Dual frequency comb vibrational optical activity spectroscopy

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Abstract

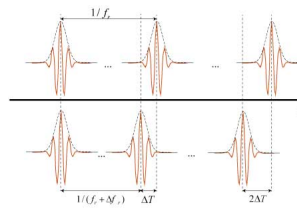We present dual-frequency comb optical activity spectroscopy(DFC-OAS) of chiral molecules in condensed phase. By measuring two interferograms corresponding to the horizontally- and vertically-polarized transmitted electric fields, the difference of the complex susceptibility spectra between left and 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 (R)-(+)-limonene and (S)-(-)-limonene by using two Mid IR OFCs generated by difference frequency generation around 3.3 μm with 240MHz repetition rate and 200 fs pulse width. First, We measured auto--correlation signal of each comb by Mach-zehnder interferometer and cross-correlation signal of dual frequency comb. 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

$$f_n = f_{ceo} + nf_r$$
$$f_n = nf_r$$

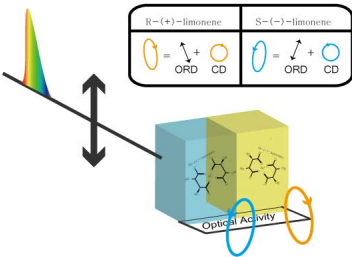Asynchronous optical sampling(ASOPS) : automatic time-delay generation

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

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

$$\Delta A(\omega) = \frac{\Delta\kappa_g(\omega)L}{2.303} = \frac{4\pi\omega L}{2.303n(\omega)c}\text{Im}[\Delta\chi(\omega)]$$

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

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

Linear polarization vector induced by chiral material is given by

$$P^{(1)}(r,t) = \int_0^\infty dt_1 \hat{S}^{(1)}(t_1) E_1(r, t-t_1)$$

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

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

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

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

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

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

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

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

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

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

If simplifying 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
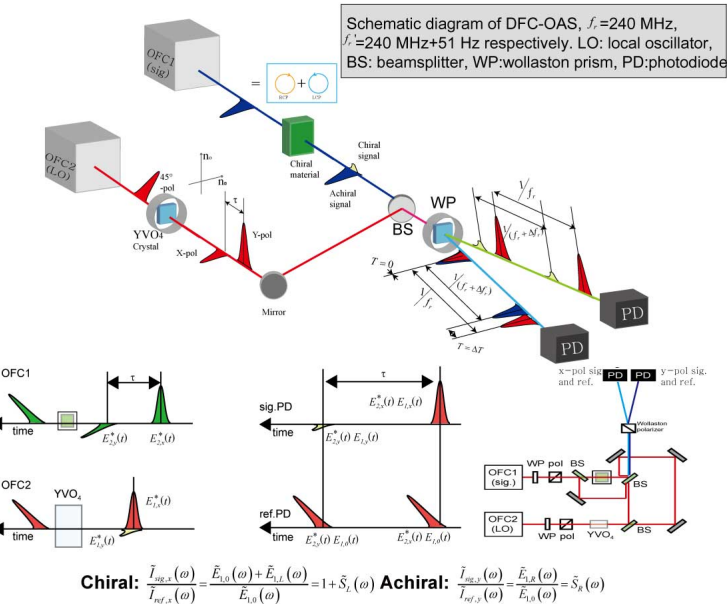
$$\Delta A(\omega) = \frac{\Delta\kappa_a(\omega)L}{2.303} = \frac{4\pi\omega L}{2.303n(\omega)c}\text{Im}[\Delta\chi(\omega)]$$
$$= \frac{4}{2.303}\text{Im}\left[\frac{\tilde{I}_y(\omega)}{\tilde{I}_x(\omega)}\right] \text{ :CD}$$

$$\Delta\varphi(\omega) = \frac{\Delta n(\omega)\omega L}{2c} = \frac{\pi\omega L}{n(\omega)c}\text{Re}[\Delta\chi(\omega)]$$
$$= \frac{\sqrt{2}}{2}\text{Re}\left[\frac{\tilde{I}_y(\omega)}{\tilde{I}_x(\omega)}\right] \text{ :ORD}$$
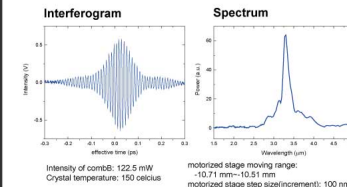
Experimental setup

Schematic diagram of DFC-OAS, f_r=240 MHz, f_r'=240 MHz+51 Hz respectively. LO: local oscillator, BS: beamsplitter, WP:wollaston prism, PD:photodiode
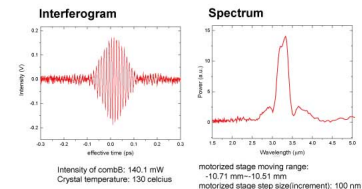
Chiral: $\frac{\tilde{I}_{sig,x}(\omega)}{\tilde{I}_{ref,x}(\omega)} = \frac{\tilde{E}_{L,0}(\omega)+\tilde{E}_{L,L}(\omega)}{\tilde{E}_{L,0}(\omega)} = 1+\tilde{S}_L(\omega)$ Achiral: $\frac{\tilde{I}_{sig,y}(\omega)}{\tilde{I}_{ref,y}(\omega)} = \frac{\tilde{E}_{L,R}(\omega)}{\tilde{E}_{L,0}(\omega)} = \tilde{S}_R(\omega)$

The Spectrum of Optical frequency comb
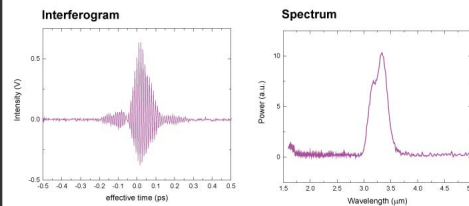
Comb A

Interferogram   Spectrum

Intensity of comb: 122.5 mW
Crystal temperature: 150 celcius

motorized stage moving range: -10.71 mm~-10.51 mm
motorized stage step size(increment): 100 nm

Comb B

Interferogram   Spectrum

Intensity of comb: 140.1 mW
Crystal temperature: 130 celcius

motorized stage moving range: -10.71 mm~-10.51 mm
motorized stage step size(increment): 100 nm

Dual frequency comb

Interferogram   Spectrum

-Repetition rate
Comb A: 240 MHz
Comb B: 240.000051 MHz
-Number of data: 1144 S
-External reference: 10 MHz
-Sampling rate: 80 MHz

The spectrum of each comb and dual frequency comb shows that spectral bandwidth of comb is about 3.1~3.5 μm and this optical frequecy comb laser is appropriate to investigate optical activity of limonene molecules of which CH stretching mode is shown around 3.3 μm ~ 3.5 μm.

Theoretical description

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

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

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

Acknowledgements