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On electric-quadrupole and magnetic-dipole contributions to optical rectification in isotropic media near optical resonance

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<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p> <p>Zawodny-Manuscript.tex Zawodny-Table1.tex Zawodny-Table2.tex</p>	



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12 **On electric-quadrupole and magnetic-dipole contributions to**
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32 Resonant electric-quadrupole and magnetic-dipole contributions to
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Abstract

A molecular theory of resonant optical rectification via the second-order electric-dipole polarizability related to magnetic-dipole and electric-quadrupole interaction of an electromagnetic radiation with atoms and molecules of an isotropic medium is presented. The magnetic-dipole and electric-quadrupole contributions to Dc electric-dipole polarization can be produced by arbitrarily polarized light which has to be at resonance with a molecule. This effect can appear in an isotropic medium composed of molecules with arbitrary symmetries.

Key words: optical rectification, isotropic media, chiral molecule, electric -quadrupole and magnetic-dipole polarizabilities, the second-order nonlinear process.

1. Introduction

Linear and nonlinear multipolar interaction of laser light with atoms and molecules induces in them multipole moments [1-8] which contribute to the electric and magnetic polarization of the molecular system. In the nonlinear case, the frequencies of their oscillations are given, in general, by combinations of the frequencies of the interacting fields. In particular cases a static magnetization and/or a static electric polarization can be induced in isotropic media.

A static magnetization can be induced by electric dipole interaction of circularly or elliptically polarized light with matter and can appear in any medium [9-11]. The effect is referred to as the inverse Faraday effect (IFE) and has been verified experimentally [9]. The behaviour of the IFE near optical resonances has also been analyzed [12].

It has been shown [13] that a coherent beam of light of arbitrary polarization travelling in a medium composed of randomly oriented chiral molecules can also induce a static magnetization. The effect is caused by magnetic dipole and electric quadrupole interaction of molecules with the radiation field and is referred to as the inverse magnetochiral birefringence (IMCHB). The effect may exist outside optical resonances as well as within absorption bands of the system [14]. Both effects (IFE and IMCHB) are related to the second-order magnetic susceptibility.

The light-induced static electric polarization (optical rectification - OR) is electric-dipole-forbidden via the second-order electric susceptibility in nondissipative isotropic media (i.e. far from optical resonances) for symmetry reasons [15-17]. Non-resonant optical rectification is electric-dipole-allowed in optically active liquids and solutions only via the fourth-order electric susceptibility, arising from the nonlinear electric dipole interaction of chiral molecules with the electromagnetic field [17]. However, in absorption bands of optically active molecular systems, optical rectification is also allowed via the imaginary part of the second-order electric susceptibility [15,16,18,19].

The aim of this paper is to present a molecular approach to the description of the induction of optical rectification via the second-order electric-dipole polarizabilities related to electric-quadrupole and magnetic-dipole transitions in a medium composed of noninteracting molecules. We show that the second-order electric-quadrupole and magnetic-dipole contributions to Dc electric-dipole polarization can be produced by an arbitrarily polarized optical

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4 wave with a frequency that has to lie in an absorption band of the molecule and appears in
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6 an isotropic medium composed of molecules with arbitrary symmetries. Finally, we discuss
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8 the effect for all magnetic point groups.

10 2. Theory

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12 We consider an arbitrary system of volume V containing N uncorrelated atoms or
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14 molecules in which an intense monochromatic light wave with the electric vector

$$15 \mathbf{E}(\mathbf{r}, t) = \frac{1}{2} \mathbf{E}(\omega, r) \exp(-i\omega t) + c.c., \quad (1)$$

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17 oscillating with the circular frequency ω , propagates in the \mathbf{s} direction. This optical wave
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19 induces in a molecule a static electric-dipole moment, which can be written as follows [1-8]

$$20 \mu_j^d(0) = \mu_j^d(0) + \mu_j^q(0) + \mu_j^m(0). \quad (2)$$

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22 The term $\mu_j^d(0)$ denotes the static electric-dipole moment induced in a single molecule via
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24 the pure electric-dipole mechanism and is defined as follows:

$$25 \mu_j^d(0) = \frac{1}{2} \alpha_{ee}^{(1,1)}(0; -\omega, \omega) E_k^*(\omega, r) E_l(\omega, r) + c.c. \quad (3)$$

26
27 The last two terms $\mu_j^q(0)$ and $\mu_j^m(0)$ represent the Dc electric-dipole moments related
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29 with the electric-quadrupole and the magnetic-dipole interaction of a single molecule with
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31 the optical wave, respectively, and are defined in the following form:

$$32 \mu_j^q(0) = \frac{1}{6} [\alpha_{ee}^{(1,2)}(0; -\omega, \omega) E_k^*(\omega, r) \nabla_u E_l(\omega, r) \\ 33 + \alpha_{ee}^{(2,1)}(0; -\omega, \omega) E_l(\omega, r) \nabla_u E_k^*(\omega, r)] + c.c., \quad (4)$$

$$34 \mu_j^m(0) = \frac{1}{2} [\alpha_{em}^{(1,1)}(0; -\omega, \omega) E_k^*(\omega, r) B_l(\omega, r) \\ 35 + \alpha_{me}^{(1,1)}(0; -\omega, \omega) B_k^*(\omega, r) E_l(\omega, r)] + c.c. \quad (5)$$

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37 In these expressions the asterisk $*$ and the symbol $c.c.$ stand for complex conjugate
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39 quantities.

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41 The quantum mechanical form of the second-order nonlinear electric-dipole polarizability
42
43 $\alpha_{BC}^{(b,c)}(0; -\omega, \omega)$ can be obtained on putting $\omega_1 = -\omega$ and $\omega_2 = \omega$ in the quantum
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45 mechanical expression for the polarizability $\alpha_{BC}^{(b,c)}(-\omega_1 - \omega_2; \omega_1, \omega_2)$ which can be found in
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Refs. [4-6,20-22]. The polar tensor of the fourth rank ${}^{(1)}\alpha_{ee\ jk(ul)}^{(1,2)}(0; -\omega, \omega)$ describes the second-order nonlinear electric-dipole polarizability related to electric-dipole and electric-quadrupole transitions between the stationary ground state and virtual excited states (in the absence of resonance) or the stationary excited states (in the presence of resonance). Similarly, the axial tensor of the third rank ${}^{(1)}\alpha_{em\ jkl}^{(1,1)}(0; -\omega, \omega)$ represents the second-order nonlinear electric-dipole polarizability related to electric-dipole and magnetic-dipole transitions. The subscripts in semicircular parentheses (...) label the components of the electric-quadrupole moment; these parentheses at the same time serve to denote the invariance (symmetry) of the respective components with regard to transposition of the subscripts. Keeping in mind that the quadrupole electric moment operator is trace-less we arrive additionally at the relations

$${}^{(2)}\alpha_{e\ (kk)j}^{(1)}(-\omega; \omega) = 0, \quad {}^{(1)}\alpha_{e\ j(kk)}^{(2)}(-\omega; \omega) = 0, \quad {}^{(1)}\alpha_{ee\ ij(kk)}^{(1,2)}(0; -\omega, \omega) = 0. \quad (6)$$

For a molecule with complex wavefunctions, the nonlinear electric-dipole polarizability is complex and can be written as the complex sum

$${}^{(1)}\alpha_{BC}^{(b,c)}(0; -\omega, \omega) = {}^{(1)}\tilde{\beta}_{BC}^{(b,c)}(0; -\omega, \omega) + i\ {}^{(1)}\tilde{\gamma}_{BC}^{(b,c)}(0; -\omega, \omega). \quad (7)$$

and, in the presence of damping (the widths of the energy levels are taken into account) the two real polarizabilities ${}^{(1)}\tilde{\beta}_{BC}^{(b,c)}(0; -\omega, \omega)$ and ${}^{(1)}\tilde{\gamma}_{BC}^{(b,c)}(0; -\omega, \omega)$ can be split

$${}^{(1)}\tilde{\beta}_{BC}^{(b,c)}(0; -\omega, \omega) = {}^{(1)}\beta_{BC}^{(b,c)}(0; -\omega, \omega) + {}^{(1)}\xi_{BC}^{(b,c)}(0; -\omega, \omega), \quad (8)$$

$${}^{(1)}\tilde{\gamma}_{BC}^{(b,c)}(0; -\omega, \omega) = {}^{(1)}\gamma_{BC}^{(b,c)}(0; -\omega, \omega) + {}^{(1)}\vartheta_{BC}^{(b,c)}(0; -\omega, \omega), \quad (9)$$

with the quantum mechanical forms given in Appendix A. If the frequency of an optical wave lies very far from an absorption band of a molecule we can omit the widths of the energy levels as well as the polarizabilities ${}^{(1)}\xi_{BC}^{(b,c)}(0; -\omega, \omega)$ and ${}^{(1)}\vartheta_{BC}^{(b,c)}(0; -\omega, \omega)$ as quantities which are proportional to these widths. From (A3)-(A6) we see that ${}^{(1)}\tilde{\beta}_{BC}^{(b,c)}(0; -\omega, \omega)$ is even in ω and satisfies the relation

$${}^{(1)}\tilde{\beta}_{BC}^{(b,c)}(0; -\omega, \omega) = {}^{(1)}\tilde{\beta}_{CB}^{(c,b)}(0; -\omega, \omega) \quad (10)$$

whereas ${}^{(1)}\tilde{\gamma}_{BC}^{(b,c)}(0; -\omega, \omega)$ is odd in ω , and fulfils the transposition relation

$${}^{(1)}\tilde{\gamma}_{BC}^{(b,c)}(0; -\omega, \omega) = -{}^{(1)}\tilde{\gamma}_{CB}^{(c,b)}(0; -\omega, \omega) \quad (11)$$

owing to this

$$[{}^{(1)}\alpha_{\mathcal{BC}}^{(b,c)}(0; -\omega, \omega)]^* = {}^{(1)}\alpha_{\mathcal{BC}}^{(b,c)}(0; \omega, -\omega), \quad (12)$$

$${}^{(1)}\alpha_{\mathcal{BC}}^{(b,c)}(0; -\omega, \omega) = {}^{(1)}\alpha_{\mathcal{CB}}^{(c,b)}(0; \omega, -\omega) = [{}^{(1)}\alpha_{\mathcal{CB}}^{(c,b)}(0; -\omega, \omega)]^*. \quad (13)$$

The reality of the electric field $\mathbf{E}(r, t)$ of the optical wave requires that its spectral amplitude shall obey the condition [23] $\mathbf{E}(\omega, r)^* = \mathbf{E}(-\omega, r)$. The first relation (12) ensures that the static electric dipole-moment is real for the real electric field (1). The second relation (13) is very often called Bloembergen's transposition relation [3], it expresses the invariance of the polarizability under the 2! permutations of the triads $-\omega b\mathcal{B}$, $\omega c\mathcal{C}$.

The invariance of the Schrödinger equation with respect to the time reversal operator \mathcal{T} implies [24,25] that if the function Ψ is a solution of the Schrödinger equation, then the function $\mathcal{T}\Psi$ is also a solution of this equation with the same energy $E_{\Psi} = E_{\mathcal{T}\Psi}$. A physical quantity Q is invariant with respect to time reversal if its expectation value is the same in the states Ψ and $\mathcal{T}\Psi$, and it is antisymmetrical if the two values are of opposite sign. Of course, for real wavefunctions, we have the relation $\mathcal{T}\Psi = \Psi$, which rules out the quantities antisymmetrical with respect to time inversion referred to by Birss as c -tensors [26].

Using the quantum mechanical definitions (A3)-(A6), it is easy to check that the polarizabilities

$$\begin{aligned} & {}^{(1)}\gamma_{ee\ j[kl]}^{(1,1)}(0; -\omega, \omega), & {}^{(1)}\gamma_{ee\ jk(ul)}^{(1,2)}(0; -\omega, \omega), & {}^{(1)}\beta_{em\ jkl}^{(1,1)}(0; -\omega, \omega), \\ & {}^{(1)}\xi_{ee\ j(kl)}^{(1,1)}(0; -\omega, \omega), & {}^{(1)}\xi_{ee\ jk(ul)}^{(1,2)}(0; -\omega, \omega), & {}^{(1)}\vartheta_{em\ jkl}^{(1,1)}(0; -\omega, \omega), \end{aligned} \quad (14)$$

are antisymmetrical with respect to time reversal (c -tensors) and can only exist for molecules with complex wavefunctions (paramagnetic molecules), whereas

$$\begin{aligned} & {}^{(1)}\beta_{ee\ j(kl)}^{(1,1)}(0; -\omega, \omega), & {}^{(1)}\beta_{ee\ jk(ul)}^{(1,2)}(0; -\omega, \omega), & {}^{(1)}\gamma_{em\ jkl}^{(1,1)}(0; -\omega, \omega), \\ & {}^{(1)}\vartheta_{ee\ j[kl]}^{(1,1)}(0; -\omega, \omega), & {}^{(1)}\vartheta_{ee\ jk(ul)}^{(1,2)}(0; -\omega, \omega), & {}^{(1)}\xi_{em\ jkl}^{(1,1)}(0; -\omega, \omega), \end{aligned} \quad (15)$$

are symmetrical with respect to time inversion (i -tensors) and can also exist for molecules with real wavefunctions (diamagnetic molecules).

To find the static electric-dipole polarization induced by an intense optical wave in an isotropic medium composed of like noninteracting molecules we have to average the static

electric-dipole moment (2) over all possible orientations. Using the classical Boltzmann procedure of averaging [27-29] we obtain

$$P_j(0) = P_j^d(0) + P_j^q(0) + P_j^m(0). \quad (16)$$

where the Dc electric-dipole polarizations $P_j^d(0)$, $P_j^q(0)$ and $P_j^m(0)$ induced, respectively, by the pure electric-dipole, electric-dipole/electric-quadrupole and electric-dipole/magnetic-dipole interaction are defined as follows

$$P_j^d(0) = \frac{1}{V} \sum_{mol} \{ \langle \mu_j^0 \rangle_{U^d} + \frac{1}{2} [\langle {}^{(1)}\alpha_{ee}^{(1,1)}(0; -\omega, \omega) \rangle E_k^*(\omega, r) E_l(\omega, r) + c.c.] \}, \quad (17)$$

$$P_j^q(0) = \frac{1}{V} \sum_{mol} \{ \langle \mu_j^0 \rangle_{U^q} + \frac{1}{6} [\langle {}^{(1)}\alpha_{ee}^{(1,2)}(0; -\omega, \omega) \rangle E_k^*(\omega, r) \nabla_u E_l(\omega, r) + \langle {}^{(1)}\alpha_{ee}^{(2,1)}(0; -\omega, \omega) \rangle E_l(\omega, r) \nabla_u E_k^*(\omega, r) + c.c.] \}, \quad (18)$$

$$P_j^m(0) = \frac{1}{V} \sum_{mol} \{ \langle \mu_j^0 \rangle_{U^m} + \frac{1}{2} [\langle {}^{(1)}\alpha_{em}^{(1,1)}(0; -\omega, \omega) \rangle E_k^*(\omega, r) B_l(\omega, r) + \langle {}^{(1)}\alpha_{me}^{(1,1)}(0; -\omega, \omega) \rangle B_k^*(\omega, r) E_l(\omega, r) + c.c.] \}. \quad (19)$$

Here the symbol $\langle \rangle_{U^a}$ stands for the statistical average in the presence of the electric-dipole $a = d$, electric-quadrupole $a = q$ and magnetic-dipole $a = m$ interactions of the intense electric field (1) of the optical beam with a single molecule, the following $\langle \rangle$ denotes the isotropic average, μ_j^0 is the j th Cartesian component of the permanent electric dipole moment of a molecule and the summation runs over all molecules. More exactly, U^d , U^q and U^m are of the form

$$U^d = -\frac{1}{2} \{ {}^{(1)}\alpha_{e kl}^{(1)}(-\omega, \omega) E_k^*(\omega, r) E_l(\omega, r) + c.c. \}, \quad (20)$$

$$U^q = -\frac{1}{6} \{ {}^{(1)}\alpha_{e k(ul)}^{(2)}(-\omega, \omega) E_k^*(\omega, r) \nabla_u E_l(\omega, r) + {}^{(2)}\alpha_{e(kul)}^{(1)}(-\omega, \omega) E_l(\omega, r) \nabla_u E_k^*(\omega, r) + c.c. \}, \quad (21)$$

$$U^m = -\frac{1}{2} \{ {}^{(1)}\alpha_{m kl}^{(1)}(-\omega, \omega) E_k^*(\omega, r) B_l(\omega, r) + {}^{(1)}\alpha_{e kl}^{(1)}(-\omega, \omega) B_k^*(\omega, r) E_l(\omega, r) + c.c. \} \quad (22)$$

and represent, respectively, the electric-dipole, electric-quadrupole and magnetic-dipole contributions to the time-averaged potential energy of the molecule in an intense optical beam

[7,29,30], which is given by

$$U = -\frac{1}{2}[m_k^e(r, \omega) E_k(r, \omega) + m_k^m(r, \omega) B_k(r, \omega) + c.c.] = U^d + U^q + U^m. \quad (23)$$

An optical wave propagating through a medium modifies its polarization state. This process is governed by the linear response of the medium to the action of the optical field which is represented by the electric $\mathbf{m}^e(r, t)$ and magnetic $\mathbf{m}^m(r, t)$ moment induced in a molecule by the optical wave oscillating with the frequency ω , of the spectral amplitude looking as follows [4-7]

$$m_k^e(r, \omega) = \mu_k(r, \omega) - \frac{1}{3} \nabla_u q_{uk}(r, \omega) + \dots, \quad (24)$$

$$m_k^m(r, \omega) = m_k(r, \omega) + \dots \quad (25)$$

Here $\mu_k(r, \omega)$, $q_{uk}(r, \omega)$ and $m_k(r, \omega)$ denote, respectively, the Cartesian components of the spectral amplitude of the electric-dipole, electric-quadrupole and magnetic-dipole moment induced in a molecule by the optical wave, which are given by [4-7]

$$\begin{aligned} \mu_k(r, \omega) = & \quad ({}^1_e\alpha_{e\ kl}^{(1)}(-\omega, \omega) E_l(r, \omega) + \frac{1}{3} ({}^1_e\alpha_{e\ k(ul)}^{(2)}(-\omega, \omega) \nabla_u E_l(r, \omega) \\ & + ({}^1_m\alpha_{m\ kl}^{(1)}(-\omega, \omega) B_l(r, \omega) + \dots, \end{aligned} \quad (26)$$

$$q_{(uk)}(r, \omega) = ({}^2_e\alpha_{e\ (uk)l}^{(1)}(-\omega, \omega) E_l(r, \omega) + \dots, \quad (27)$$

$$m_k(r, \omega) = ({}^1_m\alpha_{e\ kl}^{(1)}(-\omega, \omega) E_l(r, \omega) + \dots, \quad (28)$$

where $({}^1_e\alpha_{e\ kl}^{(1)}(-\omega, \omega)$, $({}^1_e\alpha_{e\ k(ul)}^{(2)}(-\omega, \omega)$ and $({}^1_m\alpha_{m\ kl}^{(1)}(-\omega, \omega)$ represent the linear electric-dipole polarizabilities related to the electric-dipole, electric-quadrupole and magnetic-dipole transitions, respectively, whereas the last two symbols $({}^2_e\alpha_{e\ (uk)l}^{(1)}(-\omega, \omega)$ and $({}^1_m\alpha_{e\ kl}^{(1)}(-\omega, \omega)$ describe the electric-quadrupole and magnetic-dipole polarizabilities related to the electric-dipole transitions between the electronic ground state and virtual (in the absence of resonance) or excited (in the presence of resonance) states.

The quantum mechanical form of the linear electric $\mathcal{A} = e$ and magnetic $\mathcal{A} = m$ multipolar polarizabilities of the a th order related to the transition of the electric $\mathcal{B} = e$ and magnetic $\mathcal{B} = m$ multipole moment of the b th order between the stationary ground state and virtual/excited states $({}^a_{\mathcal{A}}\alpha_{\mathcal{B}}^{(b)}(-\omega, \omega)$ can be found in Refs. [4-7,29,30]. Here, we should keep in mind that this polarizability for molecules with complex wavefunctions is

complex, and if the widths of the energy levels are taken into account, is not Hermitian and can be written as the sum of the four parts [29,30]

$${}^{(a)}\alpha_B^{(b)}(-\omega, \omega) = {}^{(a)}\beta_B^{(b)}(-\omega, \omega) + i {}^{(a)}\gamma_B^{(b)}(-\omega, \omega) + i [{}^{(a)}\xi_B^{(b)}(-\omega, \omega) + i {}^{(a)}\vartheta_B^{(b)}(-\omega, \omega)], \quad (29)$$

which satisfy the following transposition relations

$${}^{(a)}\beta_B^{(b)}(-\omega, \omega) = {}^{(b)}\beta_A^{(a)}(-\omega, \omega), \quad {}^{(a)}\xi_B^{(b)}(-\omega, \omega) = {}^{(b)}\xi_A^{(a)}(-\omega, \omega), \quad (30)$$

$${}^{(a)}\gamma_B^{(b)}(-\omega, \omega) = - {}^{(b)}\gamma_A^{(a)}(-\omega, \omega), \quad {}^{(a)}\vartheta_B^{(b)}(-\omega, \omega) = - {}^{(b)}\vartheta_A^{(a)}(-\omega, \omega). \quad (31)$$

The polarizabilities

$${}^{(a)}\beta_e^{(b)}(-\omega, \omega), \quad {}^{(a)}\xi_e^{(b)}(-\omega, \omega), \quad {}^{(a)}\gamma_m^{(b)}(-\omega, \omega), \quad {}^{(a)}\vartheta_m^{(b)}(-\omega, \omega), \quad (32)$$

can exist for molecules with real as well as complex wavefunctions and are *i*-tensors (time even), whereas

$${}^{(a)}\gamma_e^{(b)}(-\omega, \omega), \quad {}^{(a)}\vartheta_e^{(b)}(-\omega, \omega), \quad {}^{(a)}\beta_m^{(b)}(-\omega, \omega), \quad {}^{(a)}\xi_m^{(b)}(-\omega, \omega), \quad (33)$$

can only exist for molecules with complex wavefunctions and are *c*-tensors (time odd) for arbitrary *a* and *b*. In the absence of damping, the polarizabilities ${}^{(a)}\xi_B^{(b)}(-\omega, \omega)$ and ${}^{(a)}\vartheta_B^{(b)}(-\omega, \omega)$ are equal to zero, and owing to this ${}^{(a)}\alpha_B^{(b)}(-\omega, \omega)$ becomes Hermitian.

The two kinds of classical Boltzmann averages mentioned in (17)-(19) can be obtained using the formulae [27-29]

$$\langle \mu_j^0 \rangle_{U^a} = \langle \mu_j^0 \rangle - \frac{1}{k_B T} (\langle \mu_j^0 U^a \rangle - \langle \mu_j^0 \rangle \langle U^a \rangle) \quad (34)$$

and isotropic averages over all possible orientations for the second-, third- and fourth-rank tensors which look as follows

$$\langle \alpha_{kl} \rangle = \frac{1}{3} \delta_{kl} \delta_{\sigma\nu} \alpha_{\sigma\nu}, \quad (35)$$

$$\langle \alpha_{jkl} \rangle = \frac{1}{6} \delta_{jkl} \delta_{\sigma\nu\epsilon} \alpha_{\sigma\nu\epsilon}, \quad (36)$$

$$\langle \alpha_{jklu} \rangle = [\mathcal{X}_{\sigma\nu\epsilon\zeta} \delta_{jk} \delta_{lu} + \mathcal{Y}_{\sigma\nu\epsilon\zeta} \delta_{jl} \delta_{ku} + \mathcal{Z}_{\sigma\nu\epsilon\zeta} \delta_{ju} \delta_{kl}] \alpha_{\sigma\nu\epsilon\zeta} \quad (37)$$

where

$$\begin{aligned} \mathcal{X}_{\sigma\nu\epsilon\zeta} &= \frac{1}{30} (4\delta_{\sigma\nu} \delta_{\epsilon\zeta} - \delta_{\sigma\epsilon} \delta_{\nu\zeta} - \delta_{\sigma\zeta} \delta_{\nu\epsilon}), \\ \mathcal{Y}_{\sigma\nu\epsilon\zeta} &= \frac{1}{30} (-\delta_{\sigma\nu} \delta_{\epsilon\zeta} + 4\delta_{\sigma\epsilon} \delta_{\nu\zeta} - \delta_{\sigma\zeta} \delta_{\nu\epsilon}), \\ \mathcal{Z}_{\sigma\nu\epsilon\zeta} &= \frac{1}{30} (-\delta_{\sigma\nu} \delta_{\epsilon\zeta} - \delta_{\sigma\epsilon} \delta_{\nu\zeta} + 4\delta_{\sigma\zeta} \delta_{\nu\epsilon}). \end{aligned} \quad (38)$$

Here the tensors α_{jk} , α_{jkl} and α_{jklu} represent the particular polarizability tensors in the Cartesian laboratory frame $\{xyz\}$, k_B denotes the Boltzmann constant, T is the absolute temperature, the greek indices σ, ν, ε and ζ take the values 1, 2, 3, the symbols $\delta_{\sigma\nu}$ and $\delta_{\sigma\nu\varepsilon}$ represent, respectively, the Kronecker second-rank symmetric and the Levi-Civita third-rank antisymmetric unit tensors in the Cartesian molecular frame $\{123\}$.

Assuming that the optical wave propagates along the z -axis of the Cartesian laboratory frame and applying the classical Boltzmann average (34)-(38) we obtain

$$P_z^q(0) = [G^q + \underline{G}^q + \frac{1}{k_B T} G_T^q] \frac{dS_0(z)}{dz} + [G^q + \underline{G}^q + \frac{1}{k_B T} \underline{G}_T^q] \epsilon_+(z), \quad (39)$$

$$P_z^m(0) = [G^m + \underline{G}^m + \frac{1}{k_B T} G_T^m] \frac{dS_0(z)}{dz} + [G^m + \underline{G}^m + \frac{1}{k_B T} \underline{G}_T^m] \epsilon_+(z), \quad (40)$$

where

$$G^q = \frac{\rho}{90} \left\{ - {}^{(1)}\beta_{ee\sigma\sigma(\nu\nu)}^{(1,2)}(0; -\omega, \omega) + 3 {}^{(1)}\beta_{ee\sigma\nu(\sigma\nu)}^{(1,2)}(0; -\omega, \omega) \right\}, \quad (41)$$

$$G_T^q = \frac{\rho}{90} \left\{ - {}^{(1)}\beta_{e\sigma(\nu\nu)}^{(2)}(-\omega, \omega) + 3 {}^{(1)}\beta_{e\nu(\sigma\nu)}^{(2)}(-\omega, \omega) \right\} \mu_\sigma^0, \quad (42)$$

$$G^m = \frac{\rho}{12\omega} \delta_{\sigma\nu\varepsilon} \left\{ {}^{(1)}\gamma_{em\sigma\nu\varepsilon}^{(1,1)}(0; -\omega, \omega) - {}^{(1)}\gamma_{em\sigma\varepsilon\nu}^{(1,1)}(0; -\omega, \omega) \right\}, \quad (43)$$

$$G_T^m = \frac{\rho}{12\omega} \delta_{\sigma\nu\varepsilon} \left\{ {}^{(1)}\gamma_{m\nu\varepsilon}^{(1)}(-\omega, \omega) - {}^{(1)}\gamma_{m\varepsilon\nu}^{(1)}(-\omega, \omega) \right\} \mu_\sigma^0, \quad (44)$$

$$\underline{G}^q = \frac{\rho}{45} \left\{ - {}^{(1)}\vartheta_{ee\sigma\sigma(\nu\nu)}^{(1,2)}(0; -\omega, \omega) + 3 {}^{(1)}\vartheta_{ee\sigma\nu(\sigma\nu)}^{(1,2)}(0; -\omega, \omega) \right\}, \quad (45)$$

$$\underline{G}^m = \frac{\rho}{6\omega} \delta_{\sigma\nu\varepsilon} \left\{ - {}^{(1)}\xi_{em\sigma\nu\varepsilon}^{(1,1)}(0; -\omega, \omega) + {}^{(1)}\xi_{em\sigma\varepsilon\nu}^{(1,1)}(0; -\omega, \omega) \right\}, \quad (46)$$

$$\underline{G}_T^q = \frac{1}{90V} \sum_{mol} \left\{ - {}^{(1)}\xi_{ee\sigma\sigma(\nu\nu)}^{(1,2)}(0; -\omega, \omega) + 3 {}^{(1)}\xi_{ee\sigma\nu(\sigma\nu)}^{(1,2)}(0; -\omega, \omega) \right\}, \quad (47)$$

$$\underline{G}_T^m = \frac{1}{12V\omega} \delta_{\sigma\nu\varepsilon} \sum_{mol} \left\{ {}^{(1)}\vartheta_{em\sigma\nu\varepsilon}^{(1,1)}(0; -\omega, \omega) - {}^{(1)}\vartheta_{em\sigma\varepsilon\nu}^{(1,1)}(0; -\omega, \omega) \right\}, \quad (48)$$

$$\underline{\underline{G}}^q = \frac{1}{45V} \sum_{mol} \left\{ - {}^{(1)}\gamma_{ee\sigma\sigma(\nu\nu)}^{(1,2)}(0; -\omega, \omega) + 3 {}^{(1)}\gamma_{ee\sigma\nu(\sigma\nu)}^{(1,2)}(0; -\omega, \omega) \right\}, \quad (49)$$

$$\underline{\underline{G}}_T^q = \frac{1}{45V} \sum_{mol} \left\{ - {}^{(1)}\gamma_{e\sigma(\nu\nu)}^{(2)}(-\omega, \omega) + 3 {}^{(1)}\gamma_{e\nu(\sigma\nu)}^{(2)}(-\omega, \omega) \right\} \mu_\sigma^0, \quad (50)$$

$$\underline{\underline{G}}^m = \frac{1}{6V\omega} \delta_{\sigma\nu\varepsilon} \sum_{mol} \left\{ - {}^{(1)}\beta_{em\sigma\nu\varepsilon}^{(1,1)}(0; -\omega, \omega) + {}^{(1)}\beta_{em\sigma\varepsilon\nu}^{(1,1)}(0; -\omega, \omega) \right\}, \quad (51)$$

$$\underline{\underline{G}}_T^m = \frac{1}{6V\omega} \delta_{\sigma\nu\varepsilon} \sum_{mol} \left\{ - {}^{(1)}\beta_{m\nu\varepsilon}^{(1)}(-\omega, \omega) + {}^{(1)}\beta_{m\varepsilon\nu}^{(1)}(-\omega, \omega) \right\} \mu_\sigma^0, \quad (52)$$

$$\epsilon_+(z) = \frac{i}{2} [E_x^*(\omega, z) \nabla_z E_x(\omega, z) + E_y^*(\omega, z) \nabla_z E_y(\omega, z) - c.c.], \quad (53)$$

$\rho = \tilde{N}/V$ is the number of molecules in unit volume and

$$S_0(z) = |E_x(\omega, z)|^2 + |E_y(\omega, z)|^2 \quad (54)$$

is the well known Stokes parameter for a pathlength z in the medium, which in fact corresponds to the total intensity of the light beam. Above we have omitted the expression for the z th component of the static electric-dipole polarization induced by the pure electric-dipole mechanism $P_z^d(0)$ which was calculated in Ref. [18] and denoted by $P_z(0)$.

To perform the summation in (47) - (52) over all molecules contained in the unit volume of our medium we have to take into account that all the standing polarizabilities in these formulae are c -tensors (their values in the state $|p\rangle$ and $\mathcal{T}|p\rangle$ differ in sign). Owing to this, the underlined parameters \underline{G}^q , \underline{G}^m , $\underline{\mathcal{G}}^q$, $\underline{\mathcal{G}}^m$, \underline{G}_T^q and \underline{G}_T^m will be proportional to the difference $\tilde{N} = \frac{1}{2}N(\rho_{pp}^0 - \rho_{\mathcal{T}p\mathcal{T}p}^0)$ which can differ from zero only if we take into account the variation of the population of these two states induced by the optical beam. Following the procedure described in Refs. [13,29,31], it is easy to show that G_T^q and G_T^m represent the static electric polarization due to the variation of the populations of the two states. The polarizabilities standing in (41)-(46) are time-even, and therefore the parameters G^q and G^m , \mathcal{G}^q , \mathcal{G}^m , G_T^q , and G_T^m are proportional to $\tilde{N} = \frac{N}{2}(\rho_{aa}^0 + \rho_{\mathcal{T}a\mathcal{T}a}^0)$ which is always much greater than the difference. Because our aim is to find the optical rectification based only on the quadratic electric nonlinearity, which leads to the linearly intensity-dependent Dc electric polarization, we have additionally $\rho_{aa}^0 + \rho_{\mathcal{T}a\mathcal{T}a}^0 \approx 2$. Due to this, we arrive at (39) and (40) with the additional condition

$$\underline{G}^q = \underline{G}^m = \underline{\mathcal{G}}^q = \underline{\mathcal{G}}^m = \underline{G}_T^q = \underline{G}_T^m \approx 0. \quad (55)$$

In Ref [32] on putting the DC magnetic field B^0 equal to zero we can find how the electric field $E_j(\omega, z)$ of the optical wave depends on the path z traversed by the optical beam in our medium which permit us to find how the Stokes parameter $S_0(z)$ and $\epsilon_+(z)$ depend on z . It is easy to check that these dependences look as follows

$$S_0(z) = \frac{2I_0}{c\epsilon_0 n(\omega)_{inc}} F(z), \quad (56)$$

$$\epsilon_+(z) = -\frac{2\omega n_0 I_0}{c^2 \epsilon_0 n(\omega)_{inc}} \left\{ F(z) - \frac{g}{n_0} f(z) \right\}, \quad (57)$$

where

$$F(z) = \left\{ \cosh\left(\frac{2\omega g' z}{c}\right) + \sin 2\eta_0 \sinh\left(\frac{2\omega g' z}{c}\right) \right\} \exp[-\kappa(\omega)z], \quad (58)$$

$$f(z) = \left\{ \sinh\left(\frac{2\omega g' z}{c}\right) + \sin 2\eta_0 \cosh\left(\frac{2\omega g' z}{c}\right) \right\} \exp[-\kappa(\omega)z], \quad (59)$$

and we have used the relation

$$S_0 = |E_x(\omega, 0)|^2 + |E_y(\omega, 0)|^2 = \frac{2I_0}{c\epsilon_0 n(\omega)_{inc}} \quad (60)$$

to express the Stokes parameter S_0 by the intensity of the incident optical wave I_0 (for $z = 0$) in SI units (W/m^2). Above

$$\kappa(\omega) = \frac{\rho\omega}{3n_0\epsilon_0 c} {}^{(1)}\xi_{e\nu\nu}^{(1)}(-\omega, \omega) \quad (61)$$

represents the light absorption coefficient, the molecular parameters

$$g = \frac{\rho}{3c\epsilon_0} {}^{(1)}\gamma_{m\nu\nu}^{(1)}(-\omega, \omega) \quad \text{and} \quad g' = \frac{\rho}{3c\epsilon_0} {}^{(1)}\vartheta_{m\nu\nu}^{(1)}(-\omega, \omega) \quad (62)$$

are responsible for the natural optical activity and the natural circular dichroism,

$$n_0 = \sqrt{1 + \frac{\rho}{3\epsilon_0} {}^{(1)}\beta_{e\nu\nu}^{(1)}(-\omega, \omega)} \quad (63)$$

describes the light refractive index, η_0 is the initial ellipticity, c is the light velocity in vacuum, ϵ_0 is the electric permittivity of vacuum and $n(\omega)_{inc}$ denotes the refractive index of the incident optical wave in an incident medium.

The static polarization leads to a potential difference $\mathcal{U}(z = d)$ on the transparent plates of the capacitor introduced into the measuring cuvette along the direction of propagation of the optical wave

$$\mathcal{U}(d) = -[\mathcal{U}_1 + \mathcal{U}_2 + \mathcal{U}_T] \{1 - F(d)\} - \mathcal{U}_3 \{\sin(2\eta_0) - f(d)\}, \quad (64)$$

where

$$\mathcal{U}_1 = \frac{2I_0 [G^q + G^m]}{c\epsilon_0^2(\epsilon - 1)n(\omega)_{inc}}, \quad (65)$$

$$\mathcal{U}_T = \frac{2I_0 [G_T^q + G_T^m]}{k_B T c\epsilon_0^2(\epsilon - 1)n(\omega)_{inc}}, \quad (66)$$

$$\mathcal{U}_2 = \frac{2I_0\omega [G^q + G^m] \left[n_0\kappa - \frac{2\omega g g'}{c} \right]}{c^2\epsilon_0^2(\epsilon - 1)n(\omega)_{inc} \left[\kappa^2 - \left(\frac{2\omega g'}{c} \right)^2 \right]}, \quad (67)$$

$$\mathcal{U}_3 = \frac{2I_0\omega [G^q + G^m] \left[-g\kappa + \frac{2\omega n_0 g'}{c} \right]}{c^2\epsilon_0^2(\epsilon - 1)n(\omega)_{inc} \left[\kappa^2 - \left(\frac{2\omega g'}{c} \right)^2 \right]}, \quad (68)$$

and d is the distance between the capacitor plates (the first is situated at $z = 0$), ϵ denotes the static dielectric constant.

Using the Tables [26,33] giving the form of the polar and axial i -tensors we can determine, for all magnetic point groups, the explicit forms of the parameters G^q , G^m , G_T^q , G_T^m , \mathcal{G}^q and \mathcal{G}^m which are responsible for the electric-quadrupole and magnetic-dipole contributions to the DC electric-dipole polarization as well as g' and $\kappa(\omega)$ which describe the parameters $F(z)$ and $f(z)$ when the frequency of the optical field is close to the molecular resonance frequency. The results are assembled in Table 1.

From this Table we see that both the parameter G^q and G^m exist for molecules with arbitrary symmetries (for all the magnetic point groups), whereas the other parameters G_T^q and G_T^m differ from zero for all the molecules with a permanent electric dipole moment. Earlier, we showed that pre-resonant optical rectification via the second-order electric dipole mechanism [15,16,18,19] can appear in an isotropic medium composed of chiral molecules and can be induced only by an optical wave which has to be circularly ($\eta_0 = \pi/4$) or elliptically polarized ($\eta_0 \neq 0$) at incidence on the medium. The use of a linearly polarized or unpolarized ($\eta_0 = 0$) pre-resonant optical wave reduces the space function $F(d)$ and $f(d)$ to the form

$$F(d) = \cosh\left(\frac{2\omega g' d}{c}\right) \exp[-\kappa(\omega)d], \quad (69)$$

$$f(d) = \sinh\left(\frac{2\omega g' d}{c}\right) \exp[-\kappa(\omega)d], \quad (70)$$

and allows us to observe only the electric-quadrupole and magnetic-dipole contributions to optical rectification in a medium composed of noninteracting molecules with arbitrary symmetries. The first two columns of Table 1 denote the form of the function $F(d)$ and $f(d)$. We see that κ can appear in an isotropic medium composed of molecules with arbitrary symmetries but g' as well as $f(d)$ can only exist in a medium composed of chiral molecules. It is easy to notice that the potential difference $\mathcal{U}(z = d)$ may differ from zero in the presence of resonance because only in this case $F(d)$ is less than 1. To estimate the magnitude of the potential differences given by equations (64)-(68) it is necessary to have available the numerical value of the parameters G^q , G^m , G_T^q , G_T^m , \mathcal{G}^q , \mathcal{G}^m , κ , g and g' for the appropriate frequency ω .

We shall now attempt to estimate the electric-quadrupole and magnetic-dipole contributions to the potential difference $\mathcal{U}(d)$ induced by linearly polarized light in absorption bands of a chiral ruthenium-tris-phenanthroline salt soluted in an optically transparent solvent at a concentration of 0.1 mole of $[\text{Ru phen}_3]^{2+}$ per litre.

The Fig. 31 in Ref. [34] and Fig. 2 in [35] present a plot of the molar extinction coefficient $\tilde{\epsilon}(\lambda)$ and the molar decadic absorption coefficient $\Delta\tilde{\epsilon}(\lambda) = \tilde{\epsilon}_L(\lambda) - \tilde{\epsilon}_R(\lambda)$ for left (L) and right (R) circular polarized light for $[\text{Ru phen}_3]^{2+}$ in the region of the wavelengths from $\lambda = 250$ nm to $\lambda = 545$ nm. To find the values of the absorption coefficient $\kappa(\lambda)$ and the parameter $\frac{2\omega g'(\lambda)}{c}$ for ruthenium-tris-phenanthroline salt soluted in an optically transparent solvent with a concentration $x_c = 0.1$ moles per litre of $[\text{Ru phen}_3]^{2+}$ we can apply in the first approximation the following formula

$$\kappa(\omega) = \tilde{\epsilon}(\lambda) \ln(10)x_c, \quad \frac{2\omega g'(\omega)}{c} = \frac{\Delta\tilde{\epsilon}(\lambda) \ln(10)x_c}{2}, \quad \text{with } \omega = \frac{2\pi c}{\lambda}. \quad (71)$$

On the basis of molar absorption and circular dichroism measurements [34,35], we assign the following transitions from the ground state A_1 (symmetry A_1 under D_3) to electronically excited states $a'(A_2)$ at $\lambda_{a'} = 464$ nm, $a''(E)$ at $\lambda_{a''} = 418$ nm, $b'(E)$ at $\lambda_{b'} = 269$ nm and $b''(A_2)$ at $\lambda_{b''} = 258$ nm. The values of the molar extinction $\tilde{\epsilon}(\lambda)$ and molar decadic absorption $\Delta\tilde{\epsilon}(\lambda)$ coefficients for the above mentioned excited states and the several wavelengths lying outside absorption bands taken from the plot 31 of Ref. [34] and 2 of [35] are assembled in Table 2. Speaking more exactly, from this Table we see that in the region of the wavelengths $250 \text{ nm} \leq \lambda \leq 545 \text{ nm}$ the molar extinction coefficient is $\tilde{\epsilon}(\lambda) \geq 755 \text{ l mol}^{-1}\text{cm}^{-1}$ with the minimal value $\tilde{\epsilon}(\lambda)_{\min} = 755 \text{ l mol}^{-1}\text{cm}^{-1}$ for $\lambda = 545$ nm and it is easy to check, that the molar decadic absorption coefficient satisfies the relation $\Delta\tilde{\epsilon}(\lambda)/2\tilde{\epsilon}(\lambda) = \frac{2\omega g'}{c\kappa} \leq 3.6 \times 10^{-3}$ (see Table 2).

Taking into account the expressions (69) and (70) together with (71) it is easy to show that the space parameters $F(d)$ and $f(d)$ reach their maximal value for $\lambda = 545$ nm, which for $d = 0.001\text{m}$ are $F(d = 0.001\text{m}) = 2.85 \times 10^{-8}$ and $f(d = 0.001\text{m}) = 9.7 \times 10^{-10}$ or for $d = 0.01\text{m}$ are $F(d = 0.01\text{m}) = 3.25 \times 10^{-76}$ and $f(d = 0.01\text{m}) = 1.08 \times 10^{-76}$. Owing to this we can take $1 - F(d) = 1$ for all the wavelengths belonging to the above mentioned region.

The parameter \mathcal{U}_3 being proportional to g and g' can exist only in an isotropic medium composed of chiral molecules and it satisfies the following relation

$$\frac{\mathcal{U}_3}{\mathcal{U}_2} = \frac{\frac{2\omega g'}{c\kappa} - \frac{g}{n_0}}{1 - \frac{2\omega g' g}{c\kappa n_0}}. \quad (72)$$

On time-consuming calculations we have estimated that for all the wavelengths belonging to the region $250 \text{ nm} \leq \lambda \leq 545 \text{ nm}$ the parameter \mathcal{U}_3 is not greater than $0.004 \mathcal{U}_2$, owing to this \mathcal{U}_3 can be discarded. To reach this result we have had to know the values of the ratio g/g' for all λ with the region $250 \text{ nm} \leq \lambda \leq 545 \text{ nm}$. The calculated values of g/g' for the exact resonances ($\lambda = \lambda_{a'}$, $\lambda = \lambda_{a''}$, $\lambda = \lambda_{b''}$) and the several wavelengths lying outside absorption bands are assembled in Table 2.

From Table 1 we see that in our case (the symmetry $32(D_3)$) the potential difference can only be generated by the parameters G_1^q and G_1^m . Unfortunately, we have lacked the experimental values of the suitable components of the nonlinear polarizabilities ${}^{(1)}\tilde{\beta}_{ee\,jk(ul)}^{(1,2)}(0; -\omega, \omega)$, and ${}^{(1)}\tilde{\gamma}_{em\,jkl}^{(1,1)}(0; -\omega, \omega)$. It has been shown [2] that the interaction between macroscopic nondissipative media and time-varying electromagnetic fields can be described by a time-averaged potential function, the free energy density. Knowing this energy we can find an expression describing the static macroscopic electric polarization which, after comparing with (39) and (40), enables us to check that the nonlinear polarizabilities ${}^{(1)}\beta_{ee\,jk(ul)}^{(1,2)}(0; -\omega, \omega)$ and ${}^{(1)}\gamma_{em\,jkl}^{(1,1)}(0; -\omega, \omega)$ satisfy the additional conditions

$$\begin{aligned} {}^{(1)}\beta_{ee\,jk(ul)}^{(1,2)}(0; -\omega, \omega) &= {}^{(1)}\beta_{e\,k(ul)j}^{(2)e}(-\omega; \omega, 0), \\ {}^{(1)}\gamma_{em\,jkl}^{(1,1)}(0; -\omega, \omega) &= {}^{(1)}\gamma_m^{(1)e}{}_{klj}(-\omega; \omega, 0). \end{aligned} \quad (73)$$

The linear electric-dipole polarizabilities ${}^{(1)}\beta_{e\,k(ul)j}^{(2)e}(-\omega; \omega, 0)$ and ${}^{(1)}\gamma_m^{(1)e}{}_{klj}(-\omega; \omega, 0)$ describe, respectively, the variation of the linear electric-dipole/electric-quadrupole polarizability ${}^{(1)}\beta_{e\,k(ul)}^{(2)}(-\omega; \omega, E^0)$ and the linear electric-dipole/magnetic-dipole polarizability ${}^{(1)}\gamma_m^{(1)}(-\omega; \omega, E^0)$ of a single molecule in the presence of a DC electric field \mathbf{E}^0 which are proportional to the first power of \mathbf{E}^0 and, of course, in the case when the frequency of the optical wave lies far from a resonance. The above linear electric variations of the linear electric-dipole polarizabilities are responsible for the reflection of an optical wave from a fluid in a uniform electric field [36-38] predicted by Buckingham and the electric-field-induced differential scattering of right and left circularly polarized light in a fluid [39,40].

The above mentioned optical phenomena (linear in an applied DC electrostatic field) have already been observed [36,37,40] but unfortunately they permit only the calculation of the magnitude of ${}^{(1)}\gamma_m^{(1)}(-\omega, \omega) = -{}^{(1)}\gamma_m^{(1)}(-\omega, \omega) = (-0.34 \pm 0.04) \times 10^{-34} \text{AV}^{-1}\text{m}^3$ for the achiral molecule CH_3Cl (methyl chloride whose symmetry is described by the point group $3m(C_{3v})$) [40] giving a contribution to \mathcal{U}_T^m which in our case is forbidden. In accordance with Refs. [41,42] ${}^{(1)}\beta_e^{(2)e}(-\omega; \omega, 0) = -1.807 \times 10^{-61} \text{J}^{-2}\text{C}^3\text{m}^4$ and $\omega^{-1} {}^{(1)}\gamma_m^{(1)e}(-\omega; \omega, 0) = 0.2255 \times 10^{-61} \text{J}^{-2}\text{C}^3\text{m}^4$ for atomic hydrogen in its ground state at low frequency.

From Table 1 we see that the parameters G^q and G^m exist for molecules with arbitrary symmetries. Owing to this, the molecules of the solvent also give contributions to the potential difference. To estimate the magnitude of the potential difference $\mathcal{U}^q + \mathcal{U}^m$ we assume the same value $2 {}^{(1)}\tilde{\beta}_{ee}^{(1,2)} + {}^{(1)}\tilde{\beta}_{ee}^{(1,2)} + 2 \left[{}^{(1)}\tilde{\beta}_{ee}^{(1,2)} + {}^{(1)}\tilde{\beta}_{ee}^{(1,2)} + {}^{(1)}\tilde{\beta}_{ee}^{(1,2)} \right] + \frac{10}{\omega} \left[{}^{(1)}\tilde{\gamma}_{em}^{(1,1)} + {}^{(1)}\tilde{\gamma}_{em}^{(1,1)} + {}^{(1)}\tilde{\gamma}_{em}^{(1,1)} \right] = \times 10^{-60} \text{J}^{-2}\text{C}^3\text{m}^4$, for $[\text{Ru phen}_3]^{2+}$ as well as for the molecule of the solvent. Owing to this, the number density ρ can take the value $\rho = 10^{28} \text{m}^{-3}$ (typical values for the number density of liquids are $10^{27} - 10^{28} \text{m}^{-3}$).

Then taking $\epsilon_0 = 8.854188 \times 10^{-12} \text{CV}^{-1}\text{m}^{-1}$, $c = 2.997925 \times 10^8 \text{ms}^{-1}$, $\epsilon - 1 = 10$, $n_{inc} = 1$ and the initial intensity of the linearly polarized optical wave $I_0 = 1.5 \times 10^{11} \text{Wm}^{-2}$, we obtain $\mathcal{U} \approx 0.4 \text{ nV}$.

Appendix A

Setting $\omega_1 = -\omega$ and $\omega_2 = \omega$ in the quantum mechanical definition of the second-order nonlinear electric-dipole polarizability ${}^{(1)}\alpha_{\mathcal{B}\mathcal{C}}^{(b,c)}(-\omega_1 - \omega_2; \omega_1, \omega_2)$ given in Refs. [4-6,20-22], we can find the quantum mechanical definition of the polarizability ${}^{(1)}\alpha_{\mathcal{B}\mathcal{C}}^{(b,c)}(0; -\omega, \omega)$ responsible for optical rectification, which in the presence of damping looks as follows

$$\begin{aligned} {}^{(1)}\alpha_{\mathcal{B}\mathcal{C}}^{(b,c)}(0; -\omega, \omega) = & \frac{\rho_{pp}^0}{2!\hbar^2} \sum_{v,w} \left\{ \frac{1}{\omega_{wp} - i\Gamma_{wp}} \left[\frac{\mathcal{P}_{e\mathcal{B}\mathcal{C}}^{1bc}}{\omega_{vp} + \omega - i\Gamma_{vp}} + \frac{\mathcal{P}_{e\mathcal{C}\mathcal{B}}^{1cb}}{\omega_{vp} - \omega - i\Gamma_{vp}} \right] \right. \\ & + \frac{1}{\omega_{wp} + \omega + i\Gamma_{wp}} \left[\frac{\mathcal{P}_{\mathcal{B}\mathcal{C}e}^{bc1}}{\omega_{vp} + i\Gamma_{vp}} + \frac{\mathcal{P}_{\mathcal{B}e\mathcal{C}}^{b1c}}{\omega_{vp} + \omega - i\Gamma_{vp}} \right] \\ & \left. + \frac{1}{\omega_{wp} - \omega + i\Gamma_{wp}} \left[\frac{\mathcal{P}_{\mathcal{C}\mathcal{B}e}^{cb1}}{\omega_{vp} + i\Gamma_{vp}} + \frac{\mathcal{P}_{\mathcal{C}e\mathcal{B}}^{c1b}}{\omega_{vp} - \omega - i\Gamma_{vp}} \right] \right\}, \quad (\text{A1}) \end{aligned}$$

with

$$\begin{aligned} \mathcal{P}_{e\mathcal{B}\mathcal{C}}^{1bc} &= (\boldsymbol{\mu}_e^{(1)})_{pw} (\boldsymbol{\mu}_{\mathcal{B}}^{(b)})_{wv} (\boldsymbol{\mu}_{\mathcal{C}}^{(c)})_{vp}, & \mathcal{P}_{e\mathcal{C}\mathcal{B}}^{1cb} &= (\boldsymbol{\mu}_e^{(1)})_{pw} (\boldsymbol{\mu}_{\mathcal{C}}^{(c)})_{wv} (\boldsymbol{\mu}_{\mathcal{B}}^{(b)})_{vp}, \\ \mathcal{P}_{\mathcal{B}\mathcal{C}e}^{bc1} &= (\boldsymbol{\mu}_{\mathcal{B}}^{(b)})_{pw} (\boldsymbol{\mu}_{\mathcal{C}}^{(c)})_{wv} (\boldsymbol{\mu}_e^{(1)})_{vp}, & \mathcal{P}_{\mathcal{B}e\mathcal{C}}^{b1c} &= (\boldsymbol{\mu}_{\mathcal{B}}^{(b)})_{pw} (\boldsymbol{\mu}_e^{(1)})_{wv} (\boldsymbol{\mu}_{\mathcal{C}}^{(c)})_{vp}, \\ \mathcal{P}_{\mathcal{C}\mathcal{B}e}^{cb1} &= (\boldsymbol{\mu}_{\mathcal{C}}^{(c)})_{pw} (\boldsymbol{\mu}_{\mathcal{B}}^{(b)})_{wv} (\boldsymbol{\mu}_e^{(1)})_{vp}, & \mathcal{P}_{\mathcal{C}e\mathcal{B}}^{c1b} &= (\boldsymbol{\mu}_{\mathcal{C}}^{(c)})_{pw} (\boldsymbol{\mu}_e^{(1)})_{wv} (\boldsymbol{\mu}_{\mathcal{B}}^{(b)})_{vp}. \end{aligned} \quad (\text{A2})$$

$(\boldsymbol{\mu}_{\mathcal{B}}^{(b)})_{pw} = \langle p | \boldsymbol{\mu}_{\mathcal{B}}^{(b)} | w \rangle$ denotes the transition matrix element of an electric ($\mathcal{B} = e$) or magnetic ($\mathcal{B} = m$) multipole moment of the b -th order between the ground state $|p\rangle$ and a stationary state $|w\rangle$, and ρ_{pp}^0 is the quantum mean value of the unperturbed density matrix in the ground state. According to Kielich's notation [4-6] the symbol ${}^{(a)}\alpha_{\mathcal{A}\mathcal{B}\mathcal{C}}^{(b,c)}(0; -\omega, \omega)$ is a tensor of the rank $a+b+c$ which describes the second-order nonlinear electric multipole $\mathcal{A} = e$ polarizability of the a th order (for $a = 1, 2$ we have, respectively, the dipole and quadrupole moment) related to an electric $\mathcal{B} = e$ or magnetic $\mathcal{B} = m$ multipole transition of order b and an electric $\mathcal{C} = e$ or magnetic $\mathcal{C} = m$ multipole transition of order c between the stationary ground state $|p\rangle$ and excited states $|w\rangle$ and $|v\rangle$.

For a molecule with complex wavefunctions, the polarizability ${}^{(1)}\alpha_{\mathcal{B}\mathcal{C}}^{(b,c)}(0; -\omega, \omega)$ may be expressed in the form (7)-(9), with ${}^{(1)}\beta_{\mathcal{B}\mathcal{C}}^{(b,c)}(0; -\omega, \omega)$, ${}^{(1)}\xi_{\mathcal{B}\mathcal{C}}^{(b,c)}(0; -\omega, \omega)$, ${}^{(1)}\gamma_{\mathcal{B}\mathcal{C}}^{(b,c)}(0; -\omega, \omega)$ and ${}^{(1)}\vartheta_{\mathcal{B}\mathcal{C}}^{(b,c)}(0; -\omega, \omega)$ defined by

$${}^{(1)}\beta_{\mathcal{B}\mathcal{C}}^{(b,c)}(0; -\omega, \omega) = \frac{\rho_{pp}^0}{\hbar^2} \sum_{v,w} \left\{ \frac{\mathcal{R}_{e\mathcal{B}\mathcal{C}}^{1bc+} \Omega_1}{N_1} + \frac{\mathcal{R}_{\mathcal{B}e\mathcal{C}}^{b1c+} \Omega_2}{2N_2} \right\}, \quad (\text{A3})$$

$${}^{(1)}\gamma_{eBC}^{(b,c)}(0; -\omega, \omega) = \frac{\omega\rho_{pp}^0}{\hbar^2} \sum_{v,w} \left\{ \frac{\mathcal{I}_{eBC}^{1bc-} \Omega_3}{N_1} + \frac{\mathcal{I}_{BeC}^{b1c-} \Omega_4}{2N_2} \right\}, \quad (\text{A4})$$

$${}^{(1)}\xi_{eBC}^{(b,c)}(0; -\omega, \omega) = \frac{\rho_{pp}^0}{\hbar^2} \sum_{v,w} \left\{ \frac{\mathcal{I}_{eBC}^{1bc+} \Omega'_1}{N_1} + \frac{\mathcal{I}_{BeC}^{b1c+} \Omega'_2}{2N_2} \right\}, \quad (\text{A5})$$

$${}^{(1)}\vartheta_{eBC}^{(b,c)}(0; -\omega, \omega) = \frac{\omega\rho_{pp}^0}{\hbar^2} \sum_{v,w} \left\{ \frac{\mathcal{R}_{eBC}^{1bc-} \Omega'_3}{N_1} + \frac{\mathcal{R}_{BeC}^{b1c-} \Omega'_4}{2N_2} \right\}, \quad (\text{A6})$$

where

$$\mathcal{R}_{eBC}^{1bc\pm} = \frac{1}{2} [\mathcal{P}_{eBC}^{1bc} \pm \mathcal{P}_{eCB}^{1cb} + c.c.], \quad \mathcal{R}_{BeC}^{b1c\pm} = \frac{1}{2} [\mathcal{P}_{BeC}^{b1c} \pm \mathcal{P}_{CeB}^{c1b} + c.c.], \quad (\text{A7})$$

$$\mathcal{I}_{eBC}^{1bc\pm} = \frac{i}{2} [\mathcal{P}_{eBC}^{1bc} \pm \mathcal{P}_{eCB}^{1cb} - c.c.], \quad \mathcal{I}_{BeC}^{b1c\pm} = \frac{i}{2} [\mathcal{P}_{BeC}^{b1c} \pm \mathcal{P}_{CeB}^{c1b} - c.c.]. \quad (\text{A8})$$

and the frequency-dependent functions are given by

$$\begin{aligned} \Omega_1 &= (\omega_{vp}\omega_{wp} - \Gamma_{vp}\Gamma_{wp})(\omega_{vp}^2 - \omega^2 + \Gamma_{vp}^2) - 2\omega^2\Gamma_{vp}\Gamma_{wp}, \\ \Omega_2 &= [(\omega_{vp}^2 + \omega^2 + \Gamma_{vp}^2)(\omega_{wp}^2 + \omega^2 + \Gamma_{wp}^2) + 4\omega^2\omega_{vp}\omega_{wp}](\omega_{vp}\omega_{wp} + \omega^2 + \Gamma_{vp}\Gamma_{wp}) \\ &\quad - 2\omega^2(\omega_{vp} + \omega_{wp})[\omega_{vp}(\omega_{wp}^2 + \omega^2 + \Gamma_{wp}^2) + \omega_{wp}(\omega_{vp}^2 + \omega^2 + \Gamma_{vp}^2)], \\ \Omega_3 &= \omega_{wp}(\omega_{vp}^2 - \omega^2 - \Gamma_{vp}^2) - 2\omega_{vp}\Gamma_{vp}\Gamma_{wp}, \\ \Omega_4 &= -[(\omega_{vp}^2 + \omega^2 + \Gamma_{vp}^2)(\omega_{wp}^2 + \omega^2 + \Gamma_{wp}^2) + 4\omega^2\omega_{vp}\omega_{wp}](\omega_{vp} + \omega_{wp}) \\ &\quad + 2[\omega_{vp}(\omega_{wp}^2 + \omega^2 + \Gamma_{wp}^2) + \omega_{wp}(\omega_{vp}^2 + \omega^2 + \Gamma_{vp}^2)](\omega_{vp}\omega_{wp} + \omega^2 + \Gamma_{vp}\Gamma_{wp}), \\ \Omega'_1 &= (\Gamma_{vp}\omega_{wp} + \Gamma_{wp}\omega_{vp})(\omega_{vp}^2 - \omega^2 + \Gamma_{vp}^2) + 2\omega^2\Gamma_{vp}\omega_{wp}, \\ \Omega'_2 &= [(\omega_{vp}^2 + \omega^2 + \Gamma_{vp}^2)(\omega_{wp}^2 + \omega^2 + \Gamma_{wp}^2) + 4\omega^2\omega_{vp}\omega_{wp}](\Gamma_{vp}\omega_{wp} - \Gamma_{wp}\omega_{vp}) \\ &\quad - 2\omega^2(\Gamma_{vp} - \Gamma_{wp})[\omega_{vp}(\omega_{wp}^2 + \omega^2 + \Gamma_{wp}^2) + \omega_{wp}(\omega_{vp}^2 + \omega^2 + \Gamma_{vp}^2)], \\ \Omega'_3 &= -\Gamma_{wp}(\omega_{vp}^2 - \omega^2 - \Gamma_{vp}^2) - 2\Gamma_{vp}\omega_{vp}\omega_{wp}, \\ \Omega'_4 &= [(\omega_{vp}^2 + \omega^2 + \Gamma_{vp}^2)(\omega_{wp}^2 + \omega^2 + \Gamma_{wp}^2) + 4\omega^2\omega_{vp}\omega_{wp}](\Gamma_{vp} - \Gamma_{wp}) \\ &\quad - 2[\omega_{vp}(\omega_{wp}^2 + \omega^2 + \Gamma_{wp}^2) + \omega_{wp}(\omega_{vp}^2 + \omega^2 + \Gamma_{vp}^2)](\Gamma_{vp}\omega_{wp} - \Gamma_{wp}\omega_{vp}), \end{aligned} \quad (\text{A9})$$

$$\begin{aligned} N_1 &= (\omega_{wp}^2 + \Gamma_{wp}^2)\{(\omega_{vp}^2 - \omega^2 + \Gamma_{vp}^2)^2 + 4\omega^2\Gamma_{vp}^2\}, \\ N_2 &= \{(\omega_{vp}^2 - \omega^2 + \Gamma_{vp}^2)^2 + 4\omega^2\Gamma_{vp}^2\}\{(\omega_{wp}^2 - \omega^2 + \Gamma_{wp}^2)^2 + 4\omega^2\Gamma_{wp}^2\}, \end{aligned} \quad (\text{A10})$$

It is easy to check that the polarizabilities ${}^{(1)}\tilde{\gamma}_{ee}^{(b,c)}(0; -\omega, \omega)$ and ${}^{(1)}\tilde{\beta}_{em}^{(b,c)}(0; -\omega, \omega)$ differ from zero only for molecules with complex wavefunctions (paramagnetic molecules) whereas the other polarizabilities ${}^{(1)}\tilde{\beta}_{ee}^{(b,c)}(0; -\omega, \omega)$ and ${}^{(1)}\tilde{\gamma}_{em}^{(b,c)}(0; -\omega, \omega)$ can also exist

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4 for molecules with real wavefunctions (diamagnetic molecules). For a molecule with real
5 wavefunctions, the matrix element of the transition of the electric multipole moment of the
6 b -th order $(\boldsymbol{\mu}_e^{(b)})_{pw}$ is real whereas the matrix element of the transition of the magnetic
7 multipole moment of the b -th order $(\boldsymbol{\mu}_m^{(b)})_{pw}$ is imaginary; owing to this $\mathcal{I}_{eee}^{\pm 1bc}$, $\mathcal{I}_{eee}^{\pm b1c}$ and
8 $\mathcal{R}_{eem}^{\pm 1bc}$, $\mathcal{R}_{eem}^{\pm b1c}$, $\mathcal{R}_{eme}^{\pm 1bc}$, $\mathcal{R}_{eem}^{\pm b1c}$ vanish.
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Table 1. The molecular parameters $\kappa(\omega)$, g' , G^q , G_T^q , G^m and G_T^m for all magnetic point groups. The molecules with the symmetries described by the magnetic point groups in parentheses { } admit of a resonant electric-dipole contribution to optical rectification [18].

Magnetic point groups	g'	κ	$P_z^q(0)$		$P_z^m(0)$	
			G^q	G_T^q	G^m	G_T^m
{1},	g'	κ	G^q	$G_{T0}^q + G_{T1}^q$	G^m	$G_{T0}^m + G_{T1}^m$
m , \underline{m} ,	0	κ	G^q	G_{T0}^q	G^m	G_{T0}^m
{2, 2},	g'	κ	G^q	G_{T1}^q	G^m	G_{T1}^m
$mm2$, $\underline{mm2}$, $\underline{2mm}$,	0	κ	G^q	G_{T1}^q	G^m	G_{T1}^m
$\bar{1}$, $\underline{\bar{1}}$, $2/m$, $\underline{2/m}$, $2/\underline{m}$, $\underline{2/\underline{m}}$, mmm , \underline{mmm} ,	0	κ	G^q	0	G^m	0
\underline{mmm} , \underline{mmm} ,						
{222, 222},	g'	κ	G^q	0	G^m	0
{4, 4, 3, 6, 6, ∞ },	g'_1	κ_1	G_1^q	G_{T2}^q	G_1^m	G_{T2}^m
$4mm$, $\underline{4mm}$, $\underline{4mm}$, $3m$, $\underline{3m}$, $6mm$, $\underline{6mm}$,	0	κ_1	G_1^q	G_{T2}^q	G_1^m	G_{T2}^m
$\underline{6mm}$, ∞m , $\infty \underline{m}$,						
{ $\bar{4}$, $\underline{\bar{4}}$ }, $4/m$, $\underline{4/m}$, $4/\underline{m}$, $\underline{4/\underline{m}}$, { $\bar{4}2m$, $\underline{\bar{4}2m}$,	0	κ_1	G_1^q	0	G_1^m	0
$\underline{\bar{4}m2}$, $\underline{\bar{4}m2}$ }, $4/mmm$, $\underline{4/mmm}$, $4/\underline{mmm}$,						
$4/\underline{mmm}$, $4/\underline{mmm}$, $\underline{4/mmm}$, $\bar{3}$, $\underline{\bar{3}}$, $\bar{3}m$, $\underline{\bar{3}m}$,						
$\bar{3}m$, $\underline{\bar{3}m}$, $\bar{6}$, $\underline{\bar{6}}$, $6/m$, $\underline{6/m}$, $6/\underline{m}$, $\underline{6/\underline{m}}$, $\bar{6}m2$,						
$\underline{\bar{6}m2}$, $\underline{\bar{6}m2}$, $\bar{6}m2$, $6/mmm$, $\underline{6/mmm}$, $6/\underline{mmm}$,						
$6/\underline{mmm}$, $6/\underline{mmm}$, $\underline{6/mmm}$, ∞/m , ∞/\underline{m} ,						
∞/mm , ∞/\underline{mm} , ∞/\underline{mm} ,						
{422, $\underline{422}$, $\underline{422}$, 32, 32, 622, $\underline{622}$, $\underline{622}$ },	g'_1	κ_1	G_1^q	0	G_1^m	0
{23},	g'_2	κ_2	G_2^q	0	G_2^m	0
$m3$, $\underline{m3}$,	0	κ_2	G_2^q	0	G_2^m	0
{432, $\underline{432}$, Y, K},	g'_2	κ_2	G_3^q	0	G_3^m	0
$\bar{4}3m$, $\underline{\bar{4}3m}$, $m3m$, $\underline{m3m}$, $m3m$, $\underline{m3m}$, Y_h , K_h	0	κ_2	G_3^q	0	G_3^m	0

where:

$$g'_1 = \frac{\rho}{3\epsilon_0} \left[2 \left({}^1\vartheta_{m11}^{(1)}(-\omega, \omega) + {}^1\vartheta_{m33}^{(1)}(-\omega, \omega) \right), \right]$$

$$g'_2 = \frac{\rho}{\epsilon_0} \left({}^1\vartheta_{m33}^{(1)}(-\omega, \omega) \right),$$

$$\kappa_1 = \frac{\rho\omega}{3n_0\epsilon_0c} \left[2 \left({}^1\xi_{e11}^{(1)}(-\omega, \omega) + {}^1\xi_{e33}^{(1)}(-\omega, \omega) \right), \right]$$

$$\kappa_2 = \frac{\rho\omega}{n_0\epsilon_0c} \left({}^1\xi_{e33}^{(1)}(-\omega, \omega) \right),$$

$$G^q = \frac{\rho}{30} \left[\left({}^1\tilde{\beta}_{ee1111}^{(1,2)} + {}^1\tilde{\beta}_{ee2222}^{(1,2)} + {}^1\tilde{\beta}_{ee3333}^{(1,2)} + {}^1\tilde{\beta}_{ee12(12)}^{(1,2)} + {}^1\tilde{\beta}_{ee13(13)}^{(1,2)} + {}^1\tilde{\beta}_{ee21(21)}^{(1,2)} + {}^1\tilde{\beta}_{ee23(23)}^{(1,2)} \right. \right. \\ \left. \left. + {}^1\tilde{\beta}_{ee31(31)}^{(1,2)} + {}^1\tilde{\beta}_{ee32(32)}^{(1,2)} \right), \right]$$

$$G_1^q = \frac{\rho}{30} \left\{ 2 \left({}^1\tilde{\beta}_{ee1111}^{(1,2)} + {}^1\tilde{\beta}_{ee3333}^{(1,2)} + 2 \left[{}^1\tilde{\beta}_{ee12(12)}^{(1,2)} + {}^1\tilde{\beta}_{ee13(13)}^{(1,2)} + {}^1\tilde{\beta}_{ee31(31)}^{(1,2)} \right] \right\},$$

$$G_2^q = \frac{\rho}{10} \left[\left({}^1\tilde{\beta}_{ee1111}^{(1,2)} + {}^1\tilde{\beta}_{ee12(12)}^{(1,2)} + {}^1\tilde{\beta}_{ee21(12)}^{(1,2)} \right), \right]$$

$$G_3^q = \frac{\rho}{10} \left[\left({}^1\tilde{\beta}_{ee1111}^{(1,2)} + 2 \left({}^1\tilde{\beta}_{ee12(12)}^{(1,2)} \right) \right), \right]$$

Table 1 (continued)

$$\begin{aligned}
G^m &= \frac{\rho}{6\omega} \left[{}_e^{(1)}\tilde{\gamma}_{em\ 123}^{(1,1)} + {}_e^{(1)}\tilde{\gamma}_{em\ 231}^{(1,1)} + {}_e^{(1)}\tilde{\gamma}_{em\ 312}^{(1,1)} - {}_e^{(1)}\tilde{\gamma}_{em\ 213}^{(1,1)} - {}_e^{(1)}\tilde{\gamma}_{em\ 321}^{(1,1)} - {}_e^{(1)}\tilde{\gamma}_{em\ 132}^{(1,1)} \right], \\
G_1^m &= \frac{\rho}{3\omega} \left[{}_e^{(1)}\tilde{\gamma}_{em\ 123}^{(1,1)} + {}_e^{(1)}\tilde{\gamma}_{em\ 231}^{(1,1)} + {}_e^{(1)}\tilde{\gamma}_{em\ 312}^{(1,1)} \right], & G_2^m &= \frac{\rho}{2\omega} \left[{}_e^{(1)}\tilde{\gamma}_{em\ 123}^{(1,1)} - {}_e^{(1)}\tilde{\gamma}_{em\ 132}^{(1,1)} \right], \\
G_3^m &= \frac{\rho}{\omega} {}_e^{(1)}\tilde{\gamma}_{em\ 123}^{(1,1)}, \\
G_{T0}^q &= \frac{\rho}{30} \left\{ \mu_1^0 \left[{}_e^{(1)}\beta_{e\ 1(11)}^{(2)} + {}_e^{(1)}\beta_{e\ 2(12)}^{(2)} + {}_e^{(1)}\beta_{e\ 3(13)}^{(2)} \right] + \mu_2^0 \left[{}_e^{(1)}\beta_{e\ 1(21)}^{(2)} + {}_e^{(1)}\beta_{e\ 2(22)}^{(2)} + {}_e^{(1)}\beta_{e\ 3(23)}^{(2)} \right] \right\}, \\
G_{T1}^q &= \frac{\rho}{30} \mu_3^0 \left[{}_e^{(1)}\beta_{e\ 1(31)}^{(2)} + {}_e^{(1)}\beta_{e\ 2(32)}^{(2)} + {}_e^{(1)}\beta_{e\ 3(33)}^{(2)} \right], & G_{T2}^q &= \frac{\rho}{30} \mu_3^0 \left[2 {}_e^{(1)}\beta_{e\ 1(31)}^{(2)} + {}_e^{(1)}\beta_{e\ 3(33)}^{(2)} \right], \\
G_{T0}^m &= \frac{\rho}{6\omega} \left\{ \mu_1^0 \left[{}_e^{(1)}\gamma_{m\ 23}^{(1)} - {}_e^{(1)}\gamma_{m\ 32}^{(1)} \right] + \mu_2^0 \left[{}_e^{(1)}\gamma_{m\ 31}^{(1)} - {}_e^{(1)}\gamma_{m\ 13}^{(1)} \right] \right\}, \\
G_{T1}^m &= \frac{\rho}{6\omega} \mu_3^0 \left[{}_e^{(1)}\gamma_{m\ 12}^{(1)} - {}_e^{(1)}\gamma_{m\ 21}^{(1)} \right], & G_{T2}^m &= \frac{\rho}{3\omega} \mu_3^0 {}_e^{(1)}\gamma_{m\ 12}^{(1)}.
\end{aligned}$$

Table 2. The calculated values of the ratio of U_3/U_2 for ruthenium-tris-phenanthroline (salt soluted in an optically transparent solvent with a concentration $x_c = 0.1$ moles per litre of $[\text{Ru phen}_3]^{2+}$), induced by linearly polarized optical wave of frequency exactly tuned to each of the four electronic levels as well as the other to be outside absorption bands. The molar extinction coefficient $\tilde{\epsilon}(\lambda)$ and the molar decadic absorption coefficient $\Delta\tilde{\epsilon}(\lambda)$ have been taken from Ref. [35].

State Ψ	λ_Ψ [nm]	$\tilde{\epsilon}(\lambda)$ [$\text{l mol}^{-1}\text{cm}^{-1}$]	$\Delta\tilde{\epsilon}(\lambda)$ [$\text{l mol}^{-1}\text{cm}^{-1}$]	$\frac{2\omega g'}{c \kappa}$	$\frac{g}{g'}$	g	U_3/U_2	U_2 [nV]
–	545	755	3.0	0.0020	78.4	0.00012	0.0018	2.74
–	500	3640	9.0	0.0012	34.3	0.00014	0.0009	2.08
–	472	13660	17.5	0.0006	7.0	0.00005	0.0005	1.67
$a'(A_2)$	464	15035	16.9	0.0006	9×10^{-6}	6×10^{-11}	0.0006	1.68
–	440	22040	–8.1	–0.0002	–81.3	0.00026	–0.0007	0.25
$a''(E)$	418	19110	–13.5	–0.0004	0.002	-8×10^{-9}	–0.0004	–0.6
–	400	14890	–9.6	–0.0003	–32.5	0.00011	–0.0005	–0.42
–	338	3640	0.6	0.0001	106.2	0.00002	0.00006	0.14
–	314	8290	12.7	0.0008	72.4	0.00026	0.0003	0.09
–	300	20240	2.7	0.0001	52.5	0.00004	–0.00001	0.05
–	277	69790	254.0	0.0018	15.9	0.00102	–0.0002	–0.03
$b'(E)$	269	115480	566.6	0.0025	–0.025	-4×10^{-6}	0.0024	–0.02
–	266	124110	145.8	0.0006	–11.1	–0.00039	0.0014	0.09
$b''(A_2)$	258	80575	–440.0	–0.0027	0.045	-5×10^{-6}	–0.00269	0.77
–	250	40190	–200.0	–0.0025	–12.7	0.00058	–0.0037	0.64