

# Artifact-free balanced detection for the measurement of circular dichroism with a sub-picosecond time resolution

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## Supplementary information

We provide here the details on our Jones calculations for the balanced detection of static circular dichroism (CD) and time-resolved CD (TRCD) signals. The effect of the different optical components on the incident probe fully polarized laser electric field can be described by the Jones formalism. The Jones vector for the horizontally polarized incoming probe light along the (Ox) axis is given by:

$$E^{\text{in}} = E_0 \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad (\text{S1})$$

The Jones matrix associated to the QWP oriented at  $\pm 45^\circ$  with respect to its fast axis (Ox) corresponds to:

$$M_{\text{QWP}}^{\pm 45^\circ} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & \pm i \\ \pm i & 1 \end{bmatrix} \quad (\text{S2})$$

The outgoing probe laser field after the Wollaston prism (Fig. 1) reads as:

$$E^{\text{out}} = M_{\text{QWP}} \cdot M_{\text{sample}} \cdot E^{\text{in}} \quad (\text{S3})$$

### 1- Pump-induced polarization artefacts

Taking into account that the Jones matrices for the sample LB and CD do not commute, we consider the total sample matrix that contains the sample CD, CB, LB and LD, previously defined by Xie et al. [1]:

$$M_{\text{sample}}^{\text{CD,CB,LB,LD}} = e^{i \frac{2\pi}{\lambda} (n + \Delta n) \cdot L - \frac{(\alpha + \Delta \alpha) L}{2}} \times \begin{bmatrix} 1 - (ig + \beta) \cos(2\phi) & i(\gamma + \Delta\gamma) - (\theta + \Delta\theta) - (ig + \beta) \sin(2\phi) \\ -i(\gamma + \Delta\gamma) + (\theta + \Delta\theta) - (ig + \beta) \sin(2\phi) & 1 + (ig + \beta) \cos(2\phi) \end{bmatrix} \quad (\text{S4})$$

where  $L$  is the sample thickness,  $n$ , the refractive index and  $\alpha$ , the sample absorption coefficient.  $4\gamma$  and  $\theta$  corresponds to the sample CD and CB, respectively.  $\phi$  is the angle between the pump and probe linear polarizations.  $4\beta$  and  $g$  are the sample LD and LB, respectively.

Under these conditions, the output laser probe field with the pump, for the QWP orientations at  $\pm 45^\circ$ , reads as:

$$\begin{aligned} E_{\pm 45^\circ}^{\text{out pump}} &= M_{\text{QWP}}^{\pm 45^\circ} \cdot M_{\text{sample}}^{\text{CD,CB,LB,LD}} \cdot E^{\text{in}} \\ E_{\pm 45^\circ}^{\text{out pump}} &= \frac{1}{\sqrt{2}} \cdot e^{i \frac{2\pi}{\lambda} (n+\Delta n)L - \frac{(\alpha+\Delta\alpha)L}{2}} \times \end{aligned} \quad (\text{S5})$$

$$\left[ \begin{array}{l} 1 \pm (\gamma + \Delta\gamma) \pm i(\theta + \Delta\theta) - \beta \cdot \cos(2\phi) - ig \cdot \cos(2\phi) \mp i\beta \cdot \sin(2\phi) \pm g \cdot \sin(2\phi) \\ \pm i - i(\gamma + \Delta\gamma) \pm (\theta + \Delta\theta) \mp i\beta \cdot \cos(2\phi) \pm g \cdot \cos(2\phi) - \beta \cdot \sin(2\phi) - ig \cdot \sin(2\phi) \end{array} \right]$$

At first order, the intensities measured on the two detectors are:

$$I_{\pm 45^\circ \text{ Det1}}^{\text{out pump}} = \frac{1}{2} E_0^2 e^{-(\alpha+\Delta\alpha)L} \cdot [1 \pm 2(\gamma + \Delta\gamma) - 2\beta \cdot \cos(2\phi) \pm 2g \cdot \sin(2\phi)] \quad (\text{S6})$$

$$I_{\pm 45^\circ \text{ Det2}}^{\text{out pump}} = \frac{1}{2} E_0^2 e^{-(\alpha+\Delta\alpha)L} \cdot [1 \mp 2(\gamma - \Delta\gamma) - 2\beta \cdot \cos(2\phi) \mp 2g \cdot \sin(2\phi)]$$

Neglecting the contribution of the pump-induced LD ( $2\beta \cdot \cos(2\phi) \ll 1$ ), the measured CD signals with the pump read as:

$$\begin{aligned} S_{\pm 45^\circ}^{\text{pump}} &= 2 \cdot \frac{I_{\pm 45^\circ \text{ Det1}}^{\text{out pump}} - I_{\pm 45^\circ \text{ Det2}}^{\text{out pump}}}{I_{\pm 45^\circ \text{ Det1}}^{\text{out pump}} + I_{\pm 45^\circ \text{ Det2}}^{\text{out pump}}} = \frac{4(\gamma + \Delta\gamma) \pm 4g \cdot \sin(2\phi)}{1 - 2\beta \cdot \cos(2\phi)} \\ S_{\pm 45^\circ}^{\text{pump}} &= \pm 4(\gamma + \Delta\gamma) \pm 4g \cdot \sin(2\phi) \end{aligned} \quad (\text{S7})$$

The measured CD signals without the pump read as:

$$S_{45^\circ}^0 = 2 \cdot \frac{I_{\pm 45^\circ \text{ Det1}}^{\text{out}} - I_{\pm 45^\circ \text{ Det2}}^{\text{out}}}{I_{\pm 45^\circ \text{ Det1}}^{\text{out}} + I_{\pm 45^\circ \text{ Det2}}^{\text{out}}} = \pm 4\gamma \quad (\text{S8})$$

Therefore, differential TRCD signals can be retrieved as:

$$S_{\pm 45^\circ} = S_{\pm 45^\circ}^{\text{pump}} - S_{\pm 45^\circ}^0 = \pm 4\Delta\gamma \pm 4g \cdot \sin(2\phi) \quad (\text{S9})$$

## 2- Sample cell birefringence artefacts

Effects of a small birefringence from the front or the back cell window can be modeled with the Jones matrix [2]:

$$M_{\text{Cell}}^{\text{LB}} = \begin{bmatrix} 1 & 2ib\psi \\ 2ib\psi & 1 \end{bmatrix} \quad (\text{S10})$$

Taking into account the effect of the front cell window LB, the output laser probe field without the pump, at first order, for the orientations of the QWP at  $\pm 45^\circ$ , becomes:

$$\begin{aligned} E_{\pm 45^\circ}^{\text{out}} &= M_{\text{QWP}}^{\pm 45^\circ} \cdot M_{\text{sample}}^{\text{CD,CB}} \cdot M_{\text{Cell}}^{\text{LB}} \cdot E^{\text{in}} \\ E_{\pm 45^\circ}^{\text{out}} &= \frac{1}{\sqrt{2}} \cdot e^{i \frac{2\pi}{\lambda} nL - \frac{\alpha L}{2}} \cdot \begin{bmatrix} 1 \pm \gamma \pm i\theta \mp 2b\psi \\ \pm i - i\gamma + \theta + 2ib\psi \end{bmatrix} \end{aligned} \quad (\text{S11})$$

The intensities measured on the two detectors are:

$$\begin{aligned} I_{\pm 45^\circ \text{ Det1}}^{\text{out}} &= \frac{1}{2} E_0^2 e^{-\alpha L} \cdot [1 \pm 2\gamma \mp 4b\psi] \\ I_{\pm 45^\circ \text{ Det2}}^{\text{out}} &= \frac{1}{2} E_0^2 e^{-\alpha L} \cdot [1 \mp 2\gamma \pm 4b\psi] \end{aligned} \quad (\text{S12})$$

CD measurements without the pump read as:

$$S_{\pm 45^\circ}^0 = 2 \cdot \frac{I_{\pm 45^\circ \text{ Det1}}^{\text{out}} - I_{\pm 45^\circ \text{ Det2}}^{\text{out}}}{I_{\pm 45^\circ \text{ Det1}}^{\text{out}} + I_{\pm 45^\circ \text{ Det2}}^{\text{out}}} = \pm 4\gamma \mp 8b\psi \quad (\text{S13})$$

If there is no coupling with the pump-induced artefacts, CD signals measured with the pump also read as:

$$S_{\pm 45^\circ}^{\text{pump}} = \pm 4(\gamma + \Delta\gamma) \mp 8b\psi \quad (\text{S14})$$

This leads to differential TRCD signals that are not affected by the cell window birefringence:

$$S_{\pm 45^\circ} = S_{\pm 45^\circ}^{\text{pump}} - S_{\pm 45^\circ}^0 = \pm 4\Delta\gamma \quad (\text{S15})$$

### 3- Unbalanced probe transmission artefacts

Considering the difference in the transmission ( $T_{\text{Det1}}$  and  $T_{\text{Det2}}$ ) of the two probe intensities on the detectors after the Wollaston prism, without the pump, we obtain for the QWP orientations at  $\pm 45^\circ$ :

$$\begin{aligned} I_{\pm 45^\circ \text{ Det1}}^{\text{out}} &= \frac{1}{2} \cdot E_0^2 \cdot T_{\text{Det1}} \cdot e^{-\alpha L} (1 \pm 2\gamma) \\ I_{\pm 45^\circ \text{ Det2}}^{\text{out}} &= \frac{1}{2} \cdot E_0^2 \cdot T_{\text{Det2}} \cdot e^{-\alpha L} (1 \mp 2\gamma) \end{aligned} \quad (\text{S16})$$

This leads to the measured CD signals without the pump:

$$S_{\pm 45^\circ}^0 = 2 \cdot \frac{I_{\pm 45^\circ \text{ Det1}}^{\text{out}} - I_{\pm 45^\circ \text{ Det2}}^{\text{out}}}{I_{\pm 45^\circ \text{ Det1}}^{\text{out}} + I_{\pm 45^\circ \text{ Det2}}^{\text{out}}} = \pm 4\gamma + 2\Delta T \quad (\text{S17})$$

with:

$$\Delta T = \frac{T_{\text{Det1}} - T_{\text{Det2}}}{T_{\text{Det1}} + T_{\text{Det2}}} \quad (\text{S18})$$

The difference of the CD signals measured for the two QWP orientations are free from artefacts and read as:

$$\frac{1}{2} \cdot [S_{45^\circ}^0 - S_{-45^\circ}^0] = 4\gamma \quad (\text{S19})$$

Similarly, with the pump, we obtain the measured intensities and CD signals for the QWP orientation at  $\pm 45^\circ$ :

$$\begin{aligned} I_{\pm 45^\circ \text{ Det1}}^{\text{out pump}} &= \frac{1}{2} \cdot E_0^2 \cdot T_{\text{Det1}} \cdot e^{-\alpha L} (1 \pm 2\gamma \pm 2\Delta\gamma) \\ I_{\pm 45^\circ \text{ Det2}}^{\text{out pump}} &= \frac{1}{2} \cdot E_0^2 \cdot T_{\text{Det2}} \cdot e^{-\alpha L} (1 \mp 2\gamma \mp 2\Delta\gamma) \end{aligned} \quad (\text{S20})$$

The measured CD signals with the pump read as:

$$S_{\pm 45^\circ}^{\text{pump}} = 2 \cdot \frac{I_{\pm 45^\circ \text{ Det1}}^{\text{out pump}} - I_{\pm 45^\circ \text{ Det2}}^{\text{out pump}}}{I_{\pm 45^\circ \text{ Det1}}^{\text{out pump}} + I_{\pm 45^\circ \text{ Det2}}^{\text{out pump}}} = \pm 4\gamma \pm 4\Delta\gamma + 2\Delta T \quad (\text{S21})$$

This leads to the differential TRCD signals that do not depend on  $\Delta T$ :

$$S_{\pm 45^\circ} = S_{\pm 45^\circ}^{\text{pump}} - S_{\pm 45^\circ}^0 = \pm 4\Delta\gamma \quad (\text{S22})$$

#### 4- Unbalanced probe separation artefacts

Using the Jones formalism, a slight QWP misalignment from  $\pm 45^\circ$  can be expressed as follows:

$$M_{\text{QWP}}^X = \begin{bmatrix} \cos(X) & i \cdot \sin(X) \\ i \cdot \sin(X) & \cos(X) \end{bmatrix} \quad (\text{S23})$$

with  $X = \pm(45^\circ + \delta)$  and  $\delta$ , the angular deviation. Chiral samples exhibiting small optical activity can be described with the Jones matrix [2]:

$$M_{\text{sample}}^{\text{CD,CB}} = e^{i\frac{2\pi}{\lambda}nL - \frac{\alpha L}{2}} \begin{bmatrix} 1 & i(\theta + \gamma) \\ -i(\theta + \gamma) & 1 \end{bmatrix} \quad (\text{S24})$$

##### 4.1 Measured signals without the pump: achiral samples

Considering first an achiral sample ( $\gamma = 0$  and  $\theta = 0$ ), the output laser probe field without the pump, at first order, for the QWP orientation at  $X$ , is:

$$\begin{aligned} E_X^{\text{out}} &= M_{\text{QWP}}^X \cdot M_{\text{sample}}^{\text{CD}=0, \text{CB}=0} \cdot E^{\text{in}} \\ E_X^{\text{out}} &= E_0 e^{i\frac{2\pi}{\lambda}nL - \frac{\alpha L}{2}} \begin{bmatrix} \cos(X) \\ i \cdot \sin(X) \end{bmatrix} \end{aligned} \quad (\text{S25})$$

This leads to the measured intensities on the two detectors:

$$\begin{aligned} I_{X \text{ Det1}}^{\text{out}} &= E_0^2 \cdot e^{-\alpha L} [\cos(X)^2] \\ I_{X \text{ Det2}}^{\text{out}} &= E_0^2 \cdot e^{-\alpha L} [\sin(X)^2] \end{aligned} \quad (\text{S26})$$

With  $X = \pm(45^\circ + \delta)$ , the measured intensities become:

$$\begin{aligned} I_{\pm(45^\circ + \delta) \text{ Det1}}^{\text{out}} &= \frac{1}{2} \cdot E_0^2 \cdot e^{-\alpha L} [1 - \sin(2\delta)] \\ I_{\pm(45^\circ + \delta) \text{ Det2}}^{\text{out}} &= \frac{1}{2} \cdot E_0^2 \cdot e^{-\alpha L} [1 + \sin(2\delta)] \end{aligned} \quad (\text{S27})$$

The measured CD signals of achiral samples, without the pump, read as:

$$S_{\pm(45^\circ + \delta)}^0 = 2 \cdot \frac{I_{\pm(45^\circ + \delta) \text{ Det1}}^{\text{out}} - I_{\pm(45^\circ + \delta) \text{ Det2}}^{\text{out}}}{I_{\pm(45^\circ + \delta) \text{ Det1}}^{\text{out}} + I_{\pm(45^\circ + \delta) \text{ Det2}}^{\text{out}}} = -2 \cdot \sin(2\delta) \quad (\text{S28})$$

Without the pump, the difference of the CD signals measured for achiral samples, for the two QWP orientations, are free from artefacts and read as:

$$\frac{1}{2} \cdot [S_{45^\circ + \delta}^0 - S_{-45^\circ - \delta}^0] = 0 \quad (\text{S29})$$

#### 4.2 Measured signals without the pump: chiral samples

The output laser probe field without the pump, at first order, for the QWP orientation at X, is:

$$\begin{aligned} E_X^{\text{out}} &= M_{\text{QWP}}^X \cdot M_{\text{sample}}^{\text{CD,CB}} \cdot E^{\text{in}} \\ E_X^{\text{out}} &= E_0 e^{i\frac{2\pi}{\lambda}nL - \frac{\alpha L}{2}} \begin{bmatrix} \cos(X) + \gamma \cdot \sin(X) + i\theta \cdot \sin(X) \\ \theta \cdot \cos(X) - i\gamma \cdot \cos(X) + i \cdot \sin(X) \end{bmatrix} \end{aligned} \quad (\text{S30})$$

This leads to the measured intensities on the two detectors:

$$\begin{aligned} I_{X \text{ Det1}}^{\text{out}} &= E_0^2 \cdot e^{-\alpha L} [\cos(X)^2 + 2\gamma \cdot \sin(X) \cdot \cos(X)] \\ I_{X \text{ Det2}}^{\text{out}} &= E_0^2 \cdot e^{-\alpha L} [\sin(X)^2 - 2\gamma \cdot \sin(X) \cdot \cos(X)] \end{aligned} \quad (\text{S31})$$

With  $X = \pm(45^\circ + \delta)$ , the measured intensities become:

$$\begin{aligned} I_{\pm(45^\circ + \delta) \text{ Det1}}^{\text{out}} &= \frac{1}{2} \cdot E_0^2 \cdot e^{-\alpha L} [1 - \sin(2\delta) \pm 2\gamma] \\ I_{\pm(45^\circ + \delta) \text{ Det2}}^{\text{out}} &= \frac{1}{2} \cdot E_0^2 \cdot e^{-\alpha L} [1 + \sin(2\delta) \mp 2\gamma] \end{aligned} \quad (\text{S32})$$

The measured CD signals, without the pump, read as:

$$S_{\pm(45^\circ + \delta)}^0 = 2 \cdot \frac{I_{\pm(45^\circ + \delta) \text{ Det1}}^{\text{out}} - I_{\pm(45^\circ + \delta) \text{ Det2}}^{\text{out}}}{I_{\pm(45^\circ + \delta) \text{ Det1}}^{\text{out}} + I_{\pm(45^\circ + \delta) \text{ Det2}}^{\text{out}}} = \pm 4\gamma - 2 \cdot \sin(2\delta) \quad (\text{S33})$$

Without the pump, the difference of the CD signals measured for the two QWP orientations are free from artefacts and read as:

$$\frac{1}{2} \cdot [S_{45^\circ + \delta}^0 - S_{-45^\circ - \delta}^0] = 4\gamma \quad (\text{S34})$$

### 4.3 Measured signals with the pump: achiral samples

With the pump, considering first an achiral sample ( $\gamma = 0$  and  $\theta = 0$ ), Eq. SI14 becomes with  $\phi=0$ :

$$M_{\text{sample}}^{\text{LB,LD}} = e^{i\frac{2\pi}{\lambda}nL - \frac{\alpha L}{2}} \cdot e^{i\frac{2\pi}{\lambda}\Delta nL - \frac{\Delta\alpha L}{2}} \begin{bmatrix} 1 - (ig + \beta) & 0 \\ 0 & 1 + (ig + \beta) \end{bmatrix} \quad (\text{S35})$$

Using Eq. 24, the output laser probe field with the pump, at first order, for the QWP orientation at X, is:

$$E_X^{\text{out pump}} = M_{\text{QWP}}^X \cdot M_{\text{sample}}^{\text{LD,LB}} \cdot E^{\text{in}} \quad (\text{S36})$$

$$E_X^{\text{out pump}} = E_0 e^{i\frac{2\pi}{\lambda}nL - \frac{\alpha L}{2}} \begin{bmatrix} \cos(X) \cdot (1 - \beta - ig) \\ \sin(X) \cdot (i - i\beta + g) \end{bmatrix}$$

This leads to the measured intensities on the two detectors:

$$I_{X \text{ Det1}}^{\text{out pump}} = E_0^2 \cdot e^{-\alpha L} [\cos(X)^2 \cdot (1 - 2\beta)] \quad (\text{S37})$$

$$I_{X \text{ Det2}}^{\text{out pump}} = E_0^2 \cdot e^{-\alpha L} [\sin(X)^2 \cdot (1 - 2\beta)]$$

With  $X = \pm(45^\circ + \delta)$ , the measured intensities become:

$$I_{\pm(45^\circ + \delta) \text{ Det1}}^{\text{out pump}} = \frac{1}{2} \cdot E_0^2 \cdot e^{-\alpha L} [(1 - \sin(2\delta)) \cdot (1 - 2\beta)] \quad (\text{S38})$$

$$I_{\pm(45^\circ + \delta) \text{ Det2}}^{\text{out pump}} = \frac{1}{2} \cdot E_0^2 \cdot e^{-\alpha L} [(1 + \sin(2\delta)) \cdot (1 - 2\beta)]$$

The measured CD signals, with the pump, read as:

$$S_{\pm(45^\circ + \delta)}^{\text{pump}} = 2 \cdot \frac{I_{\pm(45^\circ + \delta) \text{ Det1}}^{\text{out pump}} - I_{\pm(45^\circ + \delta) \text{ Det2}}^{\text{out pump}}}{I_{\pm(45^\circ + \delta) \text{ Det1}}^{\text{out pump}} + I_{\pm(45^\circ + \delta) \text{ Det2}}^{\text{out pump}}} = -2 \cdot \sin(2\delta) \cdot (1 - 2\beta) \quad (\text{S36})$$

The differential TRCD signals, with and without the pump, read as:

$$S_{\pm(45^\circ + \delta)} = S_{\pm(45^\circ + \delta)}^{\text{pump}} - S_{\pm(45^\circ + \delta)}^0 = 4\beta \cdot \sin(2\delta) \quad (\text{S37})$$

The difference of the TRCD signals measured for the two QWP orientations are free from artefacts and read as:

$$\frac{1}{2} \cdot [S_{45^\circ + \delta} - S_{-45^\circ - \delta}] = 0 \quad (\text{S38})$$

### 4.4 Measured signals with the pump: chiral samples

With the pump, considering now a chiral sample, Eq. SI14 becomes, with  $\phi=0$ :

$$M_{\text{sample}}^{\text{CD,CB,LD,LD}} = e^{i\frac{2\pi}{\lambda}nL - \frac{\alpha L}{2}} \cdot e^{i\frac{2\pi}{\lambda}\Delta nL - \frac{\Delta\alpha L}{2}} \begin{bmatrix} 1 - (ig + \beta) & i(\gamma + \Delta\gamma) - (\theta + \Delta\theta) \\ -i(\gamma + \Delta\gamma) + (\theta + \Delta\theta) & 1 + (ig + \beta) \end{bmatrix} \quad (\text{S39})$$

The output laser probe field with the pump, at first order, for the QWP orientation at X, is:

$$\begin{aligned}
E_X^{\text{out pump}} &= M_{\text{QWP}}^X \cdot M_{\text{sample}}^{\text{CD,CB,LD,LB}} \cdot M_{\text{Cell}}^{\text{LB}} \cdot E^{\text{in}} \\
E_X^{\text{out pump}} &= E_0 e^{i\frac{2\pi}{\lambda}nL - \frac{\alpha L}{2}} \cdot e^{i\frac{2\pi}{\lambda}\Delta nL - \frac{\Delta\alpha L}{2}} \times \\
&\begin{bmatrix} -\beta \cdot \cos(X) - ig \cdot \cos(X) + \cos(X) + (\gamma + \Delta\gamma) \cdot \sin(X) + i(\theta + \Delta\theta) \cdot \sin(X) \\ -i \cdot (\gamma + \Delta\gamma) \cdot \cos(X) + (\theta + \Delta\theta) \cdot \cos(X) - i\beta \cdot \sin(X) + g \cdot \sin(X) + i \cdot \sin(X) \end{bmatrix}
\end{aligned} \tag{S40}$$

This leads to the measured intensities on the two detectors:

$$\begin{aligned}
I_{X \text{ Det1}}^{\text{out pump}} &= E_0^2 \cdot e^{-(\alpha + \Delta\alpha)L} [(1 - 2\beta) \cdot \cos(X)^2 + 2(\gamma + \Delta\gamma) \cdot \sin(X) \cdot \cos(X)] \\
I_{X \text{ Det2}}^{\text{out pump}} &= E_0^2 \cdot e^{-(\alpha + \Delta\alpha)L} [(1 - 2\beta) \cdot \sin(X)^2 - 2(\gamma + \Delta\gamma) \cdot \sin(X) \cdot \cos(X)]
\end{aligned} \tag{S41}$$

With  $X = \pm(45^\circ + \delta)$ , the measured intensities become:

$$\begin{aligned}
I_{\pm(45^\circ + \delta) \text{ Det1}}^{\text{out pump}} &= \frac{1}{2} \cdot E_0^2 \cdot e^{-(\alpha + \Delta\alpha)L} [(1 - 2\beta) \cdot (1 - \sin(2\delta)) \pm 2(\gamma + \Delta\gamma)] \\
I_{\pm(45^\circ + \delta) \text{ Det2}}^{\text{out pump}} &= \frac{1}{2} \cdot E_0^2 \cdot e^{-(\alpha + \Delta\alpha)L} [(1 - 2\beta) \cdot (1 + \sin(2\delta)) \mp 2(\gamma + \Delta\gamma)]
\end{aligned} \tag{S42}$$

The measured CD signals, with the pump, read as:

$$S_{\pm(45^\circ + \delta)}^{\text{pump}} = 2 \cdot \frac{I_{\pm(45^\circ + \delta) \text{ Det1}}^{\text{out pump}} - I_{\pm(45^\circ + \delta) \text{ Det2}}^{\text{out pump}}}{I_{\pm(45^\circ + \delta) \text{ Det1}}^{\text{out pump}} + I_{\pm(45^\circ + \delta) \text{ Det2}}^{\text{out pump}}} = \pm 4(\gamma + \Delta\gamma) - 2 \cdot \sin(2\delta) \cdot (1 - 2\beta) \tag{S43}$$

The differential TRCD signals, with and without the pump, read as:

$$S_{\pm(45^\circ + \delta)} = S_{\pm(45^\circ + \delta)}^{\text{pump}} - S_{\pm(45^\circ + \delta)}^0 = \pm 4\Delta\gamma + 4\beta \cdot \sin(2\delta) \tag{S44}$$

The difference of the TRCD signals measured for the two QWP orientations are free from artefacts and read as:

$$\frac{1}{2} \cdot [S_{45^\circ + \delta} - S_{-45^\circ - \delta}] = 4\Delta\gamma \tag{S45}$$

## References :

1. X. Xie, and J. D. Simon, "Picosecond circular dichroism spectroscopy: a Jones matrix analysis," J. Opt. Soc. Am. B **7**, 1673-1684 (1990).
2. C. Niezborala, and F. Hache, "Measuring the dynamics of circular dichroism in a pump-probe experiment with a Babinet-Soleil compensator," J. Opt. Soc. Am. B **23**, 2418-2424 (2006).