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# 1 Photoexcitation Circular Dichroism in Chiral Molecules

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11 *many*

12 **Chirality is ubiquitous in nature and fundamental in science, from particle physics to meta-**  
13 **materials. The most established technique of chiral discrimination - photoabsorption circu-**  
14 **lar dichroism - relies on the magnetic properties of a chiral medium and yields an extremely**  
15 **weak chiral response. We propose and demonstrate a new, orders of magnitude more sen-**  
16 **sitive type of circular dichroism in neutral molecules: photoexcitation circular dichroism. It**  
17 **does not rely on weak magnetic effects, but takes advantage of the coherent helical motion**  
18 **of bound electrons excited by ultrashort circularly polarized light. It results in an ultra-**  
19 **fast chiral response and the efficient excitation of a macroscopic chiral density in an initially**  
20 **isotropic ensemble of randomly oriented chiral molecules. We probe this excitation without**

21 **the aid of further chiral interactions using linearly polarized laser pulses. Our time-resolved**  
22 **study of vibronic chiral dynamics opens a way to the efficient initiation, control and moni-**  
23 **toring of chiral chemical change in neutral molecules at the level of electrons.**

24 The macro-world gives us many examples of chiral dynamics created by helical structures  
25 which convert rotations in a plane into translational motion orthogonal to it, from the Archimedes  
26 screw to plane propellers and household fans. In the micro-world, the electrons bound inside chiral  
27 molecules should develop a similar helical motion when excited by planar rotation of the electric  
28 field of circularly polarized light. Electronic excitation by circularly polarized light has been used  
29 to distinguish right-handed from left-handed molecules since 1896 <sup>1</sup>. The technique, called the  
30 photoabsorption circular dichroism (CD) <sup>2</sup>, is based on the difference in the absorption of left-  
31 and right-circularly polarized light in chiral molecules and remains the go-to tool <sup>3</sup> for analysing  
32 properties of biological molecules, providing indispensable information on their structure, kinetics  
33 and thermodynamics, interaction with the environment and with other molecules. However, it does  
34 not rely on the helical nature of bound electron currents <sup>4</sup>, but uses the helical pitch of the light  
35 wave instead. This pitch, given by the wavelength of the absorbed light,  $\lambda \gtrsim 2500\text{\AA}$  ( $1\text{\AA} = 10^{-8}$   
36 cm), is barely noticeable on the molecular scale of  $\sim 1\text{\AA}$ , leading to very weak signals, three to  
37 four orders of magnitude less than the light absorption itself. Formally, the chiral-sensitive part of  
38 the light-induced excitation requires the excited electrons to respond to both the electric and the  
39 magnetic field of the light wave<sup>5</sup>, see Fig.(1a).

40 Remarkably, in spite of extraordinary recent advances in developing new methods for chiral

41 discrimination that do not rely on the magnetic properties of the medium <sup>7-18</sup>, none has relied on  
 42 detecting the helical motion of bound electrons. Is it possible to excite and probe such motion? We  
 43 demonstrate both theoretically and experimentally that one can (i) induce chiral stereodynamics of  
 44 bound electrons without the help of magnetic field effects, a new phenomenon we call PhotoeX-  
 45 citation Circular Dichroism (PXCD); (ii) probe it with linearly polarized light without the help of  
 46 the further chiral interactions that are usually presumed to be a prerequisite for chiral discrimina-  
 47 tion. Coherent excitation substitutes further chiral interactions at the probe step by coupling to a  
 48 different quantum state of the same chiral molecule.

## 49 **1 Exciting chiral dynamics in bound states**

50 A hallmark of helical motion of bound electrons is the appearance of an induced dipole orthogonal  
 51 to the polarization plane of the exciting circular light. We first show that an ultrashort pulse creates  
 52 such a dipole in a randomly oriented molecular ensemble. Let the electric field of the pulse,  
 53 rotating in the x-y plane, coherently excites two states (Fig.1b) of a chiral molecule. As shown in  
 54 the Supplementary Information (SI), the orientation-averaged induced dipole acquires the desired  
 55 component along the light propagation direction  $z$ :

$$d_z^{PXCD} \propto \sigma[\vec{d}_{01} \times \vec{d}_{02}] \vec{d}_{12} \sin(\Delta E_{21} t), \quad (1)$$

56 Here  $\vec{d}_{01}$ ,  $\vec{d}_{02}$  and  $\vec{d}_{12}$  are the dipole transition vectors connecting the ground  $|0\rangle$  and the two excited  
 57 states  $|1\rangle, |2\rangle$  (Fig. 1b),  $\Delta E_{21}$  is the energy spacing between the excited states. For more than two  
 58 states, Eq.(1) will contain the sum over all pairs of excited states  $n, m$ , leading to oscillations at all  
 59 relevant frequencies  $\Delta E_{nm}$ . As a function of time the induced dipole vector maps out a helix (Fig.

60 1b) and the z-component of the helical current is

$$j_z^{PXCD} \propto \sigma [\vec{d}_{01} \times \vec{d}_{02}] \vec{d}_{12} \Delta E_{21} \cos(\Delta E_{21} t). \quad (2)$$

61 Both  $d_z^{PXCD}$  and  $j_z^{PXCD}$  are quintessential chiral observables (see e.g. <sup>19,20</sup>). Indeed, both are

62 proportional to the light helicity  $\sigma = \pm 1$  and to the triple product of three vectors  $[\vec{d}_{01} \times \vec{d}_{02}] \vec{d}_{12}$ .

63 This product presents a fundamental measure of chirality: it changes sign upon reflection and thus

64 has an opposite sign for left and right enantiomers. For randomly oriented non-chiral molecules

$$65 \quad d_z^{PXCD} = j_z^{PXCD} = 0.$$

66 Eqs.(1,2) lead to the following conclusions. First, the coherent excitation of electronic states

67 leads to a charge displacement in the light propagation direction. Hence, a macroscopic dipole

68  $d_z^{PXCD}$  and the corresponding chiral density are created in the excited states, with a chiral cur-

69 rent oscillating out of phase for the two enantiomers. Second, PXCD requires no magnetic or

70 quadrupole effects. Hence, it is orders of magnitude stronger than standard photoabsorption CD.

71 While photoabsorption CD exploits the helical pitch of the laser field in **space**, PXCD takes ad-

72 vantage of the sub-cycle rotation of the light field in **time** and is inherently ultrafast. Indeed,

73 PXCD arises only if the excitation dipoles  $\vec{d}_{01}$ ,  $\vec{d}_{02}$  are non-collinear: for the angle  $\phi$  between

74 the two transition dipoles, the PXCD (Eqs. (1,2)) is proportional to  $\sigma \sin(\phi)$ . Since  $\sigma = \pm 1$ ,

75  $\sigma \sin(\phi) = \sin(\sigma\phi) = \sin(\sigma\omega\tau)$ , where  $\omega$  is light frequency and  $\tau = \phi/\omega$  is the required time for

76 the light field to rotate by the angle  $\phi$ . PXCD vanishes if the coherence between excited states  $|1\rangle$

77 and  $|2\rangle$  is lost and reflects dynamical symmetry breaking in an isotropic medium.

78 The oscillations of the PXCD signal Eqs.(1,2) appear to suggest that probing it requires the

79 combination of ultrafast time resolution and chiral sensitivity. We now show that time-resolving  
80 PXCD does not, in fact, require a chiral probe. The coherence underlying PXCD allows a chiral  
81 object to 'interact with itself', albeit in a different quantum state, thus mimicking interaction with  
82 "another chiral object" and removing any need for other chiral interactions during the probe step.  
83 One such non-chiral probe, termed PhotoExcitation-induced photo-Electron Circular Dichroism  
84 (PXECD), is introduced below.

## 85 2 Probing chiral dynamics in bound states

86 One way to probe the excited chiral density is to promote the chiral wave-packet to the electron  
87 continuum using a **linearly** polarized pulse (Fig 1c). As shown in the SI, the standard photoion-  
88 ization observable, the photoelectron current averaged over molecular orientations, is:

$$J_z^{PXECD}(k) = \sigma[\vec{d}_{01} \times \vec{d}_{02}] \vec{D}_{12}^r(k) \sin(\Delta E_{21}\tau) - \sigma[\vec{d}_{01} \times \vec{d}_{02}] \vec{D}_{12}^i(k) \cos(\Delta E_{21}\tau), \quad (3)$$

89 with  $J_x^{PXECD}(k) = J_y^{PXECD}(k) = 0$ . Here  $\tau$  is the pump-probe delay,  $\vec{D}_{12}(k) = \vec{D}_{12}^r(k) +$   
90  $i\vec{D}_{12}^i(k)$  is the Raman-type photoionization vector (see the SI) which connects the excited bound  
91 states via the common continuum and plays the role of  $\vec{d}_{12}$  of Eq.(1,2) and  $k$  is the photoelectron  
92 momentum.

93 First, the electron current Eq. (3) is proportional to the helicity  $\sigma$  of the pump pulse. Second,  
94 as transitions to the continuum are described by complex dipole vectors, it contains two triple  
95 products. Just like the triple product  $[\vec{d}_{01} \times \vec{d}_{02}] \vec{d}_{12}$  earlier, both  $[\vec{d}_{01} \times \vec{d}_{02}] \vec{D}_{12}^r$  and  $[\vec{d}_{01} \times \vec{d}_{02}] \vec{D}_{12}^i$   
96 will change sign upon reflection. Thus, the electron current reverses its direction if the handedness

97 of the pump pulse or of the enantiomer is swapped, showing that PXECD is a genuine chiral effect.  
 98 The chiral nature of the response arises only if the participating bound states are coherently excited.  
 99 Once the coherence is lost, the chiral signal will also disappear.

100 Importantly, the state of the continuum (Fig 1c) does not need to be chiral, as it only provides  
 101 a link between the two chiral bound states.  $J_z^{PXECD}(k)$  remains chiral even for a plane wave  
 102 continuum (see the SI), in this case  $\vec{D}_{12}(k)$  only has an imaginary component:

$$J_{z,PW}^{PXECD}(k) = -\sigma[\vec{d}_{01} \times \vec{d}_{02}] \vec{D}_{12}^{i,PW}(k) \cos(\Delta E_{21}\tau). \quad (4)$$

103 The total photoelectron current  $J_{tot}^{PXCD} = \int J_{z,PW}^{PXECD}(k) dk$  measures the helical current excited in  
 104 bound states  $j_z^{PXCD}$  (Eq. 2) distorted by the partial alignment of the molecular ensemble induced  
 105 by the pump (see the SI). One might think that partial alignment of the excited molecular ensemble  
 106 could already be fully responsible for enabling non-chiral probes of chiral dynamics. It is not true  
 107 in our case. Indeed, the effect of alignment persists for a single excited electronic state and for the  
 108 two excited electronic states with collinear dipoles, but in both cases it leads to zero PXECD cur-  
 109 rent. Finally, removing the effect of partial alignment from Eq.(4) shows that the PXECD current  
 110 remains chiral for every  $k$ , while  $J_{tot}^{PXCD}$  becomes directly proportional to the chiral component of  
 111 the helical current in bound states:  $J_{tot}^{PXCD} \propto j_z^{PXCD}$  (see the SI).

112 Probing the created chiral excitation using photo-electron imaging with linearly polarized  
 113 light constitutes yet another new phenomenon, PhotoExcitation-induced photoElectron Circular  
 114 Dichroism (PXECD). PXECD is reminiscent of the Photoelectron Circular Dichroism (PECD)  
 115 <sup>7-9, 16-18, 21</sup>, which arises when a circularly polarized light is used to photoionize a chiral molecule.

116 However, there is a fundamental difference. PECD can only exist if the molecular potential felt by  
117 the emitted electron is chiral <sup>7</sup> (the effect becoming negligible for photoelectron energies above 10  
118 eV), while the initial orbital may or may not be chiral at all <sup>22</sup>. It is also clear from the diagram of  
119 PECD in Fig 1 (d). The continuum state cannot merely serve as a non-chiral link, as in this case  
120 it will only mediate the coupling of the chiral object, the molecule in the ground state, "to itself"  
121 rather than to another chiral object.

122 In contrast to PECD, the PXECD requires neither chiral light, nor chiral scattering of the  
123 photo-electron. Since PXECD does not require the technically challenging use of ultrashort cir-  
124 cularly polarized XUV pulses <sup>23-27</sup>, it opens unique perspectives for ultrafast chiral-sensitive mea-  
125 surements using readily available linearly polarized UV and XUV light from table-top high har-  
126 monic generation sources, with no restrictions on photoelectron energies.

127 We shall now confirm both numerically and experimentally that our scheme provides a sen-  
128 sitive time-resolved probe of chiral molecular dynamics in bound states.

### 129 **3 Theoretical analysis in fenchone**

130 To quantify the PXECD effect we performed quantum mechanical calculations on fenchone molecules  
131 (see the SI). First, we simulated the PXCD phenomenon and calculated the excitation of the s- and  
132 p-manifold of Rydberg states in fenchone by a circular pump pulse. The resulting electron density  
133 of the Rydberg wave-packet is asymmetric in the  $z$ -direction in the momentum space. The asym-  
134 metry reverses if the helicity of the pump pulse or the handedness of the molecule is reversed. The



135 strength of the PXCD can be quantified by the magnitude of the chiral component of the excited  
136 electron density. It is obtained by subtracting the momentum space density  $D$  obtained with right  
137 (R) and left (L) polarized light:  $PXCD = 2(D(L) - D(R)) / (D(L) + D(R))$ . Even after averaging  
138 over molecular orientations, the calculated PXCD reaches very high values (35%, Fig. 2(a)). The  
139 asymmetry of the charge distribution corresponds to a macroscopic dipole moment  $d_z^{PXCD}$  which  
140 reaches 3 Debye (Fig. 2(b)) and oscillates at frequencies determined by the energy differences  
141 between the states forming the electronic wave-packet. The calculated pump-probe PXECD signal  
142 reveals these oscillations (Fig. 2c). While few-femtosecond pulses would be needed to resolve  
143 them, the PXECD signal can also be detected with much longer pulses. Fig. 2(d) shows that both  
144 PXCD and PXECD survive temporal averaging over 100 fs duration of a probe pulse.

#### 145 **4 Observation of PXECD in fenchone**

146 In our experiment, a circularly polarized femtosecond pump pulse at 201 nm (6.17 eV photon  
147 energy, 80 meV at 1/e bandwidth) photoexcites enantiopure fenchone molecules from a supersonic  
148 gas jet in the interaction zone of a velocity map imaging spectrometer. The molecules are excited  
149 to their first (*s*- and *p*-) Rydberg bands through single-photon absorption (Fig. 3 (a), see the SI).  
150 A time-delayed, linearly polarized probe pulse at 405 nm (3.1 eV photon energy, 35 meV FWHM  
151 bandwidth) induces one-photon ionization of the excited molecules. The cross-correlation of the  
152 pump and the probe pulses is 170 fs. The photoelectrons are accelerated and projected by an  
153 electrostatic lens onto a set of dual microchannel plates and imaged by a phosphor screen and  
154 a CCD camera. The photoelectron images are recorded alternatively using left (LCP) and right

155 (RCP) circularly polarized pump pulses. The difference (LCP-RCP) and sum (LCP+RCP) of these  
 156 two images are reconstructed using a least-square fitting algorithm (see the SI). We define the  
 157 PXECD signal as  $PXECD = \frac{2(LCP-RCP)}{(LCP+RCP)}$  and the photoelectron spectrum (PES) as  $PES =$   
 158  $(LCP + RCP)/2$ . Both are shown in Fig. 3(b) for a 200 fs pump-probe delay. As expected, a  
 159 significant PXECD signal is observed, reaching 1 %<sup>28</sup> in good agreement with our calculations  
 160 (Fig. 2(d)).

161 The photoelectron spectrum contains a single broad component, corresponding to ionization  
 162 from the outermost orbital (vertical ionization potential 8.72 eV). The position of this component  
 163 does not shift with the pump-probe delay (Fig. 4 (b)) and decays in 3.3 ps, reflecting simple vi-  
 164 bronic relaxation of the Rydberg population onto lower states which cannot be photoionized by  
 165 the 3.1 eV probe photons. The temporal evolution of the PXECD image shows much richer spec-  
 166 troscopic features, which can be analyzed by decomposing it in odd Legendre polynomials (Fig.  
 167 4(a)). We note that a sum of first- and third-order Legendre polynomials, with coefficients  $\alpha$  and  
 168  $\alpha'$ , is enough to get the PXECD images. Both coefficients maximize around  $\sim 50$  meV below  
 169 the maximum of the PES. The PXECD signal (Fig. 4(b)) can be decomposed into two compo-  
 170 nents: below and above the maximum of the PES. The low-energy component of  $\alpha$  undergoes a  
 171 rather smooth decay. On the contrary, its high-energy component decays very quickly and even  
 172 changes sign around 1 ps. For  $\alpha'$  the behaviour is opposite, *i.e.* the high-energy component shows  
 173 much slower dynamics than the low-energy part. Such time- and electron energy- dependent be-  
 174 haviour is characteristic of internal vibrational torsional motion and may indicate the change of the  
 175 chiral structure of the molecule induced by such motion. Indeed, the electronic excitation of the

176 molecules is expected to be accompanied by a significant vibrational excitation, since the equilib-  
177 rium geometries of the 3s and 3p Rydberg states are quite different from that of the ground state.  
178 The molecules will tend to relax towards the equilibrium geometry of the Rydberg states, and os-  
179 cillate around it. Figure 5 illustrates the influence of this change of molecular geometry on the  
180 calculated PXECD signal. Even small bond length changes ( $\leq 7\%$ ) lead to significant modifica-  
181 tion of the PXECD signal. This demonstrates the remarkable sensitivity of PXECD to molecular  
182 vibrations, which follow the electronic excitation. At 4 ps (not shown), the PXECD completely  
183 vanishes while the Rydberg population is still significant. This result unambiguously reflects the  
184 loss of wave-packet coherence which halts chiral dynamics in our experiment.

## 185 **5 Vibrational PXCD: experiments in camphor**

186 Is it possible to create PXCD from purely vibrational excitation of a chiral molecule? Theoretically,  
187 the two excited states in Eqs.(1,2) needed for PXCD do not have to be different electronic states.  
188 Vibrational states within the same electronic state can also fulfil the PXCD condition as long as  
189 their dipoles are not collinear, see Eqs. (1,2). As shown in the SI, this requires the breakdown  
190 of the Franck-Condon approximation, which is caused by a strong dependence of the electronic  
191 wave-function on the position of the nuclei. In turn, such dependence leads to the appearance of  
192 electronic currents stimulated by the nuclear motion, which is triggered by the pump pulse. Thus,  
193 vibrational PXCD is intertwined with the underlying chiral motion of electrons. Note that this  
194 strong dependence of the electronic wave-functions on the nuclear positions naturally arises in  
195 the vicinity of conical intersections between electronic potential surfaces. Thus, we expect that

196 PXECD could be used to excite and reveal coherent chiral dynamics at conical intersections.

197 To gain further insight into the role of electronic versus vibrational dynamics in PXECD, we  
198 performed measurements in (1R)-(+)-camphor, a very similar structural isomer of fenchone. The  
199 *s*- and *p*- Rydberg bands of camphor are upshifted by additional several tens of meV compared  
200 to fenchone, preventing direct excitation of the *p*- states and thus of an electronic chiral wave-  
201 packet. Nevertheless, the experiment still reveals a strong PXECD signal, indicating that a chiral  
202 vibronic wave-packet has been created in the *s*- Rydberg band of camphor. The  $\alpha'$  coefficients in  
203 camphor and fenchone are of opposite sign as seen in multiphoton<sup>29</sup> and one-photon PECD<sup>17</sup>.  
204 In our experiment, this could be a consequence of PXECD sensitivity to isomerism (see Figure 5  
205 to gauge the sensitivity to nuclear configuration), but it could also be a signature of the different  
206 nature of the excited chiral electronic currents in fenchone and camphor. Changing the excitation  
207 wavelength from 202 nm to 200 nm does not affect the monoexponential decay of the PES. In  
208 contrast, a strong change is observed in the PXECD: the  $\alpha'$  magnitude is almost twice as large  
209 and it is shifted in energy towards the red wing of the photoelectron spectrum. The drastic change  
210 observed in the PXECD signal in camphor once the pump photon energy is increased by only 60  
211 meV illustrates the extreme sensitivity of this measurement to the excited vibrational dynamics.

## 212 **6 Conclusions and outlook**

213 We have demonstrated two new phenomena. First, we have shown the efficient excitation of  
214 a macroscopic bound chiral electron density in the excited states of randomly oriented chiral

215 molecules without the help of magnetic interactions (the PXCD phenomenon). In the dipole ap-  
216 proximation the chiral pitch of circularly polarized light vanishes. This means that the creation of  
217 the macroscopic chiral density in the isotropic ensemble of chiral molecules is based not on the  
218 helical structure of light, but on its planar rotation.

219         Second, we have shown that the resulting chiral dynamics can be probed without the help of  
220 further chiral interactions and thus in an efficient and versatile way. The detection relies on photo-  
221 electron circular dichroism arising from the ionization of excited molecules by linearly polarized  
222 light pulses (the PXECD phenomenon), but is not limited to this scheme. The application of a  
223 linearly polarized XUV probe in PXECD would enable genuine probing of ultrafast chiral bound  
224 dynamics, since PXECD does not require chiral interaction in the continuum, which becomes neg-  
225 ligible for sufficiently high-energy electrons.

226         The ensemble-averaged chiral charge density arising in PXCD implies asymmetry in charge  
227 distribution along the light propagation direction. Depending on the medium density, this could  
228 lead to a very large coherently oscillating macroscopic dipole. The phase of this oscillation is  
229 opposite for two enantiomers, leading to macroscopic enantio-sensitive effects. The existence  
230 of the enantio-sensitive macroscopic dipole opens the way to the separation of enantiomers in  
231 isotropic racemic mixtures in the gas phase.

232         The PXCD phenomenon opens the way to direct visualization of chiral electronic density us-  
233 ing time-resolved X-ray diffraction imaging, both in the gas and condensed phase. Intense ultrafast  
234 sources of X-ray radiation, such as Free Electron Lasers, combined with measurements, sensitive

235 to valence-shell dynamics in the gas phase<sup>30</sup> should lead to few-fs time resolution of chiral charge  
236 dynamics.

237 Finally, PXCD could be used to drive molecular reactions in chiral systems in a stereo-  
238 specific way, by imprinting a chiral torque via the helicity of the exciting circularly polarized pulse.  
239 The ultrafast charge dynamics triggered by coherent electronic excitation is reminiscent of ultrafast  
240 charge migration triggered by photo-ionization<sup>31–34,36–38</sup> recently observed in ref.<sup>39</sup> and speculated  
241 to underlie charge-directed reactivity in cations<sup>35</sup>. Chiral electron stereo-dynamics in neutral  
242 molecules may open similar opportunities for controlling charge and energy flow in molecules  
243 at the level of electrons, offering new perspectives for such intriguing problems as asymmetric  
244 synthesis, a major challenge in stereochemistry.

## 245 **Methods**

246 An Even-Lavie valve is used as a pulsed enantiopure fenchone source with helium as carrier gas  
247 to avoid cluster formation. (1R)-(-) and (1S)-(+)-fenchone correspond to (1R,4S) and (1S,4R) fen-  
248 chone respectively. The 170 fs cross-correlation time as well as the 0 fs delay are determined on the  
249 lightest fragment  $C_4H_5O^+$  produced by dissociative ionization with both linearly polarized pump  
250 and probe. The high voltage of the repeller electrode was -3kV for the experiment done in fen-  
251 chone and only -2kV for the experiment done in Camphor, which increases the energy resolution.  
252 Note that the latter, along with the energy calibration, that has been determined by photoionizing  
253 krypton. Typically the energy resolution is 80 meV at 0.7 eV kinetic energy. The presented re-  
254 sults are obtained by scanning the pump-probe delays typically 30 times. At each delay, helicity is

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263 4. For non-magnetic materials, light absorption is proportional to the scalar product of the in-  
264 duced polarization current and electric component of the light field. Thus, even if the motion  
265 of bound electrons underlying the induced current were helical, moving out of the polarization  
266 plane of the circular light, it would have not contributed to the CD signal. For magnetic materi-  
267 als light absorption includes an additional term: a scalar product between magnetic field vector  
268 and the time-derivative of induced magnetization. It does not change our conclusion: CD is  
269 only sensitive to electron dynamics in light polarization plane also for magnetic materials.

270 5. Electric quadrupole effects vanish in isotropic ensembles of chiral molecules <sup>6</sup>.

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## 377 **8 Additional information**

378 **Competing Interests** The authors declare that they have no competing financial interests. Requests  
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382 S.B., A.C., R.G., Y.M., V.B., performed the experiment. D.D. and S.P. operated the laser system.  
383 S.B., A.C., B.F., G.G., L.N., B.P., Y.M. and V.B. analyzed the data. B.F. and B.P. performed the  
384 molecular geometry and dynamical calculations. A.H., Z.M. and O.S. developed the analytical

385 theory, A.F.O. and O.S. derived chirality measures for PXCD and PXECD. S.B. wrote the first  
386 version of the manuscript, all authors contributed to writing the manuscript.

387 **FIGURE 1:** Chiral discrimination schemes. C.C. denotes complex conjugated, i.e. time-  
388 reversed process. Downarrows denote C.C. of driving fields. (a) CD requires magnetic dipole  
389 transition up and electric dipole transition down and vice-versa. (b) PXCD (Eq.1) requires coher-  
390 ent excitation of two states by ultrashort circularly polarized pulse. The stimulated dipole transition  
391 to state  $|2\rangle$  is followed by dipole transition to state  $|1\rangle$  and stimulated dipole transition to state  
392  $|0\rangle$ . Insert: Induced dipole maps out a helix as a function of time. (c) In PXECD (Eq.3) the two  
393 excited states are connected by Raman-type transitions via continuum, stimulated by linearly po-  
394 larized pulse. (d) PECD requires circularly polarized light and photoelectron scattering off chiral  
395 potential  $V_{ch}$ .

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398 **FIGURE 2:** Theoretical analysis of electron chiral dynamics in (1S)-(+)-fenchone. (a) Mo-  
399 mentum space electron density underlying PXCD. The asymmetry signifying chirality of the elec-  
400 tron density is formed in light propagation direction  $z$ . (b) Temporal evolution of the  $x$ -,  $y$ - and  
401  $z$ -components of the macroscopic dipole associated with the (3s,3p) Rydberg wave-packet created  
402 by a pump pulse (shaded area). Only the  $z$ -component, along the direction of propagation of the  
403 pump and probe pulses, survives orientational averaging. (c) Momentum space PXECD signals at  
404 various pump-probe delays  $t$ . (d) Time-averaged PXECD to account for the temporal resolution of  
405 the experiment.

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408 **FIGURE 3 : PXECD in fenchone molecules.** (a) Absorption of circularly polarized pulse at  
409 201 nm with helicity  $\sigma = \pm 1$  promotes an electron from the highest occupied molecular orbital to  
410 the *s*- and *p*- Rydberg bands, creating a chiral electron wave-packet. A linear probe pulse at 405  
411 nm photoionizes the molecule, revealing the chiral asymmetry of the Rydberg wave-packet in the  
412 angular distribution of the photoelectrons. The absorption spectrum of fenchone is adapted from  
413 <sup>40</sup> (b) Experimental image of photoelectron spectrum (PES) and PXECD images at 200 fs pump-  
414 probe delay for (1S)-(+)-fenchone. The characteristic forward-backward asymmetry is observed  
415 in light propagation direction *z*.

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418 **FIGURE 4:** Time-Resolved PXECD in fenchone and camphor. (a) Legendre polynomi-  
419 als decomposition of the PXECD image for (1S)-(+)-Fenchone at 200 fs pump-probe delay. The  
420  $\alpha, \alpha'$  coefficients are multiplied by their associated Legendre polynomials  $P_i(\theta)$ :  $P_1 = \cos(\theta)$ ,  
421  $P_3 = (5/2 \cdot \cos^3(\theta) + 3/2 \cdot \cos(\theta))$ . (b) Evolution of the PES and PXECD coefficients as a func-  
422 tion of pump-probe delay, in (1S)-(+)-fenchone with 201 nm pump, (1R)-(+)-camphor with 202  
423 nm pump and with 200 nm pump. The black dotted lines represent energies corresponding to the  
424 maximum of PES.  $\alpha$  and  $\alpha'$  are normalized to the maximum value of PES.

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427 **FIGURE 5:** Sensitivity of PXECD in (1S)-(+)-fenchone to the evolution of the chiral molec-  
428 ular structure. (a) The equilibrium geometries of the ground (dark) and 3s (shadowed) electronic  
429 states, and the PXECD signal computed at the ground state geometry for both pump excitation  
430 and probe ionization. (b) The representation of the geometries are exchanged and the PXECD is  
431 computed assuming that pump excitation occurs at the ground state geometry while probe ioniza-  
432 tion occurs once the vibronic wave-packet has reached the 3s equilibrium geometry. The PXECD  
433 image is averaged over random molecular orientations and the 100 fs duration of the probe pulse.

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