Double-Photon Elastic Light Scattering by Liquids Having Centrosymmetric Molecules

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First measurements of double-photon elastic scattering performed on liquids with centrosymmetric molecules yield good agreement with statistical molecular theory of nonlinear 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[1] 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.[2] 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.[2,3]

Theoretical considerations.—Consider a laser light wave of frequency ω_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[2,3]

$$M_i(2\omega_L, 2\vec{k}_L) = \tfrac{1}{4}[(n_{2\omega_L}{}^2+2)/3][(n_{\omega_L}{}^2+2)/3]^2 \sum_{p=1}^{N} C_{ijkl}{}^{2\omega_L(p)} E_j{}^{\omega_L} E_k{}^{\omega_L} F_1{}^{(p)} \exp[i(2\vec{k}_L\cdot\vec{r}_p)]. \tag{1}$$

$C_{ijkl}{}^{2\omega_L(p)}$ 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)

$$I_{yz}{}^{2\omega_L} = H_v{}^{2\omega_L} + \tfrac{1}{40}(2\omega_L/c)^4[(n_{2\omega_L}{}^2+2)/3]^2[(n_{\omega_L}{}^2+2)3]^4(1+\Delta^{2\omega_L})S^{2\omega_L}I_L{}^2, \tag{2}$$

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

where I_L is the incident intensity, and

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

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

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

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

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

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.[2,3]

In the case of isotropically polarizable molecules[4]

$$C_{ijkl}{}^{2\omega L}=\tfrac{1}{3}C_{2\omega_L}(\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}),$$

where $C_{2\omega_L}=\frac{1}{5}C_{iijj}{}^{2\omega L}$ is the mean nonlinear polarizability. This yields the following relation between the scattering factors (5) and (6):

$$S_{is}{}^{2\omega L}=\tfrac{3}{5}R_{is}{}^{2\omega L}=\tfrac{5}{3}C_{2\omega_L}{}^2\Big\langle\sum_{p=1}^{N}\sum_{q=1}^{N}\vec{\mathrm{F}}_p\vec{\mathrm{F}}_q\exp[i(\Delta\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}_{pq})]\Big\rangle, \tag{8}$$

whence $\Delta^{2\omega}$ [Eq. (4)] vanishes, and we obtain from Eqs. (2) and (3)

$$V_v{}^{2\omega L}=9H_v{}^{2\omega L}=\tfrac{9}{40}(2\omega_L/c)^4S_{is}{}^{2\omega L}I_L{}^2. \tag{9}$$

The depolarization ratio $D_v{}^{2\omega L}$ due to isotropic scattering takes the value $\frac{1}{9}$ in accordance with an earlier theoretical result.[2]

Let us consider now the case of anisotropically polarizable molecules. Obviously, the anisotropic part of $C_{ijkl}{}^{2\omega L}$ must also be taken into account. If we restrict ourselves to paired molecular correlations and omit the interference factor $\exp[i(\Delta\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}_{pq})]\approx 1$, factors (5) and (6) now become in the case of quadrupolar molecules

$$R_{\mathrm{anis}}{}^{2\omega L}=\tfrac{2}{15}N(5C_{ijjk}{}^{2\omega L}C_{illk}{}^{2\omega L}\theta_{mn}\theta_{mn}-3C_{ijjk}{}^{2\omega L}\theta_{ik}C_{lmmn}{}^{2\omega L}\theta_{ln})\langle r_{pq}{}^{-8}\rangle, \tag{10}$$

$$S_{\mathrm{anis}}{}^{2\omega L}=\tfrac{2}{147}N(49C_{ijkl}{}^{2\omega L}C_{ijkl}{}^{2\omega L}\theta_{mn}\theta_{mn}-18C_{ijjk}{}^{2\omega L}\theta_{ik}C_{lmmn}{}^{2\omega L}\theta_{ln})\langle r_{pq}{}^{-8}\rangle, \tag{11}$$

where N is the number of molecules, θ_{ij} is their electric quadrupole moment tensor, and $\langle r_{pq}{}^{-8}\rangle$ is the radial correlation factor defined by

$$\langle r_{pq}{}^{-8}\rangle=(4\pi N/V)\int r_{pq}{}^{-8}g(r_{pq})r_{pq}{}^2dr_{pq}. \tag{12}$$

This factor can be calculated theoretically if the shape of the paired radial correlation function $g(r_{pq})$ is known[5] or can be determined experimentally.

On inspection of Eqs. (10) and (11), we note that $\Delta^{2\omega}$ [Eq. (4)] is now nonzero but does not depend on the statistical factor (12) and consequently it defines the effective anisotropy of nonlinear polarizability of the molecules. The tensor elements $C_{ijkl}{}^{2\omega L}$ for various point-group symmetries are available,[4] allowing the calculation of the anisotropy. Particularly, in the case of the point groups D_{3d}, C_{4h}, D_{4h}, S_6, C_{6h}, and D_{6h}, we find by Eqs. (4), (10), and (11) that

$$\Delta^{2\omega L}=[490(5C_{ijkl}{}^{2\omega L}C_{ijkl}{}^{2\omega L}-3C_{ijjk}{}^{2\omega L}C_{illk}{}^{2\omega L})-3(3C_{3ii3}{}^{2\omega L}-C_{ijji}{}^{2\omega L})^2]\times\{70[49C_{ijkl}{}^{2\omega L}C_{ijkl}{}^{2\omega L}-3(3C_{3ii3}{}^{2\omega L}-C_{ijji}{}^{2\omega L})^2]\}^{-1}. \tag{13}$$

In the case of axially symmetric molecules, one has simply to a satisfactory approximation that

$$\Delta^{2\omega L}=\tfrac{51}{175}[(C_{3333}{}^{2\omega L}-C_{1111}{}^{2\omega L})/(C_{3333}{}^{2\omega L}+2C_{1111}{}^{2\omega L})]^2. \tag{13a}$$

Thus, in the present model, the effective anisotropy $\Delta^{2\omega L}$ always tends to raise the depolarization ratio [Eq. (7)]; the more anisotropic the molecules, the larger the depolarization of SHLS in accordance with the present measurements.

Experimental setup.—We used a vertically polarized ruby laser, Q switched by a saturable absorber, of 5 MW peak power and 30-nsec pulse duration (see Fig. 1). A beam splitter permits the coherent generation—far from the index matching condition—of a 3471-Å reference signal proportional to the square of the incident intensity. Lens L_3 focuses the light beam so obtained on scattering plate D. The signal, after being filtered by F_6 and F_8, is detected by the photomultiplier tube PM_r. Filter F_3 may be used to reduce incident intensity. Dust is carefully removed from the sample, avoiding the breakdown at the focus of lens L. The detection system for the scattered harmonic is made quite sensitive by using a polarizer P, filters F_7 and F_5, and a lens L_2 of large diameter. The weakness of the signals did not permit the use of a monochromator and we could not measure the spectral width of the scattered light. Therefore, we carefully insured the absence of significant signals in the violet-indigo range by the use of interference filters F_5 centered at 4000 and 4400 Å. Under our experimental conditions, we did not observe the presence of backward stimulated Brillouin scattering which, after amplification by the ruby,

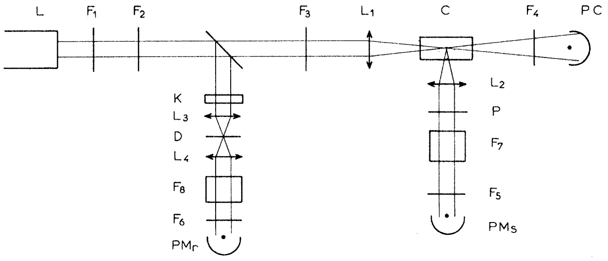

FIG. 1. Experimental setup: L, Q-switched ruby laser; F_1, Schott filter RG 610/1; F_2, Métallisations et Traitements Optiques filter J.625; F_3, F_4, Schott filters NG 4; F_5, F_6, interference filters, $\lambda = 3471$ Å, $\tau = 0.3$, $\Delta\lambda = 160$ Å; F_7, F_8, 6-cm saturated $CuSO_4$ solution filters; L_1, L_2, L_3, L_4, lenses $C \cong +14$ diopters, diam≅ 3 cm; D, scattering opaline glass; K, KH_2PO_4 plate; P, Polaroid HNP'B; C, liquid cell $l \cong 15$ cm; $P.C.$, photocell Compagnie de Télégraphie sans Fil C. P. A. 1143; PM_r, photomultiplier tube la Radiotechnique 53 A. V. P., $V \cong 1.2$ kV, $G \cong 320\,000$; PM_s, photomultiplier tube la Radiotechnique XP 1002, $V \cong 1.6$ kV, $C_T \cong 820\,000$.

would have provoked a spurious signal detectable by our apparatus. We did not look for the eventual presence of self-focusing and stimulated Raman scattering. Polaroid P allows the successive detection of the $H_v^{2\omega L}$ and $V_v^{2\omega L}$ components. The scattered (PM_s) and reference (PM_r) signals are sent to a storage bank run by a model PDP-8 computer.[6] Figure 2 shows the dependence of the harmonic scattered component $V_v^{2\omega L}$ on the reference signal in the case of tetrachloroethylene. The large dispersion of experimental points (±25%) is due to the low number of photoevents (in the range 0-50). Detection of component $H_v^{2\omega L}$, about six times weaker, corresponds to the lower limit of sensitivity of our apparatus (a few photoevents—dispersion ±35%).

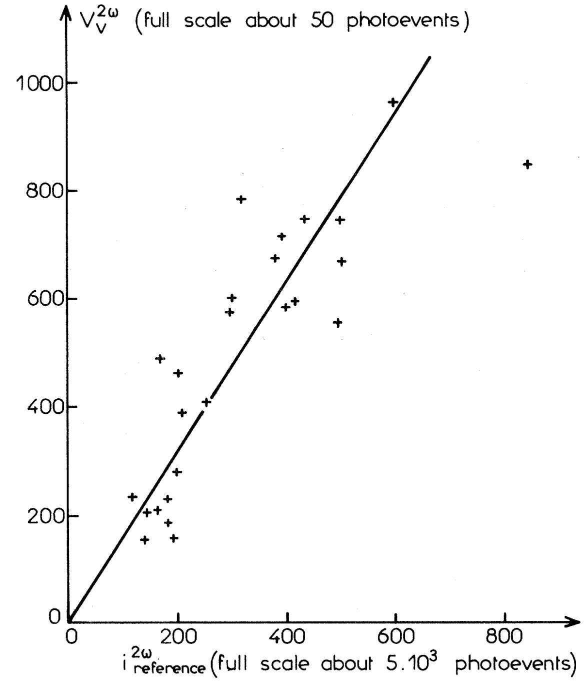

FIG. 2. Dependence of the SHLS intensity $V_v^{2\omega}$ on the reference signal $i_{\text{ref}}^{2\omega}$ for the tetrachloroethylene. The laser mean lighting at the focus of the lens L_1 is in the range 200-500 MW/cm^2.

Results and discussion.—Table I contains experimental results for $D_v^{2\omega L}$ obtained for three liquids with centrosymmetric molecules: cyclohexane, tetrachloroethylene, and trans-1, 2-dichloroethylene. It also contains the linear optical anisotropy, $\Delta^\omega = (3a_{ij}{}^\omega a_{ij}{}^\omega - a_{ii}{}^\omega a_{jj}{}^\omega)/2a_{ii}{}^\omega \times a_{jj}{}^\omega$, calculated from our direct measurements of depolarized Rayleigh scattering. For the sake of comparison, we give the number of independent elements of the tensors θ_{ij}, a_{ij}, and $C_{ijkl}{}^{2\omega}$. One can see that this number, as well as Δ^ω and $\Delta^{2\omega L}$, increases from high to low point-group symmetries.

The direct comparison between absolute scattered intensities for various liquids (made difficult by self-focusing) may allow the study of the

Table I. Experimental results from our double-photon elastic light-scattering data and calculated effective optical anisotropies of centrosymmetric molecules.

Liquid	Point group	Number of independent elements θ_{ij}	$a_{ij}{}^\omega$	$C_{ijkl}{}^{2\omega}$	Experimental nonlinear depolarization ratio $D_v^{2\omega L}$	Calculated effective optical anisotropies Linear Δ^ω	Nonlinear $\Delta^{2\omega L}$
Cyclohexane	D_{3d}	1	2	4	0.13±0.08	0.001	0.08
Tetrachlor-ethylene	D_{2h}	2	3	6	0.20±0.08	0.037	0.28
Trans-1,2-dichloroethylene	C_{2h}	3	4	9	0.24±0.14	0.064	0.37

molecular internal field F if the third-order polarizability has already been evaluated by another method (optical Kerr effect).[7]

We tried to study benzene and tetraethylene glycol under the above conditions. In both cases, important luminescence signals of intensity proportional to the square of the incident intensity (two-photon absorption of the fundamental wave) were recorded at 4000 and 4400 Å, as already noted by Maker[8] in the case of benzene. They invalidate our scattering measurements for these two compounds. An experimental setup, now being assembled, will allow the use of an inductive wavelength of 1.06 μm. In avoiding the two-photon absorption of the fundamental wave, we hope to open the door to the study of benzene and other aromatic centrosymmetric derivatives.

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Effect of a Toroidal Field on Plasma Transport in a Magnetically Perturbed Multipole*

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Field errors have been observed to cause anomalous loss to an internal hoop and produce convection patterns which have potentials $\sim kT_e/e$. A simple model of plasma flowing along field lines accounts semiquantitatively for the observed anomalous loss and the production of convection patterns. The addition of a small (5%) toroidal field reduces the anomalous loss by a factor of 60 to the level given by classical ion-neutral diffusion across the field.

Toroidal multipoles derive many of their favorable confinement properties directly from axial symmetry. However in actual experiments, all of the magnetic fields are slightly asymmetric. It is therefore important to determine the allowable level for magnetic field asymmetries in confinement experiments. The addition of small magnetic field errors to a shearless axisymmetric multipole magnetic field can cause the field lines to spiral across the entire confinement region since the shearless multipole magnetic field has no structural stability.[1] Previous experiments[2] with controlled field errors have shown that small (1%) externally applied field errors can increase the plasma loss to the internal hoop of a multipole-like device by over an order of magnitude. The plasma losses were increased when the magnetic field errors were arranged to cause field lines to cross the entire confinement region and the increased losses were negligible when the perturbation was oriented to keep the field lines closed. Reductions in plasma loss to the internal hoop by a factor of 60 have been observed with the addition of a small (5%) toroidal field. Azimuthal variations in plasma density have been produced by the addition of field errors and then subsequently reduced by the addition of a toroidal field. The sensitivity of plasma confinement in multipoles to field errors has been demonstrated[3] and may be responsible for the anomalous loss of plasma to the internal hoops of other devices.[4-6]

The apparatus consists of an internal hoop energized with dc current and an external set of coils used to guide the externally produced plasma near the internal hoop in an azimuthally symmetric manner (Fig. 1). A hydrogen plasma is continuously produced at one end of the machine by electron cyclotron breakdown in a Lisitano coil. This arrangement simulates that found in a multipole device, such as an octupole, near one of the internal conductors. Dipole coils situated outside the vacuum tank on the plane of symmetry produced the error magnetic fields. The toroidal field B_θ was produced by a current I_z flowing along the symmetry axis of the device.

The plasma loss to the internal hoop as a function of the toroidal field and applied error field