# DC ELECTRIC FIELD-INDUCED OPTICAL SECOND HARMONIC GENERATION BY INTERACTING MULTIPOLAR MOLECULES

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From classical molecular-statistical theory, second harmonic generation by multipolar substances placed in a DC or AC electric field is shown to be related not only with nonlinear electronic polarisation of molecules but essentially with orientation of the electric molecular multipoles and their interaction in the condensed state.

Terhune et al. [1] were the first to observe second harmonic generation (SHG) by calcite placed in a DC electric field. Quite recently, Mayer [2] performed similar experiments in gases and liquids and stressed the considerable role in SHG of electric dipole orientation in the DC electric field. This paper is aimed at presenting a semi-macroscopic theory of SHG by isotropic bodies in a DC or AC electric field, with a molecular-statistical discussion making apparent the role not only of molecular dipole orientation in the DC field and of mutual correlations, but moreover that of nondipolar molecules undergoing orientation in the electric fields of the quadrupoles and octupoles of the surrounding molecules in the medium.

The square of the electric field $E^M(\omega, r) = E_0^M \exp\{i(k \cdot r - \omega t)\}$ oscillating at frequency $\omega$ induces at a point $r$ in the medium a polarisation vector at frequency $2\omega$, whose $\sigma$-component in the presence of a DC electric field $E^M(0)$ is [1]:

$$P_\sigma(2\omega, r) = \chi_{\sigma\tau\nu\rho}^{2\omega} E_\tau^M(\omega) E_\nu^M(\omega) E_\rho^M(0) \, e^{i2k \cdot r} , \tag{1}$$

$\chi_{\sigma\tau\nu\rho}^{2\omega} = \chi_{\sigma\tau\nu\rho}(-2\omega, \omega, \omega, 0)$ being the nonlinear susceptibility tensor of fourth rank and $k$ the wave propagation vector.

In order to interpret microscopically the macroscopic susceptibility $\chi_{\sigma\tau\nu\rho}^{2\omega}$ of the phenomenological equation (1) for an isotropic body, we recur to the semi-macroscopic method [3, 4], expanding the polarisation vector $P(r, t)$ in a series in the electric field strength $E(t)$ in the absence of the medium (in vacuum), which is related with the mean macroscopic field $E^M$ within the medium assumed in the shape of a spherical sample of macroscopic dimensions as follows:

$$3E_\sigma^\omega = (\epsilon_{\sigma\tau}^\omega + 2\delta_{\sigma\tau})E_\tau^M(\omega, r) , \tag{2}$$

where $\epsilon_{\sigma\tau}^\omega$ is the electric permittivity tensor at frequency $\omega$. For an arbitrary isotropic medium, the method leads to the following result:

$$P_\sigma(2\omega, r) = \{Q_{is}^{2\omega} E_\sigma^0 E_\tau^\omega E_\tau^\omega + Q_{anis}^{2\omega}(3E_\sigma^\omega E_\tau^\omega E_\tau^0 - E_\sigma^0 E_\tau^\omega E_\tau^\omega)\} \, e^{i2k \cdot r} , \tag{3}$$

where the constants

$$Q_{is}^{2\omega} = \frac{1}{36V} \langle 3C_{\alpha\beta\beta\alpha}^{2\omega} + \frac{1}{kT} B_{\alpha\beta\beta}^{2\omega} M_\alpha^0 \rangle , \tag{4}$$

$$Q_{anis}^{2\omega} = \frac{1}{360V} \langle 3C_{\alpha\beta\alpha\beta}^{2\omega} + 3C_{\alpha\alpha\beta\beta}^{2\omega} - 2C_{\alpha\beta\beta\alpha}^{2\omega} + \frac{1}{kT}(3B_{\alpha\beta\alpha}^{2\omega} M_\beta^0 + 3B_{\alpha\alpha\beta}^{2\omega} M_\beta^0 - 2B_{\alpha\beta\beta}^{2\omega} M_\alpha^0) \rangle , \tag{5}$$

define respectively the isotropic and anisotropic parts of the induced polarisation. $M^0$ stands for the total electric dipole moment of the medium of volume $V$ at zero external field, whereas $B_{\alpha\beta\gamma}^{2\omega}$ and $C_{\alpha\beta\gamma\delta}^{2\omega}$

are tensors of its nonlinear polarizability of second and third order [4]. The symbol $\langle\,\rangle$ denotes classical statistical averaging.

If the medium consists of $N$ mutually interacting molecules, one can write the expansions:

$$M_\alpha^0 = \sum_{p=1}^{N} \{\mu_\alpha^{(p)} + \alpha_{\alpha\beta}^{(p)} F_\beta^{(p)} + \tfrac{1}{2}\beta_{\alpha\beta\gamma}^{(p)} F_\beta^{(p)} F_\gamma^{(p)} + \dots \},\qquad(6)$$

$$B_{\alpha\beta\gamma}^{2\omega} = \sum_{p=1}^{N} \{b_{\alpha\beta\gamma}^{2\omega(p)} + c_{\alpha\beta\gamma\delta}^{2\omega(p)} F_\delta^{(p)} + \dots \},\qquad(7)$$

$$C_{\alpha\beta\gamma\delta}^{2\omega} = \sum_{p=1}^{N} \{c_{\alpha\beta\gamma\delta}^{2\omega(p)} + \dots \},\qquad(8)$$

with $\mu$ denoting the permanent electric dipole moment of a molecule, and $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$ tensors of its electric polarizabilities [5] induced by the field $F^{(p)}$ of electric multipoles of surrounding molecules [6,7].

We now proceed to discuss the expressions (4)-(8) for several particular cases:

(i) Atomic substances, or ones consisting of nonpolar molecules. The constants (4) and (5) do not depend directly on the temperature and are a consequence solely of the mechanism of third-order nonlinear electron polarizability $c_{\alpha\beta\gamma\delta}^{2\omega}$ present in all molecular symmetries, spherical included. This distortional effect depends but weakly on the molecular correlations by way of statistical translational fluctuations [6,8], which we shall not consider here.

(ii) Dipolar substances. In addition to the preceding distortional effect, these present a temperature-dependent effect due to coupling between the second-order electric polarizability $b_{\alpha\beta\gamma}^{2\omega}$ and orientation of molecular dipoles $\mu$ in the DC electric field. In condensed states, this effect depends to a considerable extent on the molecular correlations. Indeed, by eqs. (4)-(8) and on neglecting contributions from molecular fields, we obtain:

$$Q_{is}^{2\omega} = \frac{\rho}{36}\left(c_{\alpha\alpha\beta\beta}^{2\omega} + \frac{g}{kT} b_{\alpha\beta\beta}^{2\omega}\mu_\alpha\right),\qquad(9)$$

$$Q_{anis}^{2\omega} = \frac{\rho}{180}\left\{3c_{\alpha\alpha\beta\beta}^{2\omega} - c_{\alpha\beta\beta\alpha}^{2\omega} + \frac{g}{kT}(3b_{\alpha\alpha\beta}^{2\omega}\mu_\beta - b_{\alpha\beta\beta}^{2\omega}\mu_\alpha)\right\},\qquad(10)$$

where $\rho = N/V$ is the number density of molecules,

$$g = 1 + z\langle\cos\theta_{pq}\rangle.\qquad(11)$$

Kirkwood's correlation parameter [3], $\theta_{pq}$ the angle between the axes of the $p$th and $q$th molecules, and $z$ the number of neighbours of the $p$th molecule.

To make numerical evaluations, we neglect electron dispersion in eqs. (9) and (10) which enables us to write approximately:

$$Q_{is}^{2\omega} = \tfrac{5}{2} Q_{anis}^{2\omega} = \frac{\rho}{36}\left(c_{\alpha\alpha\beta\beta}^{2\omega} + \frac{g}{kT} b_{\alpha\alpha\beta}^{2\omega}\mu_\beta\right).\qquad(12)$$

For $CH_2(CN)_2$ we have the following data [5]: $\mu = 3.56 \times 10^{-18}$ esu, $\beta \simeq \tfrac{3}{5} b_{\alpha\alpha\beta}^{2\omega} = -8 \times 10^{-30}$ esu, and $\gamma \simeq \tfrac{3}{5} c_{\alpha\alpha\beta\beta}^{2\omega} = 15 \times 10^{-36}$ esu. Hence and by eq. (12), the temperature effect is found to be $42\,g$ times larger than the distortional effect. We thus conclude that generally in dipolar substances the temperature effect is markedly predominant over the electronic distortional effect.

(iii) Molecules without a dipole but with higher electric moments. These, too, present the temperature effect, which by eqs. (4)-(8) and on neglecting electron anisotropy and dispersion of polarizability is found to be of the form:

$$Q_{is}^{2\omega} = \tfrac{5}{2} Q_{anis}^{2\omega} = \frac{\rho}{36} c_{\alpha\alpha\beta\beta}^{2\omega}\left(1 + \frac{\alpha}{kT}\langle F^2\rangle\right),\qquad(13)$$

$\alpha = \tfrac{1}{3}\alpha_{\alpha\alpha}$ being the mean electric polarizability of a molecule.

If, in particular, the axially-symmetric molecules possess only the quadrupole moment $\Theta$, the mean square molecular field of the quadrupole is [4,6]:

$$\langle F^2\rangle = \Theta^2 \langle r_{pq}^{-8}\rangle,\qquad(14)$$

where $r_{pq}$ is the distance between molecules $p$ and $q$.

Molecules having the tetrahedral symmetry ($CH_4$, $CCl_4$) possess an octupole moment $\Omega$ as well as a hexadecapole moment $\Phi$; we obtain [4]:

$$\langle F^2 \rangle = \tfrac{16}{5}\Omega^2 \langle r_{pq}^{-10} \rangle + \tfrac{80}{7}\Phi^2 \langle r_{pq}^{-12} \rangle. \tag{15}$$

In the liquid case, we obtain in Kirkwood's approximation [8]:

$$\langle r_{pq}^{-n} \rangle = \frac{4\pi\rho}{n-3}\left(\frac{\pi}{6v}\right)^{(n-3)/3}, \qquad n \geqslant 4 \tag{16}$$

with $v = \tfrac{1}{6}\pi d^3$ denoting the volume of a molecule of diameter $d$.

For benzene at $295^\circ K$ we have [7]: $\rho = 6.74 \times 10^{21}$ $cm^{-3}$, $\alpha = 10.32 \times 10^{-24}$ $cm^3$, $\langle r_{pq}^{-8} \rangle = 5 \times 10^{58}$ $cm^{-8}$ and [9] $\Theta = (15.7 \quad 26.3) \times 10^{-26}$ esu $cm^2$, whence by eqs. (13) and (15) one finds that the contribution from the temperature effect amounts to 30   80 per cent of the distortional effect.

For carbon disulphide [7], we have: $\rho = 9.98 \times 10^{21}$ $cm^3$, $\alpha = 8.74 \times 10^{-24}$ $cm^3$, $\langle r_{pq}^{-8} \rangle = 11.5 \times 10^{58}$ $cm^{-8}$ and [10] $\Theta = 28 \times 10^{-26}$ esu $cm^2$, whence the temperature effect is 1.9 times larger than the distortional effect.

As an example of an octupolar liquid, let us consider carbon tetrachloride, for which the data [7] are: $\rho = 6.22 \times 10^{21}$ $cm^{-3}$, $\alpha = 10.5 \times 10^{-24}$ $cm^3$, $\langle r_{pq}^{-10} \rangle = 6 \times 10^{72}$ $cm^{-10}$ and [11] $\Omega = (15 \div 32) \times 10^{-34}$ esu $cm^3$ (the hexadecapolar moment is not available). Eqs. (13) and (15) imply that here the temperature effect is insignificant, amounting to as little as $(1 \div 4)$ per cent of the distortional effect. Maybe in other liquids the octupole effect is more considerable.

For the time being, there is a lack of appropriate temperature measurements of DC electric field-induced SHG for deciding to what extent and in which substances the temperature effect predominates over the distortional effect. It seems that this might be decided in a different way, by replacing the DC field with an AC electric field $E^0 e^{i\omega_0 t}$ oscillating at frequency $\omega_0$ much smaller than the optical frequency $\omega$. In this case, in eqs. (4) and (5), the permanent dipole moment $M_\alpha^0$ would have to be replaced by the slowly-oscillating moment

$$M_\alpha^{\omega 0} = \frac{M_\alpha^0 e^{i\omega_0 t}}{1 + i\omega_0 \tau_\alpha}, \tag{17}$$

where $\tau_\alpha$ is Debye's relaxation time for the principal molecular axis $\alpha$. In other words, one might investigate how strongly SHG is affected by Debye dipolar dispersion in polar liquids.

Finally, let us particularize the general expression (3) to the experimental situation in the measurements of Mayer [2] i.e. with light propagation in the $z$-direction of the laboratory reference system and the DC electric field acting in the $y$-direction. This leads to polarisation components in the form:

$$P_x(2\omega, r) = 3Q_{anis}^{2\omega} E_x^\omega E_y^\omega E_y^0 e^{i2k\cdot r}, \tag{18}$$

$$P_y(2\omega, r) = \left\{ (Q_{is}^{2\omega} - Q_{anis}^{2\omega})(E_x^\omega)^2 + (Q_{is}^{2\omega} + 2Q_{anis}^{2\omega})(E_y^\omega)^2 \right\} E_y^0 e^{i2k\cdot r}, \tag{19}$$

whence, in the case under consideration, the $x$-component of polarisation is seen to be a purely anisotropic component. Similarly, other experimental conditions can be discussed [12].

Note added on 3 October 1968.

Professor Bloembergen has just communicated to the author an interesting conclusion from the phenomenological equation (1) for the components intervening in Mayer's experiment [2], if the factor describing spatial dispersion is omitted; one gets:

$$P_c(2\omega) = \chi_1^{2\omega} E_x^\omega E_y^\omega E_y^0, \tag{18a}$$

$$P_y(2\omega) = \chi_2^{2\omega}(E_x^\omega)^2 E_y^0 + \chi_3^{2\omega}(E_y^\omega)^2 E_y^0. \tag{19a}$$

On comparing the above with eqs. (18) and (19), he notes that for isotropic bodies one must have

$$\chi_1^{2\omega} + \chi_2^{2\omega} = \chi_3^{2\omega} \,. \tag{a}$$

On the other hand, if electron dispersion is negligible, eq. (12) is fulfilled, whence:

$$\chi_1^{2\omega} : \chi_2^{2\omega} : \chi_3^{2\omega} = 2 : 1 : 3\,. \tag{b}$$

The symmetry relations (a) and (b) have been derived by Bloembergen on purely macroscopic grounds and communicated to Mayer at the Gordon Conference on "Nonlinear Optic Effects" held in Meriden, New Hampshire, USA, 26 – 30 August 1968. Recent measurements of Mayer (private communication) for bromoethane are in good agreement with the relation (b).

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