

Induced Photoelectron Circular Dichroism in an Achiral Chromophore



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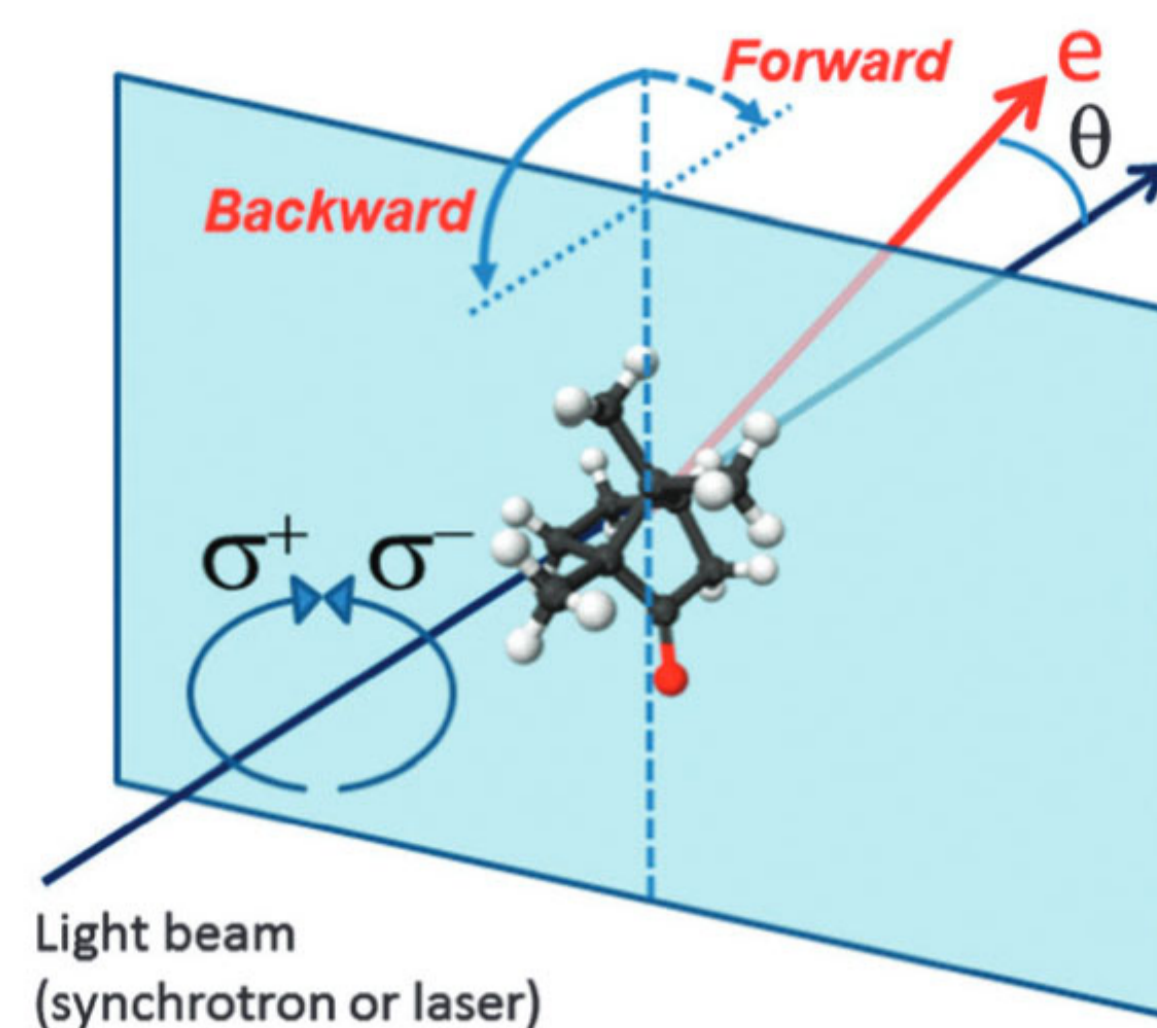
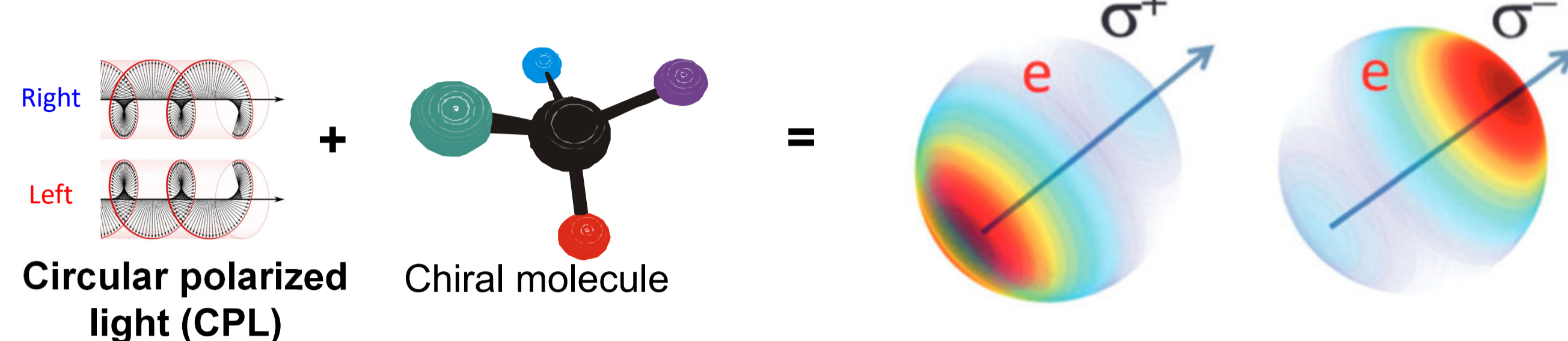


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PHOTOELECTRON CIRCULAR DICHOISM (PECD)

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.

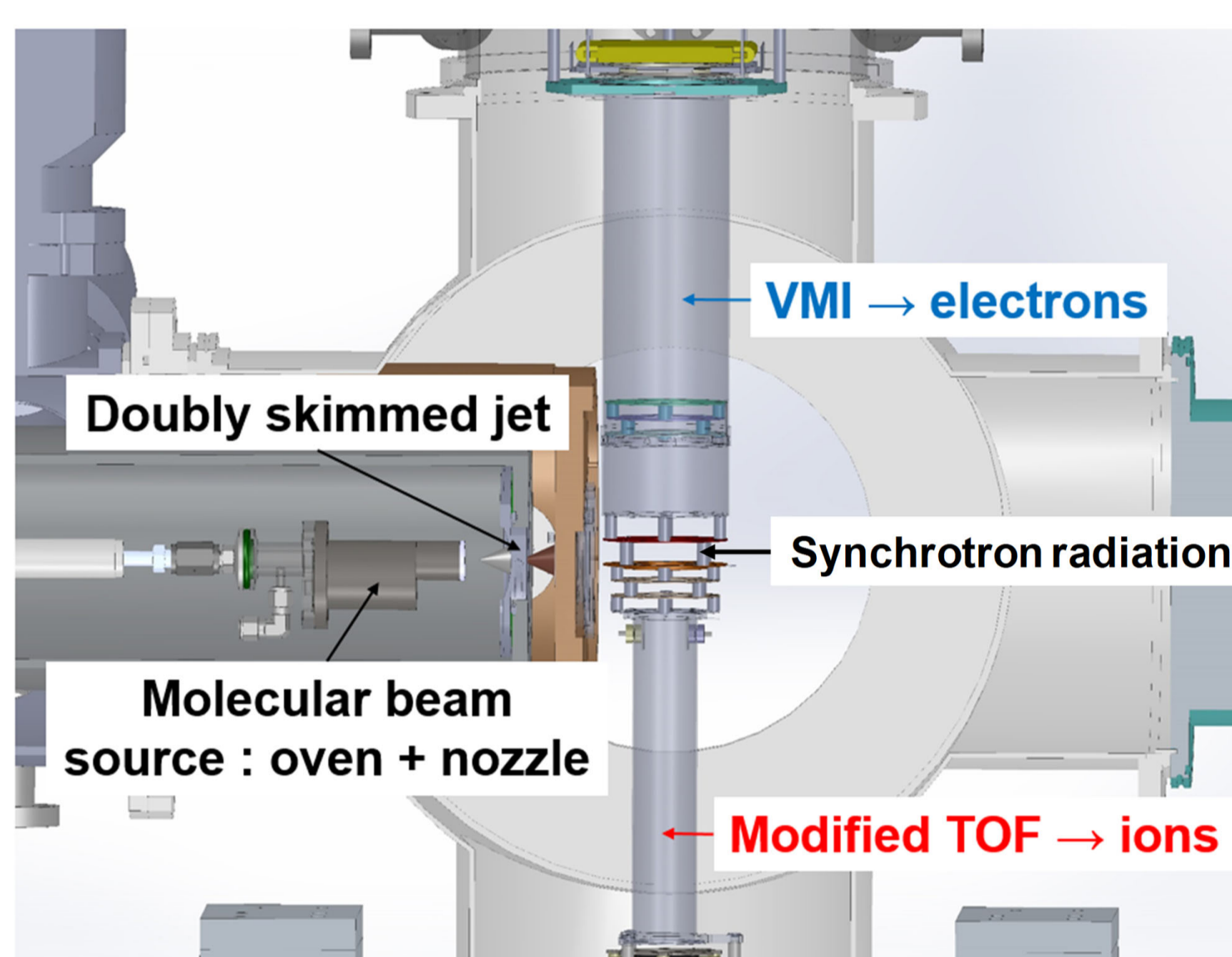


⇒ **Absolute configurations determination**

⇒ **Sensitivity to conformation**
Conformational analysis

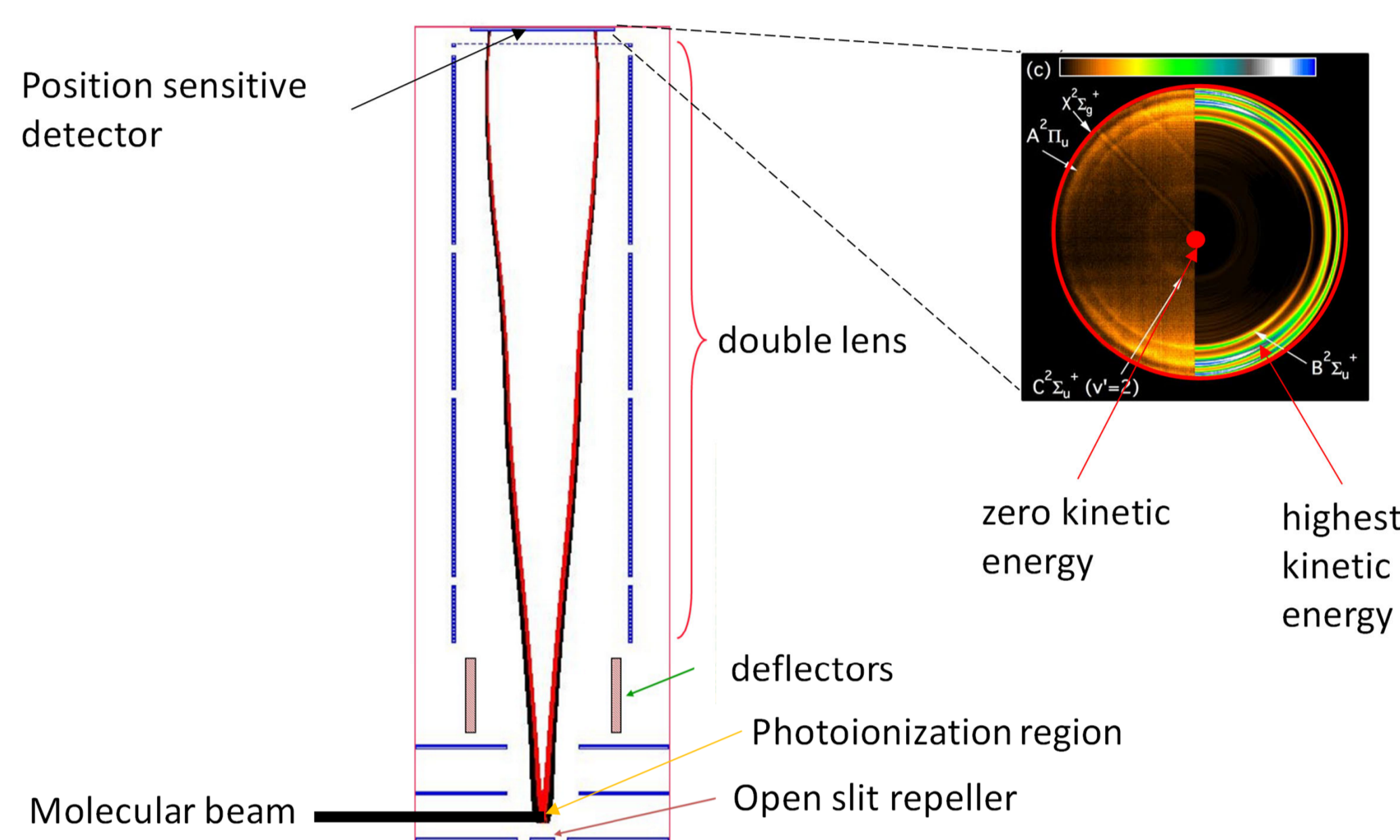
⇒ **Sensitivity to molecular interactions:**
Microsolvation, hydrogen bond formation

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,

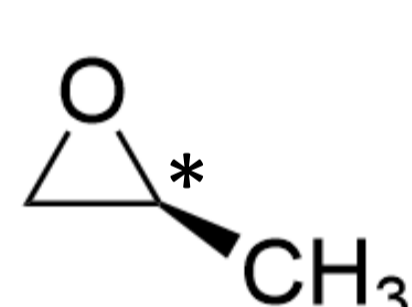
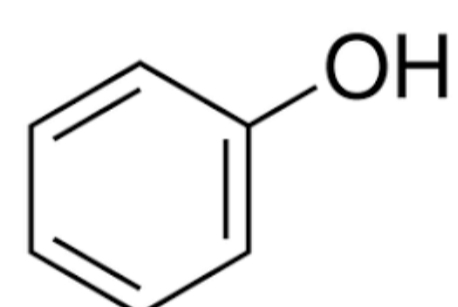
$$b_1^{(\pm 1)} \neq 0 \text{ and } b_1^{(+1)}(R) = b_1^{(-1)}(S)$$

➔ **PECD = 2b₁** ➤ from one to a few tens %

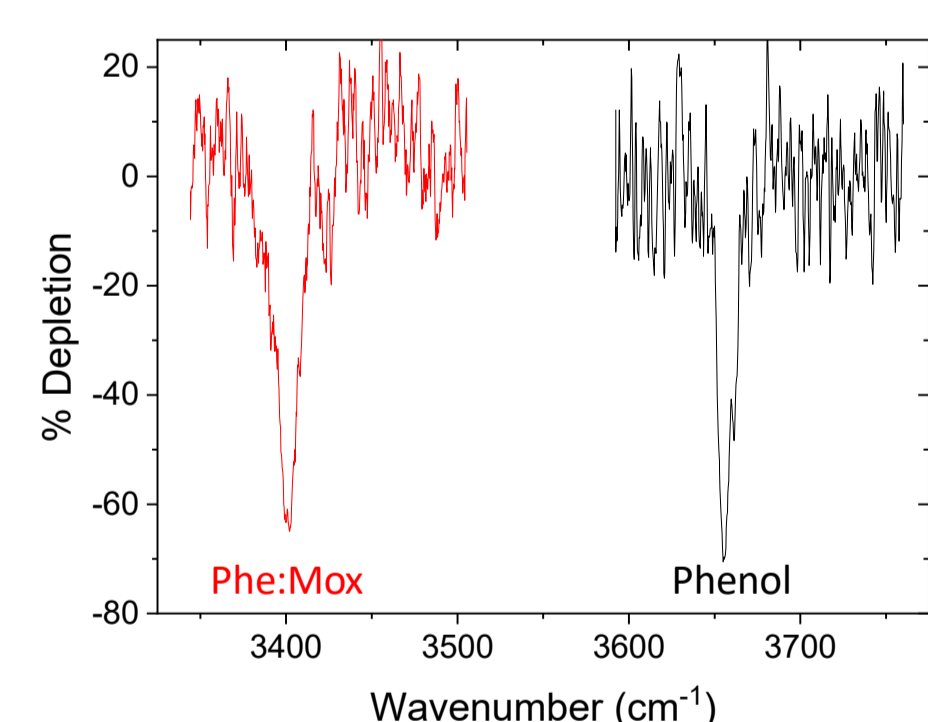
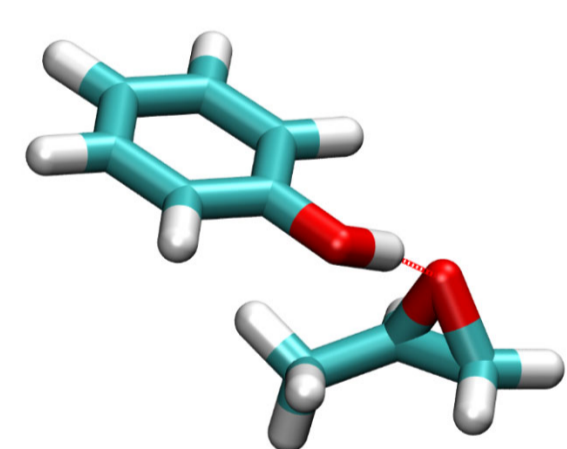
➤ depends on the **initial orbital** and the **final state (photoelectron scattering by the molecular potential of the cation)**

Complex studied

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



➔ **Bound by strong hydrogen bond OH...O**

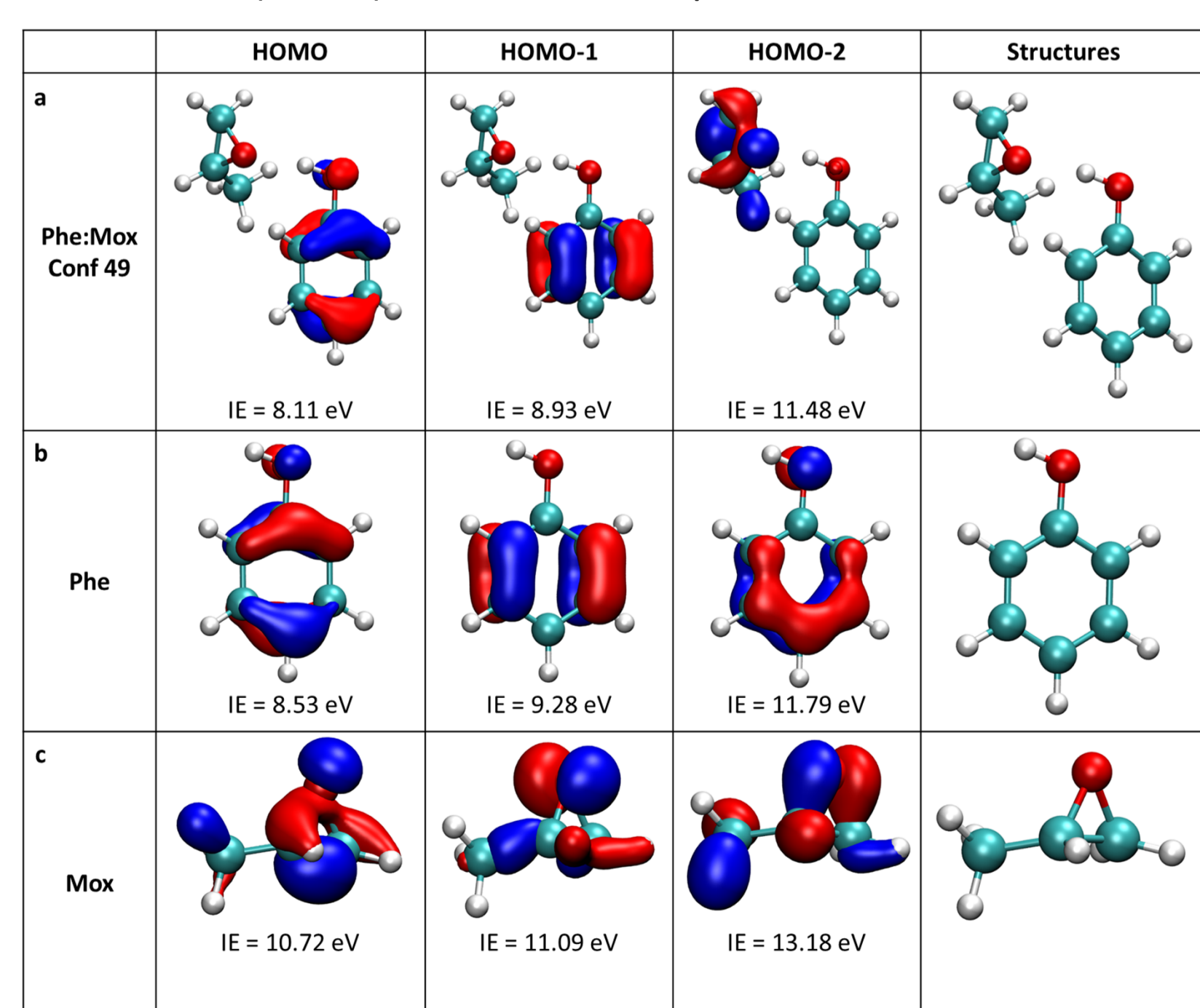


Most stable structure of the Phe-MOX complex calculated at the B3LYP-D3BJ/6-311++G(d,p) level of theory

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

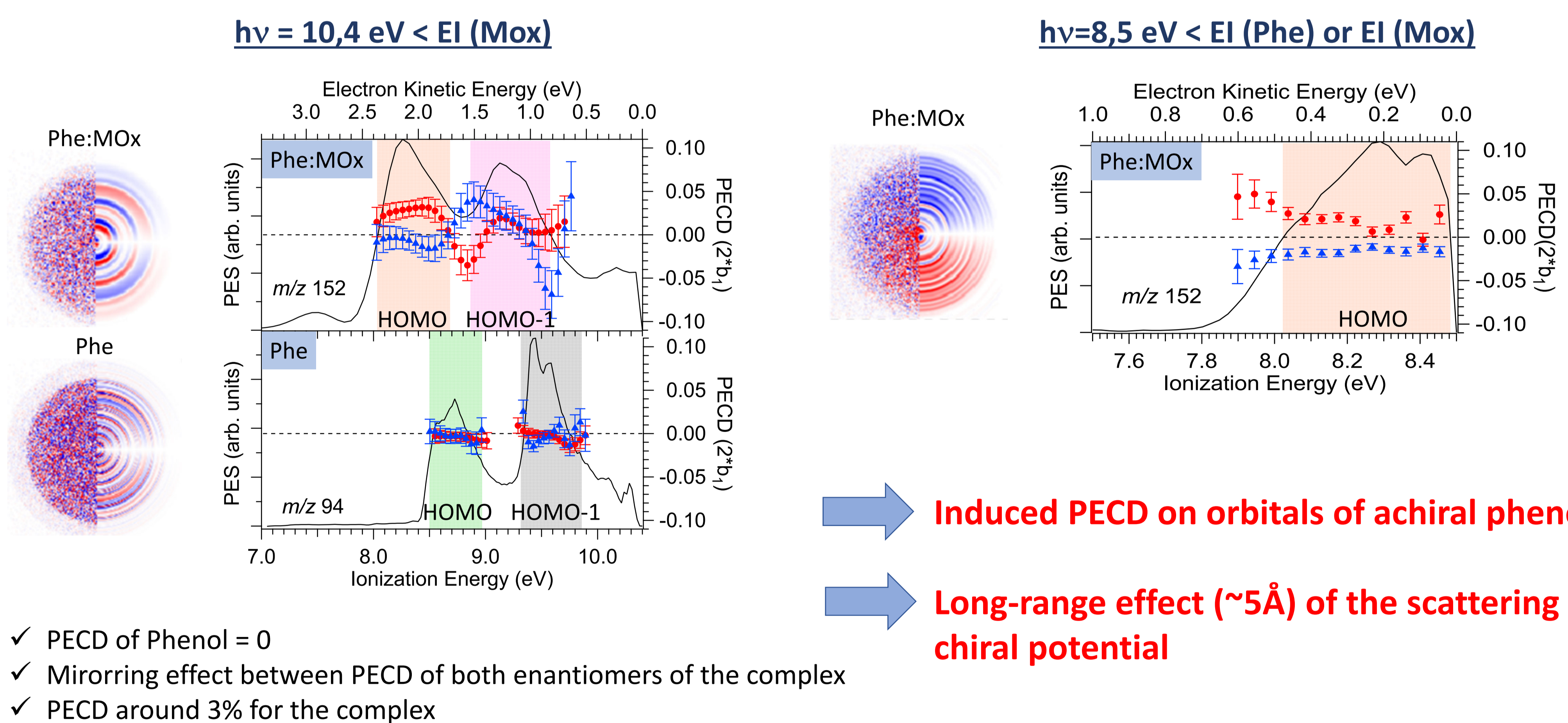
Isosurfaces of occupied orbitals for Phe:Mox, Phe and MOx calculated at the MP2/6-31++G(d,p) level.

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



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

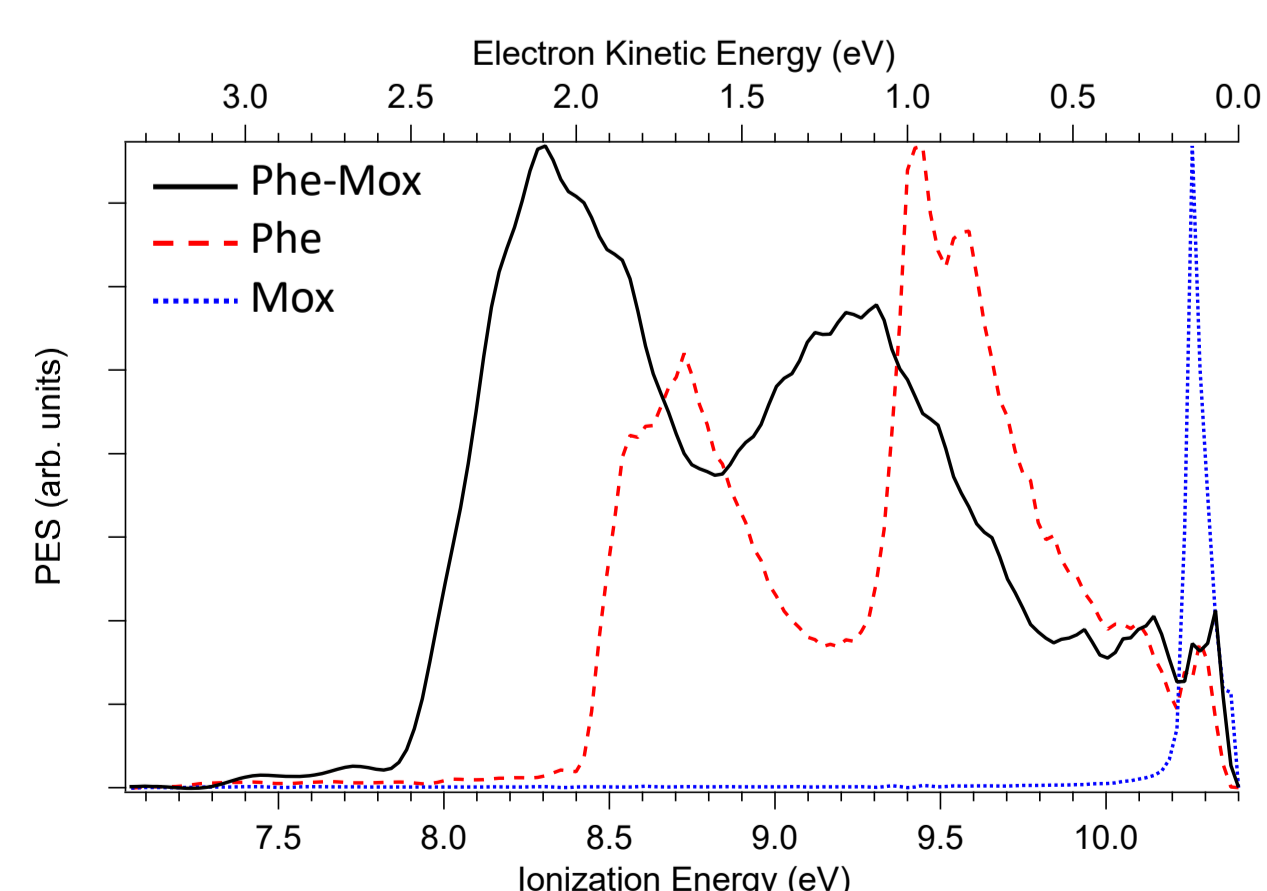
PECD Results



➔ **Induced PECD on orbitals of achiral phenol**

➔ **Long-range effect (~5Å) 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