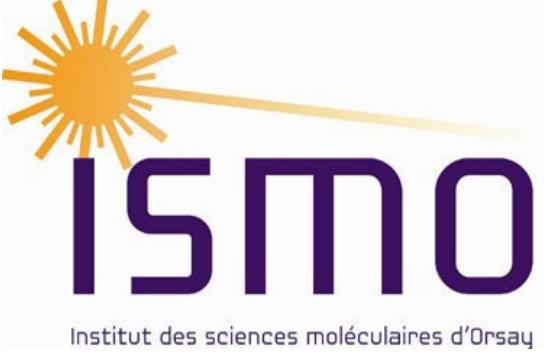


# Induced Photoelectron Circular Dichroism in an Achiral Chromophore



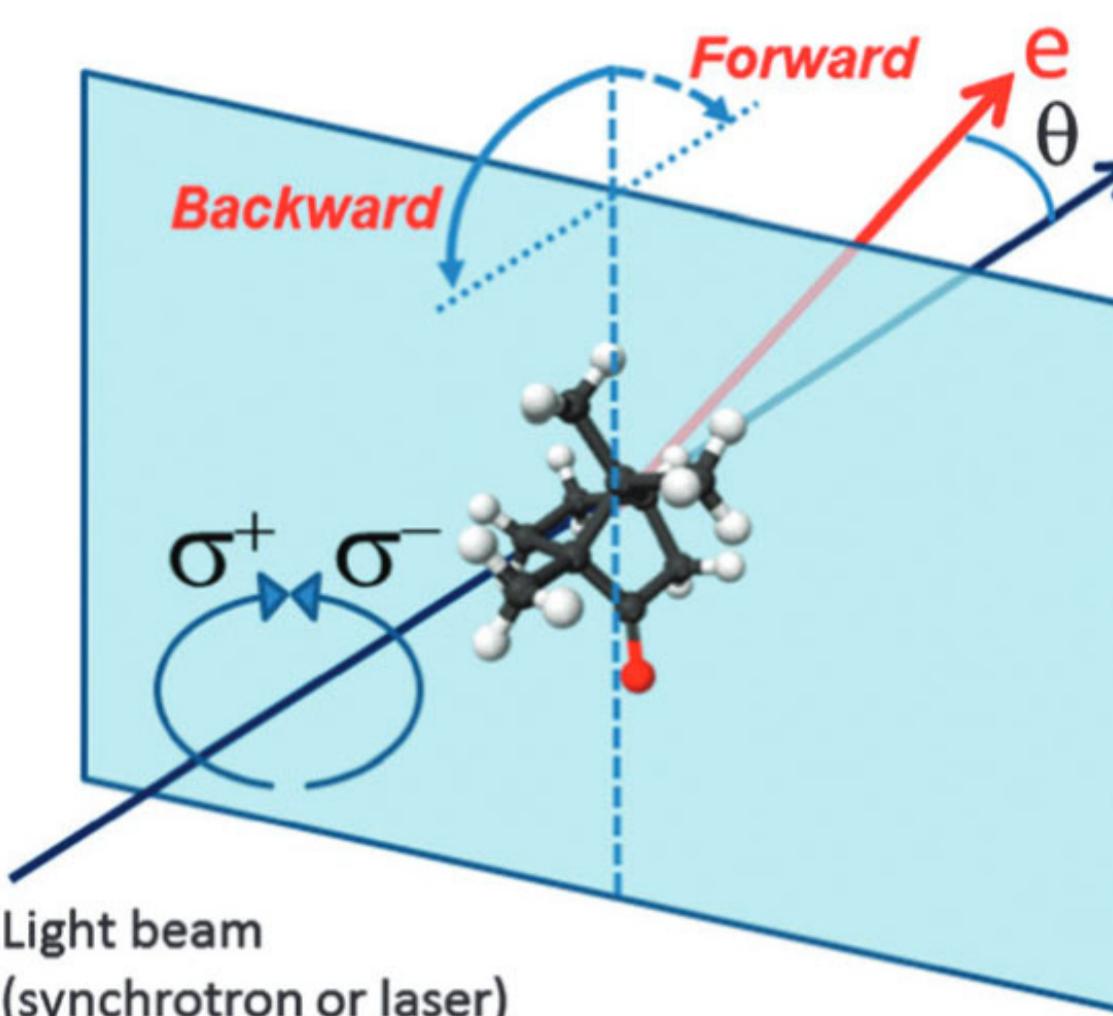
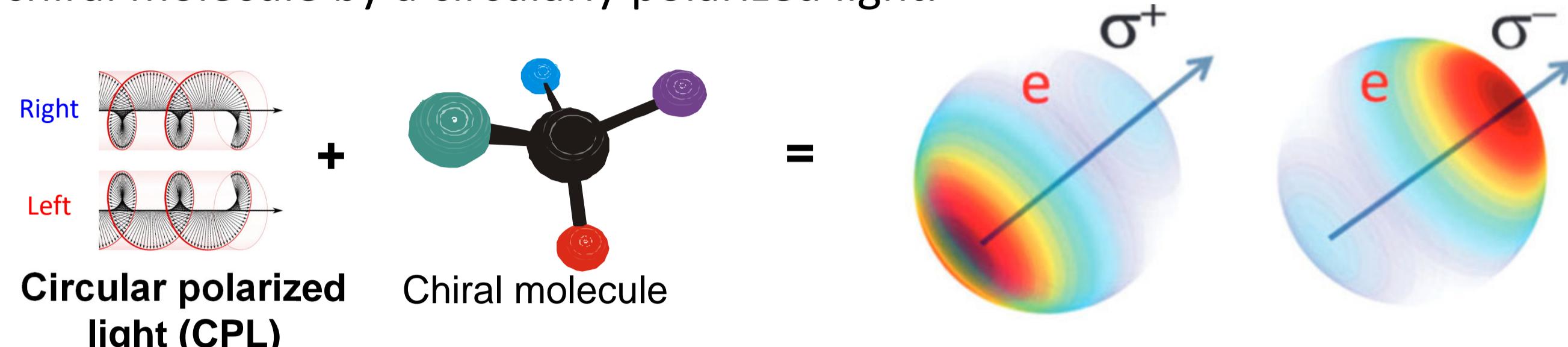
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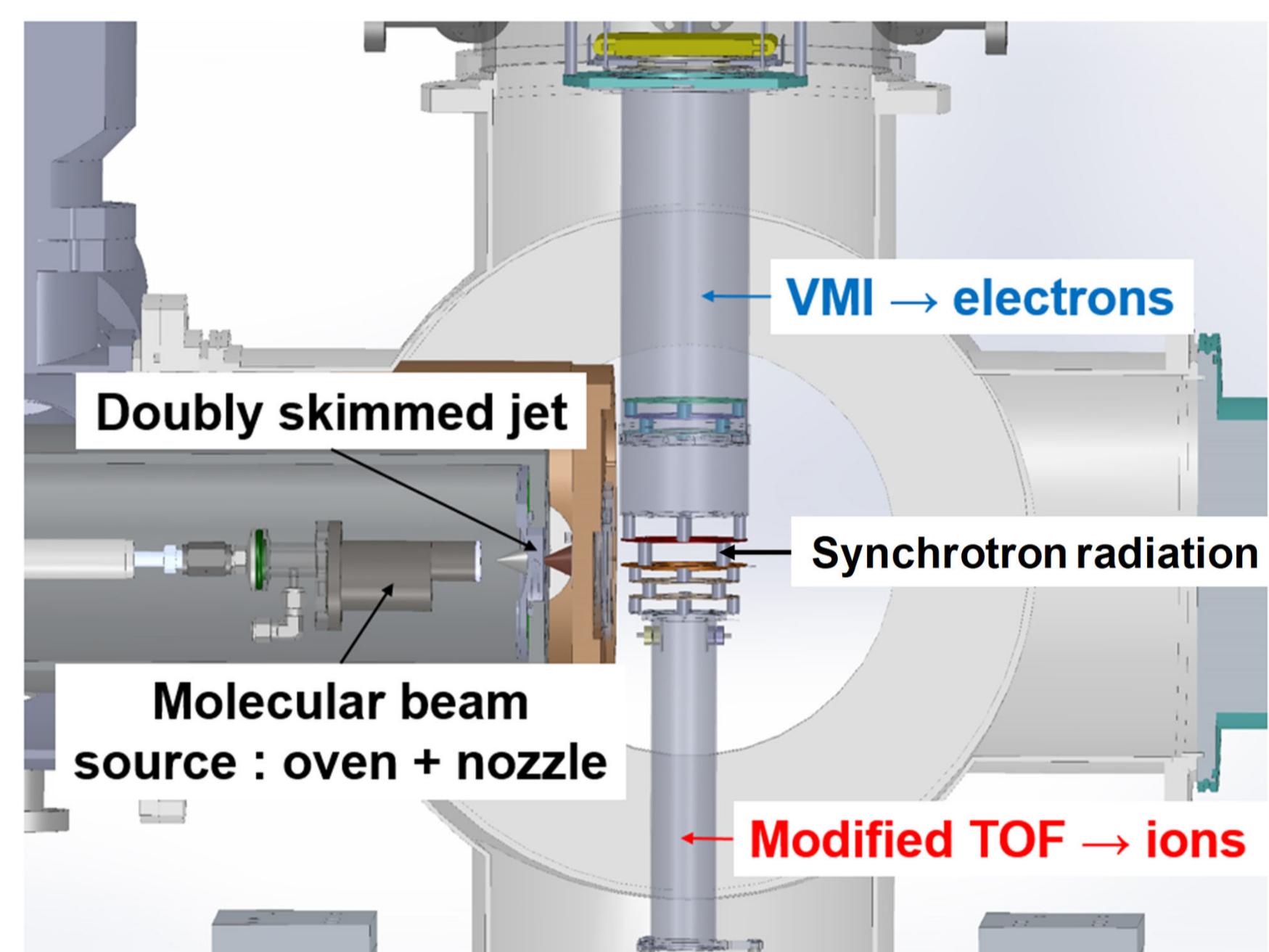
## PHOTOELECTRON CIRCULAR DICHROISM (PECD)

PECD consists in a **forward/backward asymmetry** with respect to the light propagation axis in the photoelectron angular distribution after ionization of a chiral molecule by a circularly polarized light.



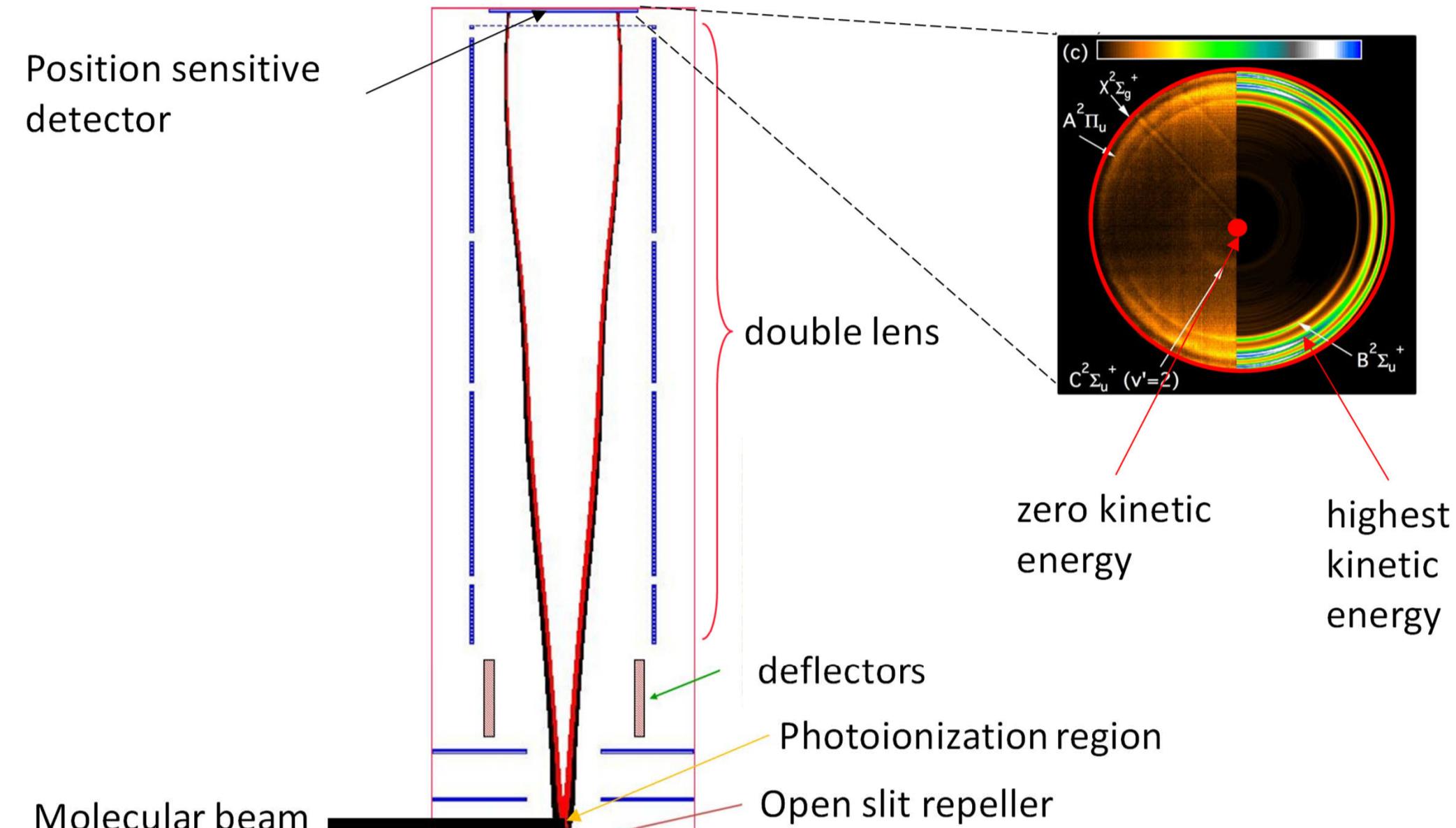
- ⇒ Absolute configurations determination
- ⇒ Sensitivity to conformation  
Conformational analysis
- ⇒ Sensitivity to molecular interactions :  
Microsolvation, hydrogen bond formation

## EXPERIMENT



The SAPHIRS experimental chambers and the DELICIOUS3 spectrometer DESIRS Beam line of Synchrotron SOLEIL

## VMI (Velocity Map Imaging)



- Focusing of the electron as a function of their kinetic energy
- Microchannel plates

## THEORY

Angular distribution of photoelectrons ejected from a randomly oriented molecule by single photon excitation process :

$$I_p(\theta) = 1 + b_1^{\{p\}} P_1(\cos \theta) + b_2^{\{p\}} P_2(\cos \theta)$$

$p = 0$  for linear polarization  
 $p = \pm 1$  for left and right circular polarization

For achiral molecules,

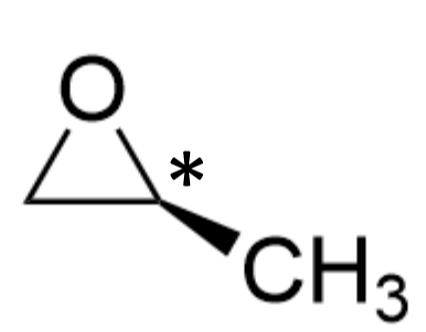
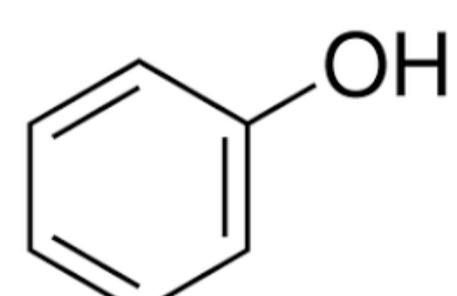
$$b_1^{\{p\}} = 0$$

For chiral molecules,

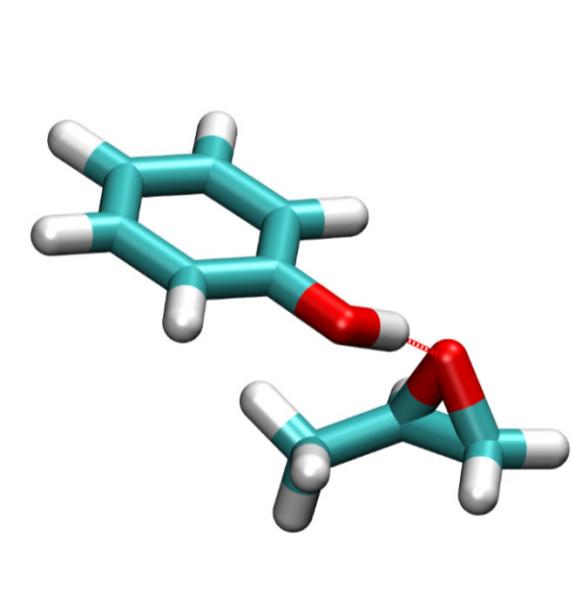
$$b_1^{\{\pm 1\}} \neq 0 \text{ and } b_1^{\{+1\}}(R) = b_1^{\{-1\}}(S)$$

## Complex studied

Phenol (Phe) = Methyloxirane (Mox) =  
achiral chromophore chiral molecule



Bound by strong hydrogen bond OH...O



Most stable structure of the Phe:Mox complex calculated at the B3LYP-D3BJ/6-311++G(d,p) level of theory

Vibrational spectrum of isolated phenol and of the Phe:Mox complex recorded by IR-UV double resonance spectroscopy

Isosurfaces of occupied orbitals for Phe:Mox, Phe and MOx calculated at the MP2/6-31++G(d,p) level.

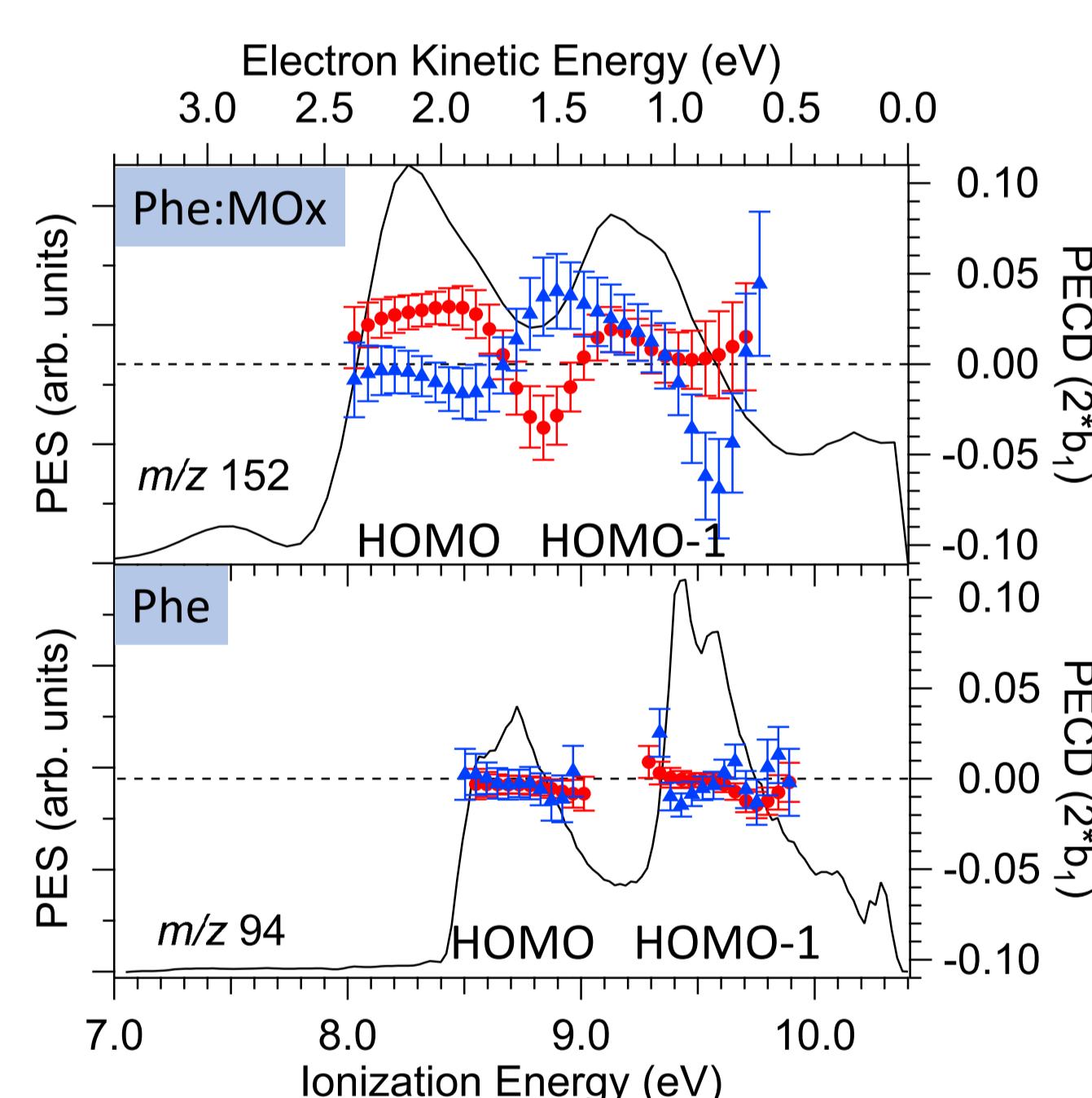
Vertical ionisation energies (VIE) calculated with the outer valence Green's function (OVGF) method and cc-pVTZ basis set.

	HOMO	HOMO-1	HOMO-2	Structures
a Phe:Mox Conf 49				
	IE = 8.11 eV	IE = 8.93 eV	IE = 11.48 eV	
b Phe				
	IE = 8.53 eV	IE = 9.28 eV	IE = 11.79 eV	
c Mox				
	IE = 10.72 eV	IE = 11.09 eV	IE = 13.18 eV	

➤ HOMO & HOMO-1 of the complex localized on the phenol part, Mox moiety being a mere spectator

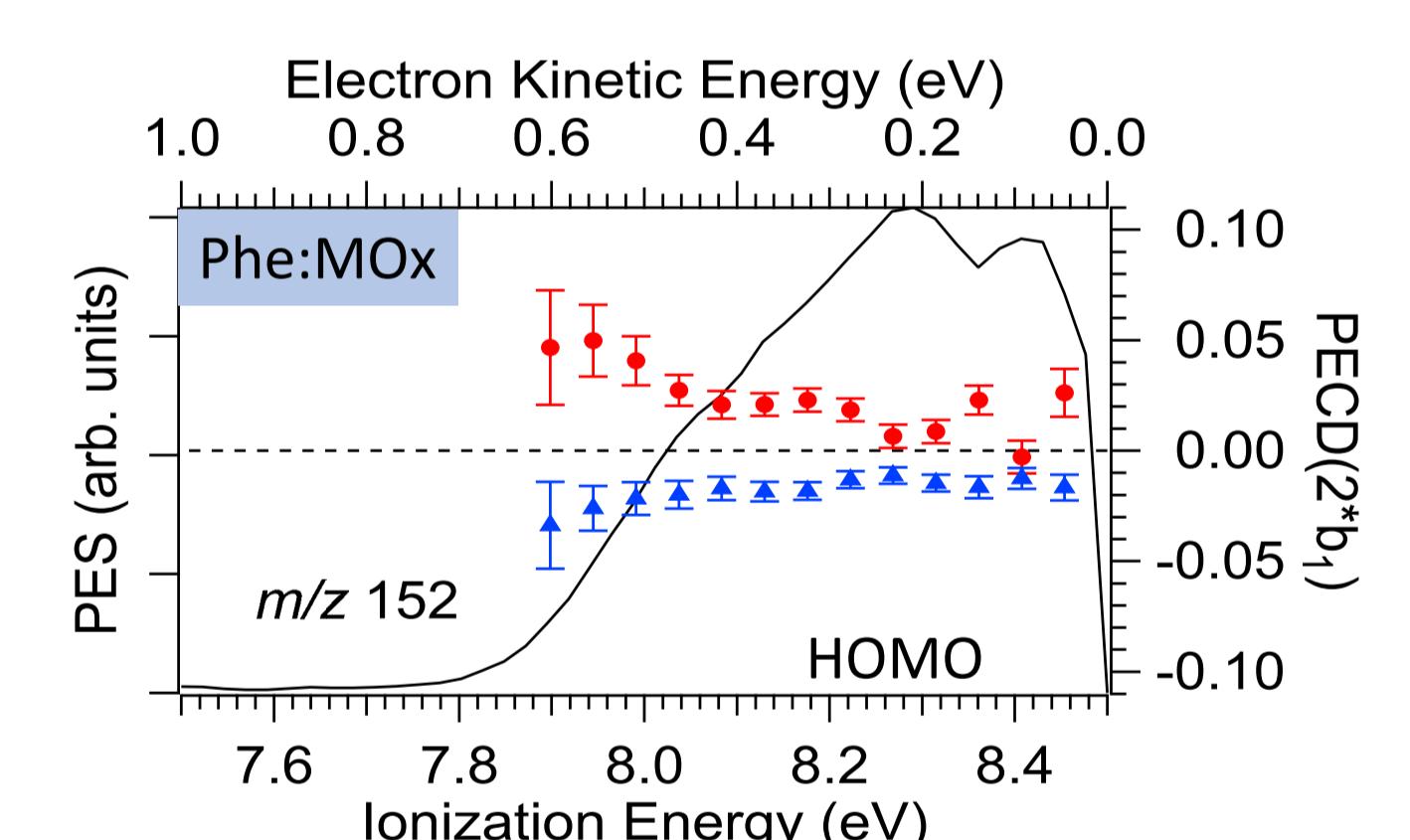
## PECD Results

$h\nu = 10.4 \text{ eV} < EI (\text{Mox})$



- ✓ PECD of Phenol = 0
- ✓ Mirroring effect between PECD of both enantiomers of the complex
- ✓ PECD around 3% for the complex

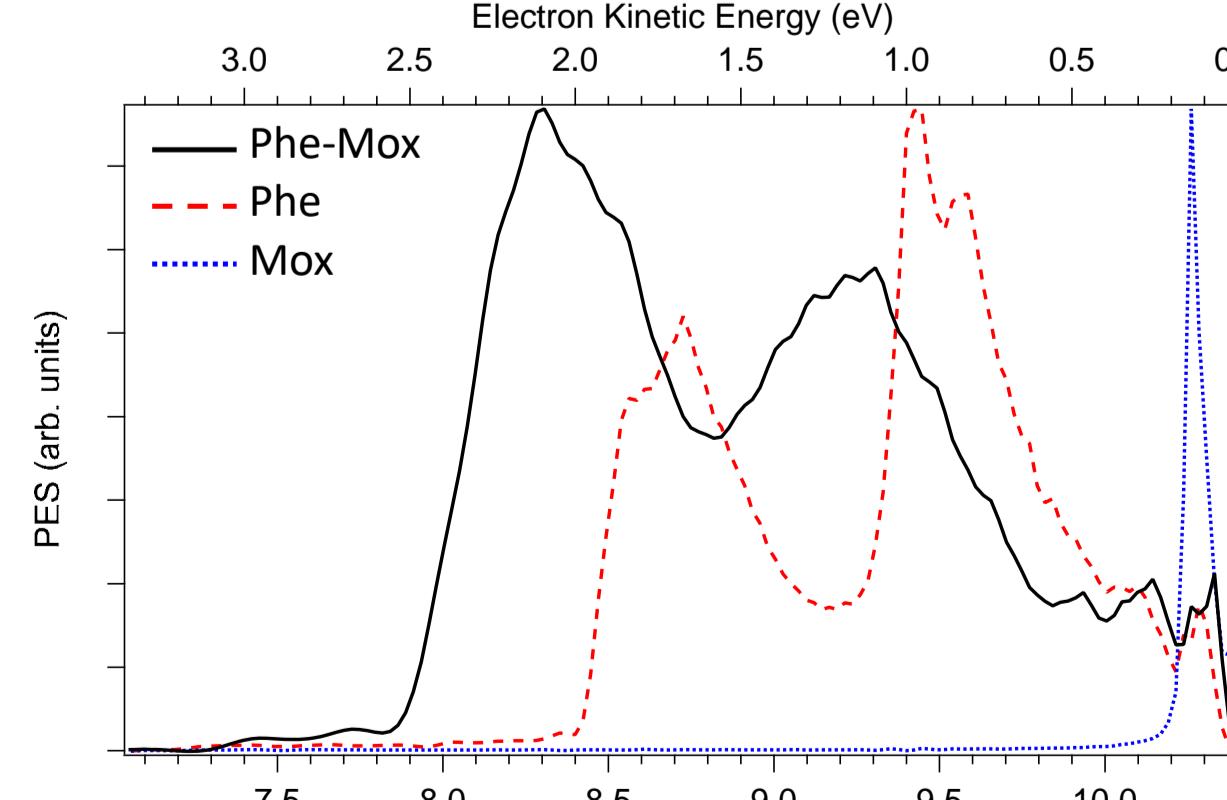
$h\nu=8.5 \text{ eV} < EI (\text{Phe}) \text{ or } EI (\text{Mox})$



➤ Induced PECD on orbitals of achiral phenol

➤ Long-range effect (~5 Å) of the scattering chiral potential

## PES Results



Comparison of Photoelectron spectra (PES) of phenol, MOx and the Phe:Mox complex, recorded at a photon energy of 10.4 eV, slightly above the adiabatic ionisation energy of MOx (10.24 eV).

➤ HOMO & HOMO-1 of the complex lower in energy than those of phenol

## CONCLUSION AND AFTER...

- First example of the manifestation of **induced chirality** in PECD on the HOMO & HOMO-1 orbitals of an achiral chromophore by complexation with a chiral tag.
- Complexation with the chiral MOx host offers the phenol departing electron a **chiral scattering potential**.
- Role of the **long-range chiral scattering potential** extending to intermolecular distances, here up to ~5 Å
- Laser chiroptical measurements possible of chiral species which cannot be excited in UV thanks to complexation with a achiral chromophore
- Induced chirality = important structural and analytical implications
- REMPI-PECD at ISMO to record conformer-selective PECD