

MOLECULAR QUADRUPOLE MOMENT DETERMINATIONS FROM MEASUREMENTS OF LASER WAVE HYPER-RAYLEIGH SCATTERING BY DENSE FLUIDS

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Hyper-Rayleigh scattering (second-harmonic scattering, SHS) of laser waves by dense fluids composed of centrosymmetric molecules permits the measurement of the mean-squared value of the internal molecular electric field $\langle F_0^2 \rangle$. In the case of quadrupolar molecules, these measured values can be used to determine the quadrupole moment of the scattering molecules. Numerical results are given for cyclohexane and *trans*-decahydronaphthalene amounting to 11 and 9.8, respectively, in 10^{-26} esu.

1. Introduction

We have shown [1-4] that despite their intrinsic incapacity to cause second-harmonic scattering (SHS) of an intense laser wave of circular frequency ω_L , an assemblage of mutually interacting centrosymmetric molecules gives rise to an effect of cooperative non-linear scattering in dense fluids. The SHS intensity is proportional to the product:

$$c_{2\omega_L}^2 \langle F_0^2 \rangle, \quad (1)$$

where $c_{2\omega_L}$ is the mean molecular polarizability of order 3 at the frequency $2\omega_L$ and $\langle F_0^2 \rangle$ the statistical mean-squared internal electric field acting on a molecule in the medium in the absence of an external electric field, $E(\omega_L) = 0$.

Expansion of the internal field in a multipole series, though not obviously justifiable with regard to dense fluids, then permits the measurement of molecular multipole moments of order 2 and higher than 2.

2. Method of measurement

We performed relative measurements and a comparison of the vertical SHS component $V_v^{2\omega_L}$ for cyclohexane and *trans*-decahydronaphthalene, given by:

$$V_v^{2\omega_L} = \frac{\rho}{24} \left(\frac{2\pi}{\lambda/2} \right)^4 \left(\frac{n_{2\omega_L}^2 + 2}{3} \right)^2 \left(\frac{n_{\omega_L}^2 + 2}{3} \right)^4 \\ \times c_{2\omega_L}^2 \frac{5(1 - \Delta^{2\omega_L})}{5 - 7\Delta^{2\omega_L}} \langle F_0^2 \rangle I_{\omega_L}^2 \quad (2)$$

and the horizontal SHS component $H_v^{2\omega_L}$ for carbon tetrachloride, of intensity:

$$H_v^{2\omega_L} = \frac{\rho}{35} \left(\frac{2\pi}{\lambda/2} \right)^4 \left(\frac{n_{2\omega_L}^2 + 2}{3} \right)^2 \left(\frac{n_{\omega_L}^2 + 2}{3} \right)^4 \\ \times b_{2\omega_L}^2 I_{\omega_L}^2 \quad (3)$$

In eqs. (2) and (3), ρ is the number density of mole-

cules per unit volume, λ the wavelength of the fundamental laser frequency of intensity I_{ω_L} , $b_{2\omega_L}$ the value of the only independent tensor element of the polarizability of order 2 for carbon tetrachloride, and $\Delta^2\omega_L$ a quantity dependent on the anisotropy of third-order nonlinear polarizability $c_{2\omega_L}$ and the molecular field F_0 .

Eqs. (2) and (3) give $\langle F_0^2 \rangle$ for the liquid compound under investigation (denoted by X at the same incident laser intensity):

$$\langle F_0^2 \rangle = \frac{24}{35} \frac{\rho_{\text{CCl}_4}}{\rho_X} \frac{(n_{2\omega_L}^2 + 2)_{\text{CCl}_4}^2 (n_{2\omega_L}^2 + 2)_{\text{CCl}_4}^4}{(n_{2\omega_L}^2 + 2)_X^2 (n_{2\omega_L}^2 + 2)_X^4} \times \left(\frac{b_{2\omega_L}^{\text{CCl}_4}}{c_{2\omega_L}^X} \right)^2 \frac{5 - 7\Delta_X^2\omega_L (V_v^2\omega_L)_X}{5(1 - \Delta_X^2\omega_L) (H_v^2\omega_L)_{\text{CCl}_4}} \quad (4)$$

Once b_{CCl_4} is available, measurements of the refractive indices at the circular frequency ω_L and $2\omega_L$, of the density ratios, of c and $\Delta^2\omega_L$, and of the ratio $(V_v^2\omega_L)_X / (H_v^2\omega_L)_{\text{CCl}_4}$, lead to the determination of $\langle F_0^2 \rangle$.

3. Experimental

The smallness of the scattered light intensities, amounting to several photoelectrons at a laser pulse of 500 MW/cm^2 , makes these determinations particularly difficult. For the full details of our experimental procedure, we refer to our earlier publications. Here, we adduce but the essentials (fig. 1).

The programmer sets off a laser shot every 2 minutes. The fast cell opens an electronic gate and permits the time-limited detection of the signals measured (noise reduction). The photomultiplier 3 ensures that no harmful effects perturb the propagation of the intense laser wave within the vessel. The photomultipliers 2 and 1 successively detect the scattered signal and a squared reference signal of the incident laser intensity. The data are supplied to the computer, which provides for visualisation and printing of the results.

The values of c are obtained in our laboratory by a comparison of results of optical Kerr measurements and Rayleigh scattering depolarisation measurements [5]. $\Delta^2\omega_L$ is derived from measurements of the SHS

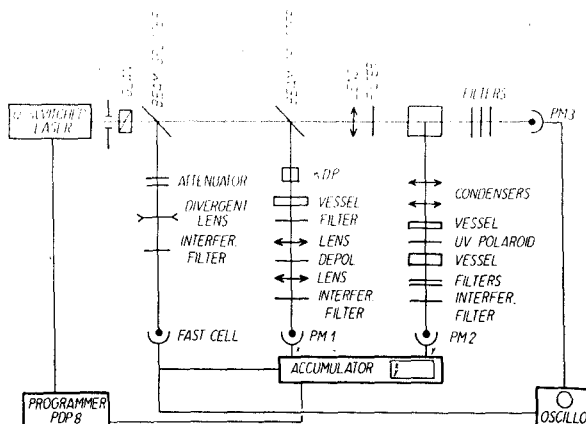


Fig. 1. Set-up for the measurement of the intensity and depolarisation ratio of scattered laser light. $\lambda_L = 0.6942 \mu$; $T = 20^\circ\text{C}$.

depolarisation ratio [4]. The quantities ρ and n are measured directly. For b , we assumed the value $\pm 0.35 \times 10^{-30}$ esu cgs of Terhune et al. [6].

4. Results of measurements, and their application to the determination of quadrupole moments

The results obtained are given in table 1. Now what is the source of the phenomenon under observation? Obviously, we are dealing with a time- and spatially-limited destruction of the centre of molecular symmetry within the zone of light scattering. We rule out many-body collision effects, leading to distortion of atomic electron shells. A recent quantal approach by Gelbart [7] to monatomic liquids shows the relevance of these distortion effects in triatomic, obviously non-centrosymmetric double-photon scattering centres. However, this effect calculated in 1974 for liquefied xenon [8], appears to contribute no more than several per cent to the phenomenon observed.

We attribute this cooperative double-photon scattering entirely to the fluctuating electric fields of neighbouring permanent molecular quadrupoles. In this treatment in the approximation of pairwise correlations, we obtain:

$$\langle F_0^2 \rangle = 12\theta^2 \left\langle \sum_{q \neq p=1}^N r_{pq}^{-8} \right\rangle \quad (5)$$

Table 1

Experimental results and determinations of the mean-squared internal field value for cyclohexane and *trans*-decahydronaphthalene. $T = 20^\circ\text{C}$; $\lambda_L = 0.6942 \mu$; $b_{\text{CCl}_4} = \pm 0.35 \times 10^{-30}$ esu cgs [6]

Liquid	ρ (10^{21} esu cgs)	n_{ω_L}	$n_{2\omega_L}$	c (10^{-36} esu cgs)	$\Delta^{2\omega_L}$	$\frac{V_V^{2\omega_L}}{(H_V^{2\omega_L})_{\text{CCl}_4}}$
cyclohexane	5.581 ± 0.010	1.4236	1.4474	3.7 ± 0.8	0.08	0.11 ± 0.01
<i>trans</i> -decahydronaphthalene	3.793 ± 0.006	1.4657	1.4958	5.8 ± 1.5	0.15	0.23 ± 0.02
carbon tetrachloride	6.242 ± 0.010	1.4555	1.4858			

Table 2

Determinations of effective quadrupole moments for liquid cyclohexane and *trans*-decahydronaphthalene at 20°C

Liquid	Symmetry group	$\langle F_0^2 \rangle$ (10^8 esu cgs)	$\langle \sum_{q \neq p=1}^N r_{pq}^{-8} \rangle$ (10^{57} cm $^{-8}$)		Θ (10^{-26} esu cm 2)
			calculated with Kirkwood's model [9]	calculated semi-empirically [10]	
cyclohexane	D $_{3d}$	9.3 ± 5.0	19.6	5.4	11
<i>trans</i> -decahydronaphthalene	C $_{2h}$	10.6 ± 5.0	7.04		9.8

where for the symmetry C $_{2h}$ (e.g., *trans*-decahydronaphthalene):

$$\Theta^2 = \frac{1}{3}(\Theta_{11}^2 + \Theta_{22}^2 + \Theta_{12}^2 + \Theta_{11}\Theta_{22}), \quad (6)$$

with the 3 independent quadrupole moment tensor elements Θ_{11} , Θ_{22} and Θ_{12} . For cyclohexane, we have $\Theta_{11} = \Theta_{22}$ and $\Theta_{12} = 0$. r_{pq} is the distance between molecules p and q . Summation extends over the N molecules of the scattering volume.

In dealing with *trans*-decahydronaphthalene, the unavailability of experimental data for $\langle r_{pq}^{-8} \rangle$ led us to apply Kirkwood's model [9]. The effective quadrupole value of 9.8×10^{-26} esu for *trans*-decahydronaphthalene is reasonable though may be too low. In dealing with cyclohexane, we had recourse to the results of a semi-empirical calculation based on a Lennard-Jones potential applied to the liquid and probably providing a much more realistic description of the molecular situation [10]. The results are given in table 2.

5. Conclusion

We have shown how hyper-Rayleigh scattering of laser waves by certain dense fluids can provide a useful method for the determination of effective electric molecular quadrupole moments.

The effective quadrupole moments determined by the present method can be subjected to a comparison with the quadrupoles of isolated molecules derived by other, direct procedures, e.g., by electric field gradient-induced birefringence in gases [11].

The inverse path is feasible too: by having recourse to known quadrupole values for the isolated molecule, and applying eq. (5), one can gain information on the binary radial correlation function. Such a comparison between experiment and theory would be highly valuable.

The method is applicable to highly symmetric molecules, like SF $_6$, whose first permanent electric moment is a hexadecapole [4], hitherto determined by indirect dielectric methods only [12,13].

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