Using chiral light pulses to probe ultrafast molecular dynamics

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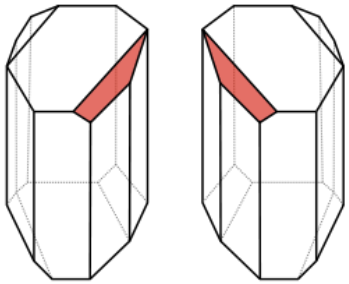
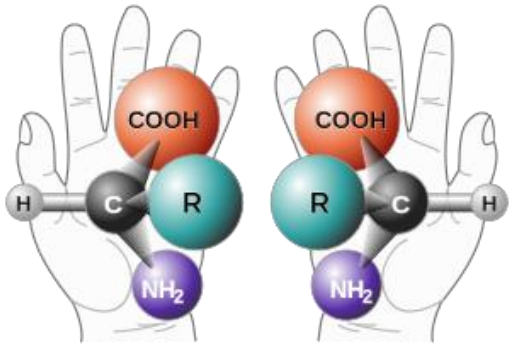
Chirality

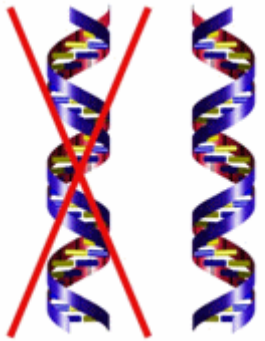
- A chiral object lacks an internal plane of symmetry and its mirror image cannot be superposed by rotations alone.



- Chirality chemistry recognised since Pasteur
- Chiral molecules (enantiomers) have almost identical physical properties. Parity violation of weak force results in $\Delta E \approx 10^{-16}$ eV
- Life is homochiral!



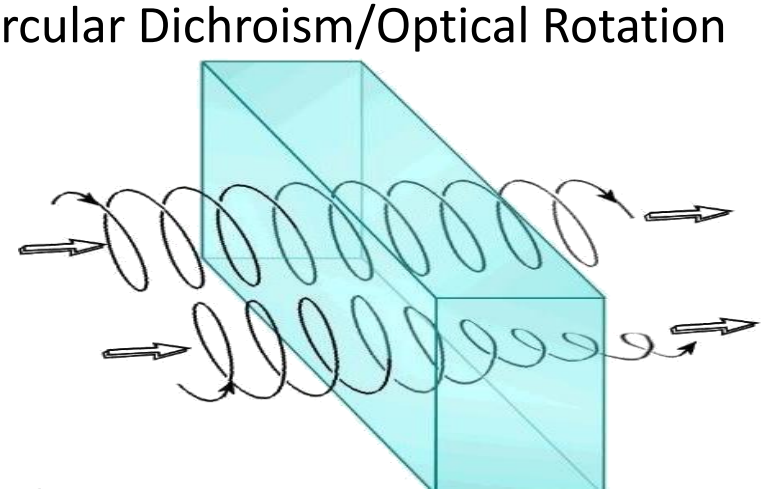
Amino acids

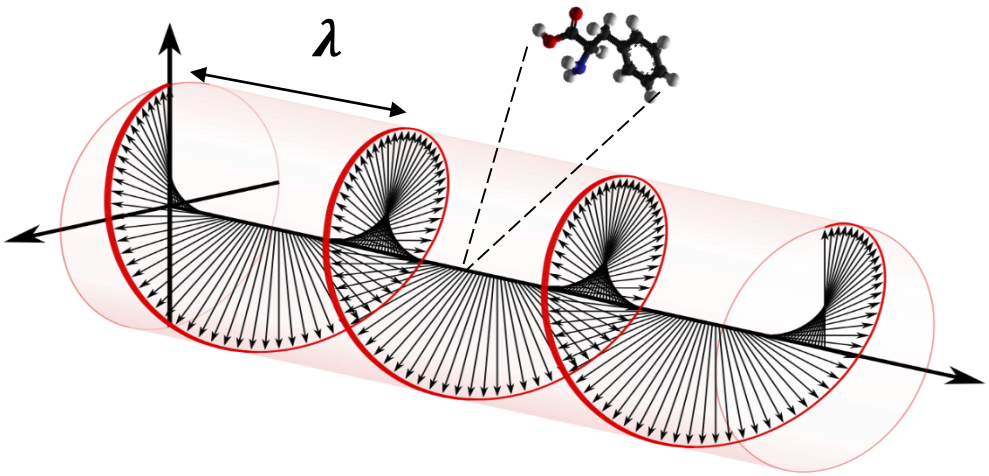


Chiral Light Interactions

- Enantiomers can only be identified through interaction with another chiral object, e.g. circularly polarised light

Circular Dichroism/Optical Rotation

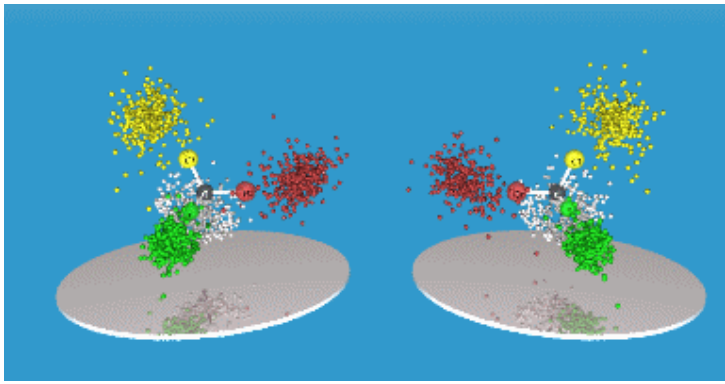




- Chiral discrimination poor (≈0.1%)
- Chiral interaction of optical light is weak
- **Need new light sources and phenomena manifested via electric dipole interactions → for studying ultrafast molecular chirality**

Chiral Electric Dipole Interactions

- X-ray regime increases circular dichroism → few %
  e.g. Rouxel et al., *Struct. Dynam.* **4**, 044006 (2017)
- Direct, coulomb explosion imaging
  Pitzer et al., *ChemPhysChem*, 17, 2465 (2016)



- Photo-Excitation Circular Dichroism (PXCD)
  S. Beaulieu et al., *Nat. Phys*., 14, 484 (2018)

- Photo-Electron Circular Dichroism (PECD)

Photo-Electron Circular Dichroism (PECD)

- "Normal" photoelectron spectroscopy

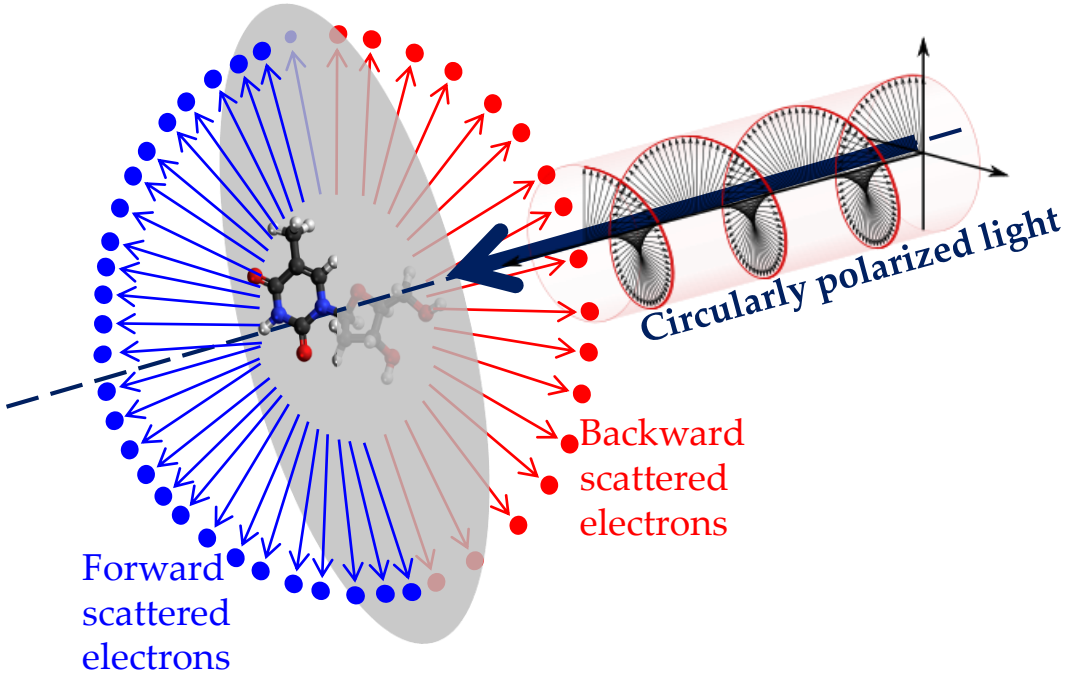
  $I(\theta) \propto 1 + \beta\, \mathrm{P}_2(\cos\theta)$ linear polarization

  $I(\theta) \propto 1 - \frac{\beta}{2}\, \mathrm{P}_2(\cos\theta)$ circular polarization

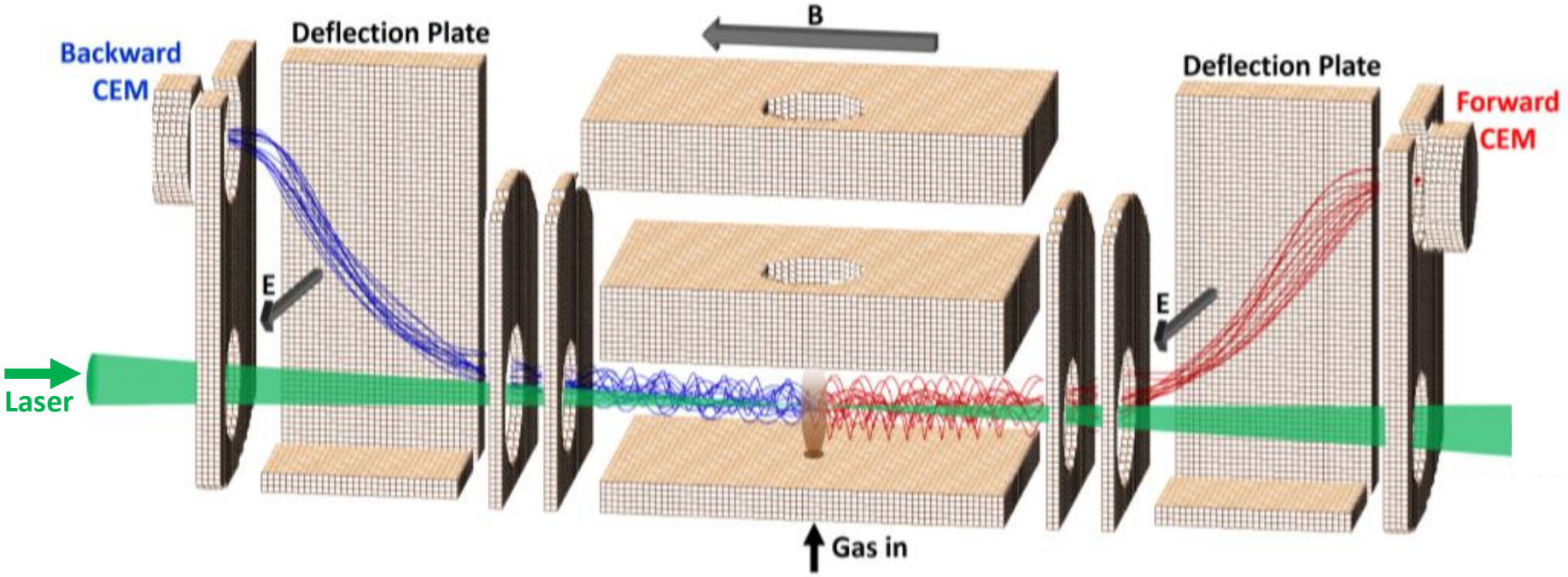
- PECD

  $I(\theta) \propto 1 + \boldsymbol{D\cos\theta} + \frac{\beta}{2}\, \mathrm{P}_2(\cos\theta)$ circular polarization

  Ritchie, PRA,13, 1411 (1976)



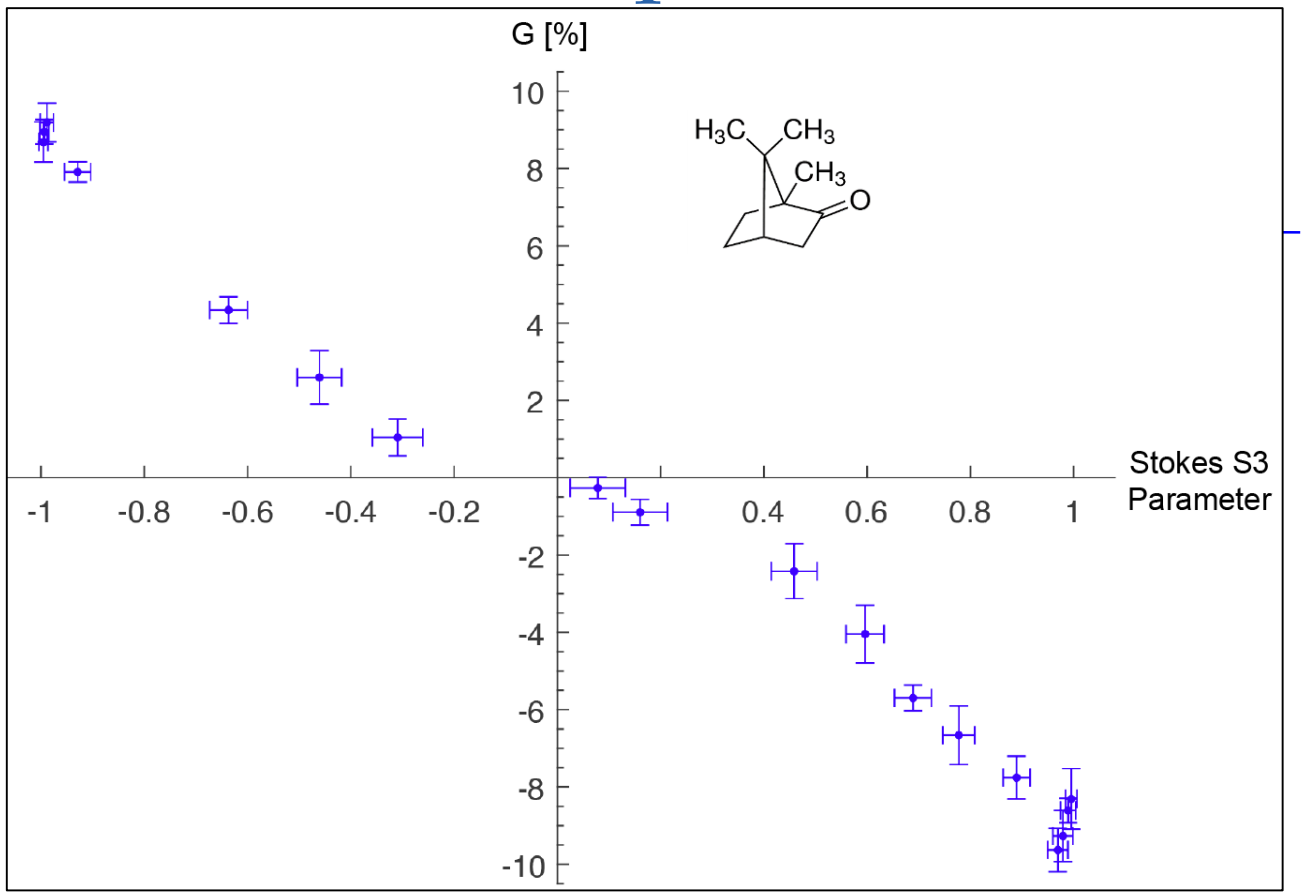
Observing PECD

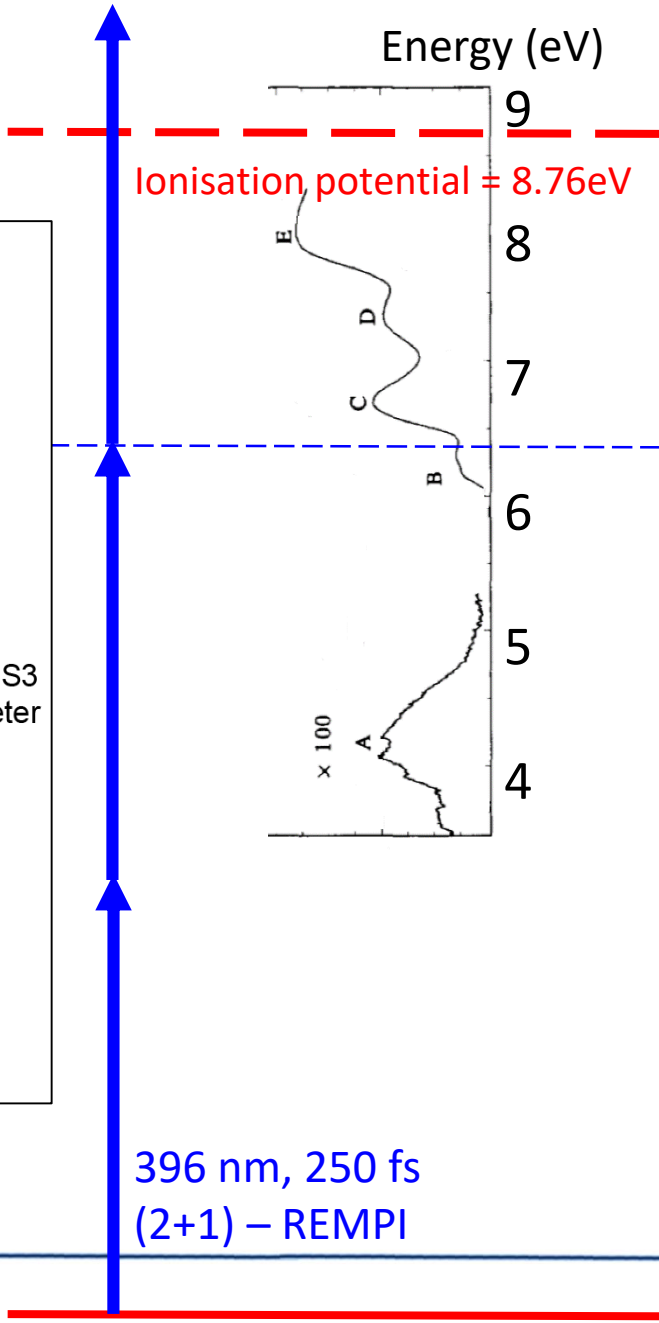


Belfast Stereo-Electron Detector

Miles et al., Analytica Chimica Acta, **984**, 134 (2017)

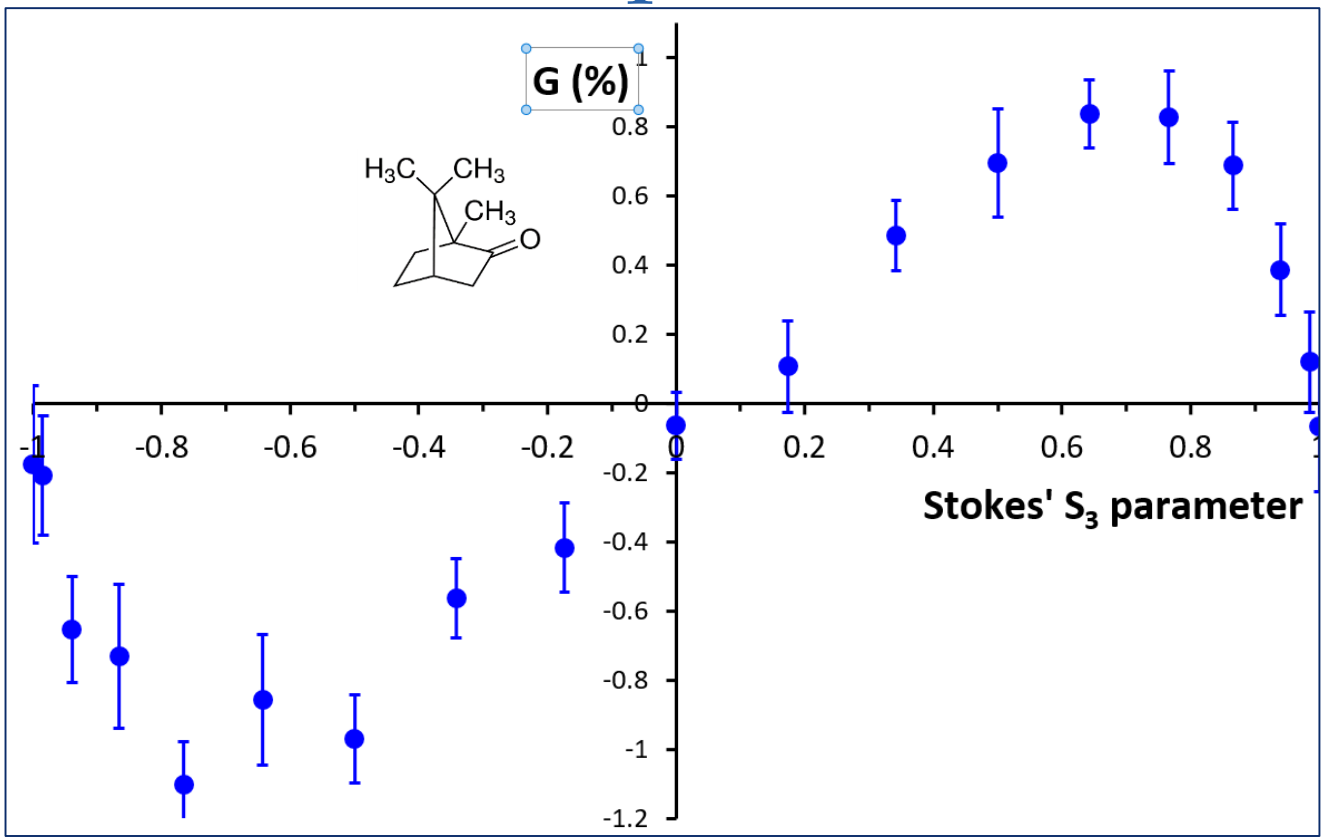
Ellipticity Dependence Camphor

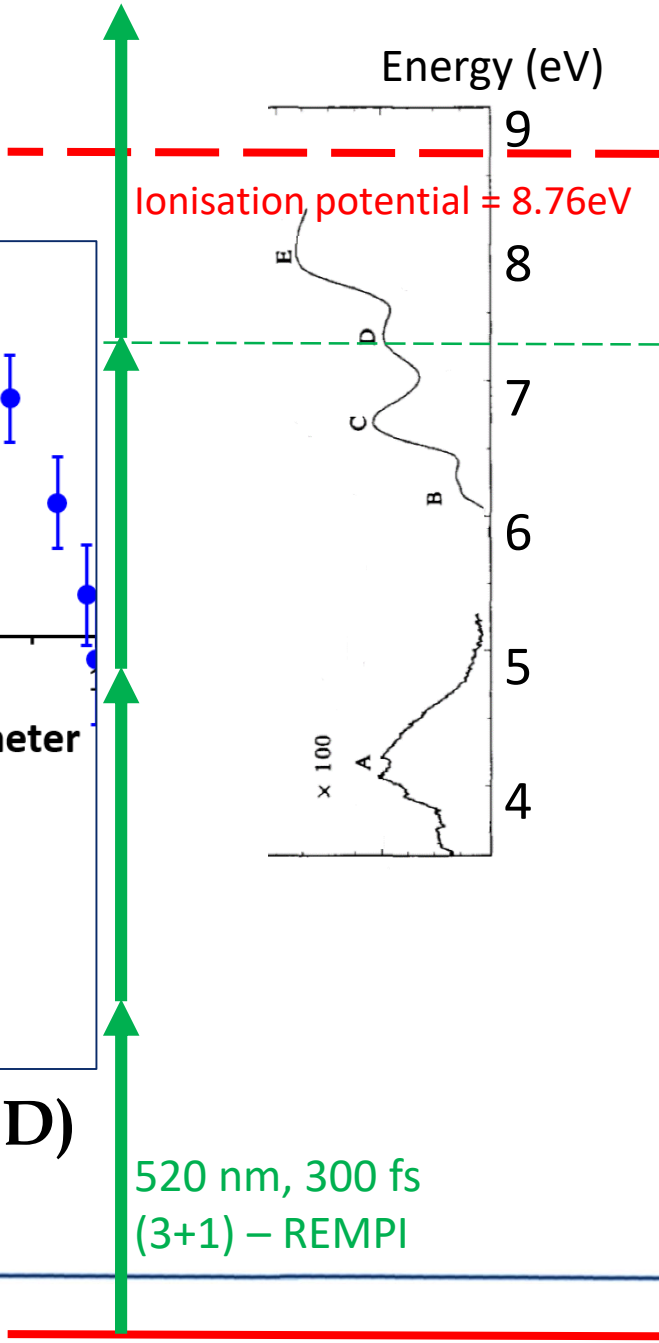




J. Miles et al., Anal. Chim. Acta, **984**, 134 (2017)

Ellipticity Dependence Camphor





Photoelectron Elliptical Dichroism (PEELD)

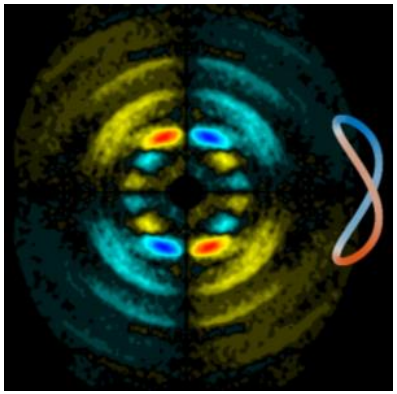
A. Comby et al., Nat. Comm., 9, 5212 (2018)

PECD – A Sensitive Observable

- **Highly sensitive to molecular structure**
  - Vibrational state
  - Isomerization
  - Clustering
  - Conformation
  - Molecular Orientation
- **Discovered in Various Ionization Regimes**
  - Single Photon Ionisation
  - Multi-Photon Ionisation
    - Resonant (REMPI)
    - Non-resonant
  - Tunnelling Ionisation

Shaping the Chiral Light Field

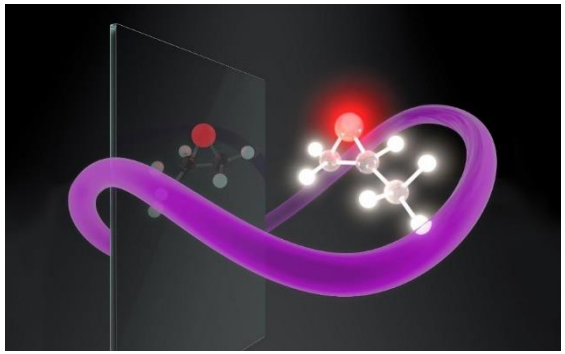
- $1\omega + 2\omega$ laser field allow sub-cycle chiral control



Rozen et al., PRA 9, 031004 (2019)

http://harmodyn.celia.u-bordeaux.fr/

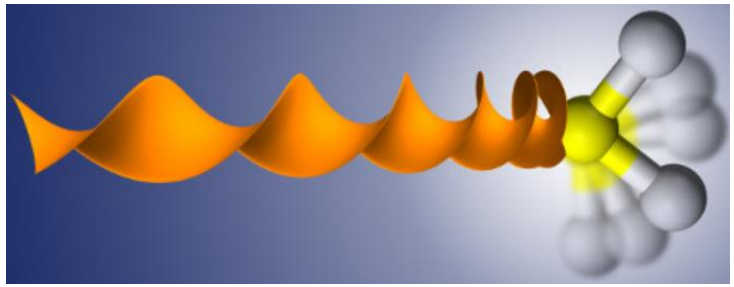
- Synthesize a 3D chiral field $\rightarrow$ electric dipole response



Ayuso et al., Nat. Phot. (2019)

https://scitechdaily.com/and-the-scientist-said-let-there-be-light-and-there-was-synthetic-chiral-light/

- Optical centrifuge – induced chirality



Owens et al., PRL, 121, 193201 (2019)

Potential of FELs

- **FEL Probe – Ultrafast Molecular Dynamics**
  - Sensitive, site-specific, inner-shell PECD
  - X-ray diffraction imaging of molecular dynamics
  - Coulomb explosion imaging
- **Combine with Optical Laser Pulses**
  - Control position, orientation, and chirality of molecules
  - Production/control of local and global chirality in pulses
  - Exploit chiral electric dipole interactions

Fundamental Questions/Challenges

- **Origin of Nature's homohirality**
  - How did enantiomeric balances first form in primordial solar system?
  - Selective photo-destruction
  - Enantiomeric separation via asymmetric PECD recoil
- **Fundamentals of Dynamic Molecular Processes**
  - Can chiral interactions, e.g. PECD, provide highly sensitive, site specific observables?
  - Can theory accurately model these interactions and yield insight?
- **Optical Synthesis and/or Separation of Enantiomers**
  - Optical fields to induce, control or flip enantiomeric state
  - Use optical forces of chiral light for physically separation

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