Nonlinear Optical Properties of Chiral Liquids – Computational Methods and Applications

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In isotropic media, within the electric dipole approximation, three-wave mixing (TWM) in second-order nonlinear optical (NLO) processes is only symmetry-allowed for sum- and difference-frequency generations when the constituents are chiral and present an enantiomeric excess [1]. The TWM in chiral liquids is related to the completely antisymmetric isotropic component of the first hyperpolarizability (β) tensor, the pseudoscalar $\bar{\beta} = \left(\beta_{xyz} - \beta_{xzy} + \beta_{zxy} - \beta_{zyx} + \beta_{yzx} - \beta_{zyx}\right)/6$ quantity. $\bar{\beta}\left(-\omega_\sigma;\omega_1,\omega_2\right)$ with $\omega_\sigma = \omega_1 + \omega_2$ is zero for second harmonic generation ($\omega_1 = \omega_2$), for dc-Pockels effect (ω_1 or $\omega_2 = 0$). Although in off-resonance conditions, the chirality-allowed sum-frequency generation (SFG) phenomenon is generally weak [2], SFG signals were observed in resonance conditions [3].

Although $\bar{\beta}$ changes sign with the handedness, SFG can however not distinguish between enantiomers because the scattering power is proportional to the square of the polarization, and therefore to the square of $\bar{\beta}$. On the other hand, using symmetry arguments, it was demonstrated that the third-order electric field-induced SFG signal, $\gamma\left(-\omega_\sigma;\omega_1,\omega_2,0\right)$, originating from the application of an electrostatic field, E(0), gives rise, in chiral liquids, to an interference term, which is linear in the static electric field as well as in $\bar{\beta}$ [5], $\mathrm{SFG(E)} \propto \mathrm{Re}\left\lfloor \beta(\bar{\gamma}_i) \right\rfloor E(0) I(\omega_1) I(\omega_2)$, where I are the respective incident intensities, Re stands for the real part, and the star indicates a complex conjugate. The $\bar{\gamma}_i$ (i = 1 - 3) quantities are scalar combinations of second hyperpolarizability tensor components, which depend on the light polarizations. Since the $\bar{\gamma}$ quantities are achiral, the contribution to the intensity that is linear in E may therefore reveal the sign of $\bar{\beta}$ and furthermore, be used to determine the absolute configuration of the chiral molecules.

This contribution will describe computational schemes to evaluate electric dipole-based NLO properties of chiral molecules in isotropic media ($\bar{\beta}$ and $\bar{\gamma}_i$). Then, it will discuss applications towards the design of compounds presenting large and specific chirality-based NLO responses [5].

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