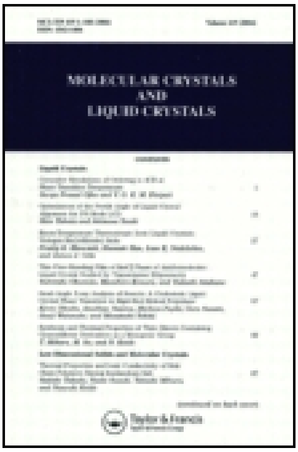

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ORGANIC MOLECULAR CRYSTALS FOR OPTICAL DATA PROCESSING

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Abstract: We report on the nonlinear optical properties of a new class of organic compounds built of trihalides interacting weakly with donor type molecules. The adducts of iodoform with sulphur ($CHI_3.3S_8$) and iodoform with quinoline ($CHI_3.3C_9H_7N$) exhibit sizeable electrooptic effects and second harmonic generation comparable to those of the most efficient organic coumpounds such as MNA (methylnitroaniline). For both iodoform compounds the angle-tuned phase matching of type I and II has been observed.

The comparison between the electrooptic effect and the second harmonic generation suggests that in these materials the electrooptic effect is mostly electronic in origin. This permits the construction of high speed electrooptical modulators and switching devices operating at very high frequencies up to the terahertz region.

The macroscopic optical nonlinearity of the adducts stems mainly from the nonlinearity of the iodoform molecule. The largest electrooptic coefficients (r_{22} = 2.2pm/V) and the largest nonlinear optical susceptibility (d_{22} = 19.1pm/V) were measured in the iodoform-sulphur compound.

INTRODUCTION

The use of glass fibers in modern data communication techniques has created a huge need for extremely fast electrooptical devices such as light modulators and light mixers.

The search for highly efficient, optically nonlinear materials is pushed worldwide in national and international research programs, and new materials for nonlinear optical applications are regularly being patented. It is obvious that optical data processing is one of the key technologies of the future. The step towards higher data rates has to be directed towards electrooptical and all-optical systems, and organic nonlinear optical materials are key components in future devices.

The research efforts range from pure materials research to complex waveguide structures. The materials may be inorganic or organic, they can exist as single crystals, poled polymers or thin films.

IODOFORM COMPOUNDS

Iodoform CHI_3 is far from the usual notion of a nonlinear organic molecule. Unlike the standard organic materials, it does not contain aromatic rings and only possesses a small permanent dipole moment; however, some iodoform compounds are transparent into the blue wavelength regime and the nonlinear efficiency can compete with that of the best organic materials known at present. The iodoform molecule is drawn in figure 1.

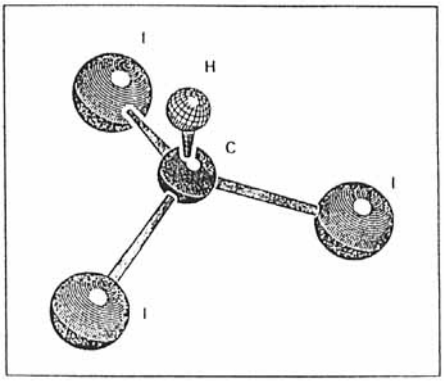

FIGURE 1 Structure of the iodoform molecule

Three iodine atoms form an equilateral triangle, the carbon and hydrogen atom merely cohere the iodine atoms. The dipole moment of the molecule is along the C-H bond. Along each C-I bond, the size of the induced electrical polarization of the molecule is different whether the electric field is applied in the C-I direction or in the I-C direction. Our measurements have shown that the nonlinearity is largest in the plane of the iodine atoms, the reason being that iodine atoms contain many electrons, and it is the polarizability of those electrons which is responsible for the optical nonlinearity of the iodoform compounds. Thus the permanent dipole moment of the iodoform molecule is orientated perpendicular to the directions of highest electrical polarizability. In this respect, the iodoform differs from the better known aromatic molecules.

In a pure iodoform crystal, the molecules are arranged in a centrosymmetric orientation so that their individual molecular nonlinearities cancel each other.

Only if a suitable complex partner is chosen, then a non-centrosymmetric alignment of the iodoform molecules is achieved in the bulk. Figure 2 shows the structure of the iodoform sulphur $CHI_3.3S_8$ complex.

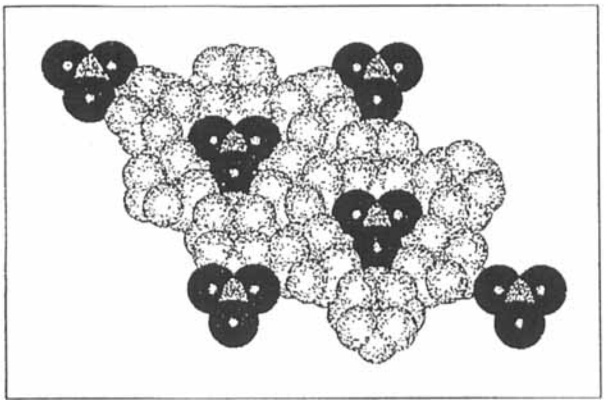

FIGURE 2 Structure of the iodoform-sulphur compound. All iodine atoms (dark) lie in a plane, and all iodoform molecules are identically orientated. The sulphur rings are drawn dotted.

The iodoform molecules are locked in planes of sulphur rings and thus are perfectly orientated along one crystal direction (the optical axis of the bulk crystal). Other suitable complex partner molecules are quinoline (C_9H_7N) and urotropine ($C_6H_{12}N_4$). Analogous to iodoform there are other similar molecules such as antimony triiodide which display a high optical nonlinearity.

The atomic force microscope has been used to record the molecular structure of iodoform-sulphur crystal platelets. The molecular resolution of the device allows the assignment of lattice parameters to the surface layer[1]. The intermolecular spacings at the surface of the crystals correspond remarkably well with those in the bulk. Furthermore, the scans show that in the crystal platelets, the dipole axis, and therefore the optical axis of the iodoform crystal, is located in the plane of the platelets.

RESULTS

The efficiency for second harmonic light generation in a material may also be considered as a measure for the maximum speed of electrooptical effects which can be achieved in the material under consideration.

We have not been able to directly measure the maximum speed of electrooptic modulators built from iodoform-sulphur crystals. Even with the fastest voltage source available (risetime 1ns), we could not detect any delay in the optical transmission. However, one can try to find the answer in an indirect way. Firstly, we had to measure the efficiency for frequency doubling, that is to say the nonlinearity of the material at light frequencies. This value can be compared with the electrooptic efficiency measured in a dc electric field. If the two values are similar, then we can conclude that an electrooptic modulator works up to the frequency of light. If the electrooptic coefficient is much larger then we can conclude that there are phonons contributing to the nonlinear effects which can not react to the fast light frequencies. In this case, we can expect an upper limit to the modulation frequency at about 1 GHz, which is the case with many of the more common inorganic electrooptic materials.

The nonlinear optical coefficients d^{SHG} characterizing the second harmonic generation (SHG) efficiency and the electrooptic coefficients r have been measured by independent experimental techniques[2,3].

The experimental results for d^{SHG} and r are compiled in table 1 for two different crystal orientations parallel (33) and perpendicular (11,22) to the dipole moment of the crystals. The electrooptic data d^{elopt}_{SHG} are calculated from the SHG experimental data d^{SHG} measured at the dye laser wavelength of λ = 940nm. The electrooptic coefficients r measured in a dc field with a HeNe laser at 632.8nm are then rewritten in terms of d^{elopt}.

Element		SHG (λ=940nm)		Elopt λ=(632.8nm)	
d_{ik}	ε	d^{SHG}	d^{elopt}_{SHG}	r	d^{elopt}
sulphur (11)	5.3	0	0	0	0
(22)	5.3	19.2	78.2	2.11	59.3
(33)	4.6	2.6	13.0	0.74	15.6
quinoline (11)	3.8	3.55	14.4	0.82	11.8
(22)	3.8	8.1	32.7	1.86	26.9
(33)	4.5	2.0	10.5	0.66	13.4

TABLE 1 Comparison between the electrooptic coefficients at high frequencies d^{elopt}_{SHG}, and the electrooptic coefficients d^{elopt} at low frequencies in the iodoform-sulphur and iodoform-quinoline compounds. The high frequency coefficients are calculated from the measured SHG coefficients d^{SHG}, while the low frequency coefficients r are rewritten in terms of d^{elopt}.

The data indicate that the iodoform adducts can be classified as moderately efficient electrooptic materials. As a comparison with good inorganic materials, a value of $r_{33} = 30.8$pm/V for $LiNbO_3$ and $r_{62} = 26.4$pm/V for KDP is reported. However, this only holds as long as the frequency of the modulating electric field is below the GHz region. In inorganic substances, where the nonlinear effects are mainly due to lattice polarization and piezoelectric interactions, the electrooptic response diminishes at higher frequencies.

As can be seen from the results in table 1, there is a good correspondence between the electrooptic data calculated at high frequencies and measured at low frequencies. This is a clear indication that the electrooptic effect in the iodoform compounds is of almost pure electronic origin. Therefore devices such as fast switches and modulators made from these materials can basically operate at speeds up to THz.

APPLICATIONS

Applications in integrated electrooptics include high speed polarization modulation and switching of lasers in optical signal processing, which is based on the Pockels effect. The figure of merit FM^{eo} for electrooptic devices is given as[4] :

$$FM^{eo} = n^3 \cdot r$$

Assuming a field of 5V/μm and a device length of 1cm, this requires $FM^{eo} \geq$ 20pm/V to produce a phase difference of π for orthogonally polarized beams in an electrooptic device. If modulation at very high frequencies is required, device capacitance must be minimal. The maximum dielectric constant ϵ may be estimated[4] from $f = d/R\epsilon\epsilon_0 A_e$, where f is the bandwidth, R the electrical impedance (50Ω), d the electrode distance and A_e the electrode area.

Setting d = 2μm and A_e = 1cm $\cdot$ 1μm, one finds $\epsilon \leq 10$ for f = 10GHz.

In iodoform-sulphur, $FM^{eo} \approx 23$ and $\epsilon \approx 5$, while in iodoform-quinoline, $FM^{eo} \approx 9$ and $\epsilon \approx 4$. The iodoform-sulphur complex is matching all these requirements.

One of the goals of our electrooptic study was to find out if these new materials could be interesting in the aspect of practical utility. Therefore we calculated the half-wave voltage $V_{1/2}$ defined as the voltage required to induce a phase retardation of π between two orthogonally polarized beams if the distance between electrodes is equal to the light path. In our compounds, The lowest half-wave voltage is obtained when the light beam is parallel to the optic axis and the electric field is applied perpendicular to it.

In this geometry the half-wave voltage is calculated at $\lambda = 632.8$ nm as

$$V_{1/2} = \frac{\lambda}{2 \cdot n^3 \sqrt{r_{11}^2 + r_{22}^2}} = \begin{cases} 9 \quad kV \quad \text{in } CHI_3 \cdot 3S_8 \\ 28 \quad kV \quad \text{in } CHI_3 \cdot 3\text{Quinoline} \end{cases}$$

The half-wave voltage in iodoform-sulphur is comparable to that in KDP (8.5kV) at low frequencies. With the electric field applied perpendicular to the light path, the voltage required in an actual device can be significantly reduced using the transverse electrooptic effect.

CONCLUSIONS

The comparison of SHG susceptibilities d^{SHG} with the electrooptic susceptibilities d^{elopt} in the iodoform compounds indicate that the electrooptic effect is predominantly electronic in origin. This result demonstrates that iodoform compounds are not only efficient frequency doublers but are, in principal, suitable for extremely fast electrooptic switches and modulators.

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