

# RESONANT OPTICAL RECTIFICATION IN CHIRAL MOLECULAR SYSTEMS: APPLICATION TO A THREE-LEVEL MODEL

S. WOŹNIAK

Nonlinear Optics Division, Institute of Physics  
A. Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland

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A molecular approach to optical rectification via the imaginary part of the second-order susceptibility related to electric dipole interaction with the radiation field is presented. A quantum-mechanical expression for the frequency dependence of the effect is obtained and its magnitude is estimated in absorption bands of a three-level model.

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Linear and nonlinear interactions of an electromagnetic wave with molecules of an isotropic medium induce in them multipole moments which contribute to electric polarization of the system [1]. Out of absorption bands optical rectification (OR) via the second-order susceptibility is forbidden but the fourth-order dipolar electric nonlinearity may cause OR in chiral liquids [2]. However, in absorption bands of optically active molecular system OR is allowed via the imaginary part of the second-order susceptibility related to electric dipole interaction with the radiation field [3].

We consider an isotropic molecular system in which a plane monochromatic light wave with the electric field

$$\mathbf{E}(z, t) = \frac{1}{2} \mathbf{E}(\omega) \exp \left( -i\omega \left( t - \frac{\tilde{n}}{c} z \right) \right) + \text{c.c.}, \quad (1)$$

oscillating with the circular frequency  $\omega$ , propagates in the  $z$ -direction. For a dissipative medium  $\tilde{n}$  is complex

$$\tilde{n} = n(1 + i\kappa) \quad (2)$$

with  $n$  the refractive index, and  $\kappa$  — the absorption coefficient.

In this paper we are interested in the calculation of a static polarization  $\mathbf{P}(0)$  induced in the medium by nonlinear interaction of chiral molecules with the light wave. Restricting our considerations to the second-order susceptibility, we have

$$P_i(0) = N \exp(-\beta z) \langle \tilde{\alpha}_{ijk}(0; \omega, -\omega) \rangle E_j(\omega) E_k^*(\omega), \quad (3)$$

where  $N$  is the number of molecules per unit volume,  $\tilde{\alpha}_{ijk}$  the nonlinear polarizability related to electric dipole transitions, whereas the asterisk represents the complex conjugate, the symbol  $\langle \rangle$  stands for the isotropic average [4], and

$$\beta = \frac{2\omega n \kappa}{c}. \quad (4)$$

In the region of absorption the tensor  $\tilde{\alpha}(0; \omega, -\omega)$  is complex

$$\tilde{\alpha}_{ijk}(0; \omega, -\omega) = \alpha_{ijk}(0; \omega, -\omega) + i\alpha'_{ijk}(0; \omega, -\omega), \quad (5)$$

where both tensors  $\alpha(0; \omega, -\omega)$  and  $\alpha'(0; \omega, -\omega)$  are now real.

The polarizability tensor  $\tilde{\alpha}(0; \omega, -\omega)$  of Eq. (3) is a time-even polar tensor of rank three and has nonzero components for molecules without a centre of symmetry. Quantum-mechanical forms of the polarizabilities  $\alpha_{ijk}$  and  $\alpha'_{ijk}$  can be obtained by perturbation theory [5]. The number of nonzero and independent components depends on the specific molecular symmetry (see, for instance, Tables 4.2a and 4.2e in Ref. [6] presenting the components of a polar tensor of rank three without permutational symmetries).

The components  $\tilde{\alpha}_{ijk}(0; \omega, -\omega)$  fulfil the additional relation

$$\tilde{\alpha}_{ijk}(0; \omega, -\omega) = \tilde{\alpha}^*_{ikj}(0; \omega, -\omega) \quad (6)$$

which leads to

$$\alpha_{ijk}(0; \omega, -\omega) = \alpha_{ikj}(0; \omega, -\omega), \quad (7)$$

$$\alpha'_{ijk}(0; \omega, -\omega) = -\alpha'_{ikj}(0; \omega, -\omega). \quad (8)$$

The relations (7) and (8) reduce the number of independent components of the polarizability tensors  $\alpha_{ijk}(0; \omega, -\omega)$  and  $\alpha'_{ijk}(0; \omega, -\omega)$  for certain well-defined symmetries.

Carrying out spatial averaging of the electric dipole moments induced in the molecules of the medium we can write the  $z$  component of the static polarization in the form convenient for a further discussion, namely

$$P_z(0) = \frac{2NI \sin 2\eta \exp(-\beta z)}{3\hbar^2 \epsilon_0 c} \sum'_m \sum'_{n>m} F_{mn}(\omega) \text{Re}[\mu_{gn} \cdot (\mu_{nm} \times \mu_{mg})], \quad (9)$$

which is nonzero only for elliptically or circularly polarized light in absorption bands of chiral molecules,  $\eta$  is the ellipticity of the light wave,  $\sum'$  stands for summation over all states except the ground state  $|g\rangle$ ,  $\mu_{mg}$  denotes an electric dipole transition between the states  $|g\rangle$  and  $\langle m|$ .  $F_{mn}(\omega)$  is a frequency-dependent function which has the form

$$F_{mn}(\omega) = A_{mn}(\omega) - A_{nm}(\omega) + B_{mn}(\omega) \quad (10)$$

with

$$A_{mn}(\omega) = \omega[\Gamma_{ng}(\omega^2 - \omega_{mg}^2) + \Gamma_{mg}(\Gamma_{mg}\Gamma_{ng} - 2\omega_{mg}\omega_{ng})]q_n^0 q_m, \quad (11)$$

$$B_{mn}(\omega) = \omega \{ 2(\omega_{mg}\omega_{ng} + \omega^2 + \Gamma_{mg}\Gamma_{ng}) \\ \times [\Gamma_{mg}(\omega_{ng}^2 - \omega^2 + \Gamma_{ng}^2) - \Gamma_{ng}(\omega_{mg}^2 - \omega^2 + \Gamma_{mg}^2)] + (\Gamma_{mg} - \Gamma_{ng}) \\ \times [(\omega_{mg}^2 - \omega^2 + \Gamma_{mg}^2)(\omega_{ng}^2 - \omega^2 + \Gamma_{ng}^2) + 4\omega^2\Gamma_{mg}\Gamma_{ng}] \} q_m q_n, \quad (12)$$

where

$$q_n^0 = (\omega_{ng}^2 + \Gamma_{ng}^2)^{-1}, \quad (13)$$

$$q_m = [(\omega_{mg}^2 - \omega^2 + \Gamma_{mg}^2)^2 + 4\omega^2\Gamma_{mg}^2]^{-1}, \quad (14)$$

$$q_n = [(\omega_{ng}^2 - \omega^2 + \Gamma_{ng}^2)^2 + 4\omega^2\Gamma_{ng}^2]^{-1}, \tag{15}$$

and  $\Gamma_{ng}^{-1}$  is a characteristic relaxation time between the states  $|n\rangle$  and  $|g\rangle$ .

Above, Eq. (9) is given in a form applicable for any isotropic molecular system, however, the summation over all states (except the ground state) is beset with difficulties and therefore some approximations are needed. A molecule represented by three levels is the simplest model to describe nonlinear effects related to the second-order susceptibility and this model can serve as a good approximation for molecules possessing two absorption bands in the optical region, if the remaining bands are situated far from them [7].

Now, the general equation (9) will be applied to a molecule represented by three levels ( $g$  the ground state,  $a$  and  $b$  the excited states). If the light frequency  $\omega$  is tuned to the absorption band with the resonance frequency  $\omega_{ag}$  (close to the resonance frequency) then the light-induced static polarization is given in the form

$$P_z(0) \cong \frac{NI \sin 2\eta \exp(-\beta z)}{3\hbar^2 \epsilon_0 c} \frac{\omega \Gamma_{ag}}{(\Delta_{ag}^2 + \Gamma_{ag}^2)\omega_{bg}(\omega_{bg} - \omega)} \times \text{Re}[\mu_{gb} \cdot (\mu_{ba} \times \mu_{ag})], \tag{16}$$

where  $\Delta_{ag} = \omega_{ag} - \omega$ . A similar expression describes optical rectification in the resonance region with the frequency  $\omega_{bg}$ .

If the frequency  $\omega$  is not close to the resonance frequency  $\omega_{ag}$  or  $\omega_{bg}$ , the conditions  $|\omega_{ag} - \omega| \gg \Gamma_{ag}$  and  $|\omega_{bg} - \omega| \gg \Gamma_{bg}$  are fulfilled, and we have

$$P_z(0) = \frac{2NI\omega\Gamma \sin 2\eta \exp(-\beta z)}{3\hbar^2 \epsilon_0 c} \times \left[ \frac{\omega^2 - \omega_{ag}^2 - 2\omega_{ag}\omega_{bg}}{\omega_{bg}^2(\omega_{ag}^2 - \omega^2)^2} - \frac{\omega^2 - \omega_{bg}^2 - 2\omega_{ag}\omega_{bg}}{\omega_{ag}^2(\omega_{bg}^2 - \omega^2)^2} + \frac{2(\omega^2 + \omega_{ag}\omega_{bg})(\omega_{bg}^2 - \omega_{ag}^2)}{(\omega_{ag}^2 - \omega^2)^2(\omega_{bg}^2 - \omega^2)^2} \right] \times \text{Re}[\mu_{gb} \cdot (\mu_{ba} \times \mu_{ag})], \tag{17}$$

where, for simplicity, we assumed  $\Gamma_{ag} = \Gamma_{bg} = \Gamma$ .

The static polarization leads to a potential difference  $U$  on the plates of a capacitor introduced into the measuring cuvette along the direction of the light wave propagation

$$U = \frac{P_z(0; z = 0) - P_z(0; z = d)}{\epsilon_0(\epsilon - 1)\beta}, \tag{18}$$

where  $P_z(0; z = 0)$  and  $P_z(0; z = d)$  are the static polarizations at  $z = 0$  and  $z = d$ , respectively;  $d$  is the distance between the capacitor plates (the first is situated at  $z = 0$ ) and  $\epsilon$  is the static dielectric constant.

If the light frequency  $\omega$  is tuned to the resonance frequency  $\omega_{ag}$  then

$$U(\omega_{ag}) \cong \frac{NI \sin 2\eta [1 - \exp(-\beta_a d)] \omega_{ag}}{3\hbar^2 \epsilon_0^2 (\epsilon - 1) c \beta_a \Gamma_{ag} \omega_{bg} (\omega_{bg} - \omega_{ag})} \text{Re}[\mu_{gb} \cdot (\mu_{ba} \times \mu_{ag})], \tag{19}$$

where  $\beta_a$  is the absorption parameter  $\beta$  of Eq. (4) at the frequency  $\omega = \omega_{ag}$ . Denoting the maximum value of the potential differences  $U(\omega_{ag})$  and  $U(\omega_{bg})$  by  $U_{\max}(\omega_{ag})$  and  $U_{\max}(\omega_{bg})$ , respectively, we have the ratio

$$R = \frac{U_{\max}(\omega_{ag})}{U_{\max}(\omega_{bg})} \cong \frac{\beta_b \Gamma_{bg} \omega_{ag}^2}{\beta_a \Gamma_{ag} \omega_{bg}^2}, \tag{20}$$

where  $\beta_b$  stands for the absorption parameter  $\beta$  at the frequency  $\omega = \omega_{bg}$ .

To estimate the potential difference given by (18) together with (16) and (17) it is necessary to have available a numerical value of the parameter  $\beta$  for the appropriate frequency  $\omega$ . We will estimate  $\beta$  from the expression [8]

$$\beta(\omega) = \frac{2N\omega^2}{3\hbar\epsilon_0cn} \sum_k' \frac{\omega_{kg}\Gamma_{kg}\langle g|\mu_\alpha|k\rangle\langle k|\mu_\alpha|g\rangle}{(\omega_{kg}^2 - \omega^2 + \Gamma_{kg}^2)^2 + 4\omega^2\Gamma_{kg}^2} \quad (21)$$

with  $\langle g|\mu|k\rangle \approx ea_0$ , where  $e$  is the electron charge and  $a_0$  the Bohr radius.

For our estimate we consider a three-level model with resonance frequencies lying in the optical region,  $\omega_{ag} = 3 \times 10^{15} \text{ s}^{-1}$ ,  $\omega_{bg} = 5 \times 10^{15} \text{ s}^{-1}$ , and with the damping factors  $\Gamma_{ag}$  and  $\Gamma_{bg}$  identical for both transitions,  $\Gamma_{ag} = \Gamma_{bg} = \Gamma = 10^{13} \text{ s}^{-1}$ . Moreover, we take  $N = 10^{27} \text{ m}^{-3}$  ( $10^{27} - 10^{28} \text{ m}^{-3}$  are typical values for the number density of liquids),  $n = 1.5$ ,  $\epsilon = 10$  and the light intensity  $I = 10^{11} \text{ W m}^{-2}$ . For a distance  $d$  between the capacitor plates fulfilling the relation  $d \gg \beta^{-1}$  we get the following values of the potential difference  $U$  at different frequencies  $\omega$ :  $\omega = 10^{15} \text{ s}^{-1} \rightarrow U = 3 \text{ }\mu\text{V}$ ;  $\omega = 2.5 \times 10^{15} \text{ s}^{-1} \rightarrow U = 30 \text{ }\mu\text{V}$ ;  $\omega = 3 \times 10^{15} \text{ s}^{-1} \rightarrow U = 60 \text{ }\mu\text{V}$ ;  $\omega = 4 \times 10^{15} \text{ s}^{-1} \rightarrow U = 175 \text{ }\mu\text{V}$ ;  $\omega = 5 \times 10^{15} \text{ s}^{-1} \rightarrow U = 100 \text{ }\mu\text{V}$ ; and  $\omega = 7 \times 10^{15} \text{ s}^{-1} \rightarrow U = 15 \text{ }\mu\text{V}$ .

The potential difference  $U$  given by Eq. (18) depends, in general, on the number density  $N$ . However, it is independent of  $N$  if  $d \gg \beta^{-1}$ , because the absorption parameter  $\beta$  (Eq. (21)) and the polarization  $P_z(0; z = 0)$  are proportional to  $N$ .

The optical rectification effect can be detected if the frequency  $\omega$  of the optical beam is tuned over the absorption band of chiral molecules. The above results show that the maximum magnitude of the potential difference  $U$  appears not at a resonance frequency where the absorption parameter  $\beta$  is high (e.g.,  $\beta = 1.4 \times 10^7 \text{ m}^{-1}$  at  $\omega = \omega_{bg}$  in the three-level model discussed) but rather out of resonance (in our case at a frequency  $\omega$  lying between  $\omega_{ag}$  and  $\omega_{bg}$ ), where the parameter  $\beta$  is smaller (e.g., in the above model  $\beta = 2.3 \times 10^3 \text{ m}^{-1}$  at  $\omega = 4 \times 10^{15} \text{ s}^{-1}$ ).

## References

- [1] S. Kielich, *Proc. Phys. Soc.* **86**, 709 (1965).
- [2] S. Woźniak, G. Wagnière, *Optics Commun.* **114**, 131 (1995).
- [3] N.I. Koroteev, *JETP* **79**, 681 (1994).
- [4] S. Kielich, *Acta Phys. Pol.* **31**, 929 (1967).
- [5] B.J. Orr, J.F. Ward, *Mol. Phys.* **20**, 513 (1971).
- [6] L.D. Barron, *Molecular Light Scattering and Optical Activity*, Cambridge University Press, Cambridge 1982.
- [7] K.E. Süsse, S. Woźniak, G. Wagnière, *Optics Commun.* **100**, 374 (1993).
- [8] S. Woźniak, R. Zawodny, *Acta Phys. Pol. A* **61**, 175 (1982).