Chirally-sensitive nolinear optical probes of vibrational excitons in proteins

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Introduction:

The nonlocal second and third order susceptibilities of an isotropic ensemble of aggregates are calculated by solving the Nonlinear Exciton Equations which map the exciton system into coupled anharmonic oscillators. The nonlinearities reflect the interplay of two mechanisms: scattering of excitons by anharmonicities and the quadratic dependence of the dipole on coordinates. The optical responses are calculated to first order in optical wavevector. Chirally sensitive signals are obtained in linear, second order and third order techniques.

Definitions:

Chiral molecules – the molecules which cannot be superimposed on their mirror images.
Enantiomer – a chiral molecule with a specified sense of chirality.
Racemate – the equal mixture of opposite enantiomers.
Chirally-sensitive signal – the signal which has the opposite sign for two enantiomers with opposite chirality

Known chirally-sensitive signals: Circular Dichrism (CD), Raman Optical Activity (ROA), Sum Frequency Generation (SFG) in dipole approximation.

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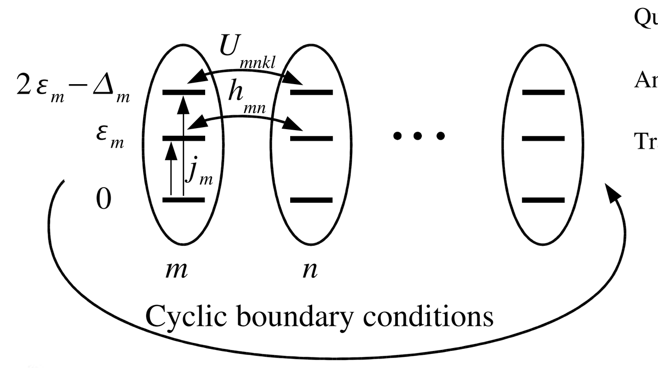
The exciton model:

Fundamental excitation energy ε_m
Quadratic couplings h_{mn}
Quartic couplings U_{mnkl}
Anharmonicity $\Delta_m = U_{mmmm}$
Transition current
$j_m = -i\omega\mu_m + i\boldsymbol{k}\times\boldsymbol{m}_m$
Electric transition contribution; Magnetic contribution



$\hat{B}^\dagger_m$ Exciton creation operator
$\hat{B}_m$ Exciton annihilation operator

System Hamiltonian

$$\hat{H} = \sum_m \varepsilon_m \hat{B}^\dagger_m \hat{B}_m + \sum_{mn}^{m\neq n} h_{m,n}\hat{B}^\dagger_m \hat{B}_n + \sum_{mn,m'n'} U_{mn,m'n'}\hat{B}^\dagger_m \hat{B}^\dagger_n \hat{B}_{m'}\hat{B}_{n'}$$

System-Field interaction

$$\hat{H}_{SF}(t) = -\frac{1}{c}\int d\mathbf{r}[\hat{\mathbb{J}}(\mathbf{r})\cdot\mathbb{A}(\mathbf{r},t)+\hat{Q}(\mathbf{r})\mathbb{A}^2(\mathbf{r},t)]$$

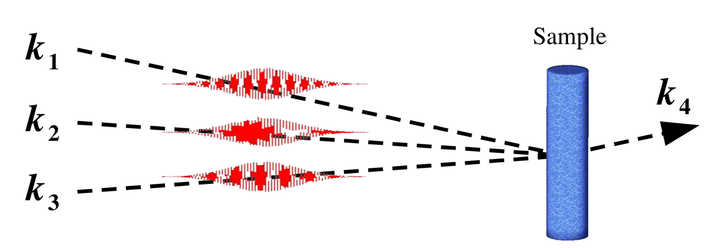
Current operator

$$\hat{\mathbb{J}}(\mathbf{r}) = \sum_m \delta(\mathbf{r}-\mathbf{r}_m)\Big\{\boldsymbol{j}_m(\hat{B}^\dagger_m+\hat{B}_m)+\boldsymbol{f}_m\hat{B}^\dagger_m\hat{B}_m + \boldsymbol{g}_m(\hat{B}^{\dagger 2}_m+\hat{B}^2_m)\Big\},$$

Charge denisty

$$\hat{Q}(\mathbf{r}) = \sum_m \delta(\mathbf{r}-\mathbf{r}_m)\Big\{j'_m(\hat{B}^\dagger_m+\hat{B}_m)+f'_m\hat{B}^\dagger_m\hat{B}_m + g'_m(\hat{B}^{\dagger 2}_m+\hat{B}^2_m)\Big\},$$

Nonlinear optical signals:



Molecular current is the source of electromagnetic radiation

$$\nabla\times\nabla\times\mathbb{E}+\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbb{E} = -\frac{4\pi}{c^2}\frac{\partial\mathbb{J}}{\partial t}$$

Molecular current in time domain

$$\mathbb{J}^{(n)}_{\nu_S}(\mathbf{r}_S\tau_S) = \sum_{\nu_n\ldots\nu_1}\int d\mathbf{r}_n\ldots\int d\mathbf{r}_1\int d\tau_n\ldots\int d\tau_1 \, R^{(n)}_{\nu_S,\nu_n\ldots\nu_1}(\mathbf{r}_S\tau_S,\mathbf{r}_n\tau_n,\ldots,\mathbf{r}_1,\tau_1)\mathbb{A}_{\nu_n}(\mathbf{r}_n,\tau_n)\ldots\mathbb{A}_{\nu_1}(\mathbf{r}_1,\tau_1)$$

Molecular current in frequency domain

$$\mathbb{J}^{(n)}_{\nu_S}(\mathbf{k}_S\omega_S) = \frac{1}{(2\pi)^{4n}}\sum_{\nu_n\ldots\nu_1}\int d\mathbf{k}_n\ldots\int d\mathbf{k}_1\int d\omega_n\ldots\int d\omega_1 \, X^{(n)}_{\nu_S\nu_n\ldots\nu_1}(-\mathbf{k}_S-\omega_S,\mathbf{k}_n\omega_n,\ldots,\mathbf{k}_1\omega_1)\mathbb{A}_{\nu_n}(\mathbf{k}_n,\omega_n)\ldots\mathbb{A}_{\nu_1}(\mathbf{k}_1,\omega_1).$$

These equations define the response function and the susceptibility

The response function will be calculated using the Nonlinear Exciton Equations (NEE) and expanded to first order in wavevector. This allows calculate nonlinear optical responses without calculating two-exciton resonances in terms of one-exciton Green's functions and exciton scattering matrix.

Expansion of the current in wavevector and orientational averagings of polarizabilities:

First order microscopic susceptibility $\quad \alpha \propto \langle\mathbb{J}(\tau)\mathbb{J}(0)\rangle_T$

Second order $\quad \beta \propto \langle\mathbb{J}(\tau_3)\mathbb{J}(\tau_2)\mathbb{J}(\tau_1)\rangle_T$

Third order $\quad \gamma \propto \langle\mathbb{J}(\tau_4)\mathbb{J}(\tau_3)\mathbb{J}(\tau_2)\mathbb{J}(\tau_1)\rangle$

Transition current relation with polarization and magnetization

$$\hat{\mathbb{J}}(\mathbf{r},t) = \frac{\partial}{\partial t}\hat{\mathrm{P}}(\mathbf{r},t)+\nabla\times\hat{\mathrm{M}}(\mathbf{r},t)$$

$$\boldsymbol{j}_l(\mathbf{k}) = -i\omega\boldsymbol{\mu}_l(\mathbf{k})+i\mathbf{k}\times\boldsymbol{m}_l(\mathbf{k})$$

$$\boldsymbol{j}_l(\mathbf{k}) \approx -i\omega\boldsymbol{\mu}_l+\omega(\mathbf{k}\cdot\mathbf{r}_l)\boldsymbol{\mu}_l+i\mathbf{k}\times\boldsymbol{m}_l$$

Parity (space inversion) transformation:

Electric dipole: $P\mu=-\mu$ Magnetic dipole: $P\boldsymbol{m}=\boldsymbol{m}$

System coordinate: $P\boldsymbol{r}=-\boldsymbol{r}$

polarizability	Contribution in the dipole approximation	parity	Contribution to first order in wavevector	parity
α	$\mu_2^{\nu_2}\mu_1^{\nu_1}$	+	$(\boldsymbol{k}^{\nu_2+2})\boldsymbol{m}_2^{\nu_2+1}\mu_1^{\nu_1}$, $(\boldsymbol{k}^{\nu_3})\boldsymbol{r}_2^{\nu_3}\mu_2^{\nu_2}\mu_1^{\nu_1}$	-
β	$\mu_3^{\nu_3}\mu_2^{\nu_2}\mu_1^{\nu_1}$	-	$(\boldsymbol{k}^{\nu_3+2})\boldsymbol{m}_3^{\nu_3+1}\mu_2^{\nu_2}\mu_1^{\nu_1}$, $(\boldsymbol{k}^{\nu_4})\boldsymbol{r}_3^{\nu_4}\mu_3^{\nu_3}\mu_2^{\nu_2}\mu_1^{\nu_1}$	+
γ	$\mu_4^{\nu_4}\mu_3^{\nu_3}\mu_2^{\nu_2}\mu_1^{\nu_1}$	+	$(\boldsymbol{k}^{\nu_4+2})\boldsymbol{m}_4^{\nu_4+1}\mu_3^{\nu_3}\mu_2^{\nu_2}\mu_1^{\nu_1}$, $(\boldsymbol{k}^{\nu_5})\boldsymbol{r}_4^{\nu_5}\mu_4^{\nu_4}\mu_3^{\nu_3}\mu_2^{\nu_2}\mu_1^{\nu_1}$	-
susceptibility	Tensor in the dipole approximation	parity	Tensor to first order in wavevector	parity
$\chi^{(1)}_{\nu_2\nu_1}$	xx	+	$(z)xy$	-
$\chi^{(2)}_{\nu_3\nu_2\nu_1}$	xyz	-	$(x)xyy$, $(x)yyx$, $(x)yxy$	+
$\chi^{(3)}_{\nu_4\nu_3\nu_2\nu_1}$	$xxyy$, $xyyx$, $xyxy$	+	$(z)xxxy$, $(z)xxyx$, $(z)xyxx$, $(z)zxyz$, $(z)zxzy$, $(z)zzxy$	-

+ parity even: not sensitive to chirality
- parity odd: chirallity-sensitive (yellow in the table) !!!

Simulations:

Calculations were performed using SPECTRON (see poster hosted by Wei Zhuang)