

## Double-Photon Elastic Light Scattering by Liquids Having Centrosymmetric Molecules

S. Kielich,\* J. R. Lalanne, and F. B. Martin

*Centre National de la Recherche Scientifique et Université de Bordeaux I, 33 Talence, France*

(Received 22 March 1971)

First measurements of double-photon elastic scattering performed on liquids with centrosymmetric molecules yield good agreement with statistical molecular theory of non-linear light scattering. Studies of this new scattering are shown to allow determination of the third-order molecular polarizability as well as its anisotropy, and to promise information on the structure of short-range molecular ordering and electric properties of molecules.

Terhune, Maker, and Savage<sup>1</sup> performed the first observation of second-harmonic laser light scattering (SHLS) in liquids whose molecules lack a center of symmetry. This communication reports first measurements of double-photon elastic scattering (DPES or SHLS) by liquids consisting of molecules having a center of symmetry in their ground state. The possibility of destroying the molecular center of inversion, owing to time and space fluctuations of the molecular electric field  $F$ , led us to predict this new scattering. This is particularly predictable in the case of liquids with molecules having permanent electric quadrupole or hexadecapole moments capable of causing very strong fluctuating molecular fields in regions of shortest-range ordering in the liquid.<sup>2</sup> Such regions in general do not possess a center of symmetry and thus cause SHLS. This is uniquely cooperative scattering by neighboring molecules whose positions and orientations are correlated.<sup>2,3</sup>

*Theoretical considerations.*—Consider a laser light wave of frequency  $\omega_L$  and propagation vector  $\vec{k}_L$  incident on such a liquid. The electric dipole moment  $\vec{M}$  induced in the medium of volume  $V$  at frequency  $2\omega_L$  is<sup>2,3</sup>

$$M_i(2\omega_L, 2\vec{k}_L) = \frac{1}{4}[(n_{2\omega_L}^2 + 2)/3][(n_{\omega_L}^2 + 2)/3]^2 \sum_{p=1}^N C_{ijk}{}^{2\omega_L(p)} E_j^{\omega_L} E_k^{\omega_L} F_l^{(p)} \exp[i(2\vec{k}_L \cdot \vec{r}_p)]. \quad (1)$$

$C_{ijk}{}^{2\omega_L(p)}$  is the tensor of third-order nonlinear polarizability induced in a molecule  $p$  at the frequency  $2\omega_L$  by the squared electric field of the light wave  $\vec{E}^{\omega_L}$  in the presence of the molecular field  $\vec{F}^{(p)}$  due to the  $N-1$  molecules surrounding molecule  $p$  with the radius vector  $\vec{r}_p$ .

With the light beam plane polarized, propagating at velocity  $c$  along  $y$  and oscillating vertically, the intensity components of light elastically scattered at frequency  $2\omega_L$  with horizontal (along  $y$ ) and vertical (along  $z$ ) oscillations, respectively, can be written in the forms (observation along  $x$ )

$$I_{yy}{}^{2\omega_L} = H_v{}^{2\omega_L} = \frac{1}{40}(2\omega_L/c)^4 [(n_{2\omega_L}^2 + 2)/3]^2 [(n_{\omega_L}^2 + 2)/3]^4 (1 + \Delta^2\omega) S^{2\omega_L} I_L^2 / 9, \quad (2)$$

$$I_{zz}{}^{2\omega_L} = V_v{}^{2\omega_L} = \frac{9}{40}(2\omega_L/c)^4 [(n_{2\omega_L}^2 + 2)/3]^2 [(n_{\omega_L}^2 + 2)/3]^4 (1 - \Delta^2\omega) S^{2\omega_L} I_L^2 / 9, \quad (3)$$

where  $I_L$  is the incident intensity, and

$$\Delta^2\omega = (5S^{2\omega_L} - 3R^{2\omega_L}) / 7S^{2\omega_L}, \quad (4)$$

$$R^{2\omega_L} = \left\langle \sum_{p=1}^N \sum_{q=1}^N C_{ijji}{}^{2\omega_L(p)} C_{ikkm}{}^{2\omega_L(q)} F_i^{(p)} F_m^{(q)} \exp[i(\Delta\vec{k} \cdot \vec{r}_{pq})] \right\rangle, \quad (5)$$

$$S^{2\omega_L} = \left\langle \sum_{p=1}^N \sum_{q=1}^N C_{ijk}{}^{2\omega_L(p)} C_{ijk}{}^{2\omega_L(q)} F_i^{(p)} F_m^{(q)} \exp[i(\Delta\vec{k} \cdot \vec{r}_{pq})] \right\rangle. \quad (6)$$

In Eqs. (5) and (6) we have  $\Delta\vec{k} = \vec{k}_2 - 2\vec{k}_L$ , where  $\vec{k}_2$  is the wave vector of the scattered second-harmonic wave and  $\vec{r}_{pq} = \vec{r}_q - \vec{r}_p$  is the vector connecting the centers of the two scattering molecules  $p$  and  $q$ .

From Eqs. (2) and (3), we define the depolarization ratio of second-harmonic scattering by

$$D_v{}^{2\omega_L} = H_v{}^{2\omega_L} / V_v{}^{2\omega_L} = \frac{1}{9}(1 + \Delta^2\omega) / (1 - \Delta^2\omega). \quad (7)$$

It is obvious from the shape of the scattering factors (5) and (6) that only cooperative SHLS is present since, in the absence of molecular correlation,  $S^{2\omega_L}$  and  $R^{2\omega_L}$  vanish. This is an important distinction with regard to SHLS by liquids consisting of molecules without centers of symmetry for which we have both a noncooperative part (isolated molecules) and a cooperative one.<sup>2,3</sup>