

# THEORY OF MOLECULAR LIGHT SCATTERING IN THE PRESENCE OF AN INTENSE LIGHT BEAM

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The possibility is considered of investigating the light scattered from a weak light beam of frequency  $\omega_1$  in the presence of the strong electric field of another light beam *e.g.* from a laser, of frequency  $\omega_2$ . It is shown quantum-mechanically to the third approximation that quite generally, under the effect of the intense light beam, there appear in addition to the component with normal Raman frequencies  $\omega_1 \pm \omega_{kl}$  two new components, the first of these of frequencies  $\omega_1 \pm \omega_2 \pm \omega_{kl}$  and  $\omega_1 \mp \omega_2 \pm \omega_{kl}$  appearing only for molecules without a centre of inversion and the other, of frequencies  $\omega_1 \pm 2\omega_2 \pm \omega_{kl}$  and  $\omega_1 \mp 2\omega_2 \pm \omega_{kl}$  — in all other cases, including optically isotropic molecules. The discussion of these non-linear contributions to the light scattering tensor is restricted to the purely classical case and is carried out strictly for gases consisting of molecules possessing a centre of inversion (point groups  $D_{4h}$ ,  $C_{6h}$ ,  $D_{6h}$ ,  $D_{\infty h}$ ,  $T_h$  and  $O_h$ ) or presenting none (point groups  $D_2$ ,  $D_{2d}$ ,  $D_{3h}$ ,  $C_{3v}$ ,  $C_{4v}$ ,  $C_{6v}$ ,  $C_{\infty v}$  and  $T_d$ ). Numerical evaluations for  $CS_2$  and  $CHCl_3$  point to the possibility of observing changes in the degree of depolarization and Rayleigh ratio if produced by a light beam with an electric field of the order of at least  $10^3$  e.s.u.

## 1. Introduction

The lasers now in existence, being sources of monochromatic and coherent light beams of very great intensity, provide the conditions for work on non-linear optical effects. Recently, the subject has been dealt with theoretically by various authors, of whom we shall quote Armstrong *et al.* (1962), and Franken and Ward (1963); the latter paper brings *i.a.* a review of the results relating to non-linear optical effects and the generation of optical harmonics, up to August 1962. Eckhardt *et al.* (1962) and Stoicheff (1963)<sup>1</sup>, using as radiation source an intense ruby laser, recently observed stimulated Raman scattering from a number of organic liquids. Quite recently, a phenomenological theory of this new effect has been proposed by Hellwarth (1963). Also, Loudon (1963) proposed a theory predicting the possi-

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bility, with the lasers now available, of observing stimulated Raman scattering from lattice vibrations in solids.<sup>2</sup>

Investigation, experimental and theoretical, of various non-linear optical effects allows *i.a.* to gain better insight into the behaviour of atoms and molecules in electric fields of an intensity unattainable several years ago, and now conveyed by laser beams. This explains the increasingly great interest on the part of physicists in the non-linear interactions between matter and light from lasers.

Non-linear interaction between atoms or molecules and an oscillating electric field is apparent specifically in the effect of light scattering in the presence of the very intense electric field of another light beam incident on the scattering medium. The possibility of laser light influencing the Rayleigh scattering of light in gases has already been discussed in some of its aspects for the case of axially-symmetric molecules and certain pre-assumed, simple conditions of observation (Kielich 1961, 1963a, c, 1964a, b, Piekara and Kielich 1963).

The present paper brings the quantum-mechanical basis of the theory of non-linear light scattering, covering the formalism of both coherent (diagonal matrix elements of the scattering tensor) and non-coherent light scattering (non-diagonal elements of the tensor). The theory is sufficiently general for applicability to molecular scattering systems of arbitrary symmetry at arbitrary conditions of observation; its detailed discussion is carried out on a purely classical level. The transition to the classical case was primarily suggested by a tendency to avoid over-complication and to obtain results in a form adapted to immediate evaluation revealing the order of the non-linear variation undergone *e.g.* by the degree of depolarization of the scattered light or by Rayleigh's ratio under the influence of the intense light beam. With the aim of rendering apparent the innermost, essential mechanism of the effect under consideration, and in order to derive our formulas in easily legible form, we shall discuss the case of a rarefied gas, where intermolecular interactions can be neglected.

## 2. Quantum-mechanical fundamentals of the theory

Let us assume a monochromatic light beam of frequency  $\omega_1$  and electric vector  $2\mathbf{E}_1 = \mathbf{E}_1^+ e^{i\omega_1 t} + \mathbf{E}_1^- e^{-i\omega_1 t}$  with  $\mathbf{E}_1^+$  and  $\mathbf{E}_1^-$  denoting (generally complex) amplitudes, incident on a quantum system (an atom or molecule or small assemblages of such). The interaction between the quantum system and the magnetic field of the light wave can be neglected in comparison with its much greater interaction with the electric field of the wave. Assuming the wavelength of the latter to be large with respect to the linear dimensions of the scattering system, we can write the Hamiltonian of the system in the following dipole approximation

$$H = H_0 + H_1 = H_0 - \frac{1}{2} (\mathbf{M} \cdot \mathbf{E}_1^+ e^{i\omega_1 t} + \mathbf{M} \cdot \mathbf{E}_1^- e^{-i\omega_1 t}), \quad (1)$$

wherein  $H_0$  relates to the non-perturbed system and  $H_1$  is the Hamiltonian of the perturbation due to the light wave,  $\mathbf{M}$  denoting the operator of the electric dipole moment of the quantum system.

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<sup>2</sup> The author expresses his thanks to Dr R. Loudon for sending him two typed copies of his papers on stimulated Raman scattering previous to their publication.

As long as the intensity of the electric field  $\mathbf{E}_1$  is small, quantum-mechanical perturbation calculus can be restricted to the first approximation, leading to the well-known result of Kramers and Heisenberg (1925) for the dipole moment induced in the system by the field  $\mathbf{E}_1$ . Albeit, we are concerned with the case when a second light wave is incident on the system under consideration, with electric vector  $2\mathbf{E}_2 = \mathbf{E}_2^+ e^{i\omega_2 t} + \mathbf{E}_2^- e^{-i\omega_2 t}$  oscillating at the frequency  $\omega_2$ . The Hamiltonian (1) has now to contain the supplementary perturbation

$$H_2 = -\frac{1}{2} (\mathbf{M} \cdot \mathbf{E}_2^+ e^{i\omega_2 t} + \mathbf{M} \cdot \mathbf{E}_2^- e^{-i\omega_2 t}). \quad (2)$$

Since we assume  $\mathbf{E}_2$  to be very large, we are no longer justified in taking into account the first approximation of perturbation calculus only, but have to consider higher approximations when computing the dipole moment induced in the system by the field  $\mathbf{E}_1$  in the presence of  $\mathbf{E}_2$ . To solve our problem, it is necessary to carry out Dirac's perturbation calculation to at least the third approximation. Thus,  $\Psi_k$  being the wave-function of the  $k$ -th perturbed state, we have

$$\Psi_k = \sum_m \{a_m^{(0)} + a_m^{(1)} + a_m^{(2)} + a_m^{(3)} + \dots\} \Psi_{0m} e^{-i\omega_m t}, \quad (3)$$

where  $a_m^{(0)} = \delta_{mk}$  and the remaining time-dependent coefficients  $a_m^{(1)}, a_m^{(2)}, \dots$ , can be computed from the differential equations

$$i\hbar \dot{a}_m^{(s+1)} = \sum_n \{\langle m|H_1|n\rangle + \langle m|H_2|n\rangle\} a_n^{(s)} e^{i\omega_{mn} t}, \quad s = 0, 1, 2, \dots \quad (4)$$

The perturbation matrix elements are

$$\langle m|H_1|n\rangle = \int \Psi_{0m}^* H_1 \Psi_{0n} d\tau, \quad \langle m|H_2|n\rangle = \int \Psi_{0m}^* H_2 \Psi_{0n} d\tau$$

$\Psi_{0m}$  and  $\Psi_{0n}$  being the wave-functions of the non-perturbed system relating respectively to the states  $m$  and  $n$ , while  $\omega_{mn}$  is the Bohr frequency for the transition  $m \rightarrow n$ .

By Eqs (1) and (2) and on integration of Eq. (4), we obtain the coefficients of the consecutive approximations as follows (cf., Kielich 1963 c):

$$\begin{aligned} a_m^{(1)} &= \frac{1}{2} \{a_\beta^{mk} (+\omega_1) E_{1\beta}^+ e^{i\omega_1 t} + a_\beta^{mk} (-\omega_1) E_{1\beta}^- e^{-i\omega_1 t} + \\ &\quad + a_\beta^{mk} (+\omega_2) E_{2\beta}^+ e^{i\omega_2 t} + a_\beta^{mk} (-\omega_2) E_{2\beta}^- e^{-i\omega_2 t}\} e^{i\omega_m t}, \\ a_m^{(2)} &= \frac{1}{4} \{b_{\beta\gamma}^{mk} (+\omega_1, +\omega_2) E_{1\beta}^+ E_{2\gamma}^+ e^{i(\omega_1 + \omega_2)t} + b_{\beta\gamma}^{mk} (+\omega_1, -\omega_2) E_{1\beta}^+ E_{2\gamma}^- e^{i(\omega_1 - \omega_2)t} + \\ &\quad + b_{\beta\gamma}^{mk} (-\omega_1, +\omega_2) E_{1\beta}^- E_{2\gamma}^+ e^{-i(\omega_1 - \omega_2)t} + b_{\beta\gamma}^{mk} (-\omega_1, -\omega_2) E_{1\beta}^- E_{2\gamma}^- e^{-i(\omega_1 + \omega_2)t} + \\ &\quad + b_{\beta\gamma}^{mk} (+\omega_2, +\omega_2) E_{2\beta}^+ E_{2\gamma}^+ e^{i2\omega_2 t} + b_{\beta\gamma}^{mk} (+\omega_2, -\omega_2) E_{2\beta}^+ E_{2\gamma}^- + \\ &\quad + b_{\beta\gamma}^{mk} (-\omega_2, +\omega_2) E_{2\beta}^- E_{2\gamma}^+ + b_{\beta\gamma}^{mk} (-\omega_2, -\omega_2) E_{2\beta}^- E_{2\gamma}^- e^{-i2\omega_2 t}\} e^{i\omega_m t}, \\ a_m^{(3)} &= \frac{1}{8} \{c_{\beta\gamma\delta}^{mk} (+\omega_1, +\omega_2, +\omega_2) E_{1\beta}^+ E_{2\gamma}^+ E_{2\delta}^+ e^{i(\omega_1 + 2\omega_2)t} + c_{\beta\gamma\delta}^{mk} (+\omega_1, +\omega_2, -\omega_2) E_{1\beta}^+ E_{2\gamma}^+ E_{2\delta}^- e^{i\omega_1 t} + \end{aligned}$$

$$\begin{aligned}
& + c_{\beta\gamma\delta}^{mk} (+\omega_1, -\omega_2, +\omega_2) E_{1\beta}^+ E_{2\gamma}^- E_{2\delta}^+ e^{i\omega_1 t} + c_{\beta\gamma\delta}^{mk} (+\omega_1, -\omega_2, -\omega_2) E_{1\beta}^+ E_{2\gamma}^- E_{2\delta}^- e^{i(\omega_1 - 2\omega_2)t} + \\
& + c_{\beta\gamma\delta}^{mk} (-\omega_1, +\omega_2, +\omega_2) E_{1\beta}^- E_{2\gamma}^+ E_{2\delta}^+ e^{-i(\omega_1 - 2\omega_2)t} + c_{\beta\gamma\delta}^{mk} (-\omega_1, +\omega_2, -\omega_2) E_{1\beta}^- E_{2\gamma}^+ E_{2\delta}^- e^{-i\omega_1 t} + \\
& + c_{\beta\gamma\delta}^{mk} (-\omega_1, -\omega_2, +\omega_2) E_{1\beta}^- E_{2\gamma}^- E_{2\delta}^+ e^{-i\omega_1 t} + c_{\beta\gamma\delta}^{mk} (-\omega_1, -\omega_2, -\omega_2) E_{1\beta}^- E_{2\gamma}^- E_{2\delta}^- e^{-i(\omega_1 + 2\omega_2)t} \} e^{i\omega_m k t},
\end{aligned} \tag{5}$$

with the notation

$$\begin{aligned}
a_{\beta}^{mk} (\pm\omega_1) &= \frac{1}{\hbar} \frac{\langle m | M_{\beta} | k \rangle}{\omega_{mk} \pm \omega_1}, \quad a_{\beta}^{mk} (\pm\omega_2) = \frac{1}{\hbar} \frac{\langle m | M_{\beta} | k \rangle}{\omega_{mk} \pm \omega_2}, \\
b_{\beta\gamma}^{mk} (\pm\omega_1, \pm\omega_2) &= \frac{1}{\hbar^2} \sum_n \left\{ \frac{\langle m | M_{\beta} | n \rangle \langle n | M_{\gamma} | k \rangle}{(\omega_{mk} \pm \omega_1 \pm \omega_2) (\omega_{nk} \pm \omega_2)} + \frac{\langle m | M_{\gamma} | n \rangle \langle n | M_{\beta} | k \rangle}{(\omega_{mk} \pm \omega_1 \pm \omega_2) (\omega_{nk} \pm \omega_1)} \right\}, \\
b_{\beta\gamma}^{mk} (\pm\omega_2, \pm\omega_2) &= \frac{1}{\hbar^2} \sum_n \frac{\langle m | M_{\beta} | n \rangle \langle n | M_{\gamma} | k \rangle}{(\omega_{mk} \pm 2\omega_2) (\omega_{nk} \pm \omega_2)}, \\
b_{\beta\gamma}^{mk} (\pm\omega_2, \mp\omega_2) &= \frac{1}{\hbar^2} \sum_n \frac{\langle m | M_{\beta} | n \rangle \langle n | M_{\gamma} | k \rangle}{\omega_{mk} (\omega_{nk} \mp \omega_2)}, \\
c_{\beta\gamma\delta}^{mk} (\pm\omega_1, \pm\omega_2, \pm\omega_2) &= \frac{1}{\hbar^3} \sum_{nr} \left\{ \frac{\langle m | M_{\beta} | n \rangle \langle n | M_{\gamma} | r \rangle \langle r | M_{\delta} | k \rangle}{(\omega_{mk} \pm \omega_1 \pm 2\omega_2) (\omega_{nk} \pm 2\omega_2) (\omega_{rk} \pm \omega_2)} + \right. \\
& + \left. \frac{\langle m | M_{\gamma} | n \rangle \langle n | M_{\delta} | r \rangle \langle r | M_{\beta} | k \rangle}{(\omega_{mk} \pm \omega_1 \pm 2\omega_2) (\omega_{nk} \pm \omega_1 \pm \omega_2) (\omega_{rk} \pm \omega_1)} + \frac{\langle m | M_{\delta} | n \rangle \langle n | M_{\beta} | r \rangle \langle r | M_{\gamma} | k \rangle}{(\omega_{mk} \pm \omega_1 \pm 2\omega_2) (\omega_{nk} \pm \omega_1 \pm \omega_2) (\omega_{rk} \pm \omega_2)} \right\}, \\
c_{\beta\gamma\delta}^{mk} (\pm\omega_1, \pm\omega_2, \mp\omega_2) &= \frac{1}{\hbar^3} \sum_{nr} \left\{ \frac{\langle m | M_{\beta} | n \rangle \langle n | M_{\gamma} | r \rangle \langle r | M_{\delta} | k \rangle}{(\omega_{mk} \pm \omega_1) \omega_{nk} (\omega_{rk} \mp \omega_2)} + \right. \\
& + \left. \frac{\langle m | M_{\gamma} | n \rangle \langle n | M_{\delta} | r \rangle \langle r | M_{\beta} | k \rangle}{(\omega_{mk} \pm \omega_1) (\omega_{nk} \pm \omega_1 \mp \omega_2) (\omega_{rk} \pm \omega_1)} + \frac{\langle m | M_{\delta} | n \rangle \langle n | M_{\beta} | r \rangle \langle r | M_{\gamma} | k \rangle}{(\omega_{mk} \pm \omega_1) (\omega_{nk} \pm \omega_1 \pm \omega_2) (\omega_{rk} \pm \omega_2)} \right\}. \tag{6}
\end{aligned}$$

By (3), the matrix element of the total dipole moment of the quantum system on the latter's transition from state  $k$  to state  $l$  as a result of the weak field  $\mathbf{E}_1$  and in the presence of the intense field  $\mathbf{E}_2$  is given by

$$\begin{aligned}
\langle k | M_{\alpha} | l \rangle_{E_1, E_2} &\equiv \int \Psi_k^* M_{\alpha} \Psi_l d\tau = \langle k | M_{\alpha} | l \rangle e^{i\omega_k t} + \\
& + \frac{1}{2} \{ A_{\alpha\beta}^{kl} (+\omega_1) E_{1\beta}^+ e^{i(\omega_1 + \omega_k)t} + A_{\alpha\beta}^{kl} (-\omega_1) E_{1\beta}^- e^{-i(\omega_1 - \omega_k)t} \} + \\
& + \frac{1}{4} \{ B_{\alpha\beta\gamma}^{kl} (+\omega_1, +\omega_2) E_{1\beta}^+ E_{2\gamma}^+ e^{i(\omega_1 + \omega_2 + \omega_k)t} + B_{\alpha\beta\gamma}^{kl} (+\omega_1, -\omega_2) E_{1\beta}^+ E_{2\gamma}^- e^{i(\omega_1 - \omega_2 + \omega_k)t} + \\
& + B_{\alpha\beta\gamma}^{kl} (-\omega_1, +\omega_2) E_{1\beta}^- E_{2\gamma}^+ e^{-i(\omega_1 - \omega_2 - \omega_k)t} + B_{\alpha\beta\gamma}^{kl} (-\omega_1, -\omega_2) E_{1\beta}^- E_{2\gamma}^- e^{-i(\omega_1 + \omega_2 - \omega_k)t} \} + \\
& + \frac{1}{16} \{ C_{\alpha\beta\gamma\delta}^{kl} (+\omega_1, +\omega_2, +\omega_2) E_{1\beta}^+ E_{2\gamma}^+ E_{2\delta}^+ e^{i(\omega_1 + 2\omega_2 + \omega_k)t} + \\
& + C_{\alpha\beta\gamma\delta}^{kl} (+\omega_1, +\omega_2, -\omega_2) E_{1\beta}^+ E_{2\gamma}^+ E_{2\delta}^- e^{i(\omega_1 + \omega_k)t} +
\end{aligned}$$

$$\begin{aligned}
& + C_{\alpha\beta\gamma\delta}^{kl}(\omega_1, -\omega_2, +\omega_2) E_{1\beta}^+ E_{2\gamma}^- E_{2\delta}^+ e^{i(\omega_1 + \omega_k)t} + \\
& + C_{\alpha\beta\gamma\delta}^{kl}(\omega_1, -\omega_2, -\omega_2) E_{1\beta}^+ E_{2\gamma}^- E_{2\delta}^- e^{i(\omega_1 - 2\omega_2 + \omega_k)t} + \\
& + C_{\alpha\beta\gamma\delta}^{kl}(-\omega_1, +\omega_2, +\omega_2) E_{1\beta}^- E_{2\gamma}^+ E_{2\delta}^+ e^{-i(\omega_1 - 2\omega_2 - \omega_k)t} + \\
& + C_{\alpha\beta\gamma\delta}^{kl}(-\omega_1, +\omega_2, -\omega_2) E_{1\beta}^- E_{2\gamma}^+ E_{2\delta}^- e^{-i(\omega_1 - \omega_k)t} + \\
& + C_{\alpha\beta\gamma\delta}^{kl}(-\omega_1, -\omega_2, +\omega_2) E_{1\beta}^- E_{2\gamma}^- E_{2\delta}^+ e^{-i(\omega_1 - \omega_k)t} + \\
& + C_{\alpha\beta\gamma\delta}^{kl}(-\omega_1, -\omega_2, -\omega_2) E_{1\beta}^- E_{2\gamma}^- E_{2\delta}^- e^{-i(\omega_1 + 2\omega_2 - \omega_k)t} \} + \dots \quad (7)
\end{aligned}$$

Here, the first term, which is independent of the electric field strengths, describes spontaneous emission or absorption of light of the frequency  $\omega_{kl}$ . The second term, together with the tensor

$$\begin{aligned}
A_{\alpha\beta}^{kl}(\pm\omega_1) &= \sum_{mn} \langle m | M_\alpha | n \rangle \{ \delta_{km} a_{\beta}^{nl}(\pm\omega_1) + a_{\beta}^{km}(\mp\omega_1) \delta_{nl} \} \\
&= \frac{1}{\hbar} \sum_m \left\{ \frac{\langle k | M_\alpha | m \rangle \langle m | M_\beta | l \rangle}{\omega_{ml} \pm \omega_1} + \frac{\langle k | M_\beta | m \rangle \langle m | M_\alpha | l \rangle}{\omega_{mk} \mp \omega_1} \right\} \quad (8)
\end{aligned}$$

accounts for the linear polarization of the system by the field  $\mathbf{E}_1$ ; this is precisely the result obtained by Kramers and Heisenberg (1925).  $A_{\alpha\beta}^{kl}$  is the optical polarizability tensor of the system in the transition  $k \rightarrow l$ .

The next two terms of Eq. (7), which are proportional to  $E_1 E_2$  and  $E_1 E_2^2$ , describe the non-linear optical polarization of the system arising through the effect thereon of the strong, oscillating electric field  $E_2$ . This non-linear polarization of the quantum system is characterized by the following tensors:

$$\begin{aligned}
B_{\alpha\beta\gamma}^{kl}(\pm\omega_1, \pm\omega_2) &= \sum_{mn} \langle m | M_\alpha | n \rangle \{ \delta_{km} b_{\beta\gamma}^{nl}(\pm\omega_1, \pm\omega_2) + \\
& + a_{\beta}^{km}(\mp\omega_1) a_{\gamma}^{nl}(\pm\omega_2) + a_{\gamma}^{km}(\mp\omega_2) a_{\beta}^{nl}(\pm\omega_1) + b_{\beta\gamma}^{km}(\mp\omega_1, \mp\omega_2) \delta_{nl} \}, \quad (9) \\
C_{\alpha\beta\gamma\delta}^{kl}(\pm\omega_1, \pm\omega_2, \pm\omega_2) &= 2 \sum_{mn} \langle m | M_\alpha | n \rangle \{ \delta_{km} c_{\beta\gamma\delta}^{nl}(\pm\omega_1, \pm\omega_2, \pm\omega_2) + \\
& + a_{\beta}^{km}(\mp\omega_1) b_{\gamma\delta}^{nl}(\pm\omega_2, \pm\omega_2) + b_{\gamma\delta}^{km}(\mp\omega_2, \mp\omega_2) a_{\beta}^{nl}(\pm\omega_1) + b_{\beta\delta}^{km}(\mp\omega_1, \mp\omega_2) a_{\gamma}^{nl}(\pm\omega_2) + \\
& + a_{\gamma}^{km}(\mp\omega_2) b_{\beta\delta}^{nl}(\pm\omega_1, \pm\omega_2) + c_{\beta\gamma\delta}^{km}(\mp\omega_1, \mp\omega_2, \mp\omega_2) \delta_{nl} \}, \quad (10)
\end{aligned}$$

wherein the coefficients depending on the frequencies  $\omega_1$  and  $\omega_2$  are given by (6) (the explicit form of Eqs (9) and (10) is given in Appendix C).

### 3. General form of the tensor of light scattering

We are now interested in the dipole moment  $\mathbf{P}$  induced in the quantum system by the field  $\mathbf{E}_1$  in the presence of the strong electric field  $\mathbf{E}_2$ . The matrix element of  $\mathbf{P}$  is given by

$$\mathbf{P}_{kl} = \langle k | \mathbf{M} | l \rangle_{E_1, E_2} - \langle k | \mathbf{M} | l \rangle e^{i\omega_{kl}t}. \quad (11)$$



It is thus seen that the intense electric field of frequency  $\omega_2$  enforces additional, non-coherent scattering of light with the frequencies  $\omega_1 \pm \omega_2 \pm \omega_{kl}$  and  $\omega_1 \pm 2\omega_2 \pm \omega_{kl}$ . In the general case, as can be seen from (13), the fundamental oscillations of frequency  $\omega_1$  and the transition frequencies  $\omega_{kl}$  are increased or diminished in the scattered light by the amounts  $\omega_2$  and  $2\omega_2$  in various combinations. The classical interpretation of the non-linear terms of Raman scattering is given in Appendix A.

In the special case when the quantum system reverts to its initial state,  $k = l$ , the scattering tensor (13) reduces to

$$I_{\sigma\tau}^{kk} = I_{\sigma\tau}^{\omega_1} + I_{\sigma\tau}^{\omega_1+\omega_2} + I_{\sigma\tau}^{\omega_1-\omega_2} + I_{\sigma\tau}^{\omega_1+2\omega_2} + I_{\sigma\tau}^{\omega_1-2\omega_2} + \dots; \quad (17)$$

herein, beside scattering with the frequency  $\omega_1$  of the primary light wave, appear additional scattering components with the harmonic frequencies  $\omega_1 \pm \omega_2$  and  $\omega_1 \pm 2\omega_2$  resulting from superposition upon  $\omega_1$  of the frequency  $\omega_2$  of the field  $\mathbf{E}_2$ .

The tensor

$$\begin{aligned} I_{\sigma\tau}^{\omega_1} = & \frac{1}{2} \omega_1^4 \left\{ \langle A_{\sigma\nu}^{\omega_1} A_{\tau\varrho}^{\omega_1} \rangle_{E_2}^{A\nu} + \frac{1}{4} \langle A_{\sigma\nu}^{\omega_1} C_{\tau\varrho\lambda\mu}^{\omega_1} + C_{\sigma\nu\lambda\mu}^{\omega_1} A_{\tau\varrho}^{\omega_1} \rangle_{E_2}^{A\nu} \dot{E}_{2\lambda} \dot{E}_{2\mu} + \right. \\ & \left. + \frac{1}{16} \langle C_{\sigma\nu\lambda\mu}^{\omega_1} C_{\tau\varrho\theta\chi}^{\omega_1} \rangle_{E_2}^{A\nu} \dot{E}_{2\lambda} \dot{E}_{2\mu} \dot{E}_{2\theta} \dot{E}_{2\chi} + \dots \right\} \dot{E}_{1\nu} \dot{E}_{1\varrho} \end{aligned} \quad (18)$$

describes coherent scattering of light, consisting of linear, Rayleigh light scattering, and non-linear light scattering due to a strong field  $E_2$  of zero oscillation frequency. The tensors  $A_{\sigma\tau}^{\omega_1} \equiv A_{\sigma\tau}^{kk}(\pm\omega_1)$  and  $C_{\sigma\tau\nu\varrho}^{\omega_1} \equiv C_{\sigma\tau\nu\varrho}^{kk}(\pm\omega_1, \pm\omega_2, \mp\omega_2)$  can be obtained explicitly from (8) and (10), respectively, putting  $k = l$ .

The remaining tensors of the expansion (17) are determined, with regard to (15) and (16), as follows:

$$I_{\sigma\tau}^{\omega_1 \pm \omega_2} = \frac{1}{8} (\omega_1 \pm \omega_2)^4 \langle B_{\sigma\nu\lambda}^{\omega_1 \pm \omega_2} B_{\tau\varrho\mu}^{\omega_1 \pm \omega_2} \rangle_{E_2}^{A\nu} \dot{E}_{1\nu} \dot{E}_{1\varrho} \dot{E}_{2\lambda} \dot{E}_{2\mu}, \quad (19)$$

$$I_{\sigma\tau}^{\omega_1 \pm 2\omega_2} = \frac{1}{128} (\omega_1 \pm 2\omega_2)^4 \langle C_{\sigma\nu\lambda\mu}^{\omega_1 \pm 2\omega_2} C_{\tau\varrho\theta\chi}^{\omega_1 \pm 2\omega_2} \rangle_{E_2}^{A\nu} \dot{E}_{1\nu} \dot{E}_{1\varrho} \dot{E}_{2\lambda} \dot{E}_{2\mu} \dot{E}_{2\theta} \dot{E}_{2\chi}, \quad (20)$$

where the notation  $B_{\sigma\tau\nu}^{\omega_1 \pm \omega_2} \equiv B_{\sigma\tau\nu}^{kk}(\pm\omega_1, \pm\omega_2)$  and  $C_{\sigma\tau\nu\varrho}^{\omega_1 \pm 2\omega_2} = C_{\sigma\tau\nu\varrho}^{kk}(\pm\omega_1, \pm\omega_2, \pm\omega_2)$  has been introduced. From (6) and (9), we have for  $k = l$

$$\begin{aligned} B_{\alpha\beta\gamma}^{\omega_1 \pm \omega_2} = & \frac{1}{\hbar^2} \sum_{mn} \left\{ \langle k | M_\alpha | m \rangle \left[ \frac{\langle m | M_\beta | n \rangle \langle n | M_\gamma | k \rangle}{(\omega_{mk} \pm \omega_1 \pm \omega_2) (\omega_{nk} \pm \omega_2)} + \frac{\langle m | M_\gamma | n \rangle \langle n | M_\beta | k \rangle}{(\omega_{mk} \pm \omega_1 \pm \omega_2) (\omega_{nk} \pm \omega_1)} \right] + \right. \\ & + \langle m | M_\alpha | n \rangle \left[ \frac{\langle k | M_\beta | m \rangle \langle n | M_\gamma | k \rangle}{(\omega_{mk} \mp \omega_1) (\omega_{nk} \pm \omega_2)} + \frac{\langle k | M_\gamma | m \rangle \langle n | M_\beta | k \rangle}{(\omega_{mk} \mp \omega_2) (\omega_{nk} \pm \omega_1)} \right] + \\ & \left. + \left[ \frac{\langle k | M_\beta | m \rangle \langle m | M_\gamma | n \rangle}{(\omega_{mk} \mp \omega_1) (\omega_{mk} \mp \omega_1 \mp \omega_2)} + \frac{\langle k | M_\gamma | m \rangle \langle m | M_\beta | n \rangle}{(\omega_{mk} \mp \omega_2) (\omega_{nk} \mp \omega_1 \mp \omega_2)} \right] \langle n | M_\alpha | k \rangle \right\}. \end{aligned} \quad (21a)$$

Similarly, we can derive explicitly the tensor  $C_{\alpha\beta\gamma}^{\omega_1\pm 2\omega_2}$  on recurring to Eqs (6) and (10), for  $k = l$ ; namely, we have

$$\begin{aligned}
C_{\alpha\beta\gamma\delta}^{\omega_1\pm 2\omega_2} = & \frac{2}{\hbar^3} \sum_{mnr} \left\{ \langle k|M_\alpha|n\rangle \left[ \frac{\langle n|M_\beta|r\rangle \langle r|M_\gamma|m\rangle \langle m|M_\delta|k\rangle}{(\omega_{nk}\pm\omega_1\pm 2\omega_2)(\omega_{rk}\pm 2\omega_2)(\omega_{mk}\pm\omega_2)} + \right. \right. \\
& + \frac{\langle n|M_\gamma|r\rangle \langle r|M_\delta|m\rangle \langle m|M_\beta|k\rangle}{(\omega_{nk}\pm\omega_1\pm 2\omega_2)(\omega_{rk}\pm\omega_1\pm\omega_2)(\omega_{mk}\pm\omega_1)} + \left. \frac{\langle n|M_\delta|r\rangle \langle r|M_\beta|m\rangle \langle m|M_\gamma|k\rangle}{(\omega_{nk}\pm\omega_1\pm 2\omega_2)(\omega_{rk}\pm\omega_1\pm\omega_2)(\omega_{mk}\pm\omega_2)} \right] + \\
& + \langle m|M_\alpha|n\rangle \left[ \frac{\langle k|M_\beta|r\rangle \langle r|M_\delta|m\rangle \langle n|M_\gamma|k\rangle}{(\omega_{rk}\mp\omega_1)(\omega_{mk}\mp\omega_1\mp\omega_2)(\omega_{nk}\pm\omega_2)} + \frac{\langle k|M_\delta|r\rangle \langle r|M_\beta|m\rangle \langle n|M_\gamma|k\rangle}{(\omega_{rk}\mp\omega_2)(\omega_{mk}\mp\omega_1\mp\omega_2)(\omega_{nk}\pm\omega_2)} + \right. \\
& + \frac{\langle k|M_\gamma|m\rangle \langle n|M_\beta|r\rangle \langle r|M_\delta|k\rangle}{(\omega_{mk}\mp\omega_2)(\omega_{nk}\pm\omega_1\pm\omega_2)(\omega_{rk}\pm\omega_2)} + \frac{\langle k|M_\gamma|m\rangle \langle n|M_\delta|r\rangle \langle r|M_\beta|k\rangle}{(\omega_{mk}\mp\omega_2)(\omega_{nk}\pm\omega_1\pm\omega_2)(\omega_{rk}\pm\omega_1)} + \\
& + \left. \frac{\langle k|M_\beta|m\rangle \langle n|M_\gamma|r\rangle \langle r|M_\delta|k\rangle}{(\omega_{mk}\mp\omega_1)(\omega_{nk}\pm 2\omega_2)(\omega_{rk}\pm\omega_2)} + \frac{\langle k|M_\gamma|r\rangle \langle r|M_\delta|m\rangle \langle n|M_\beta|k\rangle}{(\omega_{rk}\mp\omega_2)(\omega_{mk}\mp 2\omega_2)(\omega_{nk}\pm\omega_1)} \right] + \\
& + \left[ \frac{\langle k|M_\delta|r\rangle \langle r|M_\gamma|n\rangle \langle n|M_\beta|m\rangle}{(\omega_{rk}\mp\omega_2)(\omega_{nk}\mp 2\omega_2)(\omega_{mk}\mp\omega_1\mp 2\omega_2)} + \frac{\langle k|M_\beta|r\rangle \langle r|M_\delta|n\rangle \langle n|M_\gamma|m\rangle}{(\omega_{rk}\mp\omega_1)(\omega_{nk}\mp\omega_1\mp\omega_2)(\omega_{mk}\mp\omega_1\mp 2\omega_2)} + \right. \\
& \left. + \frac{\langle k|M_\gamma|r\rangle \langle r|M_\beta|n\rangle \langle n|M_\delta|m\rangle}{(\omega_{rk}\mp\omega_2)(\omega_{mk}\mp\omega_1\mp\omega_2)(\omega_{mk}\mp\omega_1\mp 2\omega_2)} \right] \langle m|M_\alpha|k\rangle \Big\}. \quad (21b)
\end{aligned}$$

#### 4. The tensor of light scattering in the classical case

We now proceed to the discussion of the scattering tensor  $I_{\sigma\tau}^{kk}$  for the purely classical case. To this purpose, we go over from the tensors  $A_{\alpha\beta}$ ,  $B_{\alpha\beta\gamma}$  and  $C_{\alpha\beta\gamma\delta}$  to the tensors  $a_{\alpha\beta}$ ,  $b_{\alpha\beta\gamma}$  and  $c_{\alpha\beta\gamma\delta}$  related with the molecular coordinate system and characterizing the classical properties of the isolated molecules. On averaging in (18)–(20) the transformation coefficients between the laboratory and molecular reference systems over all possible molecular orientations with equal probability (here, we omit the terms proportional to  $E_1^2 E_2^4$ , to be discussed in Appendix B for optically isotropic systems), we obtain

$$\begin{aligned}
I_{\sigma\tau}^{\omega_1} = & \frac{\omega_1^4}{60} \left\{ \langle a_{\alpha\gamma} a_{\beta\delta} \rangle [5\delta_{\alpha\beta} \delta_{\gamma\delta} f_{1\sigma\tau} + \sigma_{\alpha\beta\gamma\delta} f_{2\sigma\tau}] + \frac{1}{28} \langle a_{\alpha\gamma} c_{\beta\delta\epsilon\eta} + c_{\alpha\gamma\epsilon\eta} a_{\beta\delta} \rangle [35\delta_{\alpha\beta} \delta_{\gamma\delta} \delta_{\epsilon\eta} g_{1\sigma\tau} + \right. \\
& \left. + 7(\delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta} g_{2\sigma\tau} + \delta_{\gamma\delta} \sigma_{\epsilon\eta\alpha\beta} g_{3\sigma\tau} + \delta_{\epsilon\eta} \sigma_{\alpha\beta\gamma\delta} g_{4\sigma\tau}) + \sigma_{\alpha\beta\gamma\delta\epsilon\eta} g_{5\sigma\tau} + \dots \right\}, \quad (22)
\end{aligned}$$

$$\begin{aligned}
I_{\sigma\tau}^{\omega_1\pm\omega_2} = & \frac{(\omega_1\pm\omega_2)^4}{1680} \langle b_{\alpha\gamma\epsilon} b_{\beta\delta\eta} \rangle \{ 35\delta_{\alpha\beta} \delta_{\gamma\delta} \delta_{\epsilon\eta} g_{1\sigma\tau} + 7(\delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta} g_{2\sigma\tau} + \delta_{\gamma\delta} \sigma_{\epsilon\eta\alpha\beta} g_{3\sigma\tau} + \\
& + \delta_{\epsilon\eta} \sigma_{\alpha\beta\gamma\delta} g_{4\sigma\tau}) + \sigma_{\alpha\beta\gamma\delta\epsilon\eta} g_{5\sigma\tau} \}, \quad (23)
\end{aligned}$$



where we have used the notation

$$\begin{aligned}
 f_{1\sigma\tau} &= \delta_{\sigma\tau} \dot{E}_1^2 - \dot{E}_{1\sigma} \dot{E}_{1\tau}, & f_{2\sigma\tau} &= 3\dot{E}_{1\sigma} \dot{E}_{1\tau} - \delta_{\sigma\tau} \dot{E}_1^2, \\
 g_{1\sigma\tau} &= \delta_{\sigma\tau} \dot{E}_1^2 \dot{E}_2^2 + 2\dot{E}_{1\sigma} \dot{E}_{2\tau} (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2) - \dot{E}_1^2 \dot{E}_{2\sigma} \dot{E}_{2\tau} - \dot{E}_{1\sigma} \dot{E}_{1\tau} \dot{E}_2^2 - \delta_{\sigma\tau} (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2)^2, \\
 g_{2\sigma\tau} &= -\delta_{\sigma\tau} \dot{E}_1^2 \dot{E}_2^2 - 3\dot{E}_{1\sigma} \dot{E}_{2\tau} (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2) + \dot{E}_1^2 \dot{E}_{2\sigma} \dot{E}_{2\tau} + \dot{E}_{1\sigma} \dot{E}_{1\tau} \dot{E}_2^2 + 2\delta_{\sigma\tau} (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2)^2, \\
 g_{3\sigma\tau} &= -\delta_{\sigma\tau} \dot{E}_1^2 \dot{E}_2^2 - 3\dot{E}_{1\sigma} \dot{E}_{2\tau} (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2) + \dot{E}_1^2 \dot{E}_{2\sigma} \dot{E}_{2\tau} + 2\dot{E}_{1\sigma} \dot{E}_{1\tau} \dot{E}_2^2 + \delta_{\sigma\tau} (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2)^2, \\
 g_{4\sigma\tau} &= -\delta_{\sigma\tau} \dot{E}_1^2 \dot{E}_2^2 - 3\dot{E}_{1\sigma} \dot{E}_{2\tau} (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2) + 2\dot{E}_1^2 \dot{E}_{2\sigma} \dot{E}_{2\tau} + \dot{E}_{1\sigma} \dot{E}_{1\tau} \dot{E}_2^2 + \delta_{\sigma\tau} (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2)^2, \\
 g_{5\sigma\tau} &= 2\delta_{\sigma\tau} \dot{E}_1^2 \dot{E}_2^2 + 9\dot{E}_{1\sigma} \dot{E}_{2\tau} (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2) - 3\dot{E}_1^2 \dot{E}_{2\sigma} \dot{E}_{2\tau} - 3\dot{E}_{1\sigma} \dot{E}_{1\tau} \dot{E}_2^2 - 3\delta_{\sigma\tau} (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2)^2, \quad (24)
 \end{aligned}$$

and

$$\begin{aligned}
 \sigma_{\alpha\beta\gamma\delta} &= \delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}, \\
 \sigma_{\alpha\beta\gamma\delta\epsilon\eta} &= \delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta} + \delta_{\alpha\gamma} \sigma_{\delta\epsilon\eta\beta} + \delta_{\alpha\delta} \sigma_{\epsilon\eta\beta\gamma} + \delta_{\alpha\epsilon} \sigma_{\eta\beta\gamma\delta} + \delta_{\alpha\eta} \sigma_{\beta\gamma\delta\epsilon}; \quad (25)
 \end{aligned}$$

$\delta_{\alpha\beta}$  being the unit tensor.

The expressions (22) and (23) hold for scattering molecules of arbitrary symmetry, and for arbitrary mutual configurations of the vectors  $\mathbf{E}_1$  and  $\mathbf{E}_2$  as prescribed in the laboratory reference system. We shall discuss these expressions for certain types of symmetry of the scattering molecules.

### Molecules with a centre of inversion

For the case of molecules having a centre of inversion, all elements of the tensor  $b_{\alpha\beta\gamma}$  vanish, and so does the scattering tensor  $I_{\sigma\tau}^{\omega_1 \pm \omega_2}$ . Thus, we have now to consider only the scattering tensor  $I_{\sigma\tau}^{\omega_1}$  given by (22).

Let us begin by considering molecules possessing the symmetry of the point group  $D_{4h}$  (e.g.,  $C_4H_8$ ), for which the non-vanishing elements of the tensors  $a_{\alpha\beta}$  and  $c_{\alpha\beta\gamma\delta}$  are given as follows:

$$\begin{aligned}
 a_{\alpha\beta} &= a_{11} \delta_{\alpha\beta} + (a_{33} - a_{11}) k_\alpha k_\beta, \\
 c_{\alpha\beta\gamma\delta} &= (c_{1111} - c_{1122} - 2c_{1212}) (i_\alpha i_\beta i_\gamma i_\delta + j_\alpha j_\beta j_\gamma j_\delta) + (c_{1122} - c_{1133} - c_{3311} + 2c_{1212} - 4c_{1313} + c_{3333}) \times \\
 &\times k_\alpha k_\beta k_\gamma k_\delta + c_{1122} (\delta_{\alpha\beta} \delta_{\gamma\delta} - \delta_{\alpha\beta} k_\gamma k_\delta - \delta_{\gamma\delta} k_\alpha k_\beta) + c_{1212} (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) + c_{1133} \delta_{\alpha\beta} k_\gamma k_\delta + \\
 &+ c_{3311} \delta_{\gamma\delta} k_\alpha k_\beta + (c_{1313} - c_{1212}) (\delta_{\alpha\gamma} k_\beta k_\delta + \delta_{\alpha\delta} k_\beta k_\gamma + \delta_{\beta\delta} k_\alpha k_\gamma + \delta_{\beta\gamma} k_\alpha k_\delta), \quad (26)
 \end{aligned}$$

$\mathbf{i}$ ,  $\mathbf{j}$ ,  $\mathbf{k}$  being the unit vectors of the molecular reference system.

For molecules of the point groups  $C_{6h}$  (e.g.,  $C_6Cl_6$ ) and  $D_{6h}$  (e.g.,  $C_6H_6$ ), one has to put herein  $2c_{1212} = c_{1111} - c_{1122}$ , whence by (22) we have

$$I_{\sigma\tau}^{\omega_1} = \frac{\omega_1^4}{10} \left\{ 5a^2 \hat{E}_{1\sigma} \hat{E}_{1\tau} + a^2 \kappa_a (3\delta_{\sigma\tau} \hat{E}_1^2 + \hat{E}_{1\sigma} \hat{E}_{1\tau}) + \frac{a}{14} [7(2c_{1111} + 2c_{1122} + 2c_{1133} + 2c_{3311} + c_{3333}) (5g_{1\sigma\tau} + g_{2\sigma\tau} + g_{3\sigma\tau} + 5g_{4\sigma\tau} + g_{5\sigma\tau}) + 14(3c_{1111} - c_{1122} + 4c_{1313} + c_{3333}) (g_{2\sigma\tau} + g_{3\sigma\tau} + g_{5\sigma\tau}) + 2\kappa_a (c_{1122} - c_{1111} + 2c_{1313} + 2c_{3333}) (7g_{2\sigma\tau} + 7g_{3\sigma\tau} + 4g_{5\sigma\tau}) + 2\kappa_a (c_{3333} + 2c_{3311} - c_{1111} - c_{1122} - c_{1133}) (35g_{1\sigma\tau} + 7g_{2\sigma\tau} + 7g_{3\sigma\tau} + 14g_{4\sigma\tau} + 2g_{5\sigma\tau}) + 4\kappa_a (c_{3333} + 2c_{1133} - c_{1111} - c_{1122} - c_{3311}) g_{5\sigma\tau} ] \right\}, \quad (27)$$

where  $a = (a_{33} + 2a_{11})/3$  is the mean polarizability and  $\kappa_a = (a_{33} - a_{11})/3a$  — the optical anisotropy of the isolated molecule. The expression of Eq. (27) is moreover applicable to a great variety of linear molecules belonging to the point group  $D_{\infty h}$  (e.g.,  $H_2$ ,  $O_2$ ,  $CO_2$ ,  $CS_2$ ,  $C_2H_2$ ,  $C_2H_4$ , and so forth).

In particular, in the case of the point groups  $T_h$  and  $O_h$  (e.g., for  $SF_6$  and  $UF_6$ ), we have to put  $a_{11} = a_{33} = a$  and  $c_{1111} = c_{3333}$ ,  $c_{1122} = c_{1133} = c_{3311}$ ,  $c_{1212} = c_{1313}$  in Eq. (26), whence

$$a_{\alpha\beta} = a\delta_{\alpha\beta}, \quad c_{\alpha\beta\gamma\delta} = c_{1122}\delta_{\alpha\beta}\delta_{\gamma\delta} + c_{1313}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) + (c_{1111} - c_{1122} - 2c_{1313})(i_\alpha i_\beta i_\gamma i_\delta + j_\alpha j_\beta j_\gamma j_\delta + k_\alpha k_\beta k_\gamma k_\delta), \quad (28)$$

and the scattering tensor (22) reduces to

$$I_{\sigma\tau}^{\omega_1} = \frac{1}{2} \omega_1^4 \left\{ a^2 \hat{E}_{1\sigma} \hat{E}_{1\tau} + \frac{1}{10} a [(c_{1111} + 4c_{1212} - 2c_{1313}) \hat{E}_{1\sigma} \hat{E}_{1\tau} \hat{E}_2^2 + 2(c_{1111} - c_{1122} + 3c_{1313}) \hat{E}_{1\sigma} \hat{E}_{2\tau} (\hat{E}_1 \cdot \hat{E}_2)] \right\}. \quad (29)$$

In the case of isotropic molecules  $2c_{1313} = c_{1111} - c_{1122}$ , and the above formula becomes simply

$$I_{\sigma\tau}^{\omega_1} = \frac{1}{2} \omega_1^4 \left\{ a^2 E_{1\sigma} E_{1\tau} + \frac{a}{2} [c_{1122} \hat{E}_{1\sigma} \hat{E}_{1\tau} \hat{E}_2^2 + (c_{1111} - c_{1122}) \hat{E}_{1\sigma} \hat{E}_{2\tau} (\hat{E}_1 \cdot \hat{E}_2)] \right\}. \quad (30)$$

#### Molecules without a centre of inversion

We shall now consider the scattering tensor  $I_{\sigma\tau}^{\omega_1 \pm \omega_2}$ , which is non-zero for molecules possessing no centre of inversion, since in their case not all elements of the tensor  $b_{\alpha\beta\gamma}$  vanish.

The components of the tensor  $b_{\alpha\beta\gamma}$  of the symmetry group  $D_2$  are of the form

$$b_{\alpha\beta\gamma} = b_{123} (i_\alpha j_\beta + j_\alpha i_\beta) k_\gamma + b_{231} (j_\alpha k_\beta + k_\alpha j_\beta) i_\gamma + b_{312} (k_\alpha i_\beta + i_\alpha k_\beta) j_\gamma, \quad (31)$$

consequently, the scattering tensor (23) becomes

$$I_{\sigma\tau}^{\omega_1 \pm \omega_2} = \frac{(\omega_1 \pm \omega_2)^4}{840} \{ b_{123}^2 + b_{231}^2 + b_{312}^2 \} \{ 5\delta_{\sigma\tau} \hat{E}_1^2 \hat{E}_2^2 - 2\hat{E}_{1\sigma} \hat{E}_{2\tau} (\hat{E}_1 \cdot \hat{E}_2) + 3\hat{E}_1^2 \hat{E}_{2\sigma} \hat{E}_{2\tau} + 3\hat{E}_{1\sigma} \hat{E}_{1\tau} \hat{E}_2^2 + 3\delta_{\sigma\tau} (\hat{E}_1 \cdot \hat{E}_2)^2 \}. \quad (32)$$

Hence, for  $b_{231} = b_{312} \neq b_{123}$ , we obtain an expression for the point group  $D_{2d}$  (e.g.,  $C_3H_4$ ). If, in particular,  $b_{123} = b_{331} = b_{312}$ , Eq. (32) holds for molecules of symmetry  $T_d$  (e.g.,  $CH_4$ ,  $CF_4$ ,  $SiCl_4$ , etc.). Tetrahedral molecules also have a scattering tensor  $I_{\sigma\tau}^{\omega_1}$  given by (29).

Molecules of symmetry  $D_{3h}$  (e.g.,  $BCl_3$ ,  $C_3H_6$ ,  $C_6H_3Cl_3$ ) have the following non vanishing elements:

$$b_{\alpha\beta\gamma} = b_{111}\{(i_\alpha i_\beta - j_\alpha j_\beta)i_\gamma - (i_\alpha j_\beta + j_\alpha i_\beta)j_\gamma\}, \quad (33)$$

and the tensor  $I_{\sigma\tau}^{\omega_1 \pm \omega_2}$  is obtained in the form of (32) on replacing  $b_{123}^2 + b_{231}^2 + b_{312}^2$  therein by  $2b_{111}^2$ . For this group, the tensor  $I_{\sigma\tau}^{\omega_1}$  is valid in the form (27).

Let us now proceed to the symmetry of the point group  $C_{3v}$  (comprising the molecules  $NH_3$ ,  $CHCl_3$ ,  $CH_3CN$  etc.), for which

$$b_{\alpha\beta\gamma} = b_{222}\{(j_\alpha j_\beta - i_\alpha i_\beta)j_\delta - (i_\alpha j_\beta + i_\beta j_\alpha)i_\gamma\} + b_{333}k_\alpha k_\beta k_\gamma + \\ + b_{113}(\delta_{\alpha\beta}k_\gamma - k_\alpha k_\beta k_\gamma) + b_{131}(\delta_{\alpha\gamma}k_\beta + \delta_{\beta\gamma}k_\alpha - 2k_\alpha k_\beta k_\gamma); \quad (34)$$

Eq. (23) now yields the result

$$I_{\sigma\tau}^{\omega_1 \pm \omega_2} = \frac{(\omega_1 \pm \omega_2)^4}{1680} \{(b_{333}^2 + 2b_{113}^2 + 4b_{131}^2 + 4b_{222}^2) [35g_{1\sigma\tau} + 14(g_{2\sigma\tau} + g_{3\sigma\tau} + \\ + g_{4\sigma\tau}) + 6g_{5\sigma\tau}] + (b_{333} + 3b_{113})^2 (7g_{4\sigma\tau} + g_{5\sigma\tau}) + 4(b_{333} + 2b_{113}) (b_{333} + 2b_{131})g_{5\sigma\tau} + \\ + (b_{333}^2 + 2b_{131}^2 - 2b_{113}^2 + 4b_{333}b_{131} + 4b_{131}b_{113}) (7g_{2\sigma\tau} + 7g_{3\sigma\tau} + 4g_{5\sigma\tau})\}. \quad (35)$$

On putting herein  $b_{222} = 0$ , we have an expression that holds for molecules of the point group  $C_{4v}$  ( $BrF_5$ ,  $JF_5$ ),  $C_{6v}$  as well as  $C_{\infty v}$  (e.g.,  $CH$ ,  $NH$ ,  $NaCl$ ,  $OCS$ ,  $CICN$ , and the like). For the last two groups, Eq. (27) holds also.

Similarly, the scattering tensors (22) and (23) can be discussed for molecules of the low symmetry point groups  $D_{2h}$  ( $C_2J_2$ ,  $C_2H_4$ ),  $C_{2v}$  ( $H_2O$ ,  $CH_2Cl_2$ ,  $C_6H_5NO_2$  etc.),  $C_2$  ( $H_2O_2$ ),  $C_1$  ( $ONCl$ ,  $CH_3NO_2$ ), and so on. Within these groups, however, the tensors  $a_{\alpha\beta}$ ,  $b_{\alpha\beta\gamma}$  and  $c_{\alpha\beta\gamma\delta}$  possess a larger number of mutually independent components than above, and the formulas for the tensors  $I_{\sigma\tau}^{\omega_1}$  and  $I_{\sigma\tau}^{\omega_1 \pm \omega_2}$  become highly involved; we refrain from writing them out in detail here.

### 5. Non-linear variations of the Rayleigh ratio and degree of depolarization

Let us assume a weak light beam to propagate in the direction of the  $Y$ -axis of the laboratory reference system with its electric vector oscillating in the  $XZ$ -plane at an angle  $\psi$  to the plane  $XY$  (the plane of observation); thus,  $\mathbf{E}_1 = (\mathbf{x} \cos \psi + \mathbf{z} \sin \psi)E_1$ ,  $\mathbf{x}$ ,  $\mathbf{y}$  and  $\mathbf{z}$  being the unit vectors of the laboratory system  $XYZ$ . The light scattered is observed along the  $X$ -axis (perpendicularly to the direction of incidence), the configuration of the vector  $\mathbf{E}_2$  in the laboratory system being, as yet, arbitrary.

If the scattering medium consists of a gas of volume  $V$  containing  $N$  mutually non-interacting molecules, Rayleigh's ratio is given by the expression

$$S = \frac{2N}{c_1^4 V E_1^2} (I_{\sigma\tau}^{kk} y_\sigma y_\tau + I_{\sigma\tau}^{kk} z_\sigma z_\tau), \quad (36)$$

where  $c_1$  is the velocity of light propagation.

In the case of scattering by an atomic gas or by one whose molecules are optically isotropic, substitution of the tensor (30) into Eq. (36) yields the relation

$$S = \frac{\omega_1^4 N}{2V} \left\{ a^2 \sin^2 \psi + \frac{a}{2} [c_{1122} \overset{\circ}{E}_2^2 \sin^2 \psi + (c_{1111} - c_{1122}) (\overset{\circ}{E}_{2x} \overset{\circ}{E}_{2z} \sin \psi \cos \psi + \overset{\circ}{E}_{2z}^2 \cos^2 \psi) \right\} \overset{\circ}{E}_1^2, \quad (37)$$

which, for non-polarized incident light ( $\overline{\sin^2 \psi} = \overline{\cos^2 \psi} = \frac{1}{2}$ ,  $\overline{\sin \psi \cos \psi} = 0$ ), can be represented as follows:

$$\frac{S - S_0}{S_0} = \frac{1}{2} \left\{ \left( \frac{c_{1122}}{a} \right) \overset{\circ}{E}_2^2 + \left( \frac{c_{1111} - c_{1122}}{a} \right) \overset{\circ}{E}_{2z}^2 \right\}, \quad (38)$$

where  $S_0 = \frac{1}{2} (\omega_1/c_1)^4 (N/V) a^2$  is the Rayleigh coefficient in the absence of the strong light beam ( $E_2 = 0$ ).

By (38), two experiments with a strong light beam polarized and propagating with its electric vector oscillating parallel to the  $Z$ -axis in the one case and parallel to the  $Y$ -axis in the second should yield, respectively,

$$\frac{S - S_0}{S_0} = \frac{1}{2} \left( \frac{c_{1111}}{a} \right) \overset{\circ}{E}_{2z}^2 \quad \text{and} \quad \frac{S - S_0}{S_0} = \frac{1}{2} \left( \frac{c_{1122}}{a} \right) \overset{\circ}{E}_{2y}^2. \quad (39)$$

This enables us to determine separately the coefficients  $c_{1111}$  and  $c_{1122}$  of non-linear deformation of an isotropic molecule for the cases when the vector  $\mathbf{E}_2$  is parallel or perpendicular to the plane of oscillation of the vector  $\mathbf{E}_1$  (the plane  $XZ$ ).

Defining the degree of depolarization of scattered light as

$$D = \frac{I_{\sigma\tau}^{kk} y_\sigma y_\tau}{I_{\sigma\tau}^{kk} z_\sigma z_\tau} = \frac{(I_{\sigma\tau}^{\omega_1} + I_{\sigma\tau}^{\omega_1 + \omega_2}) y_\sigma y_\tau}{(I_{\sigma\tau}^{\omega_1} + I_{\sigma\tau}^{\omega_1 + \omega_2}) z_\sigma z_\tau}, \quad (40)$$

we obtain for tetrahedral molecules, on substituting herein (29) and (32),

$$D = \frac{(\omega_1 + \omega_2)^4}{140\omega_1^4 \sin^2 \psi} \left( \frac{b_{123}}{a} \right)^2 \left\{ 5\overset{\circ}{E}_2^2 + 3\overset{\circ}{E}_{2y}^2 + 3(\overset{\circ}{E}_{2x} \cos \psi + \overset{\circ}{E}_{2z} \sin \psi)^2 \right\}. \quad (41)$$

We have here an interesting result stating that, although with regard to a weak light beam tetrahedral molecules do not depolarize the scattered light at perpendicular observation, it is sufficient to project a strong light beam in any direction and with arbitrary polarization upon the scattering gas in order that some slight depolarization shall appear. We see, moreover, that this depolarization, which is impressed by the strong light beam, is due in the above approximation to the deformation  $b_{123}$  alone and is thus related essentially with the absence of a centre of inversion in the scattering molecules.

Eq. (41) yields, when the incident light is polarized with its electric vector  $\mathbf{E}_1$  oscillating in a plane perpendicular to the plane of observation ( $\psi = 90^\circ$ ),

$$D^\perp = \frac{1}{140} \left( 1 + \frac{\omega_2}{\omega_1} \right)^4 \left( \frac{b_{123}}{a} \right)^2 (8\overset{\circ}{E}_2^2 - 3\overset{\circ}{E}_{2z}^2), \quad (42)$$

or, for non-polarized incident light,

$$D^n = \frac{1}{140} \left(1 + \frac{\omega_2}{\omega_1}\right)^4 \left(\frac{b_{123}}{a}\right)^2 (13\overset{\circ}{E}_{2z}^2 + 3\overset{\circ}{E}_{2y}^2). \quad (43)$$

For the case under consideration, the change in  $S$  due to the strong light beam is given by the formula

$$\begin{aligned} \frac{S-S_0}{S_0} &= \frac{1}{140} \left(1 + \frac{\omega_2}{\omega_1}\right)^4 \left(\frac{b_{123}}{a}\right)^2 (29\overset{\circ}{E}_{2z}^2 + 4\overset{\circ}{E}_{2x}^2) + \\ &+ \frac{1}{10a} \{(c_{1111} + 4c_{1122} - 2c_{1313})\overset{\circ}{E}_{2z}^2 + 2(c_{1111} - c_{1122} + 3c_{1313})\overset{\circ}{E}_{2x}^2\}. \end{aligned} \quad (44)$$

It is thus seen that the Rayleigh ratio is affected by the two non-linear deformations  $b$  and  $c$  of tetrahedral molecules. With  $b_{123} = 0$ , Eq. (44) holds for octahedral molecules.

When calculating  $D$  for anisotropic molecules of intermediate symmetry, in order to avoid dealing with too highly complicated expressions, we shall assume the incident light to be polarized with electric vector oscillating in the plane of observation ( $\psi = 0^\circ$ ). It is readily seen from Eq. (27) that in this case in the absence of the strong light beam  $D_0 = 1$  and in the presence of the latter

$$D - D_0 = - \left(\frac{c\kappa_c}{a\kappa_a}\right) (\overset{\circ}{E}_{2z}^2 - \overset{\circ}{E}_{2y}^2), \quad (45)$$

with  $\kappa_c = (2c_{3333} - 2c_{1133} - 2c_{3311} + 7c_{1122} + 6c_{1313} - 5c_{1111})/7c$  denoting a parameter that determines the anisotropy of non-linear polarizability of molecules belonging to the symmetry groups  $C_{6h}$ ,  $D_{6h}$  and  $D_{\infty h}$ , and  $c = (c_{\alpha\alpha\beta\beta} + c_{\alpha\beta\alpha\beta} + c_{\alpha\beta\beta\alpha})/15 = \{3c_{3333} + 2(3c_{1111} + c_{1122} + c_{1133} + c_{3311} + 2c_{1212} + 4c_{1313})\}/15$ .

For  $CS_2$ , we have (Kielich 1960)  $a = 8.77 \times 10^{-24} \text{ cm}^3$ ,  $\kappa_a = 0.37$ ,  $c = 56.5 \times 10^{-36}$  e.s.u.; on the assumption of  $\kappa_c = \kappa_a$  we have, by (45),  $D - D_0 = -6.4 \times 10^{-12} (\overset{\circ}{E}_{2z}^2 - \overset{\circ}{E}_{2y}^2)$ . Hence, clearly, the non-linear variation of  $D$  should be accessible to observation in  $CS_2$  when applying a strong light beam with electric vector intensity of at least  $10^8$  e.s.u.

For molecules of the symmetry group  $D_{3h}$ , Eq. (45) has to be replaced by

$$D - D_0 = - \left\{ \frac{(\omega_1 + \omega_2)^4}{42\omega_1^4} \left(\frac{b_{111}}{a\kappa_a}\right)^2 + \left(\frac{c\kappa_c}{a\kappa_a}\right) \right\} (\overset{\circ}{E}_{2z}^2 - \overset{\circ}{E}_{2y}^2). \quad (46)$$

For a gas of molecules having the symmetry  $C_{3v}$ , Eqs (35) and (40) yield

$$D - D_0 = - \frac{(\omega_1 + \omega_2)^4}{252\omega_1^4 a^2 \kappa_a^2} \{2(b_{333} - b_{113})^2 + 6b_{222}^2 + 3b_{131}(5b_{131} + 2b_{333} - 2b_{113})\} (\overset{\circ}{E}_{2z}^2 - \overset{\circ}{E}_{2y}^2), \quad (47)$$

this result, for  $b_{222} = 0$  and  $b_{131} = 0$ , reduces to

$$D - D_0 = - \frac{(\omega_1 + \omega_2)^4}{14\omega_1^4} \left(\frac{b\kappa_b}{a\kappa_a}\right)^2 (\overset{\circ}{E}_{2z}^2 - \overset{\circ}{E}_{2y}^2), \quad (48)$$

where  $\varkappa_b = (b_{333} - b_{113}) / (b_{333} + 2b_{113}) = (b_{333} - b_{113}) / 3b$  determines the anisotropy of non-linear polarization of an axially-symmetric molecule without centre of inversion.

Applying the following values for chloroform (Kielich 1962):  $a\kappa_a = -0.78 \times 10^{-24} \text{ cm}^3$ ,  $b\kappa_b = -0.83 \times 10^{-29} \text{ e.s.u.}$ , we obtain from Eq. (48) for  $\omega_2/\omega_1 = 0.8$ ,  $D - D_0 = -86 \times 10^{-12} (\overset{\circ}{E}_{2z}^2 - \overset{\circ}{E}_{2y}^2)$ . At  $\overset{\circ}{E}_{2z} = 100 \text{ e.s.u.}$  and  $\overset{\circ}{E}_{2y} = 0$ , the non-linear change in degree of depolarization amounts to  $D - D_0 = -10^{-6}$ , whereas for  $\overset{\circ}{E}_{2z} = 10^3 \text{ e.s.u.}$  it is of the order of  $10^{-4}$  and, consequently, is accessible to observation.

If, instead of isotropic averaging of Eqs (18)–(20), we recur to averaging with Boltzmann's statistical factor  $\exp\{-\bar{u}/kT\}$  containing the time-averaged potential energy of the molecule in the strong electric field  $\mathbf{E}_2$ , additional contributions to the tensor  $I_{\sigma\tau}^{\omega_1}$  will appear accounting for the role played by the effect of optical molecular orientation in light scattering (see, Kielich 1963 a, c). For the conditions of observation specified above and on the assumption of axial symmetry of the molecular polarizability ellipsoid we have for the change in  $D$  resulting from optical molecular orientation (Kielich 1963c)

$$D - D_0 = -\frac{3a\kappa_a}{7kT} (\overset{\circ}{E}_{2z}^2 - \overset{\circ}{E}_{2y}^2). \quad (49)$$

This yields, for  $T = 300^\circ\text{K}$  and the values for  $\text{CS}_2$  already specified,  $D - D_0 = -33 \times 10^{-12} (\overset{\circ}{E}_{2z}^2 - \overset{\circ}{E}_{2y}^2)$  and, for  $\text{CHCl}_3$ ,  $D - D_0 = 8 \times 10^{-12} (\overset{\circ}{E}_{2z}^2 - \overset{\circ}{E}_{2y}^2)$ . On comparing these figures with the results calculated above, it is seen that in the case of  $\text{CS}_2$  the contribution to  $D$  due to the effect of molecular orientation is almost five times larger than that due to non-linear deformation of the molecule, whereas in  $\text{CHCl}_3$ , on the contrary, the contribution to the non-linear variation of  $D$  from the effect of molecular orientation is almost 10 times smaller than that resulting from non-linear molecular deformation. It is to be expected that in all cases of anisotropic molecules without a centre of inversion the changes in the light scattered are due chiefly to the effect of their non-linear deformation.

## 6. Results and conclusions

From the preceding considerations, two basic processes can be distinguished in the mechanism of non-linear light scattering, namely, non-linear polarization of the atoms or molecules due to an intense, optical electric field, and a process leading to some measure of ordering in this field of the polarizability ellipsoids of the optically anisotropic molecules. Which of these two processes will play the essential or sole part in any particular case will depend primarily on the structure and symmetry of the molecules, on the temperature at which the substance is investigated, on its dispersion and, in dealing with gases, on the pressure. Although the final results derived here are strictly applicable to a rarefied gas where intermolecular interactions are negligible, there are nevertheless from a formal point of view no difficulties in the way of their extension to a condensed gas or a liquid. The effect of intermolecular correlations, both radial and angular, upon measurable quantities such

as  $D$  and  $S$  can be calculated as was done for other non-linear phenomena in liquid dielectrics (see, *e.g.*, Kielich and Piekara 1959, Kielich 1962, 1963d). However, owing to the appearance therein of additional terms, the respective expressions for  $D$  and  $S$  (which, as we have seen, are already sufficiently involved for the gaseous state) become even more complicated. In this respect, a glance at the formulas of earlier papers (*e.g.* Kielich 1963b, containing a discussion of the changes in  $D$  resulting in liquids from an applied strong  $DC$  electric or magnetic field) should be convincing. It was with the aim of avoiding such complication that the present theory has been restricted, maybe justifiably, to scattering media in which intermolecular interactions are absent or, at the most, very weak. Besides, the theory in the gaseous state approximation presents the advantage of providing information as to the properties of the isolated molecule.

Since the anisotropy of linear polarizability  $\kappa_a$  is known for many kinds of isolated molecules *e.g.* from measurements of linear light scattering or Kerr's effect, Eqs (45) and (48) will allow to determine simply and directly the anisotropy of their non-linear polarization,  $\kappa_b$  or  $\kappa_c$ , as soon as the variations in degree of depolarization become accessible to measurement. On measuring some quantities, *e.g.*  $D$  and  $S$ , in different appropriately chosen experimental conditions, it will be possible to determine separately the tensor components  $b_{\alpha\beta\gamma}$  and  $c_{\alpha\beta\gamma\delta}$  not vanishing for the symmetry group considered. Thus, investigation of the effect of a laser beam on the scattering of light can provide one more method for determining the parameters of the various non-linear optical deformations of molecules.

The discussion of § 5 is easily generalized to other experimental conditions, *e.g.* to cases when the scattered light is observed at an angle differing from  $90^\circ$  with respect to the direction of incidence. For this, the reader is referred to another paper (Kielich 1964a) dealing with the simpler case when a single, very intense light beam is used only. Also the effect of an optical electric field gradient on the scattering of light can be calculated as for the case of a  $DC$  electric field gradient (Kielich 1963e).

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## APPENDIX A

Effect of the oscillations of nuclei on non-linear light scattering

We shall present here in brief a simple extension of Placzek's (1934) linear theory of polarizability to the case of non-linear Raman scattering.

Let us consider molecules in their non-degenerate ground electronic states and assume the frequencies of the own oscillations of their atoms to be small as compared with the frequencies  $\omega_1$  and  $\omega_2$  of the incident light waves.

The dipole moment component induced in the molecule by the electric field  $\mathbf{E}_1 = \mathring{\mathbf{E}}_1 \cos \omega_1 t$  in the presence of a strong electric field  $\mathbf{E}_2 = \mathring{\mathbf{E}}_2 \cos \omega_2 t$  can be written in the form of an expansion, thus

$$p_\alpha = \left\{ a_{\alpha\beta} + b_{\alpha\beta\gamma} \mathring{E}_{2\gamma} \cos \omega_2 t + \frac{1}{2} c_{\alpha\beta\gamma\delta} \mathring{E}_{2\gamma} \mathring{E}_{2\delta} \cos^2 \omega_2 t + \dots \right\} \mathring{E}_{1\beta} \cos \omega_1 t. \quad (\text{A.1})$$

On the assumption that the oscillations of the nuclei lead to distortion of the electron shell of the molecule, the tensors  $a_{\alpha\beta}$ ,  $b_{\alpha\beta\gamma}$  and  $c_{\alpha\beta\gamma\delta}$  are functions of the normal coordinates  $q_i$  ( $i = 1, 2, \dots, n$ ) and can be expanded for small oscillations in a series in powers of  $q_i$ :

$$\begin{aligned} a_{\alpha\beta} &= \overset{\circ}{a}_{\alpha\beta} + \left( \frac{\partial a_{\alpha\beta}}{\partial q_i} \right)_0 q_i + \frac{1}{2} \left( \frac{\partial^2 a_{\alpha\beta}}{\partial q_i \partial q_j} \right)_0 q_i q_j + \frac{1}{6} \left( \frac{\partial^3 a_{\alpha\beta}}{\partial q_i \partial q_j \partial q_k} \right)_0 q_i q_j q_k + \dots, \\ b_{\alpha\beta\gamma} &= \overset{\circ}{b}_{\alpha\beta\gamma} + \left( \frac{\partial b_{\alpha\beta\gamma}}{\partial q_i} \right)_0 q_i + \frac{1}{2} \left( \frac{\partial^2 b_{\alpha\beta\gamma}}{\partial q_i \partial q_j} \right)_0 q_i q_j + \dots, \\ c_{\alpha\beta\gamma\delta} &= \overset{\circ}{c}_{\alpha\beta\gamma\delta} + \left( \frac{\partial c_{\alpha\beta\gamma\delta}}{\partial q_i} \right)_0 q_i + \frac{1}{2} \left( \frac{\partial^2 c_{\alpha\beta\gamma\delta}}{\partial q_i \partial q_j} \right)_0 q_i q_j + \dots, \end{aligned} \quad (\text{A.2})$$

with  $\overset{\circ}{a}_{\alpha\beta}$ ,  $\overset{\circ}{b}_{\alpha\beta\gamma}$  and  $\overset{\circ}{c}_{\alpha\beta\gamma\delta}$  denoting the polarizability tensors of the molecule at equilibrium.

Assuming the  $i$ -th normal oscillation of the molecule to occur with frequency  $\omega_i$  and phase  $\varphi_i$ ,

$$q_i = \overset{\circ}{q}_i \cos(\omega_i t + \varphi_i), \quad (\text{A.3})$$

we can put the expansion of (A.1), with regard to (A.2), in the form

$$P_\alpha = \overset{\circ}{P}_\alpha + \Delta p_\alpha, \quad (\text{A.4})$$

wherein

$$\begin{aligned} \overset{\circ}{P}_\alpha &= \left\{ \overset{\circ}{a}_{\alpha\beta} + \frac{1}{4} \overset{\circ}{c}_{\alpha\beta\gamma\delta} \overset{\circ}{E}_{2\gamma} \overset{\circ}{E}_{2\delta} + \dots \right\} \overset{\circ}{E}_{1\beta} \cos \omega_1 t + \frac{1}{2} \overset{\circ}{b}_{\alpha\beta\gamma} \overset{\circ}{E}_{1\beta} \overset{\circ}{E}_{2\gamma} \{ \cos(\omega_1 + \omega_2) t + \\ &+ \cos(\omega_1 - \omega_2) t \} + \frac{1}{8} \overset{\circ}{c}_{\alpha\beta\gamma\delta} \overset{\circ}{E}_{1\beta} \overset{\circ}{E}_{2\gamma} \overset{\circ}{E}_{2\delta} \{ \cos(\omega_1 + 2\omega_2) t + \cos(\omega_1 - 2\omega_2) t \} + \dots \end{aligned} \quad (\text{A.5})$$

is the induced dipole moment component of the molecule at fixed positions of the nuclei, while

$$\begin{aligned} \Delta p_\alpha &= \frac{1}{2} \left\{ \left( \frac{\partial a_{\alpha\beta}}{\partial q_i} \right)_0 + \frac{1}{4} \left( \frac{\partial c_{\alpha\beta\gamma\delta}}{\partial q_i} \right)_0 \overset{\circ}{E}_{2\gamma} \overset{\circ}{E}_{2\delta} + \dots \right\} \times \\ &\times \overset{\circ}{q}_i \overset{\circ}{E}_{1\beta} \{ \cos[(\omega_1 + \omega_i) t + \varphi_i] + \cos[(\omega_1 - \omega_i) t - \varphi_i] \} + \dots \\ &+ \frac{1}{4} \left( \frac{\partial b_{\alpha\beta\gamma}}{\partial q_i} \right)_0 \overset{\circ}{q}_i \overset{\circ}{E}_{1\beta} \overset{\circ}{E}_{2\gamma} \{ \cos[(\omega_1 + \omega_2 + \omega_i) t + \varphi_i] + \cos[(\omega_1 - \omega_2 + \omega_i) t + \varphi_i] + \\ &+ \cos[(\omega_1 + \omega_2 - \omega_i) t - \varphi_i] + \cos[(\omega_1 - \omega_2 - \omega_i) t - \varphi_i] \} + \dots \\ &+ \frac{1}{16} \left( \frac{\partial c_{\alpha\beta\gamma\delta}}{\partial q_i} \right)_0 \overset{\circ}{q}_i \overset{\circ}{E}_{1\beta} \overset{\circ}{E}_{2\gamma} \overset{\circ}{E}_{2\delta} \{ \cos[(\omega_1 + 2\omega_2 + \omega_i) t + \varphi_i] + \cos[(\omega_1 - 2\omega_2 + \omega_i) t + \varphi_i] + \\ &+ \cos[(\omega_1 + 2\omega_2 - \omega_i) t - \varphi_i] + \cos[(\omega_1 - 2\omega_2 - \omega_i) t - \varphi_i] \} + \dots, \end{aligned} \quad (\text{A.6})$$



describes the change produced in the oscillating dipole moment by the oscillation of the nuclei.

By Eq. (A.5), in addition to radiation with the frequency  $\omega_1$  of the incident light wave (linear Rayleigh scattering), there occurs radiation with the harmonic frequencies  $\omega_1 \pm \omega_2$  and  $\omega_1 \pm 2\omega_2$  (non-linear Rayleigh scattering); whereas the expansion (A.6) points to the possibility of the appearance — beside normal Raman scattering with frequencies  $\omega_1 \pm \omega_i$  — of additional scattering with the frequencies  $\omega_1 \pm \omega_2 \pm \omega_i$ ,  $\omega_1 \pm \omega_2 \mp \omega_i$ ,  $\omega_1 \pm 2\omega_2 \pm \omega_i$ ,  $\omega_1 \pm 2\omega_2 \mp \omega_i$ , *etc.* characteristic of non-linear Raman scattering. Obviously, this last type of scattering requires appropriate selection rules to be established for the matrix elements of the non-linear polarizability tensors, as was done previously for the tensor of linear polarizability (see, Placzek 1934, or Bhagavantham 1942).

## APPENDIX B

The tensor of light scattering for optically isotropic molecules

On putting  $2c_{1313} = c_{1111} - c_{1122}$  in Eq. (28), the scattering tensor components of Eqs (18)–(20) are reduced to a form valid for optically isotropic scattering molecules:

$$\begin{aligned}
 I_{\sigma\tau}^{\omega_1} = & \frac{1}{2} \omega_1^4 \left\{ (a^{\omega_1})^2 \dot{E}_{1\sigma} \dot{E}_{1\tau} + \frac{1}{4} a^{\omega_1} [2c_{1122}^{\omega_1} \dot{E}_{1\sigma} \dot{E}_{1\tau} \dot{E}_2^2 + \right. \\
 & + (c_{1111}^{\omega_1} - c_{1122}^{\omega_1}) (\dot{E}_{1\sigma} \dot{E}_{2\tau} + \dot{E}_{2\sigma} \dot{E}_{1\tau}) (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2)] + \frac{1}{16} [(c_{1122}^{\omega_1})^2 \dot{E}_{1\sigma} \dot{E}_{1\tau} \dot{E}_2^4 + \\
 & + c_{1122}^{\omega_1} (c_{1111}^{\omega_1} - c_{1122}^{\omega_1}) (\dot{E}_{1\sigma} \dot{E}_{2\tau} + \dot{E}_{2\sigma} \dot{E}_{1\tau}) (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2) \dot{E}_2^2 + (c_{1111}^{\omega_1} - c_{1122}^{\omega_1})^2 \dot{E}_{2\sigma} \dot{E}_{2\tau} (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2)^2] + \dots \left. \right\}, \quad (B.1)
 \end{aligned}$$

$$\begin{aligned}
 I_{\sigma\tau}^{\omega_1 \pm 2\omega_2} = & \frac{1}{128} (\omega_1 \pm 2\omega_2)^4 \{ (c_{1122}^{\omega_1 \pm 2\omega_2})^2 \dot{E}_{1\sigma} \dot{E}_{1\tau} \dot{E}_2^4 + c_{1122}^{\omega_1 \pm 2\omega_2} (c_{1111}^{\omega_1 \pm 2\omega_2} - c_{1122}^{\omega_1 \pm 2\omega_2}) \times \\
 & \times (\dot{E}_{1\sigma} \dot{E}_{2\tau} + \dot{E}_{2\sigma} \dot{E}_{1\tau}) (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2) \dot{E}_2^2 + (c_{1111}^{\omega_1 \pm 2\omega_2} - c_{1122}^{\omega_1 \pm 2\omega_2})^2 \dot{E}_{2\sigma} \dot{E}_{2\tau} (\dot{\mathbf{E}}_1 \cdot \dot{\mathbf{E}}_2)^2 \}. \quad (B.2)
 \end{aligned}$$

Assuming for simplicity that the two light vectors  $\mathbf{E}_1$  and  $\mathbf{E}_2$  oscillate in the same direction, though the propagation directions of the waves conveying them need not be identical but lie in one plane, and taking account of  $c_{1111} = 3c_{1122} = c$ , we can rewrite (B.1) and (B.2) in much simpler form,

$$I_{\sigma\tau}^{\omega_1} = \frac{1}{2} \omega_1^4 \left\{ a^{\omega_1} + \frac{1}{4} c^{\omega_1} \dot{E}_2^2 \right\}^2 \dot{E}_{1\sigma} \dot{E}_{1\tau}, \quad (B.3)$$

$$I_{\sigma\tau}^{\omega_1 \pm 2\omega_2} = \frac{1}{128} (\omega_1 \pm 2\omega_2)^4 \{ c^{\omega_1 \pm 2\omega_2} \dot{E}_2^2 \}^2 \dot{E}_{1\sigma} \dot{E}_{1\tau}. \quad (B.4)$$

On applying the classical theory of the anharmonic oscillator under the effect of two periodic fields  $\mathbf{E}_1$  and  $\mathbf{E}_2$ , we derive directly the dependence between the molecular deforma-

tion coefficients and the frequencies  $\omega_1$  and  $\omega_2$  of the fields (see *e.g.* Kielich 1963c, 1964b):

$$\begin{aligned}
 a^{\omega_1} &= \text{Re} \sum_i \frac{e_i^2}{m_i(\omega_i^2 - \omega_1^2 + i\Gamma_i\omega_1)}, \\
 c^{\omega_1} &= \text{Re} \sum_i \frac{e_i^4 \gamma_i}{m_i^4(\omega_i^2 - \omega_1^2 + i\Gamma_i\omega_1)^2 (\omega_i^2 - \omega_2^2 + i\Gamma_i\omega_2)^2}, \\
 c^{\omega_1 \pm 2\omega_2} &= \text{Re} \sum_i \frac{e_i^4 \gamma_i}{m_i^4(\omega_i^2 - \omega_1^2 + i\Gamma_i\omega_1) (\omega_i^2 - \omega_2^2 + i\Gamma_i\omega_2)^2 [\omega_i^2 - (\omega_1 + 2\omega_2)^2 + i\Gamma_i(\omega_1 + 2\omega_2)]};
 \end{aligned} \tag{B.5}$$

herein,  $e_i$  is the electric charge of the  $i$ -th electron of mass  $m_i$  oscillating with the frequency  $\omega_i$ ,  $\gamma_i$  — the anharmonicity constant, and  $\Gamma_i$  — the damping constant. Summation in the expressions of Eq. (B.5) extends over all the electrons of the atom or molecule.

In the region very far remote from absorption lines of the gas under consideration, the coefficient of non-linear deformation  $c$  is of the order of  $10^{-36}$  e.s.u., so that  $c/a$  is at the most of order  $10^{-12}$  and the non-linear contribution to the scattering tensor is, relatively, vanishingly small. However, by (B.5), in the immediate neighbourhood of an absorption line the coefficients of non-linear deformation can attain much greater values and we can expect considerable non-linear light scattering from an atomic gas or from one consisting of optically isotropic molecules.

### APPENDIX C

Quantum-mechanical form of the tensors  $B_{\alpha\beta\gamma}^{kl}$  and  $C_{\alpha\beta\gamma\delta}^{kl}$

On substituting the coefficients of (6) in Eqs (9) and (10), we obtain

$$\begin{aligned}
 B_{\alpha\beta\gamma}^{kl}(\pm\omega_1, \pm\omega_2) &= \frac{1}{\hbar^2} \sum_{mn} \left\{ \langle k|M_\alpha|n\rangle \left[ \frac{\langle n|M_\beta|m\rangle \langle m|M_\gamma|l\rangle}{(\omega_{nl} \pm \omega_1 \pm \omega_2)(\omega_{ml} \pm \omega_2)} + \right. \right. \\
 &+ \left. \frac{\langle n|M_\gamma|m\rangle \langle m|M_\beta|l\rangle}{(\omega_{nl} \pm \omega_1 \pm \omega_2)(\omega_{ml} \pm \omega_1)} \right] + \langle m|M_\alpha|n\rangle \left[ \frac{\langle k|M_\gamma|m\rangle \langle n|M_\beta|l\rangle}{(\omega_{mk} \mp \omega_2)(\omega_{nl} \pm \omega_1)} + \right. \\
 &+ \left. \frac{\langle k|M_\beta|m\rangle \langle n|M_\gamma|l\rangle}{(\omega_{mk} \mp \omega_1)(\omega_{nl} \pm \omega_2)} \right] + \left[ \frac{\langle k|M_\beta|n\rangle \langle n|M_\gamma|m\rangle}{(\omega_{nk} \mp \omega_1)(\omega_{mk} \mp \omega_1 \mp \omega_1)} + \right. \\
 &\left. \left. + \frac{\langle k|M_\gamma|n\rangle \langle n|M_\beta|m\rangle}{(\omega_{nk} \mp \omega_2)(\omega_{mk} \mp \omega_1 \mp \omega_2)} \right] \langle m|M_\alpha|l\rangle \right\}, \tag{C.1}
 \end{aligned}$$

$$\begin{aligned}
 C_{\alpha\beta\gamma\delta}^{kl}(\pm\omega_1, \pm\omega_2, \pm\omega_2) &= \frac{2}{\hbar^3} \sum_{mnr} \left\{ \langle k|M_\alpha|n\rangle \left[ \frac{\langle n|M_\beta|r\rangle \langle r|M_\gamma|m\rangle \langle m|M_\delta|l\rangle}{(\omega_{nl} \pm \omega_1 \pm 2\omega_2)(\omega_{rl} \pm 2\omega_2)(\omega_{ml} \pm \omega_2)} + \right. \right. \\
 &+ \left. \frac{\langle n|M_\gamma|r\rangle \langle r|M_\delta|m\rangle \langle m|M_\beta|l\rangle}{(\omega_{nl} \pm \omega_1 \pm 2\omega_2)(\omega_{rl} \pm \omega_1 \pm \omega_2)(\omega_{ml} \pm \omega_1)} + \frac{\langle n|M_\delta|r\rangle \langle r|M_\beta|m\rangle \langle m|M_\gamma|l\rangle}{(\omega_{nl} \pm \omega_1 \pm 2\omega_2)(\omega_{rl} \pm \omega_1 \pm \omega_2)(\omega_{ml} \pm \omega_2)} \right] +
 \end{aligned}$$

$$\begin{aligned}
& + \langle m | M_\alpha | n \rangle \left[ \frac{\langle k | M_\beta | m \rangle \langle n | M_\gamma | r \rangle \langle r | M_\delta | l \rangle}{(\omega_{mk} \mp \omega_1) (\omega_{nl} \pm 2\omega_2) (\omega_{rl} \pm \omega_2)} + \frac{\langle k | M_\gamma | r \rangle \langle r | M_\delta | m \rangle \langle n | M_\beta | l \rangle}{(\omega_{rk} \mp \omega_2) (\omega_{mk} \mp 2\omega_2) (\omega_{nl} \pm \omega_1)} + \right. \\
& + \frac{\langle k | M_\beta | r \rangle \langle r | M_\delta | m \rangle \langle n | M_\gamma | l \rangle}{(\omega_{rk} \mp \omega_1) (\omega_{mk} \mp \omega_1 \mp \omega_2) (\omega_{nl} \pm \omega_2)} + \frac{\langle k | M_\delta | r \rangle \langle r | M_\beta | m \rangle \langle n | M_\gamma | l \rangle}{(\omega_{rk} \mp \omega_2) (\omega_{mk} \mp \omega_1 \mp \omega_2) (\omega_{nl} \pm \omega_2)} + \\
& + \left. \frac{\langle k | M_\gamma | m \rangle \langle n | M_\beta | r \rangle \langle r | M_\delta | l \rangle}{(\omega_{mk} \mp \omega_2) (\omega_{nl} \pm \omega_1 \pm \omega_2) (\omega_{rl} \pm \omega_2)} + \frac{\langle k | M_\gamma | m \rangle \langle n | M_\delta | r \rangle \langle r | M_\beta | l \rangle}{(\omega_{mk} \mp \omega_2) (\omega_{nl} \pm \omega_1 \pm \omega_2) (\omega_{rl} \pm \omega_1)} \right] + \\
& + \left[ \frac{\langle k | M_\delta | r \rangle \langle r | M_\gamma | n \rangle \langle n | M_\beta | m \rangle}{(\omega_{rk} \mp \omega_2) (\omega_{nk} \mp 2\omega_2) (\omega_{mk} \mp \omega_1 \mp 2\omega_2)} + \frac{\langle k | M_\beta | r \rangle \langle r | M_\delta | n \rangle \langle n | M_\gamma | m \rangle}{(\omega_{rk} \mp \omega_1) (\omega_{nk} \mp \omega_1 \mp \omega_2) (\omega_{mk} \mp \omega_1 \mp 2\omega_2)} + \right. \\
& \left. + \frac{\langle k | M_\gamma | r \rangle \langle r | M_\beta | n \rangle \langle n | M_\delta | m \rangle}{(\omega_{rk} \mp \omega_2) (\omega_{nk} \mp \omega_1 \mp \omega_2) (\omega_{mk} \mp \omega_1 \mp 2\omega_2)} \right] \langle m | M_\alpha | l \rangle, \quad (C.2)
\end{aligned}$$

$$\begin{aligned}
C_{\alpha\beta\gamma\delta}^{kl}(\pm\omega_1, \pm\omega_2, \mp\omega_2) &= \frac{2}{\hbar^3} \sum_{mnr} \left\{ \langle k | M_\alpha | n \rangle \left[ \frac{\langle n | M_\beta | r \rangle \langle r | M_\gamma | m \rangle \langle m | M_\delta | l \rangle}{(\omega_{nk} \pm \omega_1) \omega_{rk} (\omega_{mk} \mp \omega_2)} + \right. \right. \\
& + \left. \frac{\langle n | M_\gamma | r \rangle \langle r | M_\delta | m \rangle \langle m | M_\beta | l \rangle}{(\omega_{nk} \pm \omega_1) (\omega_{rk} \pm \omega_1 \mp \omega_2) (\omega_{mk} \pm \omega_1)} + \frac{\langle n | M_\delta | r \rangle \langle r | M_\beta | m \rangle \langle m | M_\gamma | l \rangle}{(\omega_{nk} \pm \omega_1) (\omega_{rk} \pm \omega_1 \pm \omega_2) (\omega_{mk} \pm \omega_2)} \right] + \\
& + \langle m | M_\alpha | n \rangle \left[ \frac{\langle k | M_\beta | m \rangle \langle n | M_\gamma | r \rangle \langle r | M_\delta | l \rangle}{(\omega_{mk} \mp \omega_1) \omega_{nl} (\omega_{rl} \mp \omega_2)} + \frac{\langle k | M_\gamma | r \rangle \langle r | M_\delta | m \rangle \langle n | M_\beta | l \rangle}{(\omega_{rk} \pm \omega_2) \omega_{mk} (\omega_{nl} \pm \omega_1)} + \right. \\
& + \frac{\langle k | M_\beta | r \rangle \langle r | M_\delta | m \rangle \langle n | M_\gamma | l \rangle}{(\omega_{rk} \mp \omega_1) (\omega_{mk} \mp \omega_1 \pm \omega_2) (\omega_{nl} \pm \omega_2)} + \frac{\langle k | M_\delta | r \rangle \langle r | M_\beta | m \rangle \langle n | M_\gamma | l \rangle}{(\omega_{rk} \pm \omega_2) (\omega_{mk} \mp \omega_1 \mp \omega_2) (\omega_{nl} \pm \omega_2)} + \\
& + \left. \frac{\langle k | M_\gamma | m \rangle \langle n | M_\beta | r \rangle \langle r | M_\delta | l \rangle}{(\omega_{mk} \mp \omega_2) (\omega_{nl} \pm \omega_1 \pm \omega_2) (\omega_{rl} \mp \omega_2)} + \frac{\langle k | M_\gamma | m \rangle \langle n | M_\delta | r \rangle \langle r | M_\beta | l \rangle}{(\omega_{mk} \mp \omega_2) (\omega_{nl} \pm \omega_1 \mp \omega_2) (\omega_{rl} \pm \omega_1)} \right] + \\
& + \left[ \frac{\langle k | M_\delta | r \rangle \langle r | M_\gamma | n \rangle \langle n | M_\beta | m \rangle}{(\omega_{rk} \pm \omega_2) \omega_{nk} (\omega_{mk} \mp \omega_1)} + \frac{\langle k | M_\beta | r \rangle \langle r | M_\delta | n \rangle \langle n | M_\gamma | m \rangle}{(\omega_{rk} \mp \omega_1) (\omega_{nk} \mp \omega_1 \pm \omega_2) (\omega_{mk} \mp \omega_1)} + \right. \\
& \left. + \frac{\langle k | M_\gamma | r \rangle \langle r | M_\beta | n \rangle \langle n | M_\delta | m \rangle}{(\omega_{rk} \mp \omega_2) (\omega_{nk} \mp \omega_1 \mp \omega_2) (\omega_{mk} \mp \omega_1)} \right] \langle m | M_\alpha | l \rangle \}. \quad (C.3)
\end{aligned}$$

On replacing in the foregoing expressions  $\omega_1$  by  $-\omega_1$  we obtain the tensors  $B_{\alpha\beta\gamma}^{kl}(\mp\omega_1, \pm\omega_2)$ ,  $C_{\alpha\beta\gamma\delta}^{kl}(\mp\omega_1, \pm\omega_2, \pm\omega_2)$  and  $C_{\alpha\beta\gamma\delta}^{kl}(\mp\omega_1, \pm\omega_2, \mp\omega_2)$ . For  $k = l$  the tensors of (C.1) and (C.2) reduce to the form of (20a) and (20b), for which the symmetry relations of the tensors  $B_{\alpha\beta\gamma}^{kk}$  and  $C_{\alpha\beta\gamma\delta}^{kk}$  are discussed in detail by Armstrong *et al.* (1962) for the general case of three light waves of frequencies  $\omega_1$ ,  $\omega_2$  and  $\omega_3$ , respectively.

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Note added in proof. Recently, this author had the pleasure of corresponding with Professor Neugebauer and of receiving from him reprints of papers published in *Acta Physica Hungarica*, **10**, 221 (1959); **14**, 77 (1962); **16**, 217, 227 (1963), and in *Z. Phys.*, **155** 380 (1959) containing the quantum-mechanical considerations and calculations on *das Problem der Vereinigung von zwei Photonen gleicher Frequenz an Molekülen* which originally enabled Professor Neugebauer to predict the light scattering with double frequency that can take place on entirely asymmetric molecules. Neugebauer's double-frequency scattering is a special case of the scattering considered in this paper for identical directions and frequencies of the two light beams ( $\omega_1 = \omega_2$ ) and  $\omega_{el} = 0$ ; his results can be derived from Eqs (19) and (21a) on making the appropriate assumptions.