# Observation of Magnetoelectric Jones Birefringence

T. Roth[1,2] and G. L. J. A. Rikken[1]
[1]*Grenoble High Magnetic Field Laboratory, Max Planck Institut für Festkörperforschung/CNRS, BP 166, F-38042 Grenoble, France*
[2]*Technische Universität Darmstadt, Hochschulstraße 12, 64289 Darmstadt, Germany*

(Received 25 May 2000)

In 1948, Jones showed that uniaxial media can in general show four different fundamental optical phenomena, each of which can appear in refraction and absorption. Three of these are well established: isotropic refraction and absorption, linear birefringence and dichroism, and circular birefringence and dichroism. The fourth effect, predicted by Jones, has remained unobserved so far. In this Letter, we report the first experimental observation of this missing fourth, so-called Jones effect, as an additional, tilted linear birefringence. In our experiments, this effect was induced in liquids by parallel external magnetic and electric fields perpendicular to the propagation direction.

PACS numbers: 33.55.Fi, 42.25.Lc

Numerous linear optical effects in homogeneous uniaxial media are known, either intrinsic ones due to the symmetry properties of the medium, or effects induced by external influences such as magnetic field, electric field, pressure, etc. Jones developed a matrix formalism to describe and classify these effects [1,2]. By a completeness argument, he deduced the existence of a fundamentally new type of optical effect, which we shall call the Jones effect. Jones showed that this new effect can exist only in uniaxial media, and that it represents an additional linear birefringence and dichroism, the optical axes of which bisect the optical axes of the standard linear birefringence and dichroism. The Jones formalism was immediately recognized as a very powerful tool to describe the propagation of polarized light [3], in particular, in media that show two or more of the fundamental optical effects. It has been widely applied in polarization-optical studies on crystals, biological systems, polymers, etc. [2]. Although the Jones formalism has never been explicitly disputed, the long-standing absence of experimental evidence for the existence of the Jones effect leaves some doubts concerning the validity of Jones' approach. Later theoretical work supported the existence of Jones birefringence on the basis of symmetry arguments [4,5] and offered order of magnitude estimates for it. It was shown that the effect not only occurs intrinsically in some uniaxial crystal classes, but that it can also be induced in all media by simultaneously applying parallel magnetic and electric fields perpendicular to the propagation direction. This magnetoelectric Jones birefringence $\Delta n_{\mathrm{J}}$ is predicted to be of the form [4,5] (see inset of Fig. 1),

$$\Delta n_{\mathrm{J}} \equiv n_{+45^\circ} - n_{-45^\circ} = k_{\mathrm{J}} \lambda \mathbf{E} \cdot \mathbf{B}, \tag{1}$$

where $\lambda$ is the wavelength and $\mathbf{E}$ and $\mathbf{B}$ are externally applied electric and magnetic fields, respectively, both perpendicular to the light beam. The induced magnetoelectric Jones birefringence might be easier to detect than the intrinsic effect in birefringent crystals, as the external fields can be easily controlled and modulated. This allows for high sensitivity and good discrimination against other effects, in particular, the standard linear birefringence $\Delta n = n_{\parallel} - n_{\perp}$ that always accompanies the Jones birefringence. Such a standard birefringence will be present in all media under electric and magnetic fields in the form of the Cotton-Mouton effect ($n_{\parallel} - n_{\perp} \propto B^2$) and the Kerr effect ($n_{\parallel} - n_{\perp} \propto E^2$). These birefringences will in general be stronger than the Jones birefringence and can therefore obscure the latter effect. This partly explains why Jones birefringence, in spite of its predicted ubiquitous nature, has not been observed so far. Furthermore, the fact that no simple, intuitive explanation for the nature of Jones birefringence has yet been put forward also hampers the experimental search for media that exhibit this effect.

The formal descriptions proposed for the magnitude of the Jones birefringence vary greatly. This arises from the different orders in the light-matter coupling the different authors consider to be the dominant contributions to the Jones birefringence. The type of light-matter coupling (electric vs magnetic, dipole vs quadrupole vs octupole, etc.) not only determines the strength of the effect [6], but also the molecular symmetry for which a relatively large magnetoelectric Jones effect can be expected. Graham and Raab [4] incorporate up to electric quadrupole/magnetic dipole coupling in their calculations of Jones birefringence in liquids, but Ross *et al.* [5] claim electric/magnetic dipole coupling to be sufficient. To further confuse the situation, other authors do not find magnetoelectric Jones birefringence in their theoretical analysis of the magneto-electro-optical properties of liquids [7]. These controversies clearly show that Jones birefringence constitutes a severe test of our detailed understanding of light-matter interaction and that its experimental observation is long overdue. We have therefore embarked on a search for magnetoelectric Jones birefringence in liquids containing molecules of different symmetries and present our findings below.

0031-9007/00/85(21)/4478(4)$15.00

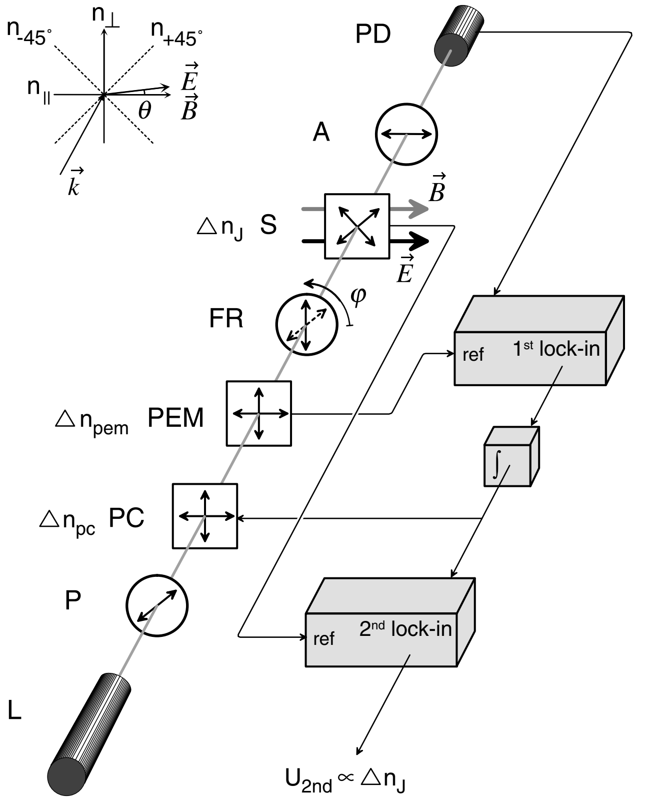

FIG. 1. Experiment to measure magnetoelectric Jones birefringence. Inset shows the optical axes of Jones birefringence $\Delta n_J = n_{+45°} - n_{-45°}$ and standard linear birefringence $\Delta n = n_{\parallel} - n_{\perp}$. Main figure shows experimental setup to observe Jones birefringence, consisting of a HeNe laser at a wavelength of 632.8 nm (L), polarizer (P), photoelastic modulator (PEM), Pockels' cell (PC), Fresnel rhomb (FR), sample cell (S), analyzer (A), and photodiode (PD). A phase sensitive feedback loop drives the Pockels' cell to compensate the sample birefringence. Path lengths of the samples varied between 5 and 30 mm. In addition to the static magnetic field **B**, a low frequency alternating electric field $\mathbf{E}\cos\Omega t$ is applied and phase sensitive detection of the resulting birefringence at the electric field frequency $\Omega$ ($\Omega \approx 60\ \mathrm{s}^{-1}$) is performed. The angle $\varphi$ of the polarization of the light incident on the sample with respect to the magnetic field can be chosen by means of the Fresnel rhomb. The angle $\theta$ between **E** and **B** can be chosen by rotating the electrode assembly. By a proper choice of $\varphi$ and $\theta$ and the external fields, this setup can be used to measure electric linear (Kerr), magnetic linear (Cotton-Mouton), and magnetoelectric Jones birefringence. The resolution was, due to noise and drift, limited to $\Delta n_J \approx 2 \times 10^{-12}$ with applied magnetic and electric fields up to 17 T and $2.5 \times 10^5$ V/m, respectively, and a path length of 25 mm.

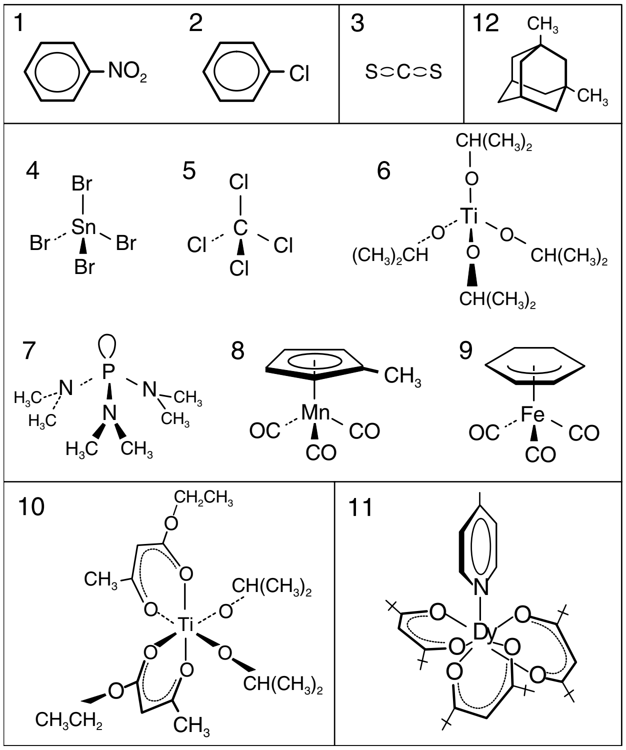

FIG. 2. Structure formulas of the molecules studied. All but **11** were liquids at room temperature and were measured as such. **11** was measured as a 43 wt % solution in toluene.

The experimental setup to observe Jones birefringence is shown in Fig. 1. It consists of a modification of a well-known setup to measure magnetic linear birefringence (the Cotton-Mouton effect) [8]. All samples were nonabsorbing at the wavelength used, and consisted of pure molecular liquids, or concentrated molecular solutions, and are shown in Fig. 2 and listed in Table I. Dipolar (**1**, **2**), quadrupolar (**3**), tetrahedral (**4**–**9**), and octahedral (**10**, **11**) molecules were studied (the symmetries being only approximative). The selection of materials was made on the basis of the presence of low-lying, high oscillator strength optical transitions and the possibility to have high concentration liquids. Our results for Kerr, Cotton-Mouton, and Jones birefringence are summarized in Table I. Where comparison is possible, our results for the Kerr and Cotton-Mouton constants agree reasonably with literature values [9]. **8**, **9**, and **10** were found to show a significant Jones birefringence. Typical results for **8** are shown in Fig. 3, where the linear dependences of $\Delta n_J$ on $E$, $B$, and $\cos\theta$ are explicitly demonstrated, thereby proving the existence of (magnetoelectric) Jones birefringence and confirming Eq. (1). In addition, we have measured the temperature dependence of $\Delta n_J$ of **8**, which gave $k_J(T) \propto T^{-x}$, $x = 0.8 \pm 0.2$. This is consistent with the mean orientation of noninteracting permanent, gaslike molecular dipole moments in an external field, which was predicted to give $x = 1$ [4]. We tentatively identify this moment as the static electric dipole moment. The static magnetic moments are mostly spin type, and as there is only weak spin-orbit coupling in the light transition elements, little effect on the optical properties can be expected. We can heuristically summarize our results by noting that a relatively large Jones birefringence is observed in molecules having a low-lying strong charge transfer transition of approximately octupolar symmetry and a permanent electric dipole moment. It should however be stressed that all liquids must exhibit magnetoelectric Jones birefringence. Our failure to observe it in the other molecules only means that for those, the effect is below our detection limit. In fact, recent calculations

TABLE I. Summary of molecular properties and birefringence results. The table gives the electric ($\mu$) and magnetic ($m$) dipole moments and the results for Jones, Kerr, and Cotton-Mouton birefringence. (Kerr and Cotton-Mouton constants are defined as $\Delta n_{\mathrm{K}} = k_{\mathrm{K}} \lambda \mathbf{E}^2$ and $\Delta n_{\mathrm{CM}} = k_{\mathrm{CM}} \lambda \mathbf{B}^2$.) For the definition of $k_{\mathrm{J}}$ see Eq. (1), for that of $\eta$, see Eq. (2). All measurements were done at room temperature. Molecules: (1) nitrobenzene; (2) chlorobenzene; (3) $CS_2$; (4) $SnBr_4$; (5) $CCl_4$; (6) Ti-isopropoxide; (7) tris (dimethylamino) phosphine; (8) methylcyclopentadienyl-Mn-tricarbonyl; (9) cyclohexadienyl-Fe-tricarbonyl; (10) Ti-bis(ethyl-acetoacetato) diisopropoxide; (11) Dy-tris(dipivaloylmethane)-pyridine 15:35 wt/wt in toluene; (12) dimethyl-adamantane.

| Molecule | $\mu$ (D) | $m(\mu_B)$ | $k_{\mathrm{J}}(\frac{10^{-12}}{\mathrm{VT}})$ | $k_{\mathrm{K}}(\frac{10^{-15}\ \mathrm{m}}{\mathrm{V}^2})$ | $k_{\mathrm{CM}}(\frac{10^{-5}}{\mathrm{m\,T}^2})$ | $\eta(10^{-5})$ |
|---|---|---|---|---|---|---|
| 1 | 4.0 | 0 | $<3$ | 3900 | 2100 | $<1$ |
| 2 | 1.6 | 0 | $<2$ | 220 | 590 | $<5$ |
| 3 | 0 | 0 | $<2$ | 39 | $-440$ | $<15$ |
| 4 | 0 | 0 | $<2$ | $<2$ | $-20$ | $\cdots$ |
| 5 | 0 | 0 | $<3$ | $<2$ | $-9$ | $\cdots$ |
| 6 | 0 | 0 | $<2$ | 2.8 | $-40$ | $<200$ |
| 7 | 0 | 0 | $<2$ | 4 | $-5$ | $<500$ |
| 8 | $\approx 4$ | 1.7 | 47 | 340 | $-51$ | 360 |
| 9 | $\approx 4$ | $\approx 3$ | 22 | 100 | $-130$ | 190 |
| 10 | $\approx 1$ | $\leqslant 0.5$ | 5.1 | 32 | $-7$ | 340 |
| 11 | $\approx 1$ | 8 | $<2$ | 30 | $-10^4$ | $<5$ |
| 12 | $\approx 0.3$ | 0 | $<2$ | 1.2 | $-2.8$ | $<1000$ |

have shown that even the vacuum, which is predicted to show both the Cotton-Mouton and the Kerr effect due to quantum-electrodynamical effects, also should show magnetoelectric Jones birefringence [10].

A further test for the validity of our experimental results consisted of measuring the magnetoelectric linear birefringence of **8** in crossed magnetic and electric fields, both perpendicular to the direction of light propagation. This birefringence, which has the same standard optical axis as the Kerr and Cotton-Mouton effects, was predicted to have exactly the same magnitude as the Jones birefringence [5,11]. We have indeed observed this to be the case [12].

Graham and Raab have estimated the strength of Jones birefringence for spherical atoms. They have found for the relative strength of Jones birefringence as compared to Cotton-Mouton and Kerr birefringence [4]:

$$\eta \equiv \left|\frac{\Delta n_{\mathrm{J}}}{\sqrt{\Delta n_{\mathrm{K}} \Delta n_{\mathrm{CM}}}}\right| = \left|\frac{k_{\mathrm{J}}}{\sqrt{k_{\mathrm{K}} k_{\mathrm{CM}}}}\right| = 0.016 . \qquad (2)$$

In spite of the different theoretical starting points, this estimate is not in strong quantitative disagreement with the predictions by Ross *et al.* [5]. The results of Ross *et al.* would imply that $\eta$ is of the order of the fine structure constant ($\approx 0.0073$). The largest value we have observed so far is $\eta = 0.0036$ for tetrahedral molecules. This is within 1 order of magnitude of both predictions. However, also values for $\eta$ that are at least 2 orders of magnitude smaller than this were found for other molecular symmetries (see Table I). Clearly, the relation between $\eta$ and the molecular structure is not understood. Still, our results imply that, in contrast to the Kerr and Cotton-Mouton effects which are determined by electric dipole transitions, the Jones birefringence is determined by higher order transition moments. The Jones birefringence therefore gives access to molecular parameters that are not accessible by Kerr or Cotton-Mouton measurements.

Estimates of the absolute strength of Jones birefringence have been made for hydrogen gas atoms [11]. A value of $k_{\mathrm{J}} = 6 \times 10^{-17}\ \mathrm{V}^{-1}\,\mathrm{T}^{-1}$ was calculated at 1 atm pressure, which translates into $k_{\mathrm{J}} \approx 10^{-14}\ \mathrm{V}^{-1}\,\mathrm{T}^{-1}$ for the densities of our molecular liquids. Electrostatic alignment of permanent dipole moments at room temperature increases this by 2 orders of magnitude [4], resulting in $k_{\mathrm{J}} \approx 10^{-12}\ \mathrm{V}^{-1}\,\mathrm{T}^{-1}$. Resonant enhancement due to the low-lying optical transitions (in **8**, $\lambda_0 = 335$ nm versus $\lambda_0 = 121$ nm for hydrogen) may give another order of magnitude, leaving us with an estimate of $k_{\mathrm{J}} \approx 10^{-11}\ \mathrm{V}^{-1}\,\mathrm{T}^{-1}$, which is in reasonable agreement with our experimental results for $k_{\mathrm{J}}$ on **8**, **9**, and **10**. Empirically, this extrapolation only seems to be valid for those molecules that have optical transitions that involve truly three-dimensional motion of electrons, as is also the case for the hydrogen atom. Still, one should keep in mind that our detection limit for Jones birefringence is only 1 order of magnitude below this estimate for $k_{\mathrm{J}}$.

Causality requires the real and imaginary parts of the refractive index to be related, so now that the existence of Jones birefringence has been experimentally established, it is inevitable that Jones dichroism also exists. Magnetoelectric Jones dichroism would represent a difference in absorption coefficient for light polarized linearly under +45° and under −45° with respect to the external fields. Our first results on **8** only give an upper limit for the ratio of magnetoelectric Jones dichroism over isotropic absorption of $3 \times 10^{-15}$ m/V T at $\lambda = 351$ nm.

An alternative description of linear birefringence would be to combine standard linear and Jones birefringence into a new linear birefringence, the optical axes of which are

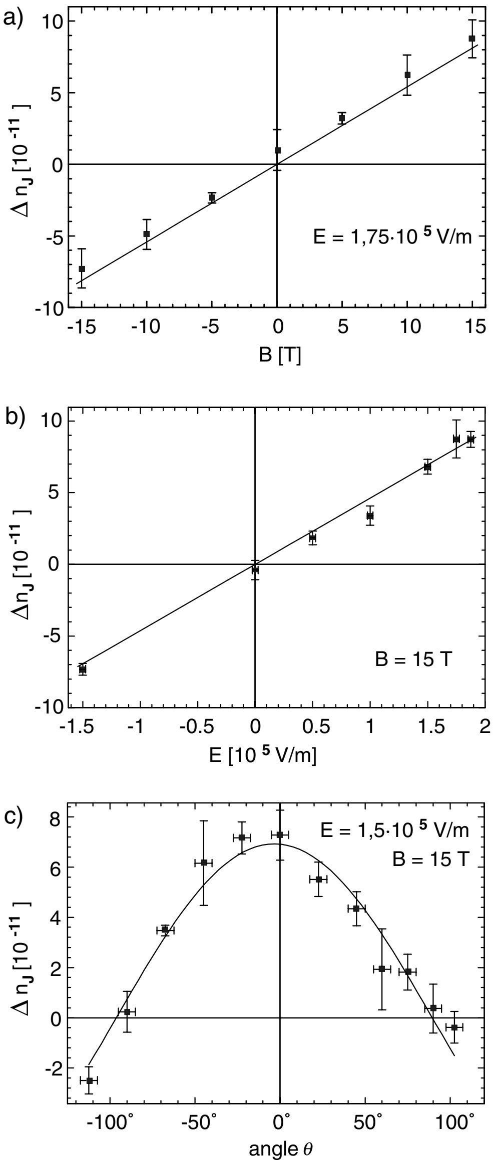

FIG. 3. Principal dependencies of Jones birefringence. $\Delta n_J$ for **8** at room temperature as a function of $B$ [(a), $\theta = 0$], $E$ [(b), $\theta = 0$], and $\theta$ (c). It was also checked that the observed $\Delta n_J$ was independent of sample length.

tilted with respect to the symmetry axes. A similar combination can be defined for the standard linear and Jones dichroism. The disadvantages of this description are that in general the tilt angles for this new birefringence and dichroism will be different and that both birefringence and dichroism and the corresponding angles have a more complicated dependence on the external fields. Along these lines, it has been suggested [13] that the intrinsic Jones birefringence in antiferromagnetic crystals forms the basis for the so-called gyrotropic birefringence [14]. Jones birefringence might also appear as a distortion of the Pockels birefringence in certain electro-optic crystals [15].

In conclusion, we have for the first time experimentally observed Jones birefringence, induced by an electric and a magnetic field in molecular liquids. This observation provides the final validation of the Jones formalism in polarization optics. Our results confirm all qualitative predictions made for this effect, but show clearly that our understanding of the relation between Jones birefringence and molecular structure is still incomplete.

We gratefully acknowledge P. Wyder, G. Martinez, B. van Tiggelen, G. Wagnière, and R. Feile for helpful discussions and C. Strohm for support. The Grenoble High Magnetic Field Laboratory is a "laboratoire conventionné aux universités UJF et INP de Grenoble."

[1] R. C. Jones, J. Opt. Soc. Am. **38**, 671–685 (1948).
[2] For an excellent review of Jones matrix calculus, see D. S. Kliger, J. W. Lewis, and C. E. Randall, *Polarized Light in Optics and Spectroscopy* (Academic Press, San Diego, 1990).
[3] *Encyclopedia of Physics,* edited by S. Flügge, Crystal Optics Diffraction (Springer-Verlag, Berlin, 1961), Vol. XXV/1.
[4] E. B. Graham and R. E. Raab, Proc. R. Soc. London A **390**, 73–90 (1983).
[5] H. J. Ross, B. S. Sherborne, and G. E. Stedman, J. Phys. B **22**, 459–473 (1989).
[6] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975), Chap. 16.
[7] N. B. Baranova, Yu. V. Bogdanov, and B. Ya. Zel'dovich, Sov. Phys. Usp. **20**, 870–877 (1977).
[8] G. Maret and G. Weil, Biopolymers **22**, 2727–2744 (1983).
[9] *Zahlenwerte und Funktionen,* Landolt-Börnstein, 6 Auflage, II. Band, 8. Teil, Optische Konstanten, 5-827 and 5-849 (Springer, Berlin, 1962).
[10] G. L. J. A. Rikken and C. Rizzo, Phys. Rev. A (to be published).
[11] E. B. Graham and R. E. Raab, Mol. Phys. **52**, 1241–1249 (1984).
[12] T. Roth and G. L. J. A. Rikken (unpublished).
[13] E. B. Graham and R. E. Raab, Ferroelectrics **162**, 161–171 (1994).
[14] R. V. Pisarev, B. B. Krichevtsov, and V. V. Pavlov, Phase Transit. B **37**, 63–72 (1991).
[15] E. M. Meintjes and R. E. Raab, J. Opt. A **1**, 146–151 (1999).