

# XUV and X-ray spectroscopy of phthalocyanines in the gas-phase

Gildas Goldsztejn

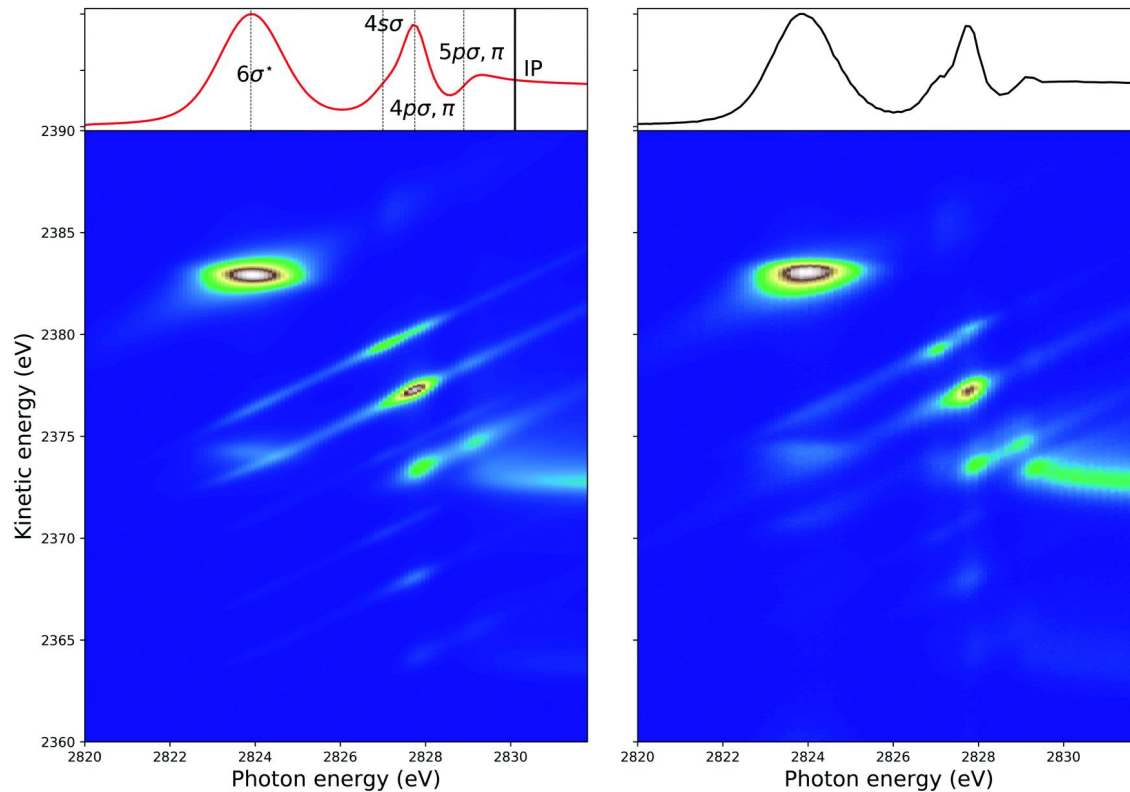
Institut des Sciences Moléculaires d'Orsay (ISMO)



SFP-MC14, July 5th 2023

# The ideal case: a diatomic molecule (HCl)

$$\sigma(\omega, \omega') \propto \sum_f \left| \sum_c \frac{\langle \Phi_f | Q | \Phi_c \rangle \langle \chi_f | \chi_c \rangle \langle \Phi_c | D | \Phi_o \rangle \langle \chi_c | \chi_o \rangle}{\omega - \omega_{co} + i\Gamma_c} \right|^2 \times \Delta(\omega - \omega' - \omega_{fo}, \Gamma_f)$$



(Relatively) Simple equations  
can describe everything

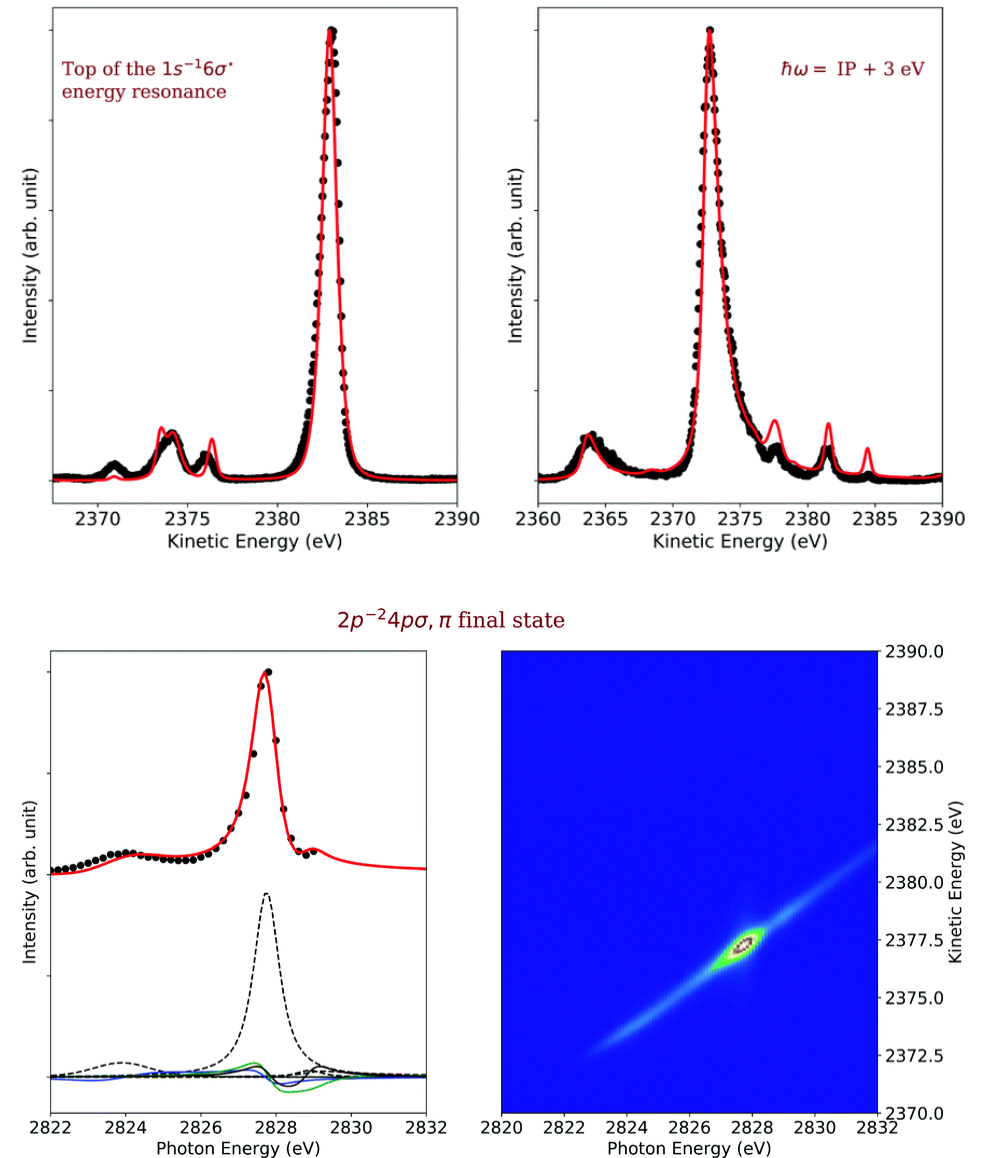
G. Goldsztejn et al., PCCP, 2022, **24**, 6590

# The ideal case: a diatomic molecule (HCl)

It can be used to simulate resonant and normal Auger spectra

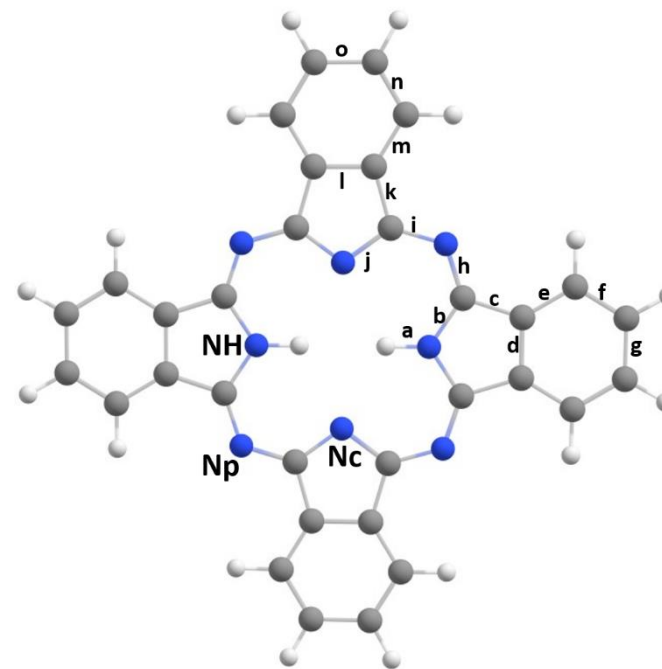
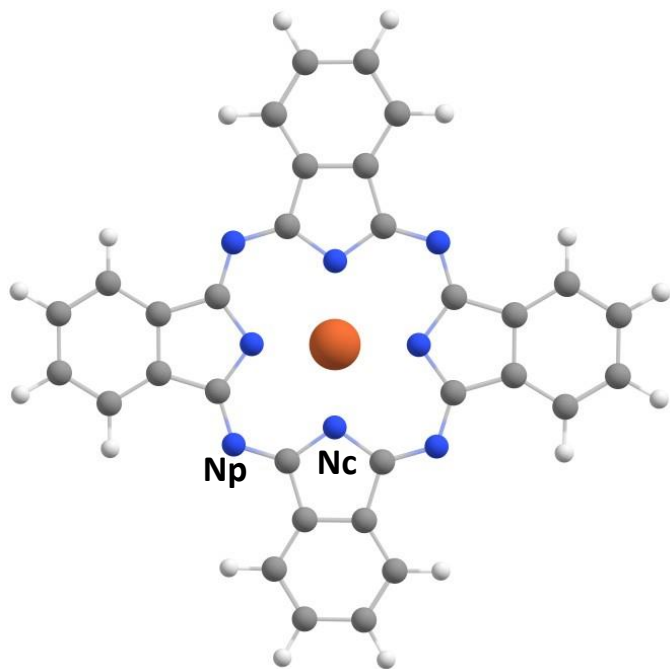
Or study a particular final electronic state and highlight (for instance) interferences between different intermediate states.

G. Goldsztejn et al., PCCP, 2022, **24**, 6590



## (Metallo-)phthalocyanines in the gas phase: a good benchmark molecule

MPC

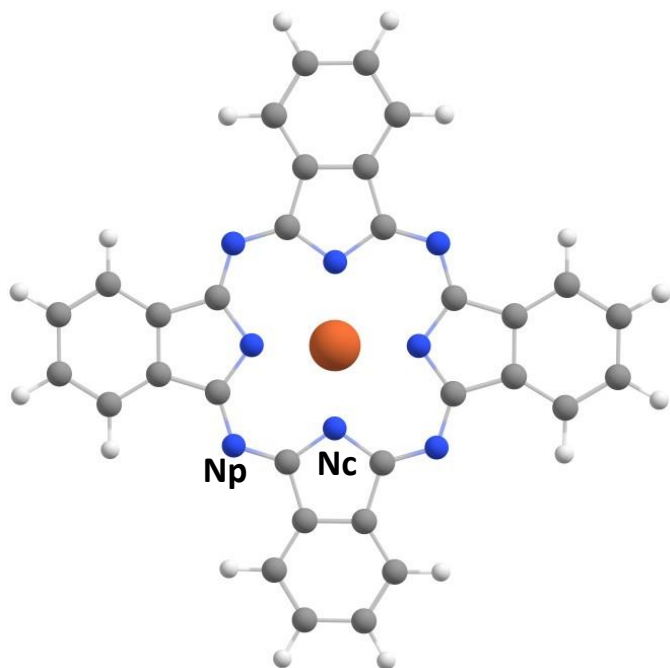


H<sub>2</sub>Pc

- Large molecule with a rich photophysics
- Transition metal: strong interaction  $3d(M)/\pi(L)$
- Symmetry helps

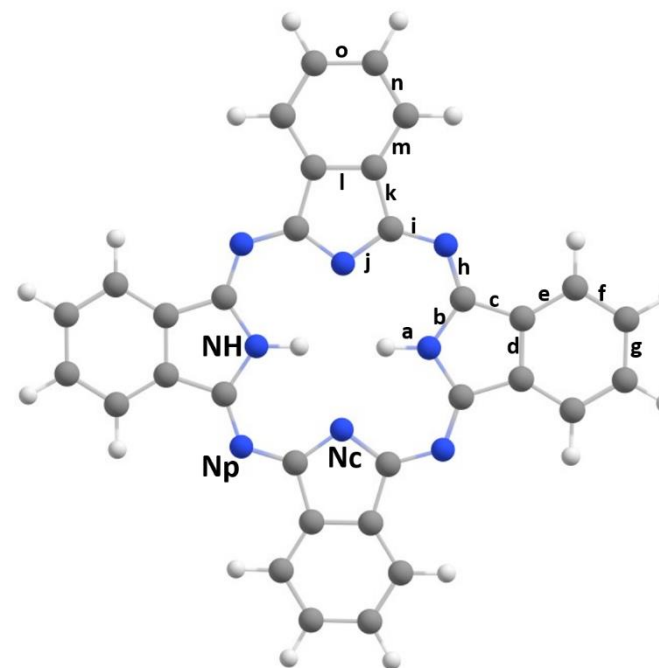
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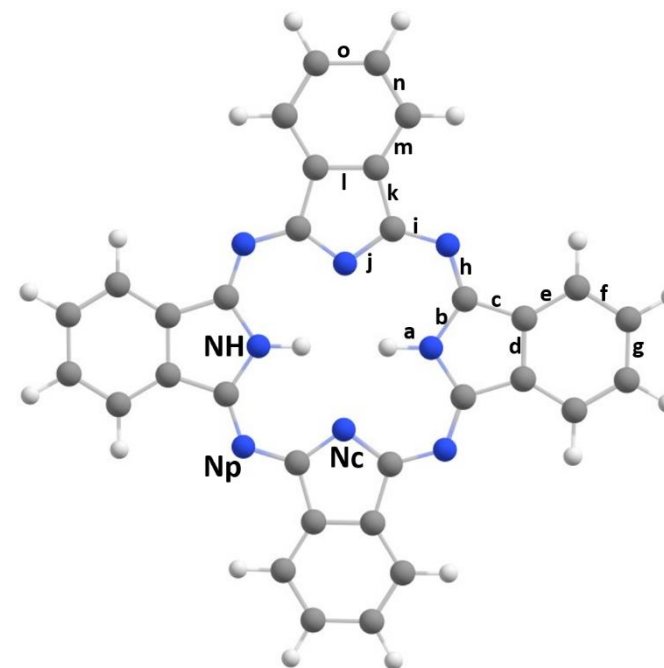
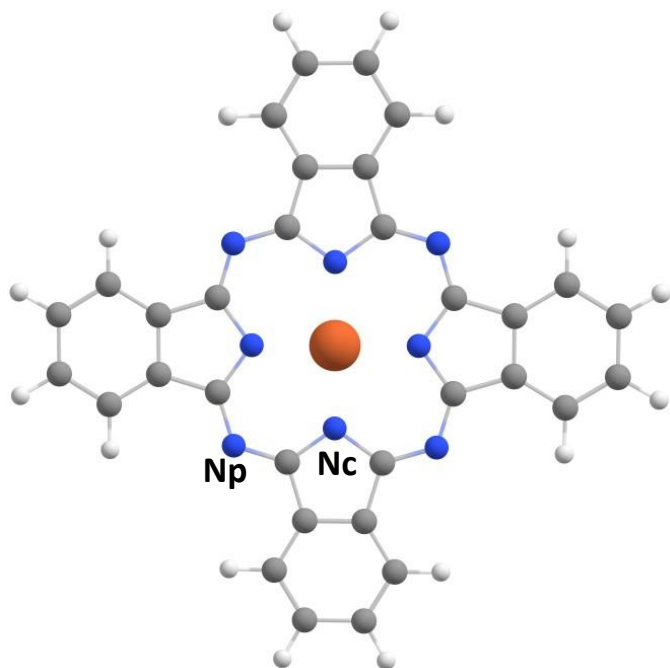
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- Electron spectroscopy to:
  - Determine the electronic configuration within M
- Resonant Auger spectroscopy as local probe of:
  - The chemical environment
  - The ultrafast electronic rearrangement

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Experiments done at PLEIADES (SOLEIL): gives access to valence and core shells. In the gas phase with an oven we designed specifically for this beamline

# What do we need to determine the metal's electronic configuration?

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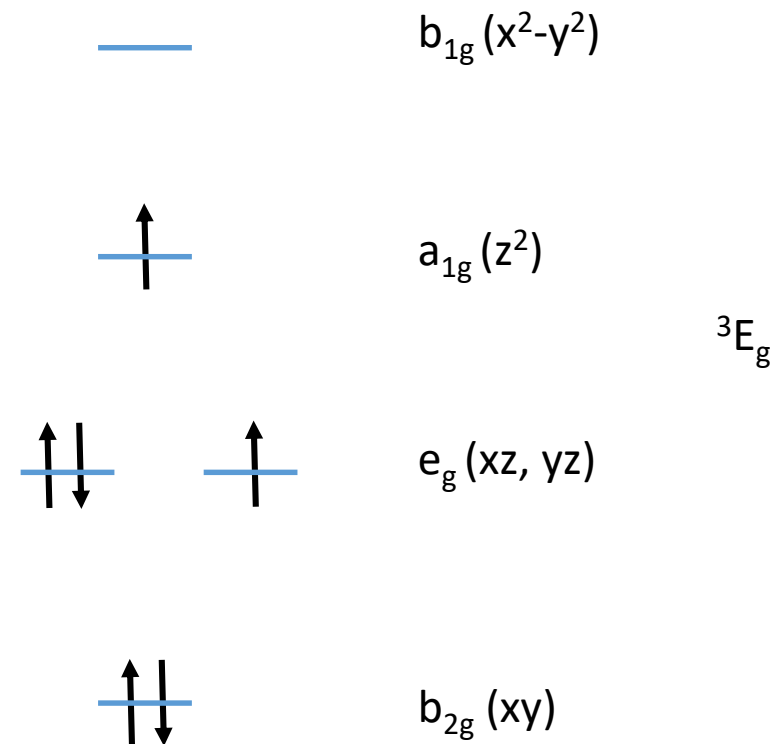
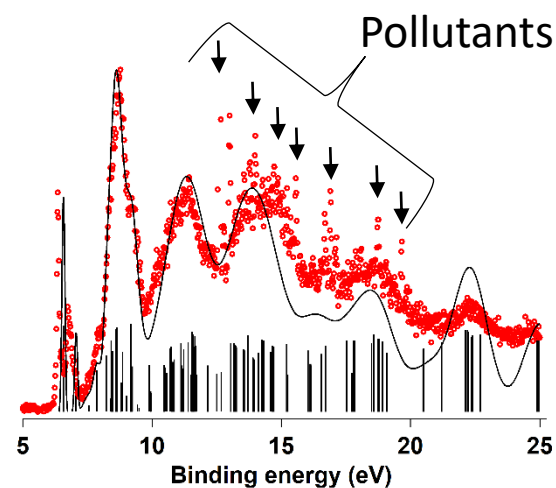
Answer: a lot of spectra and (at least) two theoretical methods to simulate them



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Valence photoelectron spectra + DFT calculation

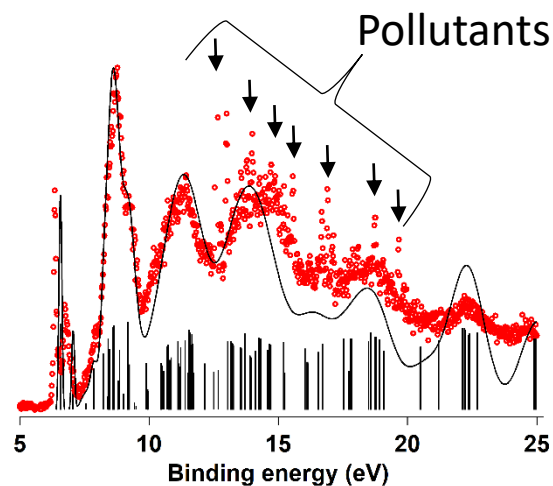


J. Laurent, ..., and G. Goldsztejn, Phys. Chem. Chem. Phys., 2022, **24**, 2656

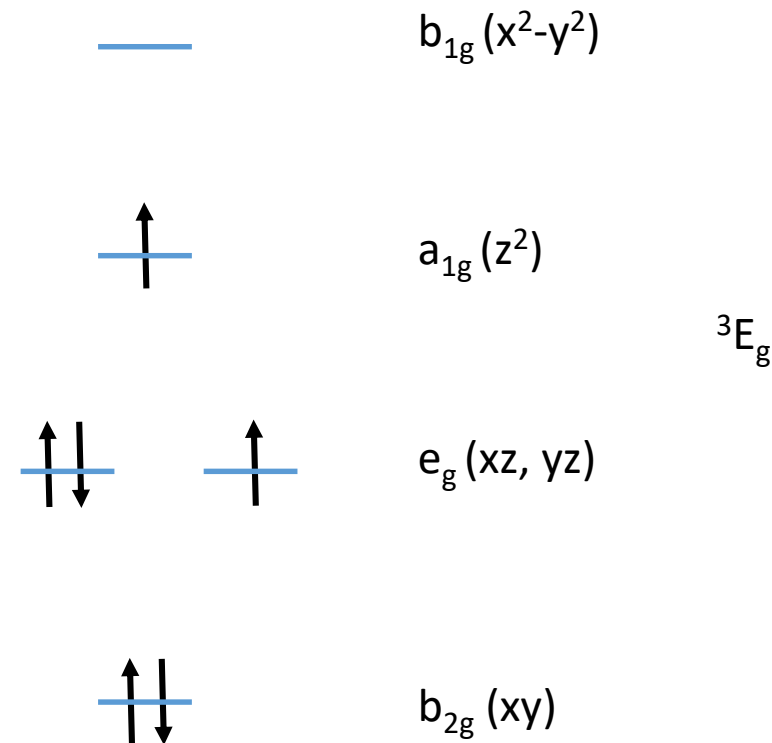
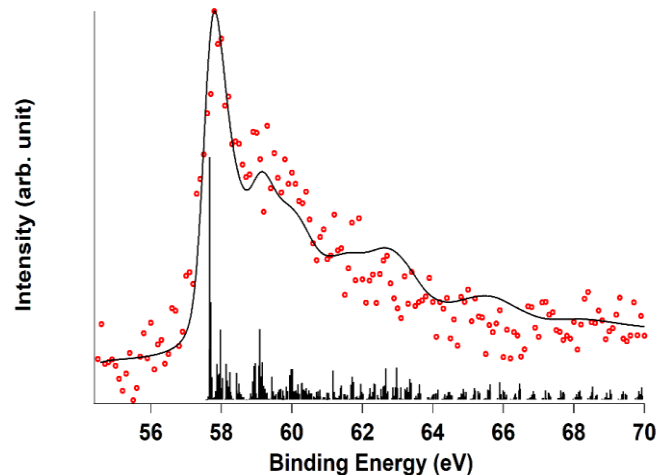
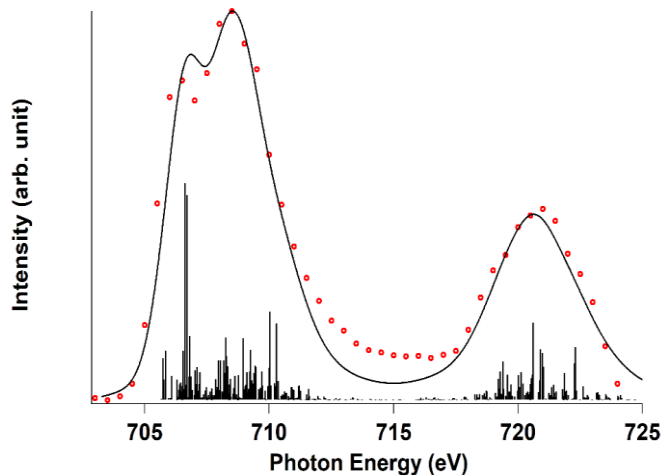
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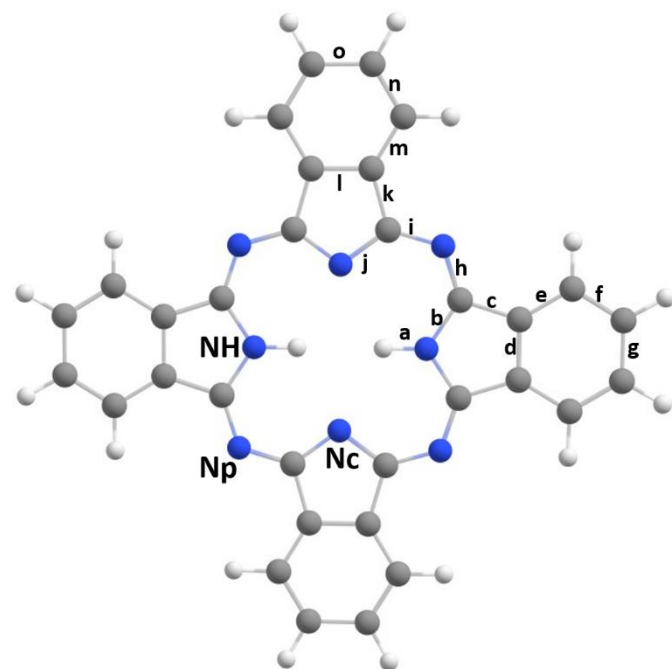


Fe 2p absorption + Fe 3p photoelectron spectra + CTM calculations



J. Laurent, ..., and G. Goldsztejn, Phys. Chem. Chem. Phys., 2022, **24**, 2656

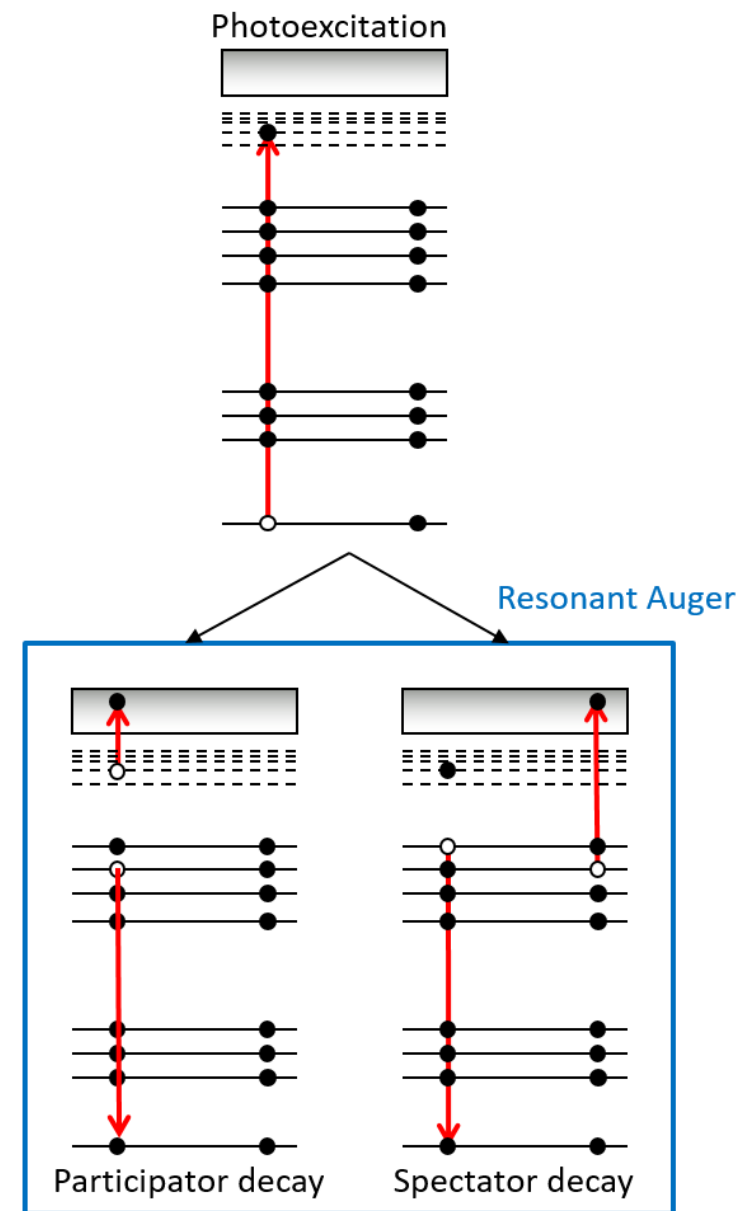
# How sensitive are we to the chemical environment?



$H_2Pc$

Resonant Auger spectroscopy:

- Local character of the core-shell excitation
- Sensitive to chemical environment because of valence holes



# How sensitive are we to the chemical environment?

$$\sigma(\omega, \omega') \propto \sum_f \left| \sum_c \frac{\langle \Phi_f | Q | \Phi_c \rangle \langle \chi_f | \chi_c \rangle \langle \Phi_c | D | \Phi_o \rangle \langle \chi_c | \chi_o \rangle}{\omega - \omega_{co} + i\Gamma_c} \right|^2 \times \Delta(\omega - \omega' - \omega_{fo}, \Gamma_f)$$

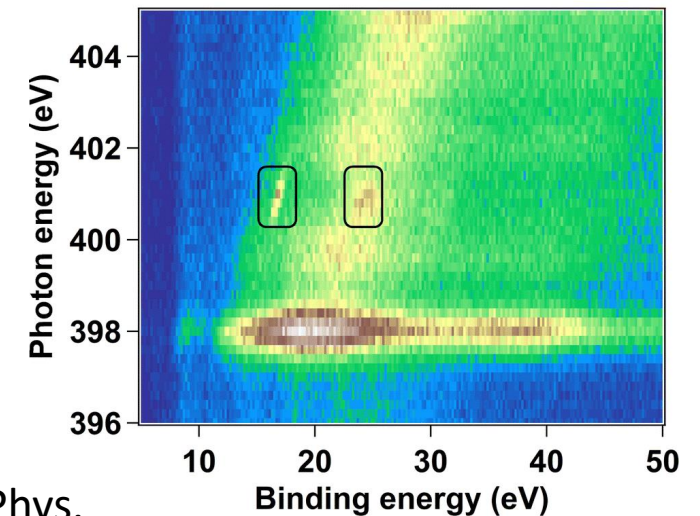
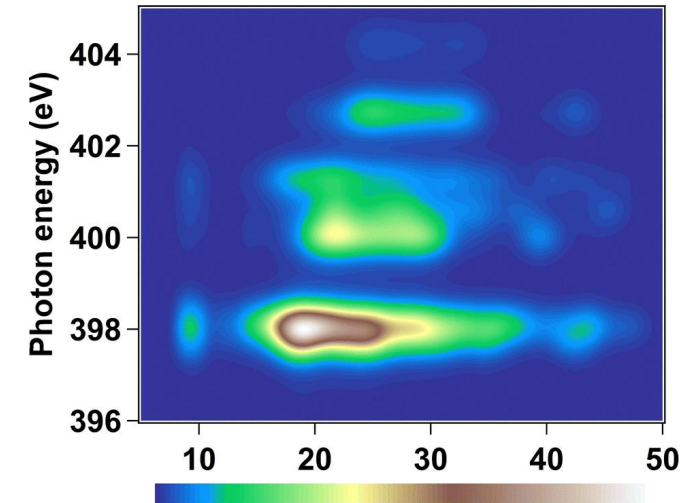
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- 2D-map: x-axis = binding energy; y-axis = incident energy



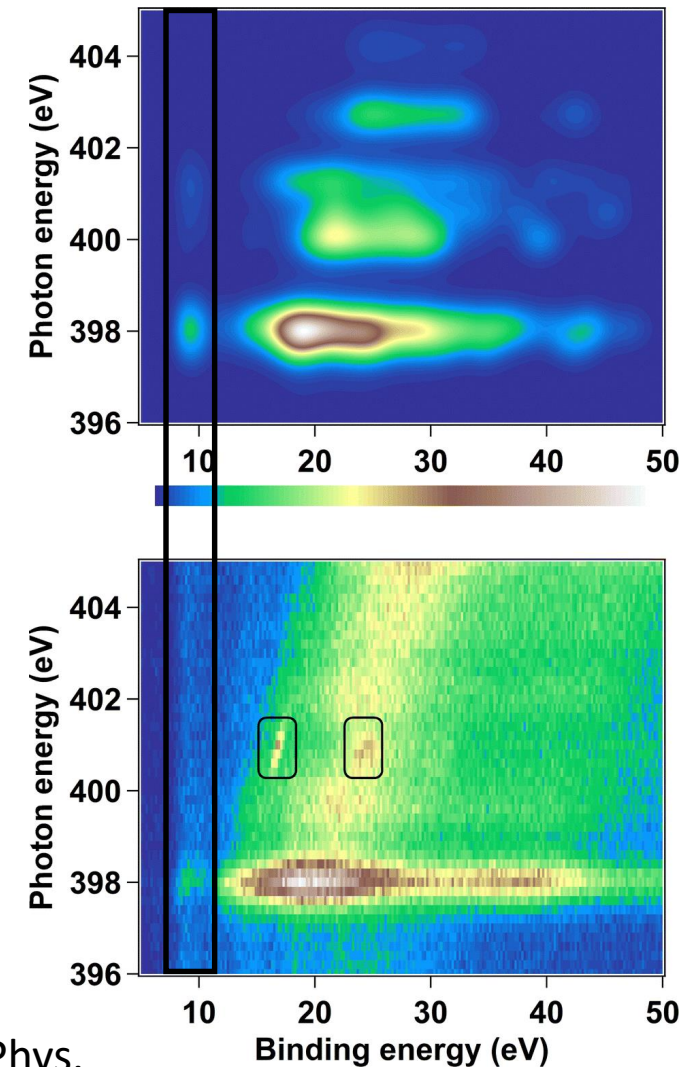
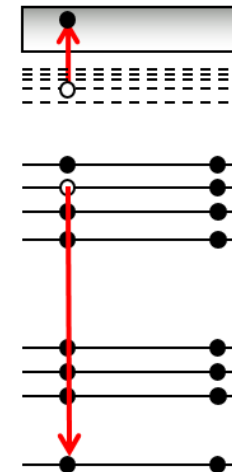
C.E.V de Moura, ..., and G. Goldsztejn, Phys. Chem. Chem. Phys., 2023, **25**, 15555

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- Vertical lines = participator Auger decay at fixed binding energies



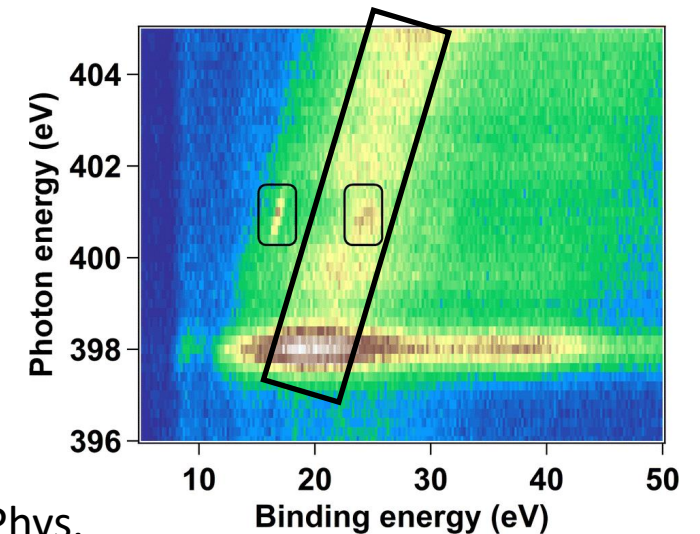
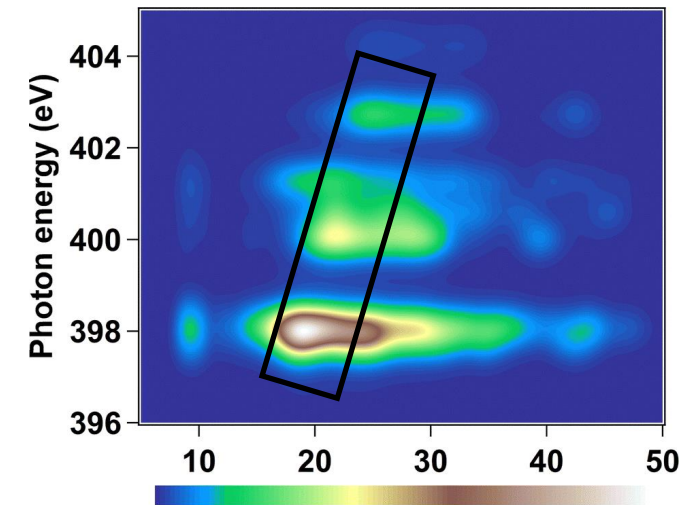
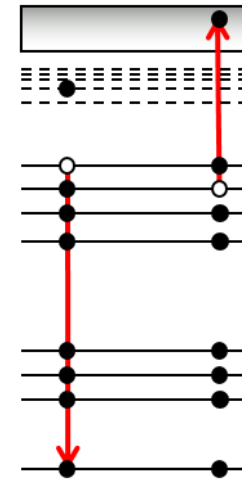
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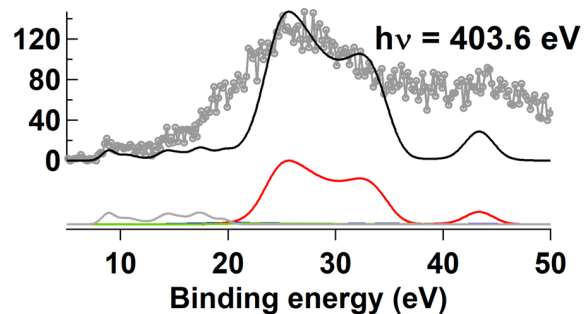
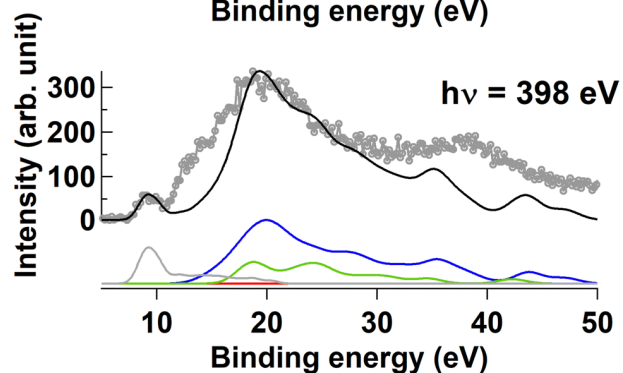
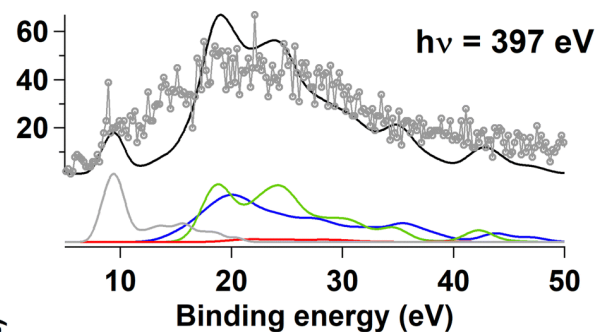
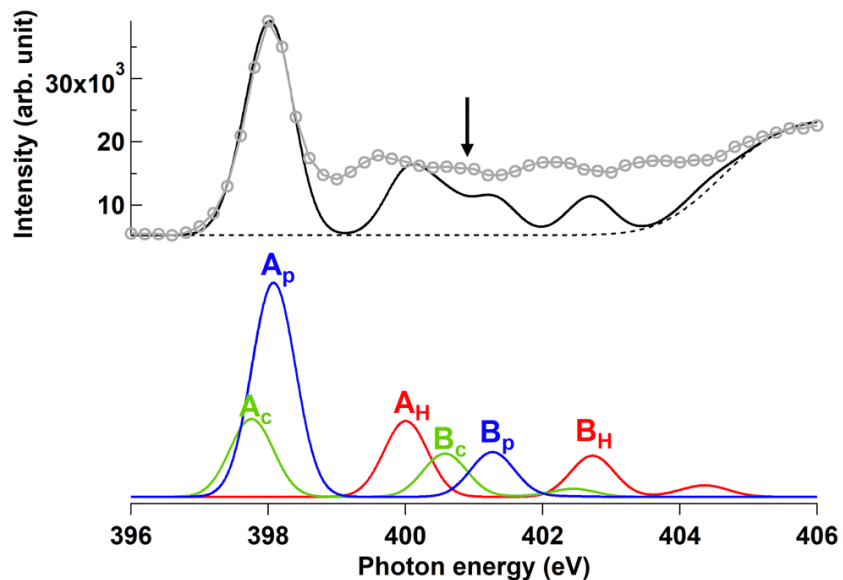
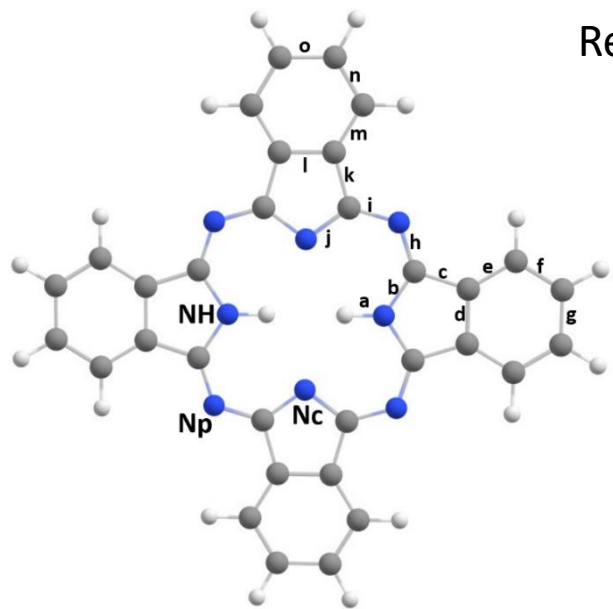
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- Diagonal lines = spectator Auger decay



C.E.V de Moura, ..., and G. Goldsztejn, Phys. Chem. Chem. Phys., 2023, **25**, 15555

# How sensitive are we to the chemical environment?

Resonant Auger spectroscopy more sensitive than absorption spectroscopy, but...

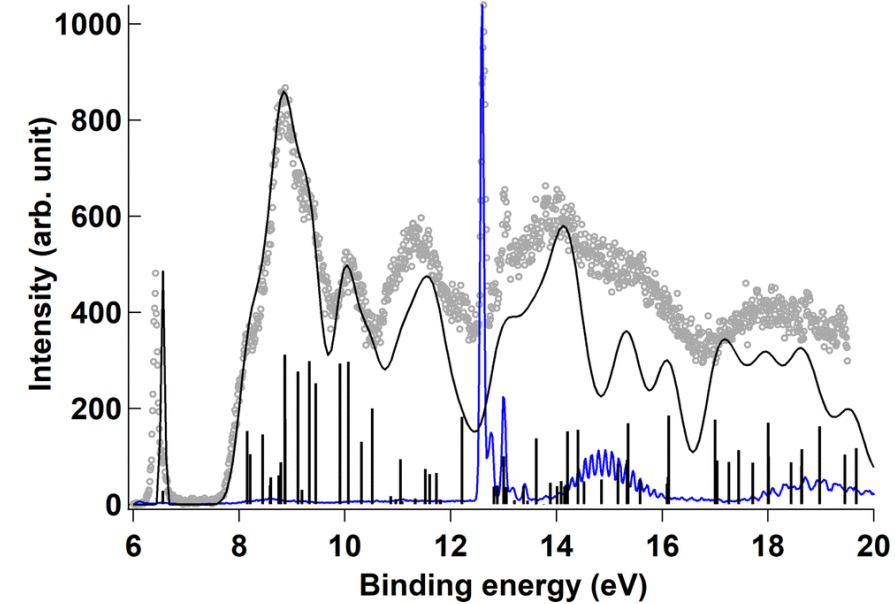
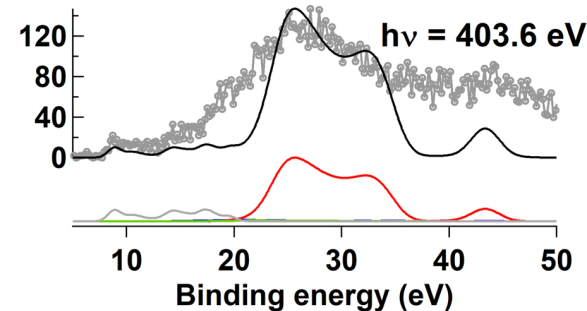
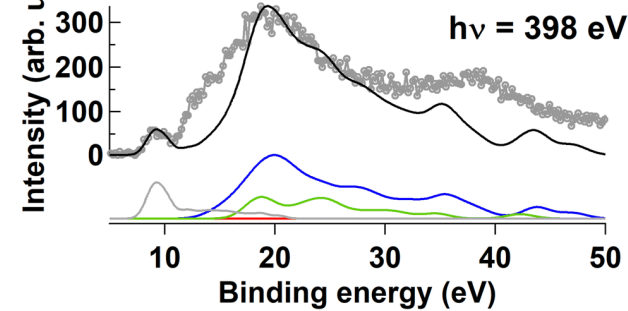
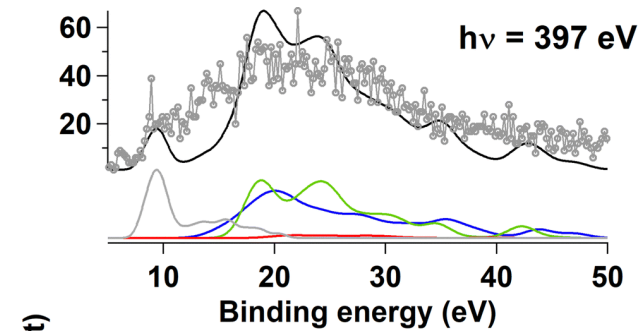
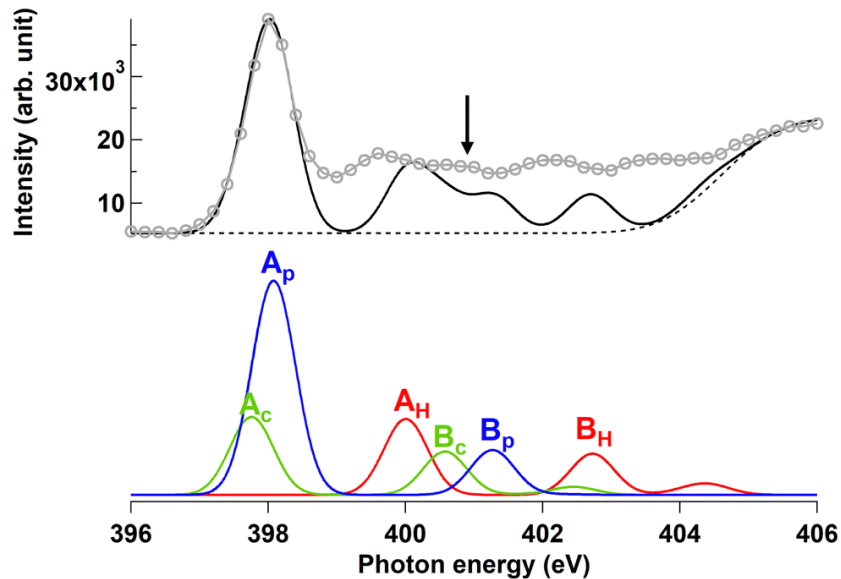
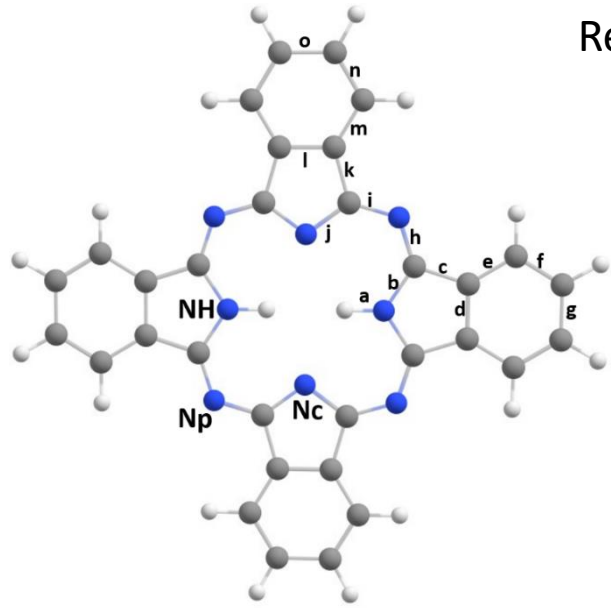


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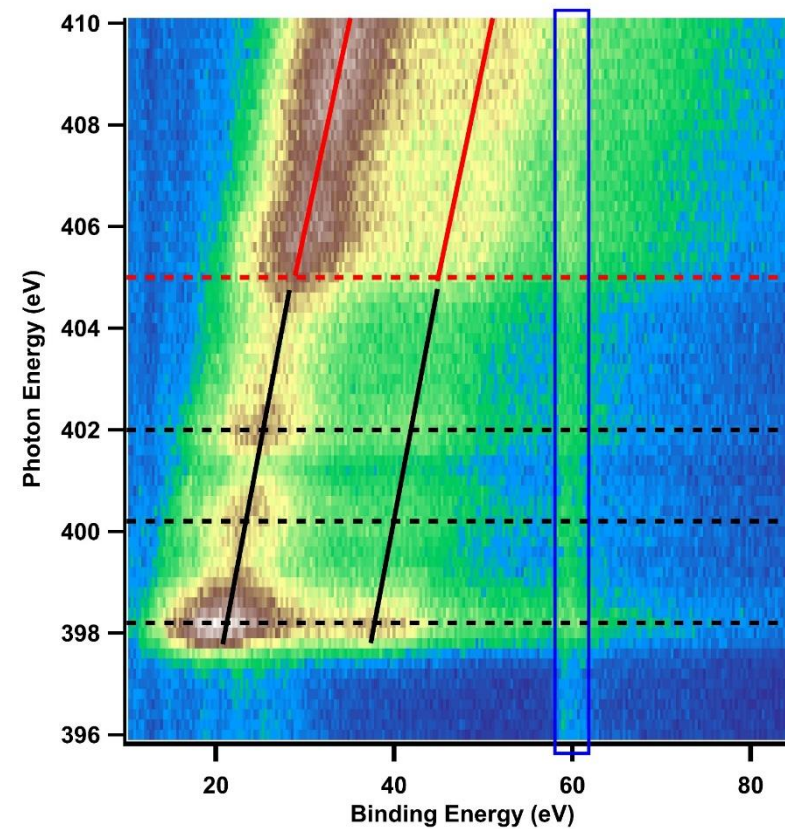
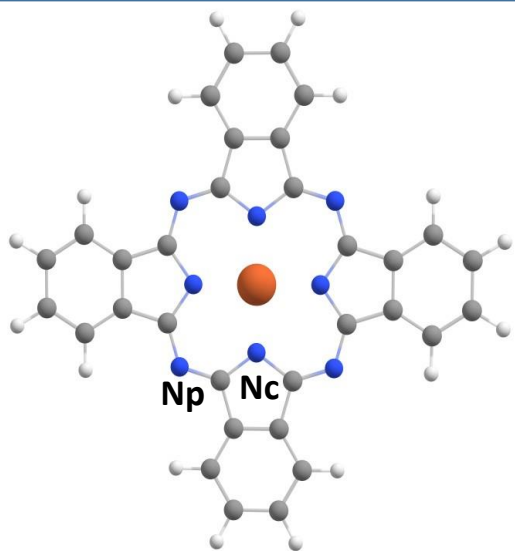
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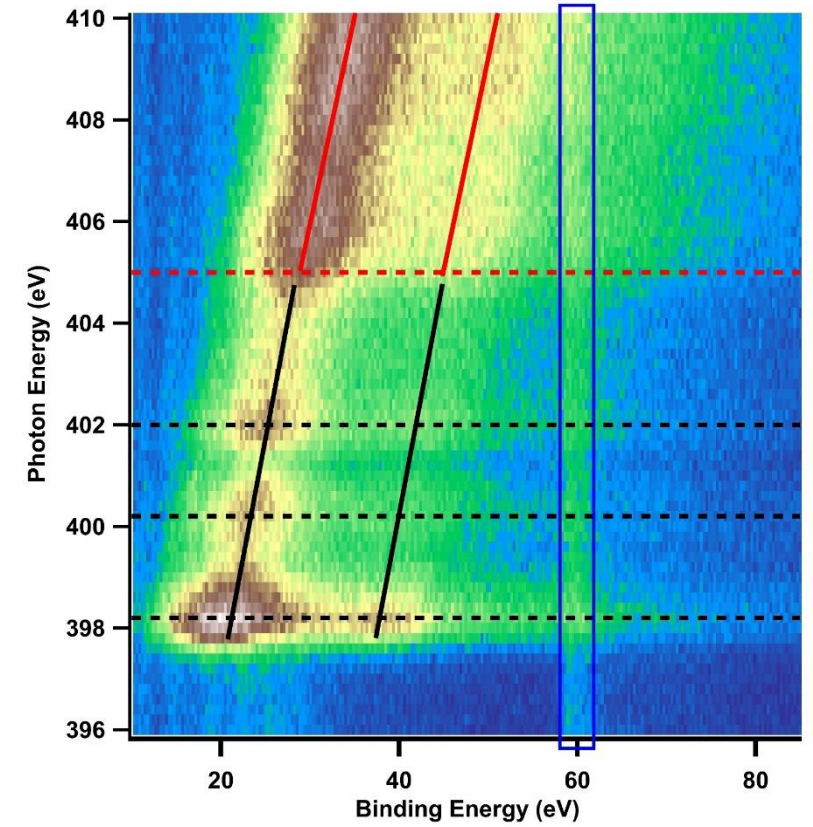
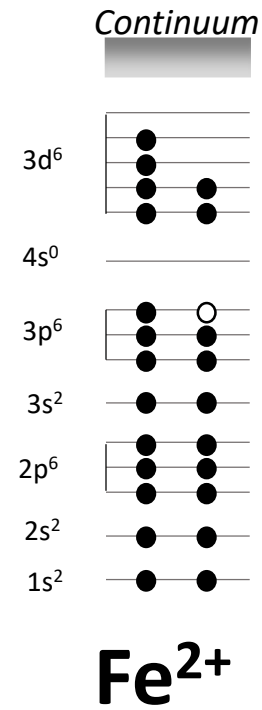
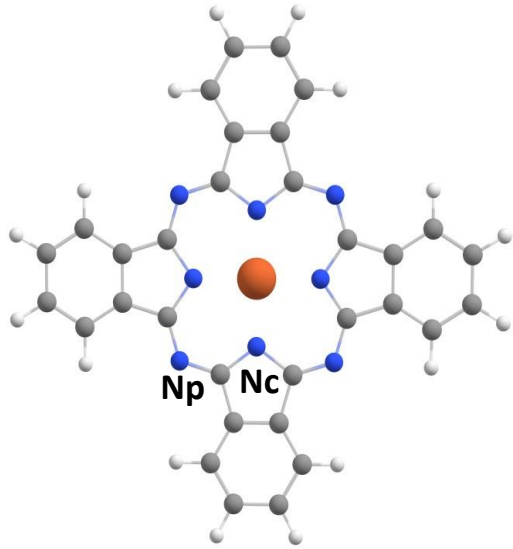
... valence spectroscopy helped us interpret the resonant Auger spectra

C.E.V de Moura, ..., and G. Goldsztejn, Phys. Chem. Chem. Phys., 2023, **25**, 15555

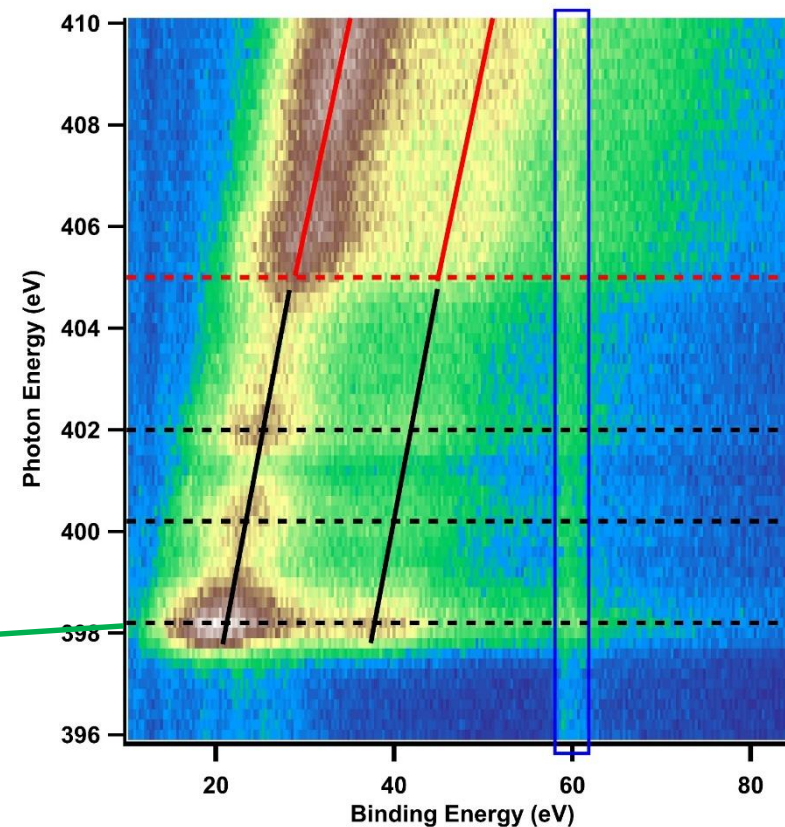
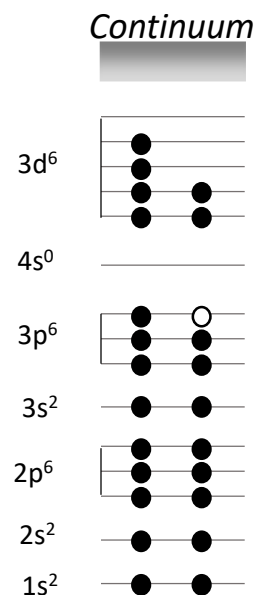
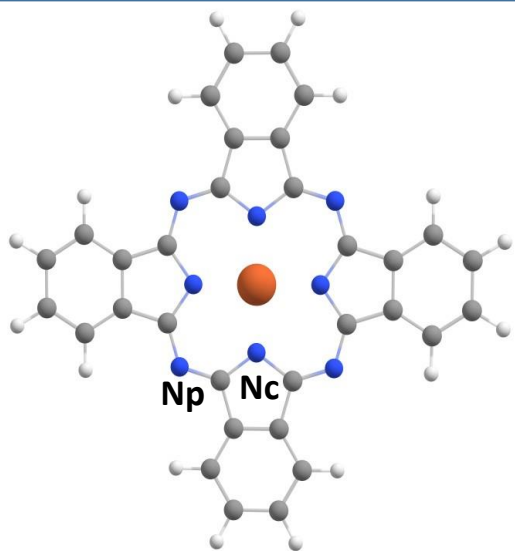
# Can we probe localized ultrafast electronic processes?



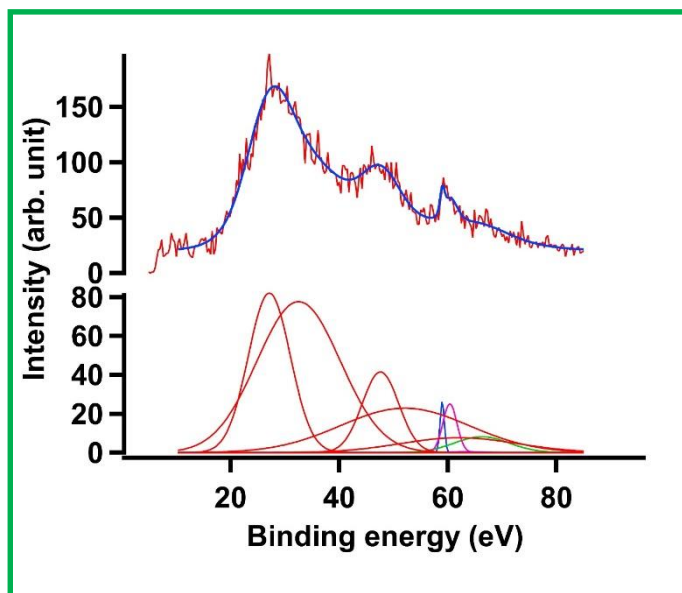
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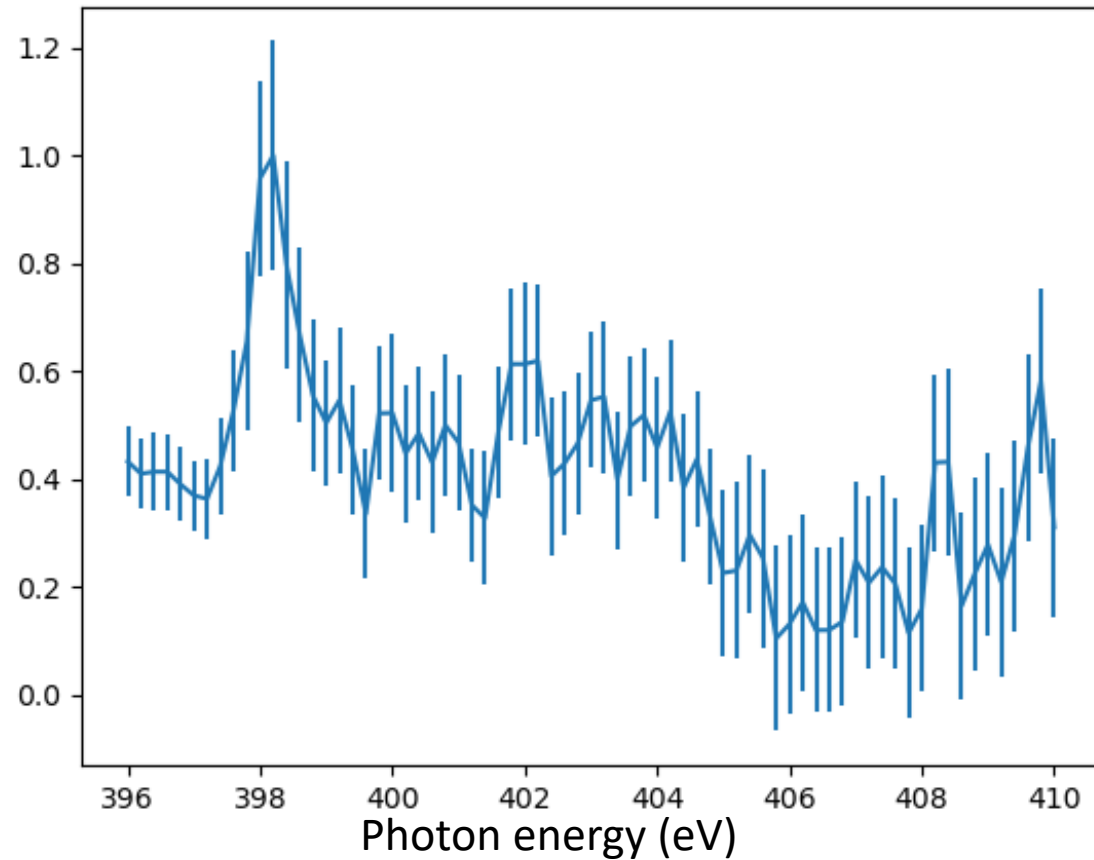


Fe<sup>2+</sup>



Step-by-step fitting methodology to extract the cross section (see Manon's poster)

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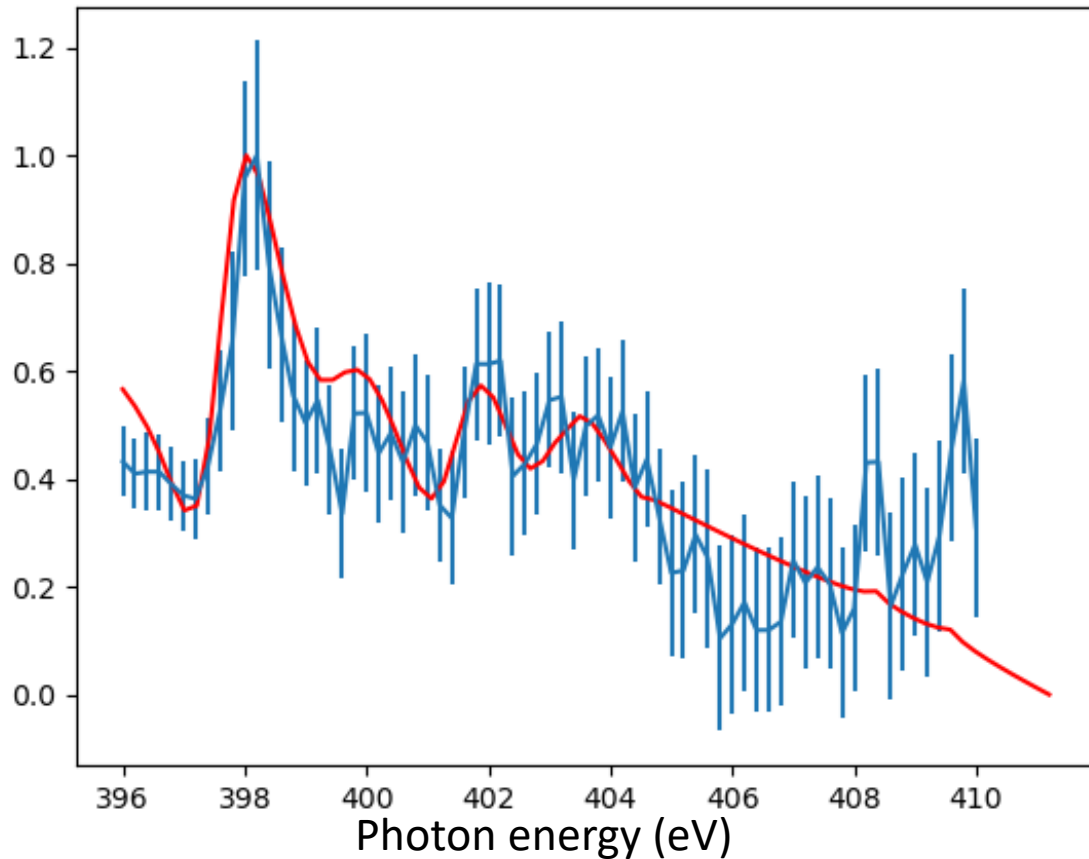


M. Carrière, ..., and G. Goldsztejn, in preparation

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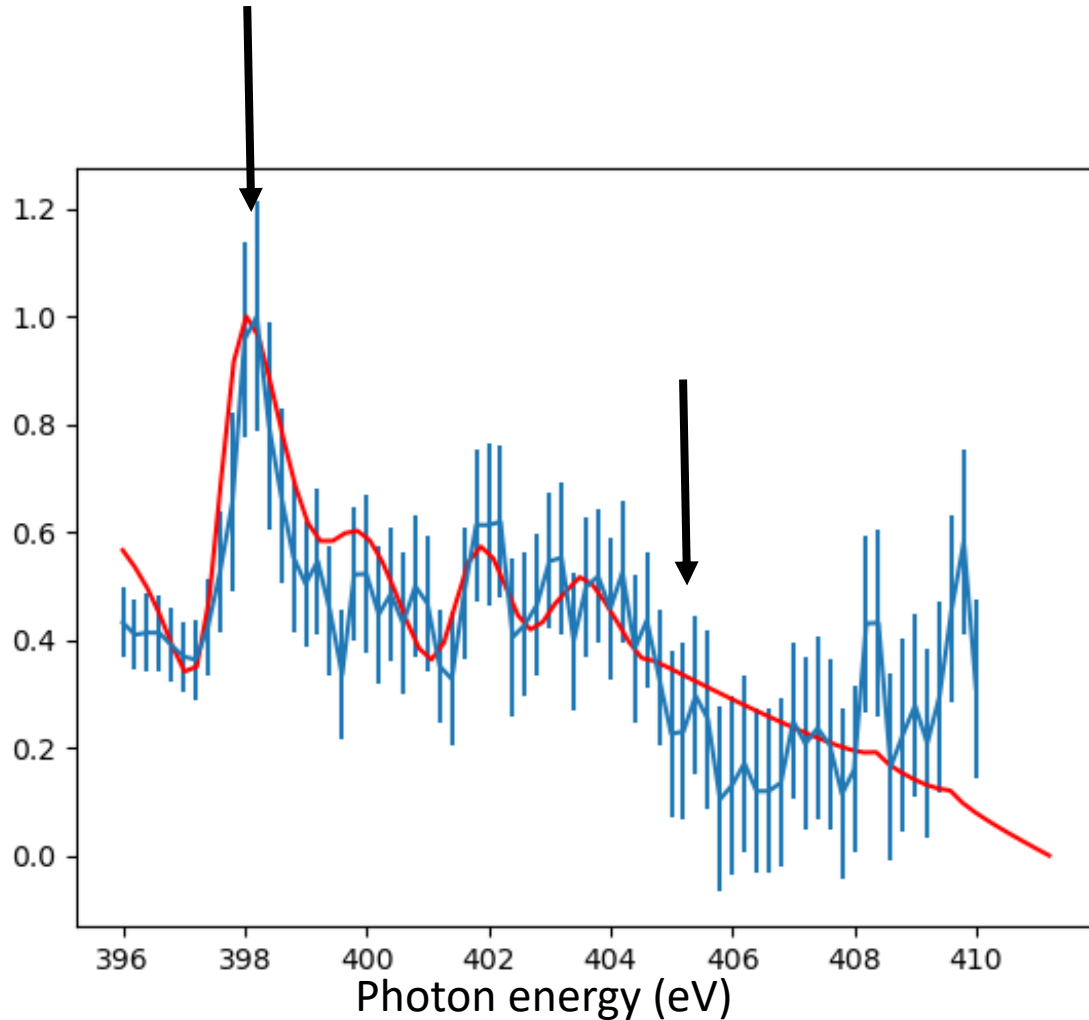
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- Resonance from a N 1s discrete state
- Decrease after ionization threshold



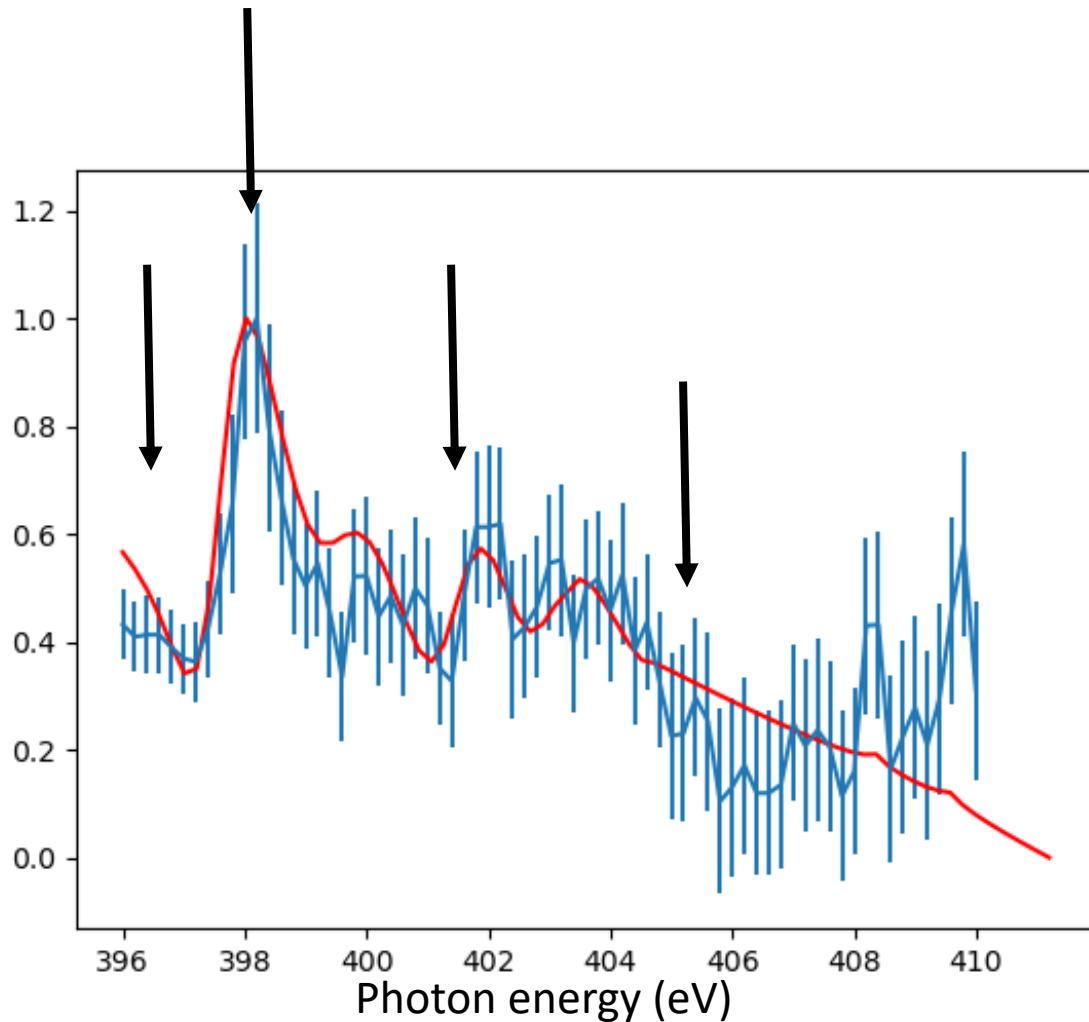
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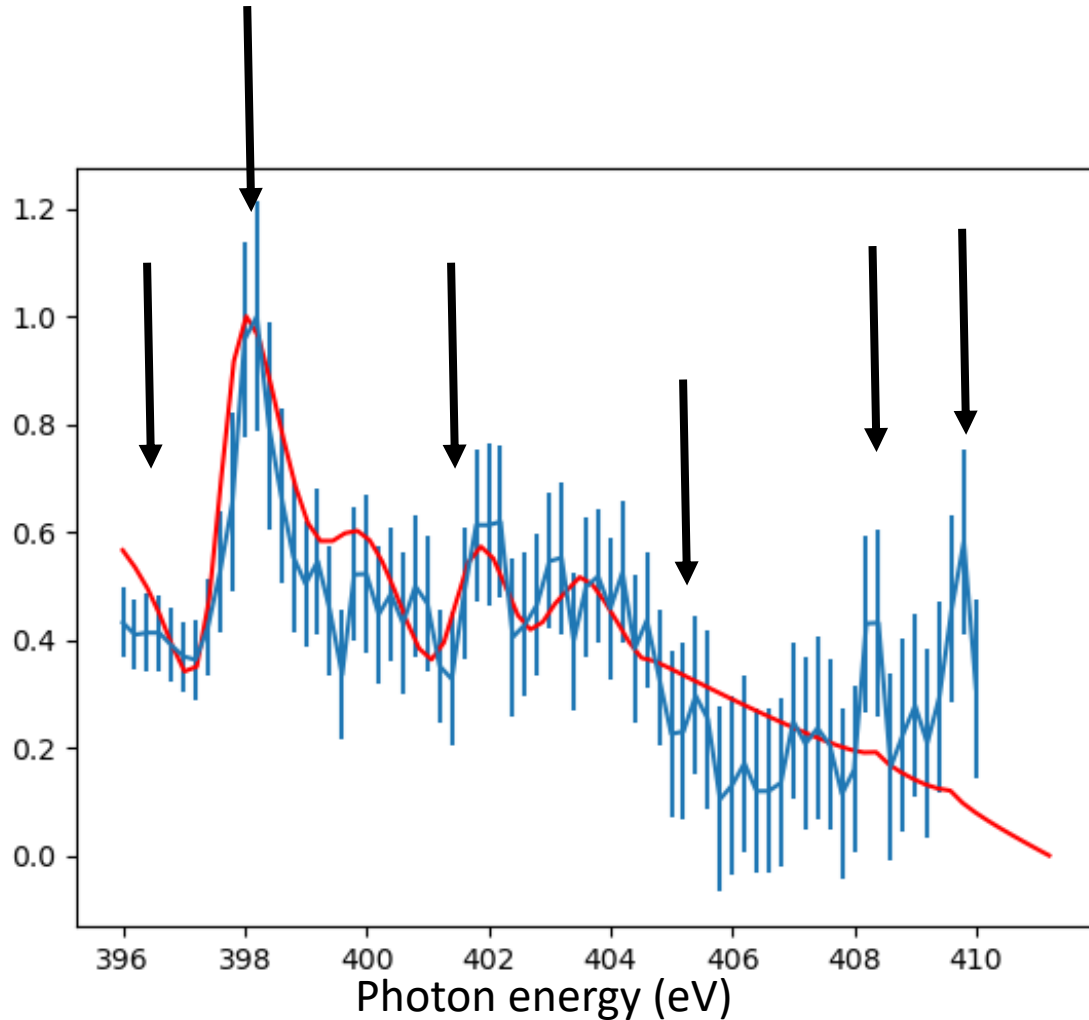


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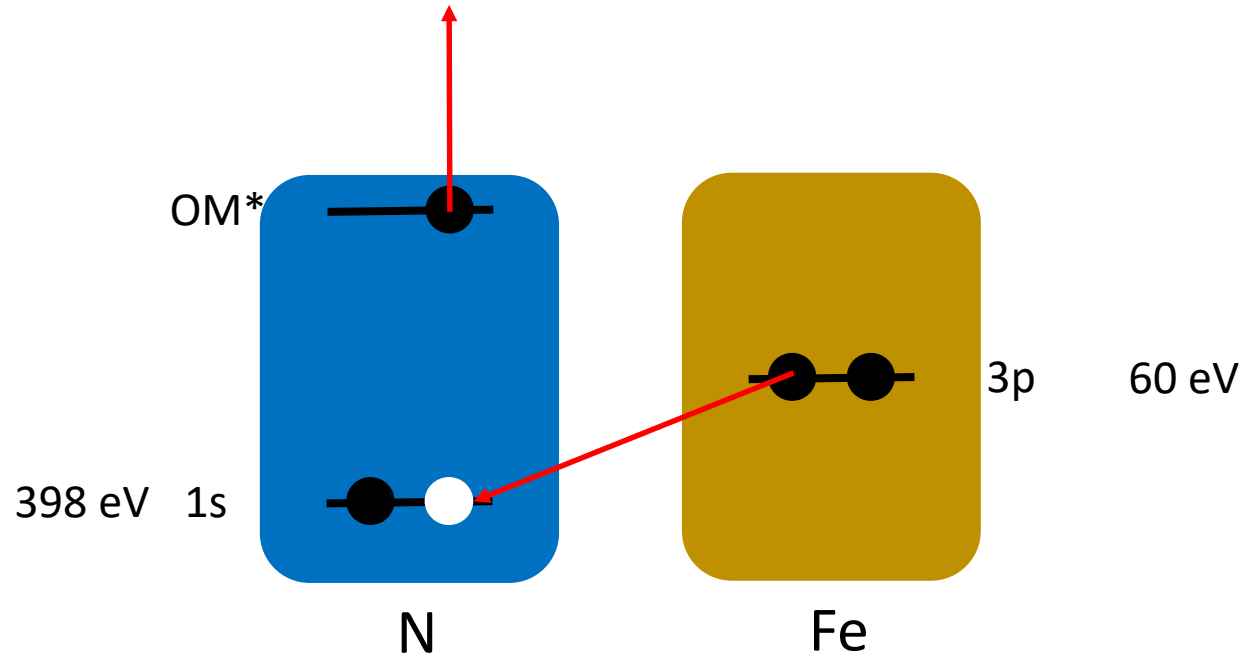
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- Resonance from a N 1s discrete state
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- Fano-type interferences between continua states



M. Carrière, ..., and G. Goldsztejn, in preparation

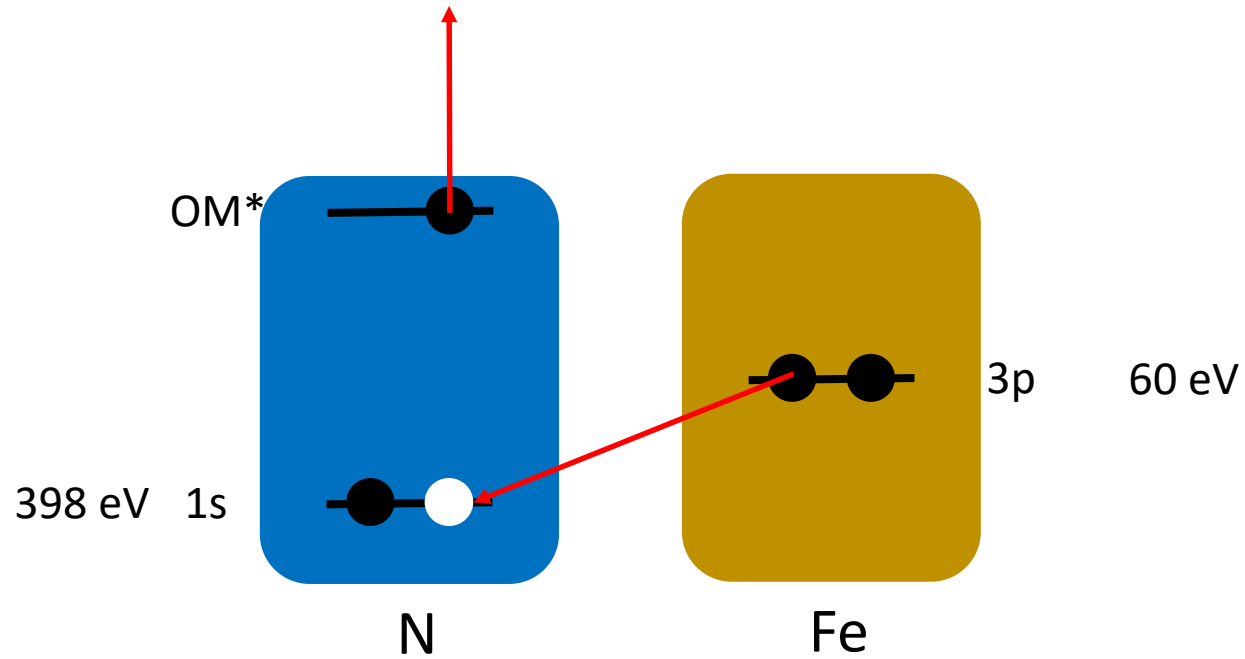
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Interatomic Coulomb decay (ICD) like  
+ electronic states' interferences

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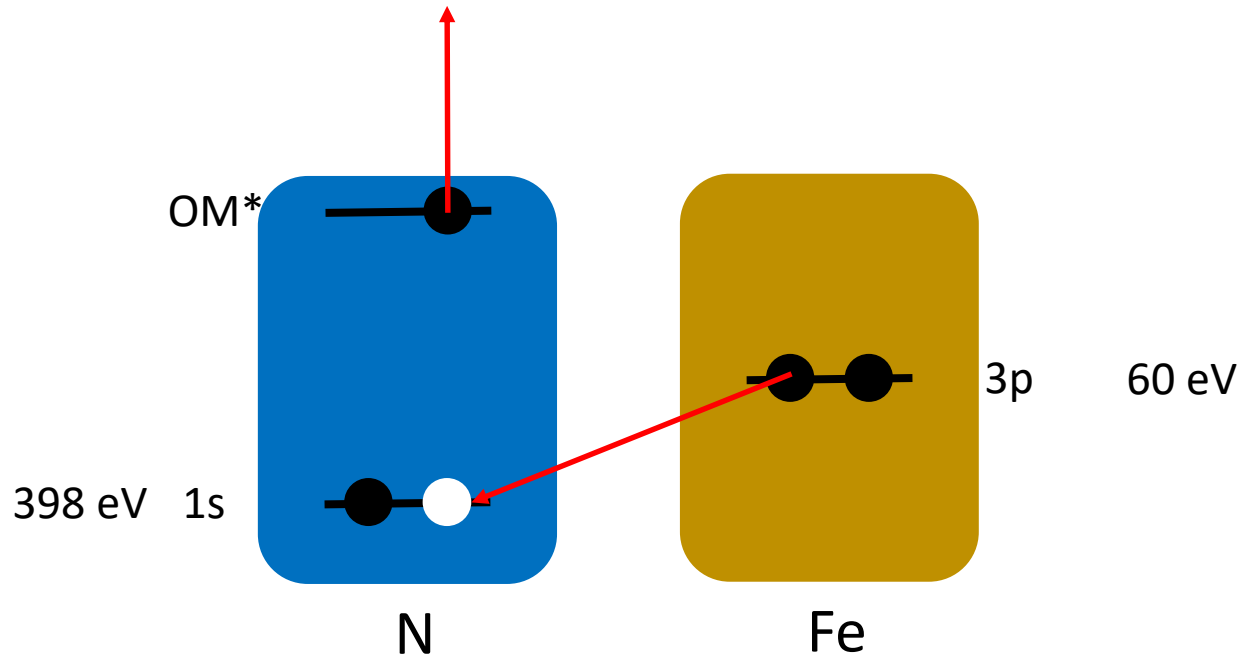


Interatomic Coulomb decay (ICD) like  
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Is it related to a particular transition  
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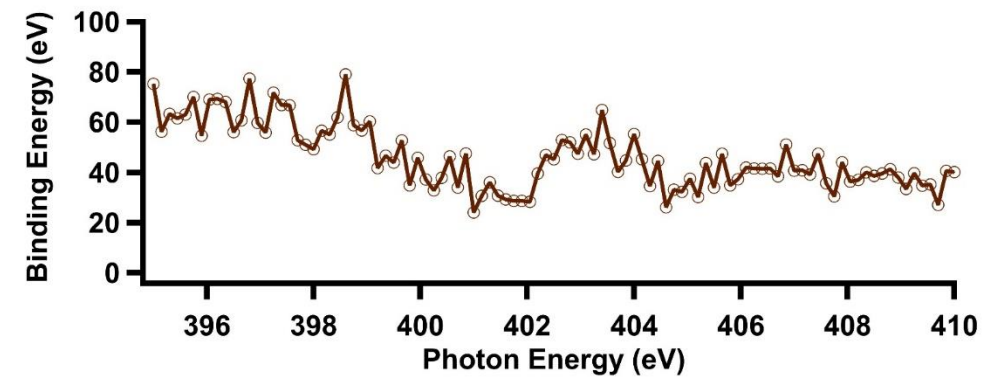
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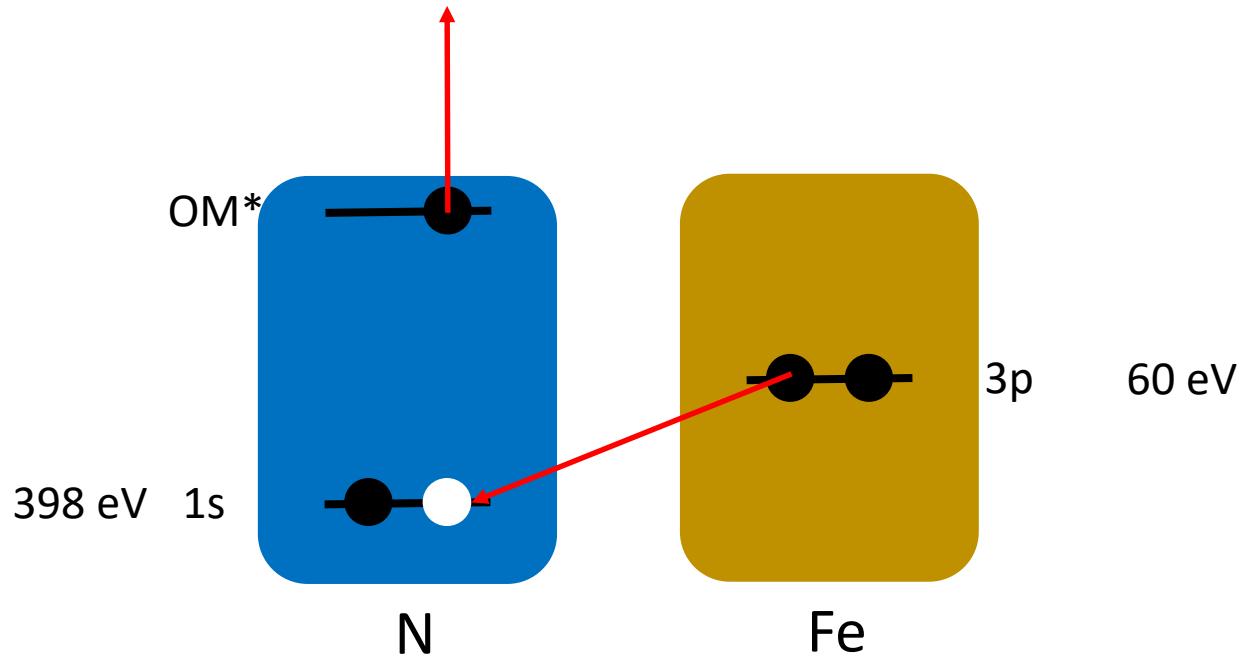
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Cobalt phthalocyanine = no clear sign of ICD



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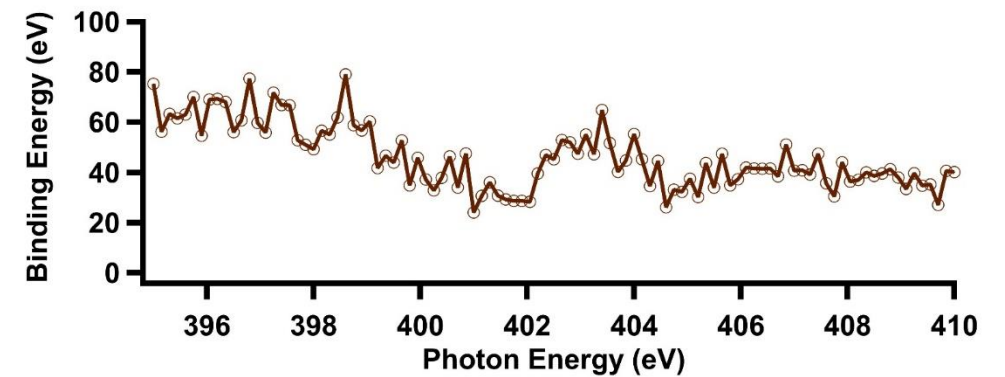


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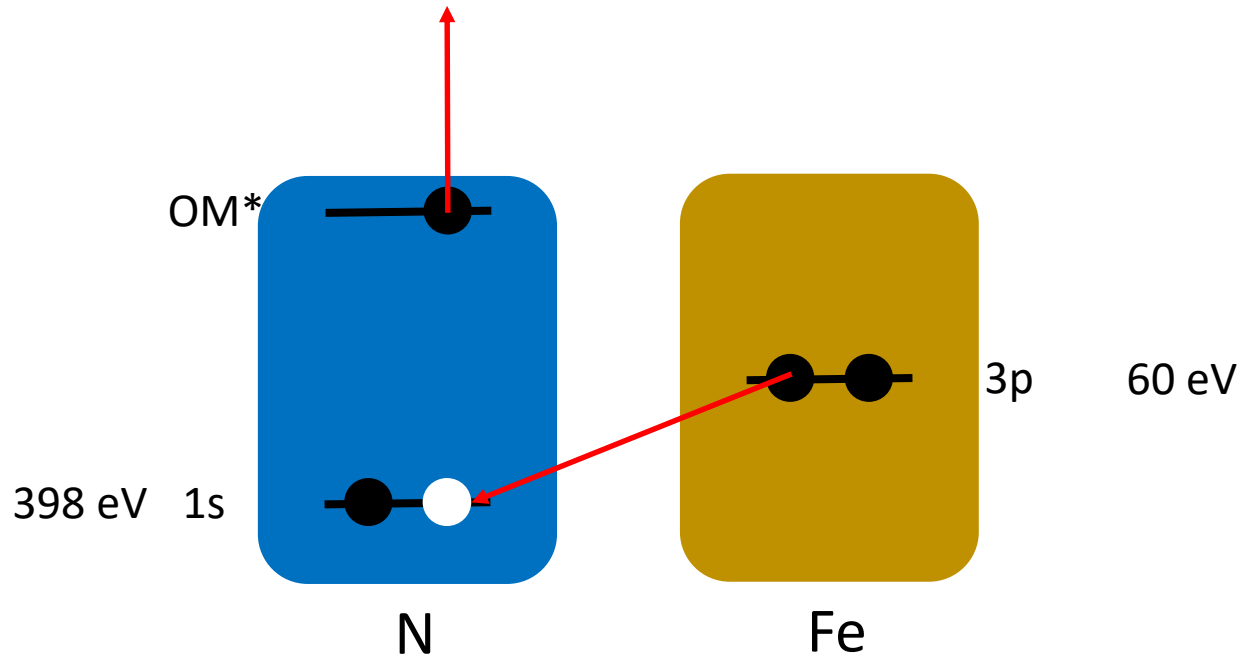
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Can you tell us why?



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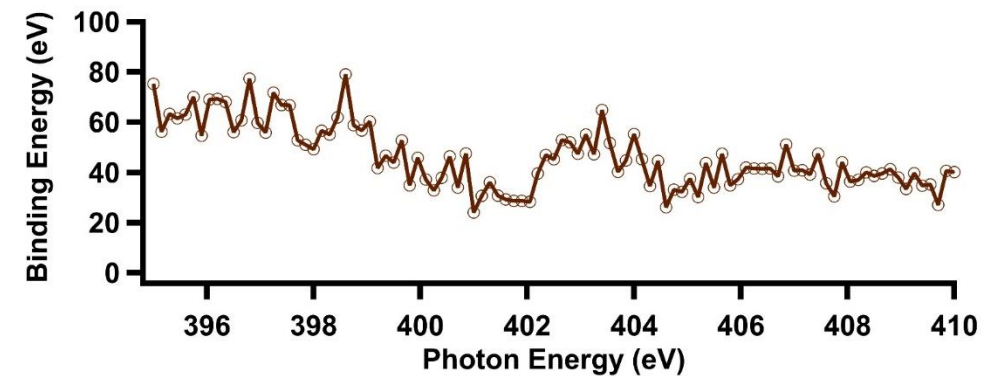
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Can you tell us why?

**NO**



M. Carrière, ..., and G. Goldsztejn, in preparation

## It is possible to have access to subtle, ultrafast, localized dynamical processes or to electronic configurations:

- Information is a bit more blurry
- Requires more spectra in various regions of the incident energy
- And on related molecules
- To accept doing (severe) approximations in the simulations

## Ways to improve:

- Having a better-resolved spectroscopy
  - New evaporation method
  - Supersonic expansion to cool the molecules
  - New spectrometer
- Having better theoretical methods

}  
} Currently under development, see A. Piard's poster

# Acknowledgments

## ISMO

M. Carrière  
A. Piard (master student)  
A. Kumar (post-doc)  
J. Laurent (master student, 2021)  
D. Cubaynes  
N. Shafizadeh  
B. Soep  
P. Çarçabal

## Collaborations

R. Püttner (Freie Universität, Berlin)  
M. Briant (NIMBE, CEA Saclay)  
M. Simon (LCPMR, Paris)

## PLEIADES

J. Bozek  
A. Milosavljević  
E. Robert

**Thank you for your attention**



# Don't forget the posters

## Manon Carrière

**Interatomic coulomb decay in molecules of biological interest**

Manon Carrière, Jonathan Laurent, J. Bozek, M. Briant, P. Carcabal, D. Cubaynes, N. Shafiqzadeh, M. Simon, B. Soep, R. Pöltner et Gildas Goldsztein  
CNRS, UMR 8214, Institut des Sciences Moléculaires d'Orsay, France.

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**Motivation**

Metallophthalocyanins (MPc) are synthetic molecules, symmetrical, the best known synthetic porphyrin analogues, essential bricks of many molecules of the living (heme, chlorophyll, vitamin B12...). These complex molecular systems present very rich photochemistry and photochemistry following photoabsorption.

**Experimental measures on iron phthalocyanin**

- Measures were carried out at the PLEIADES beamline of the French national synchrotron SOLEIL.
- X-ray electron spectroscopy was realized in the tender x-ray region

**Dominant process : Auger Effects**

◊ Dashed red line : ionization potential of Fe 3p  
 ◊ Red lines : Normal Auger  
 ◊ Black lines : Resonant Auger  
 ◊ Dashed black lines : electronic transitions  $N 1s \rightarrow 1$   
 ◊ Blue rectangle : Photoelectron peaks from the 3p shell of the iron atom

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**ICD (Interatomic coulomb decay)**

Process theoretically predicted in 1997 [1]

- Studied exhaustively and observed on small specific systems such as rare gas dimers [2, 3]) but has never been observed on systems the size of a metallophthalocyanin.
- Has been predicted to occur everywhere in living organisms[4]

**Methodology and data processing**

Determination of the iron 3p contribution using a spectrum made with an incident energy of 100 eV.

Then, we fit the whole spectrum, with the overlapping of the Auger contributions (in red) and the iron contributions (coloured blue, pink, purple and green). For each region the contributions of the electrons emitted by the iron atom are simulated by four gaussians. For the electron Auger contributions we had to do three different treatments:

- Region 1 (396; 397.4 eV) : contributions correspond to a continuous background and a low probability of exciting the first resonance under its threshold, we used three or four gaussians depending on the energy. The position of the Gaussians are fixed and their intensities are left free, the 4 Gaussian functions modeling the Fe 3p-state can only vary in intensity (fixed positions and widths).
- Region 2 (397.6; 404 eV) : for the resonant Auger we used four gaussians. We followed a shift between 0 and 0.4 eV from their previous position.
- Region 3 (404.6; 410 eV) : after the ionization threshold, the normal Auger is the dominant way of relaxation. Here we had to use five gaussians and shift them by 0.2 eV, as previously explained.

In each region, the widths of the Gaussians modeling the Auger contributions are fixed and their intensities are left free, the 4 Gaussian functions modeling the Fe 3p-state can only vary in intensity (fixed positions and widths).

**Results and interpretations**

Intensity effect on the effective cross-section of the Fe 3p<sup>1</sup> electronic state around energy 398 eV, which corresponds to the strongest resonance in the absorption spectrum.

This electronic state is populated via passage through an excited core state of an excited core state of a neighbouring nitrogen atom. This therefore proves the ICD process in the iron phthalocyanin molecule.

ICD relaxation process occurring, final state : iron with a hole on 3p shell and electron emission

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**Preliminary Results on Cobalt phthalocyanin**

Same data processing no sign of a particular intensity effect on the cross section for Auger.

Does the ICD process occurs depending on the metal at the center ?

**Cross section of the Cobalt atom in CoPc**

**Conclusion**

- Gas-phase studies give us access to the intrinsic properties of the molecules, unaffected by environmental effects.
- Real differences depending on the transition metal, enabling us to hypothesize the important ingredients for observing this process.
- Progress in the task of establishing a robust methodology for studying ICD in complex molecular systems

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## Apolline Piard

**New spectrometer for ultra-fast electron/ion coincidence measurements**

A. Piard<sup>1</sup>, A. Kumar<sup>1</sup>, P. Carcabal<sup>1</sup>, D. Cubaynes<sup>1</sup>, J. Palaudoux<sup>2</sup>, F. Perent<sup>1</sup> and G. Goldsztein<sup>1</sup>  
<sup>1</sup>Institut des sciences moléculaires d'Orsay (ISMO) UMR 8214, Université Paris-Saclay  
<sup>2</sup>Laboratoire de Chimie Physique-Matière et Rayonnement (LCPMR) UMR 7614, Sorbonne Université

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**Context**

Study of complex molecules in gas phase

- Many processes after photoabsorption
- Can be ultrafast (femtosecond)
- Can be localized on a particular atomic site
- Fragmentation caused by high temperatures

**Examples**

- Photofragmentation
- Charge transfer

**Idea**

Development of a new spectrometer

- Electron/ion coincidence measurements
- Laser desorption
- Transportable

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**Experimental setup**

Laser desorption : gentle evaporation - resolved spectroscopy  
 Transportable on ultra-fast and ultra-high frame rate XUV sources

**kHz laser desorption**

Supersonic rare gas jet allowing

- Drive the molecules towards the ionization zone
- Cool them by collisions

Drawing of the laser desorption setup

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**Electron detection**

**Magnetic bottle**

- Magnet
- Flight tube
- MCP detector

Detection and analysis of electron at 4π steradians

- Improved resolution by adding retarding grids

Schematic representation of the movement of an electron in a magnetic field induced by the magnetic bottle

**Ion detection**

Ion source

Flight tube

MCP detector

Time Of Flight

Schematic representation of an ion TOF

After ionisation by a laser, ions are pulsed by electrodes to the flight tube, then are analysed by a MCP detector

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**Progress of the project**

- Assembly of the magnetic bottle
- First electron detection

Picture of the setup (June 2023)

**Electron measurements**

262 nm nanosecond, kHz laser from a Nd:YLF 4<sup>th</sup> harmonic

First electron signal of DARCO (June 2023)

**Next steps:**

- Assembly of the Ion TOF
- Coincidence measurements
- Pump-probe measurements
- Laser desorption

DARCO (1,14-diazabicyclo[2.2.2]heptane)