Coherent Infrared Pulse Sequences for Probing Molecular Chirality

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Abstract. Novel Polarization configurations in infrared four wave mixing are proposed and simulated using the nonlinear exciton equations (NEE). Application to helical peptides demonstrates higher sensitivity than CD to molecular chirality.

1. Introduction

In third order optical techniques, three laser pulses interact with the system to generate the fourth signal pulse, The wavevector k_j and polarization ν_j configuration of all four pulses can be varied to obtain different signals (Fig 1). We demonstrate that chirality-specific polarization configurations of the field can enhance the sensitivity of the signals to peptide structure .

Time-domain optical response of molecules

The coherent optical response of molecules is determined by the induced polarization P, which serves as the source in the Maxwell equations for the generated signal field. The third-order polarization which describes four-wave mixing signals is given by[3]:

$$P^{(3)}_{\nu_4}(x_4) = \sum_{\nu_3\nu_2\nu_1} \int dx_3 \int dx_2 \int dx_1 S^{(3)}_{\nu_4\nu_3\nu_2\nu_1}(x_4,x_3,x_2,x_1) E_{\nu_3}(x_3) E_{\nu_2}(x_2) E_{\nu_1}(x_1) \qquad (1)$$

x,y,z denote the Cartesian polarization components in the lab frame; x=(r,t) is the space-time vector representing the times and coordinates of the interactions with the optical pulses. E is the optical electric field vectors. The third-order response function is a system property-tensor, which allows to calculate the induced polarization for an arbitrary incomng pulse configuration.

Within the impulsive limit, the Polarization is proportional to the response function, which can be calculated using the Nonlinear Exciton Equations (NEE) formalism[1]:

$$\begin{aligned} S^{k_l}_{\nu_4\nu_3\nu_2\nu_1}(\Omega_3,T_2,\Omega_1) = 2i \sum_{\xi_4\xi_3\xi_2\xi_1} & \left\langle d^{\nu_4}_{\xi_4}(k_1-k_2-k_3) d^{\nu_3 *}_{\xi_3}(-k_3) d^{\nu_2 *}_{\xi_2}(-k_2) d^{\nu_1}_{\xi_1}(-k_1) \right\rangle \\ & \times I^*_{\xi_1}(T_2) I_{\xi_2}(T_2) I^*_{\xi_1}(-\Omega_1) I^*_{\xi_4}(\Omega_3) \\ & \times \Gamma_{\xi_4\xi_1,\xi_3\xi_2}(\Omega_3 + E_{\xi_1} + i\gamma_{\xi_1}) \vartheta_{\xi_3\xi_2}(\Omega_3 + E_{\xi_1} + i\gamma_{\xi_1}) \end{aligned} \qquad 2)$$

l_i is single exciton states, $\langle \cdots \rangle$ represents the rotational averaging of the product of momentum space transition dipoles. . $I^*_{\xi_{l1}}(T)$ and $I^*_{\xi_{l1}}(-\Omega_j)$ are the single exciton Green's functions which describe the free propagation of excitons. $\Gamma_{\xi_1\xi_2\xi_3\xi_4}(\Omega_3 + E_{\xi_1} + i\gamma_{\xi_1})\vartheta_{\xi_3\xi_4}(\Omega_3 + E_{\xi_3} + i\gamma_{\xi_3})$ is the two exciton green function which describe the scattering of the excitons during the interaction with the field. d^{ν}_{ξ} is the exciton transition dipole.

3. Chirality-induced two dimensional signals:

Molecular chirality originates from the three dimensional distribution of local transitions in real space, signals sensitive to chirality include explicitly the real space coordinates of the local transition. We expand the rotational averages in Eq(3) to first order in wavevectors [1]:

$$\begin{aligned}\left\langle d^{\nu_1}_{\xi_1}(k_4)d^{\nu_3}_{\xi_3}(k_3)d^{\nu_1*}_{\xi_2}(-k_2)d^{\nu_1*}_{\xi_1}(-k_1)\right\rangle = &\left\langle d^{\nu_4}_{\xi_4}d^{\nu_3}_{\xi_3}d^{\nu_2}_{\xi_2}d^{\nu_1}_{\xi_1}\right\rangle + i\sum_{\kappa}k^{\kappa}_4\left\langle \bar{d}^{\kappa,\nu_4}_{\xi_4}d^{\nu_3}_{\xi_3}d^{\nu_2}_{\xi_2}d^{\nu_1}_{\xi_1}\right\rangle \\ &+ i\sum_{\kappa}k^{\kappa}_3\left\langle \bar{d}^{\kappa,\nu_3}_{\xi_3}d^{\nu_4}_{\xi_4}d^{\nu_2}_{\xi_2}d^{\nu_1}_{\xi_1}\right\rangle + i\sum_{\kappa}k^{\kappa}_2\left\langle \bar{d}^{\kappa,\nu_2}_{\xi_2}d^{\nu_4}_{\xi_4}d^{\nu_3}_{\xi_3}d^{\nu}_{\xi_1}\right\rangle \\ &+ i\sum_{\kappa}k^{\kappa}_1\left\langle \bar{d}^{\kappa,\nu_1}_{\xi_1}d^{\nu_4}_{\xi_4}d^{\nu_3}_{\xi_3}d^{\nu_2}_{\xi_2}\right\rangle\end{aligned} \tag{3}$$

where

$$d^{\nu}_{\xi} \equiv d^{\nu}_{\xi}\ (k=0) = \sum_{m}\mu^{\nu}_{m}\psi_{\xi,m} \tag{4}$$

and the tensor:

$$\bar{d}^{\kappa,\nu}_{\xi} = \sum_{m} r^{\kappa}_{m}\mu^{\nu}_{m}\psi_{\xi,m} \tag{5}$$

r_m is the coordinate for the mth transition, μ_m is the transition dipole and ψ_m is the eigenvector. The first (dipole approximation) term in Eq(3) is independent on r_m and is insensitive to chrality, the other terms go beyond the dipole approximation. For tensor components with even number of repeating indices such as xxxx, the first term is finite and dominant in the signal, thus the signal is insensitive to chirality. For tensor component such as xxxy, with odd number of repeating indices, the first term vanished and the other chiral-sensitive terms dominate.

We have simulated the electronic CD of amide band, the vibrational CD and photon echo signal with xxxy tensor component of amide I band for two structure ensembles of a 25 residue helical peptide in water. The CHARMM package[2] was used for the MD simulation. After a 10 ns equilibration, a 25 ns dynamic run was carried out and 22000 snapshots were generated for the analysis. We chose the 11000th snapshot as the reference structure and calculate the RMSD of central 20 pairs of the ramanchandran angles for each snapshot. We then selected the 1000 snapshots at each of the two wings of this distribution, denoted as group I (high RMSD) and group II (low RMSD) and calculated the spectra using *SPECTRON* package[4]. A is the vibrational CD (identical) for group I (II). B (C) are sections of the 2D XXXY photon echo signals cut along 1620 (1603) cm-1,

the red (black) line in B and C is for group I (II). CD of these two groups are identical while the third order signals are very different. In D the signal for group II is much stronger within the [-1590,-1640] region, which allows to investigate one species independently with the presence of the other.. This shows a higher sensitivity of the two dimensional signal compared to CD.

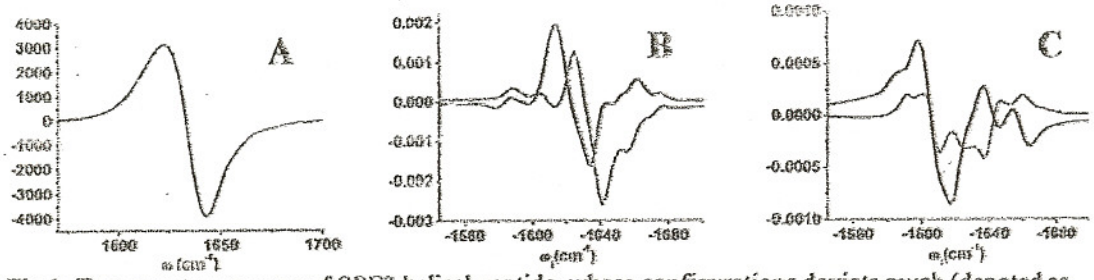

Fig 1: Two structure groups of SPE3 helical peptide, whose configurations deviate much (denoted as group I) and little (denoted as group II) from a reference helical structure, are chosen from the MD simulation trajectory and used for the spectrum calculation. A gives the virturely identical vibrational CD for group I and II. B (C) is the XXXY photon echo signals with ν_1 = 1620 (1603) cm-1, the red (black) line in B and C is for group I (II). CD of these two groups are identical while the two dimensional signals are very different. In C the signal for group II is much stronger within the [-1590,-1640] region, which allows to investigate one species independently in the presence of the other.

4. Acknowledgement:

This work was supported by the National Institutes of Health Grant 2RO1-GM59230-05 and the National Science Foundation Grant CHE-0446555.

5. References

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