

Optically induced birefringence in transparent media

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1. Introduction

A strong light beam incident onto a medium induces in it many nonlinear optical phenomena. Research on these phenomena in solids, liquids and gases and their dependence on the intensity and other parameters of the incident light is carried out by nonlinear optics. Fundamentals of this science were established as early as in the fifties, but actually, the intensive progress has been started with the development of quantum electronics. These two fields of knowledge are inseparable; from one side, nonlinear phenomena play a major role in many laser systems, from the other side, achievements of quantum electronics result in a fast development of nonlinear optics.

One of the nonlinear optical phenomena is a birefringence, optically induced in transparent media by a strong laser beam. It is also called the optical Kerr effect (OKE) [1]. As it is commonly known, the magnitude of the Kerr effect is very sensitive to differences between the components of tensor of optical polarizability of a molecule and also depends on its induced or permanent electrical momenta [2]. These properties of the molecule depend on its internal structure and conformation. Hence, the research on the OKE, together with information resulting from other measuring methods (i.e. dielectric methods, light scattering, molecular refraction, etc.), is used for determination of the molecule properties and structure and the local structure of investigated media [3].

A particular advantage of the OKE is that the electric field is applied to an investigated medium without using any electrodes. Therefore, this method is very useful for investigating systems with high electric conductivity (such as colloids or biological solutions [4, 5]) characterized by strong optical nonlinearity [6]. The optically induced birefringence has also an important role for other nonlinear processes induced by a strong laser beam [7 ÷ 11], in particular for self-focusing and

optical breakdown. These processes, as well as the induced light scattering or the thermal effect, may of course disturb the Kerr effect, but they can be eliminated by the appropriate arranging of the experiment [12].

First time the OKE was observed in 1964 in organic fluids [13, 14]. Then, it was investigated in various media using nanosecond laser pulses to induce it. At the beginning, the conventional light sources [13, 15] and next, the laser sources — continuous or pulsed — were applied to analyse this effect. Then, picosecond [18 ÷ 20] or femtosecond [21 ÷ 23] pulses were introduced, both inducing and analysing. It enabled direct measurement of the relaxation time of molecule orientation in pure liquids [18, 24 ÷ 27], liquid crystals [28] and elastic crystals [29]. Recently, the achieved increase in measuring equipment sensitivity [30] has also made it possible to investigate OKE in organic vapours [30] and in gases [32].

2. Theoretical backgrounds

Theories of the optical Kerr effect have been elaborated by many researchers. They have used various methods, most frequently the statistical-molecular one or the quantum mechanics. The review and detailed presentation of them may be found in Ref. [33]. Therefore, in this paper only the basic relations and formulas used in interpreting the experimental results, are presented.

Birefringence of a medium, induced by a strong beam of light of wavelength λ_i , may be detected and its magnitude may be determined using an analyzing beam of linearly polarized light of wavelength λ_a (similarly like in the research on the electro-optical Kerr effect). The principle of the measurement of OKE phenomenon is shown in Fig. 1. A phase difference between the ordinary and extraordinary ray (that is the magnitude of the induced birefringence) is computed from the measured data,

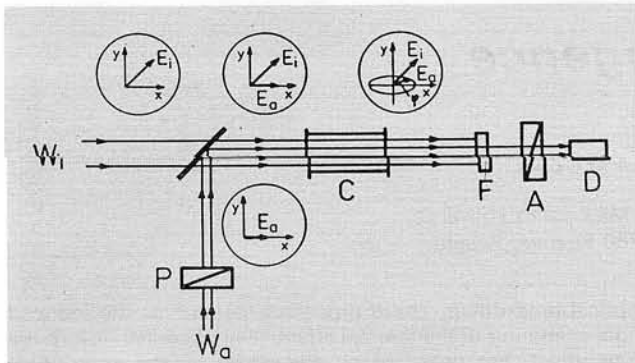


Fig. 1. Principle of the measurement of optical Kerr effect: W_i , W_a linearly polarized laser beams (inducing and analysing, respectively), C – Kerr cell, F – filter blocking the inducing beam, P – polarizer, A – analyzer, D – detector

and then a value of optical Kerr constant $B_o(\lambda_a, \lambda_i)$ is calculated. This constant describes macroscopic properties of the medium. The microscopic properties of the medium are associated with the mole Kerr constant $B_m(\lambda_a, \lambda_i)$, depending on parameters characterizing atoms and molecules and on molecular mechanisms leading to the birefringence. For dense media these constants are related each to other according to the following formula:

$$B_o(\lambda_a, \lambda_i) = 3B_m(\lambda_a, \lambda_i) / (2n_a \lambda_a V_M) \times [(n_a^2 + 2)/3]^2 \cdot [n_i^2 + 2]/3^2 \quad (1)$$

where n_a and n_i are the refractive indices for the analysing and inducing beam, respectively, and V_M is the mole volume of the investigated medium. The coefficients, binding the constants B_o and B_m , depend on the assumed model of the local field and on the method of computing of the potential energy of a molecule in the optical field. It is assumed in Eq. (1) that the local field is determined according to the spherical cavity model in Lorentz approximation. Taking into account the molecular mechanisms, which in a microscopic scale lead to the birefringence of a medium, the constant B_m may be transformed into the sum:

$$B_m(\lambda_a, \lambda_i) = B_m^{NL}(\lambda_a, \lambda_i) + B_m^{OR}(\lambda_a, \lambda_i) \quad (2)$$

Component B_m^{NL} defines the contribution of nonlinear deformation of an electron cloud of atoms or molecules in the optical field (the Voigt effect) to the OKE, and component B_m^{OR} incorporates the contribution to OKE originating from the orientation (the Langevin effect) and redistribution of atoms and molecules in the optical field. The Voigt effect depends on nonlinear properties of atoms and molecules, determined by a hyperpolarizability tensor of the second order $c_{\alpha\beta\gamma\delta}$ and on molecular interactions. The contribution of molecular interactions to the constant $B_m^{NL}(\lambda_a, \lambda_i)$ varies, depending on the kind of a medium. It may be equal from several percent up to some dozen percent for a liquid consisting of strongly interacting molecules [30]. However, in the case of a medium consisting of molecules with small, constant electric momenta and characterized by low optical anisotropy, the influence of molecular interactions may be neglected in first approximation. Then the constant $B_m^{NL}(\lambda_a, \lambda_i)$ has a simpler form:

$$B_m^{NL}(\lambda_a, \lambda_i) = 4\pi N_A c/9 \quad (3)$$

where $c = c_{\alpha\alpha\beta\beta}$ and N_A is the Avogadro number. The constant $B_m^{OR}(\lambda_a, \lambda_i)$, describing the distribution of molecule reorientation in the optical field and the statistical-molecular processes (translation, rotation, libration movements) to OKE, may be written in a general form:

$$B_m^{OR}(\lambda_a, \lambda_i) = 4\pi N_A \Gamma^2(\lambda_a, \lambda_i) / (45kT) \quad (4)$$

where Γ is the effective optical anisotropy characterizing the molecular optical anisotropy of a molecule placed in a medium. Only for rarefied gases it may be assumed, that Γ is equal to molecular optical anisotropy γ defined for an isolated molecule.

The greater is density of a medium the stronger is the interaction of the molecule's closest vicinity on its optical properties. This interaction may be quite considerable in liquids. It leads, mainly through multipole interactions apparently dependent on the molecule structure, to the creation of ordered, short-range structured zones and short-living molecule complexes in a liquid [34]. For molecules with permanent dipole momentum, the dipole-dipole interactions are the strongest and they lead to the creation of complexes usually consisting of two molecules, most often configured antiparallel or, rather seldom, parallel. Such complexes have optical properties different than in the case of single molecules. In such case the effective optical anisotropy of a molecule, including the influence of the molecule vicinity, may considerably differ from anisotropy γ of the isolated molecule. The latter is also called the optical anisotropy in the gaseous phase.

In the case of anisotropic molecules the substantial contribution to OKE are the molecular orientation and the molecular redistribution. Taking only these phenomena into consideration, the effective optical anisotropy may be written as follows:

$$\Gamma^2(\lambda_a, \lambda_i) = \gamma_a \gamma_i (1 + J_A) + (9\alpha_a^2 \alpha_i^2 + 28\alpha_a \alpha_i \gamma_a \gamma_i / 5 + \dots) J_R \quad (5)$$

where:

$$\gamma^2 = [(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2] / 2 \quad (6)$$

The average molecule polarizability in expressions (5) and (6) is $\alpha = (\alpha_1 + \alpha_2 + \alpha_3) / 3$, where α_1 , α_2 , α_3 are the main molecule polarizabilities, while J_A and J_R are the angular and radial correlation functions, respectively, defining the molecular interactions.

If the Voigt effect is taken into account, then expression (2) may be transformed to the following form (assuming the molecule properties and molecule interactions are the same as mentioned earlier):

$$B_m^{OR}(\lambda_a, \lambda_i) = 4\pi N_A c/9 + 4\pi N_A \Gamma^2(\lambda_a, \lambda_i) / (45kT) \quad (7)$$

where $\Gamma^2(\lambda_a, \lambda_i)$ given by Eq. (5), is convenient for further numerical calculations.

3. Measuring systems

For investigations of optically induced birefringence an optical and electronic instrumentation is applied, with lasers as indispensable parts of such systems used for inducing and analysing the effect. The measuring systems for OKE investigation may be divided into two groups: one of them applies a CW laser beam for analysing the effect induced by a pulsed beam, while in the second group both the inducing and analysing beams are pulsed.

In primary research on the OKE a beam emitted by the conventional light source (xenon lamp) was used for analysing. The beam was formed by an appropriate optical system. Recently the laser beams are used for this purpose and the optical system may be eliminated, thus increasing the sensitivity of the measurements.

Various types of lasers are applied in the first group of the OKE measuring systems. For example, a pulsed ruby laser ($\lambda = 694.3$ nm) is used to induce the effect and a CW-mode Cd ($\lambda = 441.6$ nm) or Ar ($\lambda = 448$ nm or 514.5 nm) laser – to analyse it. Also the pulsed Nd glass or YAG lasers ($\lambda = 1062$ nm) and CW analysing beams from Cd, Ar or He-Ne ($\lambda = 632.8$ nm) lasers may be used. The bigger is the difference in wavelength of these two beams, the more exactly the inducing beam is separated in the detecting system. Pulsed lasers used in such research, generate light beams, the power of which reaches the order of dozens or hundreds megawatts and the duration time is of the order of nanoseconds, picoseconds or femtoseconds. Single-mode laser operation is required there, as well as high homogeneity of the laser beam (i.e., the homogeneity of the inducing optical field). The analysing beams have the much lower power. Usually, it is of the order of several dozens or several hundreds of milliwatts in CW-mode lasers, while the requirements on homogeneity and single-mode emission are similar to the inducing lasers.

In measuring systems with a pulsed analysing beam, the beam may be obtained either by transforming the frequency of a part of the inducing beam (of the Nd-glass or YAG laser) into the second harmonic or using dye or excimer lasers. Since this method is much more sensitive than the previous one, this type of systems is particularly useful for investigating the media of low anisotropy. Optical elements used in the system — such as polarizers, lenses, filters, beam splitters, nonlinear crystals, etc. — must be of the high quality and must stand high power densities of laser pulses.

Photoelectric elements, such as photodiodes, photomultipliers or photocells, applied in the control and detection sections of the equipment, must feature the sensitivity matching a particular wavelength and must be high-speed, thus ensuring proper recording of ultra-short light pulses, usually with the use of fast digital oscilloscopes connected with a microcomputer.

Typical measuring systems operating in various temporal modes are shown in Figs. 2÷4. Detailed description of each

particular system may be found using references given in annotations, so they are not described here. Nevertheless, it is worth to mention about the method which allows to increase, in a simple way, the sensitivity of the equipment used for OKE measurements by more than an order of magnitude. It consists in introduction of the additional Kerr cell in the measuring system, approx. 0.1 cm long, filled with a liquid with strong anisotropy. During the action of a inducing pulse this cell plays the role of a phase plate, shifting the operation point of the photomultiplier towards a higher sensitivity region [10]. After passing the inducing pulse this extra phase difference disappears, thus the signal-to-noise ratio remains unchanged.

Another element, used in pico- and femtosecond systems, is the optical shutter (also called a light gate) described in details in [38, 39]. The principle of operation of the shutter is presented in Fig. 5. The shutter enables, among other things, measuring pico- and femtosecond pulses in the near IR, visible and ultra-violet ranges [10, 23, 41, 42]. The operation principle of

Fig. 2. Typical equipment for the OKE research with analysing CW laser beam: L — lasers (λ_i — inducing, λ_a — analysing), P — polarizers, A — analyzer, C — Kerr cell (C_1 — modifying, C_2 — measuring), M — monochromator, PMT — photomultiplier, PD — photodiodes, PM — radiation power meter, F — filters (after [35])

Fig. 3. System for OKE research with pulsed analysing beam: L_{Nd} — neodymium laser, ADP — crystal doubling the frequency of light, Q — phase plate, C — Kerr cell, P — polarizer, A — analyzer, FD — photodiode, $F1, F2$ — filters (after [36])

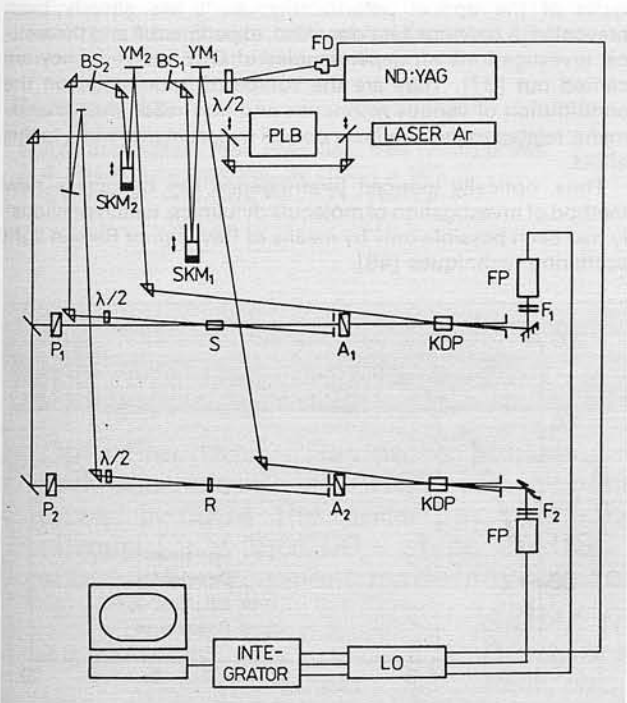
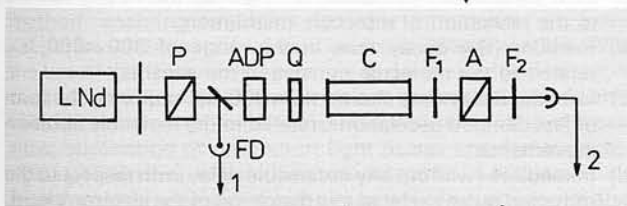
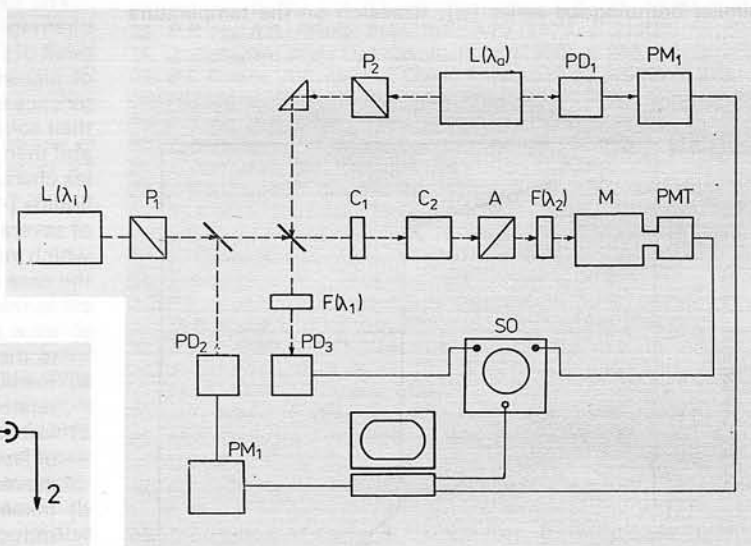


Fig. 4. Picosecond system with a Kerr reference cell (after [37]): PLB — dye ring laser, FP — photomultiplier, FD — photodiodes, LO — delay line, P — polarizers, A — analyzer, BS — beamsplitters, M — mirrors, S, R — Kerr cells (S — measuring cell, R — reference cell). Mirrors in the delay lines are moved by step motors

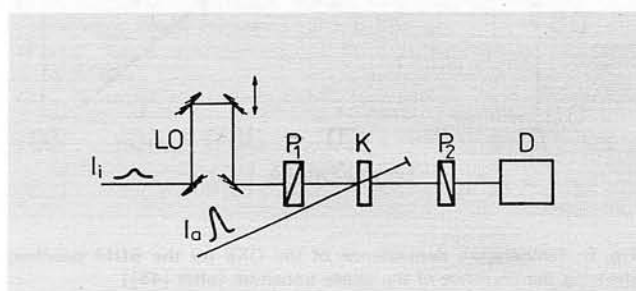


Fig. 5. Configuration of the optical shutter: K — Kerr cell, P_1, P_2 — crossed polarizers, I_i, I_a — inducing and analysing pulses, respectively, LO — optical delay line, D — detector

the optical gate is the following. The transmission of a system consisting of the Kerr cell, located between the crossed polarizers (Fig. 5) is zero. A weak analysing pulse may reach the detector only when it reaches the Kerr cell in a precisely determined time range, i.e., when the optically induced birefringence, caused by a strong pulse, occurs. The shutter opening time is of the order of picoseconds and it may still be shortened by applying perpendicular configuration of the two beams [42]. Assuming small amplitude, depending on the induced birefringence time, and negligible delay of a nonlinear response of the system, the energy of the analysing pulse, measured as a function of the delay introduced by the optical system, is proportional to the third order autocorrelation function (under fulfilment of appropriate conditions, [23]). From width of this function, after deconvolution, the duration of analysing pulse is derived.

4. Selected experimental results

In research on the optically induced birefringence two directions may be distinguished — the research on the properties of atoms, molecules or local structure of a medium and the nonlinear laser spectroscopy. Sometimes, these two directions cannot be easily separated. Within the first direction, the value of the optical Kerr constant is measured for various media and its dependence on the medium temperature, concentration or pressure (for gases) is investigated, as well as dependence on the inducing pulse duration and power. Using these values the mole Kerr constants are calculated and then, assuming a particular theoretical model, it becomes possible to determine many microscopic parameters of atoms and molecules, as well as it is possible to conclude on their shape and structure, electric charge distribution and a chemical binding orientation. The obtained information is much more certain and precise, if the research is performed for chemical compounds, which do not differ substantially and which form homologous series, or for similar homologous series [3]. Research on the temperature

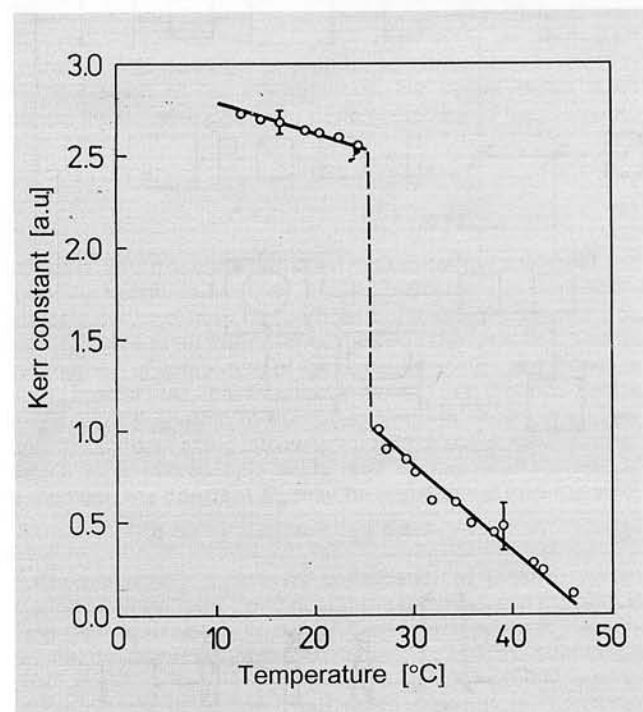


Fig. 6. Temperature dependence of the OKE for the BDM polymer, showing the presence of the phase transition (after [45])

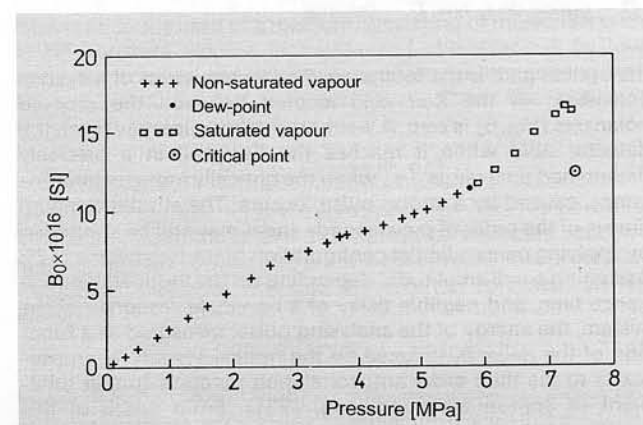


Fig. 7. OKE pressure dependence for CO_2 vapours (after [32])

dependencies of the OKE effect enables to detect the presence and localization of phase transitions (Fig. 6) [43] and to determine the critical areas in various states of aggregation. The review of the obtained results may be found in monographic papers [44, 45].

Research on OKE in the gaseous phase is particularly interesting (Fig. 7) because it gives the possibility of direct comparison of the experimental results with the theoretical predictions on the role of molecular interactions in the optical orientation phenomenon [31]. It also enables to control these interactions by changing the temperature and pressure of the investigated gas [32]. Besides, the research have enabled to develop a new method of measuring of relaxation time of molecule orientation, on the basis of the OKE measurements with the use of nanosecond pulses. As it was shown in Ref. [46], a change in the slope of the curve representing a dependence of the optical Kerr constant on the time interval between subsequent collisions of a selected gas molecule (Fig. 8), occurs when this time is equal to the orientation relaxation time.

The second direction of research on the optically induced birefringence phenomena was initiated with a direct measurement of the relaxation time of molecule orientation with the use of picosecond techniques [18–20]. Then, temporal characteristics of OKE were examined for various organic liquids and their solutions [21–27]. Application of subpicosecond pulses and then femtosecond pulses [38–40] has disclosed a complex character of decay of the optically induced birefringence in liquids [47]. It appeared that the OKE signal is a superposition of several components featuring various decay times (Fig. 9), which may be related to the respective molecular movements. In the case of anisotropic liquids it is possible to distinguish four components in this signal:

- slow component (the decay time greater than 1 ps), related to the relaxation of molecule orientation,
- medium (the decay time in the range of 300–600 fs), related to the molecule translation movements,
- fast (the decay time shorter than 200 fs), acquiring the form of fast damped oscillations, related to the molecule libration movements,
- immediate (without any noticeable delay with respect to the inducing pulse), related to a distortion of the electron cloud.

All these molecular movements correspond to characteristic types of the optical polarizability, as it has already been presented in previous sections. Also, experimental and theoretical investigations on dependencies of OKE on frequency are carried out [37]. They are the source of information on the contribution of various resonance and non-resonance phenomena, related to the nonlinear optical hyperpolarizability, to this effect.

Thus, optically induced birefringence has become a new method of investigation of molecule dynamics, which previously had been possible only by means of Rayleigh or Raman light scattering techniques [48].

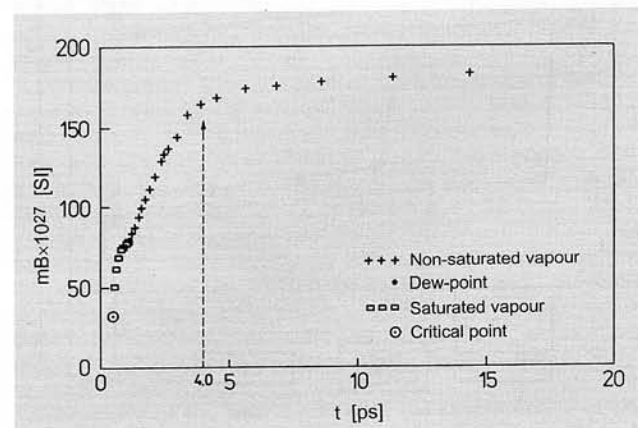


Fig. 8. Dependence of the Kerr mole constant on the time interval between subsequent collisions for a selected CO_2 molecule. The inflexion point of the curve determines the relaxation time of molecule orientation (after [46])

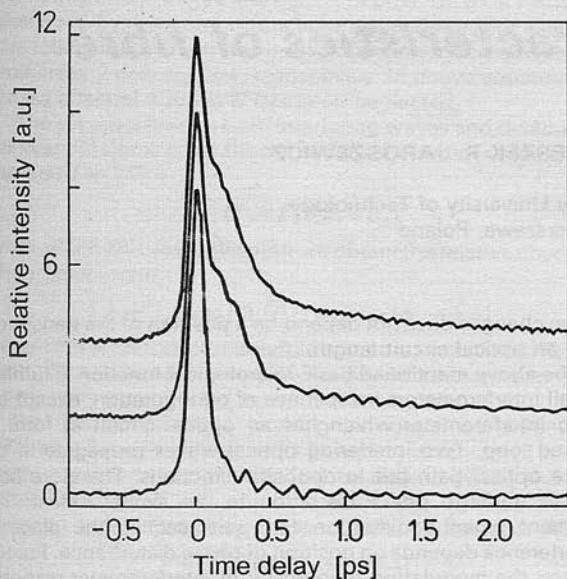


Fig. 9. OKE signals (in descending order) obtained with the use of femtosecond techniques for CH_2Cl_2 , CHCl_3 , CCl_4 . The curves are superpositions of several ones (after [47])

5. Conclusions

As follows from the presented review, the phenomenon of the optically induced birefringence constitutes a useful research method, enabling to obtain valuable information on basic properties of the matter of various states of aggregation. With the use of this method, it is possible to determine local structure of a medium, disclose phase transitions and critical regions and, besides, to investigate molecular interactions of various types. Also, application of ultra-short light pulses enabled to investigate phenomena, which up to now could be investigated only with the use of specialized techniques of light scattering. It also concerns investigations on dynamics and kinetics of various nonlinear optical phenomena of the third order, related to electron processes for which the optical Kerr effect has been, up to now, the only direct experimental method.

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