

# Anomalous Electro-Optic Effect in Polar Liquid Films

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**Abstract**—We present an anomalous electro-optic effect in polar liquid films: liquids, usually considered to be isotropic, possess the linear electro-optic effect that occurs only in materials lacking inversion symmetry. Due to the observed large effect in the low-frequency range and slow response speed, this strange effect was thought to come from the field-induced orientation of large mass. Therefore, we brought forward a physical model that contributed to the interpretation of this phenomenon: field-induced pre-oriented, short-range orderly dipole clusters in liquid films break the macroscopic symmetry and results in this asymmetric effect. Finally, combined with spectral analysis, the formation of clusters induced by an electric pulse was proved.

**Index Terms**—Electro-optic effects of liquids, nonlinear optics, Pockels electro-optic effect.

## I. INTRODUCTION

LIQUIDS are generally acknowledged to be isotropic in nature: they exhibit the same characteristics optically, magnetically, and electrically from any perspective. Although the molecules that constitute the liquids are sometimes anisometric, this will not affect the isotropic macroscopic behavior from a thermodynamics statistical point of view. However, here we report an anomalous electro-optic effect in liquid films composed of dipole linear molecules, and this electro-optic effect is believed to indicate that these liquid films are anisotropic. An electro-optic effect is an induced change in the refractive index of a material in response to an electric field, which can be divided into the Pockels and the Kerr effects. If the sample is isotropic, the refractive index response to the applied field is the Kerr electro-optic effect, as distinguished from the Pockels electro-optic effect, in which the induced index change is directly proportional to the square of the electric field instead of varying linearly with it [1]. The Pockels effect occurs only in anisotropic materials that lack inversion symmetry, such as noncentrosymmetric crystals [2], [3] or electric-field poled polymers [4], [5]. Strangely, in our experiments, a Pockels effect was measured in a polar liquid sample; this is incompatible with the nature of liquids [6]. No mechanism exists to interpret the Pockels effect in liquids, but one thing for sure is the breaking of the macroscopic symmetry

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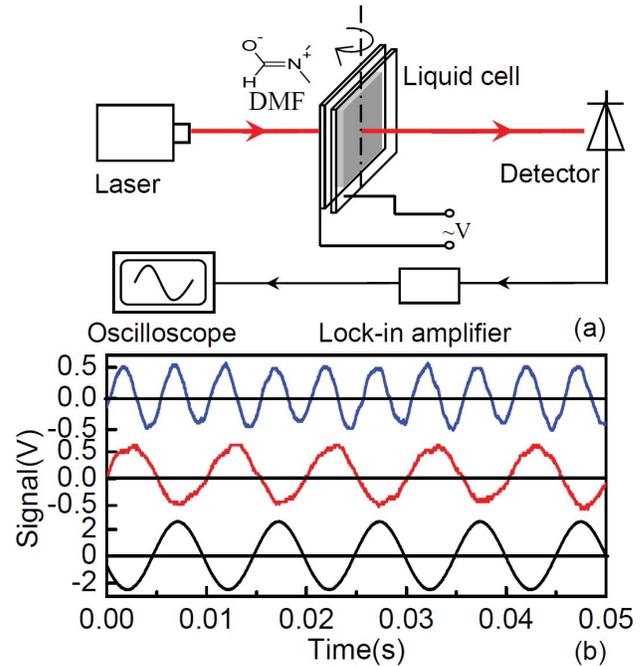


Fig. 1. Electro-optic measurement for polar liquids. (a) Schematic diagram of the setup. (b) Typical data were picked up by lock-in detection. The upper and middle curves separately show the fundamental ( $\omega$ ) and the quadratic ( $2\omega$ ) components of the electro-optic modulation signals read by the photodiode detector. The bottom curve is the applied electric signal to the sample.

of the liquids due to the principle of the Pockels effect [7]. After further experiments, the significant dependence of the Pockels effect on voltage strength and frequency was used to present the physical model of the pre-oriented and short-range orderly molecule clusters that give rise to this asymmetric effect. This dipole molecular aggregation was further confirmed in the field-induced spectral shift measurements [8], and the result demonstrated that these clusters maintained for a long time after the exciting electric pulse.

## II. PRINCIPLE

Figure 1(a) shows the schematic diagram of the setup for the electro-optic phase modulation measurement of liquids [9], [10]. As seen in Fig. 1(a), the liquid cell, which is used as an optical phase modulator, consists of a polar liquid placed in an insulating container with two indium tin oxide (ITO) electrodes. Unlike a conventional Kerr cell (usually several millimeters thick), the liquid cell is approximately  $8 \mu\text{m}$  thick. When a beam of light, generated by a  $1.3 \mu\text{m}$  continuous wave laser, travels through the liquid cell, the beam is divided

into two components. One is reflected by the interfaces of the sample, while the other passes through the sample. The electro-optic effects cause a small voltage-dependent optical path variation of the beam passing the liquid film. The liquid cell is considered as a symmetric Fabry-Perot etalon, and the transmitted light intensity  $I_{tran}$  could be expressed as:

$$I_{tran} = \frac{I_{in}}{1 + 4R \sin^2(\phi/2)/(1 - R^2)} \quad (1)$$

where,  $I_{in}$  is the intensity of the incident laser,  $R$  is the interface reflection coefficient, and  $\phi$  is the round-trip phase within the etalon. Due to the refractive index difference of glass, ITO film, and liquid film, the interface reflection coefficient  $R$  is about 10%. The round-trip phase  $\phi$  is relative to applied voltage due to the electro-optic effect, so the transmitted light carries out the information of the field-induced refractive index change. Thus, the electro-optic properties of polar liquids will be acquired by detecting the intensity signal of the transmitted light.

The application of an electric field to a polar liquid results in the reconfiguration or reorientation of the dipole molecules. Under this influence, the liquid becomes birefringent, and thus the bulk refractive index changes with the applied voltage strength. According to the equation of optical indicatrix, a refractive index change of a material under the action of an applied electric field can be expanded quantitatively in its power series [5]:

$$\Delta \left( \frac{1}{n^2} \right)_{ij} = \gamma_{ijk} : E_k + b_{ijkl} : E_k E_l + \dots \quad (2)$$

where  $\Delta \left( \frac{1}{n^2} \right)_{ij}$  is the field-induced birefringence,  $\gamma_{ijk}$  is the Pockels constant,  $b_{ijkl}$  is the Kerr constant, and  $E_k$  and  $E_l$  are the electric field across the sample. We assume the electric field has only one component  $E_k$ . For an alternating electric field,  $E_k = E_0 \cos \omega t$ , Eq. (1) gives:

$$\Delta \left( \frac{1}{n^2} \right)_{ij} = \frac{1}{2} b_{ijkk} E_0 + \gamma_{ijk} E_0 \cos \omega t + \frac{1}{2} b_{ijkk} E_0^2 \cos 2\omega t + \dots \quad (3)$$

Therefore, the Pockels and the Kerr effects are distinguished by the frequencies of the electro-optic modulation signals with respect to the applied field. The fundamental ( $\omega$ ) and the quadratic ( $2\omega$ ) signals separately represent the Pockels and the Kerr effects of the materials under the test. After having been lock-in amplified in Fig. 1(a), the fundamental ( $\omega$ ) and the quadratic ( $2\omega$ ) components are separated expediently by selecting the lock frequency [11], and the collected electro-optic modulation signals will be sent to a monitoring oscilloscope.

### III. EXPERIMENT AND DISCUSSION

A polar organic solvent, N, N-Dimethylformamide (DMF), was injected into the space of the liquid cell by capillary action. As shown in the inset of Fig. 1(a), an oxygen atom can attain one electron from a nitrogen atom, giving rise to the polar characteristics of DMF molecules. The curves in Fig. 1(b) were picked up at one measurement process, but

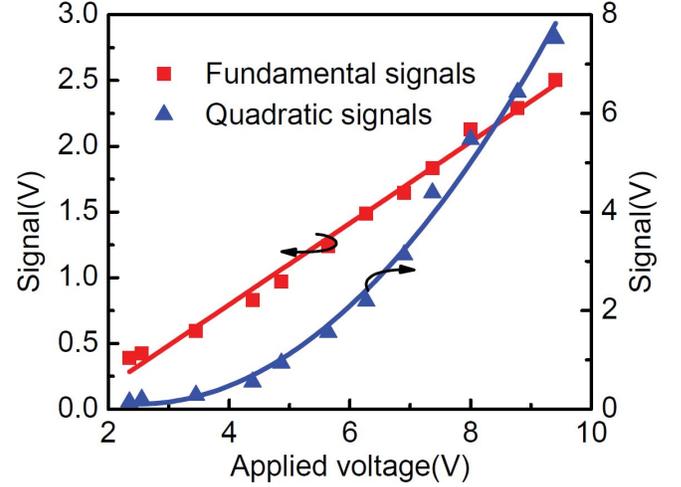


Fig. 2. Fundamental and quadratic component amplitudes of the electro-optic modulation signals as functions of the electric field strength. Note that different components have different voltage responses.

separated by the fundamental ( $\omega$ ) and the quadratic ( $2\omega$ ) lock frequencies of the applied electric signals. The origin of the modulation signals encompasses two possibilities: field-induced change of the absorption or the refractive index of the sample. In the practical measurement process, we found the modulation signal amplitudes exhibited periodic changes by rotating the sample slightly. That was a sign the modulation signals were from the field-induced refractive index changes, because the absorption change will increase monotonically with the optical path in the sample, but not periodically. Meanwhile, as we have seen, neither the fundamental ( $\omega$ ) nor the quadratic ( $2\omega$ ) components are dominant. It indicates that the liquid films of DMF simultaneously possess the Pockels and the Kerr electro-optic effects. This leads to the anomalous conclusion that the liquid film in the liquid cell is anisotropic. Moreover, this phenomenon seems to be universal by utilizing other polar liquids in the electro-optic measurements, such as dimethylacetamide, acetonitrile, and acetone.

Definitely more independent corroboration is necessary. Voltage-dependence curves are another obvious characteristic distinguishing the fundamental ( $\omega$ ) and the quadratic ( $2\omega$ ) components. Owing to differences in the manifestations of different mechanisms, that was often used to reveal the inherent essence of the origin of the modulation signals. As seen in Fig. 2, two kinds of voltage responses were respectively measured by lock-in detection. The fundamental ( $\omega$ ) component was proportional to the electric field strength, whereas the other was quadratic. The result of the experiments matched those of the theoretical expectation well. It was further proved that the Pockels effect occurred in the liquid film.

To interpret electrokinetic phenomena of polar liquids, experiments on frequency-response analysis are usually carried out [12]. The response speed of electro-optic materials relates to the mass of the entity that is moved by the electrical force. Different frequency responses can mirror different types of underlying mechanisms of the electro-optic effect. There are essentially three basic polarization mechanisms that are thought to result in the electro-optic effect: the electronic,

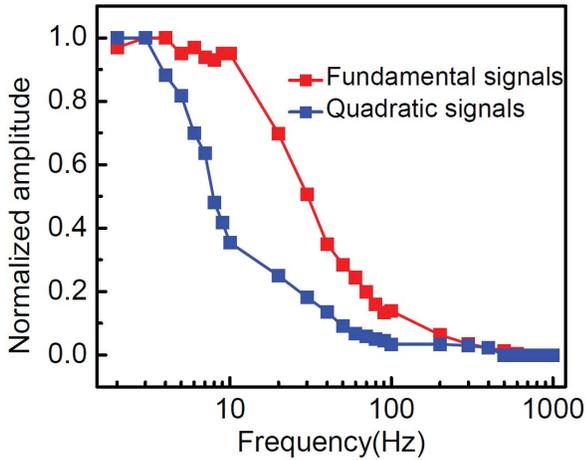


Fig. 3. Frequency response of the fundamental ( $\omega$ ) and the quadratic ( $2\omega$ ) signals. The large effect in the low-frequency range and the slow response indicate the large moving mass in the electro-optic process.

the ionic, and the orientation polarization. The orientation polarization is a large effect, but it is rather slow ( $10^3$ – $10^6$  Hz) because the electric field force moves a lot of mass, such as liquid crystal [13], [14]. In contrast, the ionic or the electronic polarization is a small effect but is relatively faster ( $10^{10}$ – $10^{14}$  Hz) because an ion or electron with less mass is moved, like inorganic crystals or poled electron chromophore polymer [2]–[5]. As seen in Fig. 3, the electro-optic effect in the low-frequency range was much larger than that in the relatively flat region of high frequency where only ionic and electronic polarization existed. This slow response speed indicates that the applied field force needs to move large mass; this gives a clue to analyze the origin of the asymmetric effect for liquids.

The temperature dependence is an important characteristic to distinguish the microcosmic mechanism of the electro-optic effect. The molecular orientation is the result of external electric field and internal thermal motion co-functioning, so the orientation polarization is a function of the material temperature, which is different from the other polarizations (the electronic or ionic polarization). We have conducted experiments of electro-optic modulation signals versus surrounding temperatures. The sample was heated by an infrared heater from 25 °C to 100 °C. At the same exerting voltage, the amplitudes of the modulation signals varied with the temperature obviously, which indicated the anomalous electro-optic effect was from molecular orientation polarization but not from other mechanisms.

Based on these measurements, we present a physical model that contributes to the interpretation of the anomalous Pockels effect: partial polar molecules form field-induced pre-oriented, short-range orderly dipole clusters [15, 16]. To some extent, these clusters resemble the liquid crystal. On the one hand, these clusters with lots of mass can explain the slow response speed, and their orientation effect leads to a large electro-optic effect coefficient in low-frequency range. On the other hand, the pre-oriented clusters break the macroscopical symmetry of the polar liquids, making it possible for the Pockels effect to occur in liquids.

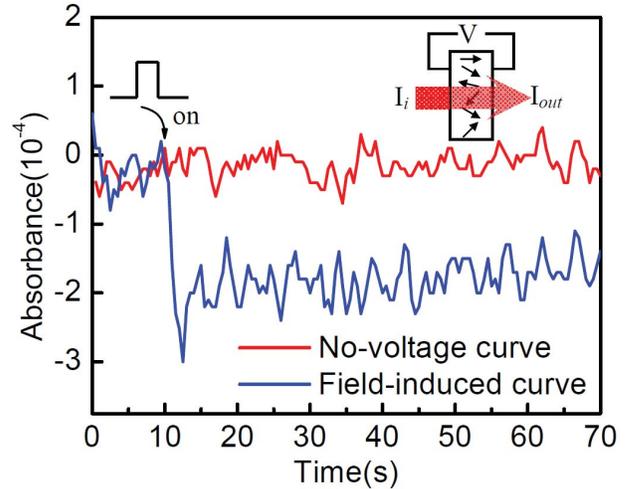


Fig. 4. Time spectral evolution measurement for certifying the physical model of field-induced pre-oriented dipole clusters. When an electric pulse was added, the spectral absorbance changed obviously, compared with the no-voltage curves. The inset shows the sample diagram for the absorbance measurement.

The field-induced aggregation of clusters was thought to result from strong intermolecular attractive forces and electrostatic forces from the liquid/ITO interfaces. These aggregates usually exhibit distinct changes in the absorption from the monomeric species [8]. Therefore, the spectral shifts of the sample were proposed to certify the field-induced clusters in the liquid cell. As shown in the inset of Fig. 4, when the spectrophotometer (UV3600, Shimadzu, Japan) was measuring the absorption spectrum of the sample around  $1.3 \mu\text{m}$ , a pulse electric field was added on the liquid film, and then we could observe the absorption changes at the wavelength of shorter than  $1.3 \mu\text{m}$ . In order to reveal the relation between the spectral changes and the input voltage, we took time as horizontal axis. Assuming that the absorption changes around  $1.3 \mu\text{m}$  are the same, Fig. 4 was converted from the field-induced spectrum change curve by recording the measurement time. Figure 4 shows a typical time spectral evolution. Therein the blue one is the spectral baseline without a field. The field-induced change was observed clearly by comparing the baseline. We applied a pulsed voltage to the sample at the other near-infrared wavelengths (1200nm–1800nm), and we got the same result. Besides, we find that these spectral changes remain for a long time after the exciting electric pulse, indicating that once the clusters are formed, they are difficult to disassemble. This phenomenon may be related to the hydrogen bonding in polar liquids induced by the exiting electric field. Thereby, the physical model for the origin of the anomalous Pockels effect was verified.

#### IV. CONCLUSION

In summary, the electro-optic effect of polar liquids was investigated. These materials are ideal candidates for the ability to control optical properties by electrical signals. Based on the anomalous and large Pockels effect in low frequency and the slow response speed, we present a physical model of field-induced pre-oriented clusters. Combined with spectral

analysis, the formation of clusters by an electric pulse was confirmed.

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