DOUBLE PHOTON SCATTERING BY INTERACTING QUADRUPOLAR AND OCTOPOLAR MOLECULES

S. KIELICH
Department of Molecular Physics, A. Mickiewicz University, Poznăn, Grunwaldzka 6, Poland

Received 20 March 1968

In accordance with experiment, double-photon scattering by tetrahedral molecules involves their octopole-induced dipole interaction and translational fluctuations. Quadrupole-induced dipole interaction can cause second-harmonic scattering by molecules with centre of inversion.

For observation at angle θ to the incident beam of intensity I, the horizontal scattering component of double frequency 2ω [1,2] is given by

$$H_{\mathrm{h}}^{2\omega} = V_{\mathrm{h}}^{2\omega} \sin^2\theta + V_{\mathrm{v}}^{2\omega} \cos^2\theta \tag{1}$$

with vertical components given as

$$V_{\mathrm{h}}^{2\omega} = H_{\mathrm{v}}^{2\omega} = \tfrac{1}{35}\left(\frac{2\omega}{c}\right)^4 F_{2\omega} I^2 , \tag{2}$$

$$V_{\mathrm{v}}^{2\omega} = \tfrac{8}{3} V_{\mathrm{h}}^{2\omega} + \tfrac{1}{30}\left(\frac{2\omega}{c}\right)^4 G_{2\omega} I^2 . \tag{3}$$

$F_{2\omega}$ and $G_{2\omega}$ describe the optical properties and molecular structure of the scattering medium [2] and for a liquid of N tetrahedral molecules:

$$F_{2\omega} = N\{\beta_{2\omega}^2(1 + \tfrac{76}{5}\alpha^2\langle r^{-6}\rangle) + \tfrac{14}{9}\gamma_{2\omega}^2\Omega^2\langle r^{-10}\rangle\} , \tag{4}$$

$$G_{2\omega} = -N\{\beta_{2\omega}^2(1 + \tfrac{22}{5}\alpha^2\langle r^{-6}\rangle) - \tfrac{76}{9}\gamma_{2\omega}^2\Omega^2\langle r^{-10}\rangle\} ; \tag{5}$$

$\beta_{2\omega}$ is the second-order nonlinear polarizability induced in the molecule by the square of the optical field E_ω [3], and $\gamma_{2\omega}$ the third-order polarizability induced by E_ω^2 and the molecular field F of electric molecular octopoles Ω at mutual distance r [4,5]; $\langle\ \rangle$ symbolizes statistical averaging with the radial correlation function $g(r)$. Terms $\langle r^{-6}\rangle$ result from translational fluctuation of molecules with linear polarizabilities α and $\langle r^{-10}\rangle$ from octopole-induced dipole interaction.

Defining the depolarization ratio $D_{2\omega}$ as of that components (2) and (3), we get by eqs. (4) and (5)

$$D_{2\omega} = \frac{2}{3}\,\frac{1 + \frac{76}{5}\alpha^2\langle r^{-6}\rangle + \frac{14}{9}(\gamma/\beta)^2\Omega^2\langle r^{-10}\rangle}{1 + \frac{118}{5}\alpha^2\langle r^{-6}\rangle + \frac{28}{3}(\gamma/\beta)^2\Omega^2\langle r^{-10}\rangle} , \tag{6}$$

whence one sees that in the absence of molecular interactions $D_{2\omega} = \frac{2}{3}$. In evaluating numerically $\langle r^{-n}\rangle$, one can recur to Kirkwood's approximation [6] yielding ($n \geqslant 4$)

$$\langle r^{-n}\rangle = 4\pi\rho \int_0^\infty g(r)\, r^{-n+2}\, \mathrm{d}r = \frac{4\pi\rho}{n-3}\left(\frac{\pi}{6v}\right)^{\frac{n-3}{3}} ; \tag{7}$$

ρ being the number density of molecules of volume v.

Using for CCl_4 $\rho V = 0.6$, $\alpha = 10.5 \times 10^{-24}$ cm^3, $\beta = 0.35 \times 10^{-30}$ e.s.u., $\gamma = 12 \times 10^{-36}$ e.s.u. [3] and assuming $\Omega = 15 \times 10^{-34}$ e.s.u. we get by eqs. (6) and (7) $D_{2\omega} = 0.34$ in accordance with experiment [1]. The value of Ω estimated recently by Weinberg [4] is about twice the value used above.

In molecules with a centre of inversion but having a quadrupole moment Θ, the quadrupole field induces additionally a nonlinear dipole, and second-harmonic scattering occurs given by

$$F_{2\omega} = \frac{5N}{72}\gamma_{2\omega}^2\Theta^2(7 + 5\kappa_\gamma)\langle r^{-8}\rangle , \tag{8}$$

$$G_{2\omega} = \frac{5N}{36}\gamma_{2\omega}^2\Theta^2(19 - 25\kappa_\gamma)\langle r^{-8}\rangle \tag{9}$$

resulting in a depolarization ratio of the form

$$D_{2\omega} = (7 + \kappa_\gamma)/(63 - 9\kappa_\gamma) . \tag{10}$$

On neglecting the anisotropy of nonlinear polarizability $\kappa_\gamma = (\gamma_{3333} - \gamma_{1111})/3\gamma$, the depolarization from quadrupole molecules amounts to $\frac{1}{9}$.

Eq. (10) permits to determine the value and sign of the anisotropy κ_γ easily, provided measurements are available.

The preceding considerations show that investigation of second-harmonic scattering by interacting molecules yields information concerning the value of their quadrupole or octopole moments allowing comparison with the values from other methods [7].

1. R.W.Terhune, P.D.Maker and C.M.Savage, Phys. Rev. Letters 14 (1964) 681.
2. S.Kielich, Physica 30 (1964) 1717; Chem. Phys. Letters 1 (1967) 441 and references therein.
3. A.D.Buckingham and B.J.Orr, Quarterly Reviews 21 (1967) 195 and references therein.
4. D.L.Weinberg, J. Chem. Phys. 47 (1967) 1307.
5. S.Kielich, Acta Phys. Polonica 24 (1963) 389; 33 (1968) 89.
6. J.G.Kirkwood, J. Chem. Phys. 4 (1936) 592.
7. D.E.Stogryn and A.P.Stgryn, Mol. Phys. 11 (1967) 371 and references therein.

* * * * *