

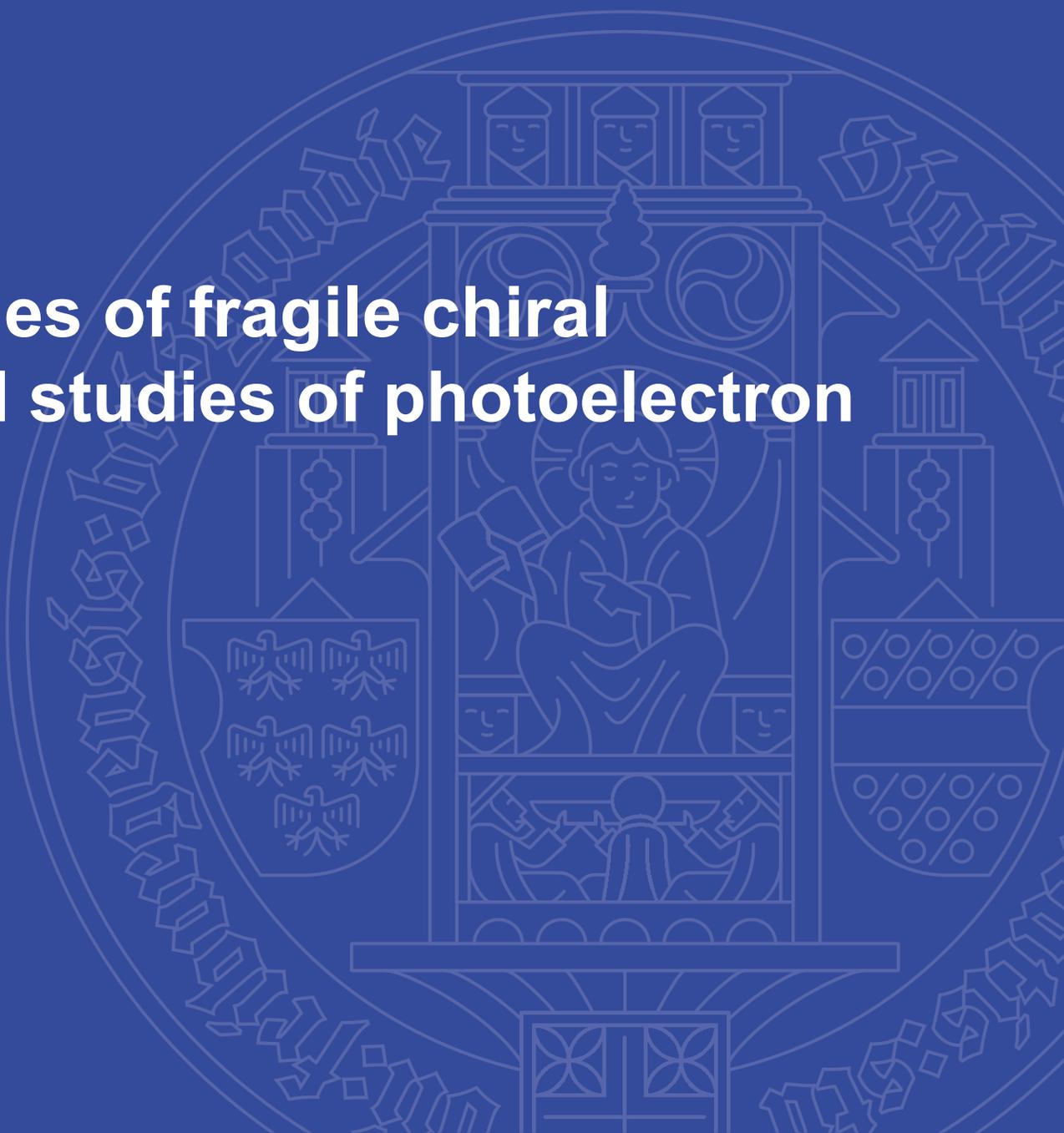
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# Toward cold molecular samples of fragile chiral compounds for time-resolved studies of photoelectron circular dichroism

ELI Ultrafast Science Workshop

Sebastian Hartweg

DESY/EuXFEL, Hamburg/Schenefeld, 12.02.2026



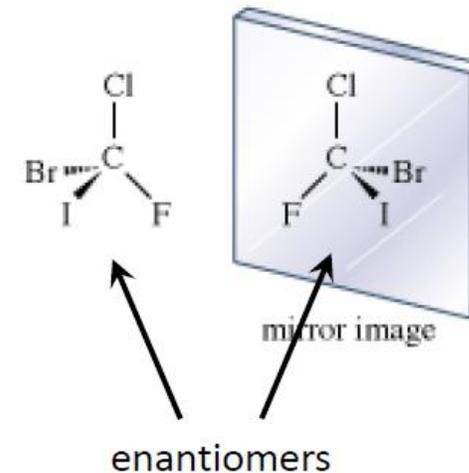
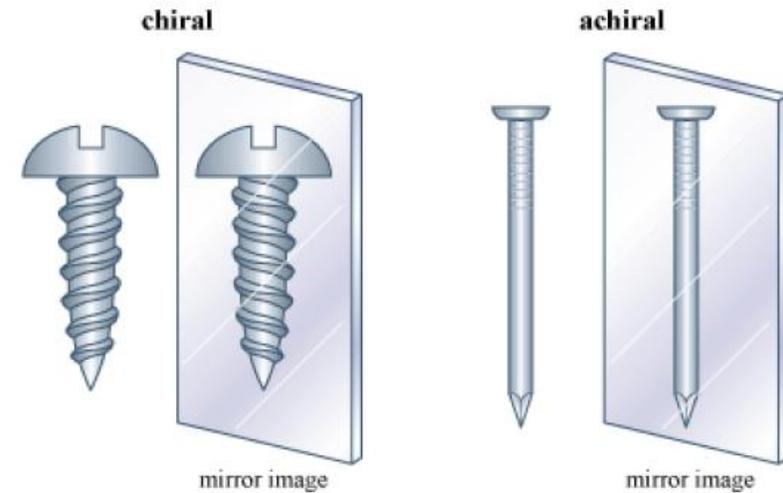
# Introduction - Chirality

Chiral objects cannot be superimposed on their mirror image

The two mirror images of a chiral molecules are called enantiomers

Most biomolecules are chiral and the smallest chiral biomolecular building blocks naturally occur as only one enantiomer

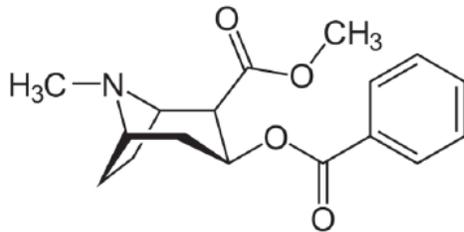
➤ D-sugars and L-amino acids



# Introduction - chiral interactions/chiral recognition

Chiral molecules have enantioselective interactions with other chiral objects/molecules

Many bioactive substances are chiral, and their activity is enantioselective

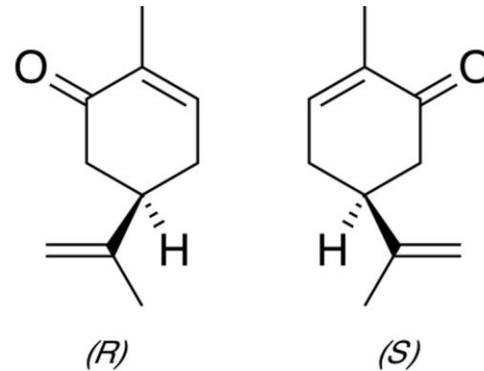


Cocaine enantiomers:

- (+)-cocaine: more active, lasts longer
- (-)-cocaine: less active



spearmint



caraway

skordo.com/products/caraway-seeds  
C I Klimov, Shutterstock

In the pharmaceutical, food and fragrance industry enantiopurity is often crucially important

- Enantioselective synthesis and catalysis
- Analytical tools with high enantioselectivity (e.g. chiral chromatography techniques)

# Introduction – chiroptical effects

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The chiral partner in a chiral interaction can also be circularly polarized light

Optical activity: refractive index in a chiral medium depends on helicity of light

- Polarization axis of linearly polarized light is rotated when light passes through chiral medium

Circular dichroism: absorption cross section in chiral medium depends on helicity of light

- Differential absorption measurements of electronic (ECD) or vibrational (VCD) transitions

Effect is zero within the electric dipole approximation of light matter interaction for non aligned molecules

- **Relatively weak effect: 0.001-0.1% of total yield**

## Photoionization:

Photoelectron angular distribution depends on the light helicity (Photoelectron circular dichroism, PECD) while total yield of photoelectrons (photoionization cross section, CD) is almost insensitive

Contained within electric dipole approximation! Ritchie, B., *Phys. Rev. A* **1976**, *13* (4), 1411-1415.

# Introduction – Photoelectron circular dichroism

**Single-photon** ionization of randomly oriented sample (achiral case)

$$I(\theta) = b_0(1 + b_2^p (3 \cos^2 \theta - 1))$$

$\theta$  is angle between emission angle and light polarization

$p = \pm 1, 0$  for circularly or linearly polarized case

Linear light polarization:  $b_2^0 = \beta$

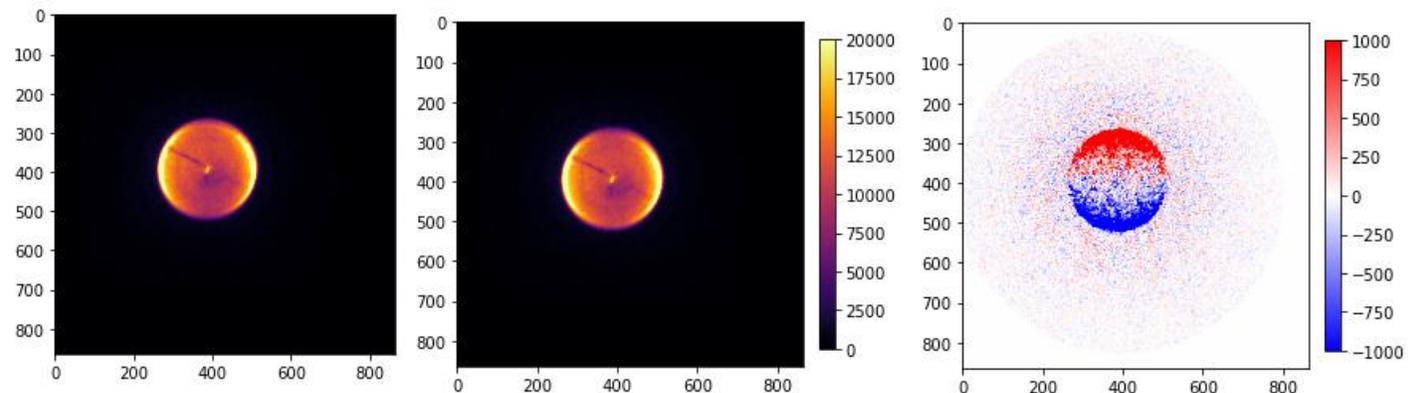
Circular light polarization:  $b_2^{\pm 1} = -\frac{\beta}{2}$

**Single-photon** ionization of randomly oriented **chiral** sample with **circularly polarized light** (chiral case)

$$I(\theta) = b_0(1 + b_1^p \cos \theta + b_2^p (3 \cos^2 \theta - 1))$$

$$b_1^{+1} = -b_1^{-1}$$

$$b_2^{+1} = b_2^{-1} = \frac{-b_2^0}{2}$$



**Multi-photon** ionization can introduce **higher order even (and odd) terms** in angular distribution of achiral (and chiral) case

# Introduction – Photoelectron circular dichroism

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## **PECD is universal with respect to the ionizing frequency**

- X-ray photoionization of core orbitals
- XUV/VUV photoionization of valence shell
- Multiphoton VIS/UV photoionization
- Above threshold ionization

## **PECD is sensitive to the shape of the ionized orbital as well as to the chiral potential of the remaining ion core**

- Sensitive to molecular conformation and nuclear structure
  - Sensitive to molecular conformation and cluster formation
- Sensitive to changes in electronic states

## **PECD is typically observed on gas phase samples**

- Many biologically-relevant chiral molecules are challenging to bring into the gas phase
- Recent studies demonstrated PECD of anions, liquid jets and free nanoparticles

# Time-resolved PECD

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**PECD is sensitive to the shape of the ionized orbital as well as to the chiral potential of the remaining ion core**

- Promising tool to study dynamical effects on nuclear and electronic degrees of freedom

Svoboda, V., et al., *Femtosecond photoelectron circular dichroism of chemical reactions. Science Advances*, 2022. **8(28): p. eabq2811.**

Faccialà, D., et al., *Time-Resolved Chiral X-Ray Photoelectron Spectroscopy with Transiently Enhanced Atomic Site Selectivity: A Free-Electron Laser Investigation of Electronically Excited Fenchone Enantiomers. Physical Review X*, 2023. **13(1): p. 011044.**

Wanie, V., et al., *Capturing electron-driven chiral dynamics in UV-excited molecules. Nature*, 2024. **630(8015): p. 109-115.**

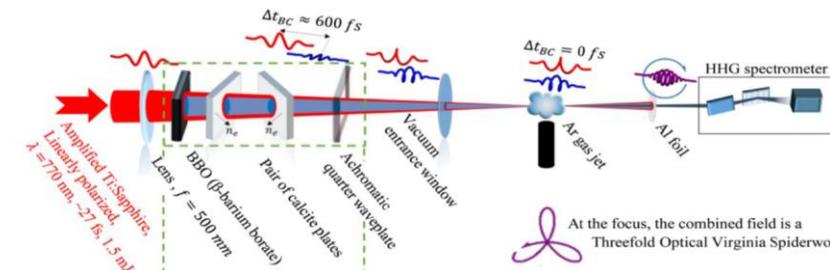
# Setup for time-resolved PECD experiments at ELI beamlines

Joint project between Prof. Dr. M. Mudrich, Dr. S. Hartweg and Prof. Dr. M. Krikunova

## Time-resolved XUV PECD studies at ELI beamlines

Prof. Dr. M. Mudrich + ELI:

- Generation and characterization of circularly polarized harmonics
- Focus on low order harmonics H7-H11 (10.5-16.5 eV)



Adapted from: Kfir, O., et al., *In-line production of a bi-circular field for generation of helically polarized high-order harmonics*. *Applied Physics Letters*, 2016. **108(21)**.

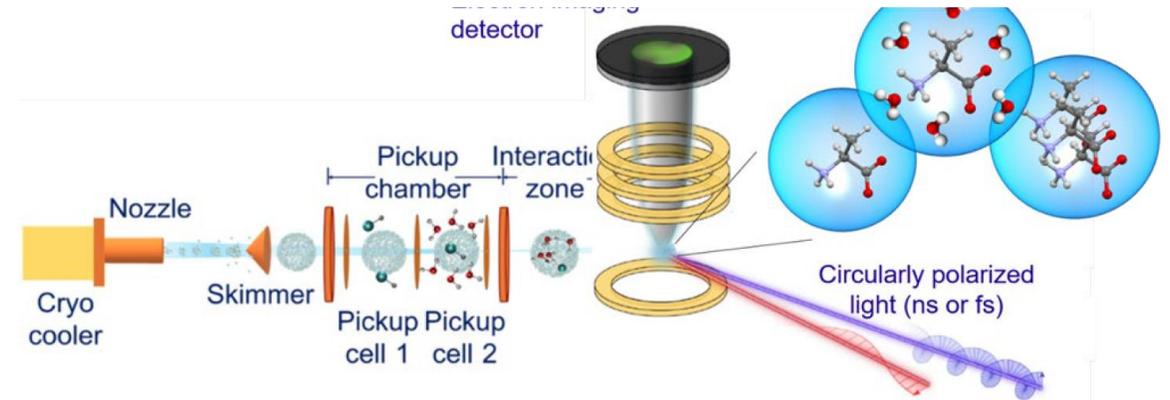


S. Hartweg:

- Improvement of sample preparation for thermally unstable, conformer-rich, low vapor pressure species
- Prototypical chiral model systems:
  - High vapor pressure
  - Thermally stable
  - Rigid small number of conformers



- Sugars? Amino acids? Pharmacologically active substances?
  - Complex conformational landscape
  - Limited thermal stability

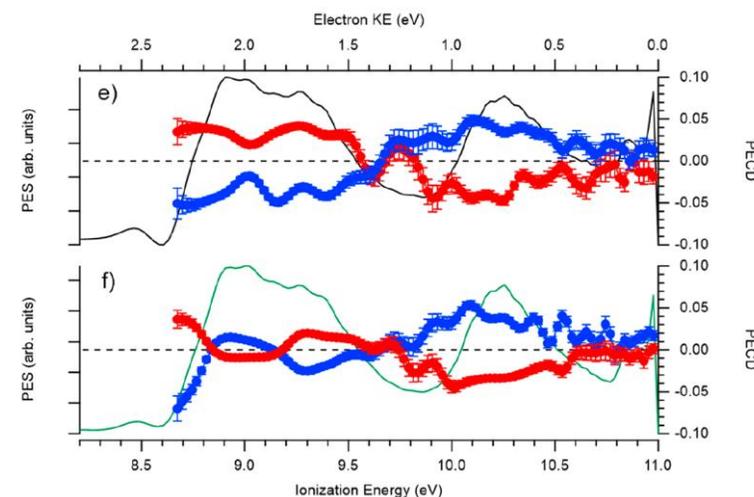
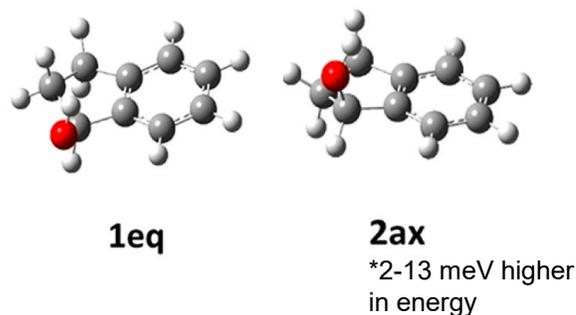
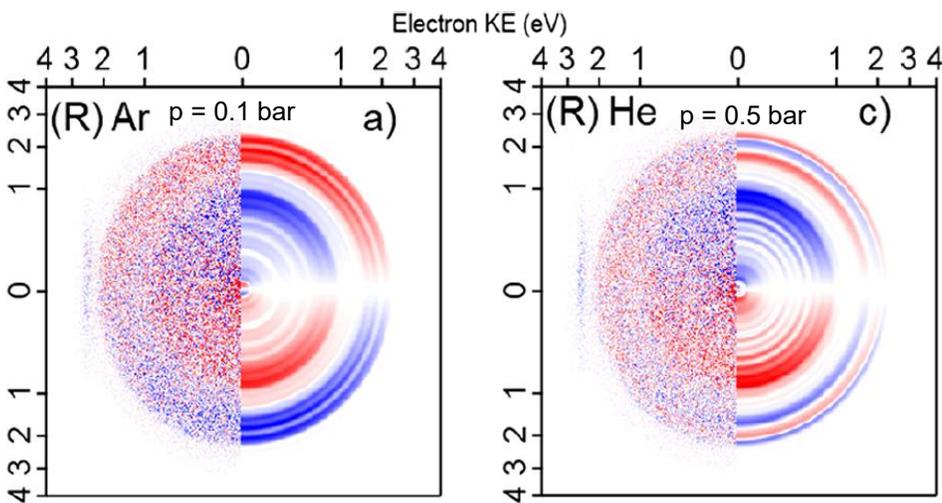
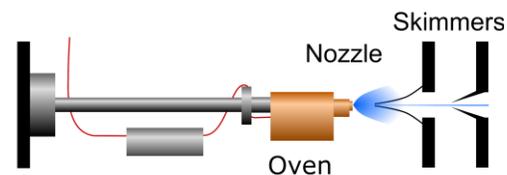


# Available preparation techniques for neutral molecules in the gas phase

Seeded molecular beam expansions

- Can produce cold molecular samples
- Can produce molecular clusters and complexes
- Can be operated pulsed or continuous

- Requires ~10 mbar of vapor pressure without inducing thermal decomposition

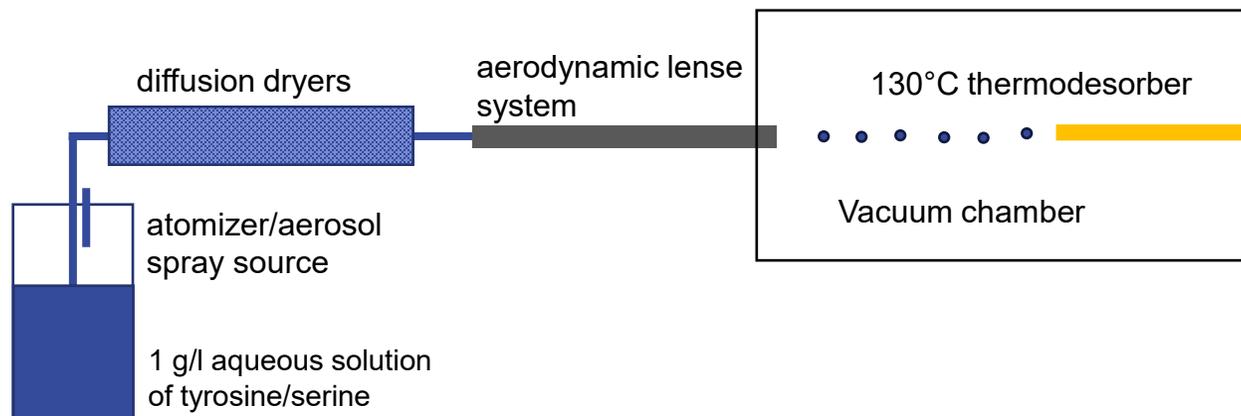


Dupont, J., et al., *Photoelectron Circular Dichroism as a Signature of Subtle Conformational Changes: The Case of Ring Inversion in 1-Indanol*. *The Journal of Physical Chemistry Letters*, 2022: p. 2313-2320.

# Available preparation techniques for neutral molecules in the gas phase

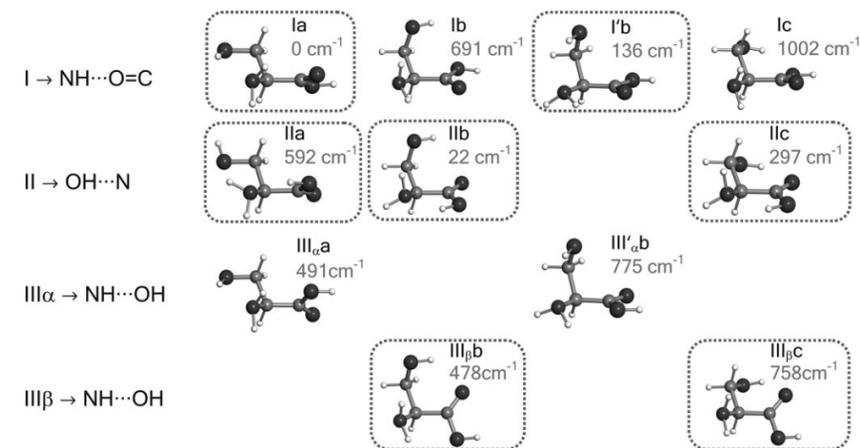
## Aerosol thermodesorption

- Desorption in high vacuum environment induces less decomposition
- Does not produce cold molecules!



Hartweg, S., et al., *Condensation Effects on Electron Chiral Asymmetries in the Photoionization of Serine: From Free Molecules to Nanoparticles*. *J. Phys. Chem. Lett.*, 2021. **12(9)**: p. 2385-2393.

Hartweg, S., et al., *Large circular dichroism in the total photoemission yield of free chiral nanoparticles created by a pure electric dipole effect*. *arXiv preprint arXiv:2510.05945*, 2025.



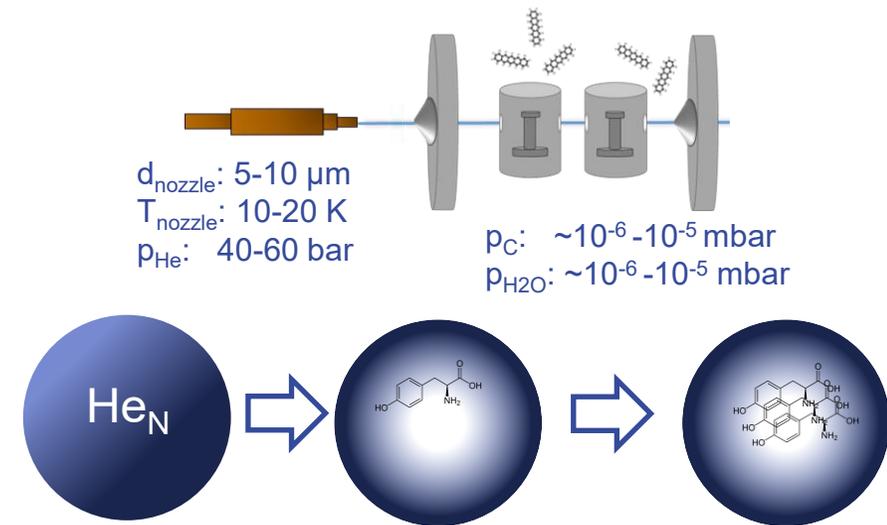
**Fig. 2.** Predicted lower-energy conformers of serine and relative energies (MP4, see text) with respect to the global minimum in cm<sup>-1</sup>. The detected conformers are encircled.

Blanco, S., et al., *Revealing the multiple structures of serine*. *PNAS*, 2007. **104(51)**: p. 20183-20188.

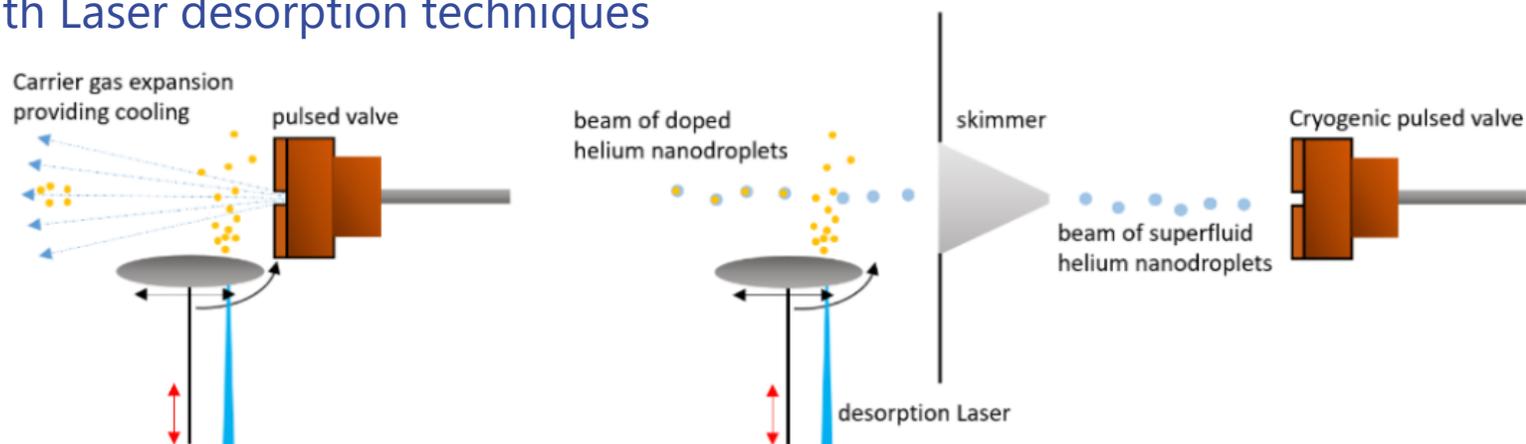
# Doping molecules into helium nanodroplets

Embedding chiral molecules into Helium nanodroplets

- Ultracold,  $T = 0.4 \text{ K}$
- Does not change molecular properties
- Can be operated pulsed or continuous
- Requires low vapor pressures  $< 10^{-5} \text{ mbar}$
- Allows extension toward clusters and complexes (e.g. chiral recognition and microsolvation)



Combination of supersonic expansions helium droplet sources with Laser desorption techniques



Sezer, U., et al., *Analytical Chemistry*, 2015. **87(11)**.  
Milešević, D., et al., *Rev. Sci. Instrum.*, 2023. **94(11)**.

# Acknowledgements

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U N I K A S S E L  
V E R S I T Ä T

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Forschungsgemeinschaft



Bundesministerium  
für Forschung, Technologie  
und Raumfahrt



Open PhD position!

If you know someone interested in pursuing a PhD in physics at the university of Freiburg focused on molecular and cluster beam techniques, Laser desorption and chiroptical effects:

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# Summary

