_o} + \frac{1}{4 A_x^2 v^2 \tau_o^2}\right) \operatorname{erfc}\left(A_x (x - vt) + \frac{1}{2 A_x v \tau_o}\right) \quad (3)$$

and

$$n_{\perp} = n_0 + \delta n_{\perp}$$

$$= n_0 + \frac{1}{2} n_2^e E_{\omega}^2(\vec{r}, t) - n_2^o \frac{\pi^{1/2}}{6 A_x v \tau_o} \overline{E}_{\omega}^2(\vec{r}, t) \exp\left(A_x^2 (x - vt)^2 + \frac{x - vt}{v \tau_o} + \frac{1}{4 A_x^2 v^2 \tau_o^2}\right) \operatorname{erfc}\left(A_x (x - vt) + \frac{1}{2 A_x v \tau_o}\right), \quad (4)$$

where  $n_0$  is the linear refractive index at the angular optical frequency  $\omega'$  of the "probe" or "test" beam, and  $\tau_o$  is the mean orientational relaxation time of the Kerr medium. The induced birefringence  $\Delta n = n_{\parallel} - n_{\perp}$  is given by

$$\Delta n = \Delta n^o + \Delta n^e, \quad (5)$$

of a short-duration optical pulse, an essentially iterative method was used. Beginning with the known solution for a plane-wave optical field,<sup>50</sup> the constant coefficients of this solution were replaced with expressions incorporating the assumed pulse-envelope model and a new set of variable but undetermined coefficients. Then, using an expression for the molecular-field interaction potential<sup>49, 50</sup> corrected to correspond to the plane-wave solution, the relaxation-diffusion equation was applied a second time to solve for this new set of coefficients.<sup>35</sup> This method was straightforward and general, and readily yielded solutions for a variety of assumed pulse models.

Specifically, in the present paper, the model adopted for the optical pulse is a three-dimensional Gaussian pulse described by

$$E_{\omega}(\vec{r}, t) = 2E_0^2 \exp[-A_x^2 (x - vt)^2 - A_y^2 y^2 - A_z^2 z^2] \times \cos^2[\omega(t - x/v)], \quad (1)$$

where  $A_x$ ,  $A_y$ , and  $A_z$  are arbitrary parameters determining the spatial and temporal variation in the pulse envelope. The pulse travels in the positive  $x$ -axis direction with a (group) velocity  $v = c/n_{\omega}$ . The factor of 2 appearing in Eq. (1) is included for convenience so that the time-averaged optical pulse envelope is

$$\overline{E}_{\omega}^2(\vec{r}, t) = E_0^2 \exp[-A_x^2 (x - vt)^2 - A_y^2 y^2 - A_z^2 z^2]. \quad (2)$$

The full-width-at-half-maximum (FWHM) duration of the pulse described by Eqs. (1) and (2) is given by  $T_{\omega} = 2(\ln 2)^{1/2}/A_x v$ , and it is assumed that the pulse envelope varies slowly relative to the period of the optical electric field, i.e.,  $T_{\omega} \gg 2\pi/\omega$ .

For the Gaussian optical pulse, the iterative molecular-optics theory yields<sup>35</sup> the refractive indices  $n_{\parallel}$  and  $n_{\perp}$  for, respectively, polarizations parallel and perpendicular to  $\vec{E}_{\omega}$ :

where the orientational and electronic contributions to the induced birefringence are, respectively,

$$\Delta n^o = n_2^o \frac{\pi^{1/2}}{2A_x v \tau_o} \overline{E}_\omega^2(\vec{r}, t) \exp\left(A_x^2(x - vt)^2 + \frac{x - vt}{v \tau_o} + \frac{1}{4A_x^2 v^2 \tau_o^2}\right) \operatorname{erfc}\left(A_x(x - vt) + \frac{1}{2A_x v \tau_o}\right) \quad (6)$$

and

$$\Delta n^e = n_2^e E_\omega^2(\vec{r}, t) = n_2^e \overline{E}_\omega^2(\vec{r}, t) [1 + \cos 2\omega(t - x/v)]. \quad (7)$$

The contribution to the total nonlinear refractive index  $n_2 = n_2^o + n_2^e$  resulting from the electronic hyperpolarizability<sup>48, 49, 55</sup> is readily found from the molecular optics theory to be<sup>48-55</sup>

$$n_2^e = \frac{2\pi\rho}{3n_o} \gamma \left(\frac{n_o^2 + 2}{3}\right)^2 \left(\frac{n_\omega^2 + 2}{3}\right)^2, \quad (8)$$

where  $\rho$  is the number density of the Kerr medium, and  $\gamma = \frac{1}{5} \gamma_{ij}^{\omega, \omega'}$  ( $i, j = 1, 2, 3$ ) where  $\gamma_{ijkl}^{\omega, \omega'}$  is a component of the fourth-rank tensor describing the electronic (second) hyperpolarizability at the angular frequency  $\omega'$  of the probe light induced<sup>47, 49, 50, 55</sup> by the optical field of angular frequency  $\omega$ . The orientational contribution  $n_2^o$  to the nonlinear refractive index  $n_2$  resulting from an anisotropy in the molecular polarizability is given by<sup>48-55</sup>

$$n_2^o = \frac{2\pi\rho}{15kTn_o} \delta^2 \left(\frac{n_o^2 + 2}{3}\right)^2 \left(\frac{n_\omega^2 + 2}{3}\right)^2, \quad (9)$$

where  $k$  is Boltzmann's constant,  $T$  is the temperature of the medium in °K, and  $\delta^2 = \frac{1}{4}(\alpha_{ii}^{\omega'} - \alpha_{jj}^{\omega'}) \times (\alpha_{ii}^\omega - \alpha_{jj}^\omega)$  ( $i, j = 1, 2, 3$ ) is a measure of the anisotropy in the molecular polarizabilities  $\alpha_{ij}^{\omega'}$  and  $\alpha_{ij}^\omega$  at frequencies  $\omega'$  and  $\omega$ , respectively. In the definitions of  $\gamma$  and  $\delta^2$ , the tensor indices  $i, j$  refer to the principal axes of the Kerr-medium molecules so that, for example,  $\alpha_{ij} = \alpha_i \delta_{ij}$ , with similar simplifying relations among the  $\gamma_{ijkl}$  components.<sup>47, 55</sup>

The above expressions for the electronic Kerr coefficient  $n_2^e$  and the orientational Kerr coefficient  $n_2^o$  were derived from a model which assumed complete independence for the individual molecules composing the Kerr medium.<sup>50</sup> While this assumption is acceptable for the electronic effect in both gases and liquids, it is invalid for the orientational effect, particularly in the case of liquids. Values of  $n_2^o$  calculated from Eq. (9) are generally considerably larger than experimentally known values<sup>57</sup> of  $n_2^o$ . It is thus necessary to reexamine the derivation of  $n_2^o$ , taking into account the effect of multiple molecular interactions on the orientating influence of an applied electric field. The most important interaction in a medium composed of anisotropic molecules is that of angular correlation between members of pairs of molecules.<sup>48-55, 58-60</sup> Because of the permanent and/or induced dipole moments in the molecules, a given molecule is no longer completely free to

align itself (i.e., its principal dipole axis) parallel to the applied electric field, but is hindered in doing so by its tendency to simultaneously align itself with nearest-neighbor molecules which, in general, have various different (though not random) orientations. Hence the net effect of binary angular correlations among the molecules is to reduce the effective value of the orientational Kerr coefficient  $n_2^o$  to a first-order corrected coefficient,  $c n_2^o$ , given by<sup>50</sup>

$$c n_2^o = n_2^o (1 + J_a), \quad (10)$$

where  $J_a$  is the integral parameter

$$J_a = \frac{\rho}{2V\delta^2} \sum_{s,t=1}^3 \alpha_s^\omega \alpha_t^{\omega'} \int \int (3\cos^2\theta_{st}^{pq} - 1) \times g^2(\Omega_p, \Omega_q) d\Omega_p d\Omega_q, \quad (11)$$

giving a measure of the degree of angular correlation for pairs of molecules. Here,  $\theta_{st}^{pq}$  denotes the angle between the principal axes  $s$  and  $t$  of molecules  $p$  and  $q$ ,  $g^2(\Omega_p, \Omega_q)$  is the correlation function for pairs of molecules having orientations specified by  $\Omega_q$  and  $\Omega_p$ ,  $V$  is the volume of the medium, and the integration is over the entire range of the set of angular coordinates symbolized by  $\Omega_q$  and  $\Omega_p$ . In practice, calculations of  $J_a$  using Eq. (11) are very approximate, since the exact form of the correlation function  $g^2(\Omega_q, \Omega_p)$  is ambiguous. However, the same parameter  $J_a$  also appears in the expression for the depolarization of scattered light  $D$  as<sup>61</sup>

$$D = \frac{6\delta^2(1 + J_a)}{45\rho k T \beta_T (\alpha^\omega)^2 + 7\delta^2(1 + J_a)}, \quad (12)$$

where  $\alpha^\omega = \frac{1}{3}(\alpha_1^\omega + \alpha_2^\omega + \alpha_3^\omega)$  is the mean polarizability and  $\beta_T$  is the isothermal compressibility of the medium. Solving for  $J_a$  and substituting into Eq. (10) gives

$$c n_2^o = \frac{6\pi\rho^2(\alpha^\omega)^2\beta_T}{n_o} \frac{D}{6 - 7D} \left(\frac{n_o^2 + 2}{3}\right)^2 \left(\frac{n_\omega^2 + 2}{3}\right)^2. \quad (13)$$

In those cases where a value for  $\alpha^\omega$  is unknown but  $\delta^2$  is known, the Lorentz-Lorenz equation may be used to arrive at an alternative but more approximate expression for  $c n_2^o$  given by

$$c n_2^o \approx \frac{3\beta_T}{8\pi n_0} \frac{D}{6-7D} \left( \frac{n_0^2+2}{3} \right)^2 (n_\omega^2-1)^2. \quad (14)$$

The usefulness of this last expression is that, apart from the refractive indices  $n_0$  and  $n_\omega$ , only a knowledge of  $\beta_T$  and  $D$  are required in order to calculate a reasonable estimate of the orientational optical Kerr coefficient. With  $n_2 = c n_2^o + n_2^e$ , the ratio  $n_2^e/n_2$  is given from Eqs. (8) and (13) by the expression

$$\frac{n_2^e}{n_2} = \left( 1 + \frac{9\rho(\alpha^\omega)^2\beta_T}{\gamma} \frac{D}{6-7D} \right)^{-1}. \quad (15)$$

For those liquids for which a value of  $\gamma$  is known (see the review by Kielich<sup>55</sup>), values of  $n_2$  calculated using Eqs. (8) and (13) consistently give better than 10% agreement with experimentally measured values<sup>62, 63</sup> of  $n_2$ . Such agreement lends strong support to at least the first-order correctness of the above expressions for  $c n_2^o$  and  $n_2^e$ . In addition, the calculations reveal that the contribution made by  $n_2^e$  to  $n_2$  is generally considerable, lying in the range 0.1–0.3 for all the liquids studied. Specifically, using Eq. (15) with experimentally determined  $\gamma$  values,<sup>55</sup> the ratio  $n_2^e/n_2$  is found to be 0.193 in carbon disulfide ( $\text{CS}_2$ ), 0.130 in benzene ( $\text{C}_6\text{H}_6$ ), 0.143 in cyclohexane ( $\text{C}_6\text{H}_{12}$ ), 0.181 in toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ), and 0.191 in chloroform ( $\text{CHCl}_3$ ), while in nitrobenzene ( $\text{C}_6\text{H}_5\text{NO}_2$ ),  $n_2^e/n_2 = 0.262$ . This finding that the contribution of  $n_2^e$  is generally substantial concurs with that expressed by Brewer and Lee,<sup>64</sup> Brewer and McLean,<sup>65</sup> and Alfano and Shapiro,<sup>66–68</sup> from their work on the self-phase-modulation spectra of picosecond pulses. Saikan and Takima<sup>69</sup> have concluded that the contribution of  $n_2^e$  to  $n_2$  is considerable from studies of the self-trapping of picosecond pulses, and Topp and Rentzepis<sup>70</sup> have arrived at the same conclusion from studies on the transmission characteristics of an OKE gate.

Substituting  $c n_2^o$  in place of  $n_2^o$  in Eq. (6), it is found that the orientational part  $\Delta n^o$  of the induced birefringence obeys the partial differential equation

$$\tau_o \frac{\partial(\Delta n^o)}{\partial t} + \Delta n^o = c n_2^o \overline{E_\omega^2}(\vec{r}, t). \quad (16)$$

In addition, provided that the condition  $\omega\tau_e \gg 1$  is met, then the electronic contribution  $\Delta n^e$  to the induced birefringence [Eq. (7)] satisfies a similar equation,

$$\tau_e \frac{\partial(\Delta n^e)}{\partial t} + \Delta n^e = n_2^e E_\omega^2(\vec{r}, t), \quad (17)$$

where  $\tau_e$  is the relaxation time for the electronic nonlinearity (approximately equal to the inverse of the ultraviolet cutoff frequency of the medium).

Moreover, since Eq. (17) yields physically acceptable and intuitively expected results even when the condition  $\omega\tau_e \gg 1$  is not met, this equation may be considered valid for arbitrary  $\omega$ . Estimates of  $\tau_e$  in most media<sup>11, 12, 17, 64</sup> lie in the range  $10^{-15} - 10^{-16}$  sec, an upper limit for  $\tau_e$  in several media of  $1.5 \times 10^{-14}$  sec having been deduced experimentally.<sup>68</sup> Values of  $\tau_o$  in most media,<sup>71, 72</sup> on the other hand, are  $\geq 10^{-12}$  sec. The distinction between these two radically different response times  $\tau_o$  and  $\tau_e$  is reflected in the appearance of the time-averaged field-squared  $\overline{E_\omega^2}(\vec{r}, t)$  in Eq. (16) governing the orientational birefringence  $\Delta n^o$  and the need to use the instantaneous field-squared  $E_\omega^2(\vec{r}, t)$  in Eq. (17) governing the electronic birefringence  $\Delta n^e$ . Equations (16) and (17) have the integral solutions

$$\begin{aligned} \Delta n^o(\vec{r}, t) &= \frac{c n_2^o}{\tau_o} \int_{-\infty}^t \overline{E_\omega^2}(\vec{r}, t'') \exp\left(\frac{-(t-t'')}{\tau_o}\right) dt'', \\ \Delta n^e(\vec{r}, t) &= \frac{n_2^e}{\tau_e} \int_{-\infty}^t E_\omega^2(\vec{r}, t'') \exp\left(\frac{-(t-t'')}{\tau_e}\right) dt''. \end{aligned} \quad (18)$$

Using the generalized molecular-optics approach described above, the induced birefringence was calculated using a number of pulse models besides the Gaussian model of Eq. (1). These included a triangular pulse, a hyperbolic sech-squared pulse, a Lorentzian pulse, and others. In all of these cases, the final solutions for  $\Delta n^o$  and  $\Delta n^e$  were found to obey Eqs. (16) and (17), respectively. From this it is surmised that these equations as written are valid in general for an arbitrary pulse shape.

The derivation of Eqs. (16) and (17) from the Buckingham-Kielich molecular-optics theory provides, to the authors' knowledge, the first real link between this very fundamental approach to the OKE and the often-used phenomenological equation found in the literature and generally written<sup>3, 4, 11, 12, 14, 17, 19, 25–27</sup>

$$\tau_o \frac{\partial(\Delta n)}{\partial t} + \Delta n = n_2 \overline{E_\omega^2}(\vec{r}, t) \quad (19)$$

or in an equivalent integral form similar to that of Eq. (18). Equation (19) is quite similar in form to Eqs. (16) and (17), with the important exception that Eq. (19) lumps together the orientational and electronic contributions and regards the total birefringence  $\Delta n$  as governed by a single relaxation equation characterized by the response time  $\tau_o$ . Thus, this latter equation fails to distinguish between the two separate contributions,  $\Delta n^o$  and  $\Delta n^e$ , with their radically different response times,  $\tau_o$  and  $\tau_e$ , and consequently could give rise to two potentially serious errors. The first stems

from the fact that Eq. (19), as written, ignores the fast-time variation  $[\propto E_\omega^2(\vec{r}, t)]$  inherent in the contribution from  $\Delta n^e$ . In certain phenomena, such as self-phase-modulation, the role played by this fast electronic contribution can be dominant even though the ratio  $n_2^e/n_2^o$  is small.<sup>68</sup> The second error implicit in Eq. (19) concerns the magnitude of the induced birefringence  $\Delta n$  when the pulsewidth  $T_\omega$  is  $\lesssim \tau_o$ . Under these conditions, the orientational effect becomes damped out, so that the electronic effect, constant in intensity as long as  $T_\omega > \tau_e$  (where  $\tau_e$  is  $\ll \tau_o$ ), becomes increasingly important as  $T_\omega$  decreases, and eventually becomes the dominant effect when  $T_\omega \ll \tau_o$ . This behavior, predicted by Eqs. (6) and (7) [or Eqs. (16) and (17)], but not by Eq. (19), will be explicitly shown by the numerical results given in the following section. In those applications where the fast-time variation of  $\Delta n^e$  may be ignored, a time-averaged  $\Delta n^e$ , given by  $\Delta n^e = n_2^e \overline{E_\omega^2}(\vec{r}, t)$  may be used. In the limit  $T_\omega \gg \tau_o$ , Eq. (6) simplifies to  $\Delta n^o = n_2^o \overline{E_\omega^2}(\vec{r}, t)$  so that the total birefringence is simply

$$\Delta n = (n_2^o + n_2^e) \overline{E_\omega^2}(\vec{r}, t) = n_2 \overline{E_\omega^2}(\vec{r}, t). \quad (20)$$

Only under the above two conditions is this equation valid. For example, it could be applied to describe the phenomenon of self-focusing or self-trapping in liquids by nanosecond-duration Q-switched laser pulses, but would be incorrect for most liquids when picosecond or subpicosecond pulses were used.

A final consideration concerns the behavior of  $n_{||}$  or  $\delta n_{||}$  separately from that of  $\Delta n$ . For many self-induced OKE phenomena, such as self-focusing and self-phase-modulation, the behavior of  $n_{||}$  rather than the birefringence  $\Delta n$  is principally of concern. The molecular-optics theory provides a specific solution for  $n_{||}$  [Eq. (3)], while the phenomenological approach represented by Eq. (19) cannot specify  $n_{||}$  separately without making further simplifying assumptions about the relationship between  $\delta n_{||}$  and  $\delta n_{\perp}$ . This latter equation is tantamount to assuming an orientational effect only ( $n_2^e = 0$ ) from which the relationships  $\delta n_{||} = -2\delta n_{\perp} = \frac{2}{3}\Delta n$  follow. However, examination of Eqs. (3), (6), and (7) shows that, in the limit  $T_\omega \gg \tau_o$ , the total birefringence  $\Delta n$  depends on  $n_2^o$  and  $n_2^e$  exactly as given in Eq. (20), while

$$\delta n_{||} = \left(\frac{2}{3}n_2^o + \frac{2}{3}n_2^e\right) \overline{E_\omega^2}(\vec{r}, t) \quad (21)$$

in this limit. Thus, the role of the electronic Kerr effect is enhanced in the case of  $\delta n_{||}$  alone, since the ratio of the electronic contribution to the orientational contribution is 2.25 times larger for  $\delta n_{||}$

than it is for  $\Delta n$ . This picture differs distinctly from that offered in connection with Eq. (19) and the assumption  $\delta n_{||} = \frac{2}{3}\Delta n$ , because this relationship predicts equal ratios of electronic to orientational contributions for both  $\delta n_{||}$  and  $\Delta n$ . Using CS<sub>2</sub> as an example, Eqs. (20) and (21) predict that the electronic contribution to the birefringence  $\Delta n$  is  $\approx 19\%$  (for  $T_\omega \gg \tau_o$ ) while for  $\delta n_{||}$  the electronic contribution is  $\approx 35\%$ . Both of these percentage figures will increase when the pulsewidth  $T_\omega$  is  $\lesssim \tau_o$ .

### III. NUMERICAL MODEL OF THE OKE INDUCED BY ULTRASHORT LASER PULSES

Comparing Eqs. (6) and (7) to Eq. (1), it is seen that the  $y$  and  $z$  dependence of  $\Delta n(\vec{r}, t)$  is identical to that of the optical pulse  $E_\omega^2(\vec{r}, t)$  while both  $\Delta n(\vec{r}, t)$  and  $E_\omega^2(\vec{r}, t)$  depend upon the variables  $x$  and  $t$  only in the form  $(x - vt)$ . Thus, for the purposes of studying the form of the induced birefringence,  $x$ ,  $y$ , and  $z$  may be set to 0 throughout the calculations with the implicit knowledge that the spatial dependence may be recovered at any point by simply multiplying by  $\exp(-A_y^2 y^2 - A_z^2 z^2)$  and replacing  $t$  by  $(t - x/v)$ . Defining the dimensionless parameters

$$\tau'_o \equiv \tau_o/T_\omega, \quad t' \equiv t/T_\omega, \quad s \equiv t''/T_\omega, \quad (22)$$

Eqs. (7), (6), and (18) may then be simplified to

$$\frac{\Delta n^e}{n_2 E_0^2} = \frac{n_2^e}{n_2} \exp[-K^2 t'^2], \quad (23)$$

$$\begin{aligned} \frac{\Delta n^o}{n_2 E_0^2} &= \frac{n_2^o}{n_2} \frac{\pi^{1/2}}{2K} \frac{1}{\tau'_o} \exp\left(-\frac{t'}{\tau'_o} + \frac{1}{(2K\tau'_o)^2}\right) \\ &\times \operatorname{erfc}\left(-Kt' + \frac{1}{2K\tau'_o}\right), \end{aligned} \quad (24)$$

and

$$\frac{\Delta n^o}{n_2 E_0^2} = \frac{n_2^o}{n_2} \frac{1}{\tau'_o} \int_{-\infty}^{t'} \exp\left[-K^2 s^2 - \left(\frac{t' - s}{\tau'_o}\right)\right] ds, \quad (25)$$

where  $K$  is the constant  $K = [4 \ln 2]^{1/2}$ , and where the time-averaged expression for  $\Delta n^e$  has been used. The quantities  $\Delta n$ ,  $\Delta n^o$ , and  $\Delta n^e$  were calculated in units of  $n_2 E_0^2$  for a number of different liquids. Figures 1 and 2 show the results of the calculations for several  $\tau'_o$  values in the liquids carbon disulfide (CS<sub>2</sub>) and nitrobenzene (C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>). In these figures, the derived values of  $n_2^o/n_2 = 0.807$  and  $n_2^e/n_2 = 0.193$  in CS<sub>2</sub>, and  $n_2^o/n_2 = 0.738$  and  $n_2^e/n_2 = 0.262$  in C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> were used. For small values of  $\tau'_o$ , Eq. (25) was used, while for larger  $\tau'_o$ , it proved more practical to use Eq. (24) and

adopt a rational approximation for the erfc function.<sup>73</sup>

Figures 1 and 2 illustrate a number of important characteristics of the behavior of the induced birefringence  $\Delta n$  with increasing values of  $\tau'_0$ , i.e., with values of  $T_\omega$  decreasing below  $\tau_0$ . The most obvious feature is the decreasing contribution made by the orientational birefringence  $\Delta n^o$  as  $\tau'_0$  increases. The peak value of  $\Delta n$  decreases

from its maximum value of  $n_2 E_0^2$  at  $\tau'_0 = 0$  to the limit  $n_2^e E_0^2$  when  $T_\omega \ll \tau_0$  (but  $T_\omega > \tau_e$ ). Figure 3 summarizes this particular feature by plotting the values of  $\Delta n_{\max}/n_2 E_0^2$  versus  $\tau'_0$  for both liquids  $\text{CS}_2$  and  $\text{C}_6\text{H}_5\text{NO}_2$ . The convergence of  $\Delta n \rightarrow \Delta n^e$  is noticeably quicker in the case of nitrobenzene than for carbon disulfide, since the electronic contribution to the induced birefringence, measured by the ratio  $n_2^e/n_2$ , is considerably larger in  $\text{C}_6\text{H}_5\text{NO}_2$

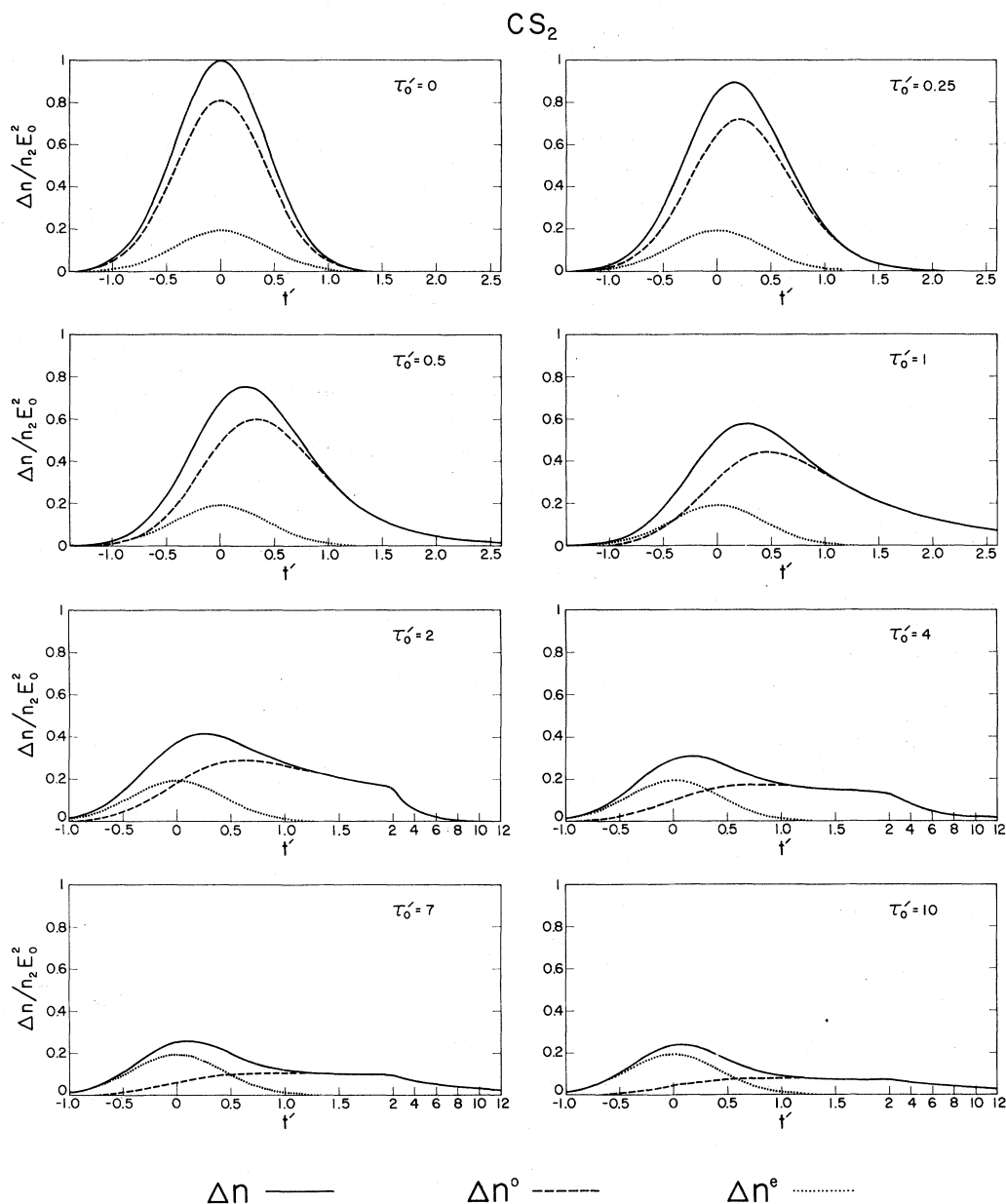


FIG. 1. Induced birefringence in liquid  $\text{CS}_2$  for selected pulsewidths ranging from  $T_\omega \gg \tau_0$  to  $T_\omega = 0.1\tau_0$ . Each set of curves shows the birefringence  $\Delta n$  (—) and the separate contributions of  $\Delta n^o$  (---) and  $\Delta n^e$  (····). Note the change of scale in the last four figures.

than in  $\text{CS}_2$ . Since  $\tau_o$  in  $\text{CS}_2$  is  $\approx 2$  psec,<sup>10, 71, 72, 74</sup> while in  $\text{C}_6\text{H}_5\text{NO}_2$   $\tau_o \approx 32$  psec,<sup>3</sup> it should be noted that, in comparing the curves in Fig. 1 to those in Fig. 2 for a given pulsewidth, the corresponding  $\tau'_o$  values will be very different. For example, for a pulse duration of  $\approx 4$  psec, the induced birefringence in  $\text{CS}_2$  would correspond approximately to the curve marked  $\tau'_o = 0.50$  in Fig. 1, while the induced birefringence in nitrobenzene would be

approximately that shown in the curve marked  $\tau'_o = 7$  in Fig. 2. Thus, in this example, the major contribution to  $\Delta n$  in  $\text{CS}_2$  comes from the orientational effect, while in  $\text{C}_6\text{H}_5\text{NO}_2$  the orientational effect is largely damped out and the electronic effect dominates.

A second important characteristic of the induced birefringence which emerges from Figs. 1 and 2 is the existence of a time lag between the peak of

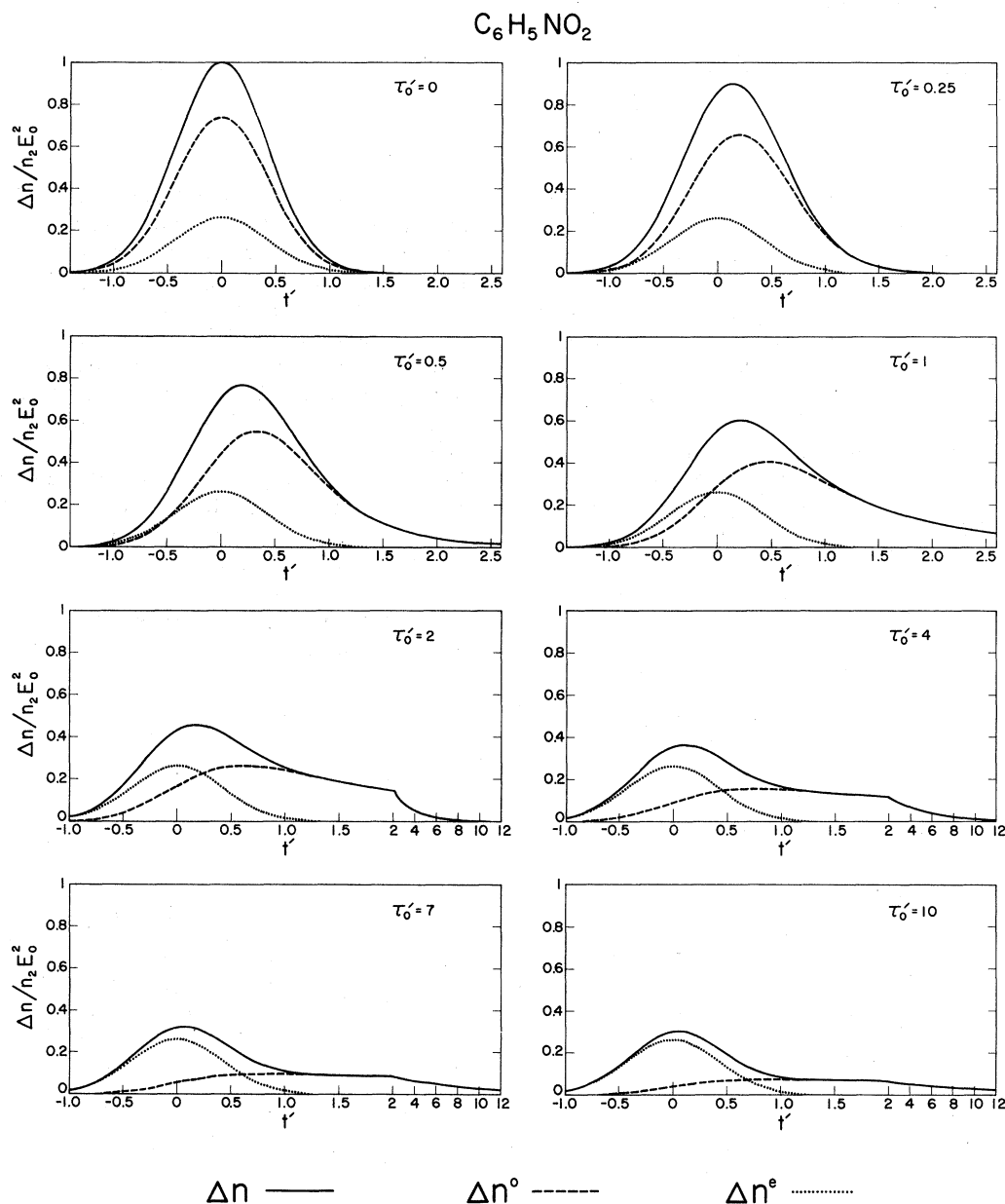


FIG. 2. Induced birefringence in liquid  $\text{C}_6\text{H}_5\text{NO}_2$  for selected pulsewidths ranging from  $T_\omega \gg \tau_o$  to  $T_\omega = 0.1\tau_o$ . Each set of curves shows the birefringence  $\Delta n$  (—) and the separate contributions  $\Delta n^o$  (----) and  $\Delta n^e$  (.....). Note the change of scale in the last four figures.

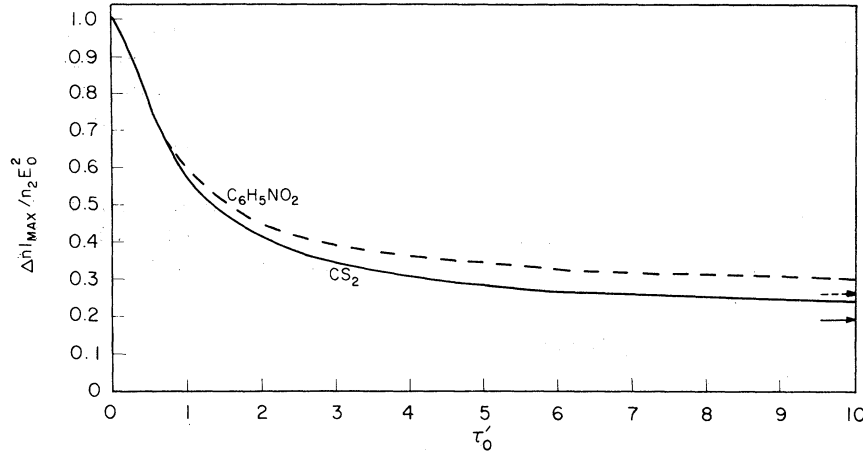


FIG. 3. Peak value of the induced birefringence versus the parameter  $\tau'_0 = \tau_0/T_\omega$  in the liquids CS<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>. The small right-hand markers indicate the limit of  $\Delta n|_{\max}$  for  $\tau'_0 \gg 1$  for carbon disulfide ( $\rightarrow$ ) and nitrobenzene ( $\dashrightarrow$ ).

the optical pulse (by definition always at  $t' = 0$ ) and the peak value of the induced birefringence. Defining  $t'_m \equiv t_m/T_\omega$  as the time at which  $\Delta n$  is a maximum,  $\Delta n(t'_m) = \Delta n|_{\max}$ , it may be seen from Figs. 1 and 2 that  $t'_m$  is initially zero when  $\tau'_0 = 0$ , increases to a maximum as  $\tau'_0$  increases, and then returns to zero in the limit of  $\tau'_0 \gg 1$ . This behavior of  $t'_m$  for carbon disulfide and nitrobenzene is shown explicitly in Fig. 4. The fact that, for a given  $\tau'_0$  value, the value of  $t'_m$  in C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> is always less than  $t'_m$  in CS<sub>2</sub>, arises from the relatively larger orientational contribution in CS<sub>2</sub> ( $c n_2^o/n_2 = 0.807$ ) than in C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> ( $c n_2^o/n_2 = 0.738$ ). The existence of this time lag  $t'_m$  has important consequences in the understanding of the phenomena of self-focusing and self-trapping<sup>75, 76</sup> and the self-steepening<sup>77</sup> of picosecond light pulses.

A third characteristic observed from Figs. 1 and 2 is the behavior of the duration of the induced birefringence versus the parameter  $\tau'_0$ . Defining the dimensionless parameters  $\Delta' \equiv (\text{FWHM of } \Delta n)/T_\omega$ , and  $\Delta'_0 \equiv (\text{FWHM of } \Delta n^o)/T_\omega$ , one observes in Figs. 1 and 2 that initially  $\Delta' = 1$  when  $\tau'_0 = 0$ , increases to a maximum as  $\tau'_0$  increases, then returns to the value  $\Delta' = 1$  when  $\tau'_0 \gg 1$ , while  $\Delta'_0$  increases without limit as  $\tau'_0$  increases. Figure 5 shows the values of  $\Delta'$  and  $\Delta'_0$  vs  $\tau'_0$  for both liquids CS<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>. The behavior illustrated in this figure is of considerable significance to the understanding of the temporal transmission characteristics of an OKE gate or shutter.

The information contained in Figs. 1 and 2 and summarized in Figs. 3–5 presents a very general picture of the temporal behavior of the OKE in-

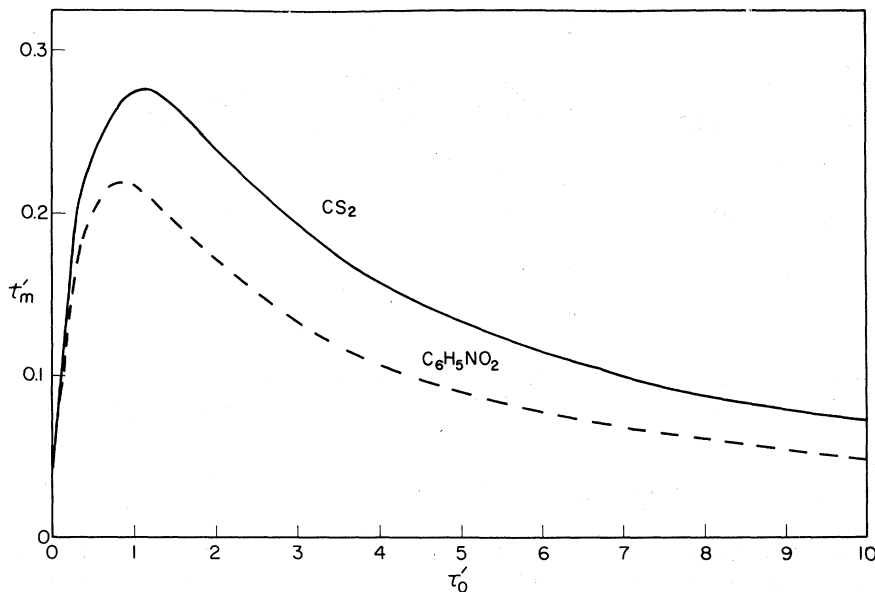


FIG. 4. Time lag  $t'_m$  in units of  $T_\omega$  between  $\Delta n|_{\max}$  and the peak of the optical pulse versus  $\tau'_0 = \tau_0/T_\omega$  in liquids carbon disulfide and nitrobenzene.

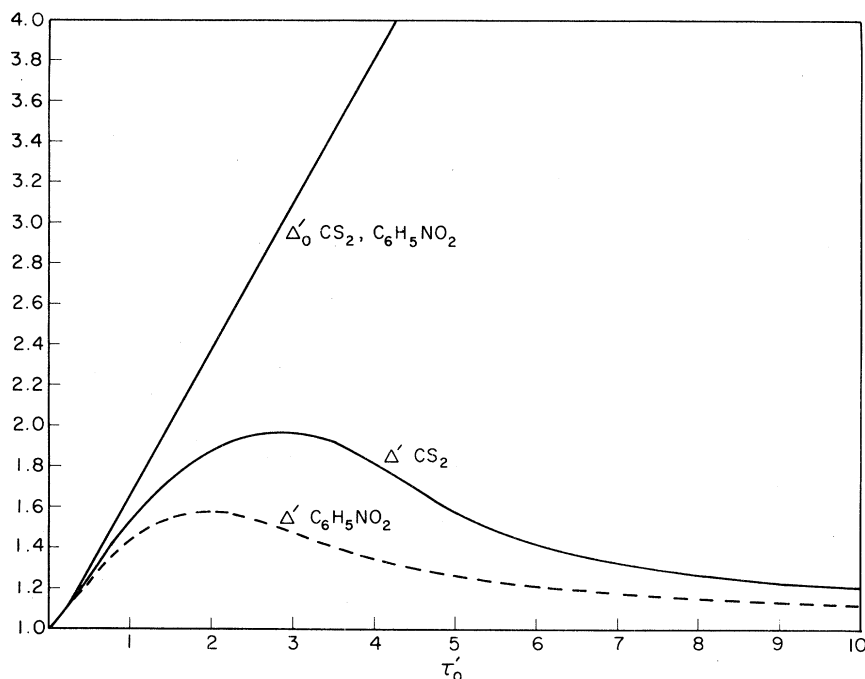


FIG. 5. FWHM durations of the birefringence  $\Delta'$  and the orientational birefringence  $\Delta'_0$  in units of  $T_\omega$  vs the parameter  $\tau'_0 = \tau_0/T_\omega$  in carbon disulfide and nitrobenzene.

duced by a short-duration laser pulse. Initially, when the pulsewidth  $T_\omega$  is much greater than the orientational relaxation time  $\tau_0$ , the intensity of the induced birefringence is a maximum with both the orientational part  $\Delta n^o$  and the electronic part  $\Delta n^e$  in synchronization with the optical pulse. There is no time lag between the induced birefringence and the pulse, and the FWHM of the birefringence is identically that of the pulse. However, when  $T_\omega \lesssim \tau_0$ , the orientational contribution  $\Delta n^o$  begins to lessen in its intensity and to lag somewhat behind the peak of the optical pulse. Because of this, the total induced birefringence  $\Delta n$  is also reduced in intensity and lags behind the pulse. In addition, the birefringence, because of its relaxing orientational part, is more spread out in time, so that its FWHM is larger than that of the pulse. In the limit  $T_\omega \ll \tau_0$  (but  $T_\omega > \tau_e$ ), the orientational contribution  $\Delta n^o$  is completely damped out, with the result that  $\Delta n = \Delta n^e$  with no time lag and the FWHM is once again equal to the pulsewidth.

This picture of the temporal behavior of the OKE induced by ultrashort laser pulses offers a practical suggestion concerning the problem of the extension of OKE photography to the subpicosecond regime. Since the time that picosecond-resolution OKE photography was first reported, it has been postulated that, with the availability of intense subpicosecond pulses, this form of photography could be extended to time scales much less than a picosecond by using glass or some similar solid

as the optical Kerr medium.<sup>12, 14</sup> In such materials, the induced birefringence is due solely to the electronic effect, and is characterized<sup>11, 12, 17, 64</sup> by response times of  $\sim 10^{-15}$  to  $10^{-16}$  sec and optical Kerr coefficients  $n_2 \lesssim 10^{-12}$  esu.<sup>78-80</sup> Aside from the practical disadvantage of requiring optically pure samples which would be subject to irreversible laser-produced damage, the use of glass would present problems of very low ( $\ll 1\%$ ) shutter transmissions stemming from the low value of  $n_2$  and the fact that the transmission is a highly nonlinear function<sup>3, 11</sup> of  $n_2$ . However, the results shown in Figs. 1 and 2 point to the possibility of using a Kerr liquid with relatively large  $\tau_0$  as the medium for a subpicosecond OKE shutter. For  $T_\omega \ll \tau_0$ , only the electronic contribution  $\Delta n^e$  with its fast response time  $\tau_e \sim 10^{-15}$  sec would remain. As an example, using nitrobenzene ( $\tau_0 \sim 32$  psec) and a 0.1-psec pulse, the orientational part  $\Delta n^o$  would be  $\cong 0$  ( $\tau'_0 > 300$ ), and thus  $\Delta n \cong \Delta n^e$ . Such a Kerr cell under these conditions could give subpicosecond exposure times. Moreover, the cell would be simple in construction, not subject to laser-produced damage, and, most importantly, the comparatively large value of  $n_2^e$  in  $C_6H_5NO_2$  of  $\approx 3 \times 10^{-12}$  esu [from Eq. (8)] would result in a marked improvement in net transmission over a comparable shutter employing glass. While it is necessary to first isolate the electronic response of a Kerr medium in order to obtain subpicosecond resolution with an OKE shutter, this condition is not in itself sufficient. Consideration must also

be given to gating geometry, the effect of finite image and pulse dimensions, and so on. Discussions of some of these more important considerations and their effect on the resolution capabilities of OKE photography are given elsewhere.<sup>12,31,81</sup>

#### IV. THE OPTICAL KERR EFFECT INDUCED IN SPHERICALLY SYMMETRIC MOLECULES

The theory and calculations given above have been limited to anisotropic molecules ( $\delta^2 \neq 0$ ). However, for spherically symmetric molecules  $\delta^2 = 0$ , and thus, from Eqs. (12) and (13),  ${}_c n_2^o = 0$ . Thus, the zero-order approximation for liquids composed of spherically symmetric molecules would be simply  $n_2 = n_2^e$ . However, as in the case for anisotropic molecules, it is necessary to consider the effect of multiple-molecular interactions explicitly in the calculation of  $\Delta n$ . It is found that the most important correction arises from the existence of radial correlations between members of pairs of molecules.<sup>50-55</sup> This leads to the phenomenon of "molecular clustering"<sup>82-84</sup> with a contribution to the induced birefringence represented by the optical Kerr clustering coefficient<sup>50</sup>

$$n_2^c = \frac{6\pi\rho(\alpha^\omega)^2(\alpha^{\omega'})^2}{5kTn_0} \left(\frac{n_0^2+2}{3}\right)^2 \left(\frac{n_\omega^2+2}{3}\right)^2 J_r, \quad (26)$$

where

$$J_r = \frac{2\rho}{V} \int \int r_{pq}^{-6} g^2(\Omega_p, \Omega_q) d\Omega_p d\Omega_q \quad (27)$$

is an integral parameter describing the strength of the radial correlation between members of pairs of molecules. In Eq. (27),  $r_{pq}$  is the distance between the centers of symmetry of molecules  $p$  and  $q$ . As in the case of  $J_a$  and for the same reasons, calculations of  $J_r$  using Eq. (27) are generally very approximate. However, this same parameter  $J_r$  also appears in the formula for the depolarization of scattered light  $D'$  for media composed of spherically symmetric molecules as<sup>61</sup>

$$D' = \frac{6(\alpha^\omega)^2 J_r}{5\rho k T \beta_T + 7(\alpha^\omega)^2 J_r}. \quad (28)$$

Solving for  $J_r$  from Eq. (28) and substituting into Eq. (26) gives the result

$$n_2^c = 6\pi\rho^2(\alpha^{\omega'})^2\beta_T \frac{D'}{6-7D'} \frac{1}{n_0} \left(\frac{n_0^2+2}{3}\right)^2 \left(\frac{n_\omega^2+2}{3}\right)^2, \quad (29)$$

with the nonlinear refractive index  $n_2$  given by  $n_2 = n_2^c + n_2^e$ . Using Eqs. (8) and (29), the values calculated for  $\text{CCl}_4$  are  $n_2^c = 0.14 \times 10^{-12}$  esu and  $n_2^e = 0.11 \times 10^{-12}$  esu (for a gating-pulse wavelength

$0.69 \mu\text{m}$  and a probe wavelength of  $0.48 \mu\text{m}$ ). The resulting value of  $n_2 = 0.25 \times 10^{-12}$  esu is in good agreement with the experimental value of Paillette.<sup>62, 63</sup> In addition, the calculated value of  $n_2^e/n_2 = 0.44$  agrees well with the experimentally measured value of  $0.54 \pm 0.16$  reported by Hellwarth *et al.*<sup>84</sup>

Although the results of the numerical calculations presented in Figs. 1-5 pertained specifically to liquids composed of anisotropic molecules for which  $n_2 = {}_c n_2^o + n_2^e$ , the results of those calculations may be applied, at least qualitatively, to liquids composed of spherically symmetric molecules for which  $n_2 = n_2^c + n_2^e$ . This follows from the fact that, like the orientational mechanism, the clustering process involves the (translational) motion of the entire molecule, and so is characterized by a relaxation time  $\tau_c$  which is of the same order of magnitude as the orientational relaxation time<sup>64</sup>  $\tau_o$ . Thus the clustering birefringence has an effect similar to that of the orientational birefringence in the numerical studies of Sec. III. Most of the conclusions arrived at there remain correct when  ${}_c n_2^o$  is replaced by  $n_2^c$ , and  $\tau_o$  by  $\tau_c$ . Also, since it would appear that, in general, the ratio  $n_2^e/n_2$  is substantially larger ( $\sim 0.5$ ) in media composed of spherically symmetric molecules than in media composed of anisotropic molecules ( $n_2^e/n_2 \sim 0.1-0.3$ ), the convergence of  $\Delta n$  to  $\Delta n^e$  with increasing  $\tau_c' (= \tau_c/T_\omega)$  will occur considerably faster in liquids composed of spherically symmetric molecules.

#### V. CONCLUSIONS

Although the above analysis of the optical Kerr effect induced in isotropic and anisotropic liquids by ultrashort laser pulses is based on a generalized theory, some idealized assumptions have been made, particularly with regard to the temporal form of the laser pulseshape. Nonetheless, several important conclusions are apparent which should be of particular relevance to the use of the OKE in the temporal diagnosis of the spatial and/or spectral features of ultrafast phenomena. It is observed that consideration of the relative contributions of the electronic and orientational effects in anisotropic liquids is essential to a correct interpretation of the induced birefringence. The temporal development of the birefringence induced by Gaussian laser pulses in carbon disulfide and nitrobenzene has been explicitly described. The theory and mode of analysis are obviously applicable to other liquid media. In addition, although a Gaussian temporal form for the laser pulseshape has been used in the present derivation of the in-

duced birefringence, it is concluded that the analysis also holds for other forms (triangular, hyperbolic sech-squared, Lorentzian, etc.) of the laser pulseshape. Although it is recognized that these do not adequately describe the random multi-structured temporal form of the output of many of today's mode-locked lasers, the general conclusions arrived at above would still remain valid. This follows, since for a structured picosecond optical pulse, the modulation in the induced birefringence will always be much less than that of the optical pulse in liquids exhibiting an orientational Kerr effect with the result that, in a first approximation, the birefringence may be treated as smoothly varying. Moreover, the choice of a Gaussian profile is still the most logical pulse-shape to include in the analysis. Bandwidth-

limited pulses apparently commonly occur in the initial generation of mode-locked Nd:glass laser pulses,<sup>85,86</sup> and in addition, there have been numerous reports recently of bandwidth-limited pulse outputs from mode-locked ruby, Nd:YAG, Nd:glass, and dye lasers.<sup>87</sup>

The present investigation also points to the possible use of the OKE induced in liquids in the sub-picosecond domain. This may partially be more suitable than utilizing the weak electronic effect induced in solid transparent media. With the provisions of laser pulses of duration much less than  $10^{-12}$  sec, the OKE would provide, through its incorporation into an optical or photographic shutter, not only a means of analysis of such pulses themselves, but also a large number of phenomena induced by ultrashort laser pulses.

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