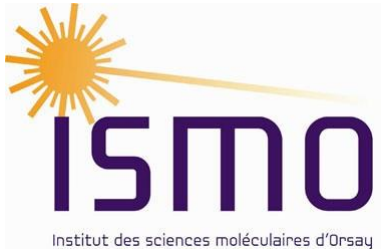
XUV and X-ray spectroscopy of phthalocyanines in the gas-phase

Gildas Goldsztejn

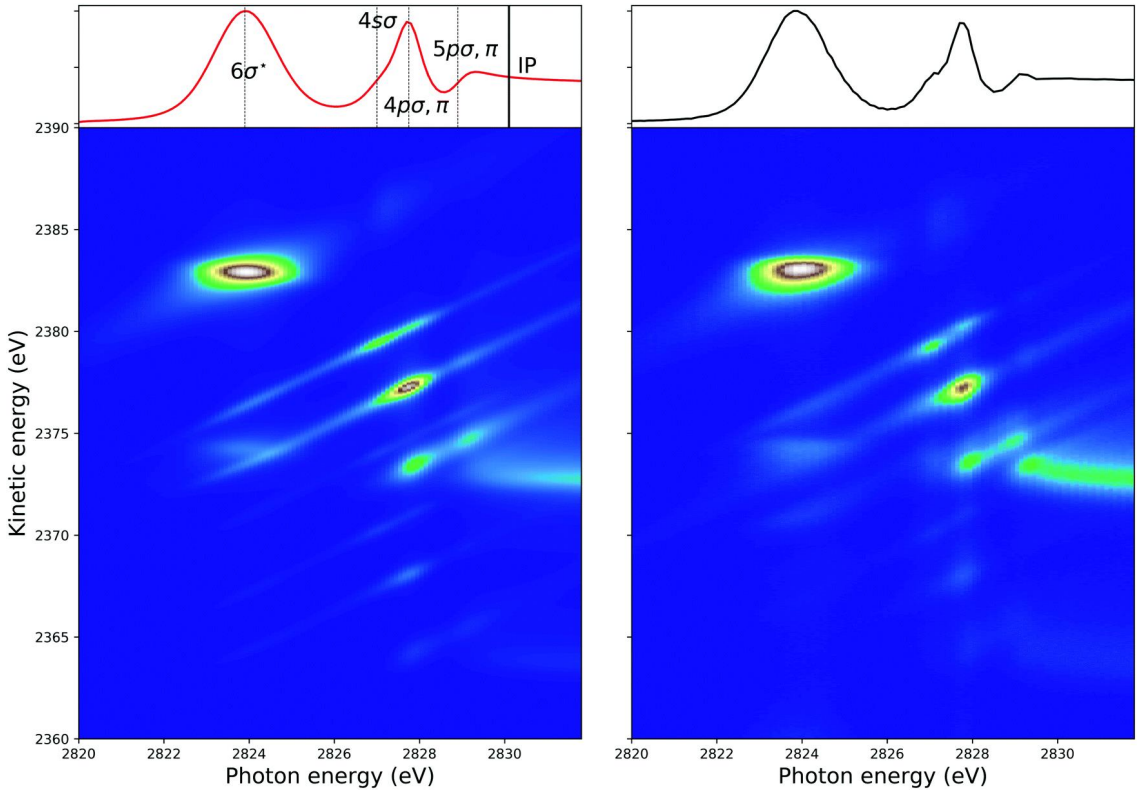
Institut des Sciences Moléculaires d'Orsay (ISMO)



SFP-MC14, July 5th 2023

The ideal case: a diatomic molecule (HCl)

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

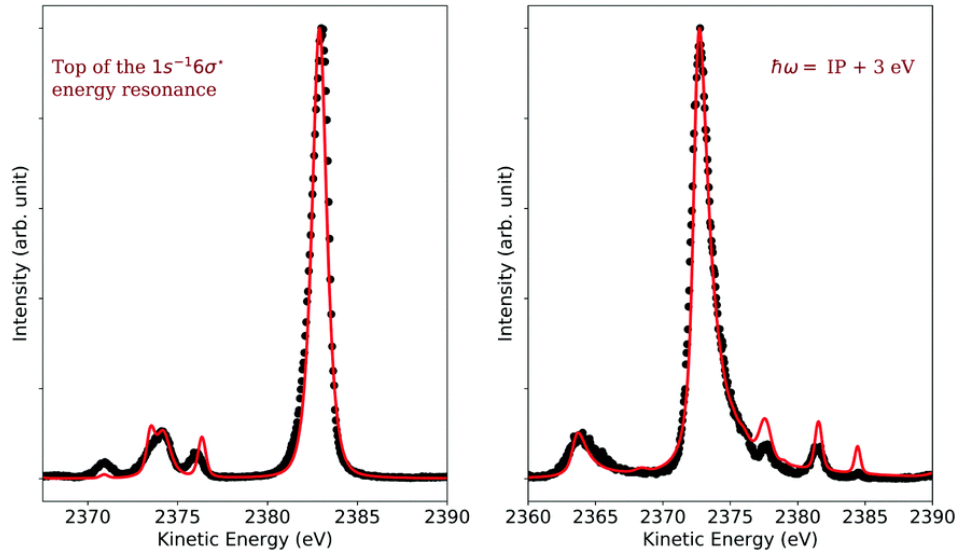


G. Goldsztejn et al., PCCP, 2022, **24**, 6590

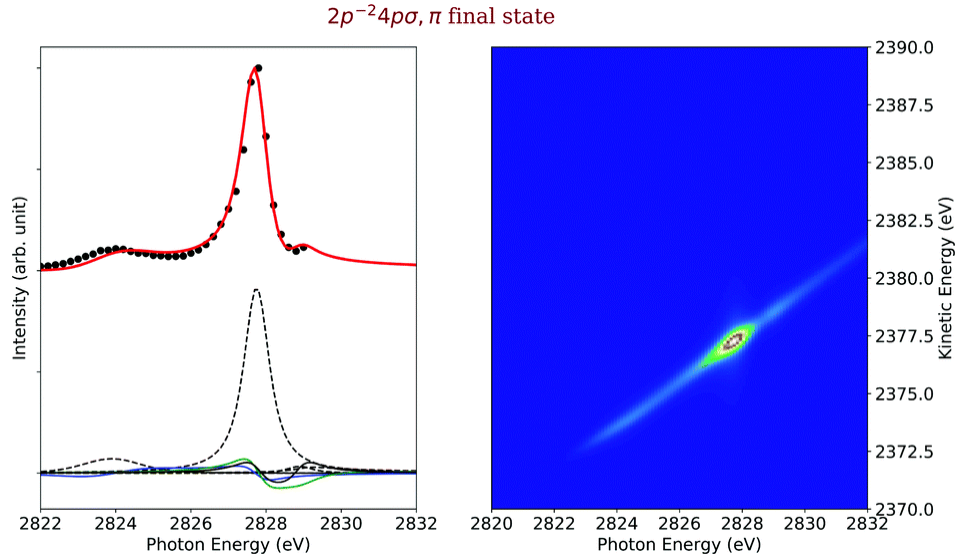
(Relatively) Simple equations can describe everything

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.

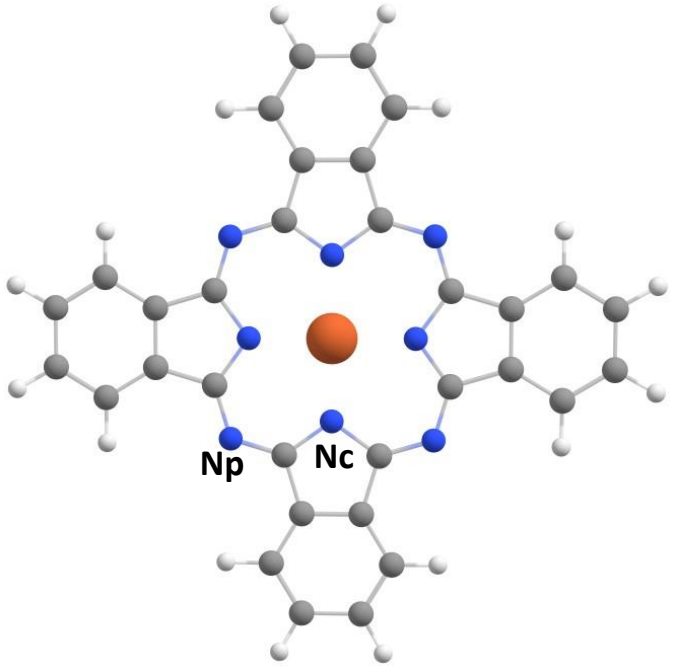


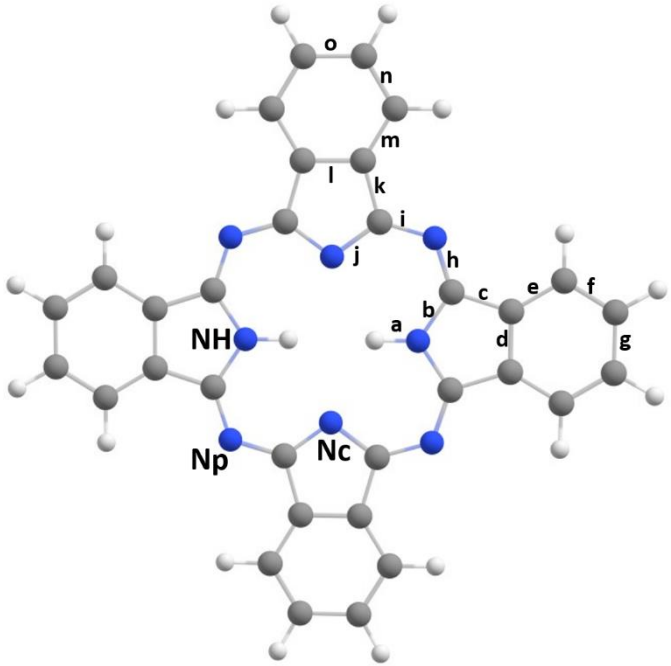
G. Goldsztejn et al., PCCP, 2022, **24**, 6590

How much can be transferred to complex molecular systems?

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

MPc





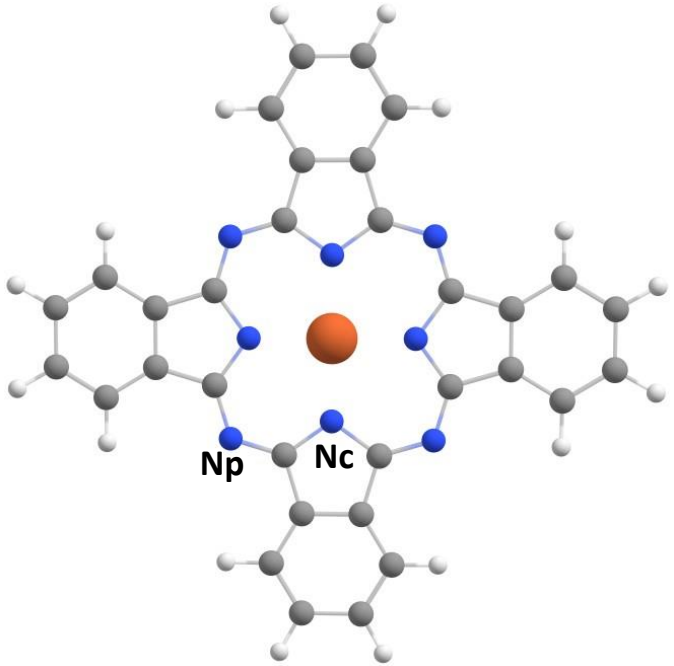
H_2Pc

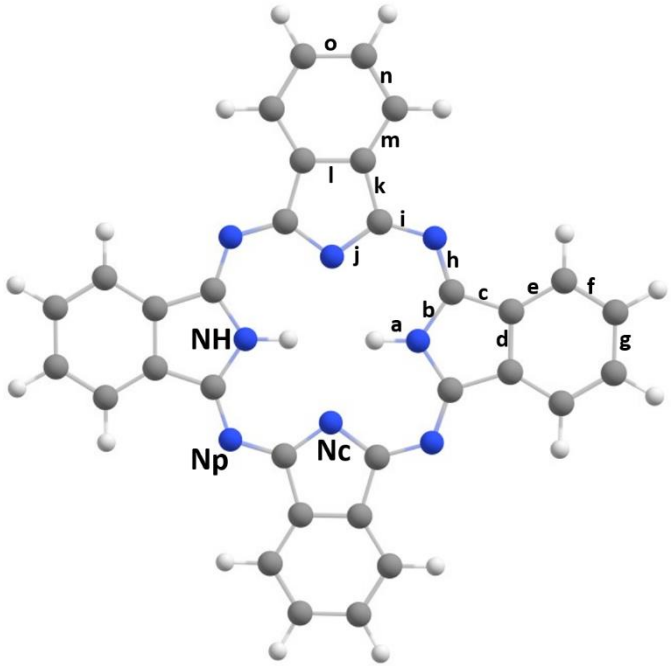
- Large molecule with a rich photophysics
- Transition metal: strong interaction *3d*(M)/π(L)
- Symmetry helps

How much can be transferred to complex molecular systems?

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

MPc





H_2Pc

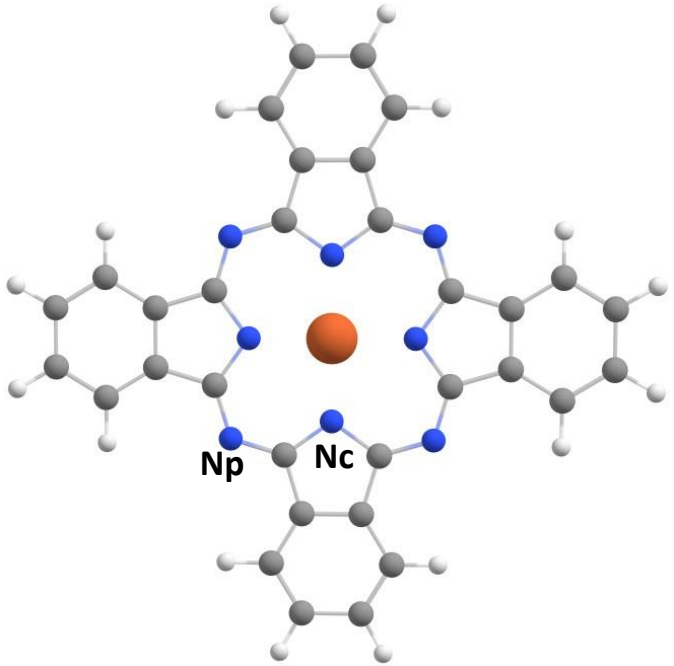
- Large molecule with a rich photophysics
- Transition metal: strong interaction *3d*(M)/π(L)
- Symmetry helps

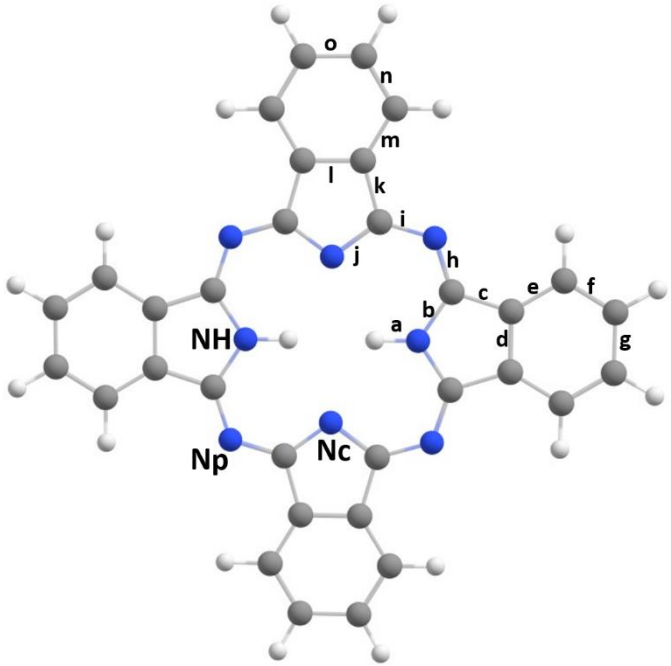
- Electron spectroscopy to:
  - Determine the electronic configuration within M
- Resonant Auger spectroscopy as local probe of:
  - The chemical environment
  - The ultrafast electronic rearrangement

How much can be transferred to complex molecular systems?

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

MPc





H_2Pc

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

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

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

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

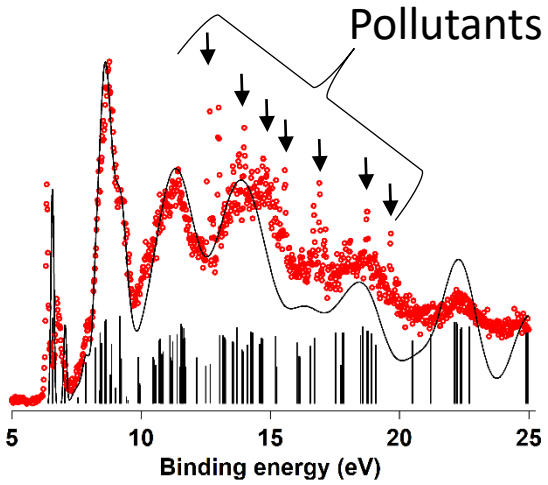
What do we need to determine the metal's electronic configuration?

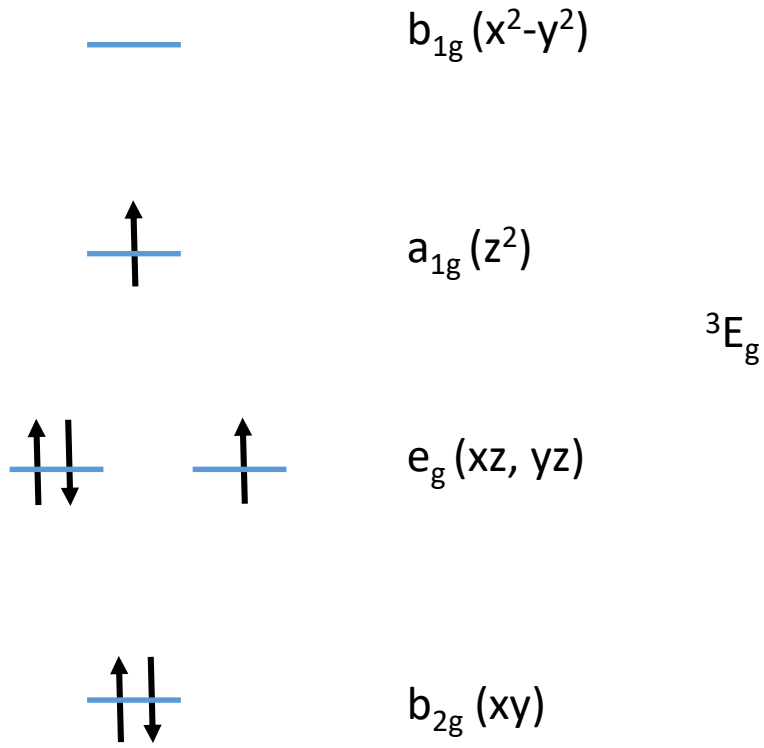
Answer: a lot of spectra and (at least) two theoretical methods to simulate them

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

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

Valence photoelectron spectra + DFT calculation



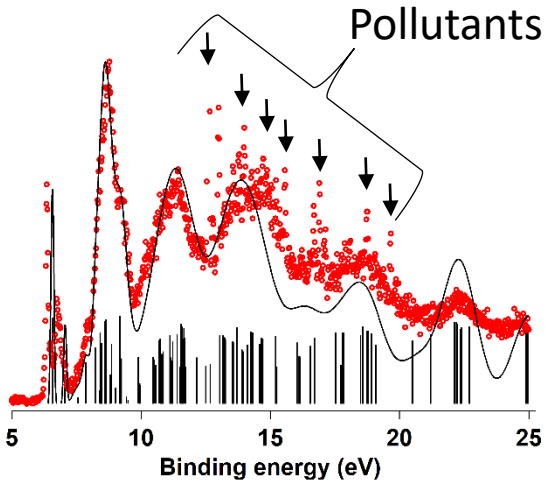


J. Laurent, …, and G. Goldsztejn, Phys. Chem. Chem. Phys., 2022, **24**, 2656

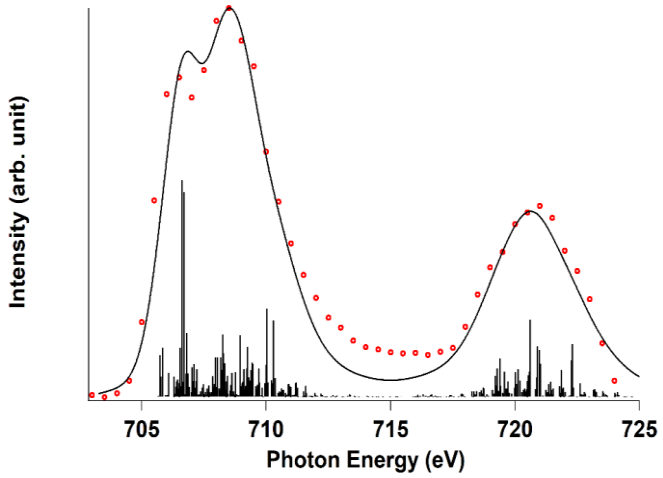
What do we need to determine the metal's electronic configuration?

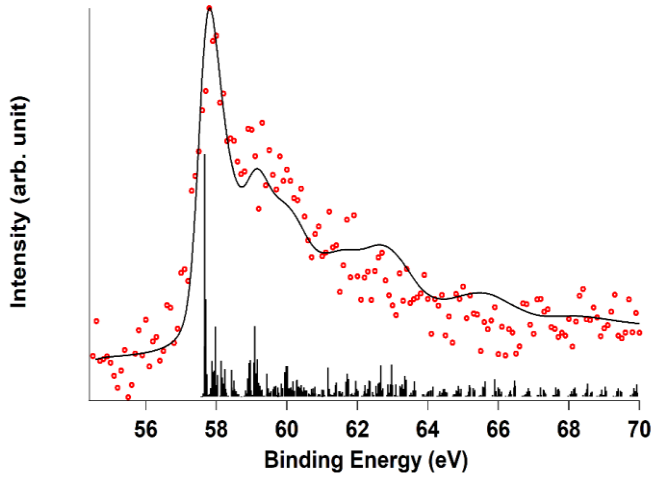
Answer: a lot of spectra and (at least) two theoretical methods to simulate them

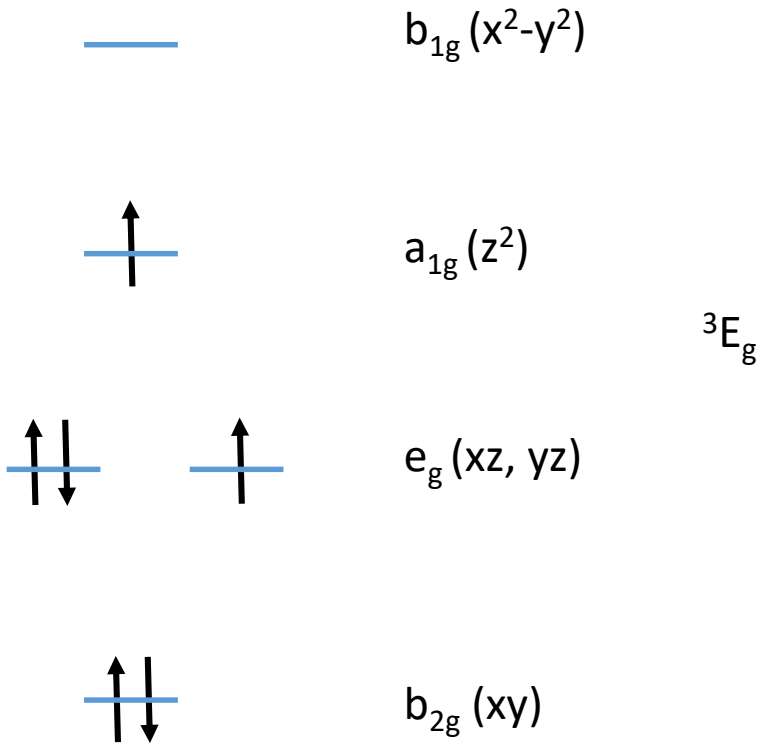
Valence photoelectron spectra + DFT calculation



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

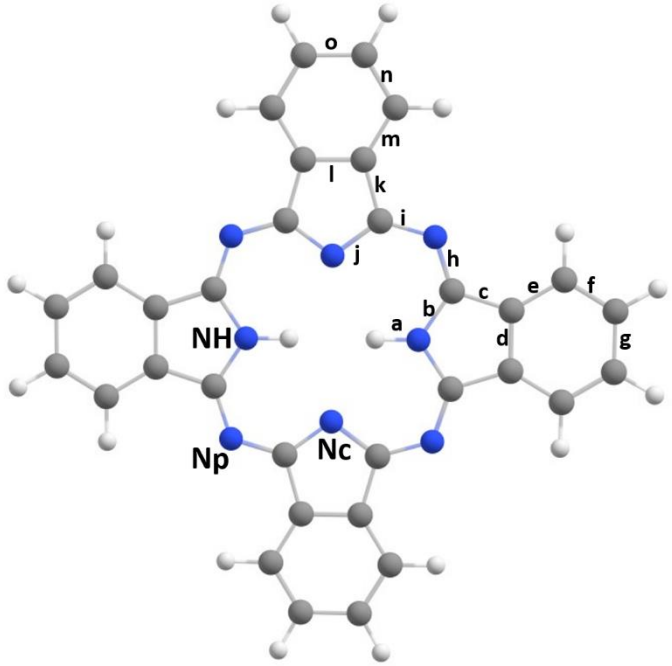




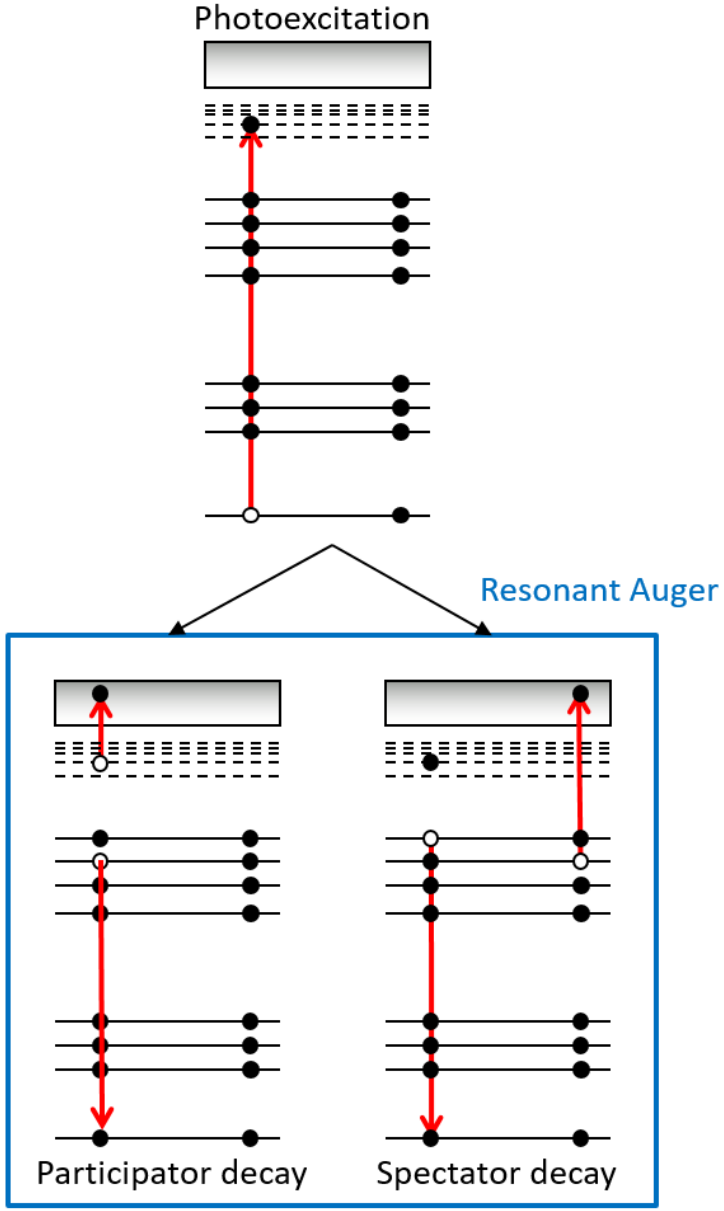


J. Laurent, …, and G. Goldsztejn, Phys. Chem. Chem. Phys., 2022, **24**, 2656

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?

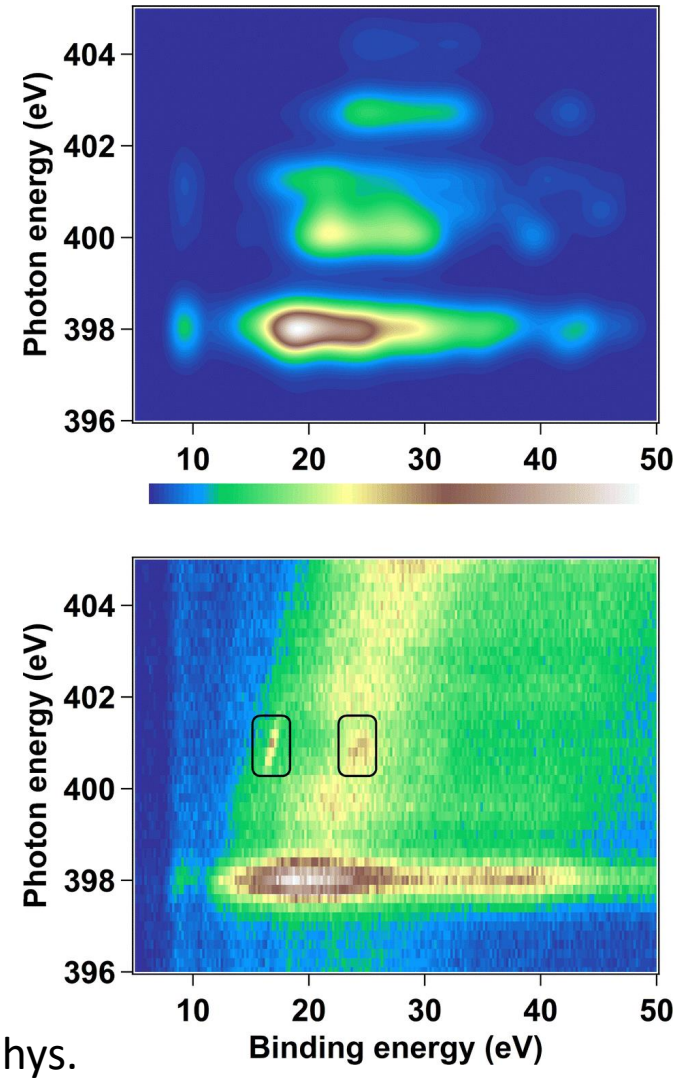
$$\sigma(\omega,\omega') \propto \sum_{f}\left|\sum_{c}\frac{\langle\Phi_f|Q|\Phi_c\rangle\langle\chi_f|\chi_c\rangle\langle\Phi_c|D|\Phi_o\rangle\langle\chi_c|\chi_o\rangle}{\omega-\omega_{co}+i\Gamma_c}\right|^2 \times\Delta\left(\omega-\omega'-\omega_{fo},\Gamma_f\right)$$

Same formula, but… few approximations later

How sensitive are we to the chemical environment?

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

Same formula, but… few approximations later



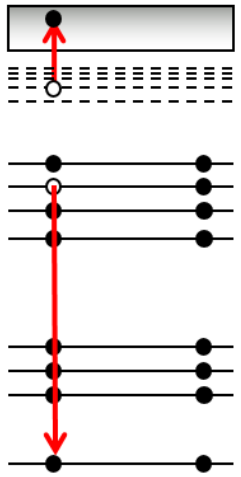
- 2D-map: x-axis = binding energy; y-axis = incident energy

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

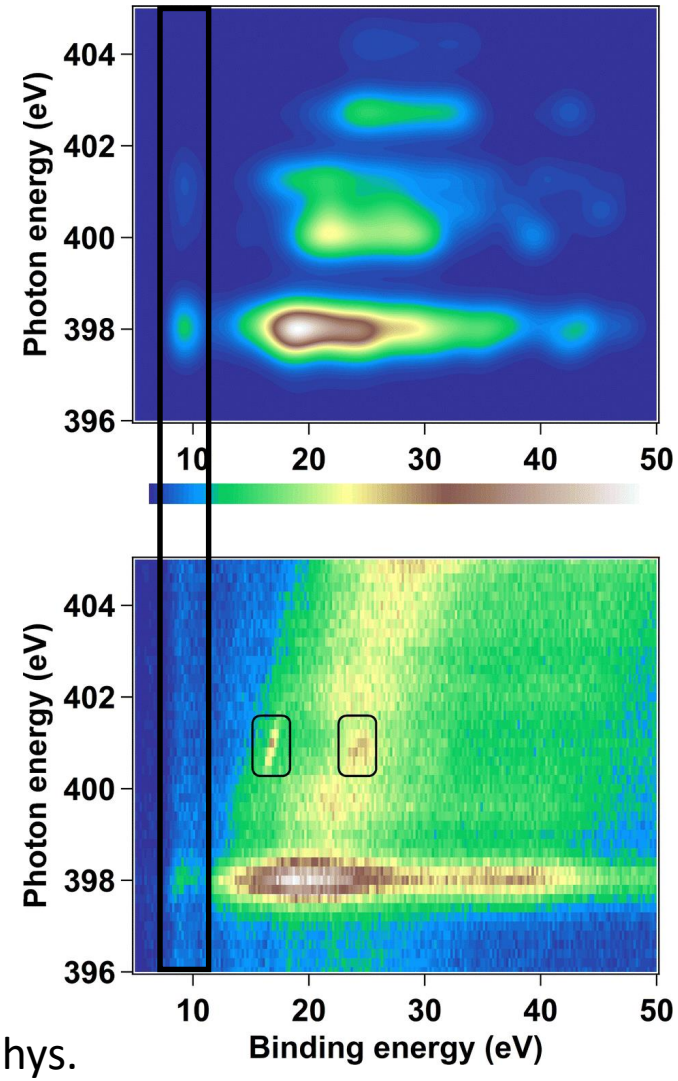
How sensitive are we to the chemical environment?

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

Same formula, but… few approximations later



- 2D-map: x-axis = binding energy; y-axis = incident energy
- Vertical lines = participator Auger decay at fixed binding energies

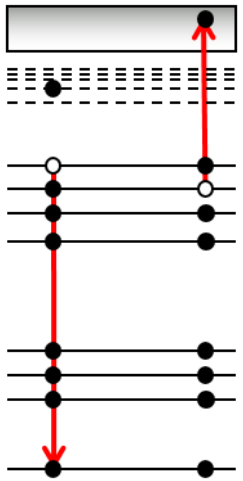


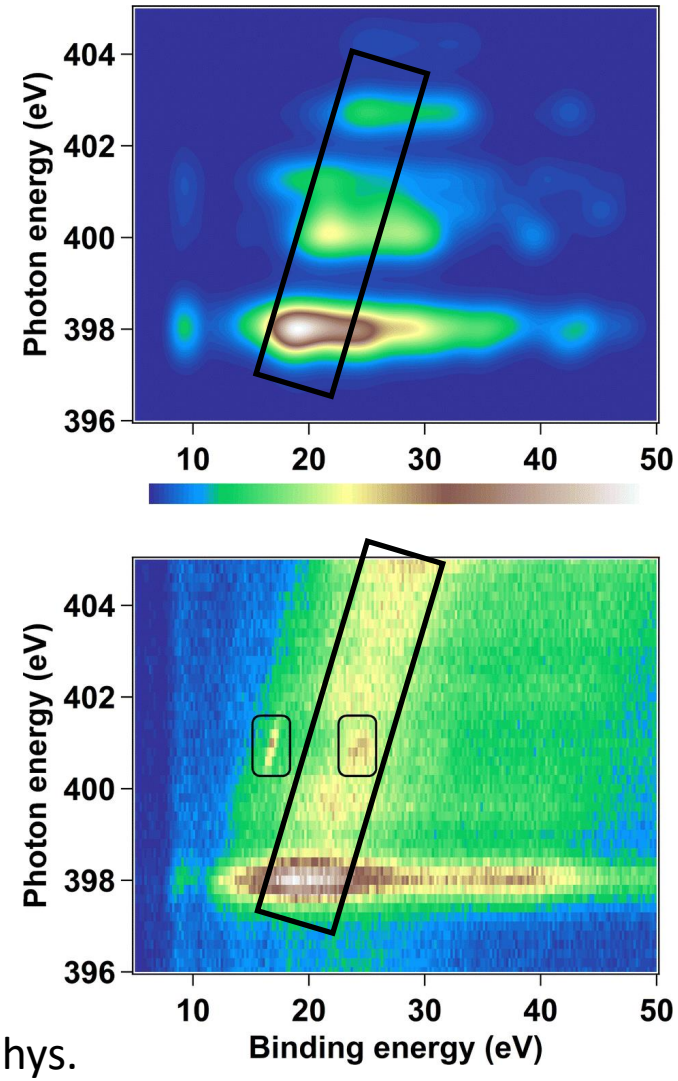
C.E.V de Moura, …, and G. Goldsztejn, Phys. Chem. Chem. Phys., 2023, **25**, 15555

How sensitive are we to the chemical environment?

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

Same formula, but… few approximations later



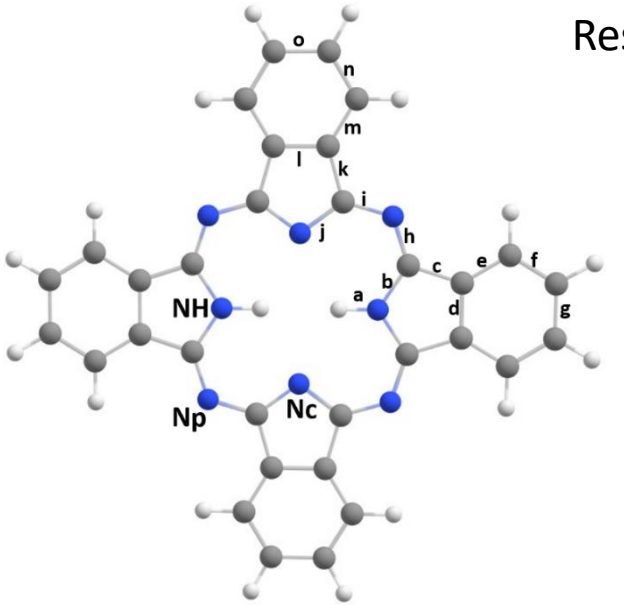


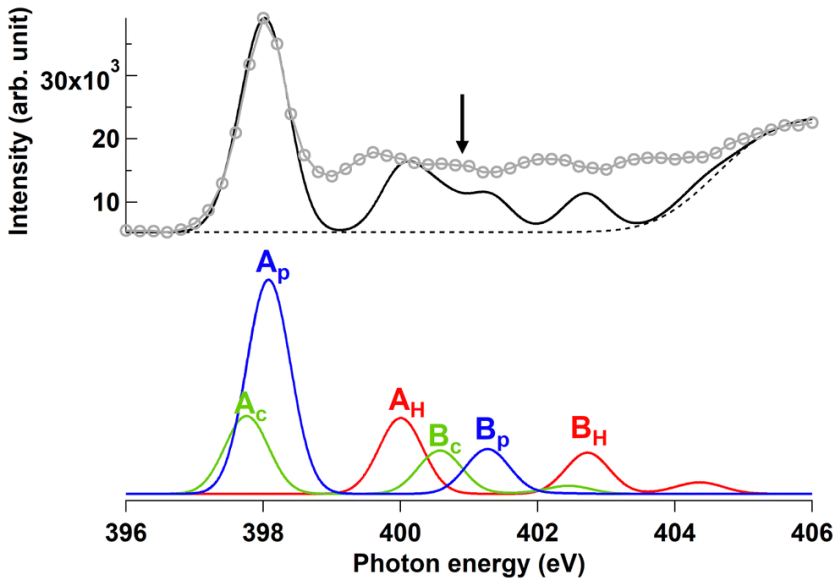
- 2D-map: x-axis = binding energy; y-axis = incident energy
- Vertical lines = participator Auger decay at fixed binding energies
- Diagonal lines = spectator Auger decay

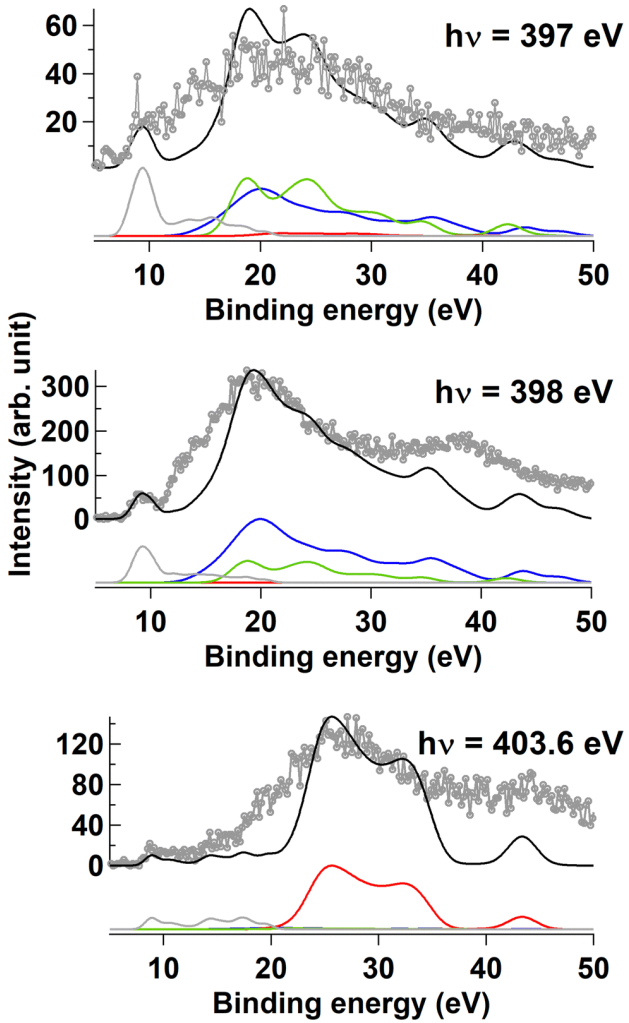
C.E.V de Moura, …, and G. Goldsztejn, Phys. Chem. Chem. Phys., 2023, **25**, 15555

How sensitive are we to the chemical environment?

Resonant Auger spectroscopy more sensitive than absorption spectroscopy, but…



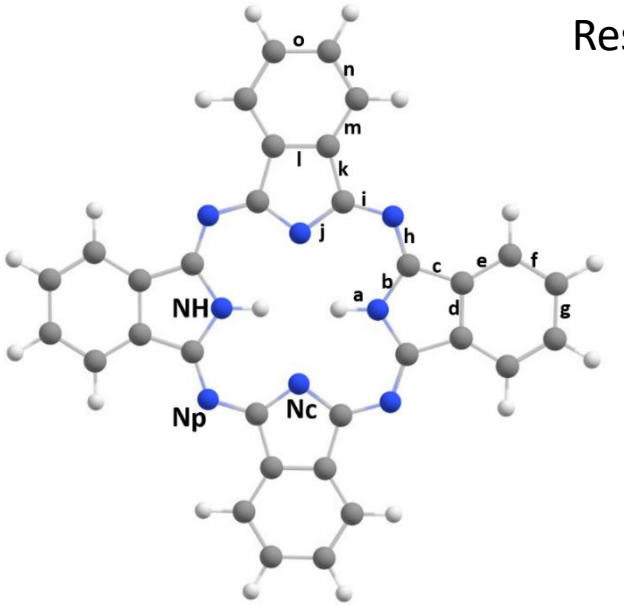


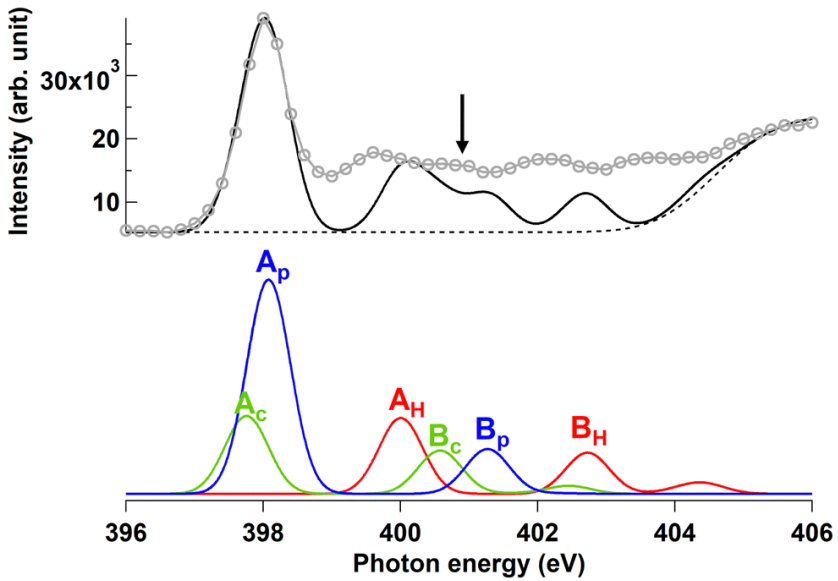


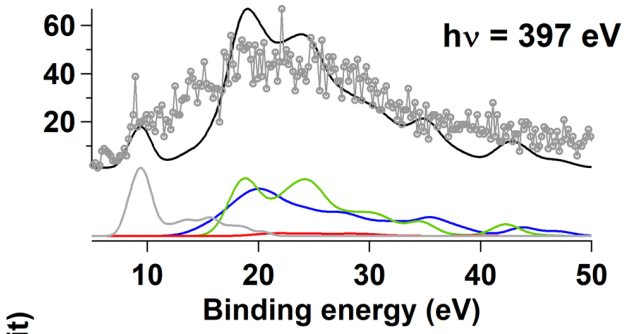
C.E.V de Moura, …, and G. Goldsztejn, Phys. Chem. Chem. Phys., 2023, **25**, 15555

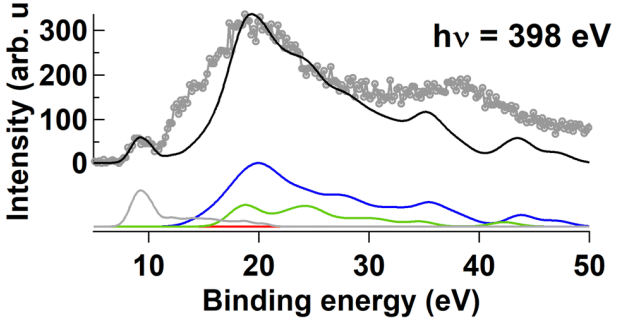
How sensitive are we to the chemical environment?

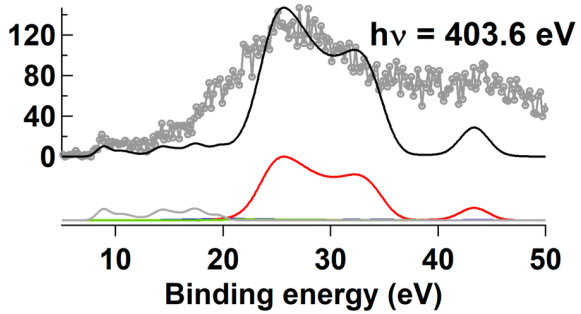
Resonant Auger spectroscopy more sensitive than absorption spectroscopy, but…

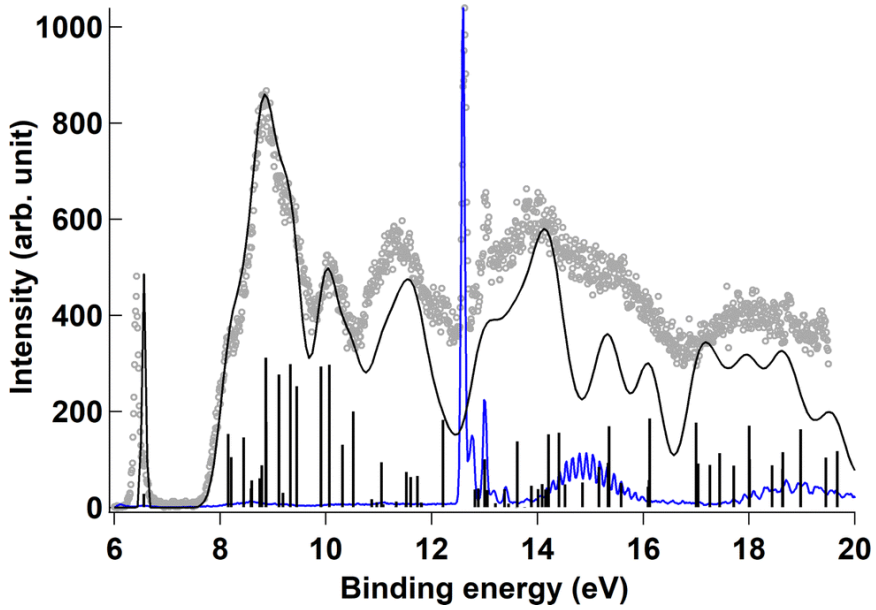








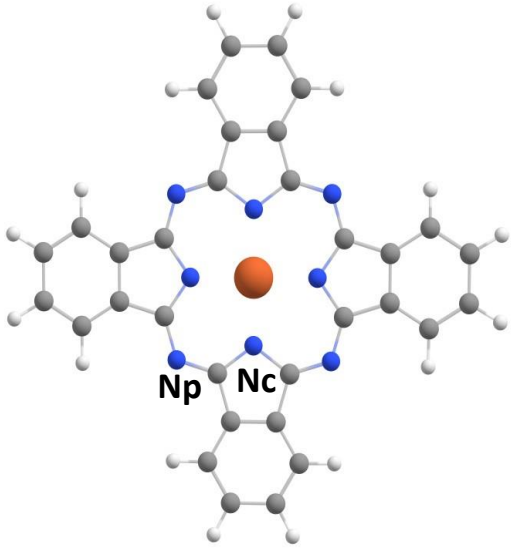


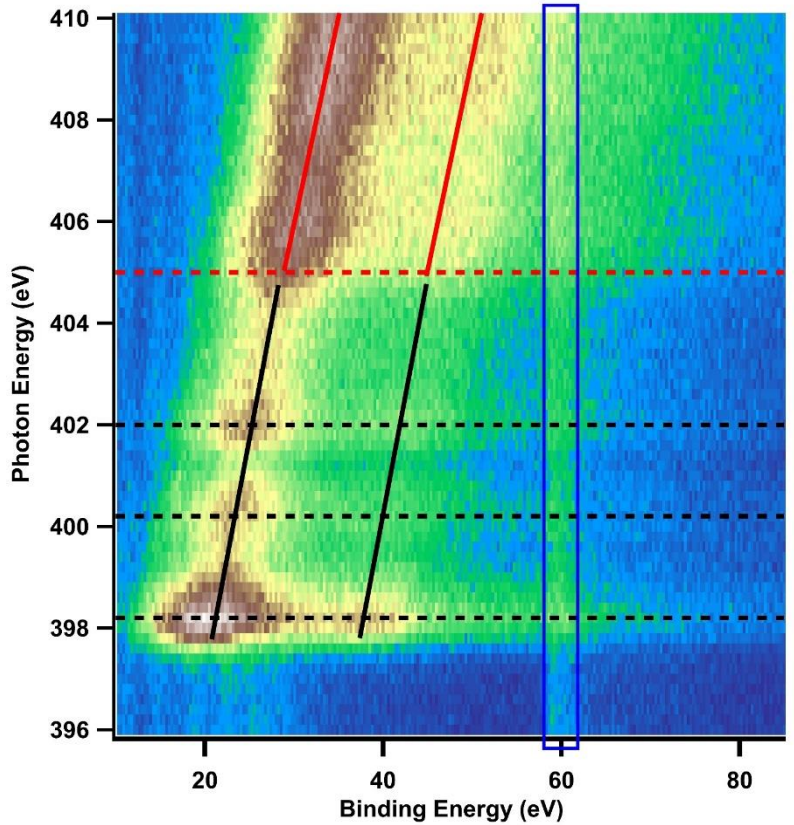


… valence spectroscopy helped us interpret the resonant Auger spectra

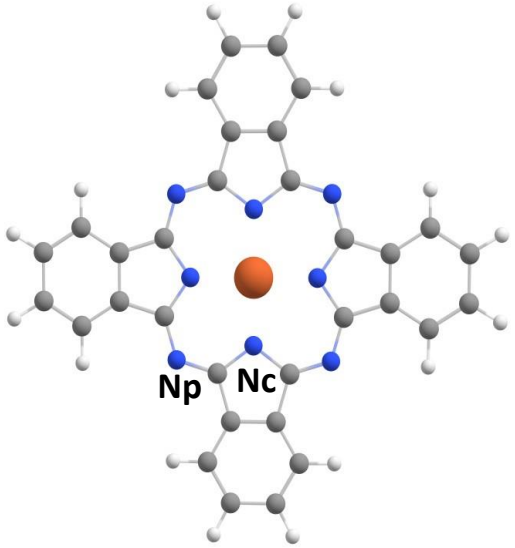
C.E.V de Moura, …, and G. Goldsztejn, Phys. Chem. Chem. Phys., 2023, **25**, 15555

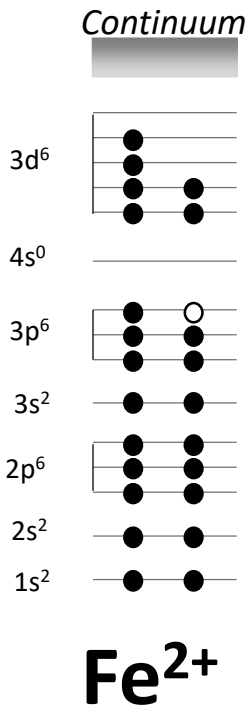
Can we probe localized ultrafast electronic processes?

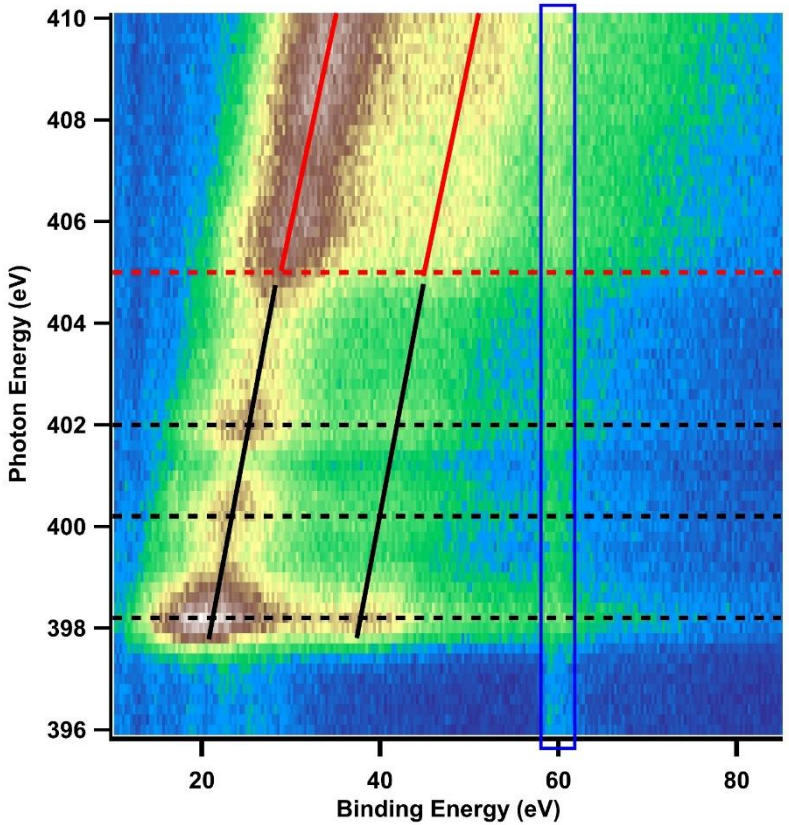




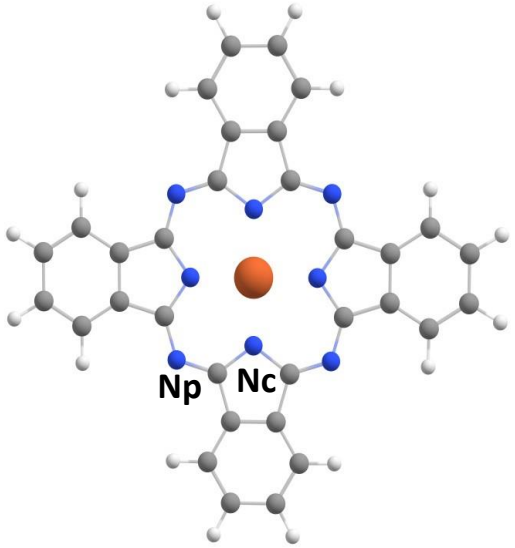
Can we probe localized ultrafast electronic processes?

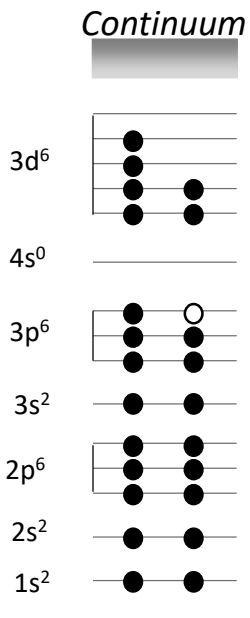




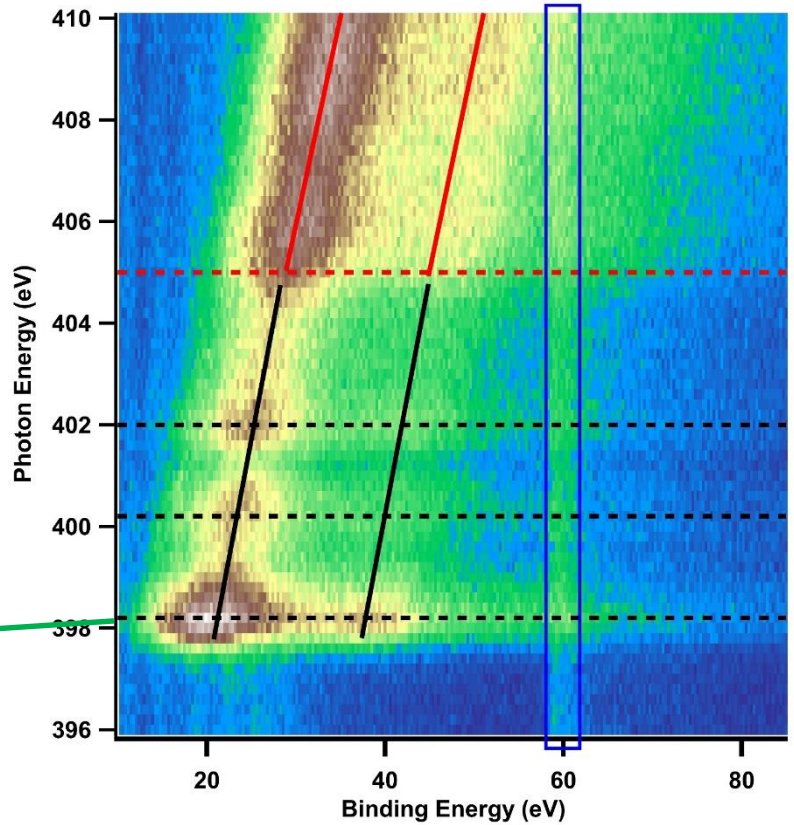


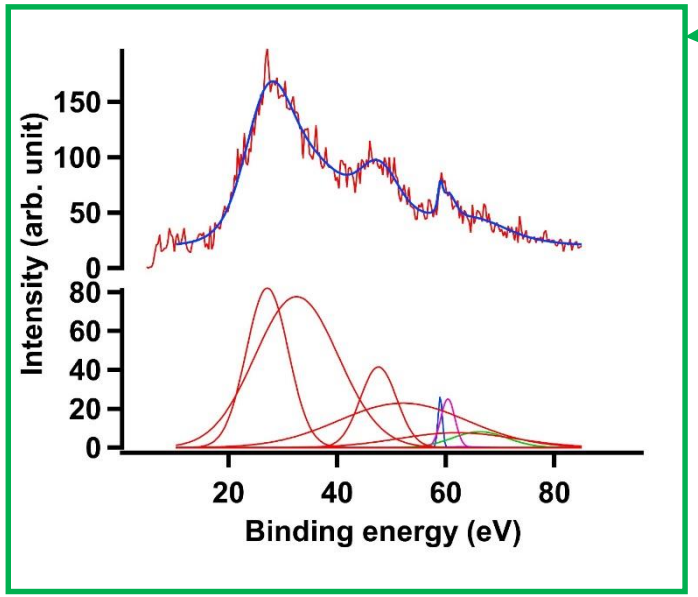
Can we probe localized ultrafast electronic processes?





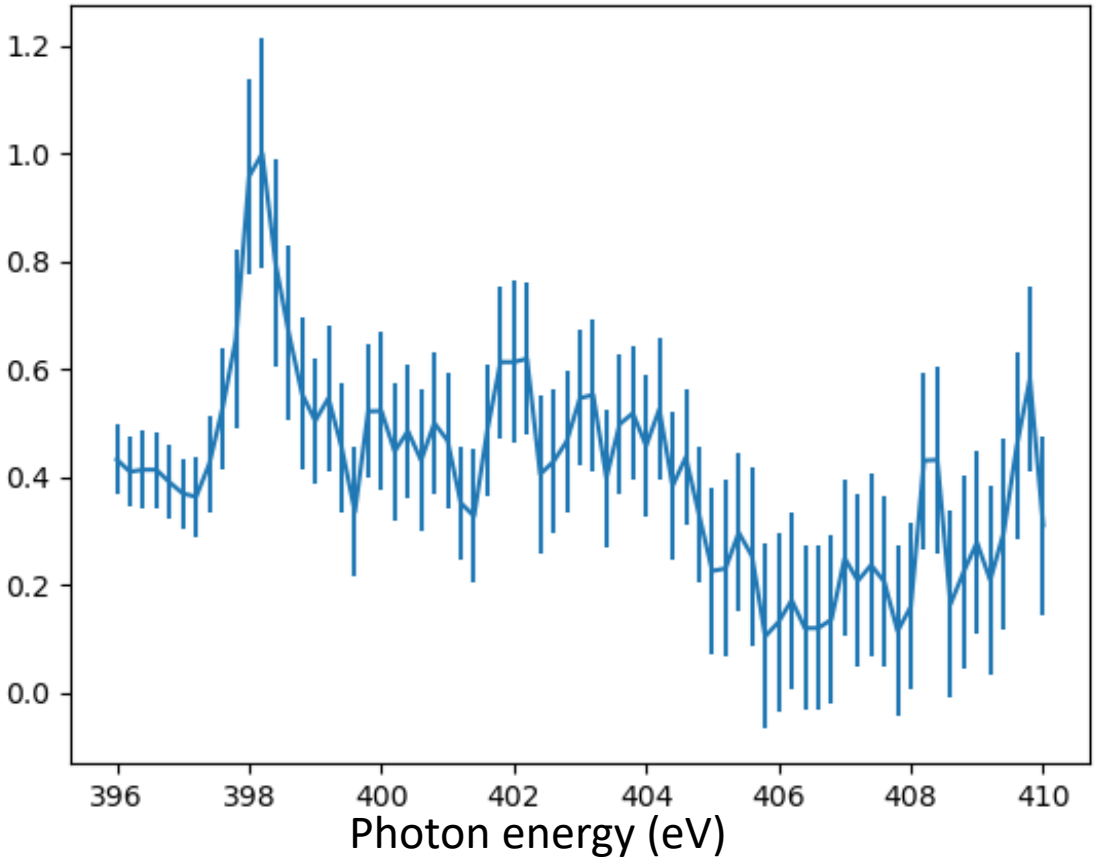
Fe^{2+}





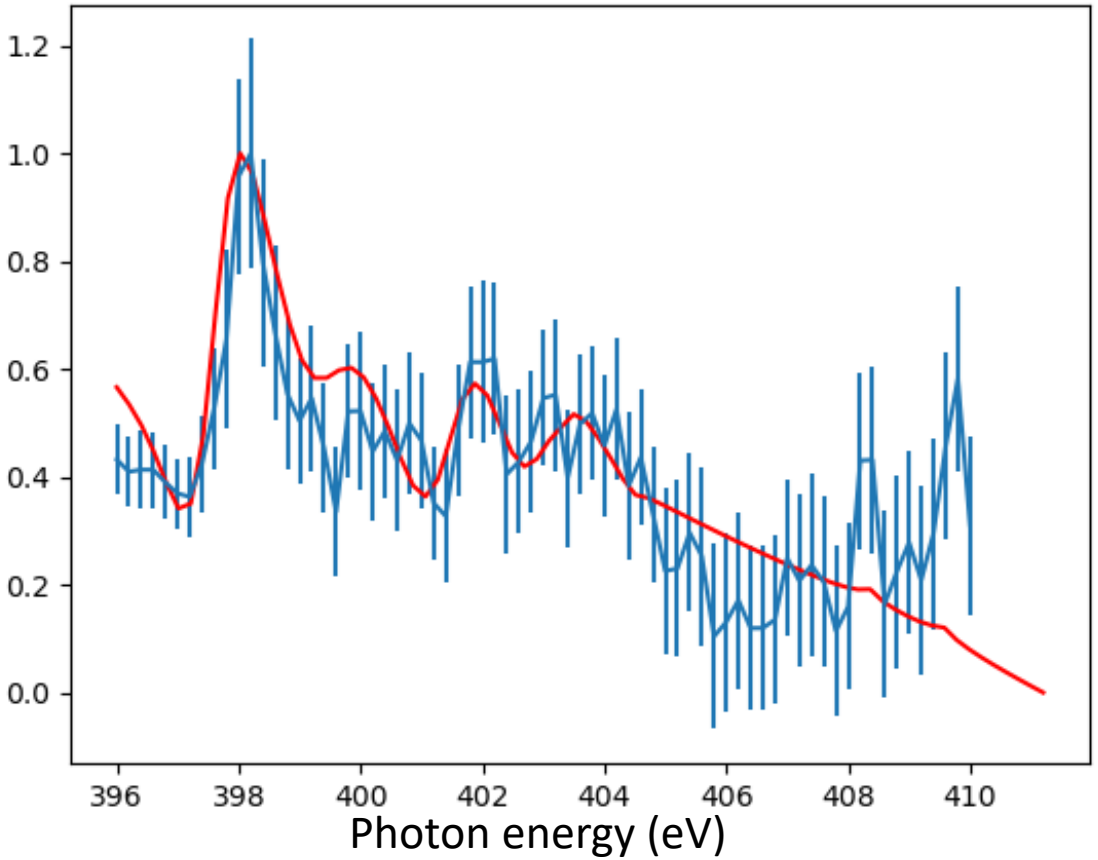
Step-by-step fitting methodology to extract the cross section (see Manon's poster)

Can we probe localized ultrafast electronic processes?



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

Can we probe localized ultrafast electronic processes?

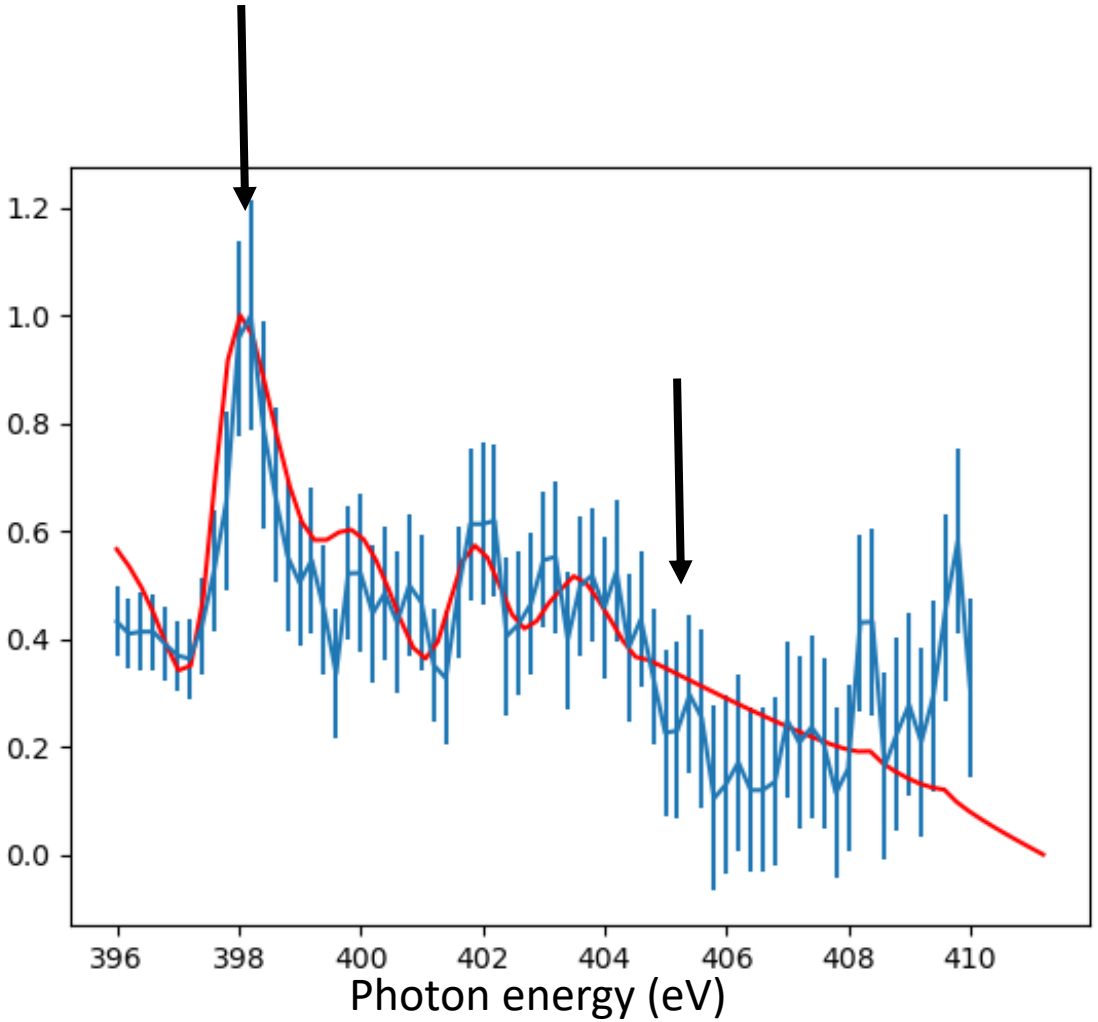


$$\sigma(\omega,\omega') \propto \sum_{\mathrm{f}} \left| \sum_{\mathrm{c}} \frac{\langle \Phi_{\mathrm{f}} \mid Q \mid \Phi_{\mathrm{c}} \rangle \langle \chi_{\mathrm{f}} \mid \chi_{\mathrm{c}} \rangle \langle \Phi_{\mathrm{c}} \mid D \mid \Phi_{\mathrm{o}} \rangle \langle \chi_{\mathrm{c}} \mid \chi_{\mathrm{o}} \rangle}{\omega - \omega_{\mathrm{co}} + i\Gamma_{\mathrm{c}}} \right|^2 \times \Delta\left(\omega - \omega' - \omega_{\mathrm{fo}}, \Gamma_{\mathrm{f}}\right)$$

Same formula, but… few approximations later

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

Can we probe localized ultrafast electronic processes?



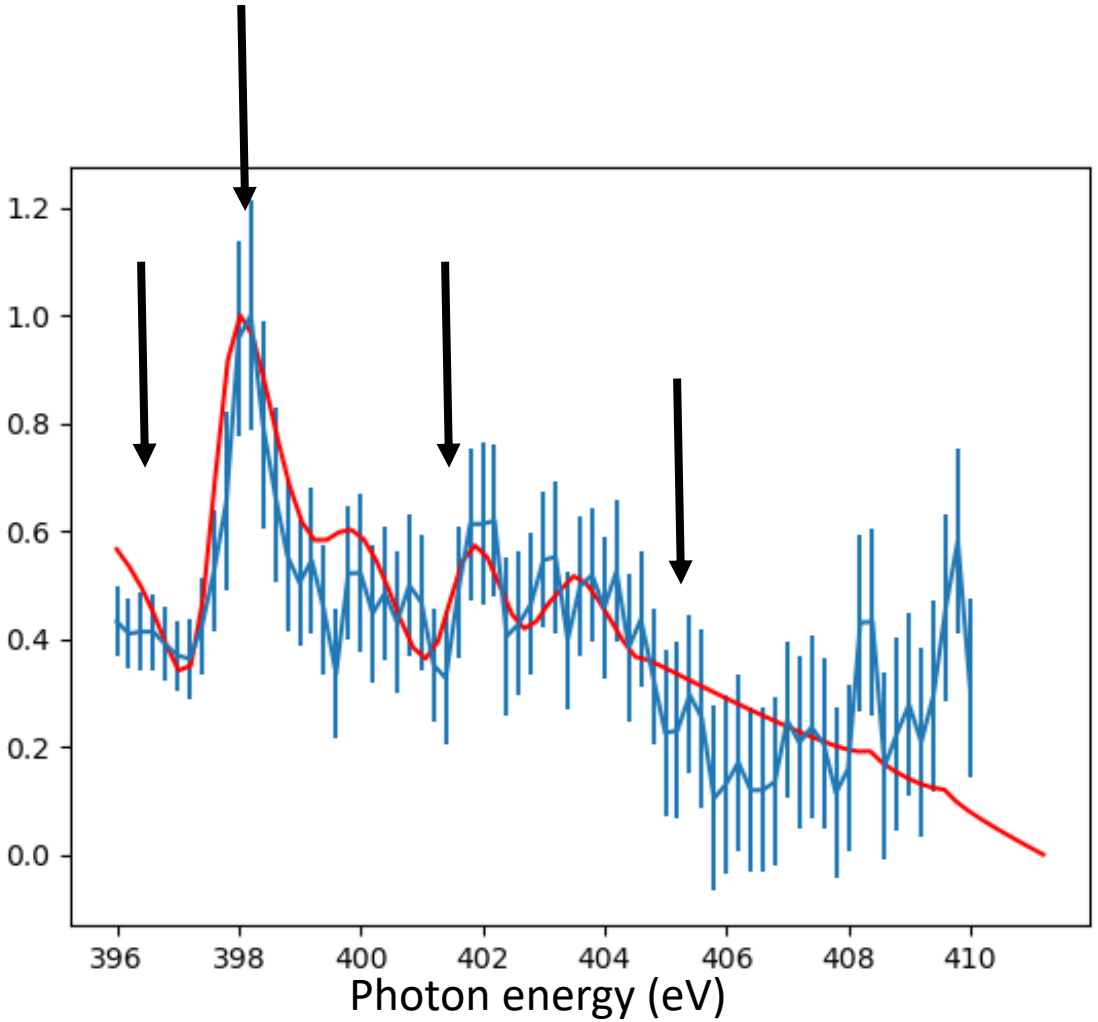
$$\sigma(\omega,\omega') \propto \sum_{\mathrm{f}} \left| \sum_{\mathrm{c}} \frac{\langle \Phi_{\mathrm{f}} \mid Q \mid \Phi_{\mathrm{c}} \rangle \langle \chi_{\mathrm{f}} \mid \chi_{\mathrm{c}} \rangle \langle \Phi_{\mathrm{c}} \mid D \mid \Phi_{\mathrm{o}} \rangle \langle \chi_{\mathrm{c}} \mid \chi_{\mathrm{o}} \rangle}{\omega - \omega_{\mathrm{co}} + i\Gamma_{\mathrm{c}}} \right|^2 \times \Delta\left(\omega - \omega' - \omega_{\mathrm{fo}}, \Gamma_{\mathrm{f}}\right)$$

Same formula, but… few approximations later

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

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

Can we probe localized ultrafast electronic processes?



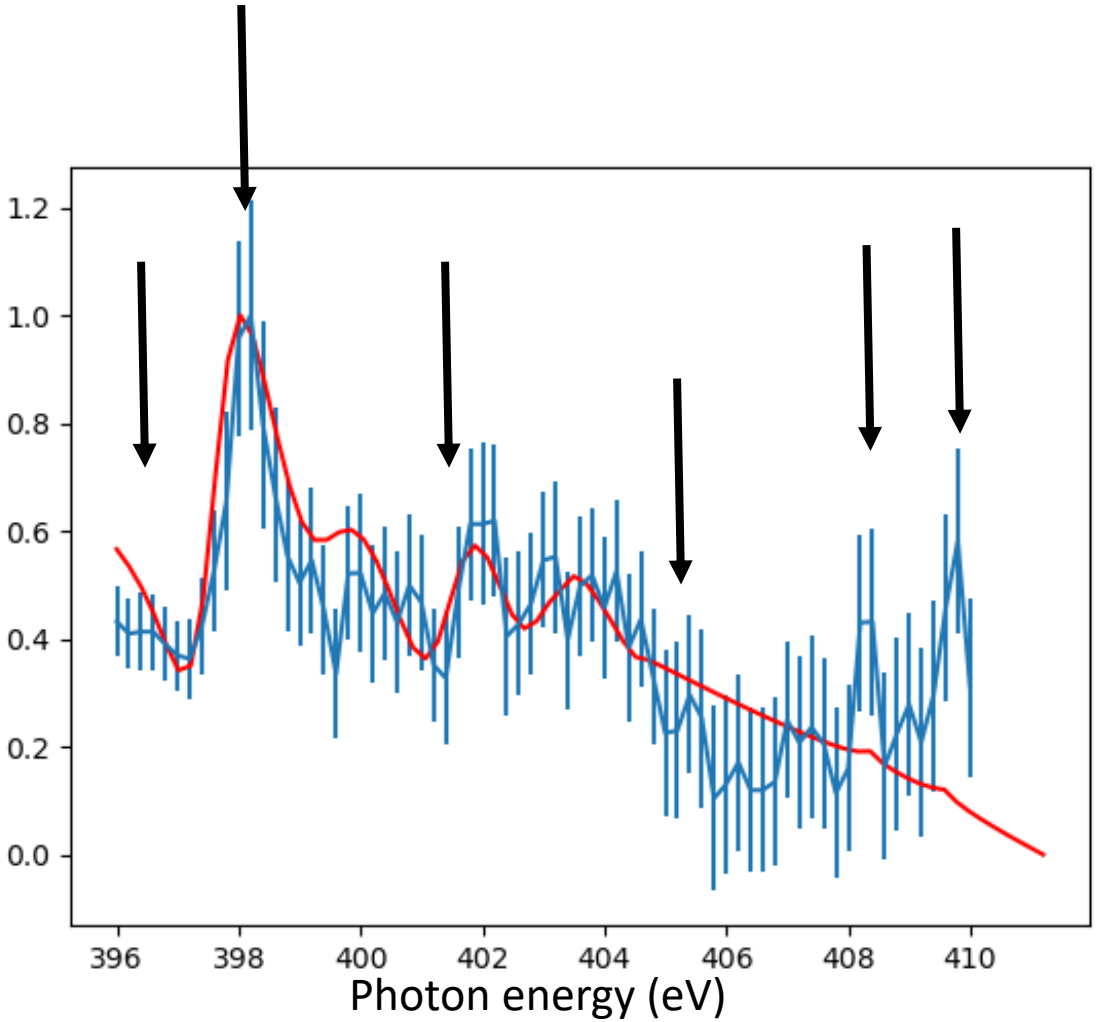
$$\sigma(\omega,\omega') \propto \sum_{\mathrm{f}} \left| \sum_{\mathrm{c}} \frac{\langle \Phi_{\mathrm{f}} \mid Q \mid \Phi_{\mathrm{c}} \rangle \langle \chi_{\mathrm{f}} \mid \chi_{\mathrm{c}} \rangle \langle \Phi_{\mathrm{c}} \mid D \mid \Phi_{\mathrm{o}} \rangle \langle \chi_{\mathrm{c}} \mid \chi_{\mathrm{o}} \rangle}{\omega - \omega_{\mathrm{co}} + i\Gamma_{\mathrm{c}}} \right|^2 \times \Delta\left(\omega - \omega' - \omega_{\mathrm{fo}}, \Gamma_{\mathrm{f}}\right)$$

Same formula, but… few approximations later

- Resonance from a N 1s discrete state
- Decrease after ionization threshold
- Plateau due to electronic interferences between discrete states

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

Can we probe localized ultrafast electronic processes?



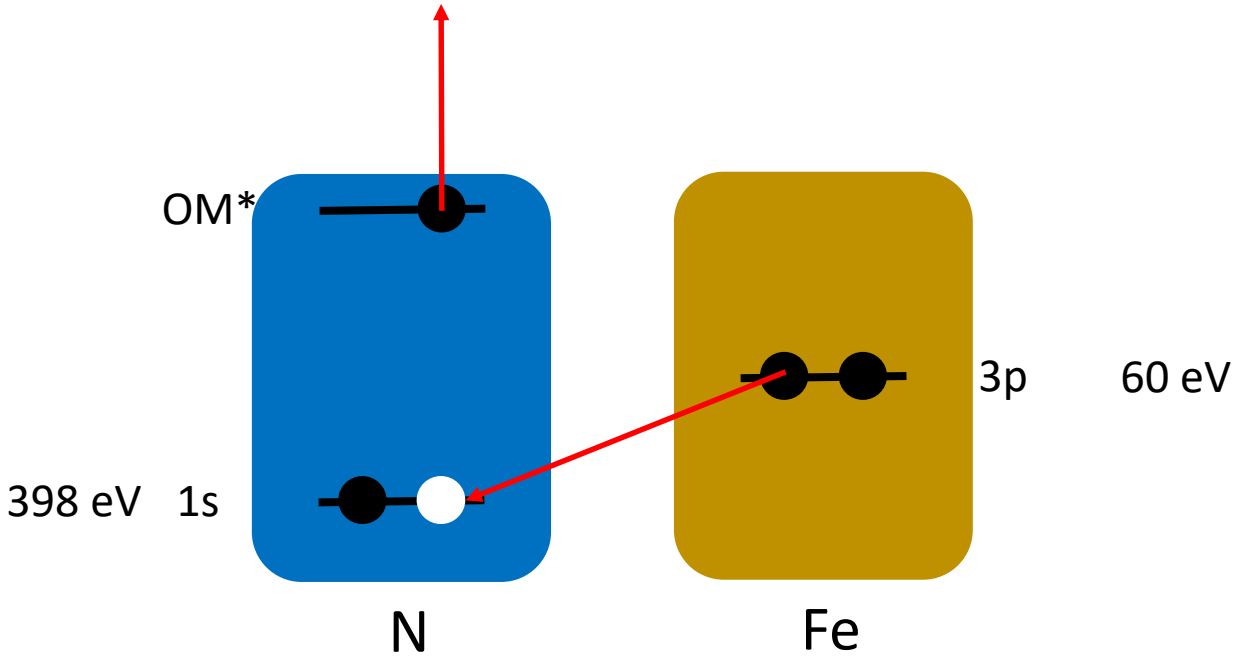
$$\sigma(\omega,\omega') \propto \sum_{\mathrm{f}} \left| \sum_{\mathrm{c}} \frac{\langle \Phi_{\mathrm{f}} | Q | \Phi_{\mathrm{c}} \rangle \langle \chi_{\mathrm{f}} | \chi_{\mathrm{c}} \rangle \langle \Phi_{\mathrm{c}} | D | \Phi_{\mathrm{o}} \rangle \langle \chi_{\mathrm{c}} | \chi_{\mathrm{o}} \rangle}{\omega - \omega_{\mathrm{co}} + i\Gamma_{\mathrm{c}}} \right|^2 \times \Delta\left(\omega - \omega' - \omega_{\mathrm{fo}}, \Gamma_{\mathrm{f}}\right)$$

Same formula, but… few approximations later

- Resonance from a N 1s discrete state
- Decrease after ionization threshold
- Plateau due to electronic interferences between discrete states
- Fano-type interferences between continua states

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

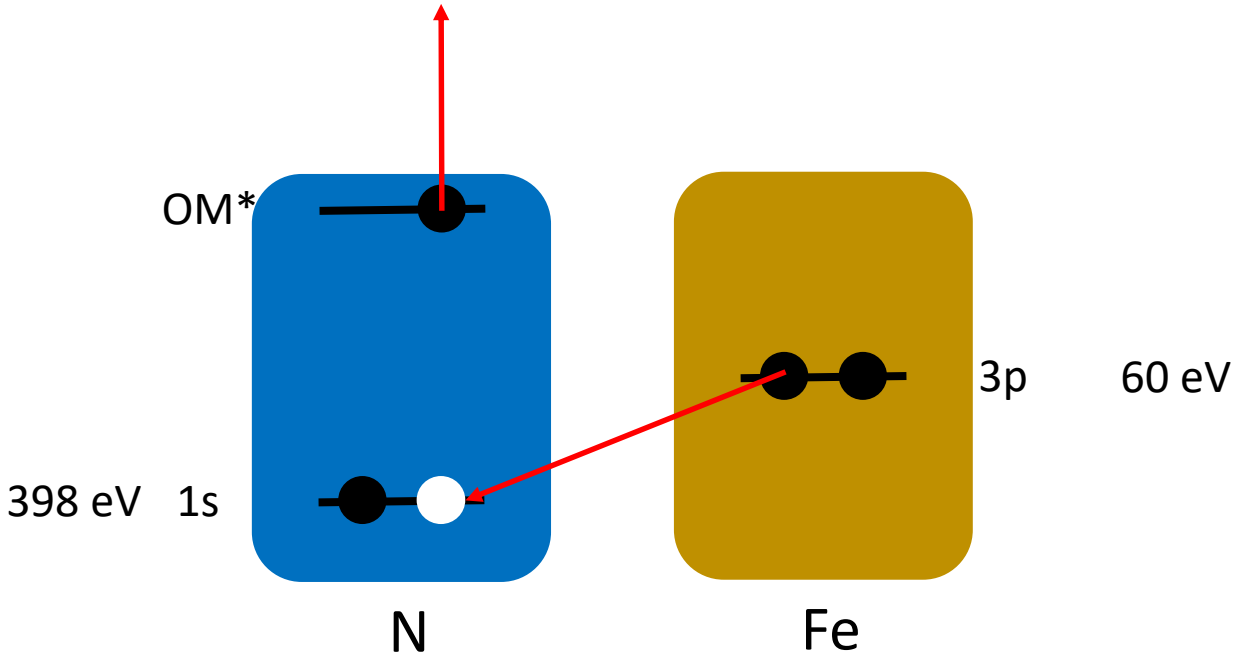
Can we probe localized ultrafast electronic processes?



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

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

Can we probe localized ultrafast electronic processes?

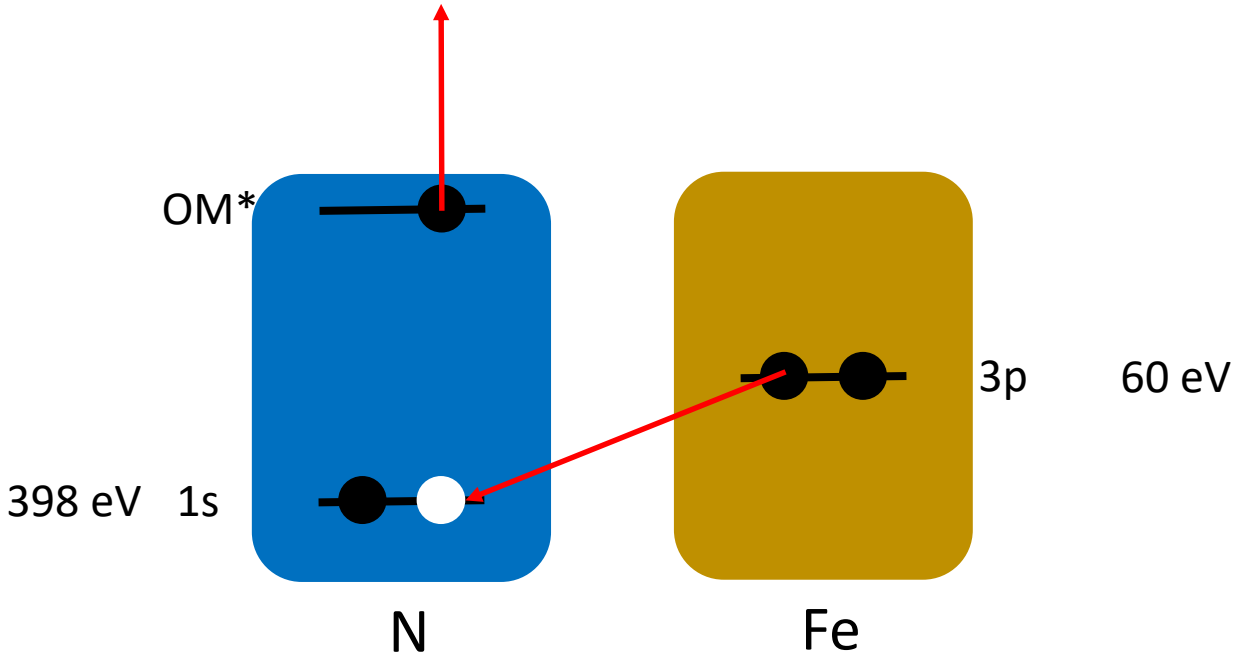


Interatomic Coulomb decay (ICD) like
+ electronic states' interferences

Is it related to a particular transition metal?

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

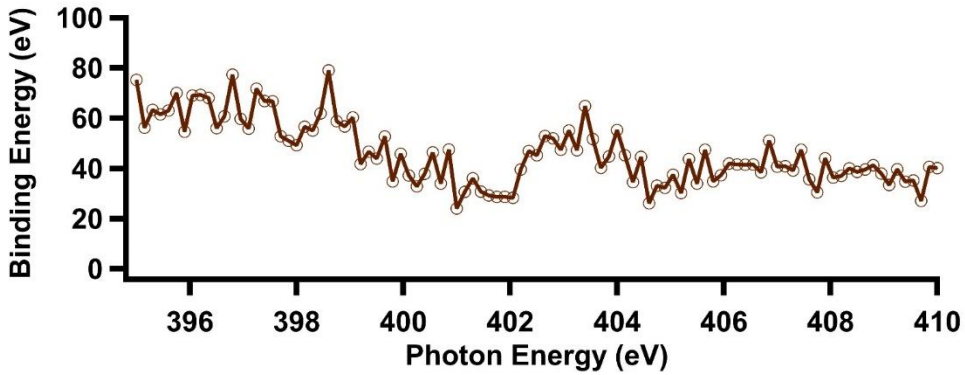
Can we probe localized ultrafast electronic processes?



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

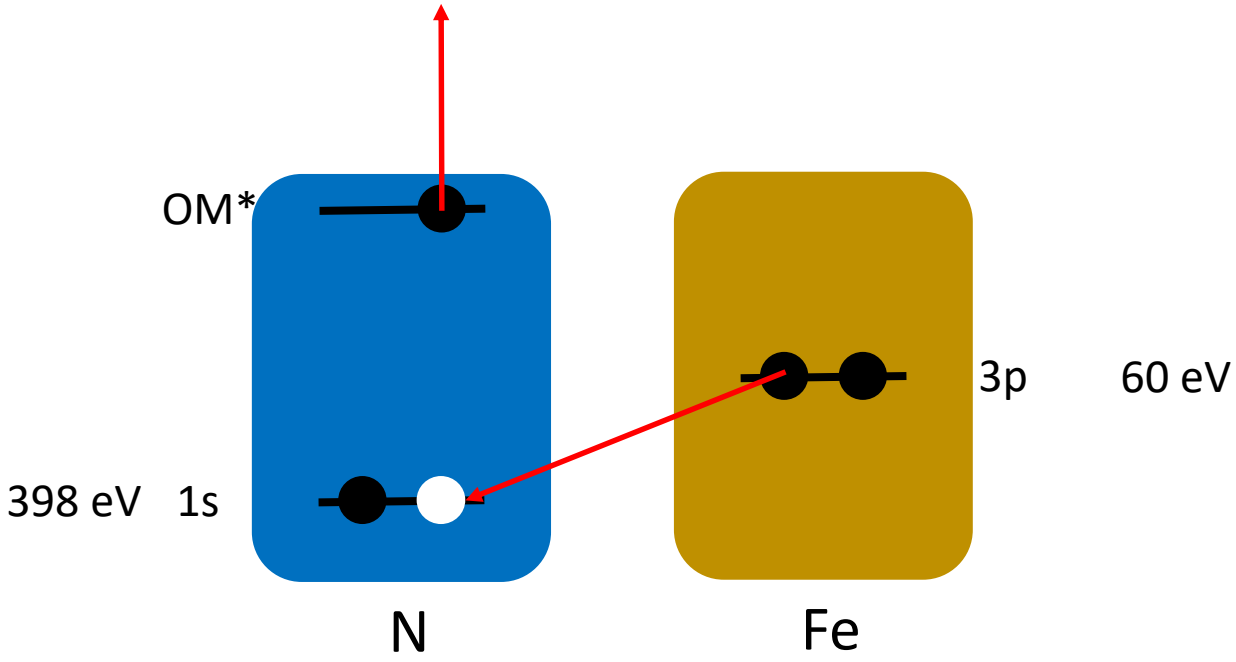
Is it related to a particular transition metal?

Cobalt phthalocyanine = no clear sign of ICD



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

Can we probe localized ultrafast electronic processes?

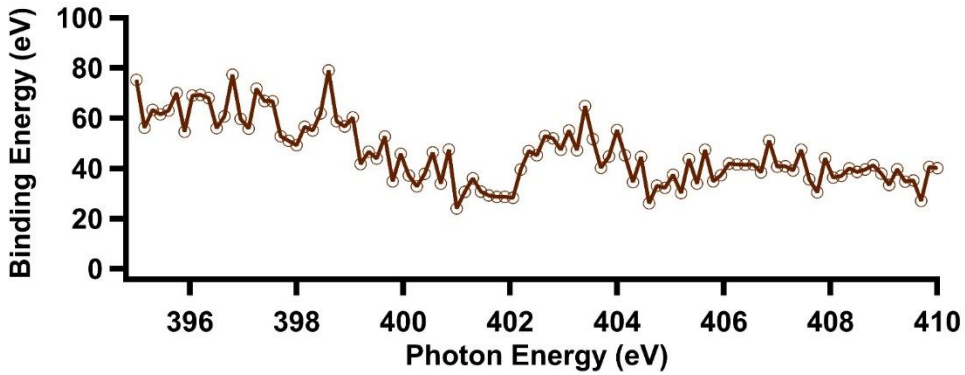


Interatomic Coulomb decay (ICD) like
+ electronic states' interferences

Is it related to a particular transition metal?

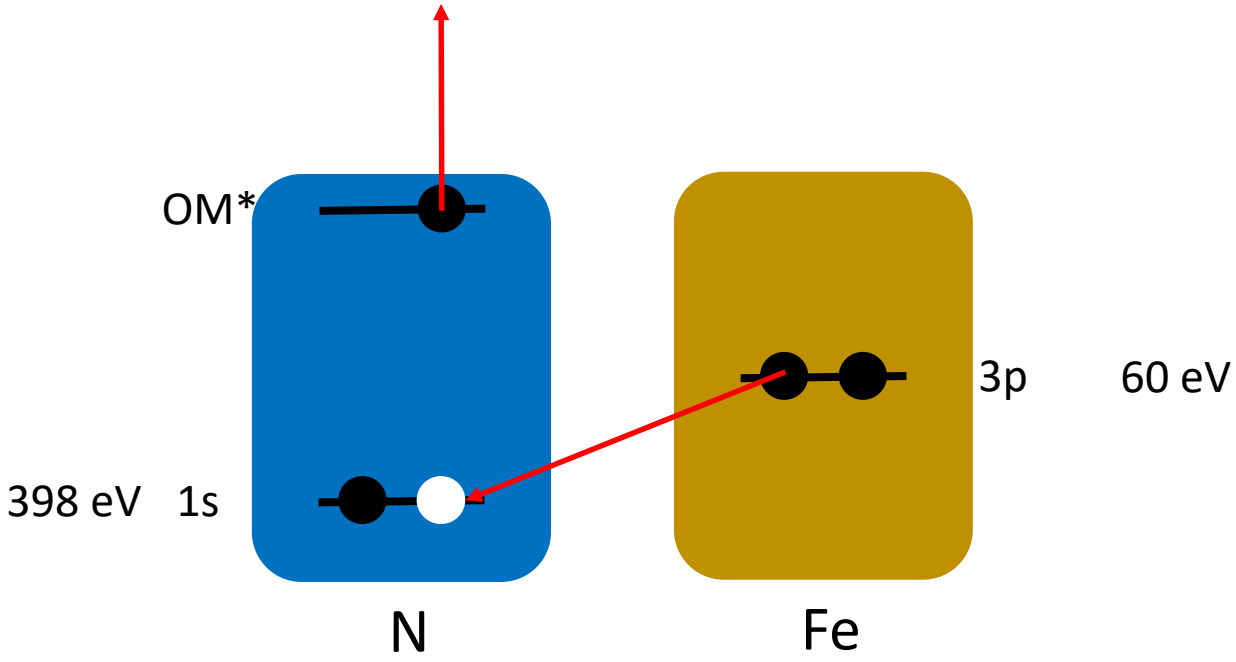
Can you tell us why?

Cobalt phthalocyanine = no clear sign of ICD



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

Can we probe localized ultrafast electronic processes?



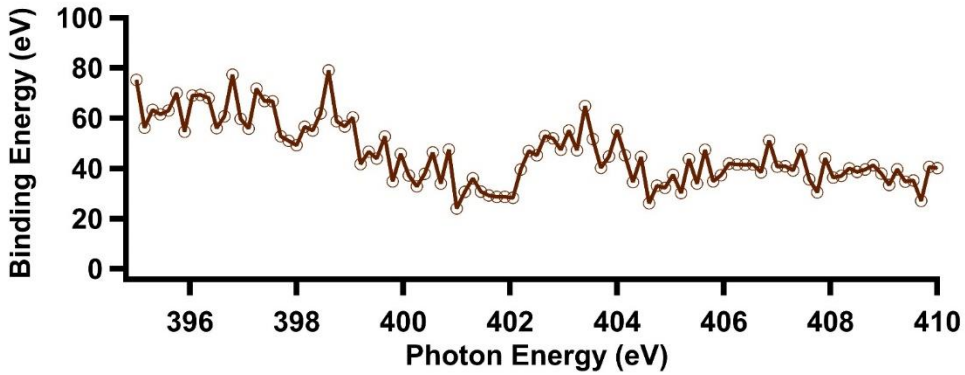
Interatomic Coulomb decay (ICD) like
+ electronic states' interferences

Is it related to a particular transition metal?

Can you tell us why?

NO

Cobalt phthalocyanine = no clear sign of ICD



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

Takeaway message

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 (Freïe Universitat, Berlin)
M. Briant (NIMBE, CEA Saclay)
M. Simon (LCPMR, Paris)

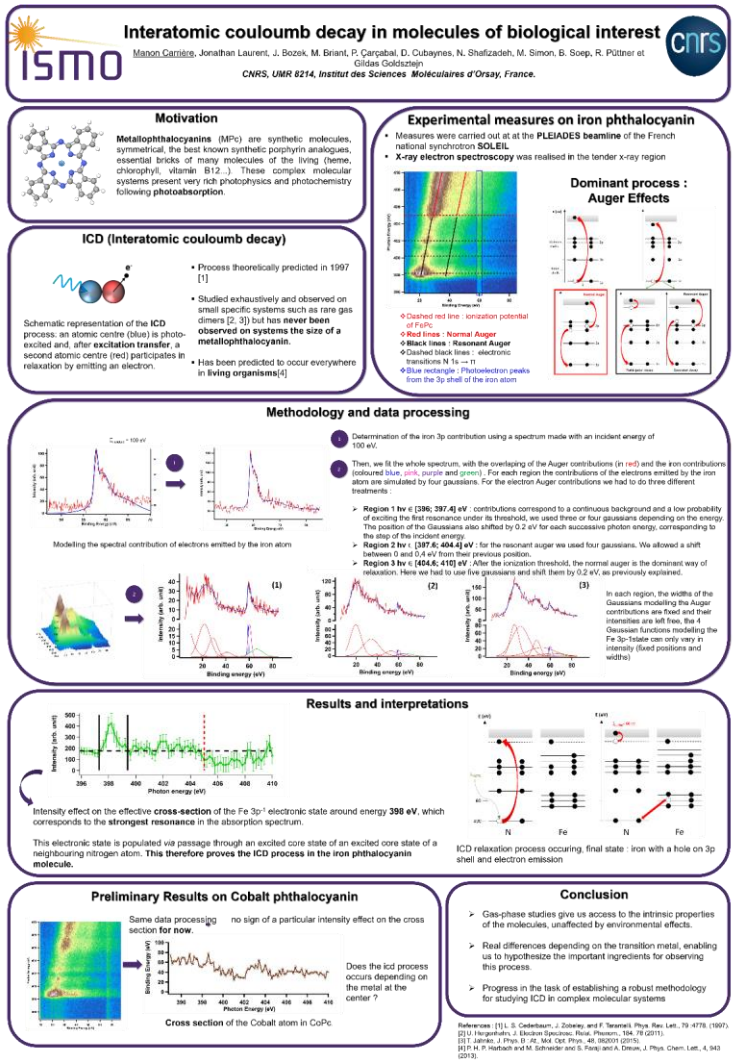
PLEIADES

J. Bozek
A. Milosavljević
E. Robert

Thank you for your attention

Don’t forget the posters

Manon Carrière



Apolline Piard