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

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Abstract: Here we present the development of a subpicosecond spectropolarimeter enabling high sensitivity balanced detection of time-resolved circular dichroism (TRCD) signals from chiral sample in solution. The signals are measured with a conventional femtosecond pump-probe set-up using the combination of a quarter-waveplate and a Wollaston prism. This simple and robust method allows access to TRCD signals with improved signal-to-noise ratio and very short acquisition times. We provide a theoretical analysis of the artifacts of such detection geometry and the strategy to eliminate them. We illustrate the potential of this new detection with the study of the [Ru(phen)₃]²⁺PF₆ complexes in acetonitrile.

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1. Introduction

Circular dichroism (CD) spectroscopy, which is the differential absorbance between left- and right-circularly polarized light, has become a tool of choice for studying the conformation of biomolecules at equilibrium in solution, under physiological conditions. Biomolecules exhibit characteristic CD signals in the ultraviolet (UV) spectral region between 200 and 300 nm that can be theoretically or phenomenologically related to their secondary structures [1]. In this context, transposition of CD measurements to the time domain (TRCD), in the UV-visible spectral domain, is a very promising strategy to access the conformational dynamics of proteins and oligonucleotides outside equilibrium that play a key role in their function. In this regard, the combination of CD detection and femtosecond pump-probe spectroscopy offers the possibility to access those dynamics over an extended time scale, ranging from femtoseconds to milliseconds, with a table top set-up.

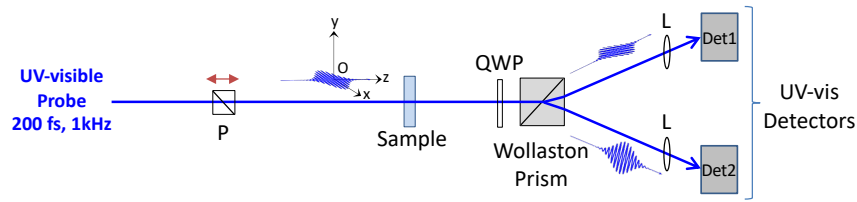
Despite the conceptual simplicity of TRCD measurements, their implementation on conventional pump-probe setups remains an experimental challenge due to their very weak signals (*i.e.* 10^{-5} - 10^{-3} in differential absorbance) subject to pump polarization artifacts [2]. Only a few groups have developed ultrafast TRCD setups in the UV-visible range (for a review, see [3, 4]). To date, only two types of detections have allowed for the comprehensive study of chiral compounds in solution [5-15]. The first one consists of direct TRCD measurements of the pump-induced differential absorbance variation of an alternately left- and right-circularly polarized probe [5, 8, 12, 13], while the second one relies on the measurement of the pump-induced ellipticity variation of a linearly polarized probe [14]. The main drawback of direct TRCD measurements stems from the detection of small absorbance changes against a strong achiral absorption background that significantly reduces their signal-to-noise (S/N) ratio. In contrast, background-free ellipticity measurements provide an enhanced detection of very small TRCD signals at a cost of an increased sensitivity to pump-induced linear birefringence (LB) artifacts due to their crossed-polarizer detection configuration [2, 16]. In addition, these two detection strategies require either the introduction of a modulation of the circularly polarized probe associated with a complex detection procedure to extract the TRCD signals [13], or of a

46 variable phase delay on the linearly polarized probe for each pump-probe delay which
 47 significantly increases the acquisition times [14]. These sequential acquisition procedures are
 48 very sensitive to pump and probe fluctuations which significantly reduces their S/N ratio.

49 Here, we specifically address these main drawbacks with the development of an alternative
 50 detection method based on the balanced detection of the pump-induced ellipticity changes of
 51 the probe linear polarization by chiral samples. The principle relies on the full characterization
 52 of the probe elliptic polarization with a single laser shot by using the combination of a
 53 broadband quarter-waveplate (QWP) and a Wollaston prism. In the following, we describe the
 54 principle and the implementation of this two-arm detection on a conventional single-
 55 wavelength detection femtosecond pump-probe set-up powered by a 1-kHz amplified Titanium
 56 Sapphire laser source. We perform a theoretical analysis of the artifacts for such detection
 57 geometry and provide a strategy to perform artifact-free TRCD measurements. We then
 58 illustrate the performances of our new set-up with the experimental study of $[\text{Ru}(\text{phen})_3] \cdot 2\text{PF}_6$
 59 complexes in acetonitrile.

60 2. Basic principle of TRCD with a balanced detection geometry

61 Taking advantage that the transmission of a linearly polarized light by a chiral medium is
 62 elliptical, the vertical and horizontal components of the ellipse can be directly accessed with
 63 the combination of a QWP and a Wollaston prism, as illustrated on Fig. 1 [4].



64

65 Fig. 1. Principle of single-shot balanced ellipsometry for a horizontally polarized incoming probe laser field along the
 66 (Ox) axis. P: Glan polarizer. QWP: quarter-waveplate. L: Lens. Det1 and Det2: sample probe detectors (photodiodes
 67 or photomultipliers).

68 The effect of the different optical components on the incident probe polarized laser electric
 69 field can be described by the Jones formalism. The Jones vector for the horizontally polarized
 70 incoming probe light along the (Ox) axis is given by:

$$71 \quad E^{\text{in}} = E_0 \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad (1)$$

72 The outgoing probe laser field reads as:

$$73 \quad E^{\text{out}} = M_{\text{QWP}} \cdot M_{\text{sample}} \cdot E^{\text{in}} \quad (2)$$

74 Each optical element is described by (2x2) matrix. The Jones matrix associated with the QWP,
 75 for an orientation at an angle of $+45^\circ$ (clockwise) with respect to its fast axis oriented along
 76 (Ox), is expressed as follows:

$$77 \quad M_{\text{QWP}}^{45^\circ} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} \quad (3)$$

78 Chiral samples exhibiting small optical activity can be described with the Jones matrix [14]:

$$79 \quad (4)$$

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

84 where L is the sample thickness, n, the refractive index and α , the sample absorption coefficient.
 85 4γ corresponds to the sample CD and θ to sample circular birefringence (CB), respectively
 86 defined as:

$$4\gamma = \ln(10) \cdot [A_L - A_R] \quad (5)$$

$$\theta = \pi \cdot \frac{n_L - n_R}{\lambda} \cdot L \quad (6)$$

91 where $A_{L,R}$ and $n_{L,R}$ are the sample absorbance and refractive index for left- and right-circularly
 92 polarized light. The outgoing laser probe field, for the QWP orientation at $+45^\circ$, becomes:

$$E_{45^\circ}^{\text{out}} = \frac{1}{\sqrt{2}} \cdot E_0 \cdot e^{i\frac{2\pi}{\lambda}nL - \frac{\alpha L}{2}} \begin{bmatrix} 1 + \gamma + i\theta \\ i(1 - (\gamma + i\theta)) \end{bmatrix} \quad (7)$$

95 The Wollaston prism then separates the output probe beam into two orthogonal polarizations.
 96 Their intensities measured with Det1 and Det2 (see Fig. 1) are respectively:

$$I_{45^\circ \text{ Det1}}^{\text{out}} = E_{x45^\circ}^{\text{out}} \cdot \overline{E_{x45^\circ}^{\text{out}}} = \frac{1}{2} \cdot E_0^2 \cdot e^{-\alpha L} (1 + 2\gamma + \gamma^2 + \theta^2) \quad (8)$$

$$I_{45^\circ \text{ Det2}}^{\text{out}} = E_{y45^\circ}^{\text{out}} \cdot \overline{E_{y45^\circ}^{\text{out}}} = \frac{1}{2} \cdot E_0^2 \cdot e^{-\alpha L} (1 - 2\gamma + \gamma^2 + \theta^2)$$

100 Neglecting the second order terms, γ^2 and θ^2 associated to the sample CD and CB that are $\ll 1$,
 101 static CD signals can be measured as follow:

$$S_{45^\circ}^0 = 2 \cdot \frac{I_{45^\circ \text{ Det1}}^{\text{out}} - I_{45^\circ \text{ Det2}}^{\text{out}}}{I_{45^\circ \text{ Det1}}^{\text{out}} + I_{45^\circ \text{ Det2}}^{\text{out}}} = 4\gamma \quad (9)$$

104 It is interesting to note that with this detection geometry, CB does not contribute to the
 105 measured signals at first order. A similar result with opposite sign can be obtained for
 106 measurements performed for a QWP orientation at -45° (anti-clockwise) with respect to its fast
 107 axis (Ox):

$$S_{-45^\circ}^0 = 2 \cdot \frac{I_{-45^\circ \text{ Det1}}^{\text{out}} - I_{-45^\circ \text{ Det2}}^{\text{out}}}{I_{-45^\circ \text{ Det1}}^{\text{out}} + I_{-45^\circ \text{ Det2}}^{\text{out}}} = -4\gamma \quad (10)$$

110 With the pump, the intensities of the two probe orthogonal polarizations measured with Det1
 111 and Det2 (see Fig.1), for a QWP orientation at $+45^\circ$, become:

$$I_{45^\circ \text{ Det1}}^{\text{out pump}} = \frac{1}{2} \cdot E_0^2 \cdot e^{-(\alpha + \Delta\alpha)L} [1 + 2(\gamma + \Delta\gamma)] \quad (11)$$

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

115 with $\Delta\alpha$ and $4\Delta\gamma$, the pump-induced variations of the sample absorption coefficient and CD,
 116 respectively.

117 Measurements with the pump lead to:

118 (12)

119
$$S_{45^\circ}^{\text{pump}} = 2 \cdot \frac{I_{45^\circ \text{ Det1}}^{\text{out pump}} - I_{45^\circ \text{ Det2}}^{\text{out pump}}}{I_{45^\circ \text{ Det1}}^{\text{out pump}} + I_{45^\circ \text{ Det2}}^{\text{out pump}}} = 4(\gamma + \Delta\gamma)$$

120 The differential TRCD signals can be retrieved by calculating the difference between the
121 signals measured with the pump ($S_{45^\circ}^{\text{pump}}$) and without the pump ($S_{45^\circ}^0$), respectively:

122 (13)

123
$$S_{45^\circ} = S_{45^\circ}^{\text{pump}} - S_{45^\circ}^0 = 4\Delta\gamma$$

124 Similarly, we obtain for the TRCD measurements performed for a QWP orientation at -45° :

125 (14)

126
$$S_{-45^\circ} = S_{-45^\circ}^{\text{pump}} - S_{-45^\circ}^0 = -4\Delta\gamma$$

127 It should be stressed that the combination of the QWP and the Wollaston prism which separates
128 the two circularly-polarized components of the transmitted probe, leads to the detection of two
129 signals of nearly equal intensity in a balanced detection geometry. The measured differential
130 signals thus give directly access to the CD variations of the sample (see Eqs. 13-14). This differs
131 from the balanced heterodyne detection previously developed by Ghosh *et al.* for the
132 measurement of the optical activity in the visible and near infrared spectral range, which
133 consists in projecting into two equal intensities the transmitted probe electric field on an analog
134 balanced photodetector with a Wollaston prism oriented at 45° [17]. With this geometry, both
135 CD and CB signals contribute to the measured differential signals. A common-path
136 interferometer is used to introduce a variable delay between the two projected probe
137 polarizations to simultaneously recover the time-domain interferograms of these two
138 contributions. Although proofs of principle for the measurement of the CD and CB spectra of
139 chiral compounds in their ground electronic state have been given, it has not yet found
140 application for ultrafast TRCD measurements [17]. It is worth noting that, despite this balanced
141 heterodyne detection has the great advantage to give access to the whole CD and CB spectra of
142 the sample with a simple set-up, its sequential acquisition procedure is expected to increase
143 considerably the acquisition times in a pump-probe geometry. One main advantage of using the
144 combination of the QWP and the Wollaston prism is to allow the characterization of the CD
145 signals with a single laser shot. Such dual-arm detection geometry, which can be classified as
146 a *non-null* ellipsometer, is commonly used in division-of-amplitude photopolarimeter (DOAP)
147 for Mueller-matrix polarimetry [18]. Similar detection geometry combining a QWP and a
148 polarization beam splitter has been also used for fast and improved S/N measurements of
149 Raman optical activity (ROA) and circularly polarized luminescence (CPL) [19-22]. Here, this
150 is the first implementation of such dual-arm *non-null* ellipsometry detection on a femtosecond
151 pump-probe set-up. This differs from previously developed UV-visible ellipsometric TRCD
152 detections, which were all based on conventional *quasi-null* ellipsometric detection
153 methods[14, 23-25].

154 3. Theoretical analysis of TRCD balanced detection artifacts

155 Our previous analysis is valid for set-ups devoid of polarization artifacts. However, cross
156 polarizer detection geometry is known to be particularly sensitive to pump-induced polarization
157 artifacts and the sample cell window strain. Those artifacts have been already discussed in
158 details by Kliger *et al.*, in the frame of the development of nanosecond-millisecond
159 ellipsometry, with a modified flash photolysis set-up [2]. Here, additional artifacts arising
160 specifically from the balanced detection geometry must be considered. In the following, for
161 simplicity, we discuss all these artifacts individually. In the experimental section, we provide
162 evidence that these artifacts do not couple and can be individually corrected.

163 **3.1 Pump-induced polarization artifacts**

164 TRCD measurements with a cross-polarizer geometry are known to be very sensitive to artifacts
 165 stemming from the partial orientation of molecules excited with a linearly polarized pump [2,
 166 14, 16]. This anisotropic effect creates sample LB and LD that can lead to strong artifacts in
 167 the TRCD signals, on the time scale of the rotational diffusion of the excited molecules.
 168 Correction of these artifacts is therefore crucial for measurements carried on the femtosecond
 169 time scale, notably for biomolecules that slowly reorient. We can evaluate these artifacts by
 170 considering the total sample matrix that contains the optical effects of the pump-induced LB
 171 and LD, in addition to the sample CD and CB, as previously defined by Xie et al. [26],
 172 expressed as:

$$173 \quad M_{\text{sample}}^{\text{CD,CB,LB,LD}} = e^{i\frac{2\pi}{\lambda}(n+\Delta n)\cdot L - \frac{(\alpha+\Delta\alpha)L}{2}} \times \quad (15)$$

$$174 \quad \begin{bmatrix} 1 - (ig + \beta) \cos(2\phi) & i(\gamma + \Delta\gamma) - (\theta + \Delta\theta) - (ig + \beta) \sin(2\phi) \\ -i(\gamma + \Delta\gamma) + (\theta + \Delta\theta) - (ig + \beta) \sin(2\phi) & 1 + (ig + \beta) \cos(2\phi) \end{bmatrix}$$

176 where ϕ is the angle between the pump and probe linear polarizations, 4β and g are the sample
 177 LD and LB, respectively, defined as:

$$178 \quad 4\beta = \frac{A_x - A_y}{\ln(10)} \quad (16)$$

$$179 \quad g = \pi \cdot \frac{n_y - n_x}{\lambda} \cdot L \quad (17)$$

182 where $A_{x,y}$ and $n_{x,y}$ are the absorbance and the refractive index along the (Ox) and (Oy) axes,
 183 respectively.

184 At first order (for the details of the calculation, see SI Eqs. S14-19), the TRCD signals measured
 185 for the two QWP orientations at $\pm 45^\circ$ read as:

$$186 \quad S_{\pm 45^\circ} = \pm 4\Delta\gamma \pm 4g \cdot \sin(2\phi) \quad (18)$$

188 This result shows that the TRCD measurements at first order are not sensitive to the pump-
 189 induced LD. However, they can be strongly affected by the pump-induced LB, if the angle of
 190 the pump and probe linear polarizations slightly deviates from 0° or 90° . Note that this is
 191 particularly pernicious since it leads to an antisymmetric artefactual contribution to the TRCD
 192 signals measured for the two QWP orientations that cannot be corrected. In this regard, *in situ*
 193 alignment of the pump and probe polarizations with a precision of less than 1° has proven to be
 194 particularly effective to avoid pump-induced LB for quasi-colinear pump-probe configurations
 195 such as ours [27].

196 **3.2 Sample cell birefringence artifact**

197 Sample cell strain birefringence is known as one of the major drawbacks in ellipsometry.
 198 Effects of a small birefringence from the front or the back cell window can be modeled with
 199 the Jones matrix [14]:

$$200 \quad M_{\text{Cell}}^{\text{LB}} = \begin{bmatrix} 1 & 2ib\psi \\ 2ib\psi & 1 \end{bmatrix} \quad (19)$$

202 where ψ is the angle between the fast axis of the birefringent window with respect to the probe
 203 polarization and $2b$ is the retardation. Taking into account the effect of the front cell window

204 LB, the measured CD signals without the pump, at first order for the QWP orientations at $\pm 45^\circ$,
 205 express as (for the details, see SI Eqs. S10-15):

$$206 \quad S_{\pm 45^\circ}^0 = \pm 4\gamma \mp 8b\psi \quad (20)$$

208 From this calculation, it is clear that sample cell LB acts as a phase retarder which alters the
 209 elliptical probe eccentricity in the opposite directions on each detection arms. This leads to an
 210 antisymmetric artefactual contribution to the measured static CD signals for the two QWP
 211 orientations. Note that a similar effect is also expected from the back cell window. Importantly,
 212 the previous studies have shown that such artifact does not couple with the pump-induced
 213 artifacts, if the pump and probe polarizations are properly aligned [2]. Under these conditions,
 214 the sample cell LB is not expected to affect the TRCD signals. Those differential measurements
 215 fully cancel out this artefactual LB that contributes equally to the signals measured with and
 216 without the pump.

217 *3.3 Unbalanced probe transmission artifacts*

218 It is practically impossible to obtain a perfectly balanced detection due to the differences
 219 between the two detection arms. Notably, one of the main artifacts arises from the difference
 220 in the probe transmission, after the Wollaston prism, on the two detection arms due to their
 221 separate optics and detectors that may respond differently to the orthogonal polarizations of the
 222 probe. It is known from the previous developments of dual-arm detection for ROA and CPL
 223 that measurements performed for the two QWP orientations at $\pm 45^\circ$, which inverts the two
 224 components of the elliptical probe polarization on the detection arms, can correct this problem
 225 [19]. This can be readily shown by calculating the CD signals for the two QWP orientations,
 226 taking into account the difference in the probe beam intensities transmitted on the two detection
 227 arms (for details, see SI Eqs. S16-22). This leads to CD signals that, at first order, are
 228 dissymmetric:

$$229 \quad S_{\pm 45^\circ}^0 = \pm 4\gamma + 2\Delta T \quad (21)$$

231 where ΔT is the normalized difference in the probe intensities transmitted on the two detection
 232 arms (T_{Det1} and T_{Det2}) expressed as:

$$233 \quad \Delta T = \frac{T_{\text{Det1}} - T_{\text{Det2}}}{T_{\text{Det1}} + T_{\text{Det2}}} \quad (22)$$

235 This dissymmetry can be fully compensated by calculating the difference of the CD signals
 236 measured for these two QWP orientations:

$$237 \quad \frac{1}{2} \cdot [S_{45^\circ}^0 - S_{-45^\circ}^0] = 4\gamma \quad (23)$$

239 Importantly, the TRCD measurements, which are differential measurements with and without
 240 the pump are expected to fully compensate the ΔT dissymmetry, regardless of the QWP
 241 orientation.

242 *3.4 Unbalanced probe separation artifacts*

243 Another source of artifact of the balanced detection pertains from the unbalanced separation of
 244 the two probe linear polarizations upstream the Wollaston prism. This can be due to
 245 imperfection and/or misalignment of the QWP. Using the Jones formalism, a slight QWP
 246 misalignment from $\pm 45^\circ$ can be expressed as follows:

247 (24)

$$248 \quad M_{\text{QWP}}^X = \begin{bmatrix} \cos(X) & i \cdot \sin(X) \\ i \cdot \sin(X) & \cos(X) \end{bmatrix}$$

249 with $X = \pm(45^\circ + \delta)$ and δ , the angular deviation.

250 Unbalanced probe separation leads to dissymmetric CD signals for the two QWP orientations
251 (for details, see SI Eqs. SI23-45):

$$252 \quad S_{\pm(45^\circ + \delta)}^0 = \pm 4\gamma - 2 \sin(2\delta) \quad (25)$$

254 Their difference allows to correct their dissymmetry:

$$255 \quad \frac{1}{2} \cdot [S_{45^\circ + \delta}^0 - S_{-45^\circ - \delta}^0] = 4\gamma \quad (26)$$

257 The situation is different for the TRCD measurements, for which the pump introduces
258 additional sample LB. Thus, the unbalanced separation of the probe polarization not only
259 affects the probe intensities, but also the amplitude of the transient absorption signals which is
260 sent on the two detection arms. To evaluate such artefactual contributions, the total sample
261 matrix that contains the optical effects of the pump-induced LB and LD, for parallel pump and
262 probe polarizations, deduced from Eq. 15, as to be considered:

$$263 \quad M_{\text{sample}}^{\text{CD,CB,LD}} = e^{i \frac{2\pi}{\lambda} (n + \Delta n) \cdot L - \frac{(\alpha + \Delta \alpha) L}{2}} \times \begin{bmatrix} 1 - (ig + \beta) & i(\gamma + \Delta\gamma) - (\theta + \Delta\theta) \\ -i(\gamma + \Delta\gamma) + (\theta + \Delta\theta) & 1 + (ig + \beta) \end{bmatrix} \quad (27)$$

265 where 4β and g are the sample LB and LD (Eqs. 16 and 17), respectively.

266 For achiral samples (*i.e.* $\gamma = 0$, $\Delta\gamma = 0$, $\theta = 0$ and $\Delta\theta = 0$), the measured TRCD signals at first
267 order, for the two QWP orientations are nonnull and read as:

$$268 \quad S_{\pm(45^\circ + \delta)} = 4\beta \cdot \sin(2\delta) \quad (28)$$

270 It is thus clear that the unbalanced separation of the probe, in the presence of the pump, induces
271 the coupling of the TRCD signals with the pump-induced sample LD. This leads to the
272 observation of the same artefactual TRCD signal for both QWP orientations, which yields:

$$273 \quad \frac{1}{2} \cdot [S_{45^\circ + \delta} - S_{-45^\circ - \delta}] = 0 \quad (29)$$

275 In a similar way, we can show that chiral samples exhibit dissymmetric TRCD signals for the
276 two QWP orientations:

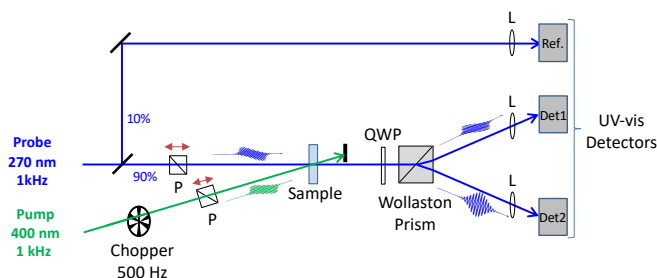
$$277 \quad S_{\pm(45^\circ + \delta)} = \pm 4\Delta\gamma + 4\beta \cdot \sin(2\delta) \quad (30)$$

279 Their difference yields TRCD signals free from artifacts:

$$280 \quad \frac{1}{2} \cdot [S_{45^\circ + \delta} - S_{-45^\circ - \delta}] = 4\Delta\gamma \quad (31)$$

282 4. Experimental set-up and processing

283 Time-resolved experiments are carried out with a single-wavelength detection pump-probe set-
 284 up using an amplified 1 kHz Ti:sapphire laser system (Spectra-Physics, Solstice), delivering
 285 100-fs pulses at 800 nm with an energy of 3 mJ. The 400-nm pump pulses are obtained from
 286 the second harmonic of the fundamental pulses. Their energy is set to 0.37 μ J to avoid photo-
 287 degradation during experiments. Probe pulses at 270 nm with an energy of 12 nJ are generated
 288 by parametric amplification of a white light continuum and second harmonic generation.
 289

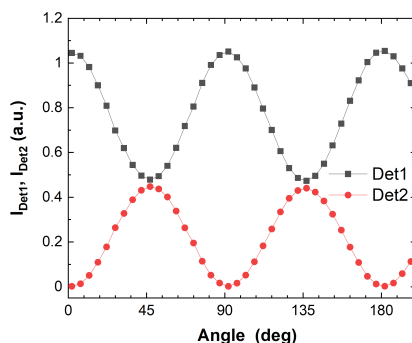


290 Fig. 2. Single-wavelength detection pump-probe set-up with a balanced ellipsometric TRCD detection. P: Glan
 291 polarizer. QWP: quarter-waveplate L: Lens. Det1 and Det2: sample probe polarization detectors. Ref: reference probe
 292 detector.
 293

294 Fig.2 illustrates the experimental set-up used for the balanced TRCD detection. The UV probe
 295 beam is split into the reference (10%) and the sample probe (90%) beams. The reference beam
 296 is directly sent to a variable gain photodiode (PDA25K2, Thorlabs) connected to a boxcar
 297 integrator (SR250, Standord Research Systems). The sample probe is focused into the sample
 298 cell with a typical diameter of about 400 μ m, after passing through a Glan α -BBO polarizer
 299 (extinction ratio 10^5 , Thorlabs) in order to get a horizontal polarization. The delay between the
 300 pump and probe beams is varied using an optical delay line driven by a stepper motor. TRCD
 301 measurements are performed by measuring the pump-induced ellipticity change of the sample
 302 probe beam with the combination of a broadband QWP (260-410 nm, Thorlabs) and a α -BBO
 303 Wollaston prism (extinction ratio 10^5 , Thorlabs). The two probe beams are then sent through a
 304 set of identical mirrors, lenses and filters on two variable gain photodiodes connected to two
 305 boxcar integrators triggered with the TTL synchronization signal of the laser source
 306 regenerative amplifier and a 16-bits data acquisition card (National Instruments). Of note
 307 analog balanced photodetectors with sensitivity in the spectral range below 300 nm being not
 308 commercially available, we choose to use two variable gain photodiodes with an enhanced
 309 sensitivity between 150 and 550 nm.

310 The TRCD signals are measured by alternating measurements of the probe beam intensity of
 311 “pumped” and “unpumped” sample, the pump being modulated by a chopper at 500 Hz.
 312 Measured TRCD signals, for the two QWP angles at $\pm 45^\circ$ with respect to its fast axis, are
 313 averaged over 100 or 250 laser shots with the pump to reach an optimum S/N ratio. In a similar
 314 way, measured static CD signals are averaged over 100 or 250 laser shots without the pump.
 315 Importantly, in order to avoid interference from pump scattered light with the TRCD
 316 measurements, one UV bandpass filter (UG11) is added in front of each detector. The pump
 317 linear polarization is set to a parallel orientation with respect to the probe polarization with a
 318 Glan-Taylor calcite polarizer (extinction ratio 10^5 , Thorlabs), in order to avoid pump-induced
 319 LB effects. The angles of the pump polarizer and the QWP are controlled with stepped-
 320 motorized rotation stages with a precision of $< 0.1^\circ$. Fig.3 illustrates the measurements
 321 performed with Det1 and Det2, for various QWP angles. As shown by Fig.3, the intensities
 322 measured with Det1 and Det2 for the QWP orientations at $+45^\circ$ and $+135^\circ$ slightly differ by

323 ca. 5% (ΔT). This dissymmetry results from a combined effect of the unbalanced separation
 324 and transmission of the probe on the two detection arms.



325
 326 Fig. 3. Measured intensities averaged over 100 laser shots measured at 270 nm with the two detectors of the balanced
 327 ellipsometric TRCD detection. Det1 for the horizontal probe polarization and Det2 for the vertical probe polarization.

328 We find the ellipticity of the probe beam field equal to: $e = \sqrt{\frac{I_{\min}}{I_{\max}}} = 0.02$

329 In the following, we denote $CD = 4\gamma/\ln(10)$ and $\Delta CD = 4\Delta\gamma/\ln(10)$, the steady-state and the
 330 transient CD signals, respectively. $A = \alpha L/\ln(10)$ and $\Delta A = \Delta\alpha L/\ln(10)$ are the sample
 331 absorbance and differential absorbance. The achiral differential ΔA signals are obtained
 332 simultaneously with the TRCD signals. In practice, for the QWP oriented at $\pm 45^\circ$, the
 333 differential achiral absorbance signals are calculated from the averaged intensities measured on
 334 the three photodiodes (Det1, Det2 and Ref.) with a home-made program as follow:
 335

$$336 \quad \Delta A_{\pm 45^\circ} = -\log \left[\frac{I_{\pm 45^\circ \text{ Det1}}^{\text{out pump}}}{I_{\pm 45^\circ \text{ Det1}}^{\text{out}}} \times \frac{I_{\pm 45^\circ}^{\text{ref}}}{I_{\pm 45^\circ}^{\text{ref pump}}} \right] - \log \left[\frac{I_{\pm 45^\circ \text{ Det2}}^{\text{out pump}}}{I_{\pm 45^\circ \text{ Det2}}^{\text{out}}} \times \frac{I_{\pm 45^\circ}^{\text{ref}}}{I_{\pm 45^\circ}^{\text{ref pump}}} \right] \quad (32)$$

337 and the TRCD signals as follows:

$$338 \quad \Delta CD_{\pm 45^\circ} = \pm \left\{ -\log \left[\frac{I_{\pm 45^\circ \text{ Det1}}^{\text{out pump}}}{I_{\pm 45^\circ \text{ Det1}}^{\text{out}}} \right] + \log \left[\frac{I_{\pm 45^\circ \text{ Det2}}^{\text{out pump}}}{I_{\pm 45^\circ \text{ Det2}}^{\text{out}}} \right] \right\} \quad (33)$$

340 which is equivalent to Eqs. 13 and 14. From these measurements performed for the two
 341 orientations of the QWP, at $\pm 45^\circ$, we calculate:

$$342 \quad \Delta A = \frac{1}{2} [\Delta A_{45^\circ} + \Delta A_{-45^\circ}] \quad (34)$$

$$343 \quad \Delta CD = \frac{1}{2} [\Delta CD_{45^\circ} - \Delta CD_{-45^\circ}] \quad (35)$$

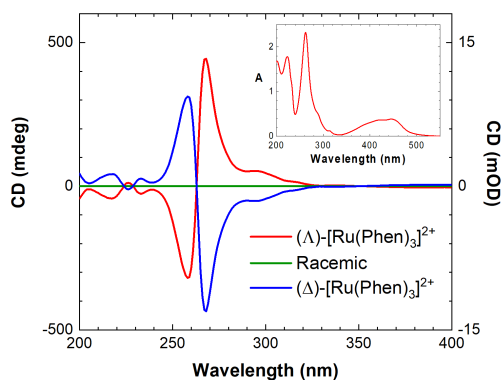
346 All measurements are performed in regular 1-mm optical path quartz cells for absorption
 347 (Hellma). In order to increase the S/N ratio of the CD and ΔCD signals, the cell is kept fixed
 348 during the measurements to avoid unwanted birefringence effects. The steady-state absorption
 349 and CD spectra of the samples are measured before and after each TRCD experiments, in order
 350 to check for any sample degradation, with, respectively, an UV-visible Agilent Cary 100
 351 spectrophotometer and a J-1500 Jasco CD spectrophotometer. The measured ΔCD kinetics
 352 traces are fitted with a Levenberg-Marquardt non-linear fitting algorithm to a sum of

353 exponential functions convoluted with a Gaussian function representing the instrumental
354 response function (IRF). The full width at half maximum (FWHM) of the Gaussian is found to
355 be ~ 0.90 ps.

356 5. Experimental results and discussion

357 5.1 Static CD measurements

358 In order to evaluate the capabilities of our experimental set-up, we first carried out static CD
359 measurements on solutions of $[\text{Ru}(\text{phen})_3] \cdot 2\text{PF}_6$ complexes of the same concentrations. Fig.4.
360 shows the CD spectra of the two enantiomers and their racemic mixture measured in acetonitrile
361 with a commercial CD spectrometer with the corresponding absorption spectrum of Λ -
362 $[\text{Ru}(\text{phen})_3]^{2+}$. Due to the propeller-twist arrangement of their phenanthroline ligands, these
363 ruthenium complexes display strong CD signals in the spectral region of their absorption
364 between 230 nm and 330 nm.



365

366 Fig. 4. Steady-state CD spectra of (Λ) - $[\text{Ru}(\text{phen})_3]^{2+}$, (Δ) - $[\text{Ru}(\text{phen})_3]^{2+}$ and their racemic mixture in acetonitrile
367 measured with our commercial spectropolarimeter. Insert : Corresponding absorption spectrum of Λ - $[\text{Ru}(\text{phen})_3]^{2+}$.

368 Table 1 gathers the static CD measurements carried out at 270 nm with our pump-probe set-up,
369 for the two QWP orientations at $\pm 45^\circ$, respectively. The CD signals retrieved from their
370 difference (Eq. 23) and those measured with our commercial spectropolarimeter are also given
371 for comparison. The CD measurements performed for the two QWP orientations all lead to
372 negative values. Notably, we observe an offset of more than 40 mOD for the racemic mixture.
373 These large offsets mainly arise from unbalanced detection artifacts (Eqs. 21 and 25) due to the
374 differences in the transmission of the two probe polarizations on the two detection arms
375 ($\Delta T=5\%$) in combination with the imperfect separation of their polarizations. Correction of
376 these artifacts allow to obtain CD values of 16.4 and -8.2 mOD, for the Λ and Δ enantiomers
377 of $[\text{Ru}(\text{phen})_3]^{2+}$ and -3.1 mOD for the racemic mixture. Although the sign and the order of
378 magnitude of the CD signals of the two enantiomers are correct, they are highly dissymmetric.
379 A significant offset from zero is also observed for the racemic mixture. Such a result is not
380 surprising since the sample cell LB is not expected to cancel out for static CD measurements,
381 as shown by the Jones calculations (Eq. 20).

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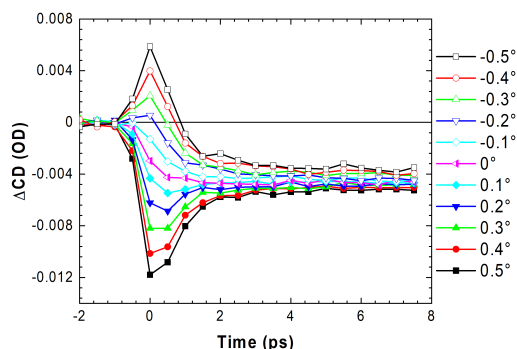
Table 1. Static CD signals measured for solutions of [Ru(phen)₃]²⁺·2PF₆ complexes in acetonitrile at 270 nm with our balanced detection (ΔT~5%) averaged over 250 laser shots and our commercial spectropolarimeter. Given errors are the standard deviations of the measured signals.

Measured signals	(Λ)-[Ru(phen) ₃] ²⁺	Racemic mixture	(Δ)-[Ru(phen) ₃] ²⁺
	CD (mOD)	CD (mOD)	CD (mOD)
$\frac{1}{\ln(10)} \cdot S_{+45^\circ}^0$	-27.7±0.4	-41.2±0.2	-54.6±0.3
$\frac{1}{\ln(10)} \cdot S_{-45^\circ}^0$	-60.5±0.4	-47.5±0.2	-38.2±0.3
$\frac{1}{2 \cdot \ln(10)} \cdot [S_{+45^\circ}^0 - S_{-45^\circ}^0]$	16.4±0.8	-3.1±0.4	-8.2±0.6
Commercial spectro.	11.5	0.0	-11.2

391 Sample cell LB is known to lead to large offsets in the CD measurements [2]. Using our
392 measurement of the racemic mixture as a baseline correction for the sample cell LB, we obtain
393 CD values of 13 mOD and -11 mOD, respectively for the Λ and Δ enantiomers, which are much
394 closer to those measured with our commercial spectropolarimeter (*i.e.* ±~11 mOD). Note,
395 however, that the correction is not perfect, as a residual skewness of 2 mOD is still observed in
396 the CD signals after the baseline subtraction. In fact, a similar result is obtained whether the
397 measurements are performed in a single sample cell or three different cells. Therefore, under
398 these experimental conditions, we deduce that the accuracy of the static CD measurements with
399 our balanced detection geometry is limited to a few mOD. Different strategies can be
400 considered to improve this accuracy, such as a careful alignment of the strained cells to reduce
401 their LB and get Ψ~0 (Eq. 20) or the use of low-stress homemade sample cells. However, we
402 show in the next section that this problem does not pose at all for the differential TRCD
403 measurements, which allow to fully cancel out this LB artifact.

404 5.2 TRCD measurements

405 The TRCD signals are measured alternatively with and without the pump at a repetition rate of
406 1 kHz. Signals recorded at 270 nm, after excitation at 400 nm, lead to significant CD changes
407 in the spectral region of the ππ* transition of the three ligands between 240 nm and 300 nm,
408 the sign of which strongly depends on the wavelength [28]. The excitation of the lowest singlet
409 excited state of [Ru(phen)₃]²⁺ pertaining from the metal-to-ligand charge transfer (¹MLCT)
410 state causes an ultrafast intersystem conversion in the sub-100-fs regime, leading to the
411 formation of a long-lived triplet state (³MLCT, τ ≈ 0.6 μs) with a quantum yield close to the
412 unity [29]. The associated TRCD changes have been attributed to a change of the excitonic
413 coupling between the ligands induced by the UV-visible excitation [28]. Note that electron
414 localization/delocalization in the MLCT excited states of Ruthenium complexes is still a matter
415 of debate (for review see [29]) and is not discussed further in this paper, which focuses on the
416 experimental development of time-resolved ellipsometry.

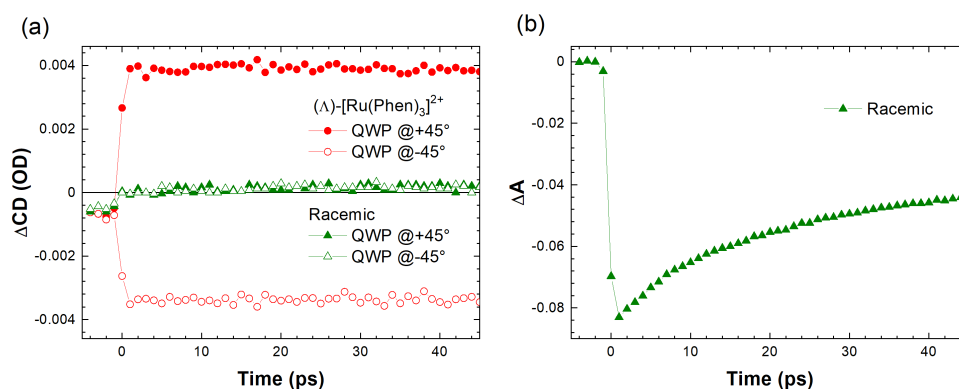


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Fig. 5. Δ CD kinetic traces averaged over 100 laser shots measured for (Δ) -[Ru(phen)₃]²⁺ in acetonitrile, at 270 nm, for different angles of the pump polarization with respect to the probe polarization, after excitation at 400 nm.

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Fig.5. shows the Δ CD signals of (Δ) -[Ru(phen)₃]²⁺ (Eq. 33) measured at 270 nm, for different angles of the pump polarization with respect to the probe polarization. The pump-induced LB leads to the observation of one antisymmetric peak around the time zero on the TRCD signals, as a function of the pump and probe polarization angle. This effect arises from the dependence of the TRCD signals with $\sin(2\phi)$ (Eq. 18) and thus disappears when the pump and probe polarizations are aligned ($\phi=0$). An alignment with a precision of 0.1° is found to properly eliminate the pump-induced LB (*i.e.* Δ CD < 5 μ OD, for the racemic mixture, for data acquisition over 500 laser shots). We found this alignment to be very robust to day-to day pump and probe alignment, as long as the angle of the input polarizer angle of the probe remains unchanged. Note that another strategy to eliminate the pump-induced LB would be to use depolarized pump pulses. However, generation of randomly polarized pump pulses with commercial depolarizers has proved ineffective to fully eliminate the pump-induced LB. An alternative strategy would be to use a common polarizer for the pump and probe, as previously done for subpicosecond ellipsometry with a Babinet-Soleil compensator [9, 10]. But under our current experimental conditions, this strategy has also proved ineffective to fully remove the pump-induced LB, probably because the polarizer has to be placed very close to the sample cell where the pump and probe beams are highly convergent.



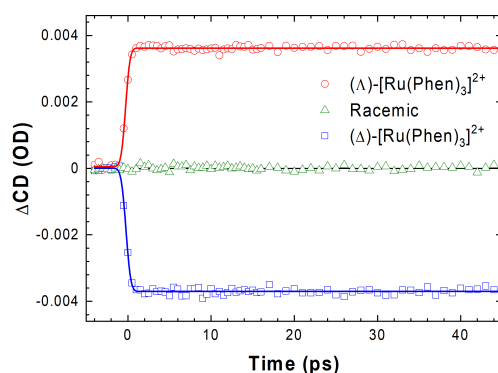
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Fig. 6. (a) Δ CD kinetic traces averaged over 250 laser shots measured at 270 nm, after excitation at 400 nm, for (Δ) -[Ru(phen)₃]²⁺ and the racemic mixture in acetonitrile, for a QWP orientation at +45° and -45°, respectively. $\Delta T = ca. 5\%$. (b) Corresponding ΔA kinetic trace measured for the racemic mixture.

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The great advantage of the balanced detection is that it does not require any modulation of the probe polarization, avoiding complex synchronization procedures to extract the TRCD signals.

443 However, as shown by the Jones calculations, such a detection may lead to specific artifacts
 444 due to imperfect separation of the two probe polarizations. Fig. 6.a illustrates effects of these
 445 artifacts on the Δ CD signals of (Λ) -[Ru(phen)₃]²⁺ and the racemic mixture measured for the two
 446 QWP orientations at +45° and -45°, respectively. It is worth noting that, in all cases, we observe
 447 residual negative signals on the order of 5×10^{-4} before the time zero. Origin of these signals has
 448 not been elucidated yet. We think they might stem from residual Δ A signals associated with the
 449 long-lived photoproduct that has not fully relaxed between two pump laser shots or residual
 450 sample pump scattering. In addition, as predicted by Eq. 30, imperfections of the balanced
 451 detection lead to the observation of dissymmetric Δ CD signals after the time zero,
 452 corresponding to an artefactual increase of the positive Δ CD signals and an attenuation of the
 453 negative ones. Concomitantly, the TRCD measurements performed on the racemic mixture
 454 exhibit small Δ CD signals after the time zero, that directly illustrates the imperfect separation
 455 of the achiral Δ A signals (Fig. 6b), as expected from Eq. 28. Importantly these artefactual
 456 signals before and after the time zero are found to be similar for the two QWP orientations and
 457 therefore can be easily removed by calculating their difference.



458
 459 Fig. 7. Δ CD kinetic traces averaged over 500 laser shots measured for (Δ) -[Ru(phen)₃]²⁺, (Λ) -[Ru(phen)₃]²⁺ and their
 460 racemic mixture, in acetonitrile at 270 nm, after excitation at 400 nm and correction for unbalanced detection
 461 artifacts. Solid lines represent the individual fits of the experimental data.

462 This is illustrated on Fig.7 which displays the Δ CD signals measured for (Λ) -[Ru(phen)₃]²⁺,
 463 (Δ) -[Ru(phen)₃]²⁺ and their racemic mixture in acetonitrile, after correction for the unbalanced
 464 detection artifacts (Eqs. 29 and 331). The Δ CD signal of the racemic mixture leads to a mean
 465 value of -3 μ OD (*i.e.* 0.1 mdeg) for data acquisitions over 500 laser shots. This result clearly
 466 shows that the TRCD measurements performed at the two QWP orientations can compensate
 467 for the imperfections of the balanced detection, before and after the time zero. Importantly, in
 468 contrast to static CD measurements, we do not observe any significant effect of the sample cell
 469 LB on the Δ CD signals of the two enantiomers, which are the mirror-image of each other. The
 470 observed changes in the Δ CD signals and their signs are consistent with an ultrafast (<100 fs)
 471 electronic relaxation pertaining from the intersystem conversion from the excited ¹MLCT state,
 472 which leads to a fast change of the CD in the excited state [28]. The associated Δ A changes are
 473 negative (see Fig. 6b), which indicate a dominant contribution of the ground state bleach arising
 474 from the ligand absorption band at 270 nm. In contrast to the Δ CD signals, which remain
 475 constant after excitation, the Δ A signals exhibit a 19-ps decay followed by a plateau. This decay
 476 time is comparable with the vibrational relaxation time of the formed ³MLCT state previously
 477 reported by the studies of the [Ru(bpy)₃]²⁺ complexes in acetonitrile studied by time-resolved
 478 resonance Raman spectroscopy and IR femtosecond spectroscopy [30, 31].

479 The fits of the Δ CD (Fig. 7) and Δ A kinetics (Fig. 6b) of the $[\text{Ru}(\text{phen})_3] \cdot 2\text{PF}_6$ complexes allow
480 to estimate the IRF of our TRCD set-up to 0.90 ± 0.05 ps. This spread of the IRF is essentially
481 due to the dispersion of the pump and probe pulses in the high extinction coefficient
482 polarization optics used to the precise control of their polarization. The fits allow to quantify
483 the Δ CD changes of the two enantiomers to values of ± 365 μOD . Thanks to the balanced
484 detection geometry, the laser probe fluctuations can be substantially compensated, which leads
485 to an accuracy on these TRCD measurements of 30 μOD , which is one order of magnitude
486 higher than that of our referenced achiral transient absorption measurements (300 μOD) for
487 data acquisition over 500 laser shots. This corresponds to an improvement by a factor 20 in the
488 data acquisition times in comparison with our previous time-resolved ellipsometry set-up using
489 a Babinet-Soleil compensator [14]. Typically, kinetics traces of Fig. 7 required acquisition
490 times of a few minutes *vs.* a few hours with our previous set-up using a Babinet-Soleil
491 compensator.

492 The present experimental results provide evidence that TRCD measurements performed for two
493 QWP orientations, respectively at $\pm 45^\circ$, fully correct artifacts inherent to the balanced detection
494 (Eqs. 21-31) and pump-induced LB (Eqs. 15-18), when pump and probe polarizations are
495 properly aligned. In addition, these differential measurements with and without the pump,
496 overcome the polarization artifacts typically encountered in static ellipsometry (Eqs. 19-20),
497 allowing artifact-free TRCD measurements to be performed in regular absorption cells. This is
498 a significant improvement compared to previous TRCD setups that usually require the use of
499 homemade weakly birefringent sample cells or even sample jets [2, 11, 14]. This also explains
500 the better accuracy we obtain for the TRCD measurements *vs.* the static CD measurements with
501 our balanced detection geometry. Thus, taken all together, these advantages allow us to propose
502 a simple and robust experimental set-up without any polarization modulation to access artifact-
503 free TRCD signals with a sub-picosecond time resolution.

504 **6. Conclusion**

505 We have described the first implementation of *non-null* ellipsometry with a balanced detection
506 geometry on a classical femtosecond pump-probe setup. The great advantage of this simple
507 detection geometry is that it does not require any polarization modulation, allowing
508 subpicosecond TRCD measurements with very reduced acquisition times (*i.e.* over 500 laser
509 shots) and an accuracy of 1 mdeg. Thanks to the rigorous control of the pump and probe linear
510 polarizations, we demonstrated the feasibility of artifact-free TRCD measurements in regular
511 quartz spectroscopic cells. These improvements represent an important technical progress
512 opening the way for the development of more amenable TRCD detections on ultrafast pump-
513 probe setups. One future challenge in the development of such a type of detection lies in the
514 improvement of its temporal resolution with the use of less dispersive polarization optics and
515 the pre-compensation of their chirp. A second challenge lies in the increase of the precision of
516 the TRCD measurements. Notably with the use of a high repetition-rate femtosecond Ytterbium
517 laser source as the probe, an accuracy of a few μOD in the TRCD measurements is expected to
518 be easily reached.

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528 **Disclosures**

529 The authors declare no conflicts of interest

530 **Supplemental document**

531 See Supplement 1 for supporting content.

532 **Data availability**

533 The data underlying the results presented herein are not publicly available currently but can be
534 obtained from the authors upon reasonable request.

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