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## Second Order Nonlinearities of Molecular Complexes

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*Abstract:* The electrooptic coefficients and second harmonic efficiencies of a group of little known molecular systems with high nonlinear optical properties will be presented. We refer to the group of the trihalogenomethanes, which are small organic molecules without  $\pi$ -bonds. By packing up those molecules with suitable complex partners, high nonlinearities can be achieved.

*Introduction:* In a nonlinear material, the dielectric polarisation  $P$  in an applied Field  $E$  is described with a Taylor series in  $E$  :

$$P = \epsilon_0 \chi^{(1)} E + \epsilon_{(0)} \chi^{(2)} E^2 + \dots$$

The second term describes a polarisation with sum- or difference frequencies :

$$P(\omega) = \epsilon_0 \chi^{(2)} E(\omega_1) E(\omega_2); \quad \omega = \omega_1 \pm \omega_2$$

*Electrooptic effect:*  $\omega_1 = 0$ ;  $\chi_{el.opt.} = n_k^2 n_i^2 r$ ;  $r$ : electrooptic coefficient

*SHG:*  $\omega_1 = \omega_2$ ;  $\chi_{SHG} = 2d$ ;  $d$ : optical nonlinear coefficient

*Electronic origin:* When both nonlinear effects are of purely electronic origin, the following equation is valid (Ref 1):

$$d = \frac{n(\omega) + 2}{n(0) + 2} \cdot \frac{n_k^2 n_i^2}{2} \cdot r$$

*Motivation:* The search for nonlinear materials capable of doubling diode laser wavelengths into the deep blue generally collides with two requirements :

- Large second order nonlinear susceptibility and
- Short cut-off wavelength (near 400nm)

Powder SHG measurements were carried out to check these requirements (with MNA and urea for comparison, 6-amino-nicotinic acid as reference).

Tab.1a: Powder SHG results

- a) Powder yield (ungraded powders < 20 $\mu$ ) at 930 nm  
 b) Trimethylamoniumjodid.trijodmethan.

	adduct	crystal class	iodoform-density [ $\frac{10^{21}}{\text{cm}^3}$ ]	$\lambda_{\text{cut-off}}$	SHG-yield vs urea <sup>a)</sup>
Iodoform- Quinoline	1:3	3	1.47	$\approx 410$ nm	1.1
Iodoform- Sulphur	1:3	3m	1.32	$\approx 460$ nm	3
Iodoform- Urotropin	1:1	mm2	3.17	$\approx 400$ nm	30
Iodoform- Ptma <sup>j</sup> <sup>b)</sup>	1:1	2	2.36	$\approx 440$ nm	12
Bromoform- Ptma <sup>j</sup>	-	-	-	-	5
Bromoform- Urotropin	1:1	-	-	$\approx 400$ nm	5.5
Urotropin	1	$\bar{4}3m$	-	< 350 nm	0.1

Tab.1b: Comparison between Electrooptic Effect and SHG

- a) measured with the Mach-Zehnder interferometer at 633 nm  
 b) measured with induced birefringence at 633 nm (Ref 2)  
 e) calculated with  $d_{\text{el.opt.}} = \frac{n_i^2 n_j^2}{2} r$   
 f) measured with the wedge - technique at 937 nm (no absorption correction),  
 calculated with  $d_{\text{SiO}_2} = 0.48 \frac{\text{pm}}{\text{V}}$

	tensor element	SHG	el.opt.effect	
		$d^f$ [ $\frac{\text{pm}}{\text{V}}$ ]	$r$ [ $\frac{\text{pm}}{\text{V}}$ ]	$d_{\text{el.opt.}}^e$ [ $\frac{\text{pm}}{\text{V}}$ ]
Iodoform- Quinoline- Complex	(33)	$1.9 \pm 0.5$	$0.66 \pm 0.13^a)$	$2.6 \pm 0.5$
	$\sqrt{(11)^2 + (22)^2}$	$8.9 \pm 3$	$1.4 \pm 0.2^a)$	$8.3 \pm 1.2$
	$\sqrt{(11)^2 + (22)^2}$	-	$2.0 \pm 0.5^b)$	$12 \pm 3$
Iodoform- Sulphur- Complex	(33)	$1.8 \pm 0.5$	$0.85 \pm 0.17^a)$	$4.3 \pm 0.9$
	$\sqrt{(11)^2 + (22)^2}$	$16 \pm 5$	$2.2 \pm 0.4^a)$	$27 \pm 5$
	$\sqrt{(11)^2 + (22)^2}$	-	$4.4 \pm 2.4^b)$	$55 \pm 30$

### Main results

- The nonlinearity is of mainly **electronic origin** .

This is shown by the comparison of  $d_{\text{el.opt.}}$  and  $d$

- The nonlinearity of iodoform is markedly improved by the complex partner

- The largest nonlinearity lies in the plane of the iodine atoms, which is also the plane of the charge-transfer bonds

- The iodoform-urotropine complex is suitable for doubling laser diode wavelengths into the deep blue

### Acknowledgement:

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