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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 π-bonds. By packing up those molecules with suitable complex partners, high nonlinearities can be achieved.

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

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

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-nicotic acid as reference).

Tab.1a: Powder SHG results

a) Powder yield (ungraded powders $< 20\mu$) at 930 nm

b) Trimethylamoniumjodid.triiodmethan.

	adduct	crystal class	iodoform-density $[\frac{10^{21}}{cm^3}]$	$\lambda_{cut-off}$	SHG-yield vs urea[a]
Iodoform- Quinoline	1:3	3	1.47	≈ 410 nm	1.1
Iodoform- Sulphur	1:3	3m	1.32	≈ 460 nm	3
Iodoform- Urotropin	1:1	mm2	3.17	≈ 400 nm	30
Iodoform- Ptmaj[b]	1:1	2	2.36	≈ 440 nm	12
Bromoform- Ptmaj	-	-	-	-	5
Bromoform- Urotropin	1:1	-	-	≈ 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 $d_{el.opt.} = \frac{n_k^2 n_l^2}{2} \quad r$

f) measured with the wedge - technique at 937 nm (no absorption correction), calculated with $d_{SiO_2} = 0.48 \frac{pm}{V}$

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

Main results

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

This is shown by the comparison of $d_{el.opt.}$ 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

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