

**Zeitschrift:** Helvetica Physica Acta

**Band:** 62 (1989)

**Heft:** 6-7

**Artikel:** Second order nonlinearities of molecular complexes

**Autor:** Kohler, D. / Staehelin, M. / Enderle, Th.

**DOI:** <https://doi.org/10.5169/seals-116159>

#### Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. [Mehr erfahren](#)

#### Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. [En savoir plus](#)

#### Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. [Find out more](#)

**Download PDF:** 08.08.2025

**ETH-Bibliothek Zürich, E-Periodica, <https://www.e-periodica.ch>**

## Second Order Nonlinearities of Molecular Complexes

D.Kohler, M.Staehelin, Th.Enderle, J. Fünfschilling, I. Zschokke-Gränacher

Institut für Physik, Universität Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland

Ch. Kröhnke

Ciba Geigy R-1060.3.40 Basel

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

**SHG:**  $\omega_1 = \omega_2; \quad \chi_{SHG} = 2d; \quad d$ : 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) Trimethylammoniumjodid.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	$\approx 410 \text{ nm}$	1.1
Iodoform- Sulphur	1:3	3m	1.32	$\approx 460 \text{ nm}$	3
Iodoform- Urotropin	1:1	mm2	3.17	$\approx 400 \text{ nm}$	30
Iodoform- Ptmaj <sup>b)</sup>	1:1	2	2.36	$\approx 440 \text{ nm}$	12
Bromoform- Ptmaj	-	-	-	-	5
Bromoform- Urotropin	1:1	-	-	$\approx 400 \text{ nm}$	5.5
Urotropin	1	43m	-	< 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  $d_{\text{el.} \text{opt.}} = \frac{n_k^2 n_l^2}{2} r$   
 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	
		$d^f) [\frac{\text{pm}}{\text{V}}]$	$r [\frac{\text{pm}}{\text{V}}]$	$d_{\text{el.} \text{opt.}}^e [\frac{\text{pm}}{\text{V}}]$
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  $d_{\text{el.} \text{opt.}}$  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:

The support of the Swiss national Science Foundation (NFP 19) is gratefully acknowledged.

### References:

- 1) J.Zyss and J.L.Oudar, Phys.Rev. A26 (1982) 2028
- 2) A.Samoc et al Material Science Vol.XIII, No.1-2 1987