

Ab initio investigation of the sum-frequency hyperpolarizability of small chiral molecules

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Abstract

Using a sum-over-states procedure based on configuration interaction singles /6-311++G**, we have computed the sum-frequency hyperpolarizability $\beta_{ijk}(-3\omega; 2\omega, \omega)$ of two small chiral molecules, R-monofluoro-oxirane and R-(+)-propylene oxide. Excitation energies were scaled to fit experimental UV-absorption data and checked with ab initio values from time-dependent density functional theory. The isotropic part of the computed hyperpolarizabilities, $\bar{\beta}(-3\omega; 2\omega, \omega)$, is much smaller than that reported previously from sum-frequency generation experiments on aqueous solutions of arabinose. Comparison is made with a single-centre chiral model. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In the electric dipole approximation, coherent three-wave mixing (TWM) processes in isotropic media are only symmetry-allowed for sum- and difference-frequency generation in chiral media [1]. Indeed, coherent second-order nonlinear optical (NLO) processes appear either in non-centrosymmetric media such as crystals and interfaces, or in isotropic media provided they contain chiral molecules and are not racemic.

Chirality-allowed sum-frequency generation (SFG) in isotropic media was first reported over 30 years ago for *d*- and *l*-arabinose solutions in water

with a sum-frequency susceptibility about one-tenth that of quartz [2,3]. In a recent joint theoretical–experimental study [4], it has been shown that the SFG phenomenon in chiral liquids is much weaker than previously reported [2,3,5]. Firstly, a single-centre chiral model and ab initio calculations on small chiral molecules indicate that the isotropic part of the SFG first hyperpolarizability, $\bar{\beta}$, is at least two orders of magnitude smaller than that reported experimentally for arabinose. Secondly, three- and four-wave mixing experiments support the absence of a strong SFG response in simple chiral liquids.

In this Letter, we describe the theoretical procedure we have adopted for computing the dynamic sum-frequency hyperpolarizability and its isotropic part. Two simple chiral molecules are considered: propylene oxide, C₃H₆O, and monofluoro-oxirane, C₂H₃OF.

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2. Methodology and computational procedure

The TWM in chiral liquids is related to the completely antisymmetric isotropic component of the second-order susceptibility $\chi^{(2)}$ or to its microscopic analog [1,6]

$$\bar{\beta} = (\beta_{xyz} - \beta_{xzy} + \beta_{yxz} - \beta_{yzx} + \beta_{zxy} - \beta_{zyx})/6 \quad (1)$$

with each tensor component written according to Boyd [7]

$$\begin{aligned} & \beta_{ijk}(-\omega_q - \omega_p; \omega_q, \omega_p) \\ &= \hbar^{-2} P_1 \sum_n \sum_m \left\{ \frac{\mu_{0n}^i \bar{\mu}_{nm}^j \mu_{m0}^k}{(\tilde{\omega}_{n0} - \omega_p - \omega_q)(\tilde{\omega}_{m0} - \omega_p)} \right. \\ &+ \frac{\mu_{0n}^j \bar{\mu}_{nm}^i \mu_{m0}^k}{(\tilde{\omega}_{n0}^* + \omega_q)(\tilde{\omega}_{m0} - \omega_p)} \\ &+ \left. \frac{\mu_{0n}^i \bar{\mu}_{nm}^k \mu_{m0}^j}{(\tilde{\omega}_{n0}^* + \omega_q)(\tilde{\omega}_{m0}^* + \omega_p + \omega_q)} \right\}, \end{aligned} \quad (2)$$

where the operator P_1 permutes simultaneously the incident frequencies and the associated Cartesian indices, (ω_q, j) and (ω_p, k) . The summations run over all the excited states m and n , $\mu_{0n}^i = \langle 0 | \hat{\mu}_i | n \rangle$ is the i th component of the transition moment between the ground state (0) and the n th excited state, $\bar{\mu}_{nm}^j = \mu_{nm}^j - \mu_{00}^j \delta_{nm}$. The validity of Eq. (2) near resonance is ensured by the complex nature of the transition frequency $\tilde{\omega}_{m0} = \omega_{m0} - (i/2)\Gamma_{m0}$, where ω_{m0} is the real transition frequency and Γ_{m0} the width at half the maximum height of the transition between states 0 and m . When we include damping in the SOS expressions we choose a linewidth of 1000 cm^{-1} for all excited states with ω_q and ω_p in the visible.

The excitation energies and transition dipole moments were computed using the GAUSSIAN94 program [8] at the configuration interaction singles (CIS) level of approximation using the 6-311++G** [9,10] atomic basis set. Then $\bar{\beta}$ was evaluated by using a modified version of the $\alpha\beta$ -SOS code [11,12]. Fig. 1 shows that for propylene oxide the variation in the $\bar{\beta}(-3\omega; 2\omega, \omega)$ [$\hbar\omega = 1.165 \text{ eV} = 0.0428 \text{ a.u.}$; $\lambda = 1064 \text{ nm}$] due to the

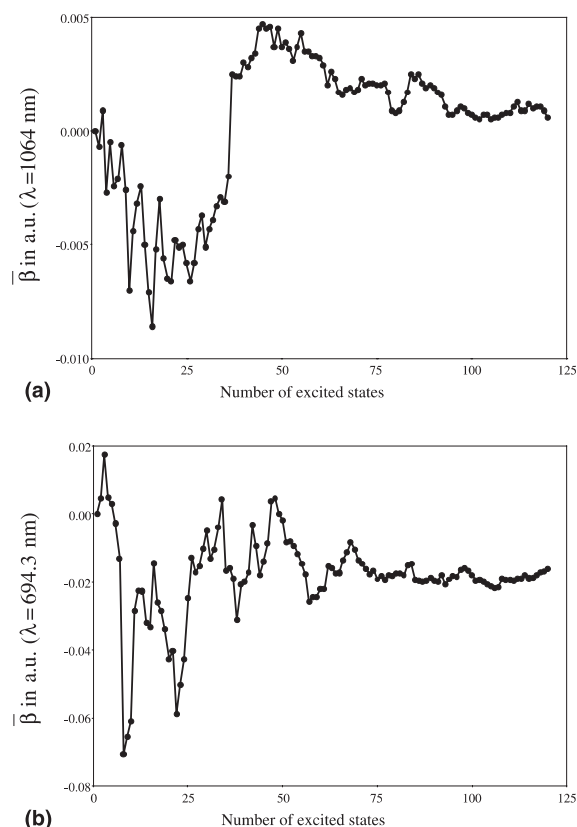


Fig. 1. CIS/6-311++G** $\bar{\beta}(-3\omega; 2\omega, \omega)$ as a function of the number of excited states included in the SOS expression. (a) R-(+)-propylene oxide, $\lambda = 1064 \text{ nm}$, scissor operator = 2.675 eV . (b) R-monofluoro-oxirane, $\lambda = 694.3 \text{ nm}$, scissor operator = 2.27 eV .

contributions from higher-energy excited states tends to decrease after the inclusion of the first ~ 80 excited states in the sum-over-states (SOS) expression. For propylene oxide $\bar{\beta}(-3\omega; 2\omega, \omega)$ converges towards a small positive value. With the exception of the sign, similar behavior is obtained for monofluoro-oxirane (Fig. 1). For the computed hyperpolarizabilities reported in this Letter we consider the first 120 excited states.

The frequency dispersion of $\bar{\beta}(-3\omega; 2\omega, \omega)$ is substantial and much larger than for the vector component of the β -tensor in the direction of the dipole moment μ , generally denoted $\beta_{\parallel} = (3/5)\mu_i \beta_{ijj} / (\mu_k \mu_k)^{1/2}$ with summation assumed over repeated indices. For instance, in the case of R-(+)-propylene oxide, $\bar{\beta}(-3\omega; 2\omega, \omega) = 0.00001$,

0.00056, and -0.0202 a.u.¹, whereas $\beta_{\parallel}(-3\omega; 2\omega, \omega)$ is -135 , -160 , and -251 a.u., respectively, for $\lambda = 1970$, 1064 and 694.3 nm ($\lambda = 2\pi c/\omega$). For the same order of wavelengths, $\bar{\beta}(-3\omega; 2\omega, \omega)$ of R-monofluoro-oxirane is -0.000004 , -0.00031 , and -0.0160 a.u. whereas, $\beta_{\parallel}(-3\omega; 2\omega, \omega)$ attains -129 , -147 , and -206 a.u., respectively. Accurate excitation energies are therefore mandatory to estimate the order of magnitude of $\bar{\beta}(-3\omega; 2\omega, \omega)$. To account for electron correlation as well as for solvatochromic effects, we have evaluated improved excitation energies by using a scissor operator to reduce all excitation energies by a fixed amount. The amplitude of the shift (2.675 eV) for propylene oxide has been determined to fit the experimental UV absorption spectra. Since monofluoro-oxirane is not commercially available and to our knowledge no experimental spectrum exists in the literature, a shift value of 2.27 eV has been obtained by comparing CIS/6-311++G** and experimental excitation energies for a set of small molecules including methanol, propylene oxide, THF and acetonitrile. Using the scissor operator, the lowest excitation energy of propylene oxide (monofluoro-oxirane) is 6.26 eV (7.26 eV) and corresponds to $\lambda_{\text{abs}} = 198$ nm (171 nm). This in turn gives a first resonance in $\bar{\beta}(-3\omega; 2\omega, \omega)$ at 594 nm (2.09 eV = 0.0767 a.u.) for propylene oxide and at 513 nm (2.42 eV = 0.0888 a.u.) for monofluoro-oxirane. The amplitude of the level shifts is supported by time-dependent density functional theory (TDDFT) [13,14] calculations of the excitation energies. Indeed, from TDDFT/6-311++G** calculations performed with GAUSSIAN98 [15], the first excitation energy of monofluoro-oxirane and propylene oxide has been estimated at 7.48 eV ($\lambda_{\text{abs}} = 188$ nm) and 6.60 eV ($\lambda_{\text{abs}} = 166$ nm), respectively. The remaining 5 – 10 nm difference is typical of solvatochromic shifts [16]. Although TDDFT provides accurate excitation energies, the $\bar{\beta}(-3\omega; 2\omega, \omega)$ calculations have been performed within the CIS scheme because the TDDFT approach has not yet been proven successful to obtain excited state dipole moments and therefore to

compute the molecular first hyperpolarizability from SOS expressions with/without damping.

The SOS expression for β_{ijk} (Eq. (2)) permits us to investigate the impact of the damping constant on $\bar{\beta}(-3\omega; 2\omega, \omega)$. This is of crucial importance near resonance. In the original experiment of Rentzepis et al. [2,3], the wavelength of the fundamental was 694.3 nm, i.e., a TWM signal at 231.4 nm (corresponding to $\hbar\omega = 5.357$ eV = 0.1969 a.u.), whereas the absorption maximum of aqueous *d*- and *l*-arabinose solutions is $\lambda_{\text{abs}} \sim 198$ nm. The impact of a non-zero linewidth on $\bar{\beta}(-3\omega; 2\omega, \omega)$ is illustrated in Fig. 2 for propylene oxide by comparing the frequency dispersion of $\bar{\beta}(-3\omega; 2\omega, \omega)$ for (a) $\Gamma_{m0} = 0$ and (b)

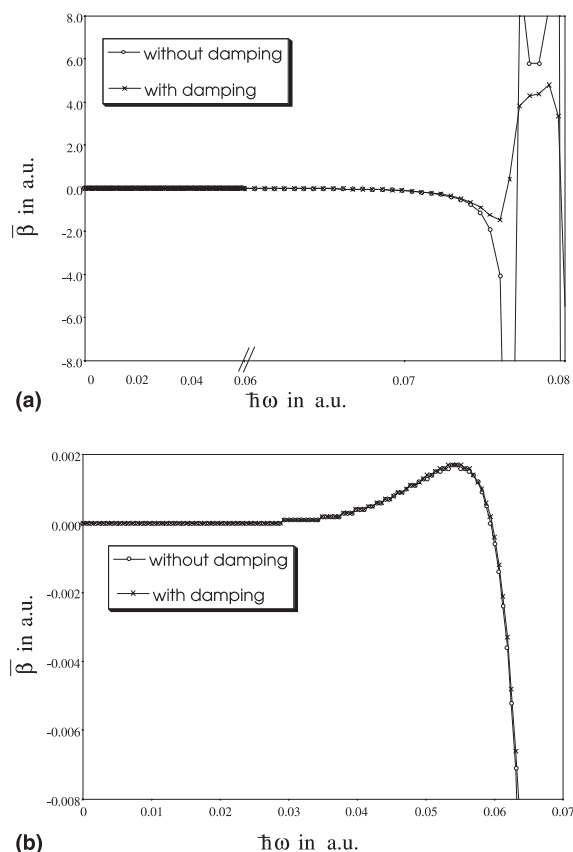


Fig. 2. Dispersion of CIS/6-311++G** $\bar{\beta}(-3\omega; 2\omega, \omega)$ of R-(+)-propylene oxide with ($\Gamma = 1000$ cm⁻¹) and without damping. When $\Gamma = 1000$ cm⁻¹, only the real part is considered. Picture (a) focuses on the resonance response, whereas picture (b) highlights the off-resonance and near-resonance regimes.

¹ 1 a.u. of the first hyperpolarizability = 3.2063×10^{-53} C³ m³ J⁻² = 8.641×10^{-33} esu.

$\Gamma_{m0} = \Gamma = 1000 \text{ cm}^{-1}$. For simplicity, the same damping constant has been chosen for all excited states. The TWM response in the resonant regime is strongly affected by neglecting the finite lifetime of the excited state, but inclusion of a damping factor has only a minor effect on the off-resonant and near-resonant responses.

The geometry of monofluoro-oxirane and propylene oxide have been fully optimized at the RHF/6-311++G** level of approximation with the help of GAUSSIAN94 [8]. The geometrical structures of the enantiomers we have considered are depicted in Fig. 3.

Provided damping is neglected, the most straightforward approach for computing $\bar{\beta}(-3\omega; 2\omega, \omega)$ is probably the time-dependent Hartree–Fock (TDHF) procedure [17]. This method has recently been implemented in the GAMESS program [18] for any pair of (ω_q, ω_p) values. By using the same scissor operator, both the CIS and TDHF procedures provide similar SFG amplitudes and dispersions for monofluoro-oxirane and propylene oxide [19]. Fig. 4 illustrates this fact for the former.

3. Single-centre chiral model

The simplest possible chiral molecule consists of a central atom bonded to three different, non-coplanar substituents. The bonding can be modeled by four sp^3 molecular orbitals $\psi_g, \psi_\ell, \psi_m$, and ψ_n

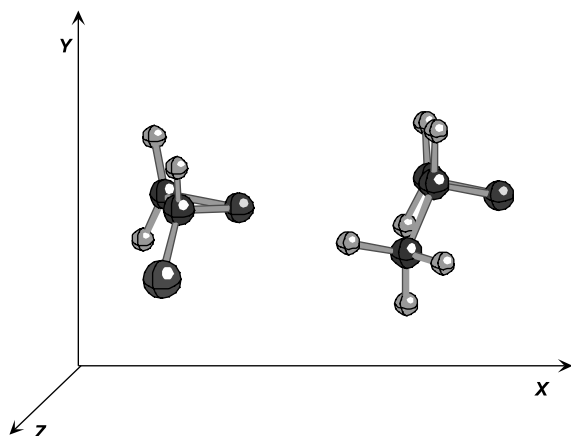


Fig. 3. Enantiomers of R-monofluoro-oxirane (left) and R-(+)-propylene oxide (right) considered in this study oriented in the Cartesian space along their principal inertial axes.

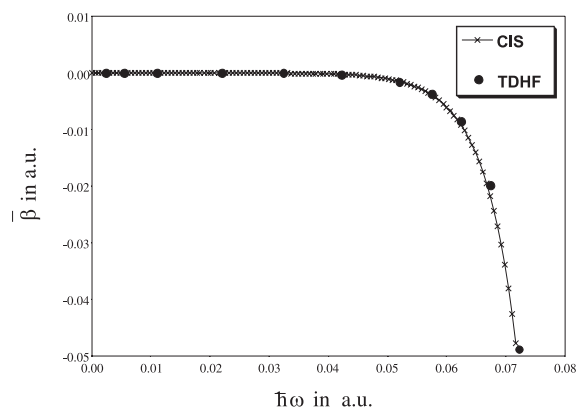


Fig. 4. Dispersion of CIS/6-311++G** $\bar{\beta}(-3\omega; 2\omega, \omega)$ of R-monofluoro-oxirane ($\Gamma = 1000 \text{ cm}^{-1}$). Corresponding TDHF/6-311++G** $\bar{\beta}(-3\omega; 2\omega, \omega)$ values are represented by filled dots ($\Gamma = 0$).

formed from the s , p_x , p_y , and p_z atomic orbitals located on the central atom. The molecular ground state is chosen to be chiral and predominately of s character. A particular set is given by

$$\begin{aligned}
 & (\Psi_g, \Psi_\ell, \Psi_m, \Psi_n) \\
 &= \begin{pmatrix} 0.93 & 0.10 & 0.20 & 0.30 \\ 0.093 & -0.99 & 0.02 & 0.03 \\ 0.26 & 0 & -0.95 & -0.16 \\ 0.26 & 0 & 0.22 & -0.94 \end{pmatrix} \begin{pmatrix} s \\ p_x \\ p_y \\ p_z \end{pmatrix}.
 \end{aligned} \tag{3}$$

In this phenomenological model the transition energies to ψ_ℓ, ψ_m , and ψ_n are taken to be 45 000, 50 000, and 55 000 cm^{-1} , respectively. The transition dipole moment $\langle s | \hat{\mu}_x | p_x \rangle = \langle s | \hat{\mu}_y | p_y \rangle = \langle s | \hat{\mu}_z | p_z \rangle$ is taken to be 1.0 debye (D) ($= 0.3935$ a.u.). From (3) it follows that the permanent dipole moment has the components $\mu_x = 0.19$ D, $\mu_y = 0.37$ D, and $\mu_z = 0.56$ D. The individual components of the hyperpolarizability tensor and its isotropic part may be computed using Eq. (3) in Eqs. (1) and (2), and are listed in Table 1 together with the results from the CIS calculation. The linewidths have been taken to be 1000 cm^{-1} .

4. Results and discussion

Our theoretical procedure, which truncates the SOS expression, satisfies several symmetry condi-

Table 1

Some components of the sum-frequency hyperpolarizability $\beta_{ijk}(-3\omega; 2\omega, \omega)$ for R-monofluoro-oxirane, R-(+)-propylene oxide (as depicted in Fig. 3) and from a single-centre chiral model^a

	R-monofluoro-oxirane	R-(+)-propylene oxide	Single-centre model
β_{\parallel}	-206.4	-250.7	29.8
β_{xyz}	16.7178	52.4195	1.3801
β_{xzy}	16.1756	55.9906	1.3805
β_{zxy}	16.8776	51.1848	0.7167
β_{yxz}	17.2439	49.9556	0.9033
β_{zyx}	15.0941	57.3314	0.9117
β_{xzx}	15.3653	55.1109	0.6725
β	-0.0159	-0.0202	0.0087

^a The input frequency is $\omega = 2\pi c/(694 \text{ nm}) = 1.786 \text{ eV}$ and $\Gamma = 1000 \text{ cm}^{-1}$. The d.c. hyperpolarizability components for the three systems are $\beta_{\parallel} = -122.5, -126.9, \text{ and } 4.7 \text{ a.u.}$, and $\beta_{xyz} = 8.7747, 18.6390, \text{ and } 0.11 \text{ a.u.}$ respectively.

tions on $\bar{\beta}(-3\omega; 2\omega, \omega)$: (i) $\bar{\beta}(-3\omega; 2\omega, \omega)$ changes sign with the enantiomer so that the macroscopic coherent response vanishes for racemic mixtures; (ii) due to its pseudoscalar nature, $\bar{\beta}(-3\omega; 2\omega, \omega)$ is independent of the molecular orientation in the Cartesian frame; and (iii) $\bar{\beta}(-3\omega; 2\omega, \omega)$ tends towards zero in the static limit, or for degenerate frequencies (second-harmonic generation). Figs. 2 and 4 show that the magnitude of $\bar{\beta}(-3\omega; 2\omega, \omega)$ of both propylene oxide and monofluoro-oxirane is small ($<10^{-3} \text{ a.u.}$) for $\hbar\omega < 0.04 \text{ a.u.}$. Closer to resonance, at $\hbar\omega = 0.07 (0.08) \text{ a.u.}$ for propylene oxide (monofluoro-oxirane), i.e., less than 0.01 a.u. below the first excited state, the magnitude of $\bar{\beta}(-3\omega; 2\omega, \omega)$ is still smaller than 0.3 a.u.. This small $\bar{\beta}(-3\omega; 2\omega, \omega)$ value is in agreement with the absence of a strong SFG signal at 355 nm for arabinose solutions, as recently reported [4]. At this stage, two remarks should be made: (i) *d*- and *l*-arabinose contain three chiral centers, whereas propylene oxide and monofluoro-oxirane have only one so that a better estimate of the arabinose $\bar{\beta}(-3\omega; 2\omega, \omega)$ might be obtained by multiplying the small molecule value by a factor of three; (ii) the nature of the substituents influences the $\bar{\beta}(-3\omega; 2\omega, \omega)$ value as indicated by the difference between the two systems investigated here and additivity of chiral centre $\bar{\beta}(-3\omega; 2\omega, \omega)$ contributions has not been demonstrated. On the other hand, this small $\bar{\beta}(-3\omega; 2\omega, \omega)$ contrasts with the 14 a.u. value obtained by Rentzepis et al. [2,3] from experiment (the SFG intensity is proportional to the square of $\bar{\beta}$).

In summary, by using a CIS/6-311++G** SOS procedure, where the excitation energies were calibrated with respect to experimental data and checked with respect to TDDFT values, we have calculated $\bar{\beta}(-3\omega; 2\omega, \omega)$ for two small chiral molecules and have concluded that the second-order susceptibility in chiral liquids is about two orders of magnitude smaller than that previously reported from experiment [2,3]. However, an improved treatment of electron correlation effects as well as a direct investigation of the chiral sugar molecules would be required to draw definitive conclusions.

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