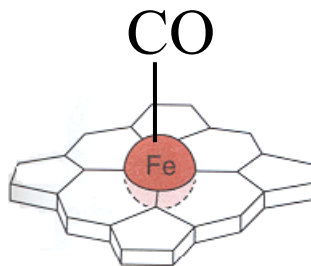


**Etude de la dynamique de relaxation des
molécules d'intérêt biologique en phase
gazeuse : la déligandation des
métalloporphyrines.**



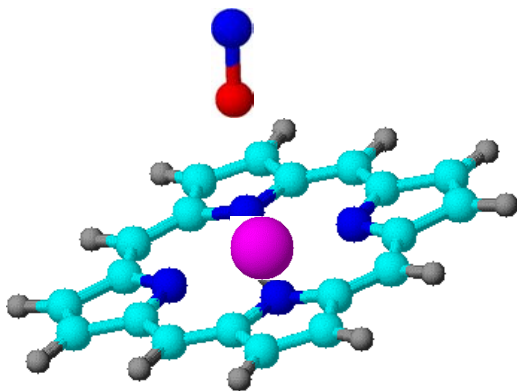
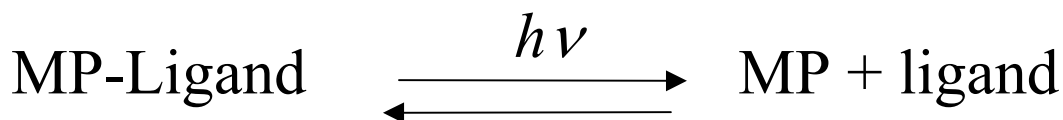
Niloufar Shafizadeh, Sébastien Sorgues

*Laboratoire de Photophysique Moléculaire bâtiment 210
Université de Paris-Sud 91405 Orsay France*

Benoît Soep

*Laboratoire Francis Perrin CEA Centre Saclay bâtiment 522,
91191 Gif- sur-Yvette France*

Dynamic of an elementary reaction in the gas phase



Porphyrin Ring

Metal

Ligand

Charge Transfer between the Metal to the Porphyrin Ring
Or

And from Porphyrin Ring to the Metal

The microscopic understanding of a reaction mechanism requires the detailed knowledge of the energetics, the transition state and of the relaxation pathways which are connected.

Comparing to the work of M. Wulff we would like to observe what happens in the first picoseconds after the excitation.

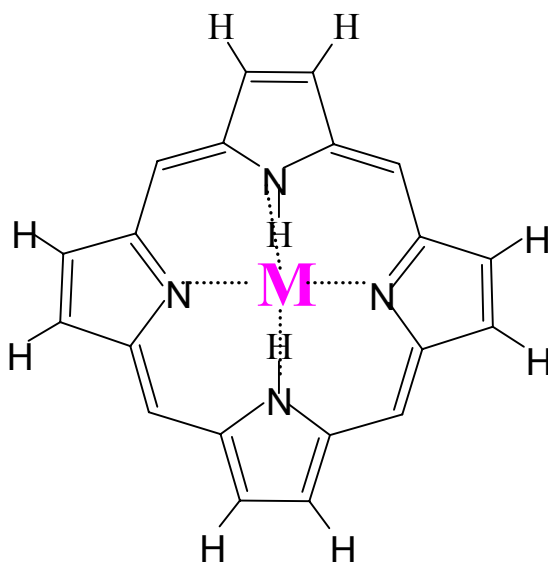
Why the gas phase

The gas phase techniques are used as analysis methods: Chromatography , MALDI (Mass Analysis of Laser Desorption Ion), Electro Spray,...

The gas phase is an unusual environment for studies of bio-molecules but these studies provides a deeper understanding :

- ♣ Of the intrinsic properties of each function or molecules without any interaction with the environment.
- ♣ They allow a very detailed analysis of structures, conformation and level energies.
- ♣ An easier comparison with theoretical models
- ♣ ease to study ions.

Metalloporphyrins



M=Fe, Mg, Co, Cu,...

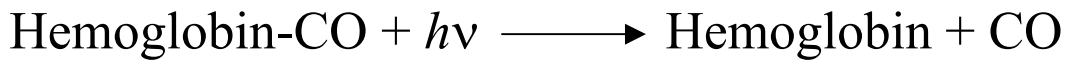
Porphyrins are most important biological molecules: they are involved in many different mechanisms of the chemistry of living systems:

Photosynthesis Chlorophyll

Or the transport and storage of O₂, CO or NO in living organisms

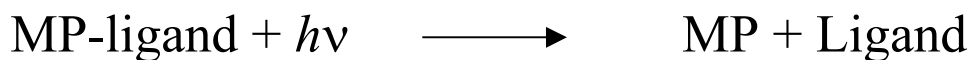
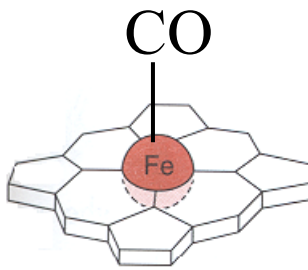
The Metalloporphyrins are present in Cytochrome P450, a catalyst of many chemical reactions in nature, which first step is an electron abstraction .

In the condensed phase



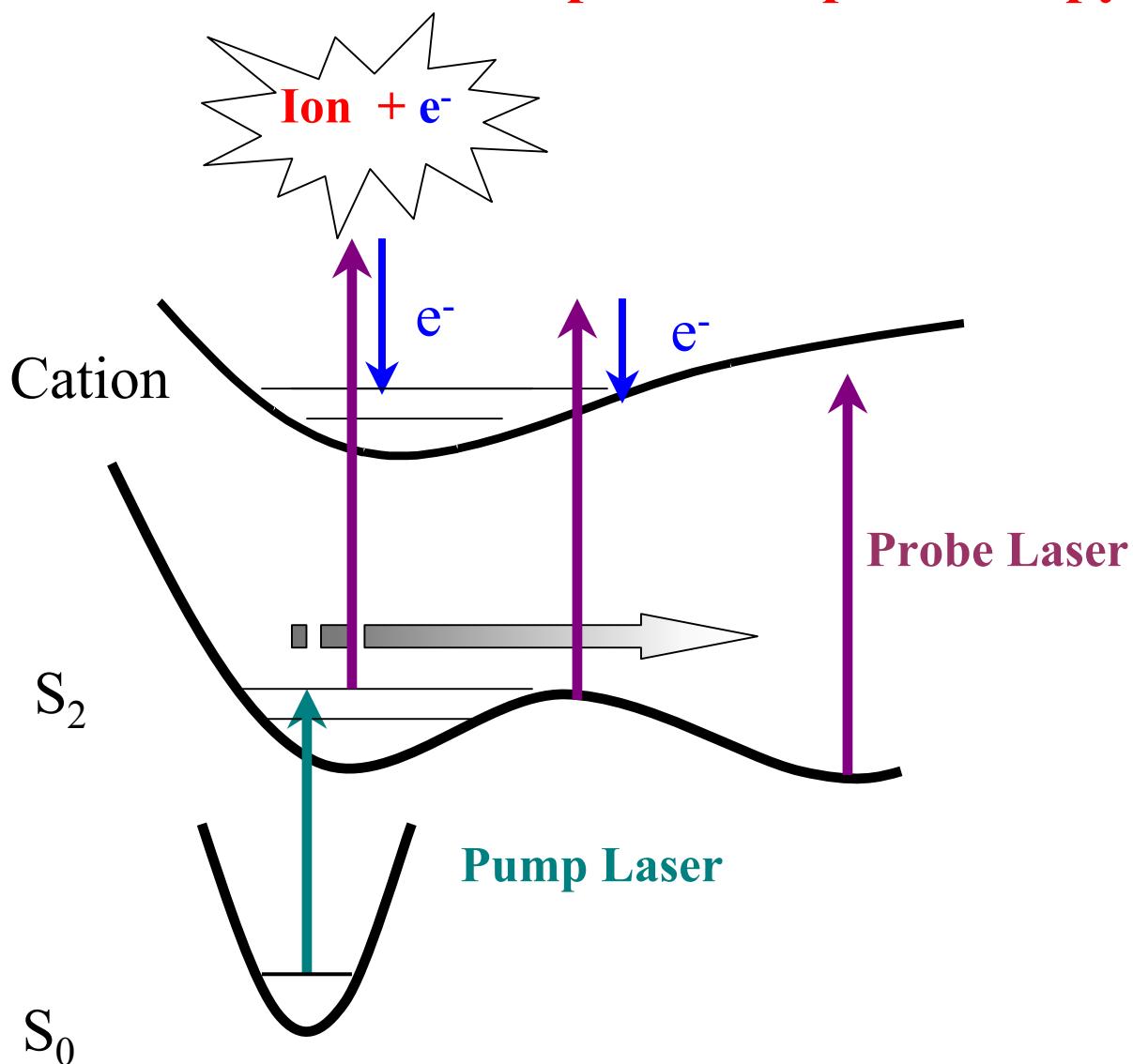
The intermediate states are not known

Change on the spin of iron



by using **time dependent mass spectrometry**
and photoelectron spectroscopy, in the gas
phase.

Ion or Electron Time dependent Spectroscopy

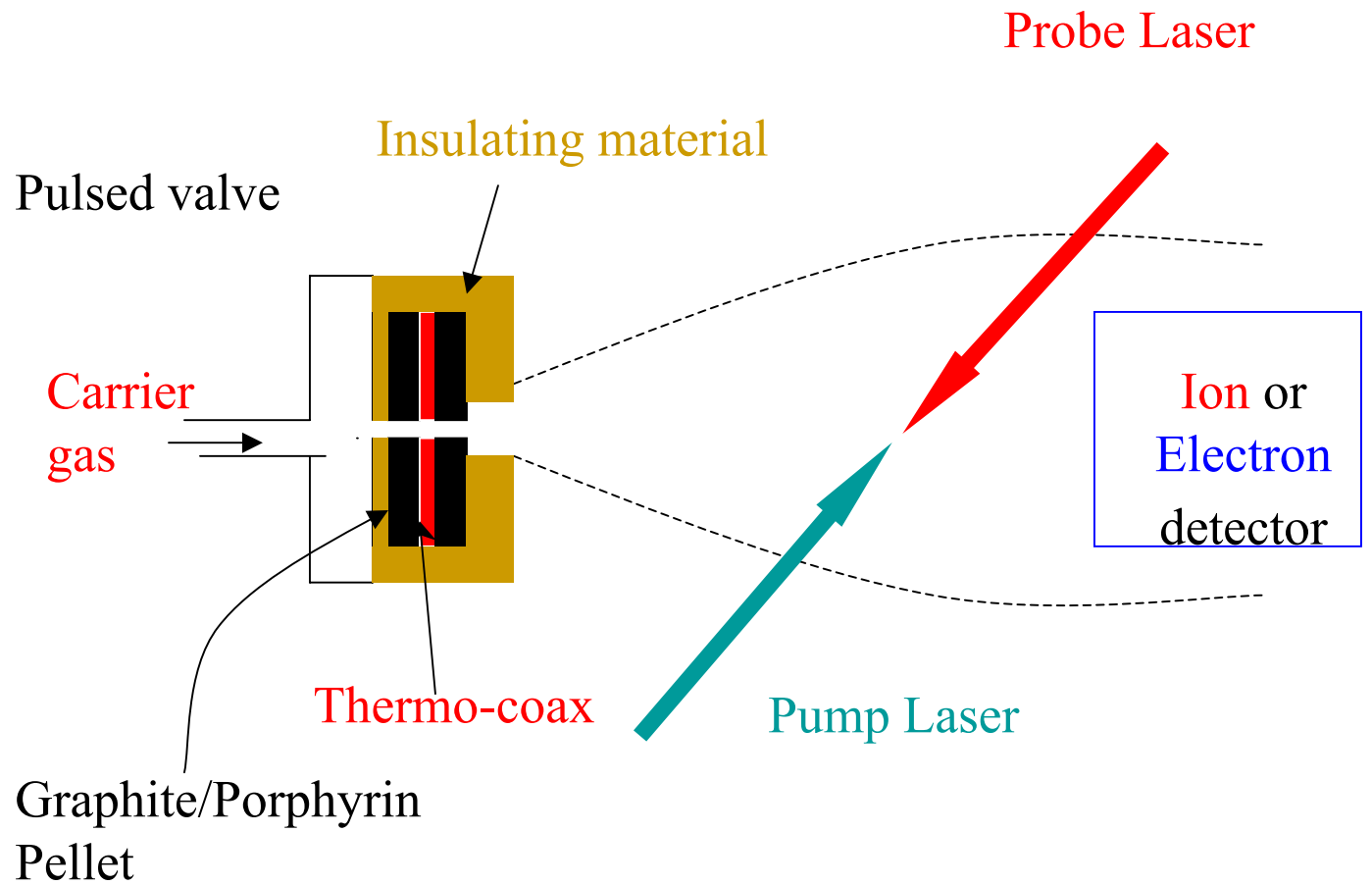


Detecting the ions leads to information on masses and fragments.

Detecting the electrons leads to information on the kinetic energy of the ejected electrons, reflecting the evolution of electronically excited intermediate states.

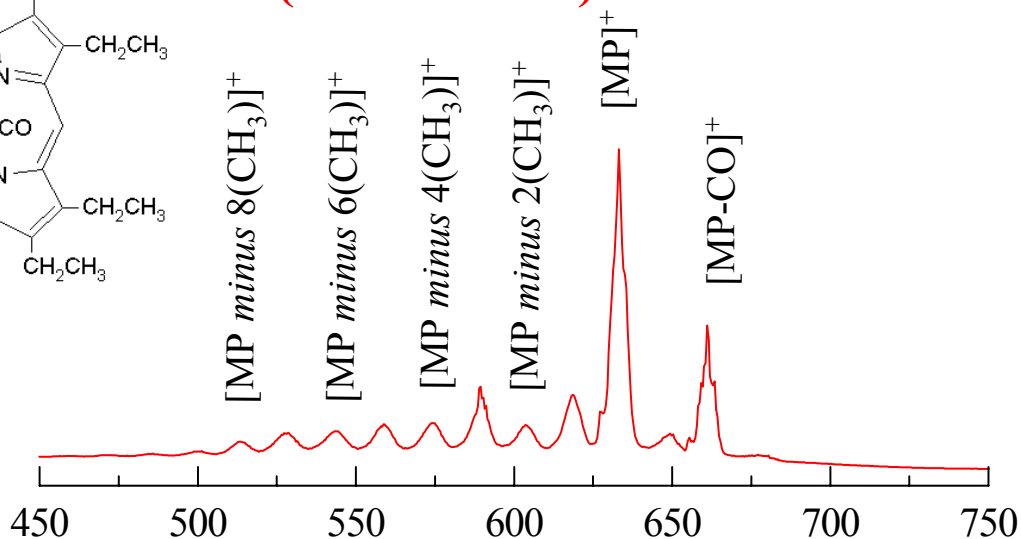
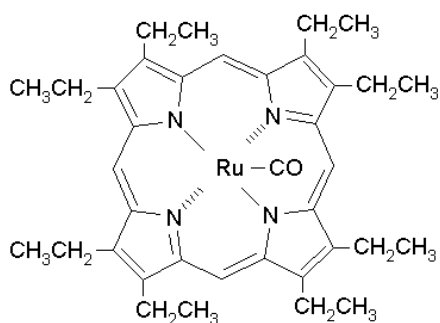
By varying the time delay between pump and probe laser, one can follow the evolution of the S_2 state.

Our vaporisation method

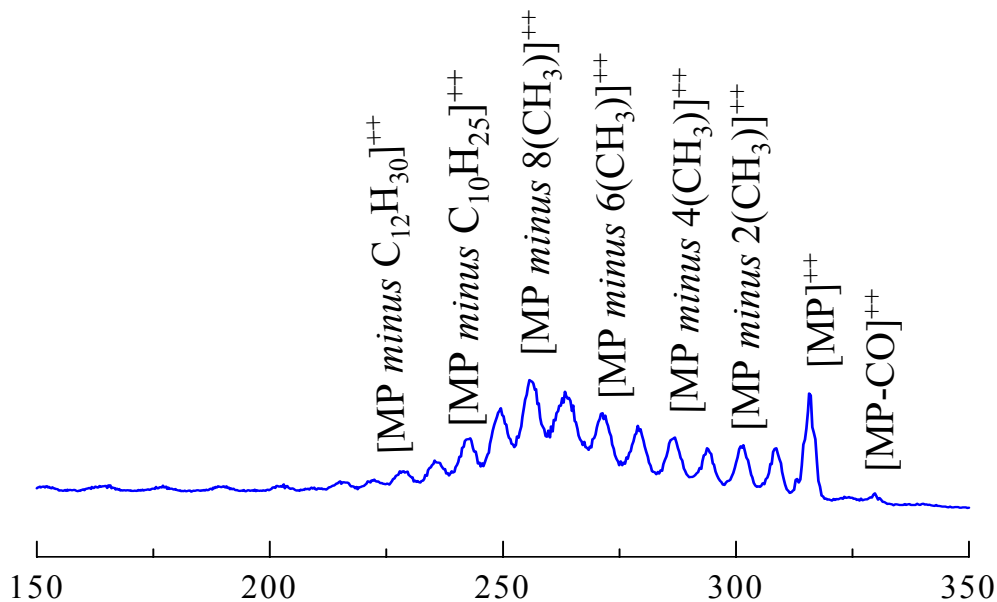
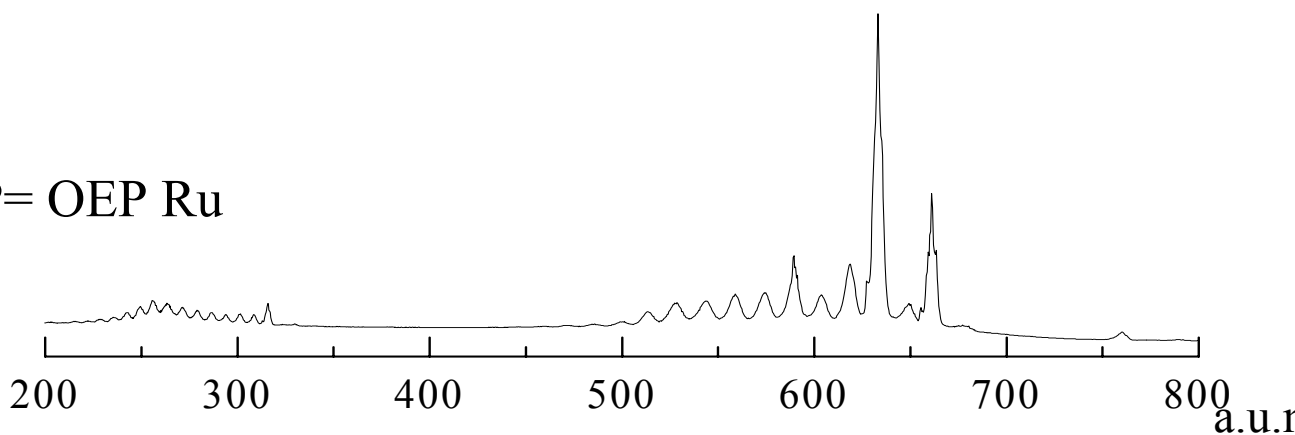


Femtosecond Resonant Ionisation 400 + 800 nm of Octaethyl-porphyrins ruthenium carbonyl

(OEP Ru CO)



MP= OEP Ru



Summary

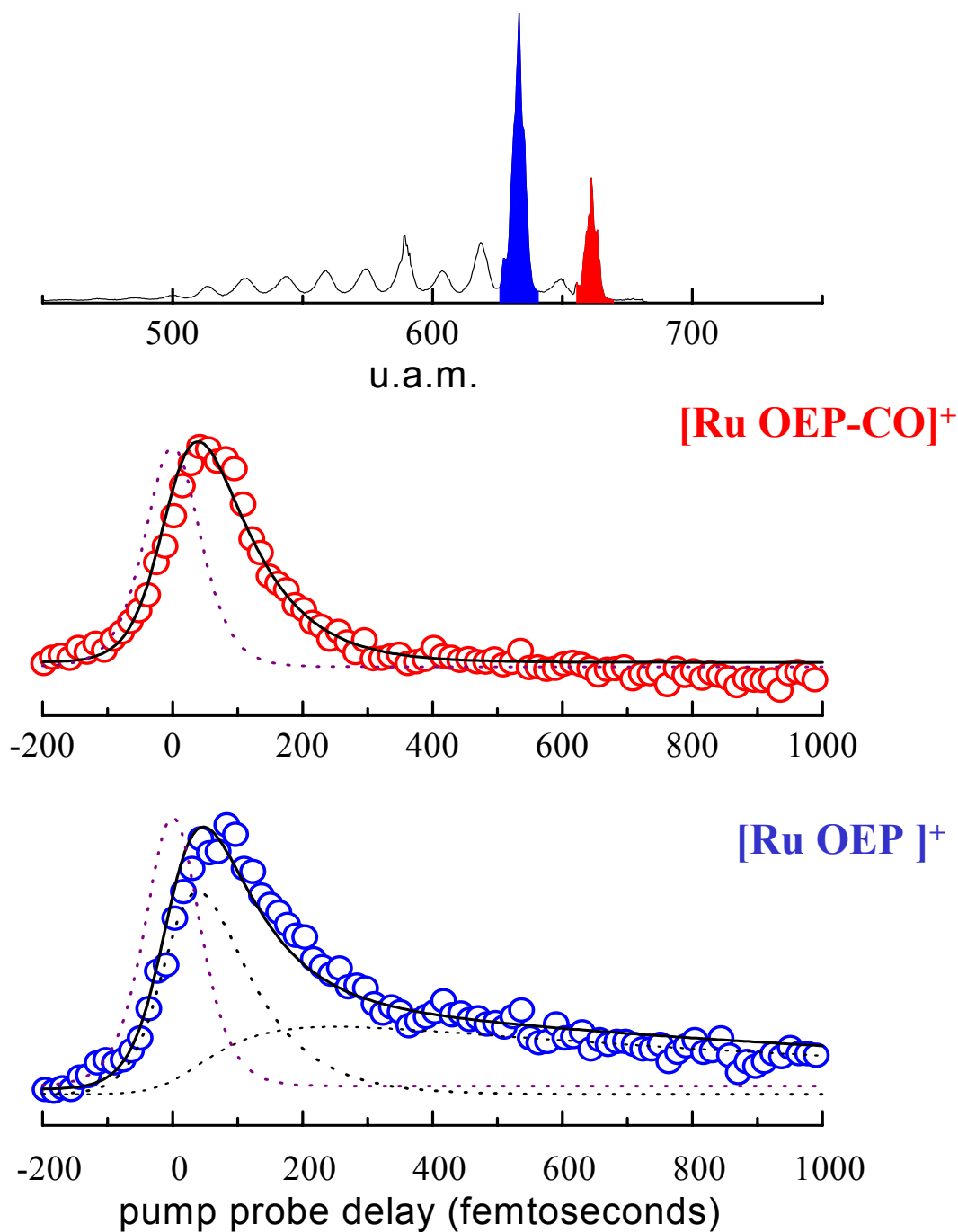
* Why are the doubly charged ion stable?

* How are the charges distributed?

* Why is $M-CO^{++}$ present in the spectra $M-CO$, while its binding is ~ 1.5 eV

The formation of $[M-8(CH_3)]^{++}$ needs at least 46 eV of energy.

Femtosecond decay of the photo-ion signals of Ruthenium Octaethyl Porphyrin Carbonyl (Ru OEP-CO) at 400+800nm



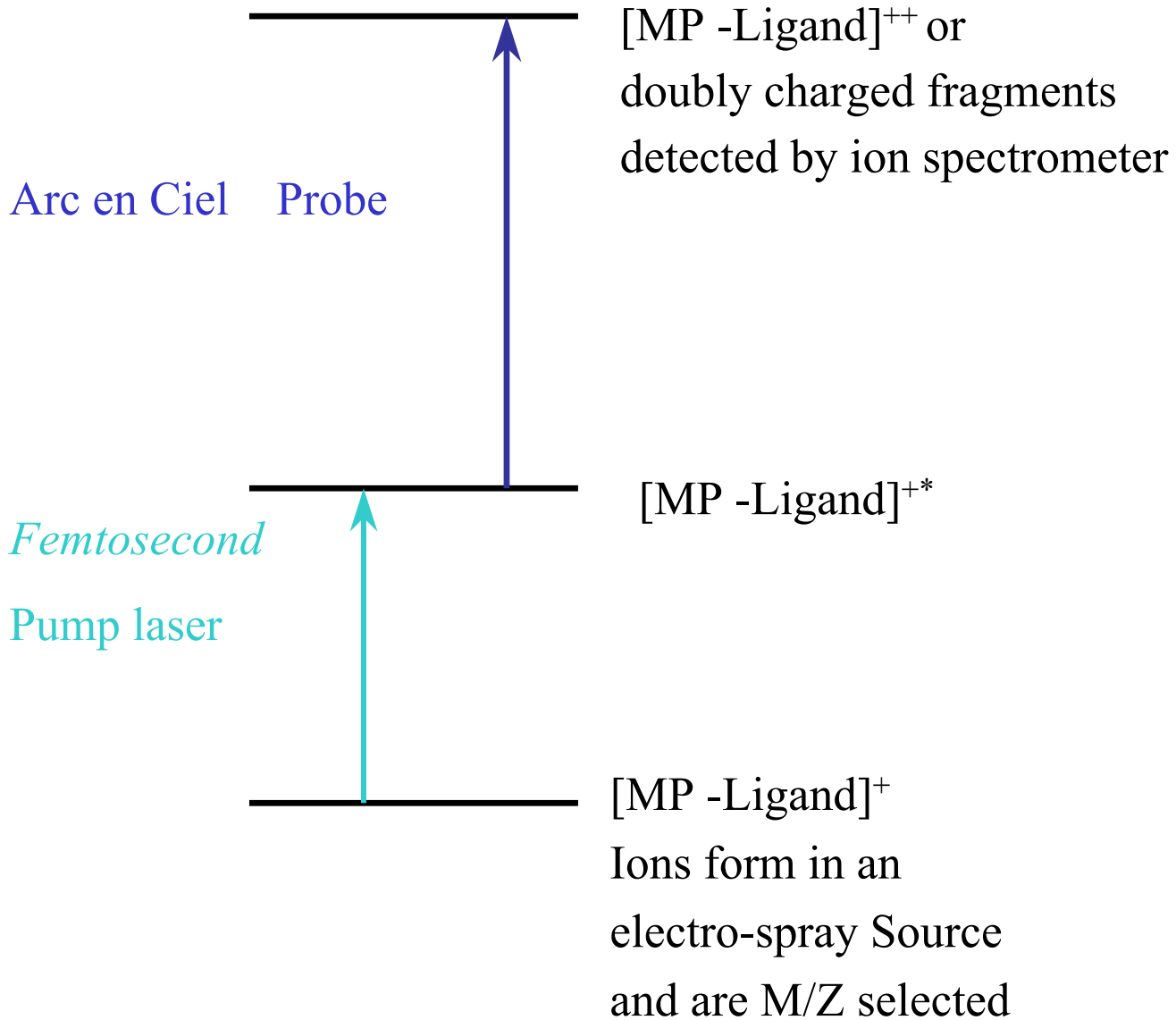
Summary

- ★ We have observed doubly charged metalloporphyrines and their fragments. The existence of these ions raises many questions
- ★ We have observed in real time the excited state dissociation of Ru OEP-CO
- ★ The dissociation of Ru OEP-CO yields an electronically excited Ru OEP* which is relatively "long lived" ~ps, certainly not the ground state. A triplet state or a charge transfer state are likely candidates, or both ...
- ★ The long lived intermediate state is the subject of further studies by photoelectron femtosecond spectroscopy .
- ★ Our soft desorption method allows : the vaporisation and cooling in supersonic jet of porphyrins and ligated metalloporphyrins of increasing complexity. We plan to use a variant of MALDI for more fragile systems.

Project with Arc en Ciel

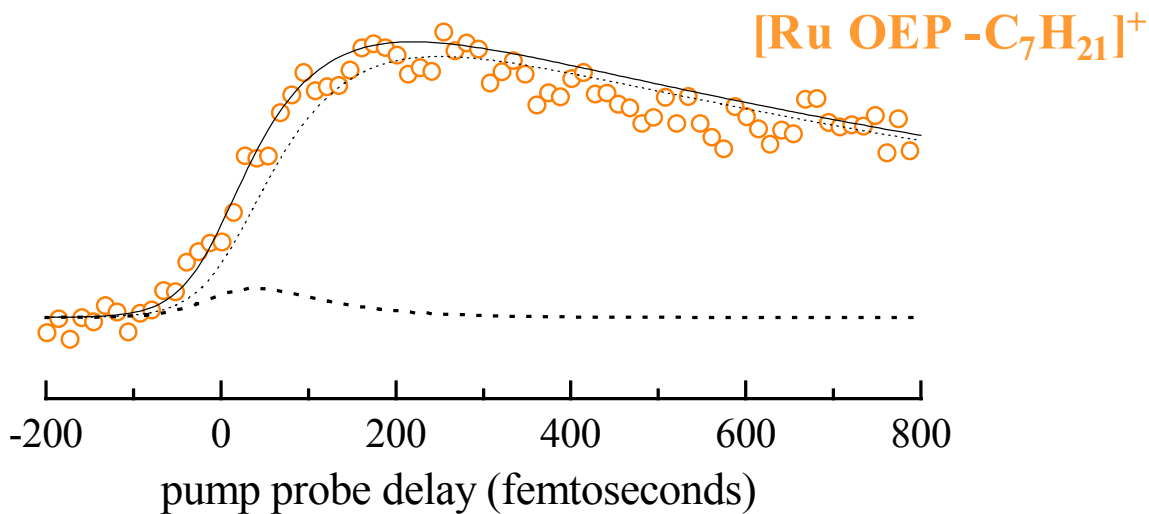
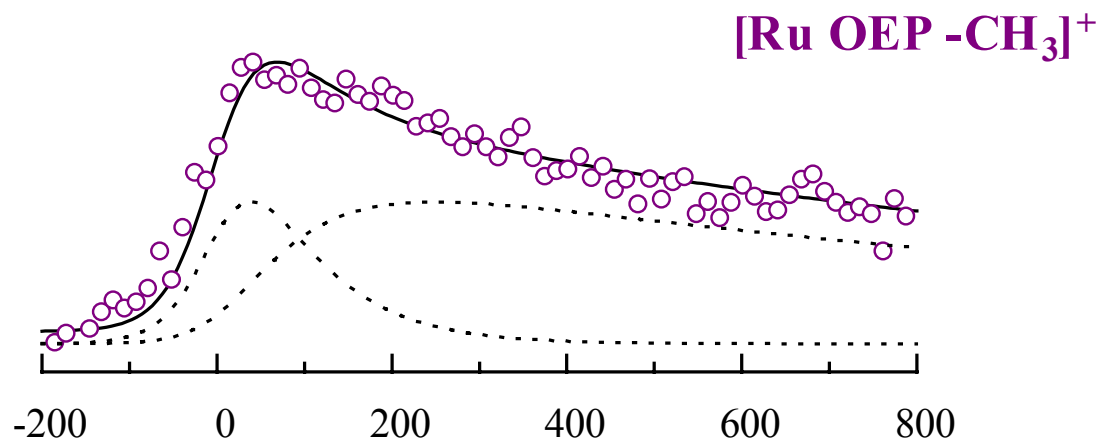
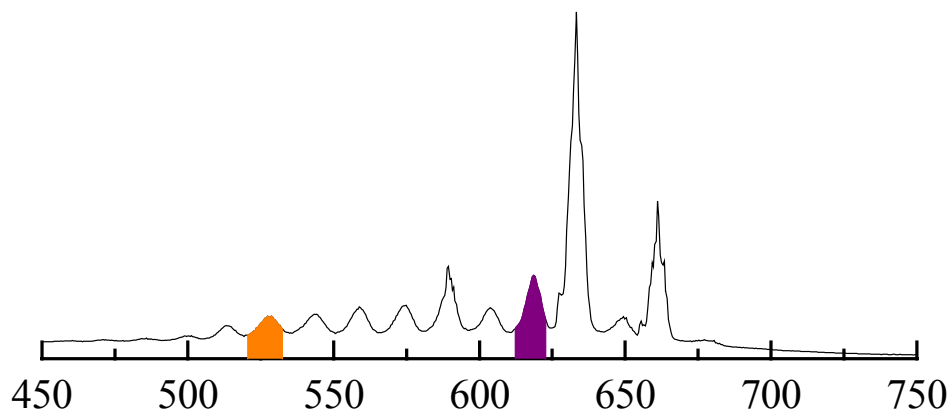
- ❖ Taking advantage from the large tuneability of the Arc en Ciel source
 - Determination of the threshold appearance of singly and doubly charged metalloporphyrins(- direct and stepwise)
 - The excited states of singly and doubly charged ions by using photoelectron spectroscopy
- ❖ By combining an electrospray source with the Arc en Ciel and a femtosecond laser we turn to the study of ionic species
 - We can evaporate more fragile and complex species
 - We will be able to follow in real time the dissociation of excited $[\text{MP-Ligand}]^+$

Project with Arc en ciel

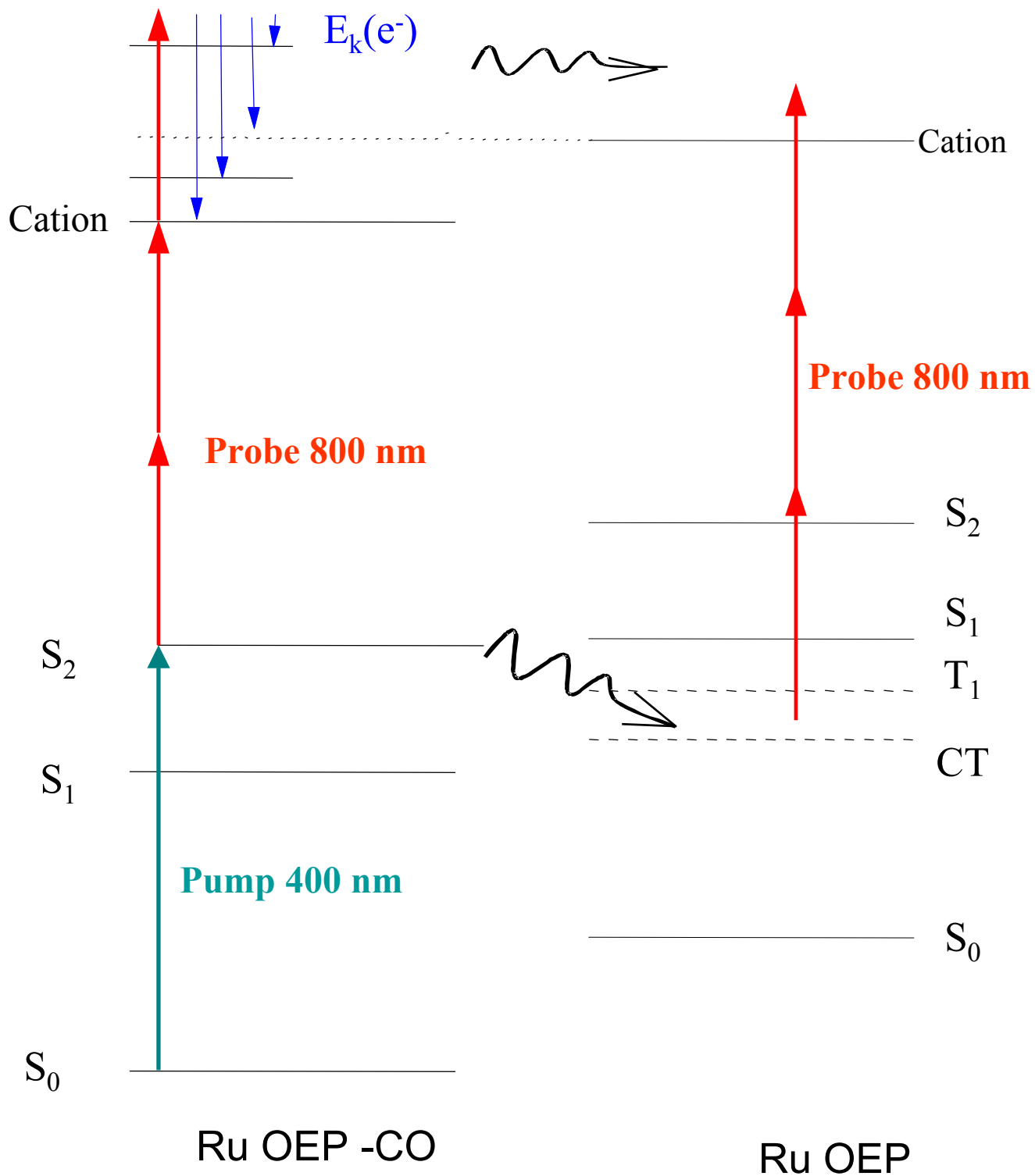


- *We can evaporate more fragile and complex species*
- *We will be able to follow in real time the dissociation of excited $[\text{MP-Ligand}]^+$*

Femtosecond decay of the photo-ion signals of Ru OEP-CO at 400+800nm



The decay pathway of Ru-OEP-CO



Ionisation potentials

	PI (eV)
TPP	6.39
MgTPP	6.48
FeTPP	6.50
NiTPP	6.44
ZnTPP	6.49

S.C.Khandelwal and J.L.Roebber CPL 34 (1975) 355

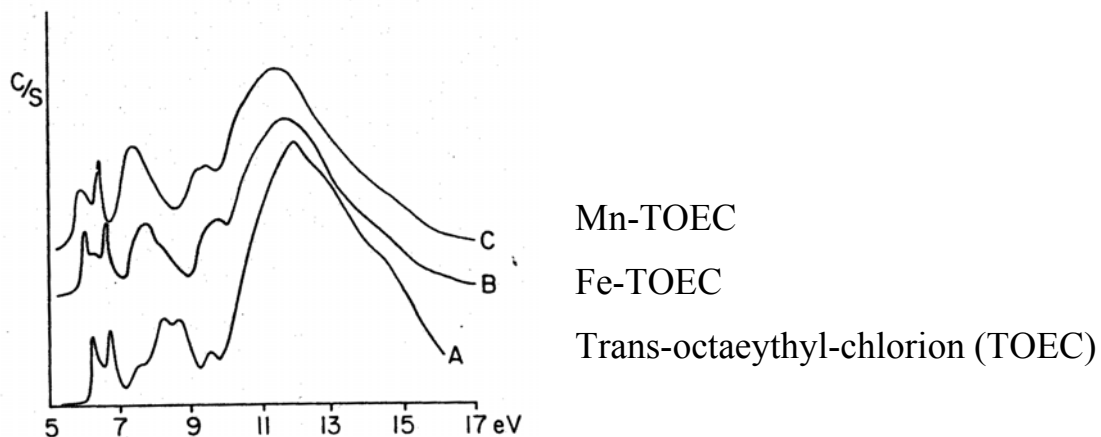
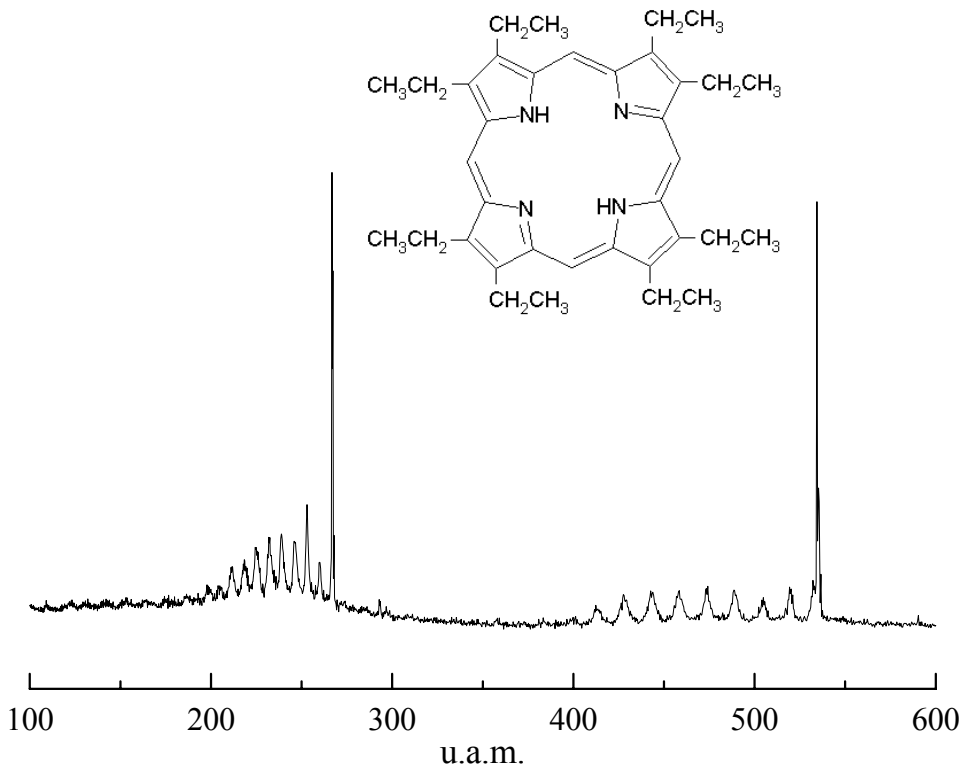


Fig. 4. The HeI photoelectron spectra of (A) trans-octaethylchlorin; (B) Fe(III)-trans-octaethylchlorin; (C) Mn(III) octaethylchlorin.

P.Dupuis, R.Roberge and C.Sandorfy CPL 75 (1980) 434

*How are the charges distributed?

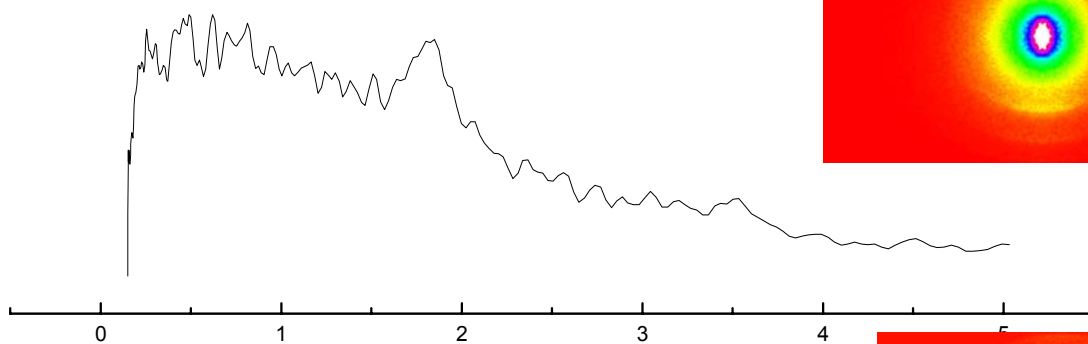
Mass Spectra of free-Octaethyl Porphyrin



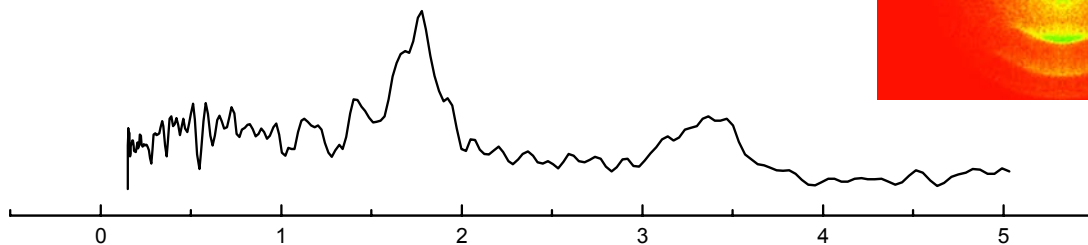
Better understanding of the oxydo-reduction processes

Photoelectron spectra of Ru OEP-CO at 400+800nm

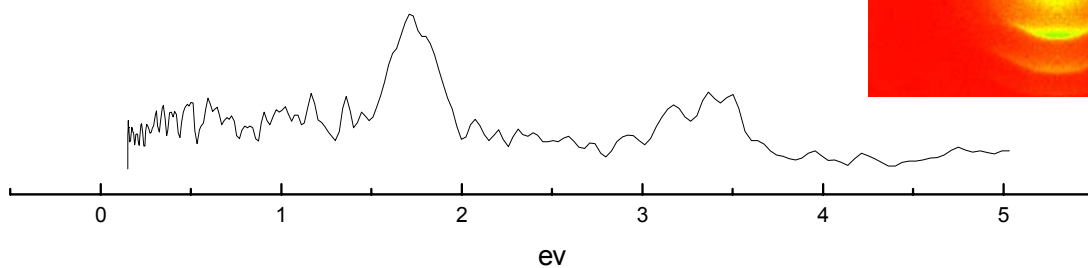
Delay=10fs



Delay=50fs



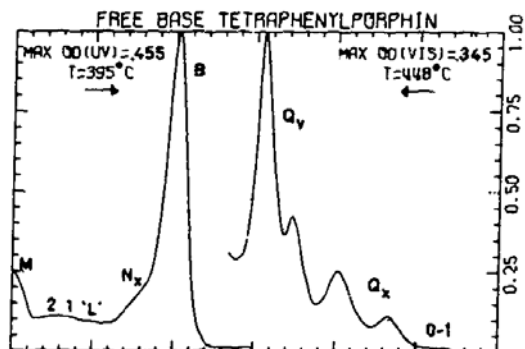
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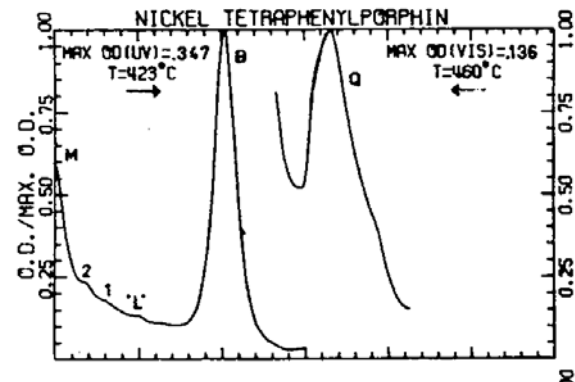
Spectroscopy of metalloporphyrins

L. Edwards, D.H. Dolphin, M. Gouterman, A.D. Adler *J. Mol. Spectr.* 38 (1971) 16

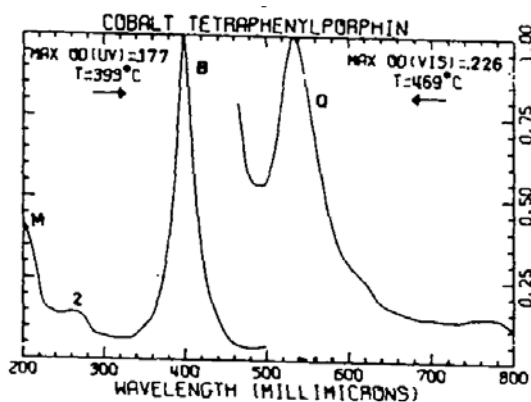
TPP H₂



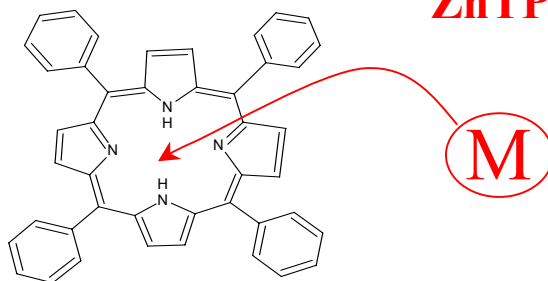
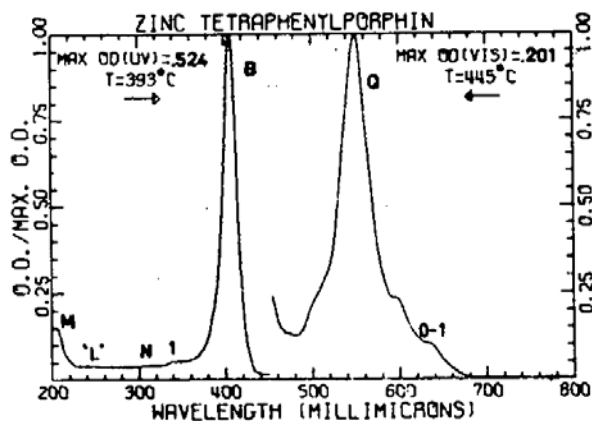
NiTPP



CoTPP



ZnTPP

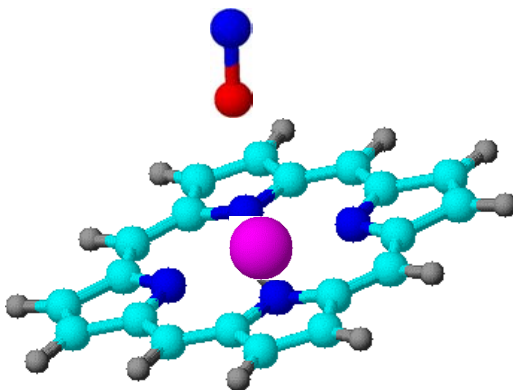


All spectra show absorption features common to all porphyrins. The high energy (~400 nm) Soret band and the low energy (550 nm) Q band. The Soret and Q bands are both due to the excitation of the macrocycle $\pi \rightarrow \pi^*$. (The metal remaining in the ground state)

The insertion of a metal atom perturbs very slightly the transition.

Metalloporphyrins

Interaction



Porphyrin Ring

Metal

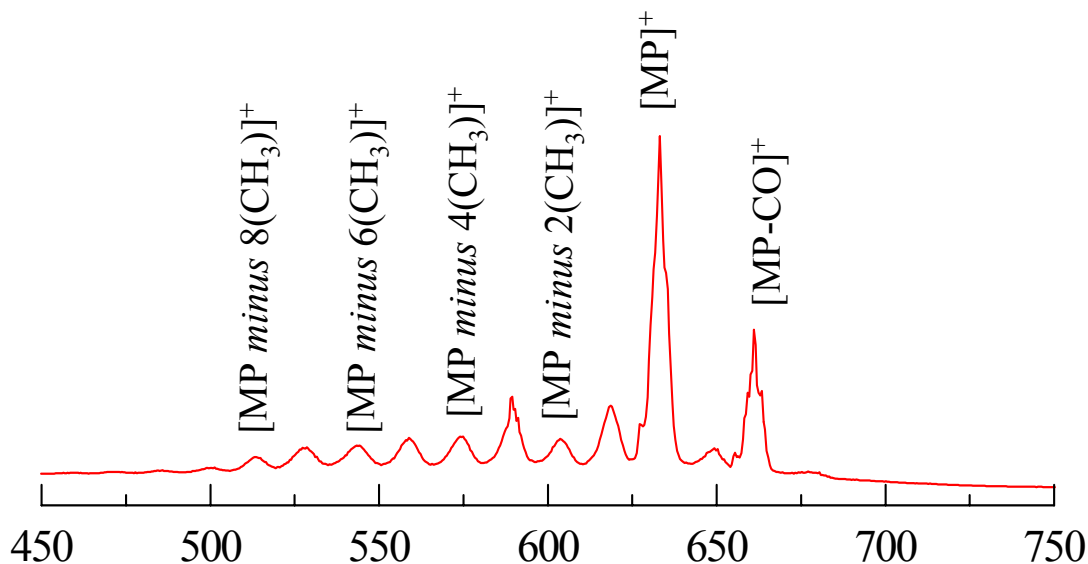
Ligand

Charge transfer between

Porphyrin Ring and **Metal**

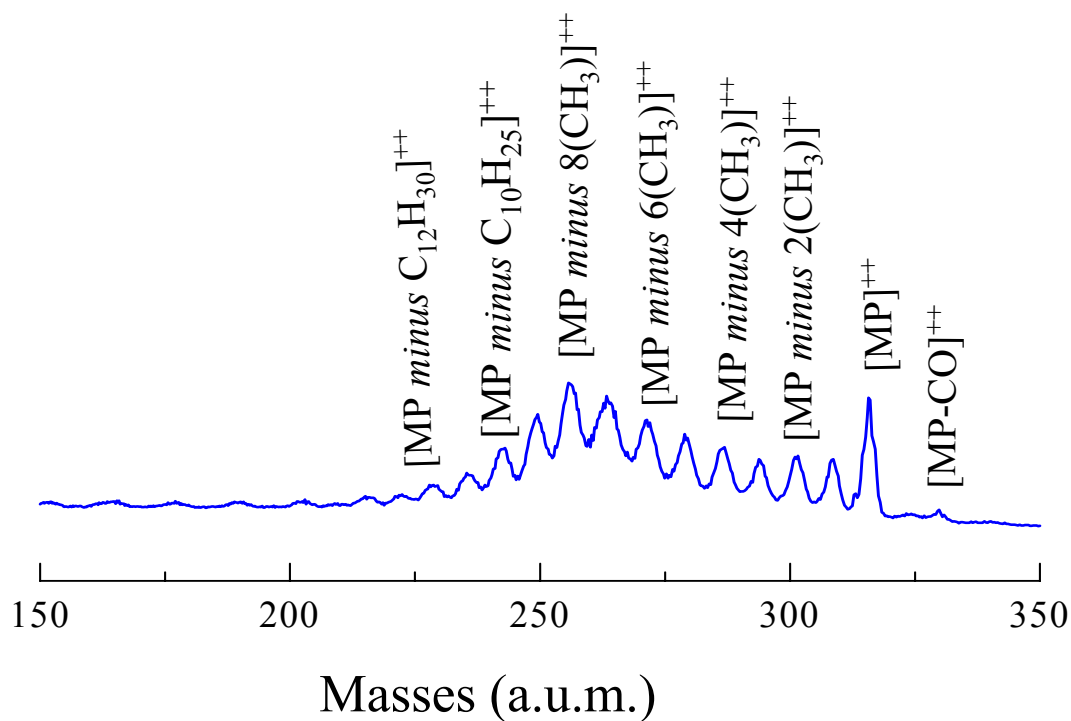
and Vice Versa

Destabilisation of **Ligand** - **Metal** bound

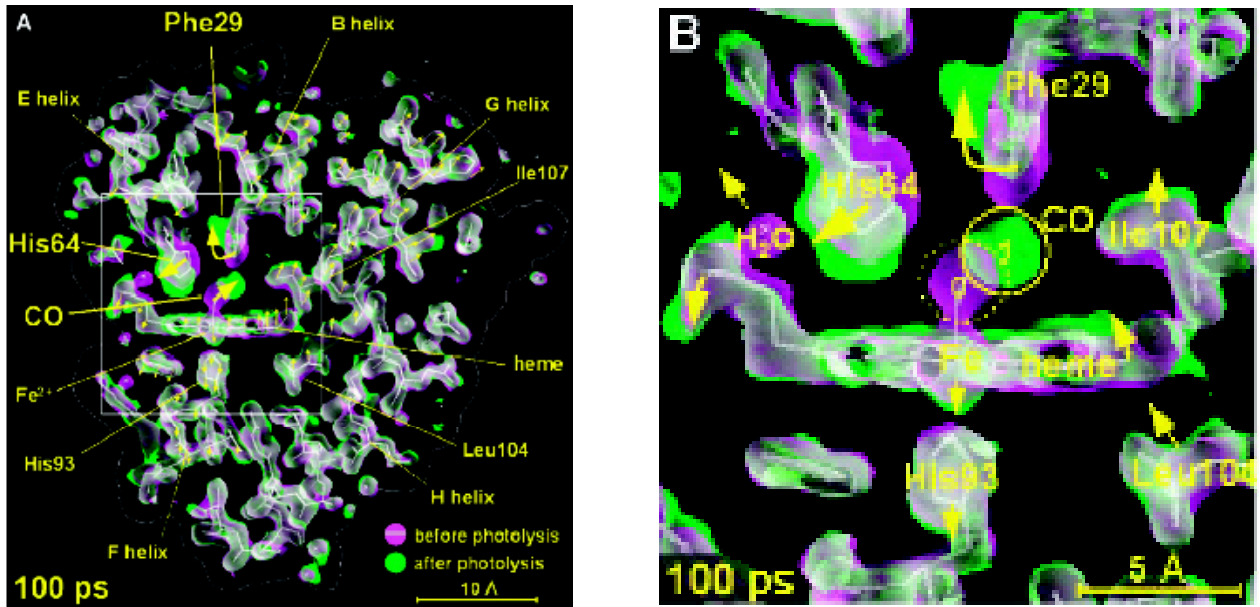


The singly charged ion can lose 8 methyl fragments after β cleavage.

Also the distribution of the fragments is different for doubly charged ions. There is an enhancement of α cleavage in doubly charged ions.

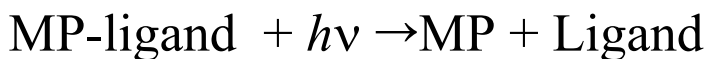


The association and dissociation of a ligand to metalloproteins is a complex process. This mechanism certainly involves multiple steps



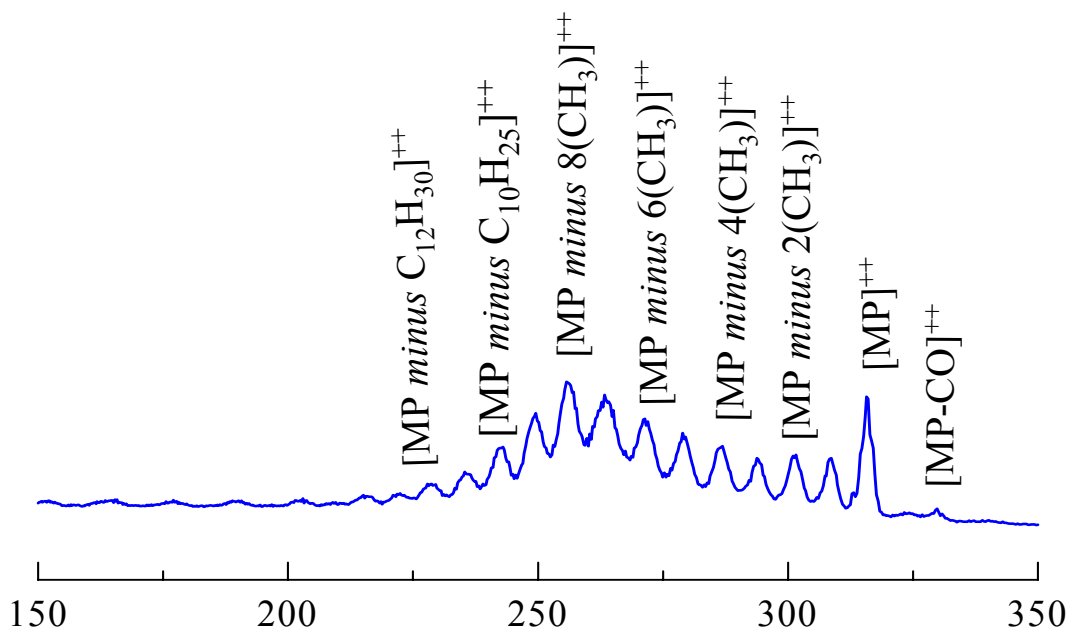
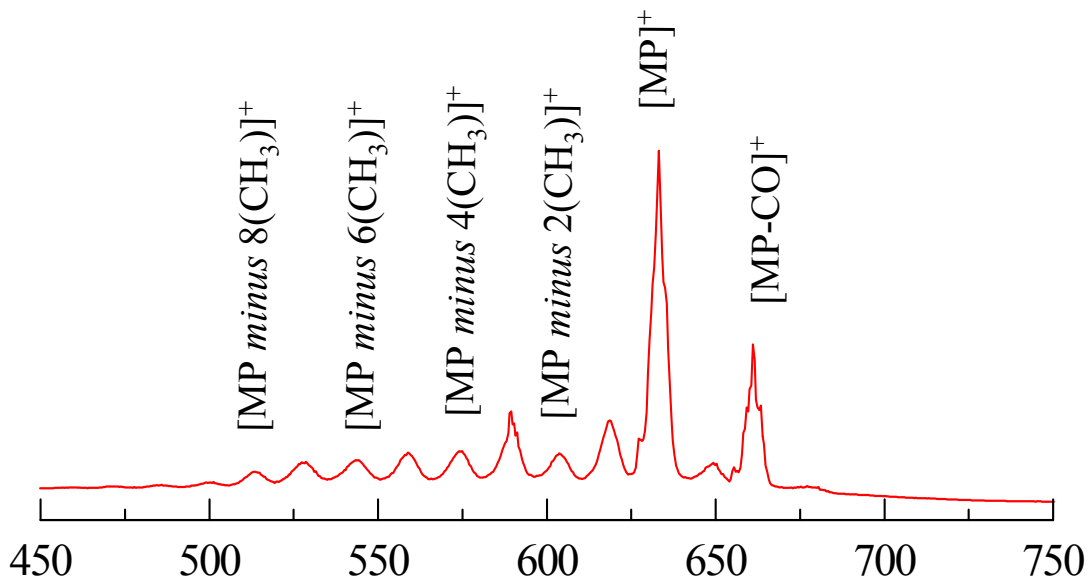
Schotte *et al.* *Science* **300** (2003) 1945

We have focused specially on the interaction between the **Ligand** and the **Metalloporphyrin**



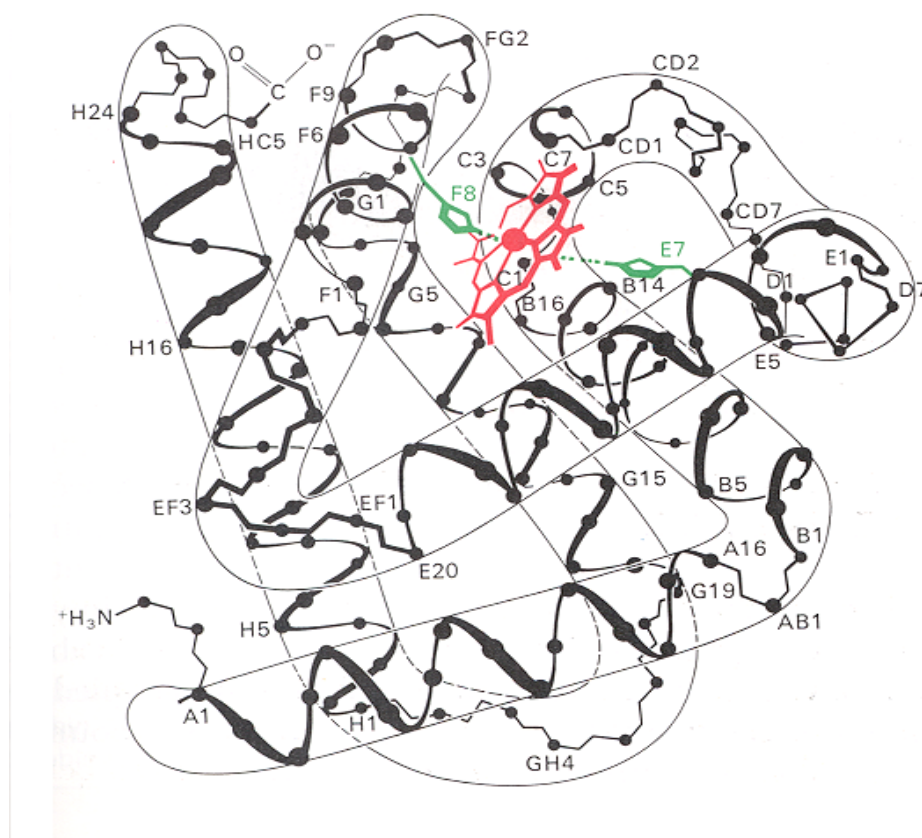
The microscopic understanding of a reaction mechanism requires the detailed knowledge of the **energetics** and of the **relaxation pathways which are connected**.

I.e. what happens in the first picoseconds after the excitation .



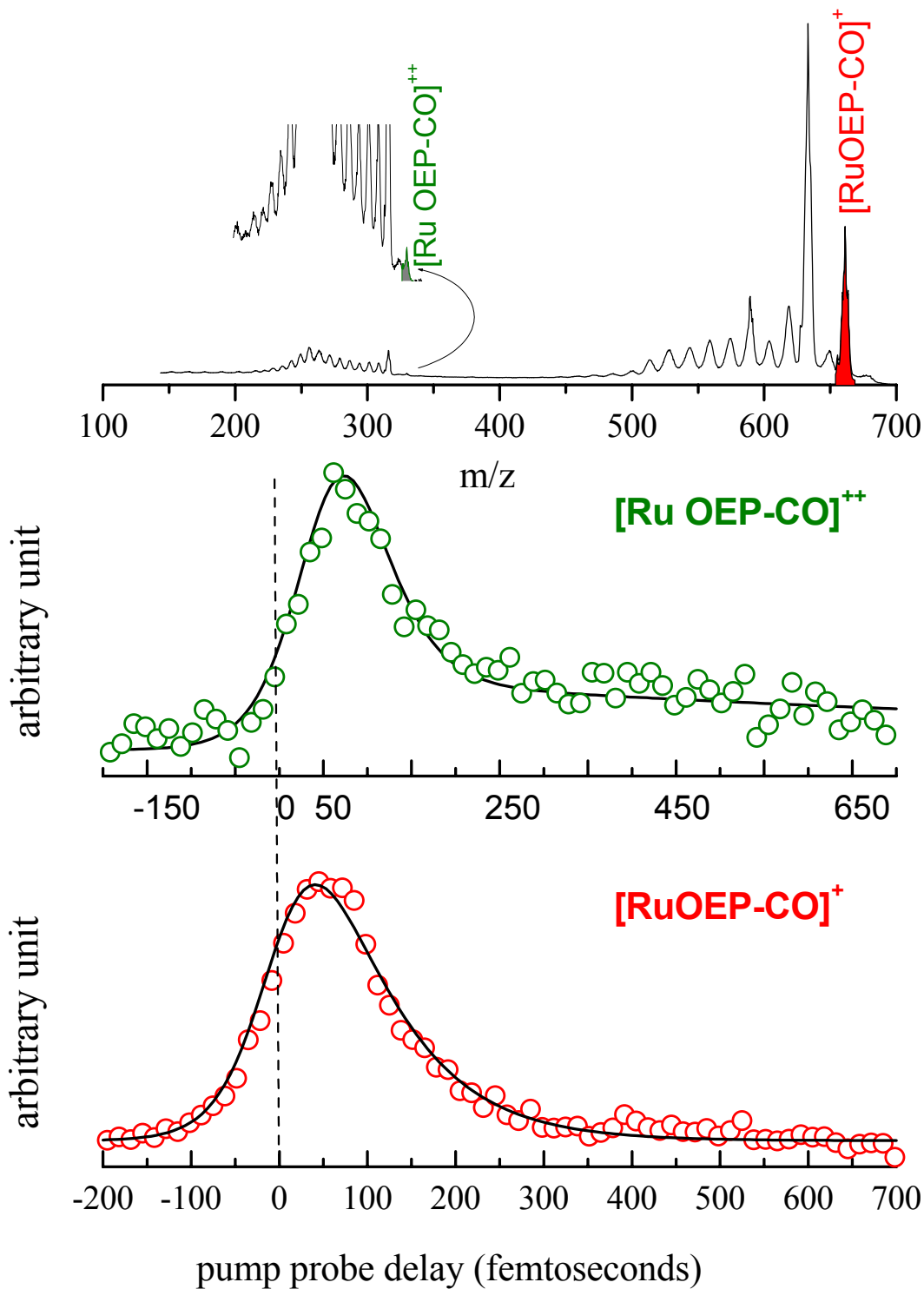
Masses (a.u.m.)

The processes of storage and transport of diatomic molecules (O_2 , CO , NO ,...) in living systems are related with the association and dissociation of a ligand with a metalloporphyrin in ground and excited states.

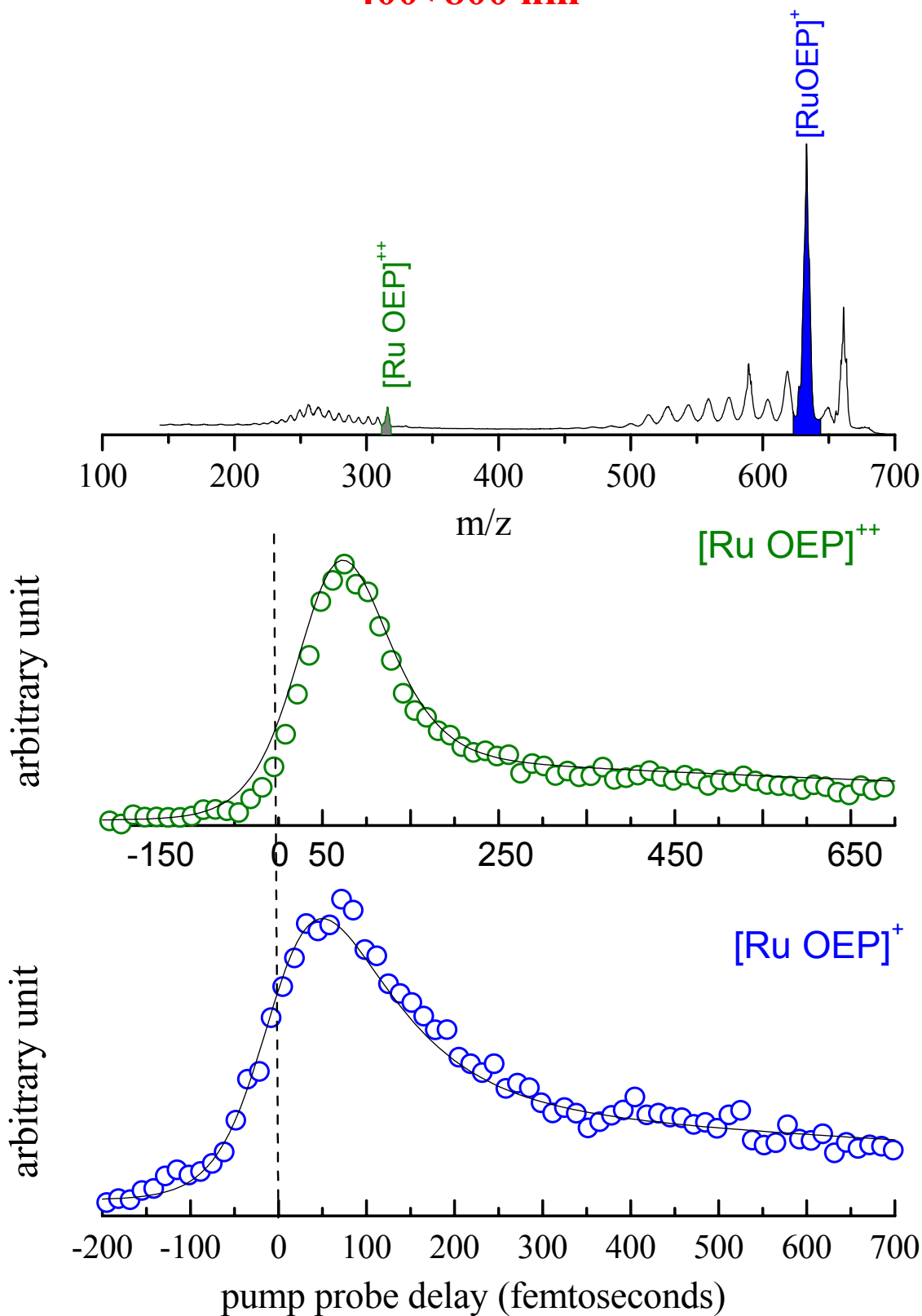


Localized phenomena between a metalloporphyrin and the ligand

Comparison of the Femtosecond decay of the photo-ion signals of $[\text{Ru OEP-CO}]^{++}$ and $[\text{Ru OEP-CO}]^+$ at 400+800 nm



Comparison of Femtosecond decay of the photoion signals of $[\text{Ru OEP}]^{++}$ and $[\text{Ru OEP}]^+$ at 400+800 nm



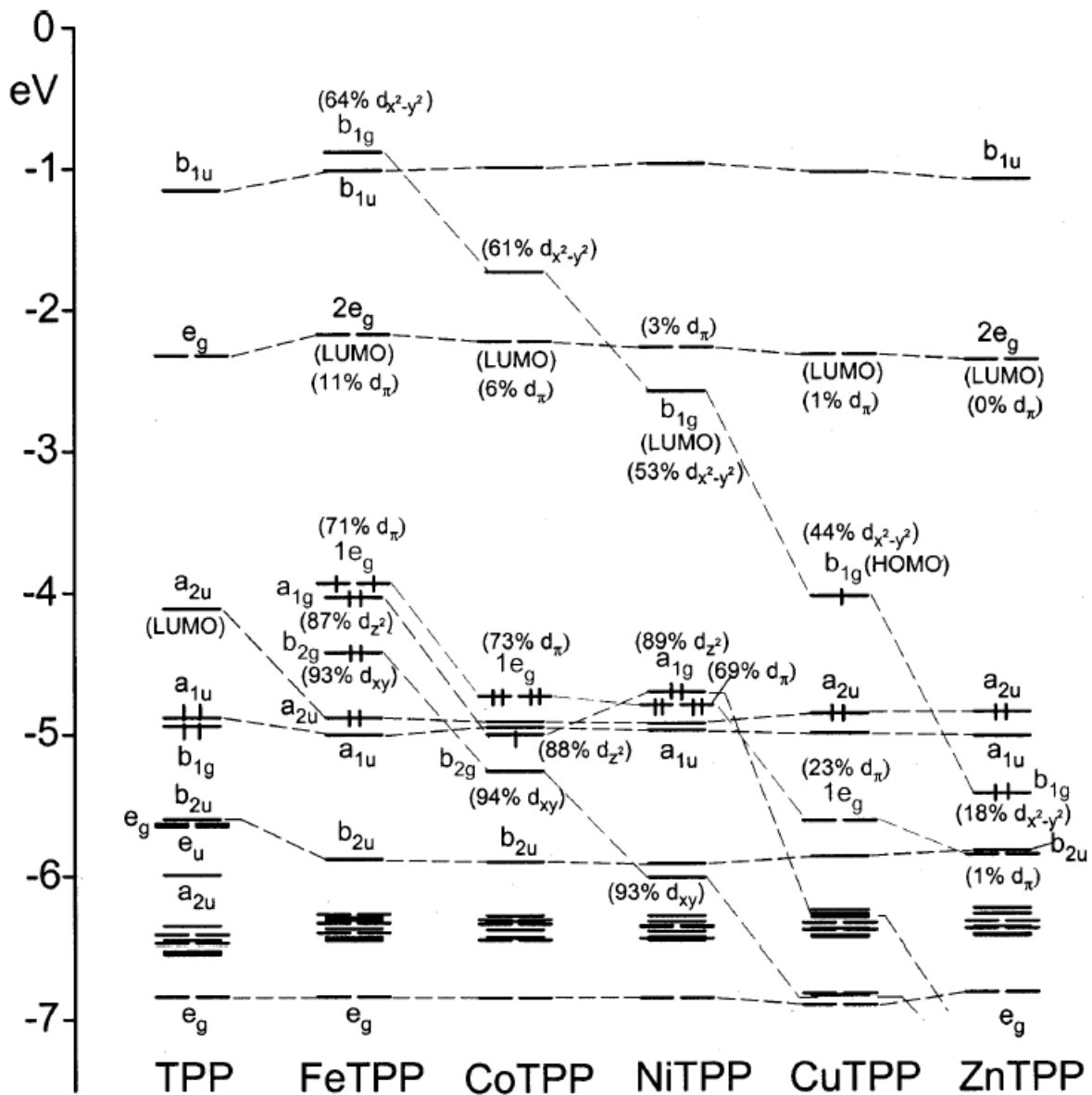
Why the Gas Phase ?

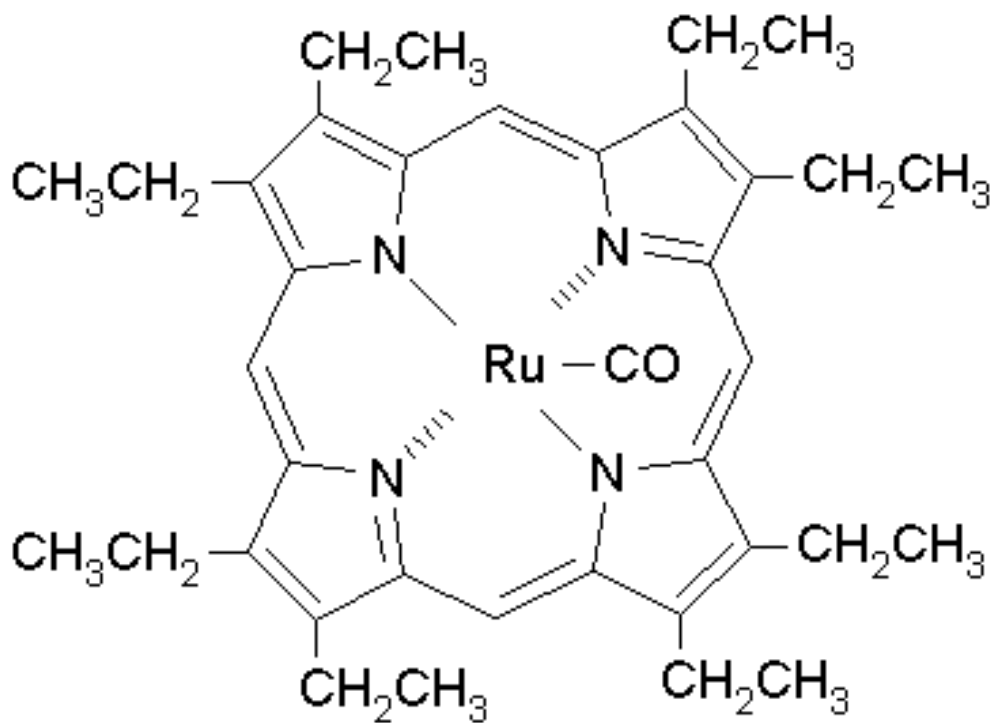
The gas phase techniques are used as analysis methods: Chromatography , MALDI (Mass Analysis of Laser Desorption Ion), Electro Spray,...

The gas phase is an unusual environment for studies of bio-molecules but these studies provides a deeper understandings :

- ♣ Of the intrinsic property of each function or molecules without any interaction with the environment.
- ♣ They allow a very detailed analysis of structures, conformation and level energies.
- ♣ An easier comparison with theoretical models
- ♣ easy to study ion

Energy diagrams of free- and metallo-porphyrins



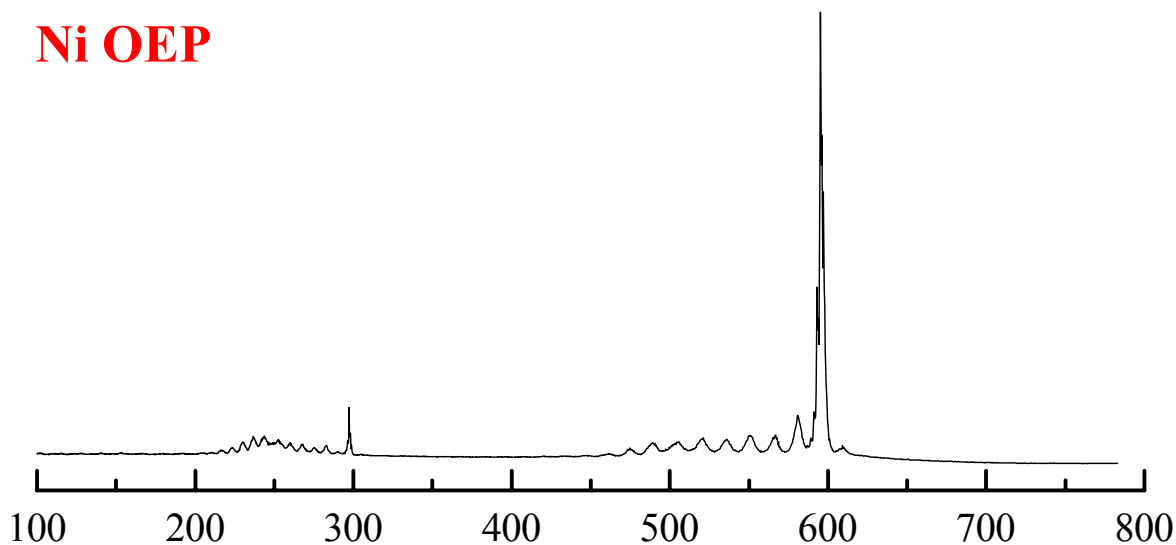


Ruthenium Octaethyl Porphyrin
(Ru OEP-CO)

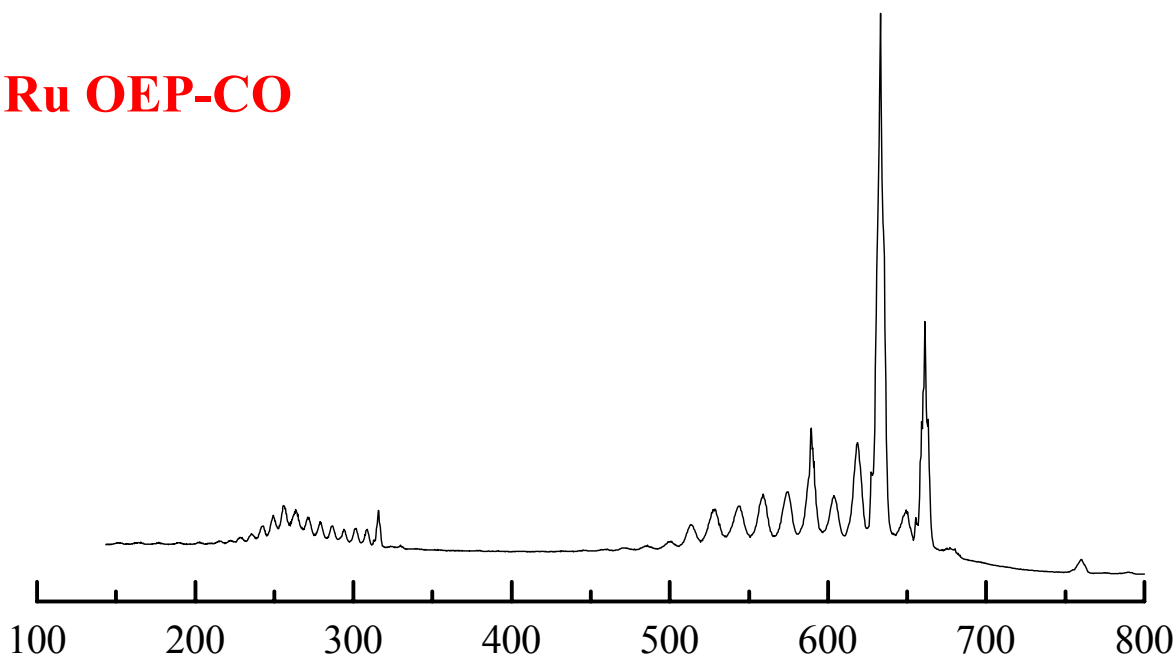
Femtosecond resonant ionisation

400 + 800 nm

Ni OEP

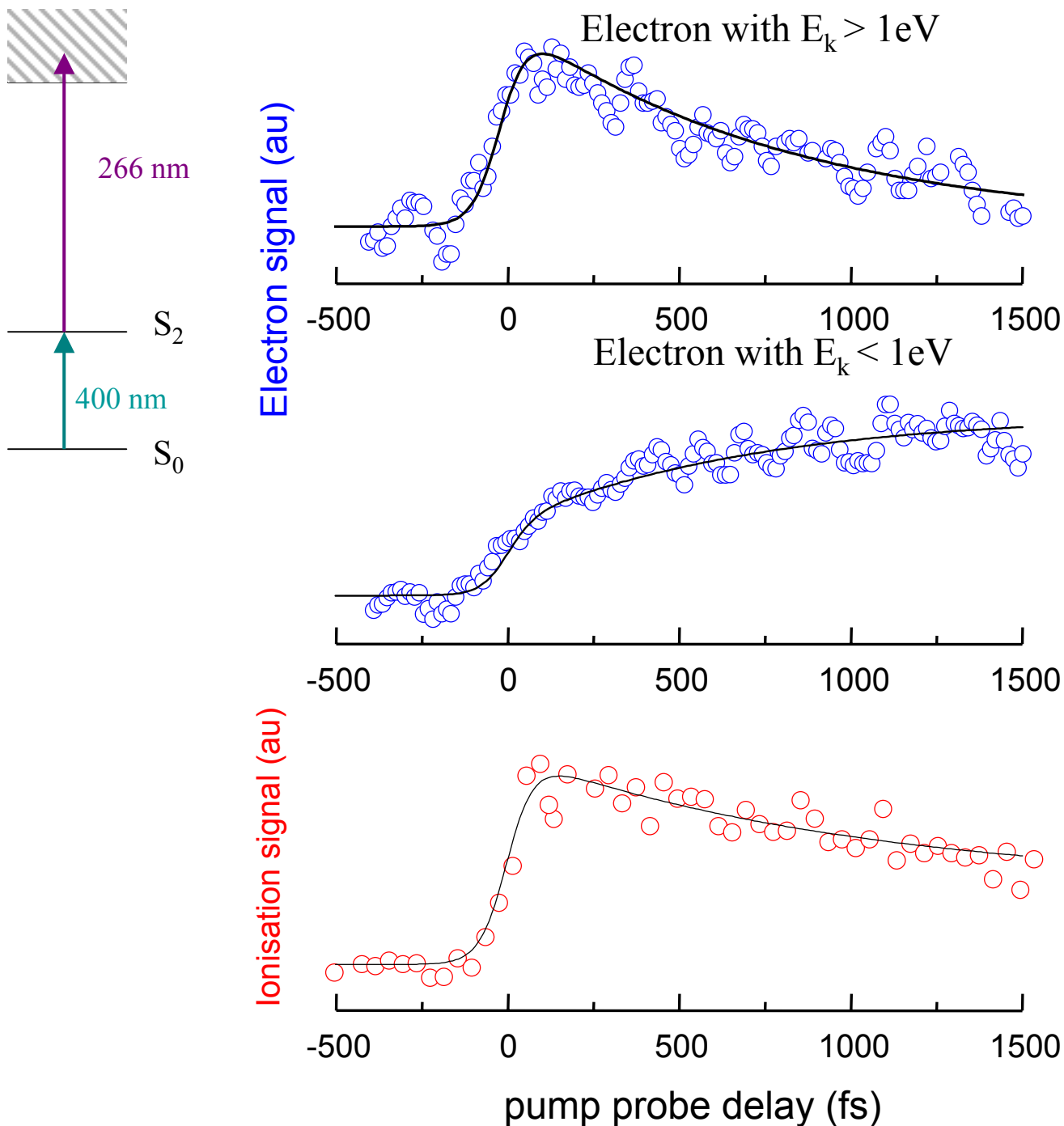


Ru OEP-CO



a.m.u.

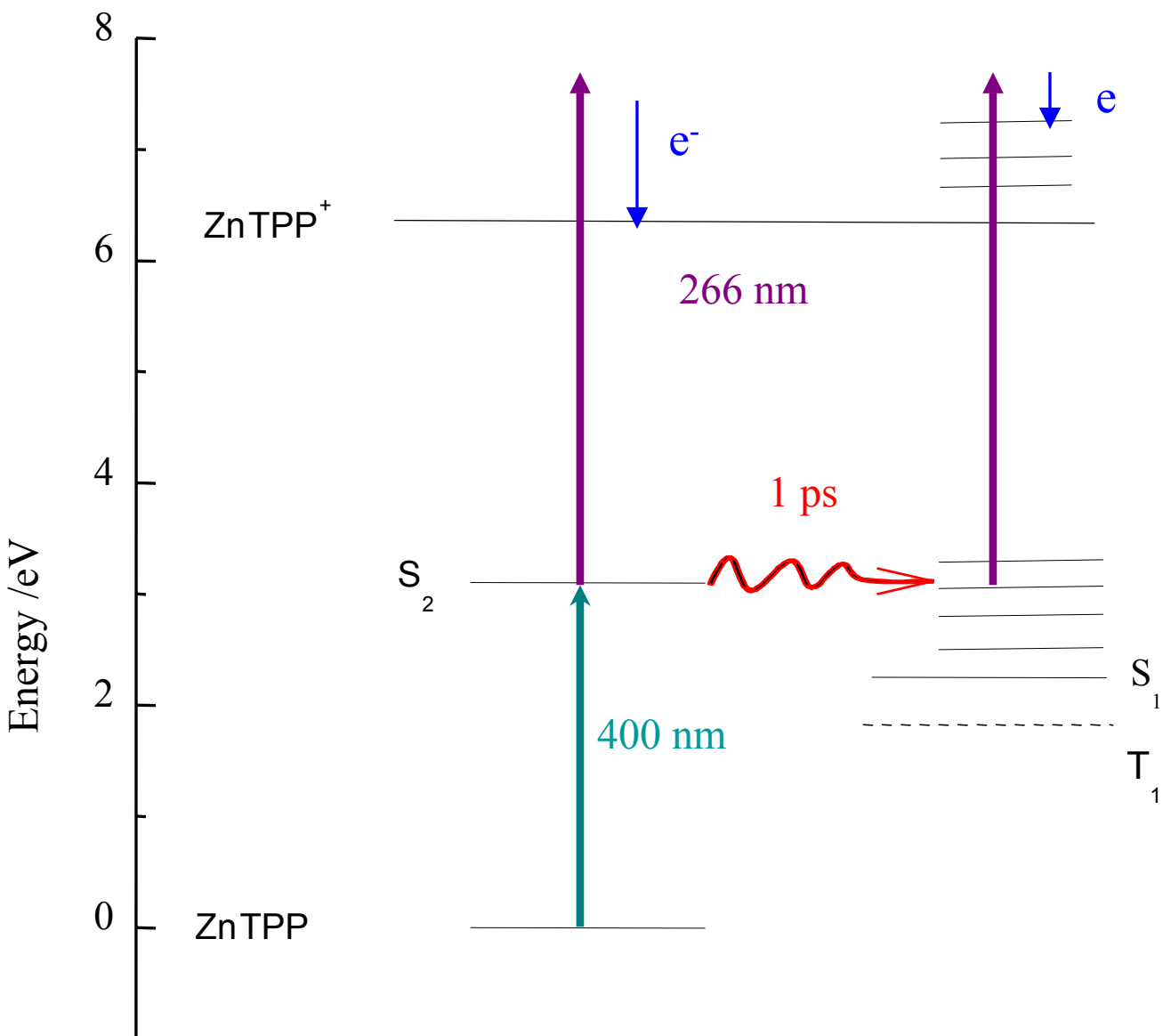
Femtosecond decay of the photo-ion and photo-electron signals of ZnTTP



The experimental points are fitted by 2 exponential decay $\tau_1=1\text{ps}$

$\tau_2=3.3\text{ns}$

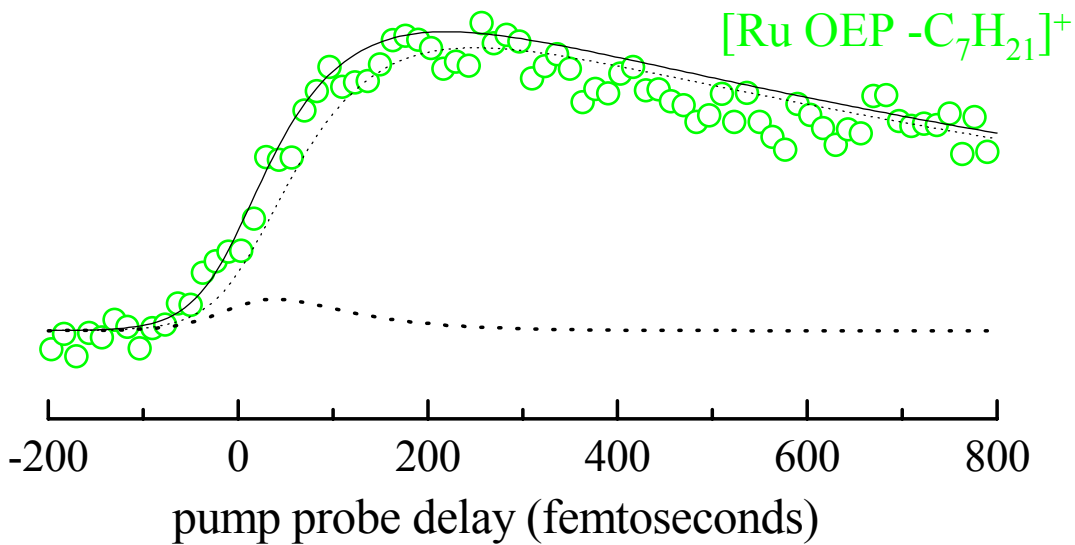
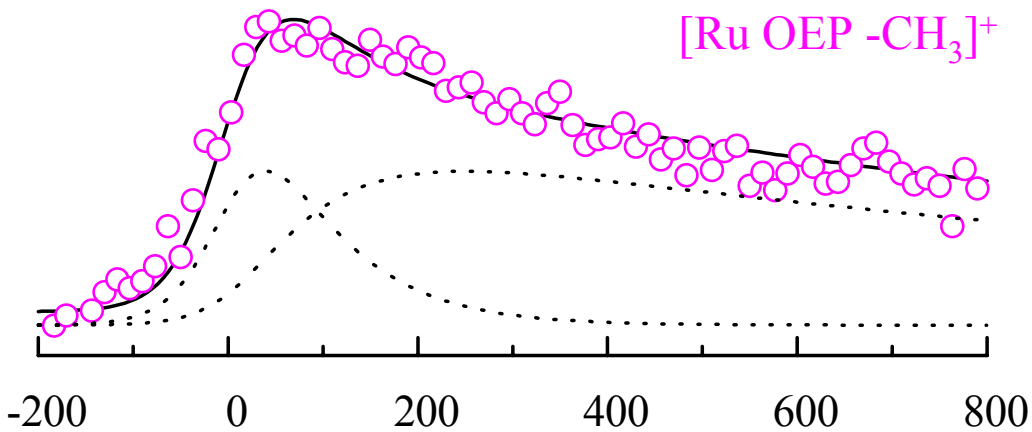
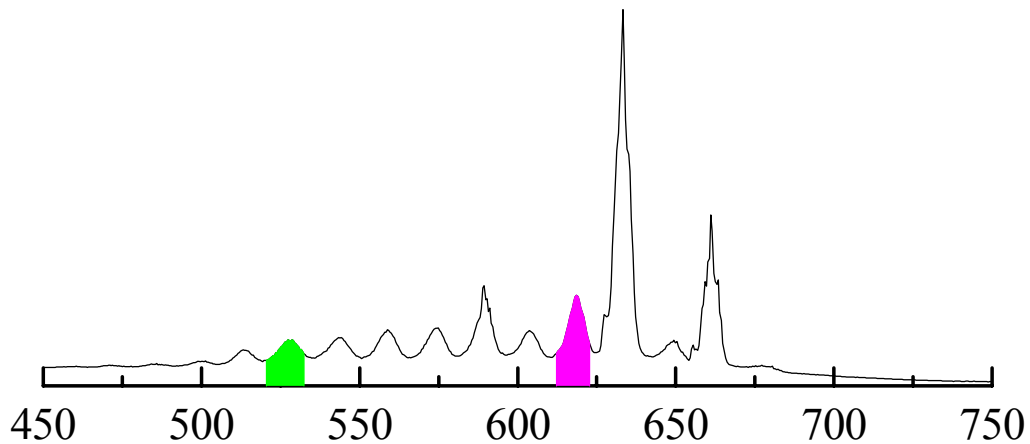
The decay pathway of ZnTPP

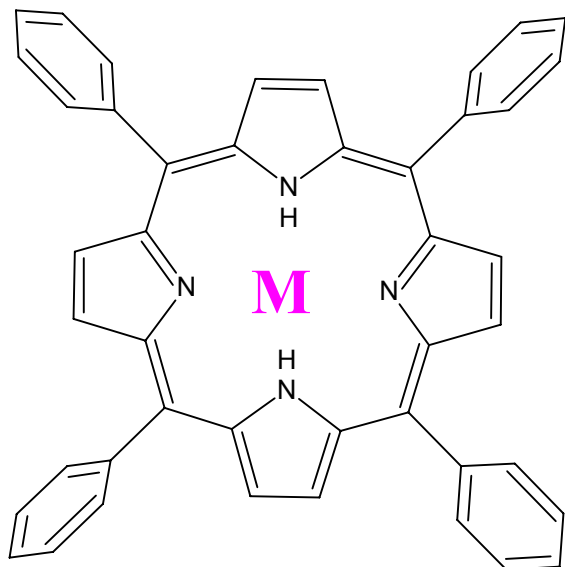


Conclusion

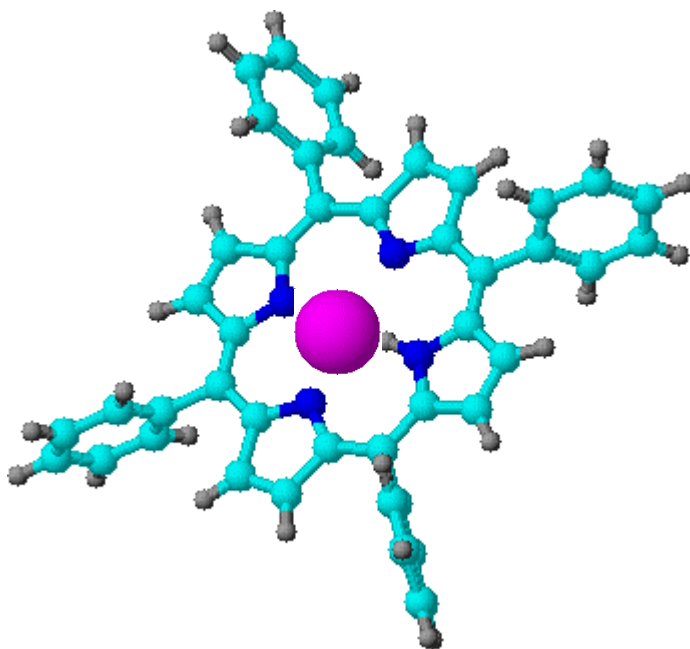
- ★ We have determined- the life time and relaxation pathways of excited states of metalloporphyrins:
- ★ Real time observation of the excited state dissociation of Ru OEP-CO
- ★ Each fragment has a different decay time constant
- ★ We have observed doubly charged metalloporphyrines and their fragments
- ★ The dissociation of Ru OEP-CO yields an electronically excited Ru OEP* which is relatively "long lived " ~ps, certainly not the ground state. A triplet state or a charge transfer state are are likely candidates, or both ...
- ★ Our soft desorption method allows : the vaporisation and cooling in supersonic jet of porphyrins and ligated metalloporphyrins of increasing complexity. We plan to use a variant of MALDI for more fragile systems

Femtosecond decay of the photo-ion signals of Ru OEP-CO at 400+800nm





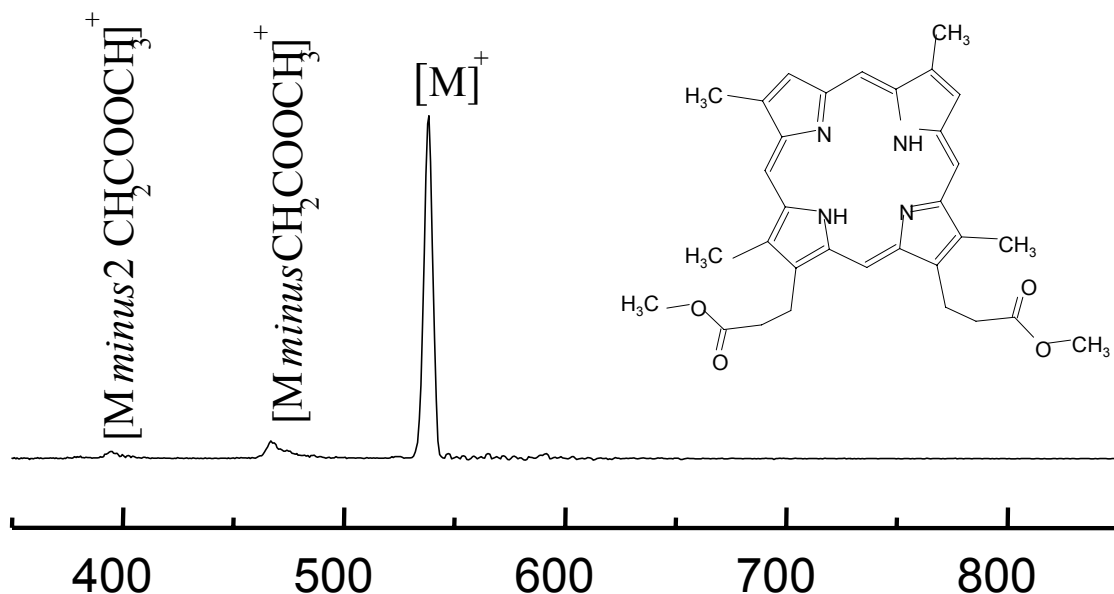
Tetraphenyl Porphyrin (TPP)



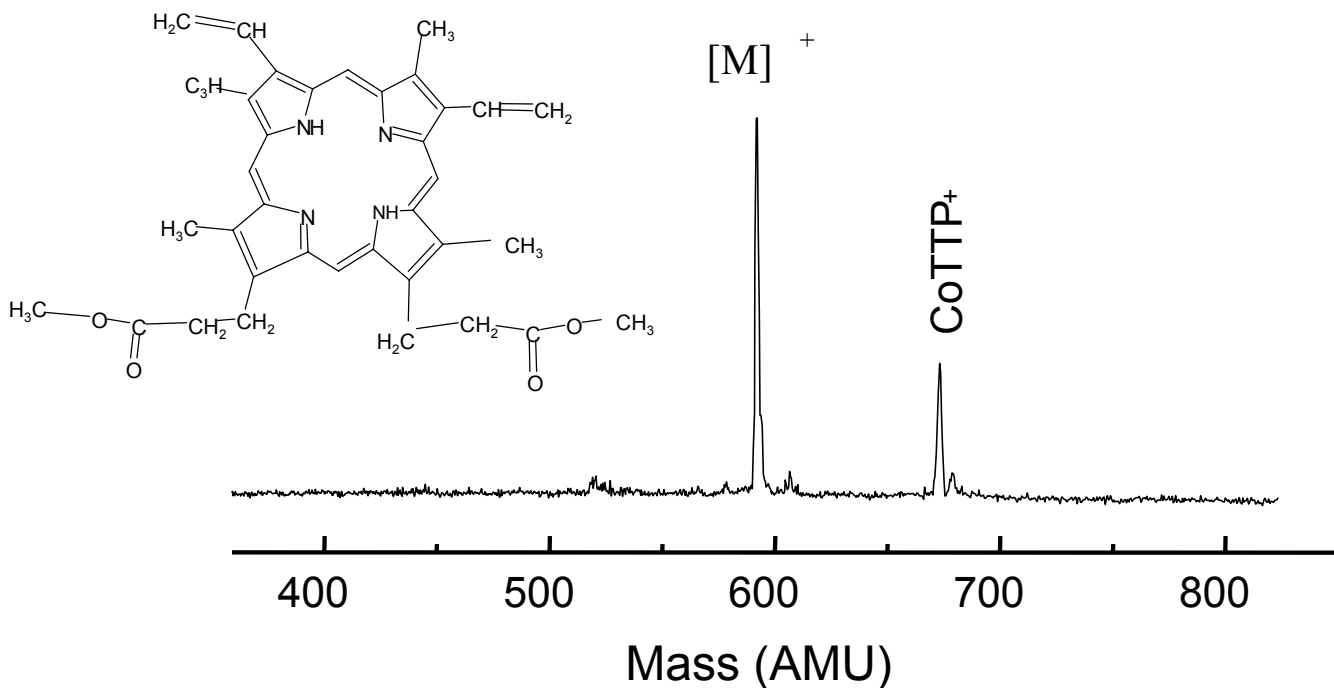
Nanosecond resonant ionisation

532 nm + 266 nm

Deuteroporphyrin IX dimethyl ester

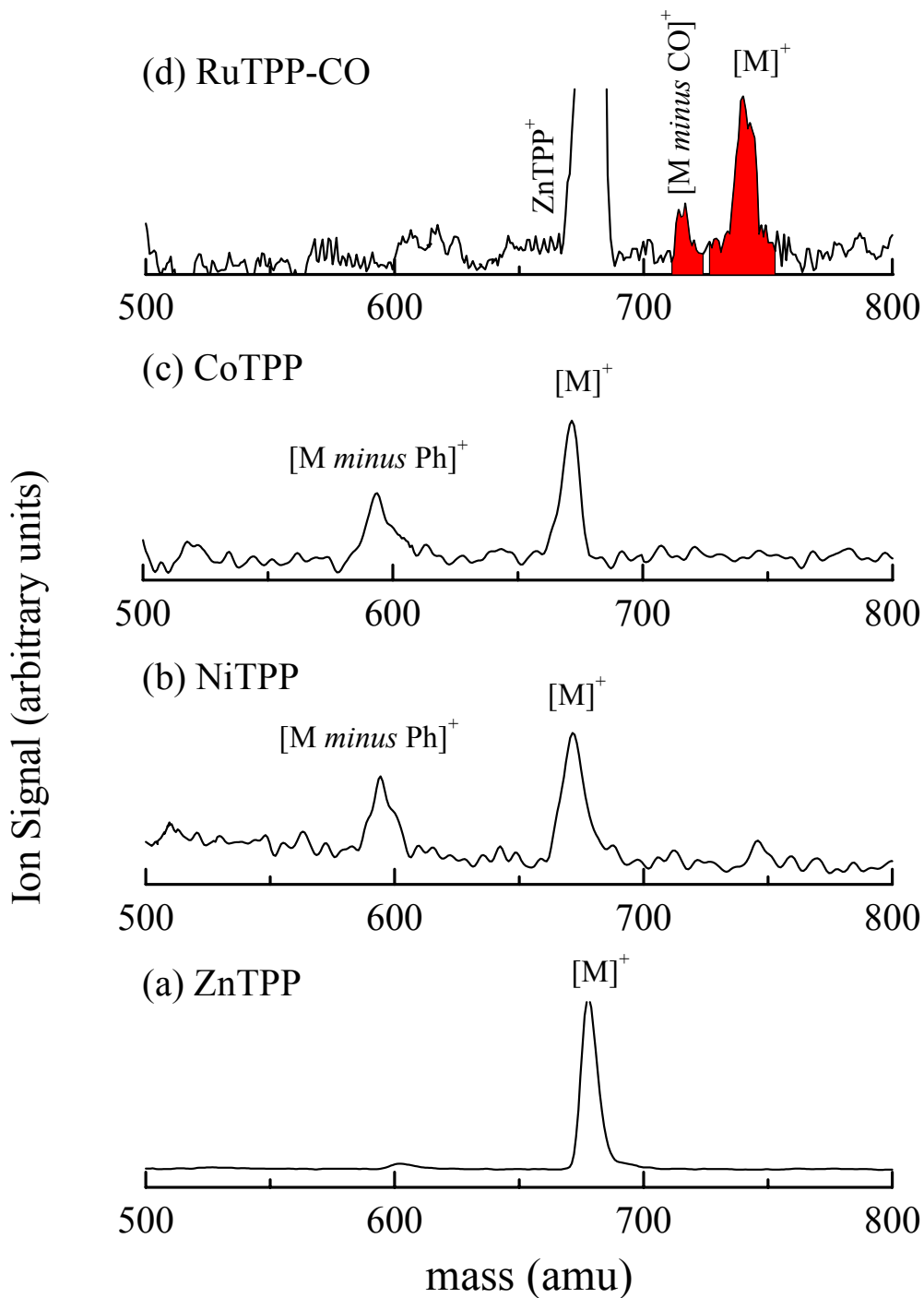


Protoporphyrin IX dimethyl ester

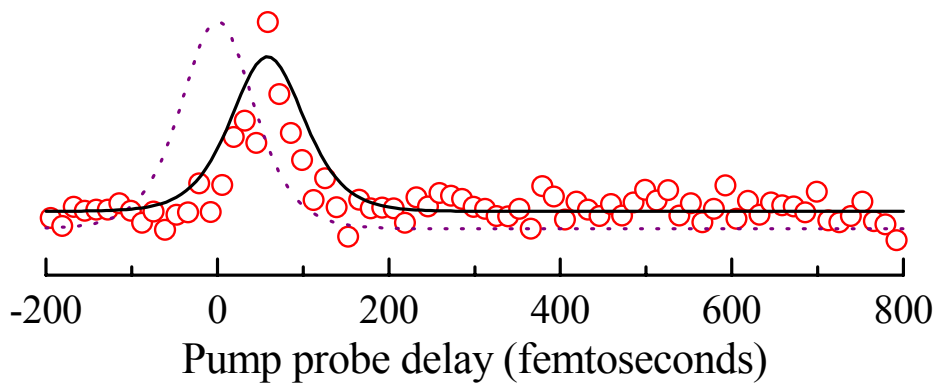
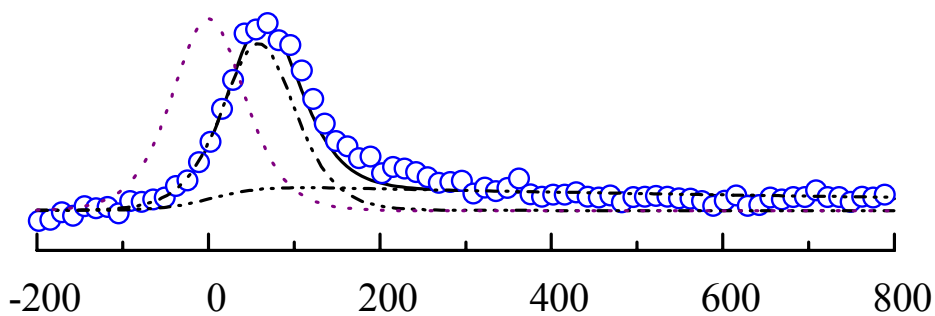
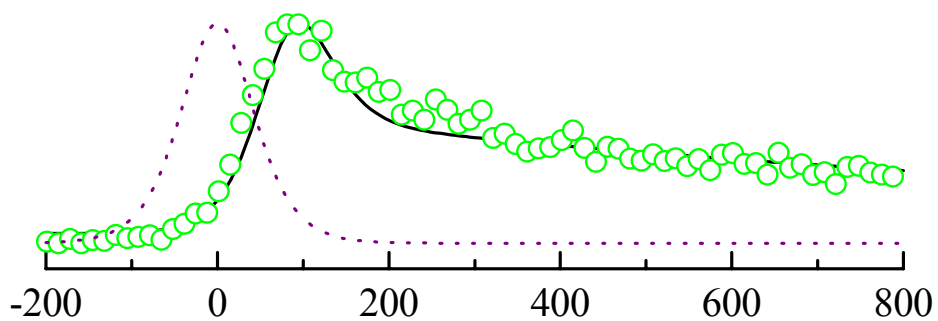
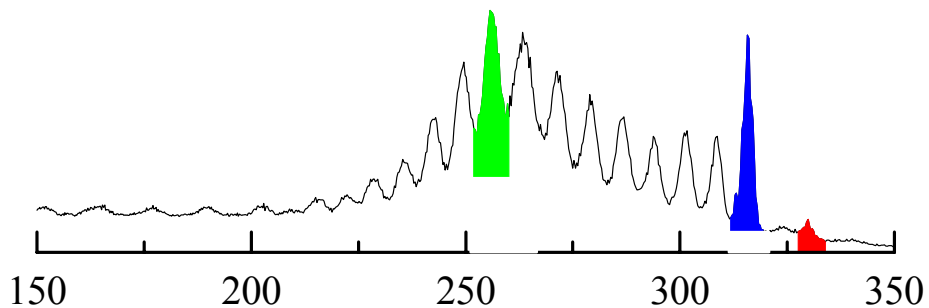


Nanosecond resonant ionisation

532 nm + 266 nm



Femtosecond decay of doubly charged Ru OEP CO at 400+800nm



The decay of the photo-ion signal of RuTPP-CO

