

ON THE MULTIPOLE MOMENTS INDUCED IN MOLECULES BY THE
ELECTRIC FIELDS OF SEVERAL LIGHT WAVES

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A consistent and general tensor formalism is proposed, allowing to compute easily the multipole electric moments induced in atoms or molecules by electric fields that are not only time-variable but are also spatially variable. The dependence of the r th-order molecular 2^n -pole moments on the r th power of the electric fields of given order inducing them is described by multipole polarizability tensors of appropriate rank. The matrix elements of these tensors for the general case of a transition $k \rightarrow l$ are derived explicitly in the first, second, third and r th-order approximations of quantum-mechanical perturbation theory. The formalism proposed can be applied for computing various non-linear effects the investigation of which is liable to provide information on the change undergone directly by the atoms or molecules under the influence of intense oscillating electric fields. The problem is discussed with regard to electric multipole light scattering and non-linear variation of the optical permittivity of a gas, as due to intense light beams from lasers.

1. Introduction

In recent years a number of papers have appeared on theories of various non-linear optical effects observed in widely differing material media subjected to illumination from a laser. The theory of generation of optical harmonics, and that of non-linear responses of macroscopic media, are discussed in papers by Braunstein (1962), Kleinman (1962), Armstrong *et al.* (1962), Bloembergen and Pershan (1962), Loudon (1962), Kogan (1962), Franken and Ward (1963), Kelley (1962), Price (1963), Butcher and McLean (1963, 1964), Caspers (1964), and others. Moreover, various scattering processes revealing non-linear interactions between electrons, atoms or molecules and light from a laser are discussed by Neugebauer (1959, 1963), Vachaspati (1962), McKenna and Platzman (1963), Mizushima (1963), Brown and Kibble (1964), and this author (Kielich 1963, 1964).

In certain non-linear optical processes, an essential role is played not only by the dipole moments induced in the atoms or molecules, but also by induced quadrupole moments (Franken and Ward 1963, Pershan 1963) and, possibly, induced moments of still higher

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orders such as octopole moments, and so forth. The role of electric and magnetic multipole moments in atomic electromagnetic radiation was discussed theoretically by Rubinowicz (1930, 1949) and others (see *e.g.* the reports of Rubinowicz and Blaton 1932, Bowen 1936 and Sommerfeld 1951). In this connection, the need may be felt of a tensor formalism allowing to derive, in a concise and simultaneously general manner, the multipole electric moments induced in molecules by time- and spatially-variable electric fields. These molecular multipoles are computed for the general case of a transition $k \rightarrow l$ to within the third order of quantum-mechanical perturbation theory, magnetic effects, radiation corrections and intermolecular interaction being neglected in the Hamiltonian for the sake of simplicity. The induced multipole moments of consecutively the first, second and third order approximations are expressed in the form of infinite series whose terms are multipole polarizability tensors of appropriate rank, n -fold contracted with the electric field of order n . The results derived here are a modification and generalization of those obtained by Armstrong *et al.* (1962) for the case of the dipole approximation.

The formalism proposed can be of use in computing various non-linear optical phenomena involving interaction effects not only dipolar but also of quadrupolar, octopolar *etc.* type between atoms or molecules and electric fields. As an example, the formalism is applied for computing the tensor of electric multipole light scattering as well as the tensor of optical permittivity and for their discussion in the first, second and third-order approximations of perturbation theory. In particular, our general results, if specialized for the dipole approximation, reduce to results obtained and discussed in detail in earlier papers (Kielich 1964 a, b, c). Investigation along these lines is clearly able to provide valuable information as to the direct and generally non-linear influence of oscillating electric fields on the properties of atoms and molecules. In the Appendix we give in explicit form the r th-order contribution to the electric 2^r -pole moment, which can be obtained with the general method elaborated by Butcher and McLean (1963, 1964) in their theory of non-linear constitutive relation in solids at optical frequencies.

2. Fundamental assumptions

We consider a system of N identical, noninteracting molecules generally assumed to be optically anisotropic. Suppose this system to be subjected simultaneously to several electric fields $\mathbf{E}_1, \mathbf{E}_2, \mathbf{E}_3, \dots$ varying periodically with the angular frequencies $\omega_1, \omega_2, \omega_3, \dots$, respectively. In general, the total incident electric field is a superposition of these perturbing fields,

$$\mathbf{E}(\mathbf{r}, t) = \sum_s \mathbf{E}_s \cos \omega_s t = \frac{1}{2} \sum_s (\mathbf{E}_s^+ e^{i\omega_s t} + \mathbf{E}_s^- e^{-i\omega_s t}). \quad (1)$$

where \mathbf{E}_s^+ and \mathbf{E}_s^- are in general complex amplitudes of the s th monochromatic component of $\mathbf{E}(\mathbf{r}, t)$.

The total Hamiltonian of a molecule is

$$H = H_0 + H' \quad (2)$$

with H_0 denoting the Hamiltonian of the nonperturbated isolated molecule and

$$H' = \frac{1}{2} \sum (H_s^+ e^{i\omega_s t} + H_s^- e^{-i\omega_s t}) \quad (3)$$

the perturbation Hamiltonian of the molecule in the electric fields.

In the electric dipole approximation we have

$$H_s^\pm = -\mathbf{M} \cdot \mathbf{E}_s^\pm, \quad (4)$$

where \mathbf{M} denotes the operator of the electric dipole moment of the molecule.

In the case when the higher-order interactions between the molecule and electric fields are taken into account, the s th perturbation Hamiltonian of (4) must be replaced by the following general expression:

$$H_s^\pm = - \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \mathbf{M}^{(n)} [n] \mathbf{E}_s^\pm, \quad (5)$$

where $\mathbf{M}^{(n)}$ is the operator of the electric 2^n -pole moment of the molecule interacting with the electric field $\mathbf{E}_s^{(n)} = \nabla^{n-1} \mathbf{E}_s(r)$ of order n . The symbol $[n]$ denotes n -fold contraction of the product of the operators $\mathbf{M}^{(n)}$ and $\mathbf{E}_s^{(n)}$, and ∇ is the differential operator.

In the perturbation Hamiltonian (5) we neglected for simplicity the interaction between the molecule and magnetic fields and have omitted the multipole radiation terms arising from retardation effects.

The electric 2^n -pole moment operator in Eq. (5) is defined as

$$\mathbf{M}^{(n)} = \sum_i e_i r_i^n \mathbf{Y}^{(n)}(\mathbf{r}_i), \quad (6)$$

where e_i is the i th electric charge of the molecule and \mathbf{r}_i is its radius vector; summation in (6) extends over all charges of the molecule. The operator $\mathbf{Y}^{(n)}$ of order n (its components are spherical harmonic functions) is given by

$$\begin{aligned} \mathbf{Y}^{(n)}(\mathbf{r}_i) &= \frac{(-1)^n}{n!} r_i^{n+1} \nabla^n \left(\frac{1}{r_i} \right) = \frac{1}{n! r_i^n} \{ (2n-1)!! \mathbf{r}_{i1} \mathbf{r}_{i2} \dots \mathbf{r}_{in} - \\ &- (2n-3)!! r_i^2 \sum \mathbf{U}_{12} \mathbf{r}_{i3}^n \dots \mathbf{r}_{in}^n + (2n-5)!! r_i^4 \sum \mathbf{U}_{12} \mathbf{U}_{34} \mathbf{r}_{i5} \dots \mathbf{r}_{in} - \\ &+ (-1)_k^k (2n-2k-1)!! r_i^{2k} \sum \mathbf{U}_{12} \dots \mathbf{U}_{2k-1, 2k} \mathbf{r}_{i2k+1} \dots \mathbf{r}_{in}^k + \dots \}, \end{aligned} \quad (7)$$

where \mathbf{U}_{12} is a unit second-rank tensor, and $\sum \mathbf{U}_{12} \mathbf{r}_{i3} \dots \mathbf{r}_{in}$ etc. are sums of the terms obtained from the one written out above by interchanging the suffixes 1, 2, ... n .

From the general expression of (5) we obtain up to the term accounting for interaction between the octopole and third-order field

$$H_s^\pm = -\mathbf{M}^{(1)} \cdot \mathbf{E}_s^{(1)} - \frac{1}{3} \mathbf{M}^{(2)} : \mathbf{E}_s^{(2)} - \frac{1}{15} \mathbf{M}^{(3)} : \mathbf{E}_s^{(3)} - \dots, \quad (8)$$

where by Eqs (6) and (7) the electric dipole, quadrupole and octopole moment operators are of the form

$$\begin{aligned} \mathbf{M}^{(1)} &\equiv \mathbf{M} = \sum_i e_i \mathbf{r}_{i1}, \\ \mathbf{M}^{(2)} &= \frac{1}{2} \sum_i e_i (3\mathbf{r}_{i1}\mathbf{r}_{i2} - r_i^2 \mathbf{U}_{12}), \\ \mathbf{M}^{(3)} &= \frac{1}{2} \sum_i e_i \{5\mathbf{r}_{i1}\mathbf{r}_{i2}\mathbf{r}_{i3} - r_i^2 (\mathbf{U}_{12}\mathbf{r}_{i3} + \mathbf{U}_{23}\mathbf{r}_{i1} + \mathbf{U}_{31}\mathbf{r}_{i2})\}. \end{aligned} \quad (9)$$

Let $\Psi^{(0)}(\mathbf{r})$ be the eigenfunction of the unperturbed Hamiltonian H_0 , and $\Psi(\mathbf{r}, t)$ that of the total Hamiltonian H . The wave-function of the molecule in the k th perturbed state may be expressed as follows:

$$\Psi_k(\mathbf{r}, t) = \sum_j \{a_{jk}^{(0)} + a_{jk}^{(1)} + a_{jk}^{(2)} + a_{jk}^{(3)} + \dots\} \Psi_j^{(0)} e^{-i\omega_j t} \quad (10)$$

with $a_{jk}^{(0)} = \delta_{jk}$, while the remaining coefficients $a_{jk}^{(1)}$, $a_{jk}^{(2)}$, $a_{jk}^{(3)}$, ... are functions of the time and can be calculated from the set of differential equations

$$\frac{da_{jk}^{(p+1)}}{dt} = \frac{1}{i\hbar} \sum_m \langle j|H'|m\rangle a_{mk}^{(p)} e^{i\omega_{jm} t}, \quad p = 0, 1, 2, \dots, \quad (11)$$

where

$$H'_{jm} = \langle j|H'|m\rangle = \int \bar{\Psi}_j^0 H' \Psi_m^0 d\tau$$

is the matrix element of the perturbation Hamiltonian H' for the transition $j \rightarrow m$ between two unperturbed states j and m and $\omega_{jm} = \omega_j - \omega_m$ is the Bohr frequency *i.e.* the unperturbed energy difference between states j and m , divided by \hbar .

On putting the integration constants equal to zero in calculating the coefficients $a_{jk}^{(p+1)}$ from Equations (11), we have

$$\begin{aligned} a_{jk}^{(1)} &= \frac{1}{2} \sum_s \{a_{jk}^{(1)}(+\omega_s) + a_{jk}^{(1)}(-\omega_s)\} e^{i\omega_{jk} t}, \\ a_{jk}^{(2)} &= \frac{1}{4} \sum_{st} \{a_{jk}^{(2)}(+\omega_s + \omega_t) + a_{jk}^{(2)}(+\omega_s - \omega_t) + a_{jk}^{(2)}(-\omega_s + \omega_t) + a_{jk}^{(2)}(-\omega_s - \omega_t)\} e^{i\omega_{jk} t}, \\ a_{jk}^{(3)} &= \frac{1}{8} \sum_{stu} \{a_{jk}^{(3)}(+\omega_s + \omega_t + \omega_u) + a_{jk}^{(3)}(+\omega_s + \omega_t - \omega_u) + a_{jk}^{(3)}(+\omega_s - \omega_t + \omega_u) + \\ &\quad + a_{jk}^{(3)}(+\omega_s - \omega_t - \omega_u) + a_{jk}^{(3)}(-\omega_s + \omega_t + \omega_u) + a_{jk}^{(3)}(-\omega_s + \omega_t - \omega_u) + \\ &\quad + a_{jk}^{(3)}(-\omega_s - \omega_t + \omega_u) + a_{jk}^{(3)}(-\omega_s - \omega_t - \omega_u)\} e^{i\omega_{jk} t}, \end{aligned}$$

with

$$\begin{aligned}
 a_{jk}^{(1)}(\pm\omega_s) &= -\frac{1}{\hbar} \frac{\langle j|H_s^\pm|k\rangle}{\omega_{jk} \pm \omega_s} e^{\pm i\omega_s t}, \\
 a_{jk}^{(2)}(\pm\omega_s \pm \omega_t) &= \frac{1}{\hbar^2} \sum_m \frac{\langle j|H_s^\pm|m\rangle \langle m|H_t^\pm|k\rangle}{(\omega_{jk} \pm \omega_s \pm \omega_t)(\omega_{mk} \pm \omega_t)} e^{\pm i(\omega_s + \omega_t)t}, \\
 a_{jk}^{(3)}(\pm\omega_s \pm \omega_t \pm \omega_u) &= -\frac{1}{\hbar^3} \sum_{mn} \frac{\langle j|H_s^\pm|m\rangle \langle m|H_t^\pm|n\rangle \langle n|H_u^\pm|k\rangle}{(\omega_{jk} \pm \omega_s \pm \omega_t \pm \omega_u)(\omega_{mk} \pm \omega_t \pm \omega_u)(\omega_{nk} \pm \omega_u)} e^{\pm i(\omega_s + \omega_t + \omega_u)t}.
 \end{aligned} \tag{12}$$

3. Induced multipole moments of a molecule

Our problem consists in calculating the 2^n -pole electric moment $\mathbf{P}^{(n)}(t)$ induced in the molecule by the oscillating electric field (1). The quantum-mechanical matrix element of $\mathbf{P}^{(n)}$ for the transition $k \rightarrow l$ is given by

$$\mathbf{P}_{kl}^{(n)}(t) = \int \bar{\Psi}_k \mathbf{M}^{(n)} \Psi_l d\tau - \int \bar{\Psi}_k^0 \mathbf{M}^{(n)} \Psi_l^0 d\tau. \tag{13}$$

By (10) and (12), we obtain from (13) to within the third approximation of Dirac's quantum-mechanical perturbation calculus

$$\mathbf{P}_{kl}^{(n)}(t) = \mathbf{P}_{kl}^{(n)(1)}(t) + \mathbf{P}_{kl}^{(n)(2)}(t) + \mathbf{P}_{kl}^{(n)(3)}(t) + \dots \tag{14}$$

We now proceed to the discussion of the contributions to $\mathbf{P}_{kl}^{(n)}$ of successive orders of approximation.

(i) First-order multipole moment. In the first-order of perturbation theory the 2^n -pole induced moment of the molecule is

$$\mathbf{P}_{kl}^{(n)(1)}(t) = \sum_{ij} \{\bar{\delta}_{jk} a_{il}^{(1)} + \bar{a}_{jk}^{(1)} \delta_{il}\} \mathbf{M}_{ji}^{(n)} e^{i\omega_{jl}t} = \frac{1}{2} \sum_s \{\mathbf{P}_{kl}^{(n)}(+\omega_s) + \mathbf{P}_{kl}^{(n)}(-\omega_s)\} e^{i\omega_{kl}t}, \tag{15}$$

with

$$\mathbf{P}_{kl}^{(n)(1)}(\pm\omega_s) = \sum_{n_s=1}^{\infty} \frac{2^{n_s} n_s!}{(2n_s)!} {}^{(n)}\mathbf{A}_{kl}^{(n_s)}(\pm\omega_s) [n_s] \mathbf{E}_s^{\pm(n_s)} e^{\pm i\omega_s t}. \tag{16}$$

Here, the tensor of rank $n + n_s$

$${}^{(n)}\mathbf{A}_{kl}^{(n_s)}(\pm\omega_s) = \frac{1}{\hbar} \sum_i \left\{ \frac{\mathbf{M}_{ki}^{(n)} \mathbf{M}_{il}^{(n_s)}}{\omega_{il} \pm \omega_s} + \frac{\mathbf{M}_{ki}^{(n_s)} \mathbf{M}_{il}^{(n)}}{\omega_{ik} \mp \omega_s} \right\} \tag{17}$$

characterizes the linear or first-order polarization of the 2^n -pole electric moment due to the electric field of order n_s .

In particular, we obtain from (16) for the induced dipole moment

$$\begin{aligned} \mathbf{P}_{kl}^{(1)}(\pm\omega_s) = & \left\{ {}^{(1)}\mathbf{A}_{kl}^{(1)}(\pm\omega_s) \cdot \mathbf{E}_s^{\pm(1)} + \frac{1}{3} {}^{(1)}\mathbf{A}_{kl}^{(2)}(\pm\omega_s) : \mathbf{E}_s^{\pm(2)} + \right. \\ & \left. + \frac{1}{15} {}^{(1)}\mathbf{A}_{kl}^{(3)}(\pm\omega_s) : \mathbf{E}_s^{\pm(3)} + \dots \right\} e^{i\omega_s t}, \end{aligned} \quad (18)$$

where ${}^{(1)}\mathbf{A}_{kl}^{(1)}$, ${}^{(1)}\mathbf{A}_{kl}^{(2)}$, ${}^{(1)}\mathbf{A}_{kl}^{(3)}$, ... are tensors of the dipole polarization caused in the molecule by the first-order electric field $\mathbf{E}_s^{(1)}$, second-order field $\mathbf{E}_s^{(2)}$, third-order field $\mathbf{E}_s^{(3)}$ etc., respectively. The explicit form of these tensors follows directly from Equation (17) for $n = 1$ and $n_s = 1$, $n_s = 2$, $n_s = 3$.

The first term of Equation (18), with (17) for $n = 1$ and $n_s = 1$, yields the result obtained by Kramers and Heisenberg (1925).

Since

$$\mathbf{E}_s^{\pm(1)} \equiv \mathbf{E}_s^{\pm} = \mathbf{E}_s(0), \quad \mathbf{E}_s^{\pm(2)} = \mp i\mathbf{k}_s \mathbf{E}_s^{\pm}, \quad \mathbf{E}_s^{\pm(3)} = -\mathbf{k}_s \mathbf{k}_s \mathbf{E}_s^{\pm}, \dots, \quad (19)$$

we can write (18) in the form

$$\begin{aligned} \mathbf{P}_{kl}^{(1)}(\pm\omega_s) = & \left\{ {}^{(1)}\mathbf{A}_{kl}^{(1)}(\pm\omega_s) \cdot \mathbf{E}_s^{\pm} \mp \frac{i}{3} {}^{(1)}\mathbf{A}_{kl}^{(2)}(\pm\omega_s) : \mathbf{k}_s \mathbf{E}_s^{\pm} + \right. \\ & \left. - \frac{1}{15} {}^{(1)}\mathbf{A}_{kl}^{(3)}(\pm\omega_s) : \mathbf{k}_s \mathbf{k}_s \mathbf{E}_s^{\pm} + \dots \right\} e^{\pm i\omega_s t}, \end{aligned} \quad (20)$$

where \mathbf{k}_s is the wave vector.

Similarly, for $n = 2$ we obtain by (15) and (19) the induced quadrupole moment

$$\begin{aligned} \mathbf{P}_{kl}^{(2)}(\pm\omega_s) = & \left\{ {}^{(2)}\mathbf{A}_{kl}^{(1)}(\pm\omega_s) \cdot \mathbf{E}_s^{\pm} \mp \frac{i}{3} {}^{(2)}\mathbf{A}_{kl}^{(2)}(\pm\omega_s) : \mathbf{k}_s \mathbf{E}_s^{\pm} + \right. \\ & \left. - \frac{1}{15} {}^{(2)}\mathbf{A}_{kl}^{(3)}(\pm\omega_s) : \mathbf{k}_s \mathbf{k}_s \mathbf{E}_s^{\pm} + \dots \right\} e^{\pm i\omega_s t}. \end{aligned} \quad (21)$$

(ii) Second-order multipole moment. The 2^n -pole induced electric moment of the molecule in the second-order approximation is:

$$\mathbf{P}_{kl}^{(n)}(t) = \sum_{ij} \left\{ \bar{\delta}_{jk} a_{ii}^{(2)} + \overline{a_{jk}^{(1)}} a_{ii}^{(1)} + \overline{a_{jk}^{(2)}} \delta_{il} \right\} \mathbf{M}_{ji}^{(n)} e^{i\omega_j t}$$

and can be rewritten by (12) as follows:

$$\begin{aligned} \mathbf{P}_{kl}^{(n)}(t) = & \frac{1}{8} \left\{ \mathbf{P}_{kl}^{(n)}(+\omega_s + \omega_t) + \mathbf{P}_{kl}^{(n)}(+\omega_s - \omega_t) + \mathbf{P}_{kl}^{(n)}(-\omega_s + \omega_t) + \right. \\ & \left. + \mathbf{P}_{kl}^{(n)}(-\omega_s - \omega_t) \right\} e^{i\omega_{kl} t}. \end{aligned} \quad (22)$$

Here, we have

$$\begin{aligned}
 \mathbf{P}_{kl}^{(2)}(\pm\omega_s \pm \omega_t) &= \sum_{n_s=1}^{\infty} \sum_{n_t=1}^{\infty} \frac{2^{n_s+n_t} n_s! n_t!}{(2n_s)!(2n_t)!} \times \\
 &\times {}^{(n)}\mathbf{A}_{kl}^{(n_s+n_t)}(\pm\omega_s \pm \omega_t) [n_s + n_t] \mathbf{E}_s^{(n_s)\pm} \mathbf{E}_t^{(n_t)\pm} e^{\pm i t(\omega_s + \omega_t)}
 \end{aligned}
 \tag{23}$$

with the tensor of rank $n + n_s + n_t$

$$\begin{aligned}
 {}^{(n)}\mathbf{A}_{kl}^{(n_s+n_t)}(\pm\omega_s \pm \omega_t) &= \frac{2}{\hbar^2} \sum_{ij} \left\{ \frac{\mathbf{M}_{ki}^{(n)} \mathbf{M}_{ij}^{(n_s)} \mathbf{M}_{jl}^{(n_t)}}{(\omega_{il} \pm \omega_s \pm \omega_t)(\omega_{jl} \pm \omega_t)} + \right. \\
 &\left. + \frac{\mathbf{M}_{ki}^{(n_s)} \mathbf{M}_{ij}^{(n)} \mathbf{M}_{jl}^{(n_t)}}{(\omega_{ik} \mp \omega_s)(\omega_{jl} \pm \omega_t)} + \frac{\mathbf{M}_{ki}^{(n_s)} \mathbf{M}_{ij}^{(n_t)} \mathbf{M}_{jl}^{(n)}}{(\omega_{ik} \mp \omega_s)(\omega_{jk} \mp \omega_s \mp \omega_t)} \right\}
 \end{aligned}
 \tag{24}$$

accounting for the nonlinear or second-order polarization of the 2ⁿ-pole electric moment due to the two electric fields $\mathbf{E}_s^{(n_s)}$ and $\mathbf{E}_t^{(n_t)}$.

On replacing in Equation (23) and (24) ω_t by $-\omega_t$ we obtain immediately the explicite form of $\mathbf{P}_{kl}^{(2)}(\pm\omega_s \mp \omega_t)$ and ${}^{(n)}\mathbf{A}_{kl}^{(n_s+n_t)}(\pm\omega_s \mp \omega_t)$.

From Equation (23) we obtain

$$\begin{aligned}
 \mathbf{P}_{kl}^{(2)}(\pm\omega_s \pm \omega_t) &= \left\{ {}^{(n)}\mathbf{A}_{kl}^{(1+1)}(\pm\omega_s \pm \omega_t) : \mathbf{E}_s^{\pm} \mathbf{E}_t^{(1)\pm} + \frac{1}{3} {}^{(n)}\mathbf{A}_{kl}^{(1+2)}(\pm\omega_s \pm \omega_t) : \mathbf{E}_s^{\pm} \mathbf{E}_t^{(2)\pm} + \right. \\
 &\left. + \frac{1}{3} {}^{(n)}\mathbf{A}_{kl}^{(2+1)}(\pm\omega_s \pm \omega_t) : \mathbf{E}_s^{(2)\pm} \mathbf{E}_t^{(1)\pm} + \frac{1}{9} {}^{(n)}\mathbf{A}_{kl}^{(2+2)}(\pm\omega_s \pm \omega_t) : \mathbf{E}_s^{(2)\pm} \mathbf{E}_t^{(2)\pm} + \dots \right\} e^{\pm i t(\omega_s + \omega_t)},
 \end{aligned}
 \tag{25}$$

or by (19)

$$\begin{aligned}
 \mathbf{P}_{kl}^{(2)}(\pm\omega_s \pm \omega_t) &= \left\{ {}^{(n)}\mathbf{A}_{kl}^{(1+1)}(\pm\omega_s \pm \omega_t) : \mathbf{E}_s^{\pm} \mathbf{E}_t^{\pm} + \right. \\
 &\mp \frac{i}{3} {}^{(n)}\mathbf{A}_{kl}^{(1+2)}(\pm\omega_s \pm \omega_t) : \mathbf{E}_s^{\pm} \mathbf{k}_t \mathbf{E}_t^{\pm} \mp \frac{i}{3} {}^{(n)}\mathbf{A}_{kl}^{(2+1)}(\pm\omega_s \pm \omega_t) : \mathbf{k}_s \mathbf{E}_s^{\pm} \mathbf{E}_t^{\pm} + \\
 &\left. - \frac{1}{9} {}^{(n)}\mathbf{A}_{kl}^{(2+2)}(\pm\omega_s \pm \omega_t) : \mathbf{k}_s \mathbf{E}_s^{\pm} \mathbf{k}_t \mathbf{E}_t^{\pm} + \dots \right\} e^{\pm i t(\omega_s + \omega_t)}.
 \end{aligned}
 \tag{26}$$

Equation (25) or (26) yields for $n = 1$ the induced dipole moment of the second approximation; similarly, for $n = 2$ we obtain the induced quadrupole moment and for $n = 3$ the induced octopole moment, etc.

(iii) Third-order multipole moment. In third-order perturbation theory we obtain for the 2ⁿ-pole induced moment of the molecule

$$\begin{aligned}
 \mathbf{P}_{kl}^{(3)}(t) &= \frac{1}{48} \sum_{stu} \left\{ \mathbf{P}_{kl}^{(3)}(+\omega_s + \omega_t + \omega_u) + \mathbf{P}_{kl}^{(3)}(+\omega_s + \omega_t - \omega_u) + \right. \\
 &+ \mathbf{P}_{kl}^{(3)}(+\omega_s - \omega_t + \omega_u) + \mathbf{P}_{kl}^{(3)}(+\omega_s - \omega_t - \omega_u) + \mathbf{P}_{kl}^{(3)}(-\omega_s + \omega_t + \omega_u) + \\
 &\left. + \mathbf{P}_{kl}^{(3)}(-\omega_s - \omega_t + \omega_u) + \mathbf{P}_{kl}^{(3)}(-\omega_s + \omega_t - \omega_u) + \mathbf{P}_{kl}^{(3)}(-\omega_s - \omega_t - \omega_u) \right\} e^{i t \omega_{kl}}
 \end{aligned}
 \tag{27}$$

with

$$\begin{aligned} \mathbf{P}_{kl}^{(3)}(\pm\omega_s \pm \omega_t \pm \omega_u) &= \sum_{n_s=1}^{\infty} \sum_{n_t=1}^{\infty} \sum_{n_u=1}^{\infty} \frac{2^{n_s+n_t+n_u} n_s! n_t! n_u!}{(2n_s)! (2n_t)! (2n_u)!} \times \\ &\times {}^{(n)}\mathbf{A}_{kl}^{(n_s+n_t+n_u)}(\pm\omega_s \pm \omega_t \pm \omega_u) [n_s + n_t + n_u] \overset{\pm}{\mathbf{E}}_s^{(n_s)} \overset{\pm}{\mathbf{E}}_t^{(n_t)} \overset{\pm}{\mathbf{E}}_u^{(n_u)} e^{\pm i t(\omega_s + \omega_t + \omega_u)}. \end{aligned} \tag{28}$$

Here, we have introduced the following tensor of rank $n + n_s + n_t + n_u$:

$$\begin{aligned} {}^{(n)}\mathbf{A}_{kl}^{(n_s+n_t+n_u)}(\pm\omega_s \pm \omega_t \pm \omega_u) &= \frac{6}{\hbar^3} \sum_{ijm} \left\{ \frac{\mathbf{M}_{ki}^{(n)} \mathbf{M}_{im}^{(n_s)} \mathbf{M}_{mj}^{(n_t)} \mathbf{M}_{jl}^{(n_u)}}{(\omega_{il} \pm \omega_s \pm \omega_t \pm \omega_u) (\omega_{ml} \pm \omega_t \pm \omega_u) (\omega_{jl} \pm \omega_u)} + \right. \\ &+ \frac{\mathbf{M}_{ki}^{(n_s)} \mathbf{M}_{im}^{(n)} \mathbf{M}_{mj}^{(n_t)} \mathbf{M}_{jl}^{(n_u)}}{(\omega_{ik} \mp \omega_s) (\omega_{ml} \pm \omega_t \pm \omega_u) (\omega_{jl} \pm \omega_u)} + \frac{\mathbf{M}_{ki}^{(n_s)} \mathbf{M}_{im}^{(n_t)} \mathbf{M}_{mj}^{(n)} \mathbf{M}_{jl}^{(n_u)}}{(\omega_{ik} \mp \omega_s) (\omega_{mk} \mp \omega_s \mp \omega_t) (\omega_{jl} \mp \omega_u)} + \\ &\left. + \frac{\mathbf{M}_{ki}^{(n_s)} \mathbf{M}_{im}^{(n_t)} \mathbf{M}_{mj}^{(n_u)} \mathbf{M}_{jl}^{(n)}}{(\omega_{ik} \mp \omega_s) (\omega_{mk} \mp \omega_s \mp \omega_t) (\omega_{jk} \mp \omega_s \pm \omega_t \pm \omega_u)} \right\} \end{aligned} \tag{29}$$

which characterizes the third-order polarization of the molecule due to the three electric fields $\mathbf{E}_s^{(n_s)}$, $\mathbf{E}_t^{(n_t)}$ and $\mathbf{E}_u^{(n_u)}$.

In a good approximation we obtain from (28), by (19),

$$\mathbf{P}_{kl}^{(3)}(\pm\omega_s \pm \omega_t \pm \omega_u) = \{ {}^{(n)}\mathbf{A}_{kl}^{(1+1+1)}(\pm\omega_s \pm \omega_t \pm \omega_u) : \mathbf{E}_s^{\pm} \mathbf{E}_t^{\pm} \mathbf{E}_u^{\pm} + \dots \} e^{\pm i t(\omega_s + \omega_t + \omega_u)}. \tag{30}$$

The expressions (18), (21), (25) and (30) contain several tensors which have been discussed phenomenologically by Franken and Ward (1963) as well as by Pershan (1963).

In the case of the electric dipole approximation, the diagonal matrix elements of the second- and third-order polarizability tensors of (24) and (29) by symmetrizing operations assume forms analogical to those derived by Armstrong *et al.* (1962). The diagonal matrix elements of the multipole polarizability tensors of (17), (24) and (29) can be calculated theoretically by methods discussed in the paper of Dalgarno (1962).

4. Electric multipole light scattering

At considerable distances R from the centre of a volume V of a gas, the electric field of the light wave scattered by a molecule is in general given by (the part with magnetic multipoles is not considered here)

$$\mathbf{E}'(\mathbf{R}, t) = \frac{1}{R} \sum_{n=1}^{\infty} \frac{2^n n!}{c^{n+1} (2n)!} \left\{ \mathbf{s} \times \left[\mathbf{s} \times \left(\frac{d^{n+1}}{dt^{n+1}} \mathbf{P}^{(n)} [n-1] \mathbf{s}^{n-1} \right) \right] \right\}, \tag{31}$$

where c is the velocity of the incident light, \mathbf{s} is the unit vector in the direction of the observation vector $\mathbf{R} = \mathbf{s}R$, and $\mathbf{P}^{(n)}$ is the 2^n -pole induced moment of the scattering molecule.

If \mathbf{u} is a unit vector perpendicular to the unit vector \mathbf{s} , i.e. $\mathbf{u} \cdot \mathbf{s} = 0$, we have by (31)

$$\begin{aligned} \mathbf{E}' \cdot \mathbf{u} &= -\frac{1}{R} \sum_{n=1}^{\infty} \frac{2^n n!}{c^{n+1} (2n)!} \frac{d^{n+1}}{dt^{n+1}} \mathbf{P}^{(n)} [n] \mathbf{u} \mathbf{s}^{n-1} \\ &= -\frac{1}{Rc^2} \left\{ \frac{d^2}{dt^2} \mathbf{P}^{(1)} \cdot \mathbf{u} + \frac{1}{3c} \frac{d^3}{dt^3} \mathbf{P}^{(2)} : \mathbf{u} \mathbf{s} + \frac{1}{15c^2} \frac{d^4}{dt^4} \mathbf{P}^{(3)} : \mathbf{u} \mathbf{s} \mathbf{s} + \dots \right\}, \end{aligned} \tag{32}$$

where the consecutive terms correspond to electric dipole, quadrupole, octopole *etc.* electromagnetic radiation.

By (32), the scattered light intensity $I_u = (\mathbf{E}' \cdot \mathbf{u})^2$, with oscillations in the direction \mathbf{u} , is given as follows:

$$I_u = \frac{1}{R^2} \sum_{n=1}^{\infty} \frac{2^{2n} (n!)^2}{c^{2(n+1)} [(2n)!]^2} \mathbf{s}^{n-1} \mathbf{u} [n] \overline{\left\{ \frac{d^{n+1}}{dt^{n+1}} \mathbf{P}^{(n)} \frac{d^{n+1}}{dt^{n+1}} \mathbf{P}^{(n)} \right\}^t} [n] \mathbf{u} \mathbf{s}^{n-1}, \tag{33}$$

where the horizontal straight line $\text{---}t$ denotes time-averaging.

With respect to (33) we introduce the tensor

$$\mathbf{I}_{kl}^{(2n)} = \overline{\left\{ \frac{d^{n+1}}{dt^{n+1}} \mathbf{P}_{kl}^{(n)} \frac{d^{n+1}}{dt^{n+1}} \mathbf{P}_{lk}^{(n)} \right\}^t}, \tag{34}$$

which describes electric 2^n -pole light scattering for the transition $k \rightarrow l$.

By the expression (14), the scattering tensor (34) can be expressed as follows:

$$\mathbf{I}_{kl}^{(2n)} = \mathbf{I}_{kl}^{(2n)(1)} + \mathbf{I}_{kl}^{(2n)(2)} + \mathbf{I}_{kl}^{(2n)(3)} + \dots \tag{35}$$

(i) First-order approximation. The scattering tensor of first-order perturbation theory is given by

$$\mathbf{I}_{kl}^{(2n)(1)} = \frac{1}{2} \sum_s \{ \mathbf{I}^{(2n)}(\omega_{kl} + \omega_s) + \mathbf{I}^{(2n)}(\omega_{kl} - \omega_s) \}, \tag{36}$$

where we have

$$\begin{aligned} \mathbf{I}^{(2n)}(\omega_{kl} \pm \omega_s) &= \frac{1}{2} (\omega_{kl} \pm \omega_s)^{2n+2} \sum_{n_s=1}^{\infty} \frac{2^{2n_s} (n_s!)^2}{[(2n_s)!]^2} {}^{(n)}\mathbf{A}_{kl}^{(n_s)} (\pm \omega_s)^{(n)} \mathbf{A}_{lk}^{(n_s)} (\mp \omega_s) \times \\ &\quad \times [2n_s] \overset{\pm}{\mathbf{E}}_s^{(n_s)} \overset{\pm}{\mathbf{E}}_s^{(n_s)}. \end{aligned} \tag{37}$$

In particular, we obtain from (37) for electric dipole scattering ($n = 1$)

$$\begin{aligned} \mathbf{I}^{(2)}(\omega_{kl} \pm \omega_s) &= \frac{1}{2} (\omega_{kl} \pm \omega_s)^4 \left\{ {}^{(1)}\mathbf{A}_{kl}^{(1)} (\pm \omega_s) {}^{(1)}\mathbf{A}_{lk}^{(1)} (\mp \omega_s) - \right. \\ &\quad \left. - \frac{1}{9} {}^{(1)}\mathbf{A}_{kl}^{(2)} (\pm \omega_s) {}^{(1)}\mathbf{A}_{lk}^{(2)} (\mp \omega_s) : \mathbf{k}_s \mathbf{k}_s + \dots \right\} : \mathbf{E}_s^{\pm} \mathbf{E}_s^{\pm}. \end{aligned} \tag{38}$$

Since ${}^{(1)}A^{(2)}/{}^{(1)}A^{(1)}$ is at the most of order 10^{-6} , the ratio of the second and first terms in (38) is approximately of order $k_s^2 10^{-16}$, and plays a role only in the case of short wave-lengths.

For $n = 2$ Equation (37) yields for the tensor of electric quadrupole scattering of light

$$\mathbf{I}^{(4)}(\omega_{kl} \pm \omega_s) = \frac{1}{2} (\omega_{kl} \pm \omega_s)^6 {}^{(2)}\mathbf{A}_{kl}^{(1)}(\pm \omega_s) {}^{(2)}\mathbf{A}_{lk}^{(1)}(\pm \omega_s) : \mathbf{E}_s^\pm \mathbf{E}_s^\pm. \tag{39}$$

(ii) Second-order approximation. In the second approximation the electric multipole scattering tensor is of the form

$$\begin{aligned} \mathbf{I}_{kl}^{(2n)} = & \frac{1}{8} \sum_s {}^{(2)}\{\mathbf{I}^{(2n)}(\omega_{kl} + 2\omega_s) + \mathbf{I}^{(2n)}(\omega_{kl} - 2\omega_s)\} + \frac{1}{4} \sum_{s \neq t} {}^{(2)}\{\mathbf{I}^{(2n)}(\omega_{kl} + \omega_s - \omega_t) + \\ & + \mathbf{I}^{(2n)}(\omega_{kl} + \omega_s + \omega_t) + \mathbf{I}^{(2n)}(\omega_{kl} - \omega_s + \omega_t) + \mathbf{I}^{(2n)}(\omega_{kl} - \omega_s - \omega_t)\} \end{aligned} \tag{40}$$

with

$$\begin{aligned} \mathbf{I}^{(2n)}(\omega_{kl} \pm \omega_s \pm \omega_t) = & \frac{1}{8} (\omega_{kl} \pm \omega_s \pm \omega_t)^{2n+2} \sum_{n_s=1}^\infty \sum_{n_t=1}^\infty \frac{2^{2(n_s+n_t)} (n_s! n_t!)^2}{[(2n_s)! (2n_t)!]^2} \times \\ & \times {}^{(n)}\mathbf{A}_{kl}^{(n_s+n_t)}(\pm \omega_s \pm \omega_t) {}^{(n)}\mathbf{A}_{kl}^{(n_s+n_t)}(\mp \omega_s \mp \omega_t) [2(n_s + n_t)] \overset{\pm}{\mathbf{E}}_s^{(n_s)} \overset{\mp}{\mathbf{E}}_s^{(n_s)} \overset{\pm}{\mathbf{E}}_t^{(n_t)} \overset{\mp}{\mathbf{E}}_t^{(n_t)}. \end{aligned} \tag{41}$$

This equation yields in the case of electric dipole scattering

$$\begin{aligned} & \mathbf{I}^{(2)}(\omega_{kl} \pm \omega_s \pm \omega_t) = \\ = & \frac{1}{8} (\omega_{kl} \pm \omega_s \pm \omega_t)^4 {}^{(1)}\mathbf{A}_{kl}^{(1+1)}(\pm \omega_s \pm \omega_t) {}^{(1)}\mathbf{A}_{lk}^{(1+1)}(\mp \omega_s \mp \omega_t) : \mathbf{E}_s^\pm \mathbf{E}_s^\mp \mathbf{E}_t^\pm \mathbf{E}_t^\mp. \end{aligned} \tag{42}$$

(iii) Third-order approximation. Similarly, we find from (34) and (27) for the third-order multipole scattering tensor (we have written here the terms for $\omega_s \neq \omega_t \neq \omega_u$ only)

$$\begin{aligned} \mathbf{I}_{kl}^{(3)} = & \frac{1}{6} \sum_{s \neq t \neq u} {}^{(3)}\{\mathbf{I}^{(2n)}(\omega_{kl} + \omega_s + \omega_t + \omega_u) + \mathbf{I}^{(2n)}(\omega_{kl} + \omega_s + \omega_t - \omega_u) + \dots + \\ & + \mathbf{I}^{(2n)}(\omega_{kl} + \omega_s - \omega_t - \omega_u) + \mathbf{I}^{(2n)}(\omega_{kl} - \omega_s - \omega_t - \omega_u)\}, \end{aligned} \tag{43}$$

where we have

$$\begin{aligned} \mathbf{I}^{(3)}(\omega_{kl} \pm \omega_s \pm \omega_t \pm \omega_u) = & \frac{1}{32} (\omega_{kl} \pm \omega_s \pm \omega_t \pm \omega_u)^{2n+2} \times \\ \times & \sum_{n_s=1}^\infty \sum_{n_t=1}^\infty \sum_{n_u=1}^\infty \frac{2^{2(n_s+n_t+n_u)} (n_s! n_t! n_u!)^2}{[(2n_s)! (2n_t)! (2n_u)!]^2} {}^{(n)}\mathbf{A}_{kl}^{(n_s+n_t+n_u)}(\pm \omega_s \pm \omega_t \pm \omega_u) \times \\ \times & {}^{(n)}\mathbf{A}_{kl}^{(n_s+n_t+n_u)}(\pm \omega_s \mp \omega_t \mp \omega_u) [2(n_s + n_t + n_u)] \overset{\pm}{\mathbf{E}}_s^{(n_s)} \overset{\mp}{\mathbf{E}}_s^{(n_s)} \overset{\pm}{\mathbf{E}}_t^{(n_t)} \overset{\mp}{\mathbf{E}}_t^{(n_t)} \overset{\pm}{\mathbf{E}}_u^{(n_u)} \overset{\mp}{\mathbf{E}}_u^{(n_u)}. \end{aligned} \tag{44}$$

In the case of electric dipole scattering, if higher-order terms are neglected, Equation (44) reduces to

$$\begin{aligned} \mathbf{I}^{(2)}(\omega_{kl} \pm \omega_s \pm \omega_t \pm \omega_u) &= \frac{1}{32} (\omega_{kl} \pm \omega_s \pm \omega_t \pm \omega_u)^4 \times \\ &\times {}^{(1)}\mathbf{A}_{kl}^{(1+1+1)}(\pm \omega_s \pm \omega_t \pm \omega_u) {}^{(1)}\mathbf{A}_{lk}^{(1+1+1)}(\mp \omega_s \mp \omega_t \mp \omega_u) :: \mathbf{E}_s^\pm \mathbf{E}_s^\mp \mathbf{E}_t^\pm \mathbf{E}_t^\mp \mathbf{E}_u^\pm \mathbf{E}_u^\mp. \end{aligned} \quad (45)$$

The tensor of (42), which determines second-order electric dipole scattering, is non-zero only in the case of molecules without a centre of inversion, and is discussed in other papers (Kielich 1964 a, b, c) for molecules presenting the point group symmetry D_{2d} , D_{3h} , C_{3v} , C_{4v} , \hat{C}_{6v} , $C_{\infty v}$ and T_d . The third-order electric dipole scattering tensor of (45) exists in all cases of molecules of arbitrary symmetry, including optically isotropic molecules. Numerical evaluations indicate that, in gases and liquids such as *e.g.* chloroform whose molecules do not possess a centre of inversion, it should be possible to observe non-linear variations in the scattered light intensity, as due to an intense light beam from the lasers now available (Kielich 1964).

5. Tensor of the optical permittivity

Let $\rho = N/V$ be the number density of molecules of a system of volume V . We assume for simplicity that intermolecular interactions in the system are absent or, at the most, very weak. The tensor of the optical permittivity of such a system is given in general by the equation (Jansen 1958 b, Kielich 1965 a)

$$(\boldsymbol{\epsilon} - \mathbf{U}) \cdot \mathbf{E}(t) = 4\pi\rho \sum_{n=1}^{\infty} (-1)^{n-1} \frac{2^n n!}{(2n)!} \nabla^{n-1} [n-1] \mathbf{P}^{(n)}, \quad (46)$$

where $\mathbf{P}^{(n)}$ is the induced multipole moment obtained by averaging its diagonal matrix elements (as given by Equation (14)) with the density matrix ρ_{kk} over all occupied states k of a molecule in the presence of the electric fields:

$$\mathbf{P}^{(n)} = \sum_k \mathbf{P}_{kk}^{(n)} \rho_{kk}. \quad (47)$$

In the approximation of dipole polarization ($n = 1$) we obtain from (46), by (14), the result

$$(\boldsymbol{\epsilon} - \mathbf{U}) \cdot \mathbf{E}(t) = 4\pi\rho \mathbf{P}^{(1)} = 4\pi\rho \{ \mathbf{P}^{(1)} + \mathbf{P}^{(1)} + \mathbf{P}^{(1)} + \dots \}, \quad (48)$$

which may be written as follows in the absence of temperature-dependent orientational effects in the system

$$(\boldsymbol{\epsilon} - \boldsymbol{\epsilon}) \cdot \mathbf{E}(t) = 4\pi\rho \{ \mathbf{P}^{(1)} + \mathbf{P}^{(1)} + \dots \}, \quad (49)$$

where

$$\begin{aligned}
 {}^{(1)}(\boldsymbol{\epsilon}-\mathbf{U}) \cdot \mathbf{E}(t) = 2\pi\rho \sum_s \sum_{n_s=1}^{\infty} \frac{2^{n_s} n_s!}{(2n_s)!} \{ {}^{(1)}\mathbf{A}^{(n_s)}(+\omega_s) \times \\
 \times [n_s] \overset{+}{\mathbf{E}}_s^{(n_s)} e^{it\omega_s} + {}^{(1)}\mathbf{A}^{(n_s)}(-\omega_s) [n_s] \overset{-}{\mathbf{E}}_s^{(n_s)} e^{-it\omega_s} \} \tag{50}
 \end{aligned}$$

is the optical permittivity tensor of the first-order approximation.

The Equation (49) with the expressions (22) and (27) for $n = 1$ determines the general form of the nonlinear change in the optical permittivity tensor of the system, as due to the electric fields of electromagnetic waves incident thereon.

In certain simpler cases, the frequency-dependence of the optical permittivity tensor can be obtained easily from classical electron theory. Let the i th electric charge e_i of a molecule of mass m_i undergo the displacement \mathbf{i}_i with respect to its equilibrium position as a result of the oscillating electric fields of Equation (1); its classical equation of motion can then be written as follows in the absence of damping of oscillations of the charges:

$$m_i \frac{d^2}{dt^2} \mathbf{r}_i + \boldsymbol{\alpha}_i \cdot \mathbf{r}_i - \frac{1}{2} \boldsymbol{\beta}_i : \mathbf{r}_i \mathbf{r}_i - \frac{1}{6} \boldsymbol{\gamma}_i : \mathbf{r}_i \mathbf{r}_i \mathbf{r}_i - \dots = e_i \sum_s \mathbf{E}_s \cos \omega_s t, \tag{51}$$

where $\boldsymbol{\alpha}_i$ is the tensor of harmonic and $\boldsymbol{\beta}_i$ and $\boldsymbol{\gamma}_i$ are the tensors of anharmonic oscillations.

Assuming for simplicity that the frequency of the harmonic oscillations ω_i are the same in all directions, *i.e.* when $\boldsymbol{\alpha}_i = m_i \omega_i^2 \mathbf{U}$, we derive from the equation (51) the displacement \mathbf{r}_i and thus the induced dipole moment of the molecule which is given by the expansion

$$\begin{aligned}
 \mathbf{m} = \sum_i e_i \mathbf{r}_i = \sum_s \mathbf{a}(\omega_s) \cdot \mathbf{E}_s \cos \omega_s t + \frac{1}{4} \sum_{st} \{ \mathbf{b}(\omega_s + \omega_t) \cos (\omega_s + \omega_t) t + \\
 + \mathbf{b}(\omega_s - \omega_t) \cos (\omega_s - \omega_t) t \} : \mathbf{E}_s \mathbf{E}_t + \frac{1}{24} \sum_{stu} \{ \mathbf{c}(\omega_s + \omega_t + \omega_u) \cos (\omega_s + \omega_t + \omega_u) t + \\
 + \mathbf{c}(\omega_s + \omega_t - \omega_u) \cos (\omega_s + \omega_t - \omega_u) t + \mathbf{c}(\omega_s - \omega_t + \omega_u) \cos (\omega_s - \omega_t + \omega_u) t + \\
 + \mathbf{c}(-\omega_s + \omega_t + \omega_u) \cos (-\omega_s + \omega_t + \omega_u) t \} : \mathbf{E}_s \mathbf{E}_t \mathbf{E}_u + \dots \tag{52}
 \end{aligned}$$

with the following tensors of the first, second and third-order dipole polarizabilities, respectively (for the case of two various frequencies ω_1 and ω_2 see *e.g.* Kielich 1964 a, b):

$$\begin{aligned}
 \mathbf{a}(\omega_s) = \sum_i \frac{e_i^2 \mathbf{U}}{m_i (\omega_i^2 - \omega_s^2)}, \\
 \mathbf{b}(\omega_s \pm \omega_t) = \sum_i \frac{e_i^3 \boldsymbol{\beta}_i}{m_i^3 (\omega_i^2 - \omega_s^2) (\omega_i^2 - \omega_t^2) [\omega_i^2 - (\omega_s \pm \omega_t)^2]}, \\
 \mathbf{c}(\omega_s \pm \omega_t \pm \omega_u) = \sum_i \frac{e_i^4}{m_i^4 (\omega_i^2 - \omega_s^2) (\omega_i^2 - \omega_t^2) (\omega_i^2 - \omega_u^2) [\omega_i^2 - (\omega_s \pm \omega_t \pm \omega_u)^2]} \left\{ \boldsymbol{\gamma}_i + \right. \\
 \left. + \frac{\boldsymbol{\beta}_i \cdot \boldsymbol{\beta}_i}{m_i [\omega_i^2 - (\omega_s \pm \omega_t)^2]} + \frac{\boldsymbol{\beta}_i \cdot \boldsymbol{\beta}_i}{m_i [\omega_i^2 - (\omega_t + \omega_u)^2]} + \frac{\boldsymbol{\beta}_i \cdot \boldsymbol{\beta}_i}{m_i [\omega_i^2 - (\omega_s \pm \omega_u)^2]} \right\}. \tag{53}
 \end{aligned}$$

In the case of a single frequency $\omega = \omega_s = \omega_i = \omega_u$, we obtain from (52) and (53) on putting $\beta_i = 2\lambda_x$ and $\gamma_i = 6\eta_x$ the result found by Armstrong *et al.* (1962). From (52) and (53) we can also derive the result of Adler (1964) for second-order polarization at frequencies $\omega_1 + \omega_2$.

By the expansion of (52) we obtain for the non-linear variation of the permittivity tensor of a gas

$$\begin{aligned} (\epsilon - \epsilon^{(1)}) \cdot \mathbf{E}(t) = & \frac{\pi}{6} \rho \sum_{stu} \langle \{ \mathbf{c}(\omega_s + \omega_t + \omega_u) \cos(\omega_s + \omega_t + \omega_u)t + \\ & + \mathbf{c}(\omega_s + \omega_t - \omega_u) \cos(\omega_s + \omega_t - \omega_u)t + \mathbf{c}(\omega_s - \omega_t + \omega_u) \cos(\omega_s - \omega_t + \omega_u)t + \\ & + \mathbf{c}(-\omega_s + \omega_t + \omega_u) \cos(-\omega_s + \omega_t + \omega_u)t \} : \mathbf{E}_s \mathbf{E}_t \mathbf{E}_u \rangle, \end{aligned} \quad (54)$$

where the symbol $\langle \rangle$ denotes averaging over all possible orientations of the molecules with respect to the reference coordinate system XYZ . We will now proceed to the discussion of this formula for several special cases.

We first consider the special case when the molecules of a gas are subjected to two electric fields $\mathbf{E}_1(t)$ and $\mathbf{E}_2(t)$. We assume the electric field strength \mathbf{E}_1 conveyed by the wave of frequency ω_1 to be small and assign to it the role of a measuring field, whereas that of the other wave, $\mathbf{E}_2(t) = \mathbf{E}_2 \cos \omega_2 t$, is of very high intensity, sufficient for producing non-linear polarization of the gas. In our subsequent considerations, the non-linear effect due to the field $\mathbf{E}_2(t)$ will be time-averaged.

If, in particular, the molecules possess the spherical symmetry, we have from (54) and (53) for the above assumptions (the terms with $\cos(\omega_1 \pm 2\omega_2)t$ vanish by time-averaging)

$$\epsilon - \epsilon^{(1)} = \pi \rho \sum_i \frac{e_i^4}{m_i^4 (\omega_i^2 - \omega_1^2)^2 (\omega_i^2 - \omega_2^2)^2} \{ \gamma_i^\perp \mathbf{U} E_2^2 + (\gamma_i^\parallel - \gamma_i^\perp) \mathbf{E}_2 \mathbf{E}_2 \}, \quad (55)$$

where γ_i^\parallel and γ_i^\perp are the anharmonicity force constants for \mathbf{E}_1 and \mathbf{E}_2 directed mutually parallel or perpendicularly and $\beta_i = 0$.

In the case when a strong *DC* electric field \mathbf{E}_2^0 is applied to the gas, *i.e.* when $\omega_2 = 0$, Equation (54) yields for spherical molecules

$$\epsilon - \epsilon^{(1)} = 2\pi \rho \sum_i \frac{e_i^4}{m_i^4 (\omega_i^2 - \omega_1^2)^2 \omega_i^4} \{ \gamma_i^\perp \mathbf{U} E_2^0 + (\gamma_i^\parallel - \gamma_i^\perp) \mathbf{E}_2^0 \mathbf{E}_2^0 \}. \quad (56)$$

If the measuring electric field \mathbf{E}_1 varies but very slowly with respect to the rapid oscillations of the polarizing field \mathbf{E}_2 (of *e.g.* optical frequency) or if $\omega_1 = 0$, Equation (54) becomes

$$\Delta \epsilon = \pi \rho \sum_i \frac{e_i^4}{m_i^4 \omega_i^4 (\omega_i^2 - \omega_2^2)^2} \{ \gamma_i^\perp \mathbf{U} E_2^2 + (\gamma_i^\parallel - \gamma_i^\perp) \mathbf{E}_2 \mathbf{E}_2 \}. \quad (57)$$

This formula determines the non-linear variations of the dielectric permittivity, *i.e.* the dielectric saturation, as produced in the gas by an intense light beam — an effect previously discussed by Piekara and the present author (1958, Kielich and Piekara 1959) without considering its dependence on the frequency of the intense light beam.

Let us assume that the measuring electromagnetic wave with field \mathbf{E}_1 propagates in the direction of the Y -axis; computations from (55) or (56) of the optical permittivity in the directions of the axes X and Z now lead to the expressions

$$\epsilon_z - \epsilon_x = \pi Q \sum_i \frac{e_i^4 (\gamma_i^{\parallel} - \gamma_i^{\perp})}{m_i^4 (\omega_i^2 - \omega_1^2)^2 (\omega_i^2 - \omega_2^2)^2} \{E_{2z}^2 - E_{2x}^2\}, \tag{58}$$

$$\epsilon_z - \epsilon_x = 2\pi Q \sum_i \frac{e_i^4 (\gamma_i^{\parallel} - \gamma_i^{\perp})}{m_i^4 (\omega_i^2 - \omega_1^2)^2 \omega_i^4} \{E_{2z}^{0^*} - E_{2x}^{0^*}\}. \tag{59}$$

Equation (58) determines the optical birefringence produced in a gas by a strong oscillating electric field as first predicted and discussed by Buckingham (1956) (who did not take into account explicitly the frequency-dependence). The Formula (59) describes the well-known effect of Voigt.

In the general case of molecules with arbitrary symmetry Equation (54) becomes

$$\begin{aligned} (\boldsymbol{\epsilon} - \boldsymbol{\epsilon}^{(1)}) \cdot \mathbf{E}(t) = & \frac{\pi Q}{180} \sum_{stu} \{ (\mathbf{U}_{st} : \mathbf{c}_{stu} : \mathbf{U}_{tu}) [4\mathbf{E}_s(\mathbf{E}_t \cdot \mathbf{E}_u) - \mathbf{E}_t(\mathbf{E}_u \cdot \mathbf{E}_s) - \mathbf{E}_u(\mathbf{E}_s \cdot \mathbf{E}_t)] + \\ & + (\mathbf{U}_{st} : \mathbf{c}_{stu} : \mathbf{U}_{su}) [3\mathbf{E}_t(\mathbf{E}_u \cdot \mathbf{E}_s) + 3\mathbf{E}_u(\mathbf{E}_s \cdot \mathbf{E}_t) - 2\mathbf{E}_s(\mathbf{E}_t \cdot \mathbf{E}_u)] \}, \end{aligned} \tag{60}$$

where by \mathbf{c}_{stu} we have denoted for simplicity the sum of the four terms in the parentheses $\{ \}$ of Equation (54).

The formalism proposed in this paper is essentially applicable to isolated atoms and molecules *i.e.* to gaseous media wherein, regrettably, non-linear effects are weaker than in solids. Nevertheless, it can be hoped that by applying more highly perfected measuring techniques it will be possible to perform various ingenious experiments on the properties of gaseous media as affected by intense light beams. Predictably, more marked non-linear effects in gases will occur in conditions when *e.g.* one or more oscillation frequencies of the intense incident light beams fall near an absorption band of the substance investigated (non-linear resonance effects). Such effects, if accessible to observation in gases, will provide us with information on the behaviour of isolated atoms or molecules in intense optical electric fields, information not biased by the presence of neighbouring molecules.

APPENDIX

The rth-order multipole moment

In general, the r th-order contribution to the electric 2^n -pole induced moment of the molecule may be written as

$$\begin{aligned} \mathbf{P}_{kl}^{(n)}(t) = & \frac{1}{2^r r!} \sum_{s_1 s_2 \dots s_r} \{ \mathbf{P}_{kl}^{(n)}(+\omega_{s_1} + \omega_{s_2} + \dots + \omega_{s_r}) + \mathbf{P}_{kl}^{(n)}(+\omega_{s_1} + \omega_{s_2} + \dots - \omega_{s_r}) + \dots + \\ & + \mathbf{P}_{kl}^{(n)}(+\omega_{s_1} - \omega_{s_2} - \dots - \omega_{s_r}) + \mathbf{P}_{kl}^{(n)}(-\omega_{s_1} - \omega_{s_2} - \dots - \omega_{s_r}) \} e^{i\omega_k t}, \end{aligned} \tag{A.1}$$

where we have

$$\begin{aligned} \mathbf{P}_{kl}^{(r)}(\pm\omega_{s_1} \pm \dots \pm\omega_{s_r}) &= \sum_{n_{s_1}=1}^{\infty} \dots \sum_{n_{s_r}=1}^{\infty} \frac{2^{n_{s_1}+\dots+n_{s_r}} n_{s_1}! \dots n_{s_r}!}{(2n_{s_1})! \dots (2n_{s_r})!} \times \\ &\times {}^{(n)}\mathbf{A}_{kl}^{(n_{s_1}+\dots+n_{s_r})}(\pm\omega_{s_1} \pm \dots \pm\omega_{s_r}) [n_{s_1} + \dots + n_{s_r}] \mathbf{E}_{s_1}^{(n_{s_1})} \dots \mathbf{E}_{s_r}^{(n_{s_r})} e^{\pm i t(\omega_{s_1} + \dots + \omega_{s_r})}. \end{aligned} \quad (\text{A.2})$$

The explicit form of the r th-order polarization tensor of rank $n + n_{s_1} + \dots + n_{s_r}$ can be obtained by using the general method of Butcher and McLean (1964); namely, we have

$$\begin{aligned} {}^{(n)}\mathbf{A}_{kl}^{(n_{s_1}+\dots+n_{s_r})}(\pm\omega_{s_1} \pm \omega_{s_2} \pm \dots \pm\omega_{s_r}) &= \frac{r!}{\hbar^r} \sum_{t=0}^r \sum_{i_1 i_2 \dots i_r} \times \\ &\times \frac{\mathbf{M}_{k i_1}^{(n_{s_1})} \mathbf{M}_{i_1 i_2}^{(n_{s_2})} \dots \mathbf{M}_{i_{t-1} i_t}^{(n_{s_t})} \mathbf{M}_{i_t i_{t+1}}^{(n)} \mathbf{M}_{i_{t+1} i_{t+2}}^{(n_{s_{t+1}})} \dots \mathbf{M}_{i_r l}^{(n_{s_r})}}{\prod_{u=1}^t (\omega_{i_u k} \mp \omega_{s_1} \mp \omega_{s_2} \mp \dots \mp \omega_{s_u}) \prod_{u=t+1}^r (\omega_{i_u l} \pm \omega_{s_u} \pm \omega_{s_{u+1}} \pm \dots \pm \omega_{s_r})}. \end{aligned} \quad (\text{A.3})$$

In the case when spatial variation of the electric fields is negligible, Equation (A.2) reduces to the following simpler form:

$$\mathbf{P}_{kl}^{(r)}(\pm\omega_{s_1} \pm \dots \pm\omega_{s_r}) = {}^{(n)}\mathbf{A}_{kl}^{(r)}(\pm\omega_{s_1} \pm \dots \pm\omega_{s_r}) [r] \mathbf{E}_{s_1}^{\pm} \dots \mathbf{E}_{s_r}^{\pm}. \quad (\text{A.4})$$

The effect of molecular interactions on the multipole polarizability tensors of appropriate orders can be calculated by a method analogical to that elaborated by Mazur and Mandel (1956) in their theory of the refractive index of non-polar gases (see also Terwiel and Mazur 1964). In this case, *i.e.* when a system of N interacting molecules is considered, the perturbation Hamiltonian is composed of two parts, one of which arises from the interaction of all molecules of the system with the oscillating electric fields (1) and is given by Equation (3) with

$$H_s^{\pm} = - \sum_{p=1}^N \sum_{n_s=1}^{\infty} \frac{2^{n_s} n_s!}{(2n_s)!} \mathbf{M}_p^{(n_s)} [n_s] \mathbf{E}_{sp}^{\pm}. \quad (\text{A.5})$$

The second part of H results from interaction between the molecules in the system and is given in general by (Jansen 1958a, Kielich 1965b)

$$H'' = \frac{1}{2} \sum_{p=1}^N \sum_{q=1}^N \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} (-1)^{n_2+1} \frac{2^{n_1+n_2} n_1! n_2!}{(2n_1)!(2n_2)!} \mathbf{M}_p^{(n_1)} [n_1] {}^{(n_1)}\mathbf{T}_{pq}^{(n_2)} [n_2] \mathbf{M}_q^{(n_2)}, \quad (\text{A.6})$$

where

$${}^{(n_1)}\mathbf{T}_{pq}^{(n_2)} = - \nabla^{n_1+n_2} \left(\frac{1}{r_{pq}} \right) = (-1)^{n_1+n_2+1} (n_1+n_2)! r_{pq}^{-(n_1+n_2+1)} \mathbf{Y}^{(n_1+n_2)}(\mathbf{r}_{pq}) \quad (\text{A.7})$$

is a tensor of rank n_1+n_2 describing the interaction between the 2^{n_1} -pole moment $M_p^{(n_1)}$ and the 2^{n_2} -pole electric moment $M_q^{(n_2)}$ of molecules p and q separated by a distance r_{pq} . The operator $Y^{(n_1+n_2)}(\mathbf{r}_{pq})$ is given by the expression (7) if n is replaced by n_1+n_2 and \mathbf{r} by \mathbf{r}_{pq} . The explicit results from calculations with the Hamiltonians of Equations (3), (A.5) and (A.6) are highly involved and we refrain from writing them here.

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