

## SECOND HARMONIC LIGHT SCATTERING INDUCED IN LIQUIDS BY FLUCTUATIONAL ELECTRIC FIELDS OF QUADRUPOLEAR MOLECULES

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The use of  $Q$ -switched neodymium glass laser with high transmission optical systems enabled us to perform a first measurement of cooperative second harmonic light scattering in liquid benzene and carbon disulphide.

In a previous communication [1], we reported the theory and first measurements of cooperative second harmonic light scattering (SHLS) by liquids having centrosymmetric molecules. We then stressed the technical impossibility of studying benzene and aromatic derivatives with our device ( $\lambda_\omega = 0.6942\mu$ ,  $\lambda_{2\omega} = 0.3471\mu$ ), since in those compounds harmonic scattering is masked by signals of unclear origin. This communication is aimed at presenting a theory and experimental results on cooperative SHLS in liquid benzene and carbon disulphide obtained from neodymium laser excitation.

### 1. Theory

The vertical and horizontal intensity components of elastically scattered laser light at frequency  $2\omega$  (for vertically polarized incident light of velocity  $c$ , frequency  $\omega$  and intensity  $I_v$ ) are [2]:

$$V_v^{2\omega} = Q_{2\omega}(F_{2\omega} + G_{2\omega})I_v^2, \quad H_v^{2\omega} = Q_{2\omega}F_{2\omega}I_v^2, \quad (1)$$

where

$$Q_{2\omega} = \left(\frac{2\omega}{c}\right)^4 \left(\frac{n_{2\omega}^2 + 2}{3}\right)^2 \left(\frac{n_\omega^2 + 2}{3}\right)^4; \quad (2)$$

$n_\omega$  and  $n_{2\omega}$  are refractive indices at frequencies  $\omega$  and  $2\omega$  respectively.

The factors  $F_{2\omega}$  and  $G_{2\omega}$  characterize the molecular mechanism of cooperative SHLS

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in a volume  $V$  containing  $N$  centrosymmetric molecules (in the absence of phase interference);

$$F_{2\omega} = \frac{1}{840V} \left\langle \sum_{p=1}^N \sum_{q=1}^N \{4c_{ijkl}^{2\omega(p)} c_{ijkm}^{2\omega(q)} - c_{ijjl}^{2\omega(p)} c_{ikkm}^{2\omega(q)}\} F_l^{(p)} F_m^{(q)} \right\rangle,$$

$$G_{2\omega} = -F_{2\omega} + \frac{1}{280V} \left\langle \sum_{p=1}^N \sum_{q=1}^N \{2c_{ijkl}^{2\omega(p)} c_{ijkm}^{2\omega(q)} + 3c_{ijjl}^{2\omega(p)} c_{ikkm}^{2\omega(q)}\} F_l^{(p)} F_m^{(q)} \right\rangle, \quad (3)$$

where  $c_{ijkl}^{2\omega}$  is the third order nonlinear polarizability of a molecule at frequency  $2\omega$ .  $F$  is the fluctuating in time and space molecular electric field which destroys the molecular center of symmetry and induces a local anisotropy in the near order region;  $\langle \rangle$  stands for statistical averaging in the presence of molecular correlations.

In the case of isotropic scattering we obtain from (3) the relations:

$$G_{2\omega}^{is} = 8F_{2\omega}^{is} = \frac{N}{27V} c_{2\omega}^2 \langle F^2 \rangle, \quad (4)$$

where, for molecules possessing the symmetry of point groups  $D_{6h}$  and  $D_{\infty h}$ , we have the mean nonlinear polarizability:

$$c_{2\omega} = c_{iiij}^{2\omega}/5 = \frac{1}{15} (3c_{3333}^{2\omega} + 12c_{3311}^{2\omega} + 8c_{1111}^{2\omega}) \quad (5)$$

and mean square of the quadrupolar molecular electric field:

$$\langle F^2 \rangle = \frac{9}{8} \Theta^2 \left\langle \sum_{q \neq p}^N \{5(\cos^2 \theta_p - \cos^2 \theta_q)^2 + 4(\cos^2 \theta_p - 2 \cos \theta_p \cos \theta_q \cos \theta_{pq} + \cos^2 \theta_q)\} r_{pq}^{-8} \right\rangle; \quad (6)$$

$\Theta$  is the permanent electric quadrupole moment,  $\theta_p$  and  $\theta_q$  being the angles between the symmetry axes of molecules  $p$  and  $q$  and the vector  $r_{pq}$ , and  $\theta_{pq}$  that between their symmetry axes.

For weak angular molecular correlations, (6) reduces to a form accessible to numerical calculations [2]:

$$\langle F^2 \rangle = 3\Theta^2 \left\langle \sum_{q \neq p}^N r_{pq}^{-8} \right\rangle. \quad (7)$$

By (1), the SHLS depolarization ratio is

$$D_v^{2\omega} = \frac{H_v^{2\omega}}{V_v^{2\omega}} = \frac{F_{2\omega}}{F_{2\omega} + G_{2\omega}} = \frac{1}{9} \frac{1 + A_{2\omega}^2}{1 - A_{2\omega}^2}, \quad (8)$$

where the nonlinear effective anisotropy is, in the case of point groups  $D_{6h}$  and  $D_{\infty h}$ :

$$A_{2\omega}^2 = \frac{17\gamma_{2\omega}^2 - 105\gamma_{2\omega}\delta_{2\omega} + 525\delta_{2\omega}^2}{525c_{2\omega}^2} \quad (9)$$

with

$$\gamma_{2\omega} = \frac{2}{7} (3c_{3333}^{2\omega} - 4c_{1111}^{2\omega} + 3c_{1133}^{2\omega}),$$

$$\delta_{2\omega} = \frac{2}{7} (c_{3333}^{2\omega} - 6c_{1133}^{2\omega} + c_{1111}^{2\omega}).$$

Eq. (9), with the assumption  $c_{1133}^{2\omega} = (c_{3333}^{2\omega} + c_{1111}^{2\omega})/6$ , gives the previous form [1]

$$A_{2\omega}^2 = \frac{51}{175} \left( \frac{c_{3333}^{2\omega} - c_{1111}^{2\omega}}{c_{3333}^{2\omega} + 2c_{1111}^{2\omega}} \right)^2. \quad (10)$$

## 2. Experimental results and discussion

With regard to our earlier device [3], the following two modifications were introduced (Fig. 1): (i) the ruby laser was replaced by a neodymium-doped glass laser of similar power ( $\approx 5$  MW) switched by means of a rotating prism, (ii) luminosity at detection was

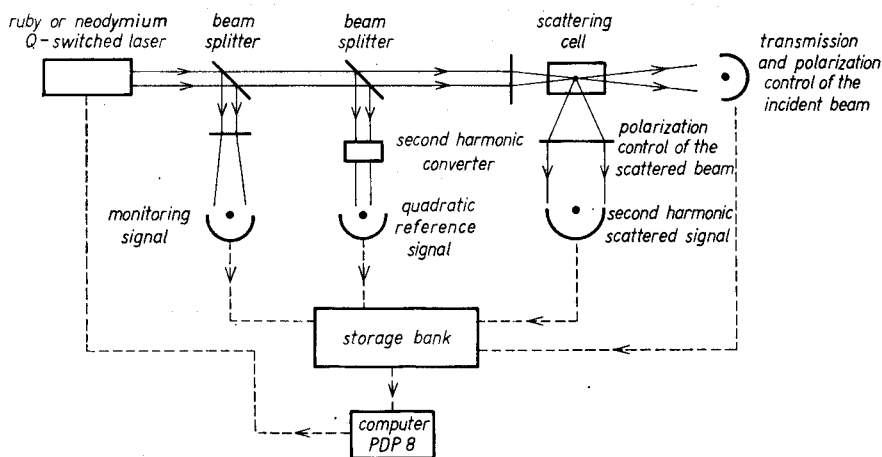


Fig. 1. Experimental set-up of SHLS using Q-switched laser excitation

considerably raised by applying lenses and condensers of large diameter ( $\varnothing = 8$  cm), open at  $f/1$ , permitting detection of the scattered flux within a cone of  $52^\circ$  aperture.

We obviously checked the proportionality of  $V_v^{2\omega} \approx I_v^2$  and  $H_v^{2\omega} \approx I_v^2$  in each case. We made sure that there were no signals on either side of the harmonic frequency and in all cases attenuated strongly the incident flux at the level of the scattering cell, so as to avoid dielectric breakdown of the sample. An experimental search for stimulated Raman radiation in the anti-Stokes region proved fruitless. Neither did we find any significant induced depolarisation of the incident laser wave in these experiments. Table I supplements

Experimental results from our SHLS data.  $\lambda = 1.06 \mu$ ,  $t = 25^\circ\text{C}$ 

Liquid	Point group	Number of independent elements*			Experimental SHLS depolarization ratio $D_v^{2\omega}$	Calculated effective optical anisotropies	
		$\Theta_{ij}$	$a_{ij}^\omega$	$c_{ijkl}^{2\omega}$		Linear $\Delta_\omega^2$	Nonlinear $\Delta_{2\omega}^2$
Cyclohexane	$D_{3d}$	1	2	4	$0.12 \pm 0.04$	0.001	0.04
Benzene	$D_{6h}$	1	2	3	$0.17 \pm 0.06$	0.032	0.21
Carbon disulphide	$D_{\infty h}$	1	2	3	$0.21 \pm 0.09$	0.190	0.31

\* $\Theta_{ij}$  — electric quadrupole moment tensor elements,  $a_{ij}^\omega$  and  $c_{ijkl}^{2\omega}$  are the linear and nonlinear polarizability tensors elements.

the one already published [1]. The value of  $D_v^{0.5300\mu}$  for cyclohexane,  $0.12 \pm 0.04$ , is very close to the one obtained previously:  $D_v^{0.3471\mu} \simeq 0.13 \pm 0.08$ . A preliminary test made on carbon tetrachloride yielded the result  $D_v^{2\omega} = 0.45 \pm 0.10$  in good agreement with experimental data concerning non-centrosymmetric molecules [4].

In benzene, noteworthy is the quite strong effective anisotropy  $\Delta_{2\omega}^2 \cong 0.21$  which appears to attain the theoretically predicted maximal value  $\Delta_{2\omega}^2 = \frac{51}{175}$ .

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