Dual frequency comb spectroscopy for optical activity measurement

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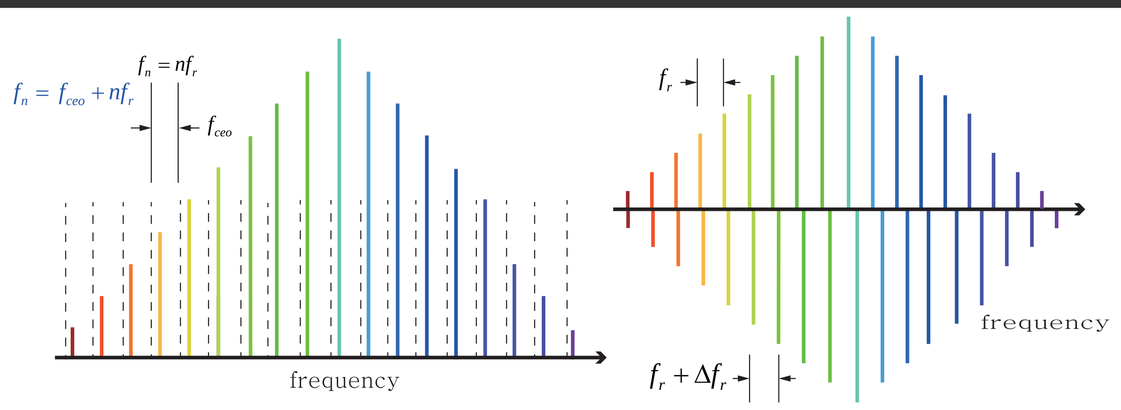
Abstract

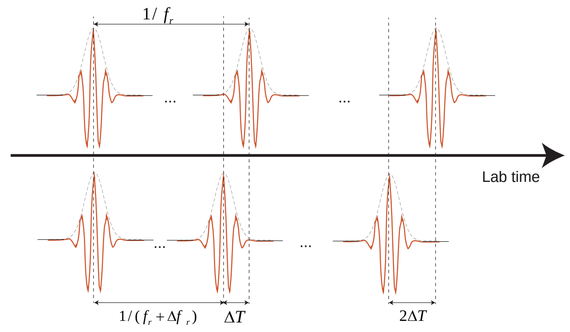
We present dual-frequency comb optical activity spectroscopy(DFC-OAS) of chiral molecules in condensed phase. By measuring two interferograms corresponding to the horizontally- and vertically-polarized transmitted electric fields, the difference of the complex susceptibility spectra between left and right-circularly polarized field can be obtained. The DFC interference signals in each polarization components will be transformed into the frequency domain by a FFT method to get the imaginary and real parts of the susceptibility spectra for the circular dichroism (CD) and circular rotatory dispersion (ORD) measurements. In this study, we consider the optical activity measurement of a metal complex of Ni-(±)-(tartrate)$_2$ by using identical broad-band OFCs from Ti:Sapphire mode-locked laser around 800 nm with 80 MHz repetition rate and 7.5 fs pulse-width. First, we calculated DFC-OAS interferograms for two-level model system to estimate the dispersion of interferograms measured by photodiode. We anticipate that the CD/ORD spectroscopy with dual frequency comb proposed in this study can be extended to time-resolved CD/ORD spectroscopy of extremely weak CD values, which has been experimental challenges for long time.

Dual frequency comb



Asynchronous optical sampling(ASOPS)

automatic time-delay generation



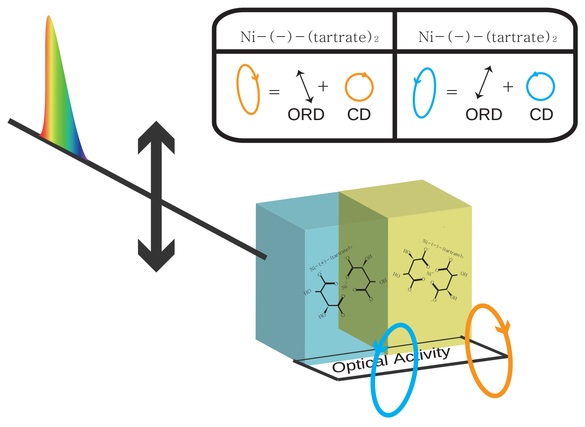
A time delay increment(ΔT) generated by two OFCs whose repetition rates are slightly different is,

$$\Delta T = \frac{1}{f_r} - \frac{1}{f_r + \Delta f_r} \cong \frac{\Delta f_r}{f_r^{\,2}}$$

Then, the time delay(T) is down-converted to laboratory time(t) by following relation,

$$T = t\frac{\Delta f_r}{f_r}$$

The cross polarization detection



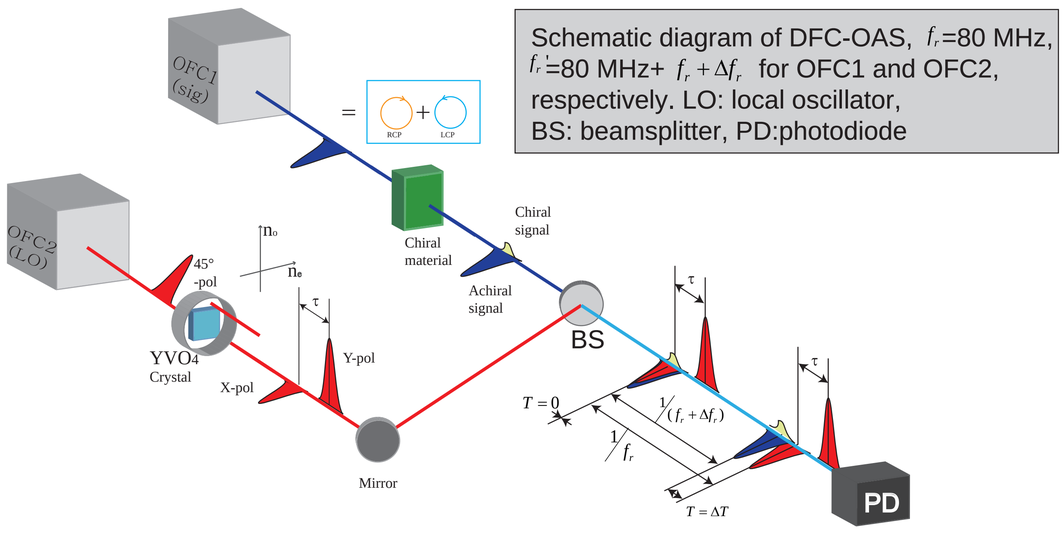
$$\Delta\chi(\omega) \cong \frac{cn(\omega)}{\pi\omega L}\frac{\tilde{E}_y^{(1)}(\omega)}{\tilde{E}_x^{(1)}(\omega)}$$

$$\Delta A(\omega) = \frac{\Delta\kappa_a(\omega)L}{2.303} = \frac{4\pi\omega L}{2.303n(\omega)c}\mathrm{Im}\left[\Delta\chi(\omega)\right]$$

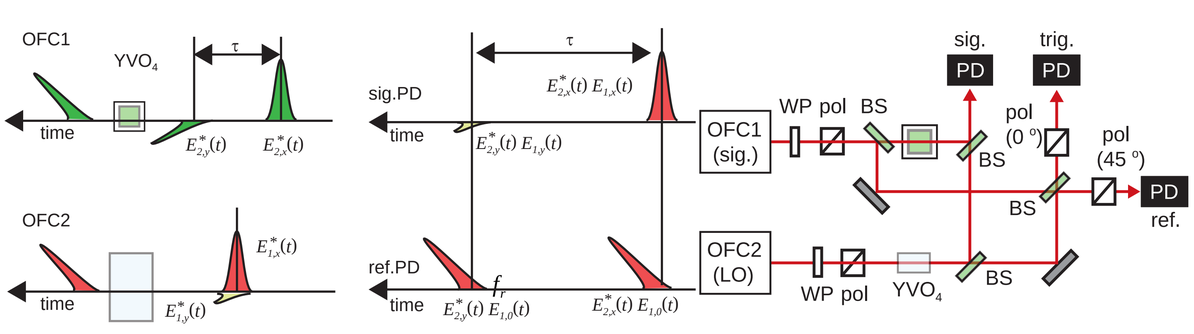
$$\Delta\varphi(\omega) = \frac{\Delta n(\omega)\omega L}{2c} = \frac{\pi\omega L}{n(\omega)c}\mathrm{Re}\left[\Delta\chi(\omega)\right]$$

Linearly polarized light ⟶ CD(ΔA(ω), ORD($\Delta\varphi(\omega)$))

Experimental setup



Schematic diagram of DFC-OAS, f_r=80 MHz, f_r'=80 MHz+ $f_r + \Delta f_r$ for OFC1 and OFC2, respectively. LO: local oscillator, BS: beamsplitter, PD:photodiode



Chiral: $\frac{\tilde{I}_{sig,x}(\omega)}{\tilde{I}_{ref,x}(\omega)} = \frac{\tilde{E}_{1,0}(\omega)+\tilde{E}_{1,L}(\omega)}{\tilde{E}_{1,0}(\omega)} = 1+\tilde{S}_L(\omega)$ **Achiral:** $\frac{\tilde{I}_{sig,y}(\omega)}{\tilde{I}_{ref,y}(\omega)} = \frac{\tilde{E}_{1,R}(\omega)}{\tilde{E}_{1,0}(\omega)} = \tilde{S}_R(\omega)$

Theoretical description

OFC field: $E_k(\mathbf{r},t) = e^{i\left[\mathbf{k}(\omega_{c,k})\cdot\mathbf{r}-\omega_{c,k}t\right]}\sum_{n=-\infty}^{\infty}A_{k,n}e^{-in\omega_{r,k}t}$

Carrier frequency: $\omega_c \equiv \omega_{c,1} = \omega_{c,2} - \Delta\omega_c$

repetition rate: $\omega_r \equiv \omega_{r,1} = \omega_{r,2} - \Delta\omega_r$

Linear polarization vector induced by chiral material is given by

$$\boldsymbol{P}^{(1)}(\mathbf{r},t) = \int_0^\infty dt_1\,\hat{\boldsymbol{S}}^{(1)}(t_1)\boldsymbol{E}_1(\mathbf{r},t-t_1)$$

$$= \int_0^\infty dt_1 \begin{pmatrix} S_L^{(1)}(t_1) & -iS_R^{(1)}(t_1) \\ iS_R^{(1)}(t_1) & S_L^{(1)}(t_1) \end{pmatrix}\begin{pmatrix} E_{1,x}(\mathbf{r},t-t_1) \\ E_{1,y}(\mathbf{r},t-t_1) \end{pmatrix}$$

If neglect $E_{1,y}(\mathbf{r},t-t_1)$ for simplicity,

$$\begin{pmatrix} P_x^{(1)}(\mathbf{r},t) \\ P_y^{(1)}(\mathbf{r},t) \end{pmatrix} = \int_0^\infty dt_1 \begin{pmatrix} S_L^{(1)}(t_1) \\ iS_R^{(1)}(t_1) \end{pmatrix} E_1(\mathbf{r},t-t_1)$$

Inserting the OFC field into $\boldsymbol{P}^{(1)}(\mathbf{r},t)$

$$\boldsymbol{P}^{(1)}(\mathbf{r},t) = \begin{pmatrix} P_x^{(1)}(\mathbf{r},t) \\ P_y^{(1)}(\mathbf{r},t) \end{pmatrix}$$

$$= \begin{pmatrix} \tilde{S}_L^{(1)}(-\omega_{c,1}-n\omega_{r,1}) \\ i\tilde{S}_R^{(1)}(-\omega_{c,1}-n\omega_{r,1}) \end{pmatrix} e^{i\left[\mathrm{k}(\omega_{c,1})\cdot\mathrm{r}-\omega_{c,1}t\right]}\sum_{n=-\infty}^{\infty}A_{1,n}e^{-in\omega_{r,1}t}$$

Since the electric field induced by the sample is approximately proportional to the linear polarization shown as

$$E^{(1)}(\mathbf{r},t) \propto iP^{(1)}(\mathbf{r},t)$$

Then the oscillating part of the intensity measured by PD is given by

$$\begin{pmatrix} I_x(t) \\ I_y(t) \end{pmatrix} \propto \mathrm{Im}\left[\sum_{n=-\infty}^{\infty}A_{2,n}^*A_{1,n}e^{i\left((\omega_c+n\omega_r)f_D+\Delta\omega_{ceo}\right)t}\begin{pmatrix} \tilde{S}_L^{(1)}(\omega_c+n\omega_r) \\ i\tilde{S}_R^{(1)}(\omega_c+n\omega_r) \end{pmatrix}\right]$$

Conversion factor: $f_D \equiv \Delta f_r / f_r$

If simplyfing the intensity as continuous function, the fourier transform can be written by,

$$\begin{pmatrix} \tilde{I}_x(\omega) \\ \tilde{I}_y(\omega) \end{pmatrix} = |A(\omega)|^2 \begin{pmatrix} i\tilde{S}_L^{(1)}\left(\frac{\omega+\omega_c f_D+\Delta\omega_{ceo}}{f_D\omega_r}\right) \\ -\tilde{S}_R^{(1)}\left(\frac{\omega+\omega_c f_D+\Delta\omega_{ceo}}{f_D\omega_r}\right) \end{pmatrix}$$

The optical activity of chiral material can be revealed from measured intensity

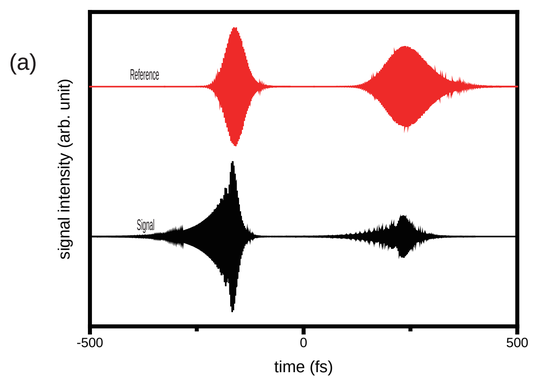
$$\Delta A(\omega) = \frac{\Delta\kappa_a(\omega)L}{2.303} = \frac{4\pi\omega L}{2.303n(\omega)c}\mathrm{Im}\left[\Delta\chi(\omega)\right]$$

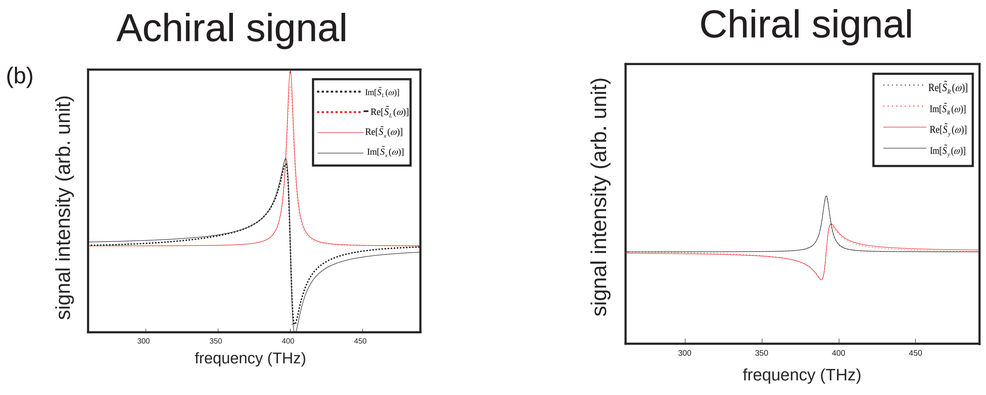
$$= \frac{4}{2.303}\mathrm{Im}\left[\frac{\tilde{I}_y(\omega)}{\tilde{I}_x(\omega)}\right] \text{ :CD}$$

$$\Delta\varphi(\omega) = \frac{\Delta n(\omega)\omega L}{2c} = \frac{\pi\omega L}{n(\omega)c}\mathrm{Re}\left[\Delta\chi(\omega)\right]$$

$$= \frac{\sqrt{2}}{2}\mathrm{Re}\left[\frac{\tilde{I}_y(\omega)}{\tilde{I}_x(\omega)}\right] \text{ :ORD}$$

Simulation for two-level model system





(a) The simulated signal (black) and reference (red) interferograms. (b) The comparison between the simulated DFC-OAS data and model response functions. Left is achiral spetrum and rightis chiral spectrum

The interferogram shows that a time delay between each interferogram is long enough that we can assume that two interferograms are independent. As you see on figure (b), the model linear susceptibility and spectrum extracted by dividing signal spectrum into reference are similar.

Acknowledgements

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