

THE LINEAR POCKELS EFFECT IN CRYSTALS OF THE IODOFORM-SULPHUR COMPLEX

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Crystals of the 1:3 adduct of iodoform and sulphur ($\text{CHI}_3 \cdot 3\text{S}_8$) have been found to exhibit a strong electro-optic effect. The values of the linear Pockels effect coefficients determined by using a modulation technique are: $|r_{12}| = (4.4 \pm 2.4) \times 10^{-12}$ m/V and $|r_{13} - 0.512r_{33}| = (0.29 \pm 0.12) \times 10^{-12}$ m/V. A comparison of the electro-optic susceptibility derived from these data with that deduced from powder second-harmonic generation tests shows the electro-optic phenomenon to be mainly of electronic origin.

Molecular crystals built of highly polarizable molecules are attractive materials for non-linear optics due to the values of the second-order susceptibilities d_{ijk} being markedly higher* than those for typical inorganic electro-optic crystals [1]. However, since for symmetry reasons all components of the tensor d_{ijk} vanish in centrosymmetric crystal space groups, high hyperpolarizabilities of organic molecules can be exploited only if the crystal structure is non-centrosymmetric. Moreover, even in such a case the crystal nonlinearities are generally much lower than those which could have been obtained had the molecular orientations been optimized [2,3].

One possible approach towards the preparation of materials having better non-linear properties is that of choosing a molecular entity of a high hyperpolarizability and embedding it into a suitable matrix. We report here on a highly non-linear crystal obtained in such a way, namely, by complexing the simple but highly polarizable molecule of iodoform (CHI_3) with sulphur. It should be noted that crystals of pure iodoform do not exhibit electro-optic properties due to

the presence of a dynamic dipolar disorder in the crystal lattice [4,5] which, if ordered, would be described by a polar P6_3 group [6]. However, in at least two addition complexes, 1:3 iodoform-sulphur [7] and 1:1 iodoform-hexamethylenetetramine [8], the iodoform molecules are fixed in non-centrosymmetric structures, the intermolecular interactions preventing the iodoform motions responsible for the disorder. We found [9] that both complexes exhibit efficient generation of the second harmonic of a Q-switched Nd:YAG laser when in powder form. Here, we present a report on the linear Pockels effect measurements in crystals of $\text{CHI}_3 \cdot 3\text{S}_8$.

Crystals of the iodoform-sulphur complex are trigonal R3m , thus the matrix of the linear Pockels effect coefficients has the following non-zero elements: $r_{12} = -r_{22} = r_{61}$, $r_{13} = r_{23}$, r_{33} and $r_{42} = r_{51}$ (e.g. ref. [10]). Application of an electric field described by the vector F_j should result in a modification of the refractive index ellipsoid according to the equation [10]

$$\Delta n_i^{-2} = r_{ij} F_j, \quad (1)$$

where $i = 1$ to 6, $j = 1$ to 3. Our measurements of the Pockels effect were performed using a simple modula-

* The second-order crystal polarization is related to the inducing electric field by $P_i = d_{ijk} E_j E_k$.

tion technique in which parallelepiped-shaped samples of the complex were used and the electric field (square-wave voltage up to 1.7 kV, 100 Hz) was applied transversely to the light path. The samples cut parallel to orthogonal x , y , z Pockels tensor axes (z being the crystal three-fold axis and the y axis lying in the symmetry plane) were mounted in an optical system consisting of a HeNe laser, a polarizer, a quarter-wave plate and an analyzer. A photodiode was used to detect the dc and ac components of the intensity of light transmitted through the system. The ac component could be observed directly using a scope or detected with a lock-in amplifier.

Simple considerations show that for the 3m point group the r_{12} coefficient can be determined by observing the modulation of light transmitted along the z direction of the crystal with the electric field applied either in the x or in the y direction. The electric-field-induced phase retardation is then given by

$$\Gamma = (2\pi L/\lambda)n_1^3 r_{12} F, \quad (2)$$

where L is the length of the light path. The value of the phase retardation is conveniently determined when the light beam entering the sample is made circularly polarized (with the quarter-wave plate) and the analyzer is positioned at 45° to the directions of the electric field induced axes of the xy section of the indicatrix (the section being circular in the absence of the field). The ratio of the ac and dc components is then simply equal to $\sin \Gamma$. Alternatively, the r_{12} coefficient was determined by applying the field in the y direction and passing the light in the x direction.

Applying the electric field in the z direction and passing the light in either the x or y direction one can measure the difference $r_{13} - (n_3^3/n_1^3)r_{33} = r_{13} - 0.512r_{33}$. Unfortunately, there is no simple way of determining the value of r_{42} since this coefficient is responsible for some slight rotation of the indicatrix only.

Table 1 shows the results obtained in this study, together with other data on the iodoform-sulphur complex taken from the literature or calculated from the present results. It should be mentioned that the relatively large spread of values of r has arisen from differences in the values measured on various samples of different optical quality. In fact, it can be anticipated that, as has been noticed for other organic electro-optic crystals [12], the crystal quality may be de-

Table 1
Properties of the iodoform-sulphur complex

| Refractive indices | 589 nm ^{a)} | 650 nm ^{a)} | 632.8 nm ^{b)} |
|--|----------------------|----------------------|------------------------|
| | $n_1 = n_2$ | 2.2528 | 2.2285 |
| n_3 | 1.7951 | 1.7860 | 1.7883 |
| Pockels effect coefficients | | | |
| $ r_{12} = (4.4 \pm 2.4) \times 10^{-12}$ m/V | | | |
| $ r_{13} - 0.512r_{33} = (0.29 \pm 0.12) \times 10^{-12}$ m/V | | | |
| Electro-optic susceptibilities | | | |
| $ d_{21}^{EO} = 55 \times 10^{-12}$ m/V | | | |
| $ d_{31}^{EO} = 2.3 \times 10^{-12}$ m/V ^{c)} | | | |

a) Ref. [11].

b) Interpolated using a single-term Sellmeier equation.

c) Assuming $|r_{33}| \ll |r_{13}|$.

cisive for obtaining large values of the electro-optic coefficients. Taking into account results obtained on the best of eleven crystals studied, one can suppose that the average values given in table 1 may be too low by a factor of two.

The relatively large value of r_{12} makes the iodoform-sulphur complex a reasonably good electro-optic crystal. The half-wave voltage for transverse electro-optic modulation and for the L/D ratio equal to unity (L being the light path and D being the distance between the electrodes) is equal to

$$V_{1/2} = \lambda/2n_1^3 r_{12}, \quad (3)$$

and from the values in table 1 there results a half-wave voltage of ≈ 6 kV. This is one of the best values for an organic molecular crystal, a much lower value of 1.3 kV being given only for 2-methyl-4-nitroaniline (MNA) [12].

For all the molecular electro-optic crystals investigated to date, it has been found that the major part of the electro-optic effect in these materials arises from the electronic contribution. Therefore, the electro-optic susceptibility d^{EO} is approximately equal to the non-linear susceptibility calculated from the second-harmonic generation experiments d^{SHG} (this is correct as long as resonance effects with optical transitions, both at the fundamental frequency and at the second harmonic, can be neglected). The components of the electro-optic susceptibility tensor may

be calculated from the equation [3]

$$d_{ijk}^{EO} = -\frac{1}{2} \sum_{l,m} \epsilon_{il} r_{lmk} \epsilon_{mj}, \quad (4)$$

given here in SI units, where ϵ_{mj} denote components of the dielectric constant tensor. The largest component of the d^{EO} matrix: $|d_{211}|$, or $|d_{21}|$ in shortened notation, is equal to $\approx 55 \times 10^{-12}$ m/V or 130×10^{-9} esu**. On the other hand, since the powder SHG efficiency of iodoform-sulphur has been found to be approximately equal to that of *m*-nitroaniline [9], the average non-linear susceptibility for the SHG phenomenon may be estimated to be $\approx 40 \times 10^{-12}$ m/V or 100×10^{-9} esu. Thus, the dispersion of the second-order susceptibility in iodoform-sulphur does not seem to be high and it can be concluded that both the SHG and the linear Pockels effect originate from non-linearities of the electronic polarizability of the iodoform-sulphur entities. Quantitatively, the molecular property responsible for crystal non-linearities is the hyperpolarizability β . The unit cell of $\text{CHI}_3 \cdot 3\text{S}_8$ contains only one molecule of the complex with the iodoform molecule on the trigonal axis and the sulphur molecules in mirror planes. Since the molecular axes coincide with the crystal axes [7], the relation between d and β is particularly simple:

$$d_{ijk} = V^{-1} f_i f_j f_k \beta_{ijk}, \quad (5)$$

where V is the unit cell volume and the f_i stand for local field correction factors (cf. ref. [3]). Approximating roughly the latter with Lorentz local field factors, one can get $\approx 83 \times 10^{-31}$ esu as the $|\beta_{222}| = |\beta_{211}|$ component of the hyperpolarizability tensor. One should note that this value is lower than, e.g., the

hyperpolarizability of the *p*-nitroaniline moiety [13], $\approx 345 \times 10^{-31}$ esu, *p*-nitroaniline being the parent molecule of MNA. However, in MNA and many similar crystals, the net crystal non-linearity arises from projecting molecular hyperpolarizabilities on crystal axes and is thus reduced while, due to the peculiarity of the crystal structure of $\text{CHI}_3 \cdot 3\text{S}_8$, the full value of the molecular hyperpolarizability is made use of in this material.

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** Using $d(\text{MKS}) = \frac{4}{3} \pi \times 10^{-4} d(\text{esu})$.