# Time-resolved Circular Dichroism in the Angular Distributions (CDAD) of photoelectrons produced by the photoionization of chiral molecules

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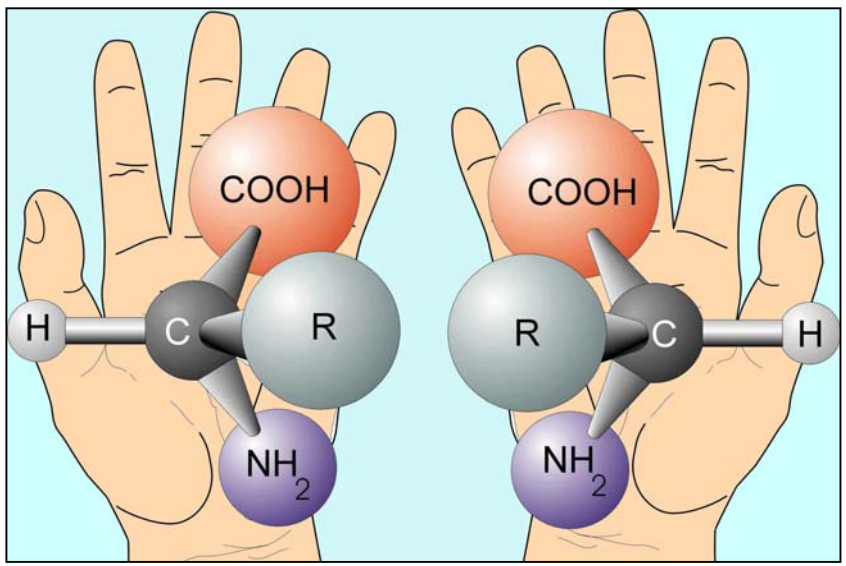



Ex : amino-acids, Sugars (DNA)

**Physical properties : OR, CD**

**Chemical properties :**
**Chiral recognition (Asym. reactivity)**

**Fundamental process of metabolism**

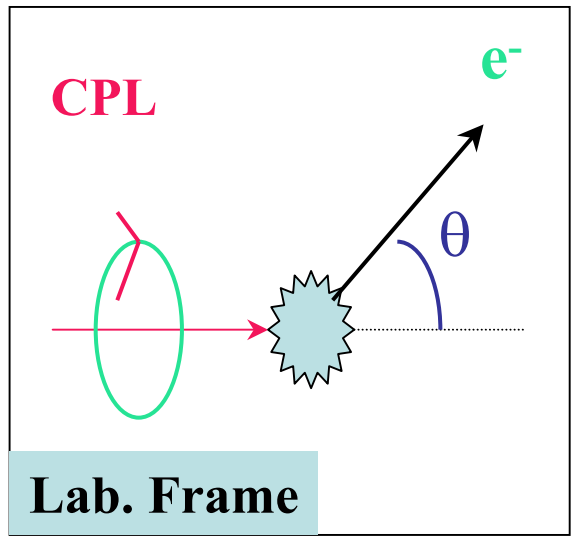
## General context : homochirality of life

# A new form of CD : Circular Dichroism in the Angular Distributions (CDAD) of photoelectrons from Randomly-oriented chiral molecules

**Chirality** ⟺ **Photoionization**

**CDAD (E1) : $I(\theta) = 1 + b_1P_1(\cos\theta) + b_2P_2(\cos\theta)$**

- $b_1 \neq 0$ if chiral molecule + CPL
- $b_1$ --> $-b_1$ if $S_3$ --> $-S_3$ or S <--> R




**Calculations : I. Powis, JCP 112, 301 (2000))**

- CDAD : 0 to few 10 % !! Especially for KE < 15 eV
- Molecular orbital dependant

**Experiment :Bowering et al., PRL 86, 1187 (2001)**

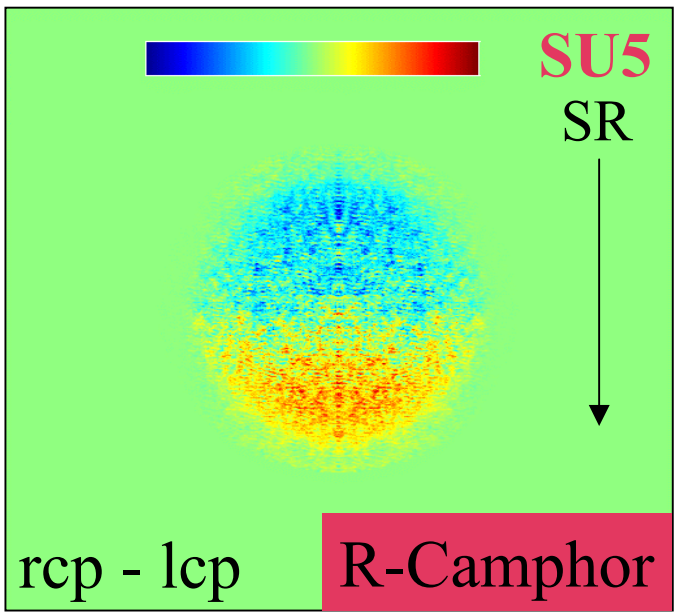
- 3 % (2b1) @ 16.2 eV on bromocamphor

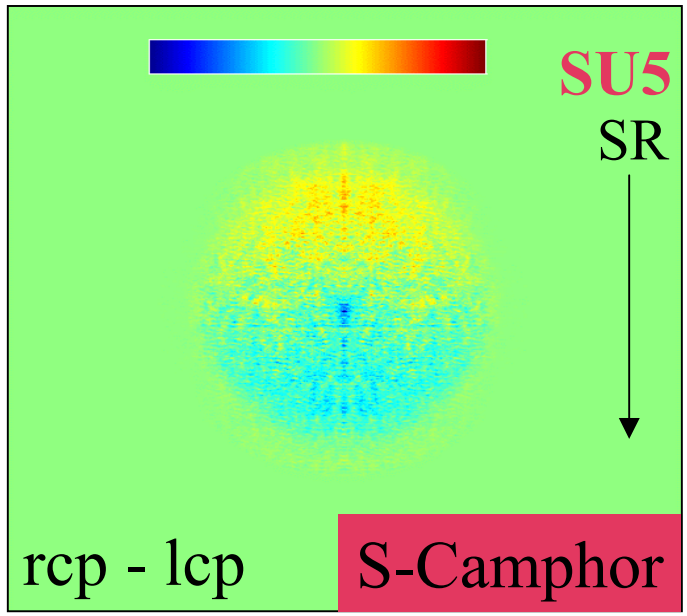
**Interests**

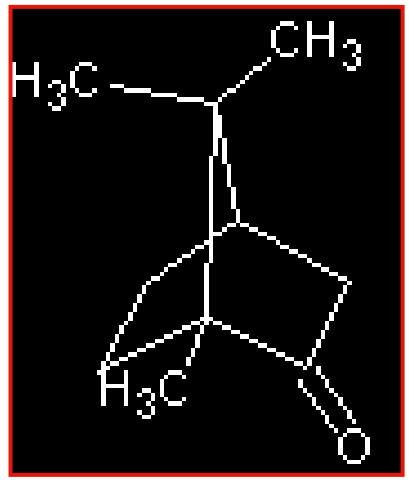
- Fundamental : Structure of molec. Potential, orbital localization, complete experiment
- Analytical : isomer/enantionmer-dependant --> Medecine, pharmacology, food industry

# CDAD of Camphor (HOMO orbital) @ 9.2 eV

**Collab. with D. Dowek and JC Houver (LCAM) : PEPICO velocity spectrometer**



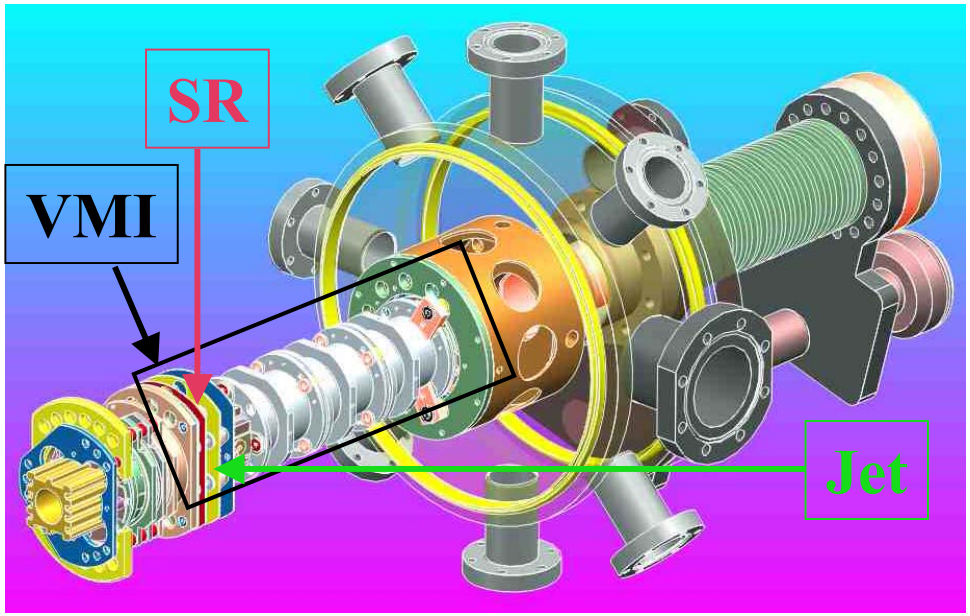

**CDAD : 3 % ($2b_1$)**

G. Garcia, L. Nahon, M. Lebech, J.-C. Houver, D. Dowek and I. Powis, J. Chem. Phys **119**, 8781 (2003)

**Output :**

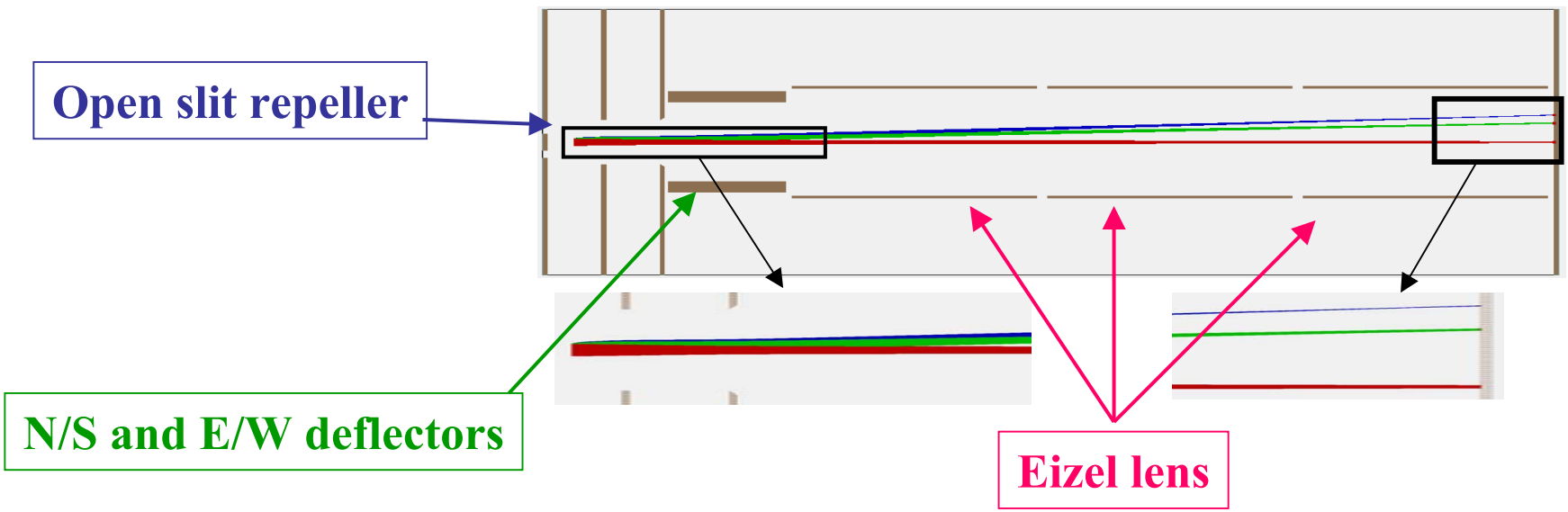
- **CDAD is macroscopic**
- **R /S Antisymetric**
- **Imaging techniques well adapted --> $b_1$ and $b_2$**

# A new imaging PEPICO Set-up : DELICIOUS

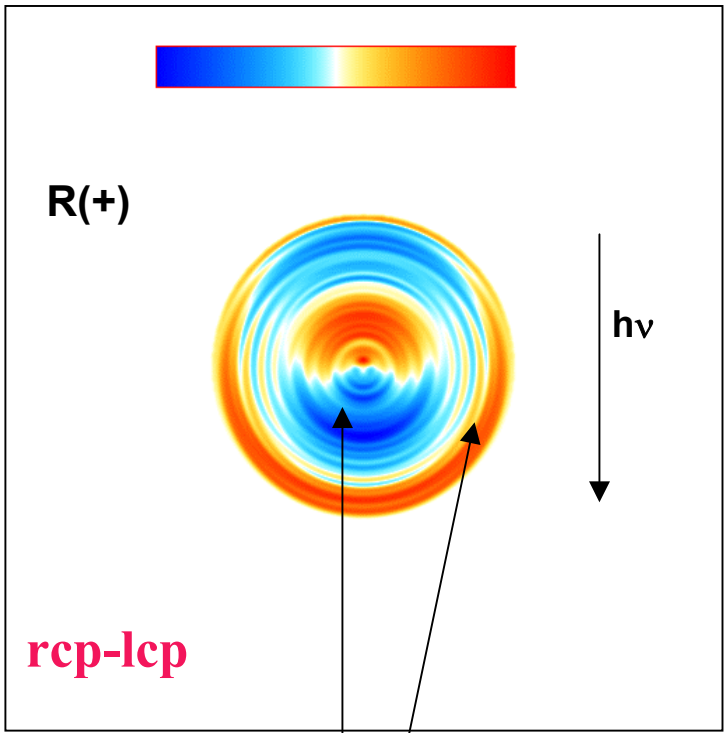


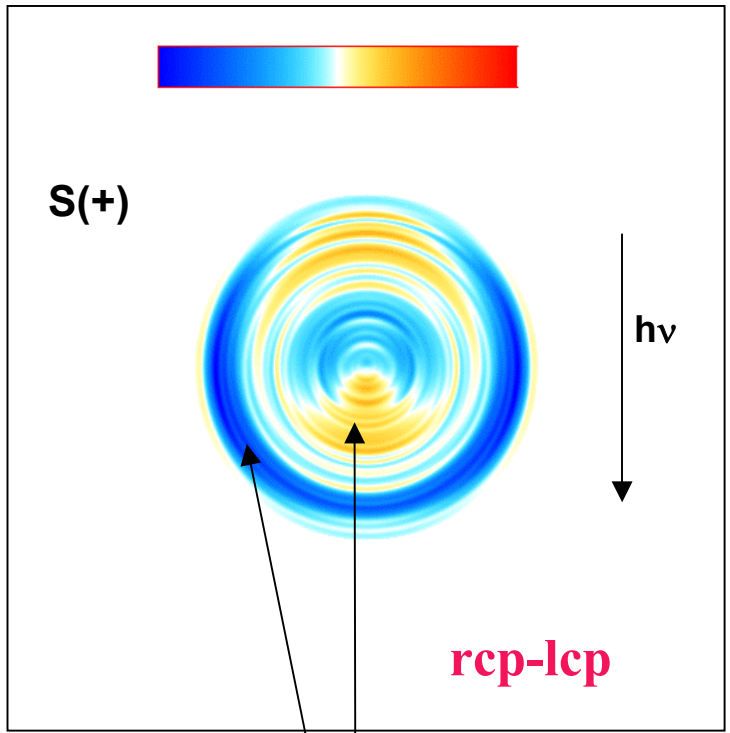

**D**ichroism and
**EL**ectron
**I**on
**C**oincidences in
**IO**nization
**U**sing
**S**ynchrotron

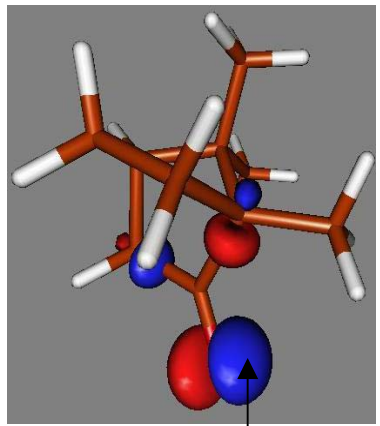
KE : 0 - 15 eV



# CDAD of Camphor @ 10.3 eV



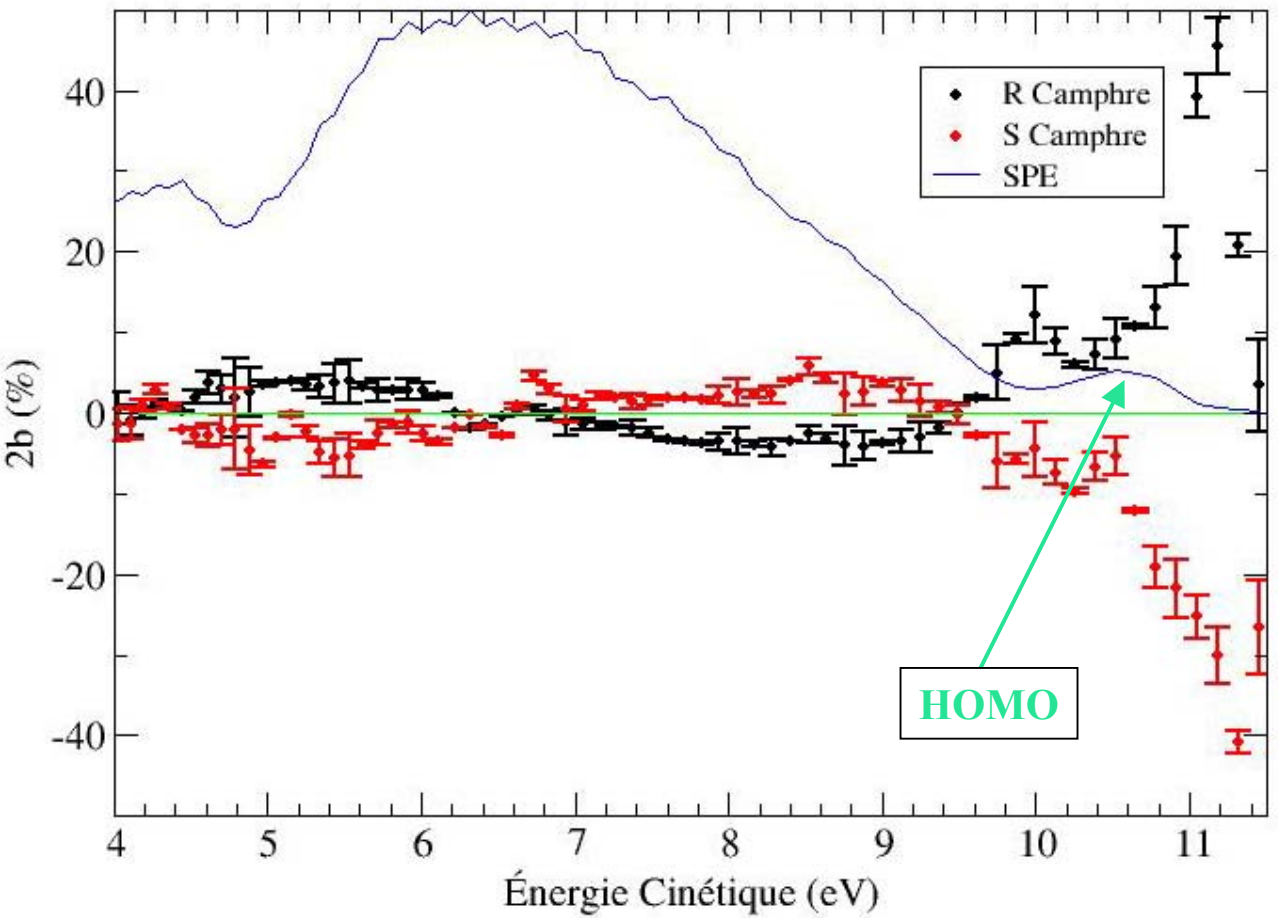



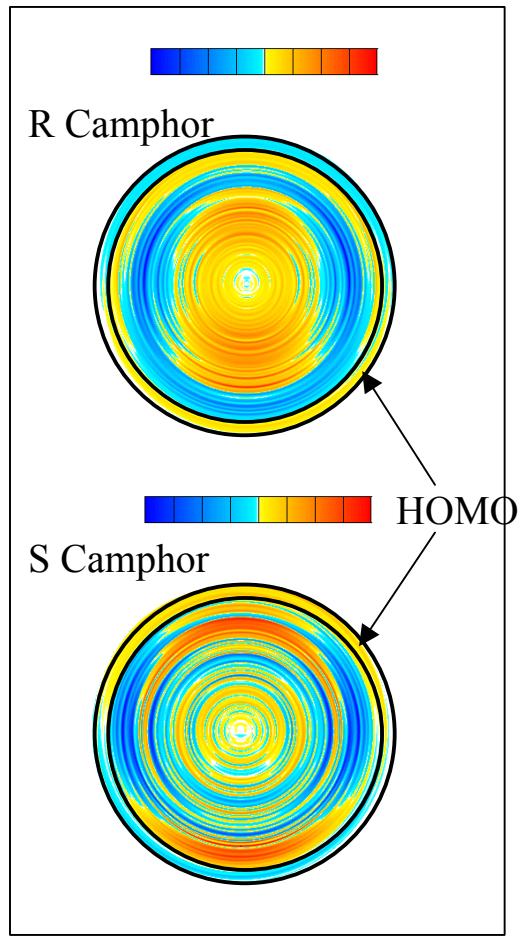
Homo orbital
O Lone pair

HOMO 7 %
HOMO -1 5 %

- CDAD is orbital dependent : localisation vs chiral centers --> initial state effect.

# CDAD of Camphor @ 20 eV



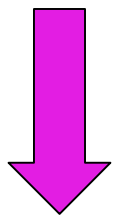

**strong resonance : final state effect**

**CDAD Max HOMO = 42 ± 4 % average HOMO > 15 %**

**CDAD resolves congested components**

# Open questions …

- **Origin of resonant features**
- **Role of vibrations**
- **Role of orbital localisation (scattering of the photoelectron by a chiral ion)**



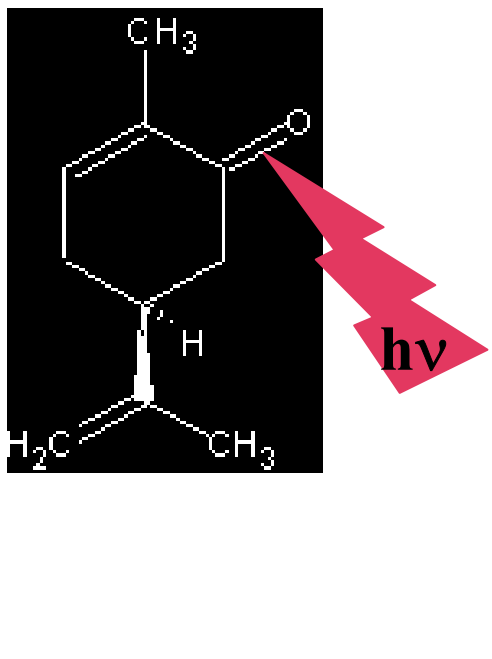
**Start from laser-excited chiral species**
(both analytical and fundamental interest)

# How ?

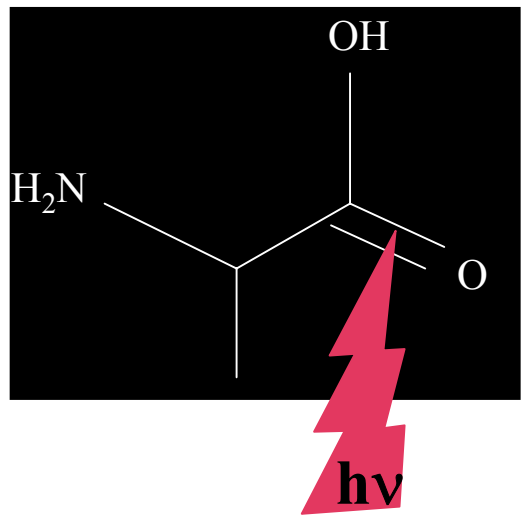
**n --> $\pi^*$ excitation (CO lone pair) around 280 - 300 nm**

**Camphor**


**Carvone**




**Alanine**



# Why ?

1. **Enhance the localization of the initial state wavefunction to be ionized : look at TR-CDAD**

2. **Probe intramolecular relaxation dynamics of $S_1$ by AR-TR imaging PES**

3. **Investigate the role of vibration on the CDAD by scanning the excess energy in $S_1$**

4. **Align the target molecules with the laser polarization ($\cos^2\alpha$ alignement of the transition moment)**

   ⇨ **enhance the handedness of the experiment probed by TR- CDAD (complete experiment <--> non-chiral species)**

# The photons that we need…

- **Spectral range :**
  - **Pump : UV (200 - 400 nm)**
  - **Probe : UV-XUV (5 - 600 eV)**
- **Repetition rates (both beams) : 100 Hz - 10 kHz**
  **Trade-off space charging / excited molecule yield**
- **Polarization (both beams) : variable linear and circular**
- **Overall Temporal cross correlation (including jitter) :**
  **~ 200 fs**

⇒ **Pump : External synch. Laser**
⇒ **Probe : ERL loop U30 @ 0.25 GeV (VUV)**
**@ 1 GeV (XUV)**