TABLE I
Experimental Results from SHLS Data ($\lambda = 1.06 \mu$; $t = 25°C$)

Liquid	Point Group	Number of Independent Elements[a,b]			Experimental SHLS Depolarization Ratio	Calculated Effective Optical Anisotropies	
		Θ_{ij}	a_{ij}^{ω}	$c_{ijkl}^{2\omega}$	$D_v^{2\omega}$	Linear[e] Δ_{ω}^2	Nonlinear $\Delta_{2\omega}^2$
Cyclo-hexane	D_3d	1	2	4	0.12 ± 0.04	0.001	0.04
Benzene	D_{6h}	1	2	3	0.17 ± 0.06	0.032	0.21
Carbon disulphide	$D_{\infty H}$	1	2	3	0.21 ± 0.09	0.190	0.31

[a] Θ_{ij}—electric quadrupole moment tensor element.
[b] a_{ij}^{ω} and $c_{ijkl}^{2\omega}$—linear and nonlinear polarizability tensor elements at frequencies ω and 2ω.
[e] Δ_{ω}^2—linear optical anisotropy defined by

$$\Delta_{\omega}^2 = \frac{3a_{ij}^{\omega}, a_{ij}^{\omega} - a_{ii}^{\omega}, a_{jj}^{\omega}}{2a_{ii}^{\omega}, a_{jj}^{\omega}}$$

permanent electric quadrupole moment Θ gives (to within binary correlation)

$$\langle F^2 \rangle = \frac{9}{8} \Theta^2 \left\{ \sum_{q \neq p}^{N} [5(\cos^2 \theta_p - \cos^2 \theta_q)^2 \right.$$
$$+ 4(\cos^2 \theta_p - 2 \cos \theta_p$$
$$\left. \cdot \cos \theta_q \cos \theta_{pq} + \cos^2 \theta_q)] r_{pq}^{-8} \right\}$$
$$\text{(4a)}$$

where θ_p and θ_q are the angles between the symmetry axes of molecules p and q and the vector r_{pq} connecting their centers. θ_{pq} is the angle between the symmetry axes of molecule p and q. Equation (4a), in the simplified case of weak angular correlations, reduces to the more accessible form

$$\langle F^2 \rangle = 3\Theta^2 \left\{ \sum_{q \neq p}^{N} r_{pq}^{-8} \right\}. \quad \text{(4b)}$$

By (1), the depolarization ration is

$$D_v^{2\omega} = \frac{H_v^{2\omega}}{V_v^{2\omega}} = \frac{F_{2\omega}}{F_{2\omega} + G_{2\omega}} \quad \text{(5)}$$

and for the isotropic scattering of (3) takes the value 1/9. Generally, we have also an anisotropic part of SHLS determined by an effective nonlinear optical anisotropy[2]

$$\Delta_{2\omega}^2 = \frac{9 D_v^{2\omega} - 1}{9 D_v^{2\omega} + 1}$$
$$= 1 - \frac{2}{9 D_v^{2\omega} + 1}. \quad \text{(6)}$$

In the case of point groups D_{6h} and $D_{\infty h}$ we have in a good approximation

$$\Delta_{2\omega}^2 = \frac{51\gamma_{2\omega}^2 + 360\ \delta_{2\omega}^2}{1575c_{2\omega}^2} \quad \text{(7)}$$

where

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

[2] S. Kielich, J. R. Lalanne, and F. B. Martin, *Phy. Rev. Lett.*, vol. 25, p. 1295, 1971.

and

$$\delta_{2\omega}^2 = (c_{3333}^{2\omega} - 6c_{1133}^{2\omega} + c_{1111}^{2\omega})$$
$$\cdot (c_{3333}^{2\omega} - 9c_{1133}^{2\omega} + 2c_{1111}^{2\omega}).$$

Equation (7), with the assumption[3] $c_{1133}^{2\omega} = 1/6(c_{3333}^{2\omega} + c_{1111}^{2\omega})$ (following also from Bloembergen's symmetry relation) leads to the previous form[2]

$$\Delta_{2\omega}^2 = \frac{51}{175} \left(\frac{c_{3333}^{2\omega} - c_{1111}^{2\omega}}{c_{3333}^{2\omega} + 2c_{1111}^{2\omega}} \right)^2 \quad \text{(8)}$$

The experimental results are given in Table I. A preliminary test made on carbon tetrachloride yielded the result $D_v^2 = 0.45 \pm 0.10$, in good agreement with experimental data concerning noncentrosymmetric molecules.[4,5]

[3] S. Kielich, *Chem. Phys. Lett.*, vol. 2, p. 569, 1968; also in *Opto-Electron.*, vol. 2, p. 5, 1970.
[4] R. W. Terhune, P. D. Maker, and C. M. Savage, *Phys. Rev. Lett.*, vol. 14, p. 681, 1965.
[5] P. D. Maker, *Phys. Rev. (A)*, vol. 1, p. 923, 1970.

A.4—Anisotropic Dispersion of the Nonlinear Susceptibility in Four-Wave Infrared Light Mixing, C. Flytzanis, E. Yablonovitch, and N. Bloembergen, *Division of Engineering and Applied Physics, Harvard University, Cambridge, Mass. 02138.*

The frequency combination $2\omega_1 - \omega_2$ was observed upon mixing laser light in cubic semiconductors when the frequencies ω_1, ω_2, and $2\omega_1 - \omega_2$ are in the transparency region of the crystal while $\omega_1 - \omega_2$ is below the phonon resonance ω_T. The ω_i were provided from the different lines of a CO_2 laser. This enabled us to measure the variation of the third-order susceptibility as the infrared frequency $\omega_1 - \omega_2$ was approaching the infrared Raman frequency ω_T from below. By making use of crystal symmetry requirements and the relationship between Raman effect and the third-order frequency mixing we have been able to account theo-

retically for the dependence of the components of the third-order susceptibility on $\omega_1 - \omega_2$.

In cubic diatomic semiconductors $\chi^{(3)}$ has two independent components $\chi_{xxxx}^{(3)}$ and $\chi_{xyxy}^{(3)}$ and a single Raman active mode with the corresponding tensor being $\alpha_{xyz}^{(1)}$. Since $\omega_1 - \omega_2$ is below the Raman frequency ω_T while ω_i and $2\omega_1 - \omega_2$ are above it, the phonon mode $\mathbf{u}_T$ is driven by a force $F_z = \frac{1}{2}N\alpha_{xyz}^{(1)}E_x(\omega_1)E_y(\omega_2)$ according to

$$\ddot{u}_z + \omega_T^2 u_z + \gamma \dot{u}_z = \frac{F_z}{m}. \quad \text{(1)}$$

This modulates the linear polarization $P_x(\omega_1) = \chi^{(1)}E_x(\omega_1)$ and provides a third-order lattice-induced nonlinear polarization in addition to the one produced by the direct coupling of the electrons with the three waves, the lattice being held fixed. Accordingly, the third-order susceptibility in the frequency range considered can be written

$$\chi_{xxxx}^{(3)} = \chi_{xxxxE}^{(3)}$$
$$\chi_{xyxy}^{(3)} = \chi_{xyxyE}^{(3)} + N$$
$$\cdot \frac{(\alpha_{xyz}^{(1)})^2}{M(\omega_T^2 - (\omega_1 - \omega_2)^2 - i(\omega_1 - \omega_2)\gamma)}$$
$$\text{(2b)}$$

where $\chi_E^{(3)}$ is the pure electronic term without dispersion in the infrared. In the experiment the ratio $\delta = \chi_{xyxy}^{(3)}/\chi_{xyxy}^{(3)}$ was measured, or

$$\delta = a$$
$$+ \frac{b}{1 - \left(\frac{\omega_1 - \omega_2}{\omega_T}\right)^2 + i\frac{\omega_1 - \omega_2}{\omega_T^2}\Gamma} \cdot$$
$$\text{(3)}$$

The experimental results for Ge were fitted by a curve of the form (3) with $\omega_T = 300\ cm^{-1}$, the Raman frequency for Ge. This allowed us to extract the value of the ratio $b = (\alpha_{xyz}^{(1)})^2/M\omega_T^2\chi_{xxxxE}^{(3)}$ and that of $a = \chi_{xyxyE}^{(3)}/\chi_{xxxxE}^{(3)}$ which is a measure of the anisotropy of the electronic distribution.

The same measurements were performed with GaAs, which is a polar compound. This technique with the latter compound allows one to obtain an absolute measurement of $\chi^{(3)}$ from that of $\chi_{SHG}^{(2)}$, the second-order susceptibility in the transparency region of the crystal. The ratio[1] $C_1 = \alpha^{(1)}e_T^*/2M\omega_T^2\chi_{SHG}^{(2)}$ and[2] $\chi_{SHG}^{(2)}$ have been measured accurately. Comparing this with (3) one obtains

$$b\chi_{xxxx}^{(3)} = 4C_1^2\{\chi_{SHG}^{(2)}\}^2/(\epsilon_0 - \epsilon_\alpha). \quad \text{(4)}$$

This technique can actually be generalized to other types of resonances, e.g., excitons.

[1] W. R. Faust and C. Henry, *Phys. Rev. Lett.*, vol. 17, p. 1265, 1966.
[2] J. J. Wynne and N. Bloembergen, *Phys. Rev.*, vol. 188, p. 1211, 1969.