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Investigation of ligand electronic effects on iron cyclopentadienyl complexes using photoelectron spectroscopy

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Introduction

➤ This project aims to study the electronic effects of several $\text{Fe}(\text{CO})_3\text{L}^1$ complexes, because the ligands bound to the metal center are able to orientate the reactivity of the complex through their steric and electronic effects^[2]. This was achieved using a gas phase approach based on photoelectron spectroscopy performed on the DESIRS^[3] beamline of the SOLEIL synchrotron. The rationalization of the electronic effects of the ligand can then be obtained from the analysis of the ionization energies and the Fe-CO dissociation energies selected.

Experiment

➤ Ionisation of the gas-phase complexes using synchrotron radiation.

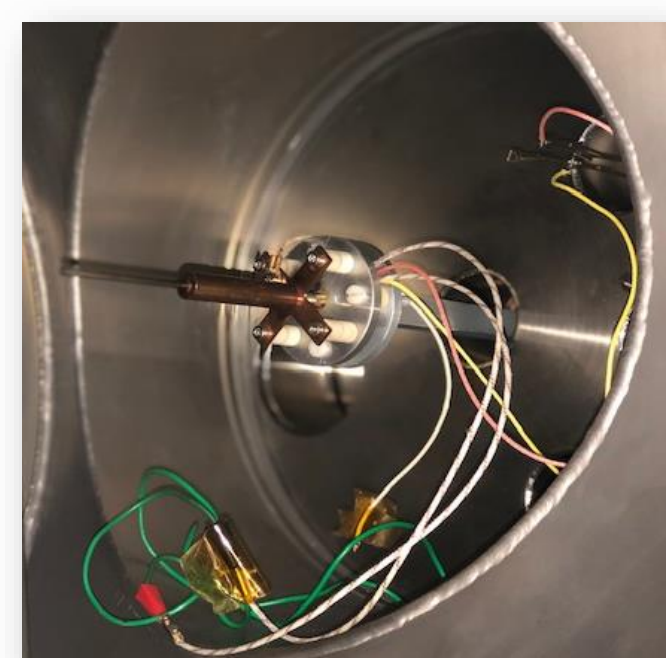


Figure 2a. Thermodesorption of aerosols.



Figure 2b. Home made oven installed in the jet chamber.

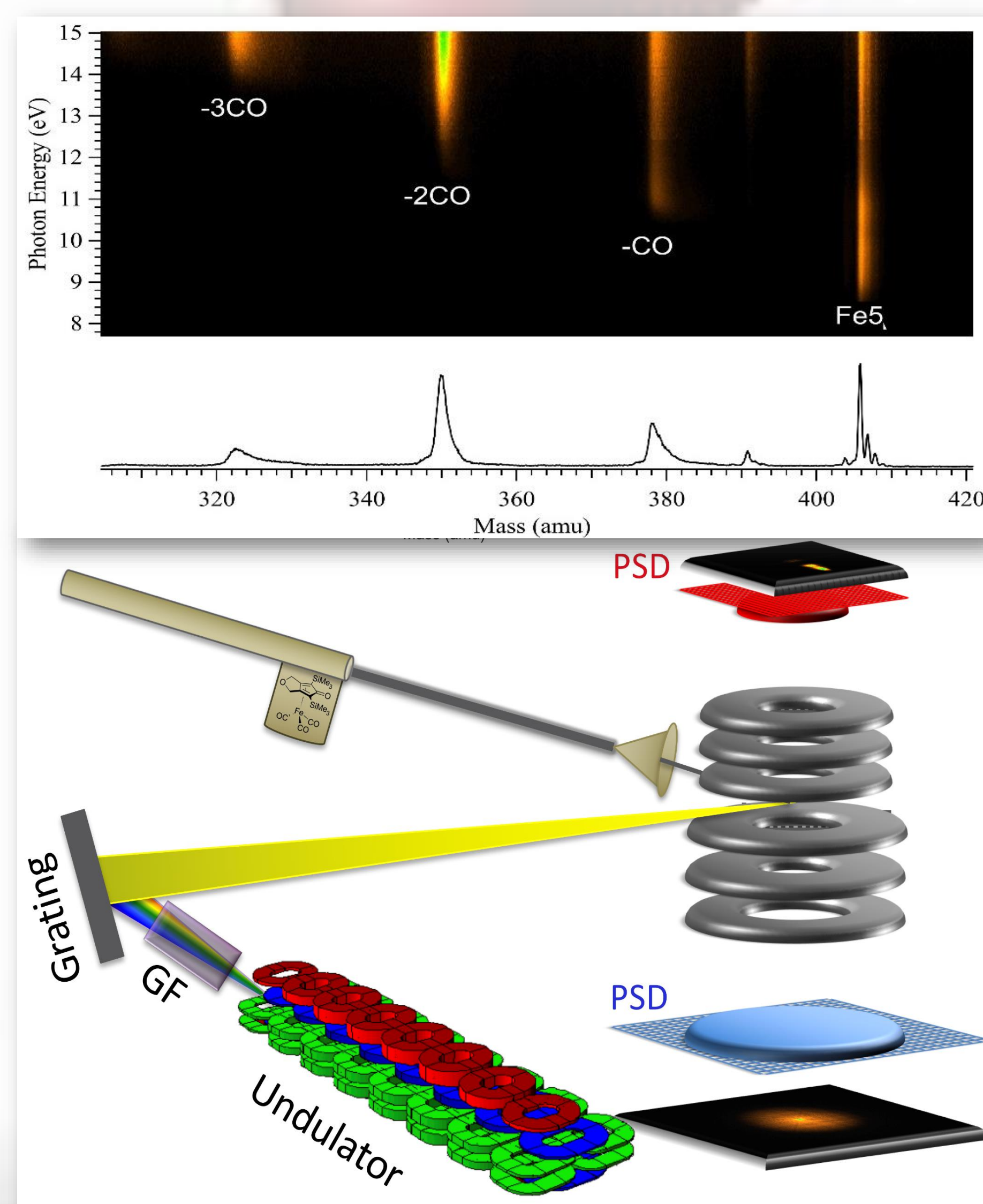


Figure 3. Experimental device showing the coupling of the DESIRS beamline to the i2PEPICO spectrometer DELICIOUS III.

Theory

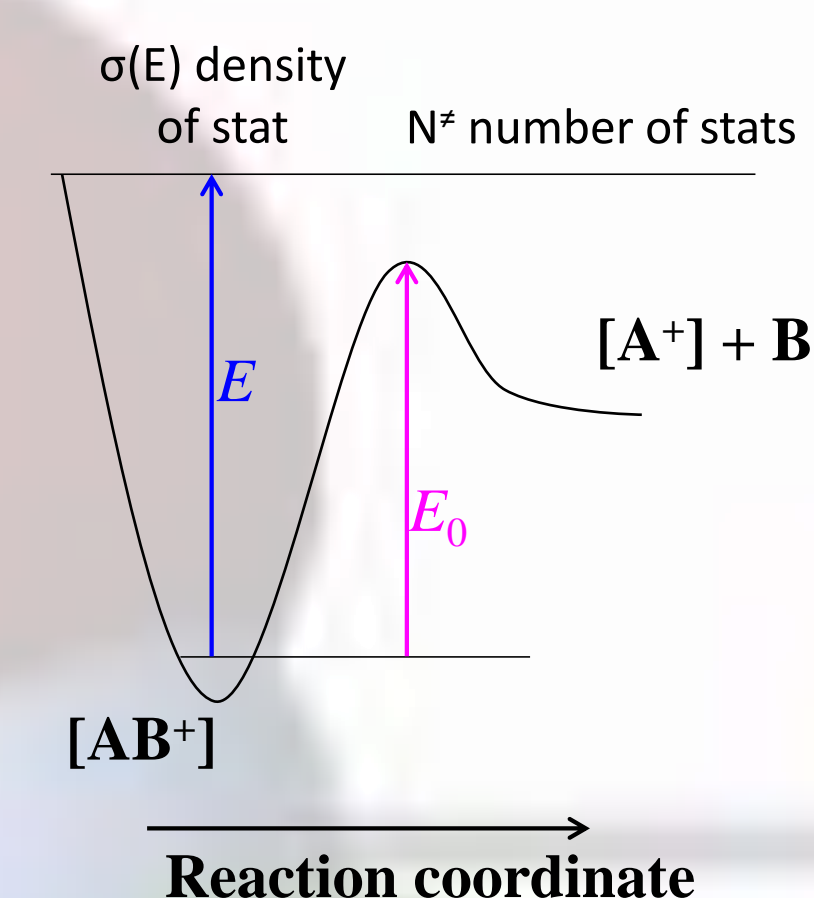
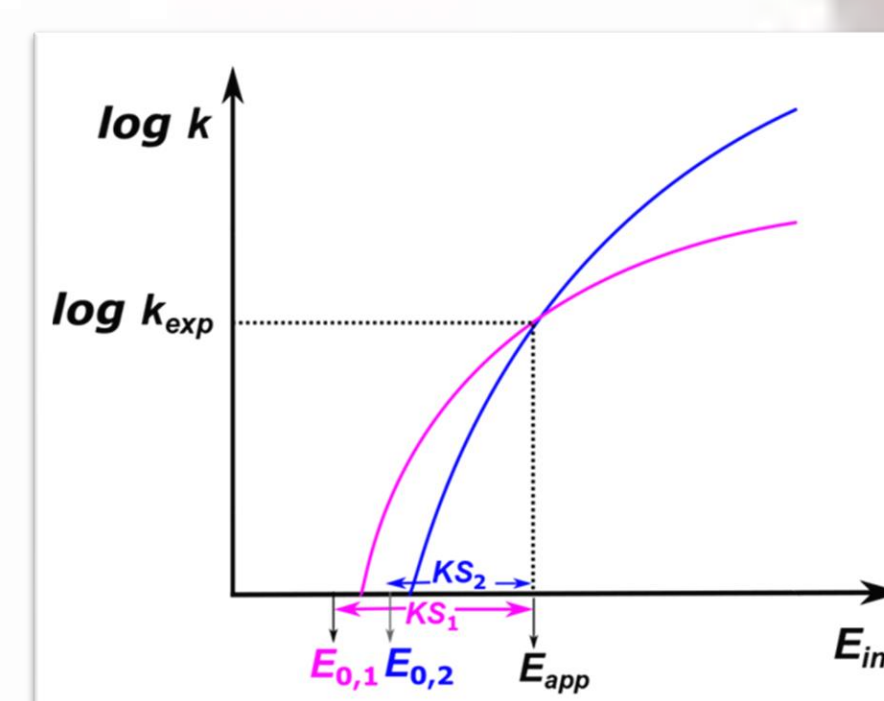
- Electronic structure calculations : PBE0/Def2-TZVP using the GAUSSIAN 09 software.
- Ionisation energy were computed with the IP-tuned LC- ω PBEh functional with the same basis set.^[4]
- Fe-L bond description : decomposition (EDA) scheme coupled to Natural Orbital for Chemical Valence (NOCV) analysis at the BP86/TZ2P(ZORA)^[5] level of theory using the ADF software.

Kinetic Modeling

➤ RRKM statistical model using *MassKinetics* software^[6]

$$k(E) = \frac{\sigma N^\ddagger (E - E_0)}{h\rho(E)}$$

E = internal energy E_0 = critical energy



➤ Kinetic Shift (KS)^[7]

- $\text{KS} = E_{\text{app}} - E_0$
- Depends on Size, Time, E_0 & ΔS

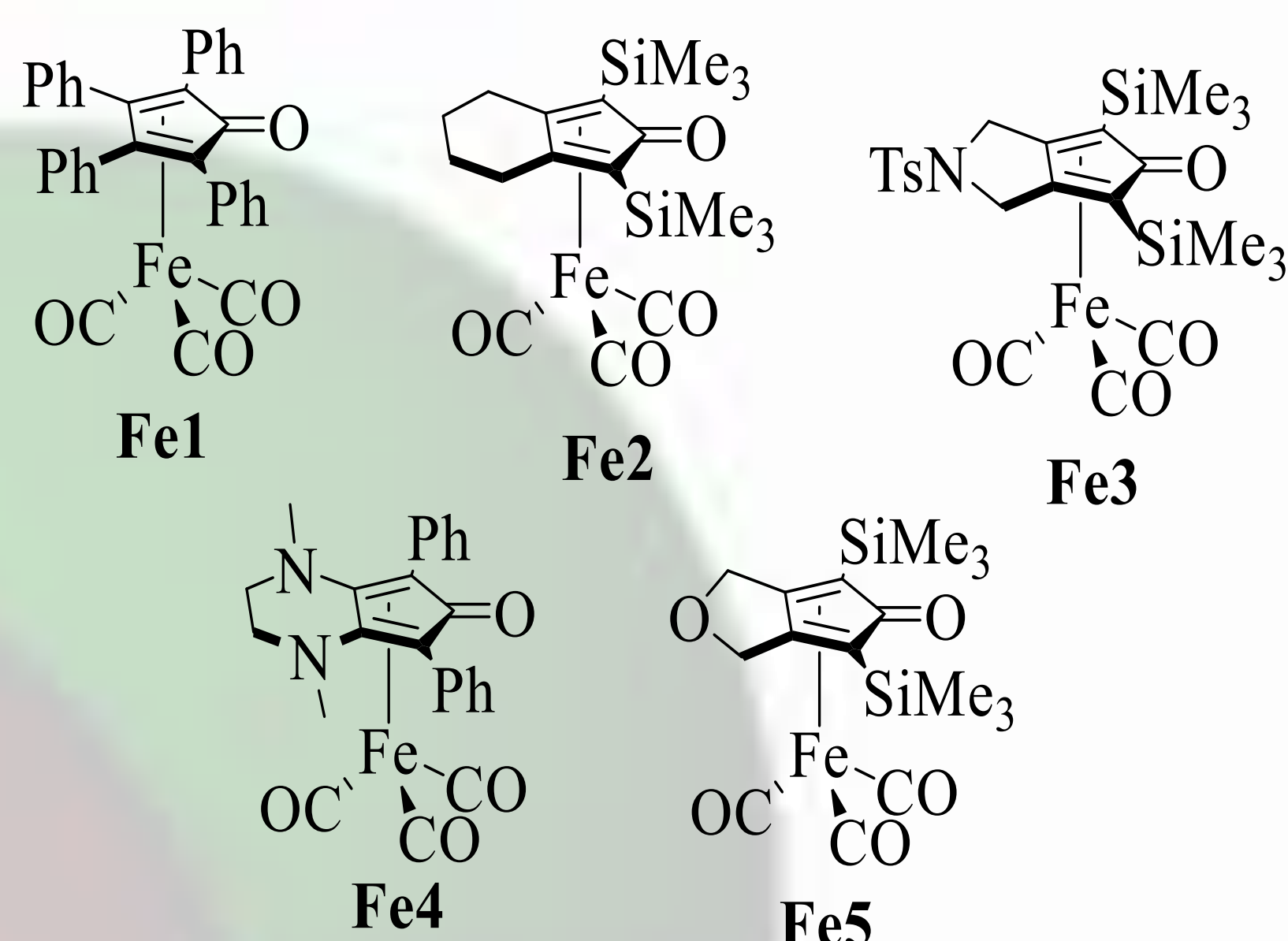


Figure 1. Structure of the synthesised organometallic iron complexes

Conclusion

- Vaporisation of thermally stable or unstable real complexes with low quantities.
- SPES provide access to the electronic structure of the complexes which showed a great agreement with the theory
- The tendency observed in the adiabatic ionisation energy is in correlation with the reaction yields of each catalyst complex.
- The first CO loss of the complexes did not show any selectivity and no trend effect was observed.

References

1. (a) Org. Lett., 2019, 21, 3057-3061. (b) Chemistry—A European Journal, 2013, 19, 17881-17890. 2. (a) Japan Institute of Heterocyclic Chemistry, 1996, vol. 43. (b) John Wiley & Sons, 2017. 3. J Synchrotron Radiat, 2012, 19, 508-520. 4. (a) Inc.: Wallingford, CT, USA, 2013. (b) The Journal of chemical physics, 1996, 105, 9982-9985. (c) The Journal of Chemical Physics, 1994, 100, 5829-5835. 5. Theoretica chimica acta, 1977, 46, 1-10. 6. J. Mass Spectrom., 1996, 31, 445-463. 7. Mass Spectrom. Rev., 1982, 1, 309-348.

Results

➤ Slow PhotoElectron Spectra (SPES)

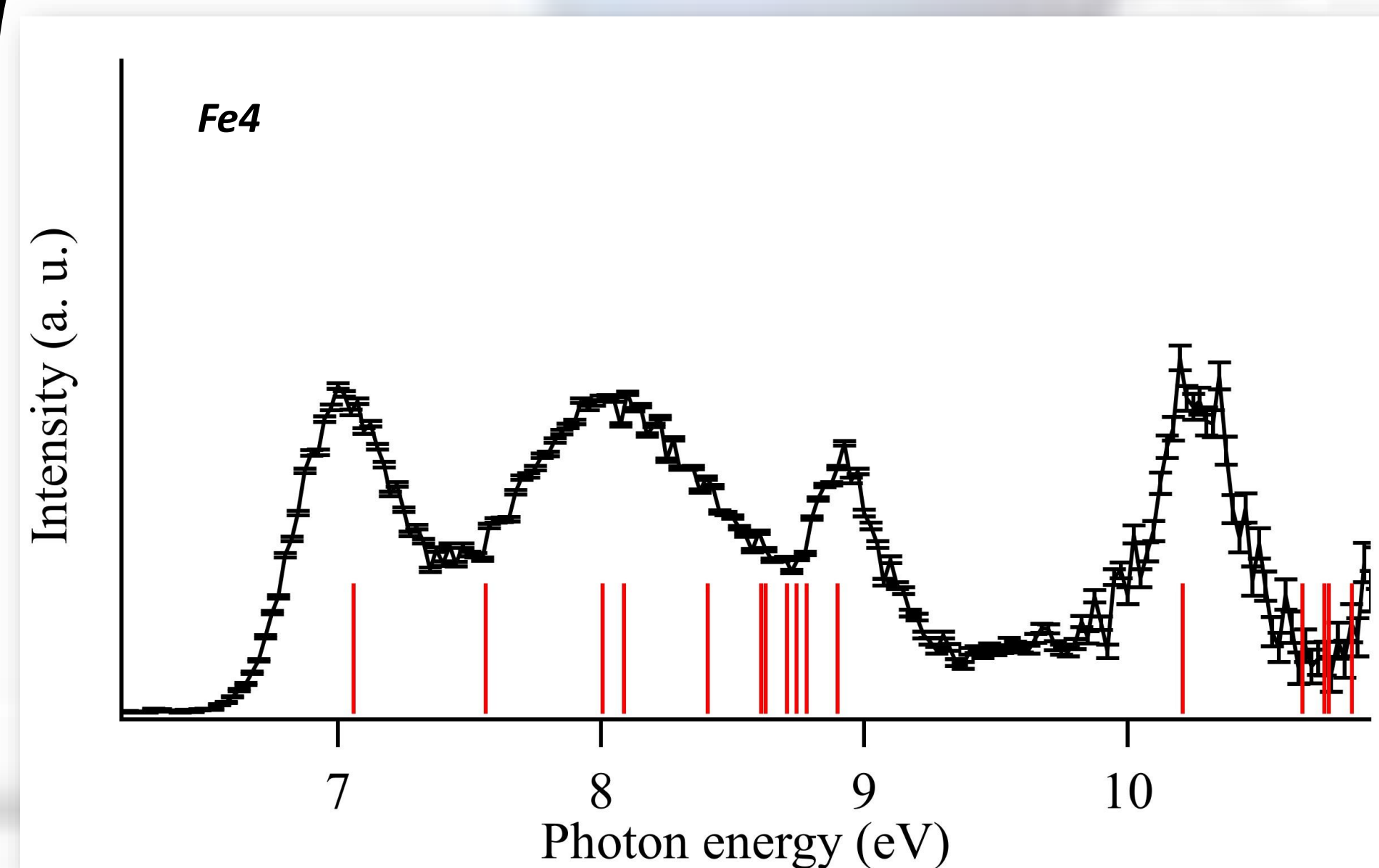


Figure 4. SPES of Fe4. Red sticks represent the calculated ionization energies of the molecular orbitals of the neutral complexes.

➤ Breakdown diagram

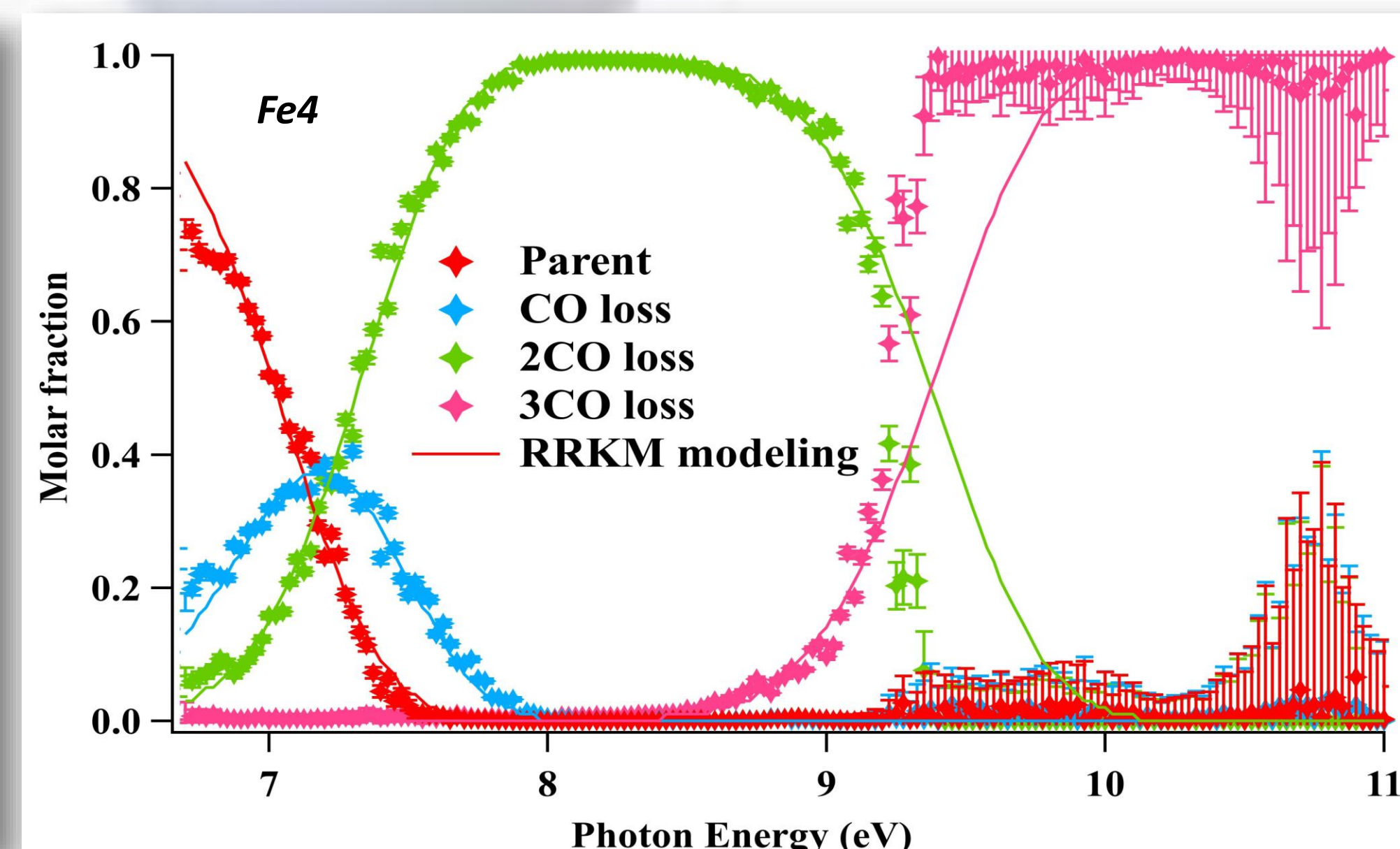


Figure 5. Breakdown diagram of Fe4 recorded in the 7.7 - 15.0 eV energy range and obtained with a 100 meV energy resolution.

Table 1. Experimental and Calculated Adiabatic and Vertical Ionization Energies of the iron Complexes (in eV).

	IE_{ad}		IE_{vert}	
	<i>exp</i>	<i>calc</i>	<i>exp</i>	<i>calc</i>
Fe1	7.20 ± 0.03	7.29	7.68 ± 0.03	7.68
Fe2	7.59	7.59	8.25	7.67
Fe3	7.49	7.57	8.13	7.95
Fe4	6.52	6.59	7.01	7.06
Fe5	7.82	7.65	8.18	7.92

Table 2. Experimental and calculated BDEs of the studied complexes in (eV)

	BDE first CO loss		BDE second CO loss	
	<i>exp</i>	<i>calc</i>	<i>exp</i>	<i>calc</i>
Fe1	0.92 ± 0.10	0.84	1.17 ± 0.11	1.30
Fe2	0.80	0.82	1.14	1.30
Fe3	0.40	0.50	0.83	1.09
Fe4	0.87	0.93	0.90	1.46
Fe5	0.99	0.96	1.24	1.34