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Polarizability and Hyperpolarizability [and Discussion]

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Polarizability and hyperpolarizability

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The oscillating charge and current distributions induced in matter by a beam of light are expressed in terms of molecular polarizabilities and hyperpolarizabilities. The symmetry of these property tensors under space and time reversal is examined and methods for their measurement considered. Depolarization of light scattering, optical rotation and differential scattering of right and left circularly polarized light are discussed, as are the effects of vibration and of collisions on the intensities of light scattering. Nonlinear polarization and the measurement of hyperpolarizabilities are briefly examined.

1. Introduction

According to classical theory, light scattering arises from oscillations in the charge and current distribution in matter induced by the incident electromagnetic wave. The dominant contribution to the scattering comes from the oscillating electric dipole $\boldsymbol{\mu}(t)$. Normally we assume that $\boldsymbol{\mu}(t)$ is linearly related to the electric field strength $\boldsymbol{E}(t) = \boldsymbol{E_0} \cos \omega t$ of the monochromatic incident wave of angular frequency ω,

$$\mu_\alpha(t) = \alpha_{\alpha\beta} E_\beta(t). \tag{1}$$

The second-rank polar tensor $\alpha_{\alpha\beta}$ is called the polarizability and is a function of ω.

In a gas at a low pressure the field $\boldsymbol{E}(t)$ is determined solely by the source. However, in a dense fluid or solid the local field is modified by the medium. It is customary to assume that the effective field may be approximated by the Lorentz field $\boldsymbol{E_L} = \frac{1}{3}(n^2+2)\boldsymbol{E}(t)$, where n is the index of refraction of the medium for the frequency ω (Lorentz 1909). This approximation has been investigated many times (Van Kranendonk & Sipe 1977; Keyes & Ladanyi 1977) and is not discussed further in this paper.

For some purposes, such as optical rotation or second-harmonic generation, equation (1) is inadequate. Some appropriate refinements are considered in this paper.

2. Polarizability

The molecular polarizability tensor $\alpha_{\alpha\beta}$ is normally a symmetric tensor with a maximum of six independent components (α_{xx}, α_{xy}, α_{xz}, α_{yy}, α_{yz}, α_{zz}). However, if the molecule possesses symmetry elements this number may be reduced. For example, there is only one independent element for spherical, tetrahedral and octahedral species, and $\alpha_{\alpha\beta} = \alpha\delta_{\alpha\beta}$ where the mean polarizability $\alpha = \frac{1}{3}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$. For molecules with a threefold or higher rotation axis, there are two independent components, and

$$\alpha_{\alpha\beta} = \alpha\delta_{\alpha\beta} + \tfrac{2}{3}(\alpha_{\parallel}-\alpha_{\perp})(\tfrac{3}{2}l_\alpha l_\beta - \tfrac{1}{2}\delta_{\alpha\beta}), \tag{2}$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the polarizabilities when the field is parallel and perpendicular to the rotation axis, and l_α is the α-component of the unit vector along this axis.

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Quantum-mechanical perturbation theory provides an equation for $\alpha_{\alpha\beta}$ for the molecule in the state n in terms of the matrix elements of the dipole moment operator $\boldsymbol{\mu}$ (Born & Huang 1954; Buckingham 1967 a),

$$\alpha_{\alpha\beta} = \alpha_{\beta\alpha} = 2\hbar^{-1} \sum_j Z(\omega, \omega_{jn}, \Gamma_{jn})\, \omega_{jn}\, \mathrm{Re}\{\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle\}, \tag{3}$$

where $\mathrm{Re}\{X\}$ is the real part of X, $\hbar\omega_{jn} = W_j - W_n$ is the difference between the energies of the unperturbed states j and n and

$$Z(\omega, \omega_{jn}, \Gamma_{jn}) = f(\omega, \omega_{jn}, \Gamma_{jn}) + \mathrm{i}g(\omega, \omega_{jn}, \Gamma_{jn}) \tag{4}$$

comprises a real dispersion function f and an imaginary absorption lineshape function $\mathrm{i}g$. If $|\omega - \omega_{jn}|$ is large compared to the width Γ_{jn} at half the maximum height of g,

$$Z = f = (\omega_{jn}^2 - \omega^2)^{-1}, \quad \text{for } |\omega - \omega_{jn}| \gg \Gamma_{jn}. \tag{5}$$

In the vicinity of a Weisskopf–Wigner absorption line at ω_{jn},

$$Z(\omega, \omega_{jn}, \Gamma_{jn}) = [\omega_{jn}^2 - \omega^2 - \mathrm{i}\omega\Gamma_{jn}]^{-1} = \frac{\omega_{jn}^2 - \omega^2}{(\omega_{jn}^2 - \omega^2)^2 + \omega^2\Gamma_{jn}^2} + \mathrm{i}\frac{\omega\Gamma_{jn}}{(\omega_{jn}^2 - \omega^2)^2 + \omega^2\Gamma_{jn}^2}. \tag{6}$$

The imaginary part of $Z(\omega, \omega_{jn}, \Gamma_{jn})$ leads to an induced dipole out-of-phase with the field $\boldsymbol{E}(t)$, and hence to absorption of the electromagnetic wave (Born & Huang 1954). This out-of-phase dipole is proportional to the time derivative $\dot{\boldsymbol{E}}(t) = -\mathrm{i}\omega\boldsymbol{E}(t)$ of the complex field

$$\boldsymbol{E}(t) = \boldsymbol{E}_0 \exp\{-\mathrm{i}(\omega t - \boldsymbol{K}\cdot\boldsymbol{r})\}, \tag{7}$$

where $\boldsymbol{K}$ is the wavevector.

If the wavefunctions n and j are necessarily complex, as in the presence of an external magnetostatic field or of electronic angular momentum (that is, if the state of the molecule is not symmetric under time-reversal), there is an imaginary part of $\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle$ and an antisymmetric contribution to the polarizability. With the use of a tilde to represent complex tensors,

$$\tilde{\mu}_\alpha(t) = \tilde{\alpha}_{\alpha\beta}\tilde{E}_\beta(t), \tag{8}$$

$$\tilde{\alpha}_{\alpha\beta} = \alpha_{\alpha\beta} - \mathrm{i}\alpha'_{\alpha\beta} = \alpha_{\beta\alpha} + \mathrm{i}\alpha'_{\beta\alpha}, \tag{9}$$

where (Buckingham & Raab 1975)

$$\alpha'_{\alpha\beta} = -\alpha'_{\beta\alpha} = -2\hbar^{-1}\omega \sum_j Z(\omega, \omega_{jn}, \Gamma_{jn})\, \mathrm{Im}\{\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle\}. \tag{10}$$

The depolarization ratio of light elastically (or rotationally inelastically) scattered in the y-direction from a beam linearly polarized in the x-direction and directed in the z-direction is

$$\rho_0 = \frac{\langle\tilde{\alpha}_{zx}^*\tilde{\alpha}_{zx}\rangle}{\langle\tilde{\alpha}_{xx}^*\tilde{\alpha}_{xx}\rangle} = \frac{\tilde{\alpha}_{\alpha\beta}^*\tilde{\alpha}_{\gamma\delta}\langle k_\alpha k_\gamma i_\beta i_\delta\rangle}{\tilde{\alpha}_{\alpha\beta}^*\tilde{\alpha}_{\gamma\delta}\langle i_\alpha i_\beta i_\gamma i_\delta\rangle}, \tag{11}$$

where $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ are unit vectors in the x, y, z directions respectively, and the angular brackets denote a statistical average. If the rotational motion of the molecules can be taken to be classical then for any Cartesian components $\alpha\beta\gamma\delta$ (Buckingham & Pople 1955),

$$\left.\begin{aligned} \langle k_\alpha k_\gamma i_\beta i_\delta\rangle &= \tfrac{1}{30}(4\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma}), \\ \langle i_\alpha i_\beta i_\gamma i_\delta\rangle &= \tfrac{1}{15}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}), \end{aligned}\right\} \tag{12}$$

and

$$\rho_0 = \frac{3\kappa^2 + 5\kappa'^2}{5 + 4\kappa^2}, \tag{13}$$

where

$$\kappa^2 = \frac{3\alpha^*_{\alpha\beta}\alpha_{\alpha\beta} - \alpha^*_{\alpha\alpha}\alpha_{\beta\beta}}{2\alpha^*_{\alpha\alpha}\alpha_{\beta\beta}}, \tag{14}$$

$$\kappa'^2 = \frac{3\alpha'^*_{\alpha\beta}\alpha'_{\alpha\beta}}{2\alpha^*_{\alpha\alpha}\alpha_{\beta\beta}}. \tag{15}$$

The anisotropies κ^2 and κ'^2 cannot be separated experimentally by measuring ρ_0 at different angles. However, this separation can be achieved through the reversal coefficient $P(\theta)$ (Placzek 1934). If the incident radiation is circularly polarized,

$$\tilde{\boldsymbol{E}}^{\pm}(t) = 2^{-\frac{1}{2}}E_0(\boldsymbol{i} \mp \mathrm{i}\boldsymbol{j})\exp\{-\mathrm{i}\omega(t - zc^{-1})\}, \tag{16}$$

where the upper and lower signs refer to right and left circular polarization respectively. The reversal coefficient $P(\theta)$ is the ratio of the intensities of left to right circularly polarized light scattered in the direction of $\boldsymbol{k}' = \cos\theta\boldsymbol{k} - \sin\theta\boldsymbol{j}$ at an angle θ to the direction of propagation $\boldsymbol{k}$, when the incident radiation is right-circular. If $\boldsymbol{j}' = \boldsymbol{k}' \times \boldsymbol{i} = \cos\theta\boldsymbol{j} + \sin\theta\boldsymbol{k}$, then

$$\begin{aligned}
P(\theta) &= \frac{\langle|\tilde{\alpha}_{\alpha\beta}\tilde{E}^+_{\beta}(i_\alpha - \mathrm{i}j'_\alpha)|^2\rangle}{\langle|\tilde{\alpha}_{\alpha\beta}\tilde{E}^+_{\beta}(i_\alpha + \mathrm{i}j'_\alpha)|^2\rangle} = \frac{\langle|\tilde{\alpha}_{\alpha\beta}(i_\beta - \mathrm{i}j_\beta)(i_\alpha - \mathrm{i}j'_\alpha)|^2\rangle}{\langle|\tilde{\alpha}_{\alpha\beta}(i_\beta - \mathrm{i}j_\beta)(i_\alpha + \mathrm{i}j'_\alpha)|^2\rangle}, \\
&= \frac{5(1 - 2\cos\theta + \cos^2\theta) + (13 + 10\cos\theta + \cos^2\theta)\kappa^2 + 5(3 - 2\cos\theta - \cos^2\theta)\kappa'^2}{5(1 + 2\cos\theta + \cos^2\theta) + (13 - 10\cos\theta + \cos^2\theta)\kappa^2 + 5(3 + 2\cos\theta - \cos^2\theta)\kappa'^2}.
\end{aligned} \tag{17}$$

For forward scattering $\theta = 0$, while for backward scattering $\theta = \pi$; from equation (17),

$$P(0) = [P(\pi)]^{-1} = \frac{6\kappa^2}{5 + \kappa^2 + 5\kappa'^2} \tag{18}$$

in agreement with the accepted result (Long 1977).

The refractive index $\tilde{n}$ is the result of interference of the forward scattering with the incident wave (Breit 1933; Kauzmann 1957; Bullough 1962). For a gas at a low pressure,

$$\tilde{n}_{\alpha\beta} = \delta_{\alpha\beta} + \frac{2\pi N}{4\pi\epsilon_0}\langle\tilde{\alpha}_{\alpha\beta}\rangle, \tag{19}$$

where N is the number of molecules in unit volume and $\langle\tilde{\alpha}_{\alpha\beta}\rangle$ is a statistical average of the polarizability of a single molecule. If the gas is isotropic,

$$\tilde{n} - 1 = \frac{2\pi N}{4\pi\epsilon_0}\langle\tilde{\alpha}\rangle. \tag{20}$$

If $\tilde{n} = n + \mathrm{i}n'$, then equations (3), (4) and (20) give

$$n - 1 = \frac{2\pi N}{4\pi\epsilon_0}\frac{2}{3\hbar}\sum_{n,j}f(\omega, \omega_{jn}, \Gamma_{jn})\omega_{jn}\langle n|\boldsymbol{\mu}|j\rangle \cdot \langle j|\boldsymbol{\mu}|n\rangle P_n, \tag{21}$$

$$n' = \frac{2\pi N}{4\pi\epsilon_0}\frac{2}{3\hbar}\sum_{n,j}g(\omega, \omega_{jn}, \Gamma_{jn})\omega_{jn}\langle n|\boldsymbol{\mu}|j\rangle \cdot \langle j|\boldsymbol{\mu}|n\rangle P_n, \tag{22}$$

where P_n is the probability that a molecule is in the state n. At equilibrium,

$$P_n = \frac{\exp(-W_n/kT)}{\sum\limits_m \exp(-W_m/kT)}.$$

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The rotation of the plane of polarization in the path-length z is determined by the anti-symmetric polarizability $\tilde{\alpha}_{xy} - \tilde{\alpha}_{yx}$ in equation (9) (Kramers 1930; Buckingham & Stephens 1966)

$$\tilde{\theta} = \theta + i\theta' = \frac{\omega z}{2c}(\tilde{n}_- - \tilde{n}_+) = \frac{2\pi N \omega z}{4\pi\epsilon_0 c}\langle\tilde{\alpha}'_{xy}\rangle. \tag{23}$$

Alkali-metal atoms with a spin $m_s = +\frac{1}{2}$ have a non-zero $\tilde{\alpha}'$ and therefore rotate the plane of polarization and depolarize light. Thus, if the nuclear spin were zero, atoms with $m_s = +\frac{1}{2}$ could absorb right but not left circularly polarized light at the resonance frequency $\omega_1 = \hbar^{-1}(W_{P_\frac{1}{2}} - W_S)$. However, the presence of an equal number of atoms with $m_s = -\frac{1}{2}$ would cancel this differential absorption, and although $\tilde{\alpha}'$ contributes to light scattering through κ'^2 (Penney 1969) (see equation (13)), it does not normally affect refraction or absorption. However, in a magnetostatic field $B_z^{(0)}$, the first-order Zeeman splitting of the $m_s = \pm\frac{1}{2}$ levels favours $m_s = -\frac{1}{2}$ and leads to a temperature-dependent optical activity. This is the T^{-1} contribution to the Faraday effect (Buckingham & Stephens 1966). Optical pumping provides another important means of favouring certain spin states (Series 1966; Happer 1972).

The magnitude of $\tilde{\alpha}'_{xy}$ in an alkali-metal atom can be estimated from equation (10). The wavefunctions $n^\pm$ and j, m representing the ground $^2S_\frac{1}{2}$ and excited $^2P_\frac{1}{2}$ and $^2P_\frac{3}{2}$ states are complex and are (Condon & Shortley 1935)

$$n^+ = (ns)\,\alpha,$$
$$n^- = (ns)\,\beta,$$
$$j, m \begin{cases} \tfrac{1}{2}, \tfrac{1}{2} = (np)_{j=\frac{1}{2}, m=\frac{1}{2}} = -(\tfrac{1}{3})^{\frac{1}{2}}p_0\alpha + (\tfrac{2}{3})^{\frac{1}{2}}p_1\beta, \\ \tfrac{1}{2}, -\tfrac{1}{2} = (np)_{j=\frac{1}{2}, m=-\frac{1}{2}} = (\tfrac{1}{3})^{\frac{1}{2}}p_0\beta - (\tfrac{2}{3})^{\frac{1}{2}}p_{-1}\alpha, \\ \tfrac{3}{2}, \tfrac{3}{2} = (np)_{j=\frac{3}{2}, m=\frac{3}{2}} = p_1\alpha, \\ \tfrac{3}{2}, \tfrac{1}{2} = (np)_{j=\frac{3}{2}, m=\frac{1}{2}} = (\tfrac{2}{3})^{\frac{1}{2}}p_0\alpha + (\tfrac{1}{3})^{\frac{1}{2}}p_1\beta, \\ \tfrac{3}{2}, -\tfrac{1}{2} = (np)_{j=\frac{3}{2}, m=-\frac{1}{2}} = (\tfrac{1}{3})^{\frac{1}{2}}p_{-1}\alpha + (\tfrac{2}{3})^{\frac{1}{2}}p_0\beta, \\ \tfrac{3}{2}, -\tfrac{3}{2} = (np)_{j=\frac{3}{2}, m=-\frac{3}{2}} = p_{-1}\beta. \end{cases} \tag{24}$$

At a frequency ω not far from the $np \leftarrow ns$ resonance but also not so close to resonance that hyperfine splitting is significant (in sodium the hyperfine splitting of both resonance lines is approximately 2 GHz):

$$\begin{aligned}(\alpha'_{xy})_{n^+} &= -\frac{2\omega}{\hbar}\left[\frac{\mathrm{Im}\{\langle n^+|\mu_x|\tfrac{1}{2}, -\tfrac{1}{2}\rangle\langle\tfrac{1}{2}, -\tfrac{1}{2}|\mu_y|n^+\rangle\}}{\omega_\frac{1}{2}^2 - \omega^2}\right.\\ &\quad\left.+\frac{\mathrm{Im}\{\langle n^+|\mu_x|\tfrac{3}{2}, \tfrac{3}{2}\rangle\langle\tfrac{3}{2}, \tfrac{3}{2}|\mu_y|n^+\rangle + \langle n^+|\mu_x|\tfrac{3}{2}, -\tfrac{1}{2}\rangle\langle\tfrac{3}{2}, -\tfrac{1}{2}|\mu_y|n^+\rangle\}}{\omega_\frac{3}{2}^2 - \omega^2}\right],\\ &= -\frac{2\omega}{3\hbar}|\langle s|\mu_z|p_z\rangle|^2\left[\frac{1}{\omega_\frac{1}{2}^2 - \omega^2} - \frac{1}{\omega_\frac{3}{2}^2 - \omega^2}\right] = -(\alpha'_{xy})_{n^-}.\end{aligned} \tag{25}$$

The mean polarizability of the atom is

$$\alpha = (\alpha_{zz})_{n^+} = (\alpha_{zz})_{n^-} = \frac{2}{3\hbar}|\langle s|\mu_z|p_z\rangle|^2\left[\frac{\omega_\frac{1}{2}}{\omega_\frac{1}{2}^2 - \omega^2} + \frac{2\omega_\frac{3}{2}}{\omega_\frac{3}{2}^2 - \omega^2}\right]. \tag{26}$$

At frequencies near resonance $|\alpha'_{xy}|^2$ may be very large, and a large depolarization ratio $\rho_0 = \kappa'^2 = |\alpha'_{xy}|^2/|\alpha|^2$ has been predicted (Placzek 1934; Penney 1969).

3. The effect of molecular vibration on polarizability

The electronic properties of a molecule depend on the relative positions of the nuclei. In a diatomic molecule the polarizabilities along and at right angles to the internuclear axis may be expressed as power series in the displacement $\xi = (r - r_e)/r_e$ from the equilibrium internuclear distance r_e:

$$\alpha = \tfrac{1}{3}(\alpha_\parallel + 2\alpha_\perp) = \alpha_e + \alpha'_e \xi + \tfrac{1}{2}\alpha''_e \xi^2 + \dots, \tag{27}$$

$$\Delta\alpha = \alpha_\parallel - \alpha_\perp = \Delta\alpha_e + \Delta\alpha'_e \xi + \tfrac{1}{2}\Delta\alpha''_e \xi^2 + \dots. \tag{28}$$

The fundamental vibrational Raman intensities are determined by α'^2_e and $\Delta\alpha'^2_e$, while the overtone depends upon $(\alpha''_e + a\alpha'_e)^2$ and $(\Delta\alpha''_e + a\Delta\alpha'_e)^2$ where a is the anharmonicity ($a\xi$ is the ratio of the cubic to the quadratic contributions to the potential energy).

Little is known of polarizability derivatives, but there is hope that the effect of centrifugal distortion on relative intensities of rotational lines in the O- and S-branches ($\Delta J = -2$ and $+2$) of the fundamental and overtone bands will permit the determination of $\Delta\alpha'_e$ and $\Delta\alpha''_e$ relative to $\Delta\alpha_e$ (James & Klemperer 1959; Buckingham & Szabo 1978). The effects are expected to be very large in H_2. Unfortunately, there does not appear to be such an easy route to α'_e and α''_e in diatomics, nor to $\Delta\alpha'_e$ and $\Delta\alpha''_e$ in polyatomics (Jacobi & Jaffe 1963).

4. Collision-induced scattering by simple gases

Depolarized Rayleigh scattering by monatomic gases is an important source of information about the effect of collisions on the polarizability (Gelbart 1974). There is inelastic depolarized scattering because the radiation field is coupled to the translational motion of the molecules by the collision-induced polarizability. The dominant contribution is that due to dipolar interaction, giving an anisotropy in the pair polarizability proportional to $\alpha_1 \alpha_2 R^{-3}$ where α_1 and α_2 are the polarizabilities of the two molecules and R is their separation (Silberstein 1917).

When a tetrahedral molecule such as CH_4 rotates, its polarizability is unchanged. However, if the molecule is in collision, there may be a change in the induced dipole on rotation of the tetrahedron by virtue of higher-order polarizabilities. The most important source of inelastic rotational scattering is probably the dipole–quadrupole polarizability $A_{\alpha\beta\gamma}$ which gives the quadrupole moment $\Theta_{\beta\gamma} = A_{\alpha\beta\gamma} E_\alpha$ induced by a uniform field E_α as well as the dipole moment $\mu_\alpha = \tfrac{1}{3}A_{\alpha\beta\gamma}\nabla_\beta E_\gamma$ induced by an electric field gradient. A tetrahedron has one independent element $A = A_{123}$ of the A-tensor and it is independent of origin. The field gradient that causes the induced dipole in molecule 1 arises from the dipole induced in a neighbour 2 by the optical field. This contribution to the anisotropy in the pair polarizability varies as $\alpha_2 A_1 R^{-4}$ and may provide a means of measuring the dipole–quadrupole polarizability of tetrahedral molecules through observations of rotational Raman transitions in the depolarized light scattered by a compressed gas (Buckingham & Tabisz 1978).

5. Differential scattering of right and left circularly polarized light

Optical activity is conventionally studied through observations of rotation of the plane of polarization or of circular dichroism. These effects result from interference of the forward scattering with the incident wave. Another manifestation of optical activity is the differential

scattering of right and left circularly polarized light. If I_R and I_L are the intensities scattered from incident beams of right and left circularly polarized light, the circular intensity differential is defined as $(I_R - I_L)/(I_R + I_L)$. It has been observed in vibrational Raman scattering from many liquids (Barron & Buckingham 1975; Barron 1978) and can be as large as 5×10^{-3}.

To account for optical activity it is necessary either that the antisymmetric polarizability α' be non-zero (as in the presence of a magnetic field) or that equation (1) be extended to allow for an oscillating dipole to be induced in a chiral molecule by the magnetic field of the incident wave (Condon 1937). In the latter case, the time-dependent electric and magnetic dipole moments and electric quadrupole moment Θ of a molecule in an electromagnetic wave may be written (Buckingham 1967a):

$$\mu_\alpha(t) = \alpha_{\alpha\beta} E_\beta(t) + G'_{\alpha\beta} \dot{B}_\beta(t)\, \omega^{-1} + \tfrac{1}{3} A_{\alpha\beta\gamma} \nabla_\beta E_\gamma(t) + \dots, \tag{29}$$

$$m_\alpha(t) = \chi_{\alpha\beta} B_\beta(t) - G'_{\beta\alpha} \dot{E}_\beta(t)\, \omega^{-1} + \dots, \tag{30}$$

$$\Theta_{\alpha\beta}(t) = A_{\gamma\alpha\beta} E_\gamma(t) + \dots. \tag{31}$$

The symmetry of a chiral molecule under time reversal requires these forms for the induced moments, since $\mu(t)$, $\Theta(t)$, $E(t)$ and $\nabla E(t)$ are symmetric under time reversal while the magnetic dipole $m(t)$ and magnetic field $B(t)$ are antisymmetric (so that the time derivative $\dot{B}(t)$ is symmetric and $\dot{E}(t)$ antisymmetric). It is also helpful to enquire into the symmetry properties of μ, m and Θ under space reversal. If the coordinates of all particles in the molecule and in the source of the fields are inverted through the origin (the parity operation) then μ, $E(t)$ and $\dot{E}(t)$ are reversed while m, Θ, $B(t)$, $\dot{B}(t)$ and $\nabla E(t)$ are unchanged. Hence α and the magnetizability χ are symmetric under parity, but G' and A are antisymmetric. Hence G' and A must vanish for centrosymmetric molecules. Perturbation theory yields the equations (Buckingham 1967a)

$$G'_{\alpha\beta} = -2\hbar^{-1}\omega \sum_j Z(\omega, \omega_{jn}, \Gamma_{jn})\ \mathrm{Im}\{\langle n| \mu_\alpha |j\rangle \langle j| m_\beta |n\rangle\}, \tag{32}$$

$$A_{\alpha\beta\gamma} = A_{\alpha\gamma\beta} = 2\hbar^{-1} \sum_j Z(\omega, \omega_{jn}, \Gamma_{jn})\ \omega_{jn}\ \mathrm{Re}\{\langle n| \mu_\alpha |j\rangle \langle j| \Theta_{\beta\gamma} |n\rangle\}. \tag{33}$$

The optical rotation $\tilde{\theta}$ is given by (Buckingham & Dunn 1971):

$$\tilde{\theta} = -\frac{2\pi N \omega}{4\pi \epsilon_0 c^2} \langle \tilde{G}'_{xx} + \tilde{G}'_{yy} + \tfrac{1}{3}\omega(\tilde{A}_{xyz} - \tilde{A}_{yxz})\rangle, \tag{34}$$

and $\langle \tilde{G}'_{xx} + \tilde{G}'_{yy}\rangle$ and $\langle \tilde{A}_{xyz} - \tilde{A}_{yxz}\rangle$ have equal but opposite values for molecules and their mirror images. For an isotropic fluid, (34) reduces to

$$\tilde{\theta} = -\frac{4\pi N \omega}{4\pi \epsilon_0 c^2} \langle \tilde{G}'\rangle, \tag{35}$$

where $\tilde{G}' = \tfrac{1}{3}\tilde{G}'_{\alpha\alpha}$. Thus $\tilde{A}$ contributes to the optical rotation only in anisotropic samples.

Differential scattering of right and left circularly polarized light results from interference of the waves scattered by the oscillating dipoles $\omega^{-1} G' . \dot{B}$ and $\tfrac{1}{3} A : \nabla E$ in (29) with that from $\alpha . E$. It provides information about polarizabilities and structure in addition to that obtainable from the optical rotation (Barron & Buckingham 1975; Barron 1978). If the polarizability tensor α is known from other measurements, polarization studies of differential Rayleigh scattering would give information about the components of G' and A.

Only chiral systems can scatter differentially right and left circularly polarized light. However, all molecules are optically active in a magnetostatic field $B_z^{(0)}$ and all also exhibit a circular intensity differential linear in $B_z^{(0)}$ (Barron & Buckingham 1972; Barron 1975). More surprisingly, it is expected that all molecules give a circular intensity differential linear in an electrostatic field $E_x^{(0)}$ (Buckingham & Raab 1975). The handedness of the frame is generated by $E_x^{(0)}$, the direction of scattering y, and the direction of propagation z; thus the circular intensity differential for an isotropic fluid changes sign if the field is reversed or if the scattering is observed in the $-y$ direction. Like the Faraday effect, the electric-field-induced circular intensity differential is a property possessed by all matter. Also like the Faraday effect (Buckingham & Stephens 1966), there are temperature-independent and temperature-dependent contributions. The latter arises from the partial orientation of the permanent electric dipoles by the field (the mean value of the cosine of the angle between the dipole axis and $E_x^{(0)}$ is

$$\overline{\cos\phi} = \frac{3\epsilon}{2\epsilon+1}\frac{\overline{\mu}E_x^{(0)}}{3kT},$$

where ϵ is the static dielectric constant and $\overline{\mu}$ the mean dipole moment of the molecule and its neighbours in a sphere of arbitrary size (Buckingham 1967 b)), and from the non-vanishing elements of G' and A possessed by all dipolar molecules. For a linear molecule with dipole moment $\mu_3 = \mu$ along the axis, the depolarized differential scattering is proportional to $(\alpha_{\parallel}-\alpha_{\perp})(G'_{12}+\frac{1}{3}\omega A_{113})\mu E_x^{(0)}(kT)^{-1}$ (Buckingham & Raab 1975).

Dr R. A. Shatwell in our laboratory is on the point of making the first measurements of this new universal property of matter.

6. HYPERPOLARIZABILITY

If the electric field E acting on a molecule is strong it may be necessary to extend equation (1) to allow for non-linear polarization (Buckingham & Pople 1955):

$$\mu_\alpha = \mu_\alpha^{(0)} + \alpha_{\alpha\beta}E_\beta + \tfrac{1}{2}\beta_{\alpha\beta\gamma}E_\beta E_\gamma + \tfrac{1}{6}\gamma_{\alpha\beta\gamma\delta}E_\beta E_\gamma E_\delta + \ldots. \tag{36}$$

For centrosymmetric molecules the permanent dipole $\boldsymbol{\mu}^{(0)}$ and the first hyperpolarizability $\boldsymbol{\beta}$ vanish. Typical values for these properties of small molecules in static fields are as follows:

$$\mu^{(0)} \approx 1\mathrm{D} = 10^{-18}\ \text{e.s.u.} = 3.33564 \times 10^{-30}\ \mathrm{C\,m}$$

$$(4\pi\epsilon_0)^{-1}\alpha \approx 1\text{Å}^3 = 10^{-24}\ \text{e.s.u.} = 10^{-30}\ \mathrm{m}^3$$

$$(4\pi\epsilon_0)^{-2}\beta \approx \pm 10^{-30}\ \text{e.s.u.} = \pm 0.29979 \times 10^{-30}\ \mathrm{C^{-1}\,m^5}$$

$$(4\pi\epsilon_0)^{-3}\gamma \approx 10^{-36}\ \text{e.s.u.} = 0.089876 \times 10^{-30}\ \mathrm{C^{-2}\,m^7}.$$

Differentiating (36) with respect to E_β gives the differential polarizability $\pi_{\alpha\beta}$,

$$\pi_{\alpha\beta} = \alpha_{\alpha\beta} + \beta_{\alpha\beta\gamma}E_\gamma + \tfrac{1}{2}\gamma_{\alpha\beta\gamma\delta}E_\gamma E_\delta + \ldots, \tag{37}$$

π may be considered to be the effective polarizability in the presence of the strong field E and its anisotropy $\overline{\pi_{zz}}-\overline{\pi_{xx}}$ in a strong static field E_z determines the Kerr constant (Buckingham & Pople 1955). According to classical theory,

$$\overline{\pi_{zz}}-\overline{\pi_{xx}} = E_z^2\left[\tfrac{1}{3}\gamma + \frac{2\mu^{(0)}\beta}{9kT} + \frac{3\kappa\kappa^{(0)}\alpha\alpha^{(0)}}{5kT} + \frac{\mu^{(0)2}(\alpha_{33}-\alpha)}{10k^2T^2}\right], \tag{38}$$

where
$$\gamma = \tfrac{1}{10}(3\gamma_{\alpha\beta\alpha\beta} - \gamma_{\alpha\alpha\beta\beta}), \tag{39}$$

$$\beta = \tfrac{3}{10}(3\beta_{\alpha3\alpha} - \beta_{\alpha\alpha3}), \tag{40}$$

$$18\kappa\kappa^{(0)}\alpha\alpha^{(0)} = 3\alpha_{\alpha\beta}\alpha^{(0)}_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha^{(0)}_{\beta\beta}, \tag{41}$$

α and $\alpha^{(0)}$ being the polarizabilities for optical and static fields respectively, and the permanent dipole $\mu^{(0)}$ is along the 3-axis of the molecule. For molecules with isotropic polarizabilities (such as Ar, CH_4, SF_6), only the term in γ survives and measurements of the Kerr effect yield second hyperpolarizabilities directly (Buckingham & Dunmur 1968). First hyperpolarizabilities can be obtained from measurements of the Kerr effect over a range of temperatures but there are difficulties because the term in β generally provides only a small part of the total birefringence (Buckingham & Orr 1967; Burnham *et al.* 1977; Bogaard *et al.* 1978).

A better route to the first hyperpolarizability of gaseous molecules is through second-harmonic generation in the presence of a strong electric field. The effective nonlinear polarizability giving second-harmonic generation through a dipole $\mu_\alpha = \tfrac{1}{2}S_{\alpha\beta\gamma}E_\beta(t)E_\gamma(t)$ oscillating at 2ω may be obtained from equation (36) and is given by:

$$S_{\alpha\beta\gamma} = \beta_{\alpha\beta\gamma} + \gamma_{\alpha\beta\gamma\delta}E_\delta + \dots = S_{\alpha\gamma\beta}. \tag{42}$$

In the presence of a static field E_z,

$$\overline{S_{zzz}} = \frac{E_z}{15}\left[\frac{\mu^{(0)}}{kT}(2\beta_{\alpha\alpha3} + \beta_{3\alpha\alpha}) + (2\gamma_{\alpha\alpha\beta\beta} + \gamma_{\alpha\beta\beta\alpha})\right], \tag{43}$$

$$\overline{S_{yyz}} = \frac{E_z}{30}\left[\frac{\mu^{(0)}}{kT}(3\beta_{\alpha\alpha3} - \beta_{3\alpha\alpha}) + (3\gamma_{\alpha\alpha\beta\beta} - \gamma_{\alpha\beta\beta\alpha})\right], \tag{44}$$

so that measurements of the intensities of second-harmonic scattering over a range of temperature yield information about both β and γ (Finn & Ward 1974; Ward & Bigio 1975; Miller & Ward 1977). The contributions of β and γ are of the same order of magnitude.

A review of the literature of polarizabilities and of first and second hyperpolarizabilities (Bogaard & Orr 1975) lists values for α, β and γ for simple molecules. Various schemes have been proposed for relating molecular polarizabilities and hyperpolarizabilities to atomic, bond or group components (Applequist 1977; Buckingham & Orr 1967; Crane & Bergman 1976; Miller *et al.* 1977). These are useful, but none is entirely successful because polarizabilities are properties of the molecule and reflect the unique electronic structure of the compound. However, it is instructive to observe that simple additivity schemes are better able to describe the isotropic properties α and γ than the anisotropic $\mu^{(0)}$, $\kappa\alpha$ and β (Miller *et al.* 1977).

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Discussion

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Some of the differences in the properties of the polarizability and hyperpolarizability are illustrated by some recent studies of hyper-Rayleigh and hyper-Raman scattering made by Dr M. J. French and myself.

Unlike the polarizability of a system which is always non-zero irrespective of its symmetry, the hyperpolarizability will be zero in a system with a centre of symmetry. Thus the intensity of hyper-Rayleigh scattering which is controlled by the equilibrium hyperpolarizability can be used as a probe of symmetry in appropriate systems.

One example is an ammonium chloride crystal which undergoes an order–disorder phase transition at $T_c = 242.3$ K. In the low temperature, ordered phase the crystal structure does not have a centre of symmetry whereas in the high-temperature, disordered phase the crystal structure has a statistical centre of symmetry. We found that a crystal of ammonium chloride which had been kept above the transition temperature for a considerable period showed virtually no hyper-Rayleigh scattering but when it was cooled below T_c, intense hyper-Rayleigh scattering was observed. However, when the crystal was subsequently allowed to warm up and pass through T_c substantial hyper-Rayleigh scattering was still observed. Only after an extended period of annealing well above T_c did the intensity of the hyper-Rayleigh scattering decrease

virtually to zero, indicating that the symmetry in the high-temperature phase depended on the thermal history of the crystal.

Other differences in the properties of the polarizability and hyperpolarizability are illustrated by the comparison of the vibrational Stokes Raman and Stokes hyper-Raman spectra of CCl_4 (liquid) given below:

CCl_4	$\Delta\tilde{\nu}/cm^{-1}$	Relative intensities	
		Raman	hyper-Raman
$\nu_3(f_2)$	776	1	10
$\nu_1(a_1)$	458	10	<1
$\nu_4(f_2)$	314	6	1
$\nu_2(e)$	218	5	inactive

The inactivity of the e class mode in the hyper-Raman effect and the radically different relative intensities in the Raman and hyper-Raman spectra are consequences of the different properties of the polarizability and hyperpolarizability.

We have recently developed a bond hyperpolarizability theory of vibrational hyper-Raman intensities analogous to the bond polarizability theory of vibrational Raman intensities. This theory affords some insight into the reasons for the different intensity distributions in the two kinds of spectra. For example the large intensity of the $\nu_1(a_1)$ mode of CCl_4 in the Raman spectrum arises because the intensity depends on the derived mean bond polarizability. However in the hyper-Raman effect the derived mean bond hyperpolarizability controls the intensity of $\nu_3(f_2)$ of CCl_4, thus accounting for its large intensity in the hyper-Raman spectrum.