

On Optical Rectification in Isotropic Media

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Abstract—Coherent nonlinear optical processes at second-order are only electric-dipole allowed in isotropic media that are optically active. Sum-frequency generation in chiral liquids has recently been observed, and difference-frequency and optical rectification have been predicted to exist in isotropic chiral media. Both Rayleigh–Schrödinger perturbation theory and the density matrix approach are used to discuss the quantum-chemical basis of optical rectification in optically active liquids. For pinene we compute the corresponding orientationally averaged hyperpolarizability, and estimate the light-induced dc electric polarization and the consequent voltage across a measuring capacitor it may give rise to near resonance.

1. INTRODUCTION

Second-order nonlinear optical processes are electric-dipole forbidden in centrosymmetric media [1]. These include crystals with cubic symmetry and most non-ordered systems (gases, liquids, amorphous solids). However, isotropic media that are optically active are necessarily also non-centrosymmetric and may thus give rise to certain second-order nonlinear optical processes. In particular, sum- and difference frequency generation are electric-dipole allowed [2], and the former has recently been observed in optically active limonene [3], and optically active solutions of 1,1'-bi-2-naphthol in tetrahydrofuran [4, 5]. Coherent second-harmonic generation and the Pockels effect remain forbidden at second-order in all isotropic media [6–8]. However, optical rectification—the generation of a static electric polarization by the application of an optical electromagnetic wave in a nonlinear medium—is predicted to exist at or near resonance in optically active isotropic media [9–11].

Optical rectification in anisotropic media is well known and was first observed in a potassium dihydrogen phosphate crystal by Bass *et al.* [12]. As predicted, the magnitude of the induced polarization was found to be proportional to the square of the optical electric-field amplitude [13]. For the effect to arise, the medium— isotropic or anisotropic—needs to be of sufficiently low symmetry such that the optically-induced dc electric polarization does not reverse exactly with the optical field [13]. We shall see that for isotropic media this necessitates the use of circularly polarized light (or a non-collinear beam geometry) and requires the optical field to be resonant with a molecular eigenstate (typically a vibrational or vibronic transition) in the chiral molecules of the optically active medium.

We first examine the quantum-mechanical form of the nonlinear second-order susceptibility that underlies optical rectification, and compute its strength *ab initio* for purely electronic resonances of pinene (see Fig. 1)— a relatively small molecule which allows the use of a

reasonably extended atomic basis set in the quantum chemical computation. We give estimates of the optically induced static polarization in liquid pinene for a typical pulsed laser.

2. THE SUSCEPTIBILITY

The real dc polarization induced in an isotropic medium by an electromagnetic wave $\mathbf{E}(\omega)$ with angular frequency ω is

$$\mathbf{P}(0) = \frac{\epsilon_0}{2} \{ \chi(0; -\omega, \omega) (\mathbf{E}^*(\omega) \wedge \mathbf{E}(\omega)) + \text{c.c.} \}. \quad (1)$$

In an isotropic medium the susceptibility tensor is given by the product of the pseudoscalar $\chi(0; -\omega, \omega)$ with the completely antisymmetric Levi Civita tensor [6]. Hence, it is the vector cross-product of the optical field amplitudes in Eq. (1) that determines the direction of the induced polarization in an isotropic medium. The macroscopic susceptibility is in turn related to the corresponding orientationally averaged molecular hyperpolarizability [6]:

$$\begin{aligned} \chi(0; -\omega, \omega) &= \frac{N}{\epsilon_0} \frac{1}{6} (\beta_{xyz} - \beta_{xzy} + \beta_{yxz} \\ &\quad - \beta_{yxz} + \beta_{zxy} - \beta_{zyx}) \equiv \frac{N}{\epsilon_0} \bar{\beta}, \end{aligned} \quad (2)$$

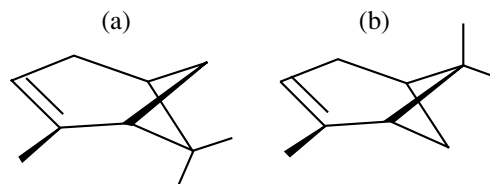


Fig. 1. Structures of (a) (1S,5S)-(-)- α -pinene and (b) (1R,5R)-(+)- α -pinene. Pinene ($C_{10}H_{16}$) is a liquid at room temperature.

where N is the number density of the optically active molecules. The isotropic component of the hyperpolarizability, $\bar{\beta}$, only exists for an ensemble of chiral¹ molecules and is of opposite sign for enantiomers. Hence, $\chi(0; -\omega, \omega)$ vanishes for a racemic mixture [6].

The quantum mechanical form of $\bar{\beta}$ describing optical rectification may be derived using a density-matrix formalism [6] or time-dependent Rayleigh–Schrödinger perturbation theory [10, 11, 14]. In both cases $\bar{\beta}$ factorizes into a triple product of transition dipole moments (common to both theories) and an energy factor [6]:

$$\begin{aligned} \bar{\beta}(0; -\omega, \omega) &= \sum_{m,n} \overline{\mu^{(3)}}(m, n) \mathcal{F}(m, n) \\ &= \sum_{m,n>m} \overline{\mu^{(3)}}(m, n) (\mathcal{F}(m, n) - \mathcal{F}(n, m)). \end{aligned} \quad (3)$$

We assume the absence of a static magnetic field and hence take the triple product of transition dipole moments

$$\overline{\mu^{(3)}}(m, n) = \frac{1}{6} \boldsymbol{\mu}_{gm} \cdot (\boldsymbol{\mu}_{mn} \times \boldsymbol{\mu}_{ng}), \quad (4)$$

where $\boldsymbol{\mu}_{gm} \equiv \langle g | \hat{\boldsymbol{\mu}} | m \rangle$, to be real. The antisymmetric nature of Eq. (4) together with the reality condition cause $\overline{\mu^{(3)}}(m, n)$ to be anti-Hermitian, i.e., $\overline{\mu^{(3)}}(m, n) = -\overline{\mu^{(3)}}(n, m)$ [15]. It follows that all diagonal ($m = n$) contributions in Eq. (3) cancel and hence that at least two nondegenerate excited states are required for $\bar{\beta}$ to be nonvanishing. It also follows that only the antisymmetric component of $\mathcal{F}(m, n)$ contributes to $\bar{\beta}$, and this allows us to write the second equality in Eq. (3). Should the optical frequency be far from any material resonances, then damping may be neglected and the hyperpolarizability tensor $\beta_{\alpha\beta\gamma}(0; -\omega, \omega)$ may be taken to be real such that the usual permutation symmetry [1] $\beta_{\alpha\beta\gamma}(0; -\omega, \omega) = \beta_{\alpha\gamma\beta}(0; -\omega, \omega)$ holds for which the sum in Eq. (2) vanishes. Thus, for optical rectification to exist in an isotropic medium, the requirement of an antisymmetric $\mathcal{F}(m, n)$ calls for the optical field to be resonant or near resonant with an electronic and/or a vibrational transition in the chiral molecule. The full Rayleigh–Schrödinger perturbation expression for a $\bar{\beta}$ that underlies optical rectification has been discussed in detail by Wozniak and coworkers [10, 11]. A corresponding expression in density matrix theory is, with the correct frequency substitutions, readily obtained from a $\bar{\beta}$ describing difference-frequency generation

[6, 16]. Both theories contain a term in $\mathcal{F}(m, n)$ that dominates whenever the optical field is near-resonant with two closely lying states. To simplify the subsequent discussion, we only retain this potentially doubly near-resonant term, and note that our computations on pinene confirm this approximation to be valid. The $(\mathcal{F}(m, n) - \mathcal{F}(n, m))$ factor in Eq. (3) is then approximately given by

$$\begin{aligned} &(\mathcal{F}(m, n) - \mathcal{F}(n, m)) \\ &\approx \frac{2i}{\hbar^2} \text{Im} \left[\frac{1}{(\omega_{mg} - \omega - i\Gamma_{mg})(\omega_{ng} - \omega + i\Gamma_{ng})} \right] \end{aligned} \quad (5)$$

using Rayleigh–Schrödinger perturbation theory, and by

$$\begin{aligned} &(\mathcal{F}(m, n) - \mathcal{F}(n, m)) \\ &\approx \frac{2i}{\hbar^2} \text{Im} \left[\frac{(\omega_{nm} + i\Gamma_{ng} + i\Gamma_{mg})}{(\omega_{nm} + i\Gamma_{nm})(\omega_{mg} - \omega - i\Gamma_{mg})(\omega_{ng} - \omega + i\Gamma_{ng})} \right] \end{aligned} \quad (6)$$

from density matrix theory. ω_{nm} is the Bohr angular frequency and Γ_{nm} is the dephasing rate constant for the macroscopic coherence between states n and m . It is also the half width at half maximum (HWHM) of the pole's spectrum for which it appears. In the absence of pure dephasing ($\Gamma_{nm} = \Gamma_{ng} + \Gamma_{mg}$) the density matrix expression in Eq. (6) correctly reduces to the corresponding Rayleigh–Schrödinger perturbation equation in Eq. (5). In the presence of pure dephasing, however, Eq. (6) suggests that, for closely lying states n , and m , additional near-resonant terms may be present that may not only affect the dispersion, but could also enhance ($\Gamma_{nm} < \Gamma_{ng} + \Gamma_{mg}$) or reduce ($\Gamma_{nm} > \Gamma_{ng} + \Gamma_{mg}$) the strength of the induced polarization. Curiously, complex damping terms in Eq. (6) are associated with a transition frequency ω_{nm} for which the sum of the incident field frequencies vanishes, yet such pure dephasing-induced near-resonance appears to be distinct from accidental secular resonances [17] as a genuine static polarization is generated in optical rectification. Formally Rayleigh–Schrödinger perturbation theory is correct provided its basis set includes states of the bath (however that is defined) as well as those of the molecules of interest. In the condensed phase this can be an unrealistic requirement and, as above, the basis set is normally limited to that of the molecule of interest. In this case bath effects have to be acknowledged by including damping of coherences. The Rayleigh–Schrödinger theory includes damping only of coherences between the excited states and the ground state (but not damping of coherences among excited states). Thus it is able to incorporate some pure dephasing as well. The density matrix approach also normally limits its basis set to that of the molecule of interest but is fully comprehensive in treating the damping, including pure dephasing, for all coherences. We see how these two theoretical approaches may be experimentally dis-

¹ A molecule that is distinct from its mirror image. The mirror image pairs are known as enantiomers.

tinguishable in the measurements of optical rectification.

Experimental observation of optical rectification in an optically active liquid will almost invariably require the use of a laser. Depending on its frequency either vibrational or electronic (vibronic) resonances may be sought. Vibrational resonances, compared to purely electronic ones, are characterized by narrower linewidths (by a factor of $\sim 10^{-2}$), lower laser- and Bohr-frequencies (by factors of $\sim 10^{-1}$ to 10^{-2}), and weaker transition dipole moments (by a factor of $\sim 10^{-1}$) [18]. Thus the relative strength of vibrational, vibronic and purely electronic contributions to the sum-over-states for optical rectification may be estimated near resonance. We expect that $\bar{\beta}$ for an infrared field that is vibrationally resonant can be an order of magnitude larger than that for the case of an incident visible or ultraviolet optical field that is resonant with electronic eigenstates in the chiral molecule. Furthermore, the case where an optical frequency can be in near resonance with two Franck–Condon vibrational levels of a single excited electronic state can also lead to a $\bar{\beta}$ comparable to that for the pure electronic case. However, since the purely electronic $\bar{\beta}$ (with optical incident frequencies) is most amenable to computation it forms the basis of the present calculations.

3. QUANTUM CHEMICAL COMPUTATIONS

We calculate the optical rectification $\bar{\beta}$ for pinene at visible and near UV-frequencies by a configuration interaction singles sum-over-states (CIS-SOS) approach. The geometry of pinene is first fully optimized with the quantum chemistry program GAUSSIAN98 [19] in a restricted Hartree-Fock calculation using the 631+G(d), 631+G(d,p), and 6311+G(d,p) basis sets [19, 20, 21]. Subsequently, the excitation energies and transition dipole moments are computed at the configuration interaction singles level of approximation using the same basis sets and program. We reduce the energy difference between the ground state and all excited states such that the first computed strongly allowed transition, with computer oscillator strength of ~ 0.23 , falls into registry with the first strong observed transition (that of the double bond excitation) having an absorption peak at 210 nm [22]. Finally, we use our own code to perform the sum in Eq. (3) over the excited states of pinene to calculate its $\bar{\beta}$. All three basis sets include diffuse and polarization functions on the carbons. The 631+G(d,p), and 6311+G(d,p) basis sets feature additional polarization functions on the hydrogens, and the latter includes additional valence functions. For pinene the 631+G(d), 631+G(d,p), and 6311+G(d,p) basis sets yield 222, 270, and 316 basis functions, respectively. Figure 2 shows the *ab initio* computed $\text{Im}[\bar{\beta}(0; -\omega, \omega)]$ in atomic units

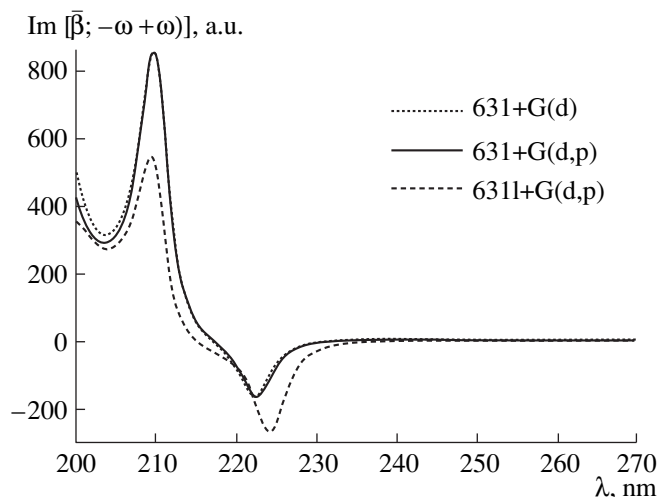


Fig. 2. The $\text{Im}[\bar{\beta}(0; -\omega, \omega)]$ for (1*R*,5*R*)-(+)- α -pinene is computed in a CIS-SOS procedure using the 631+G(d), 631+G(d,p), and 6311+G(d,p) basis sets, and is shown in atomic units ($e^3 a_0^3 / E_H^2$). The linewidths Γ_{ng} , Γ_{mg} , and Γ_{nm} are taken to be 500 cm^{-1} , and $\omega = 2\pi c/\lambda$. All terms in the sum-over-states expression for density matrix-theory are retained, yet the results are in good agreement to those obtained when the approximate energy factors in Eq. (6) are used.

as a function of the wavelength of the optical field for the three basis sets. The SOS is computed using the first 180, 80, and 60 excited states respectively. It is seen that the magnitude of $\bar{\beta}$ decreases as the size (and quality) of the basis set increases. Although the three SOS converged, more diffuse basis sets would be needed to establish whether the basis set limit has been reached, and the results in Fig. 2 are likely an upper limit to the magnitude of $\bar{\beta}$.

4. MATERIAL RESPONSE AND dc VOLTAGE ESTIMATES

The isotropic component of the optical rectification hyperpolarizability is purely imaginary and for there to be a polarization in Eq. (1) requires either a non-collinear beam geometry or an elliptically polarized incident field. We consider a circularly polarized incident electro-magnetic wave travelling in the z direction with radial frequency ω :

$$\mathbf{E}^{(\pm)}(\omega) = \frac{(\hat{e}_x \mp i\hat{e}_y)}{\sqrt{2}} E_0 e^{i(kz - \omega t)}, \quad (7)$$

where \hat{e}_x and \hat{e}_y are Cartesian unit vectors and E_0 is the amplitude. The real static polarization induced by the

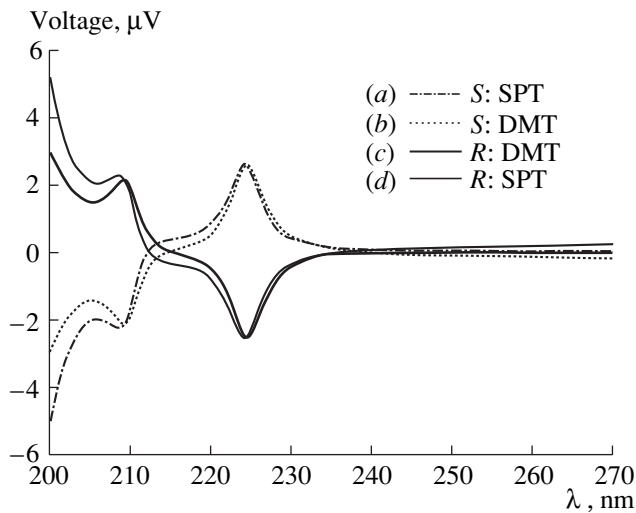


Fig. 3. DC voltage drop induced on a parallel plate capacitor (plate separation >2 mm) inserted in the direction of a laser beam with intensity $I = 10^{10}$ W/m² and wavelength λ . The 6311+G(d,p) basis set is used and estimates are for (1*S*,5*S*)-(-)- α -pinene (a) and (b), and for (1*R*,5*R*)-(+)- α -pinene (c) and (d). SPT indicates a sum-over-states based on the complete Rayleigh–Schrödinger perturbation expression. DMT indicates the sum-over-states based on the complete density matrix approach. For certain wavelengths the two theoretical treatments predict the opposite sign of $\text{Im}[\bar{\beta}(0; -\omega, \omega)]$ for the same enantiomer. The plots are in good agreement with those that are obtained from the approximate expressions given in Eq. (5) (for SPT) and Eq. (6) (for DMT).

circularly polarized wave with intensity $I = n_{\omega} c \epsilon_0 E_0^2 / 2$ is

$$\mathbf{P}_z^{(\pm)}(0) = (\pm) \frac{2000 N_A C I e^{-(\ln 10) \epsilon_{\omega} C z}}{n_{\omega} c \epsilon_0} \text{Im}[\bar{\beta}(0; -\omega, \omega)], \quad (8)$$

where N_A is Avogadro's number, and where the distance z is evaluated in cm. The absorber has concentration C (in mol/l) and a decadic molar extinction coefficient ϵ_{ω} (in 1 mol⁻¹ cm⁻¹) at the incident frequency ω . The induced static polarization may give rise to a potential difference on the plates of a parallel capacitor that is inserted in the direction of the beam [11]. The voltage drop on the capacitor, with the z direction plate separation d in cm, is then given by

$$\begin{aligned} & \delta V^{(\pm)}(d) \\ &= (\mp) \frac{20 N_A I (1 - e^{-(\ln 10) C \epsilon_{\omega} d})}{\ln(10) \epsilon_{\omega} n_{\omega} c K \epsilon_0^2} \text{Im}[\bar{\beta}(0; -\omega, \omega)], \end{aligned} \quad (9)$$

where we have further assumed that the cross section of the beam (taken to be of uniform intensity) and that of the capacitor plate are the same. The dielectric constant of the medium is K , and c is the speed of light in vacuum (in m/s). In the case of a pulsed light source it

becomes necessary to consider a time-integrated voltage in Eq. (6) and to account for the detector response-time [13].

In order to estimate the potential difference in Eq. (9) for pinene we obtain an approximate functional form of ϵ_{ω} by a Lorentzian fit to the first strong absorption peak with $\epsilon_{\omega} = 4400$ 1/(mol cm) at 210 nm [22], and we take n_{ω} to be constant and =1.6. The dielectric constant of pinene is 2.76 (at 20°C) [23]. We assume that the intensity of the laser in the ultraviolet is 10¹⁰ W/m², as could be provided by a nanosecond Excimer or the fourth-harmonic of a Q-switched YAG.

The separation of the capacitor plates is assumed to be >2 mm when plotting Fig. 3, as this ensures that the exponential in Eq. (9) is negligible (<0.01) for all wavelengths of Fig. 3. For large d , the voltage is inversely proportional to the extinction coefficient and in comparing Figs. 2 and 3 it is seen that this favors the off-resonant wavelengths.

Wozniak considers a purely electronic three-level model within Rayleigh–Schrödinger perturbation theory for solutions of chiral ruthenium-tris-phenanthroline salt and also estimates potential differences of microvolts albeit with a larger incident intensity ($I = 10^{11}$ W/m²) [11].

5. CONCLUSIONS

A circularly polarized resonant light beam in an optically active liquid may induce a static polarization, which can give rise to a potential difference on a capacitor inserted with plates perpendicular to the direction of the incident beam. The sign of this potential would, with the aid of quantum chemical calculations, constitute a direct measure of the absolute configuration of the chiral molecules in an isotropic medium. We compute a pure-electronic CIS-SOS $\bar{\beta}(0; -\omega, \omega)$ *ab initio* for pinene, and estimate that an incident intensity of $I = 10^{10}$ W/m² in the ultraviolet may give rise to potential differences of the order microvolts. Pure dephasing that is formally present in the density matrix approach appears to affect the dispersion of the optical rectification hyperpolarizability and the corresponding measured dc voltage.

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We are pleased to contribute to this special issue, on the occasion of Sven Hartmann's 70th birthday, in honor of his pioneering contributions to the field of nonlinear spectroscopy and photon echoes.

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