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# Investigation of ligand electronic effects on organometallic complexes using photoelectron spectroscopy and mass spectrometry

Lyna Bourehil<sup>1,2</sup>, Denis Lesage<sup>1</sup>, Benoit Bertrand<sup>1</sup>, Yves Gimbert<sup>1,3</sup>, Jean-Luc Renaud<sup>4</sup>, Léo Bettoni<sup>4</sup>, Nicolas Joly<sup>4</sup>, Gustavo A. Garcia<sup>2</sup>, Héroïse Dossmann<sup>1</sup>

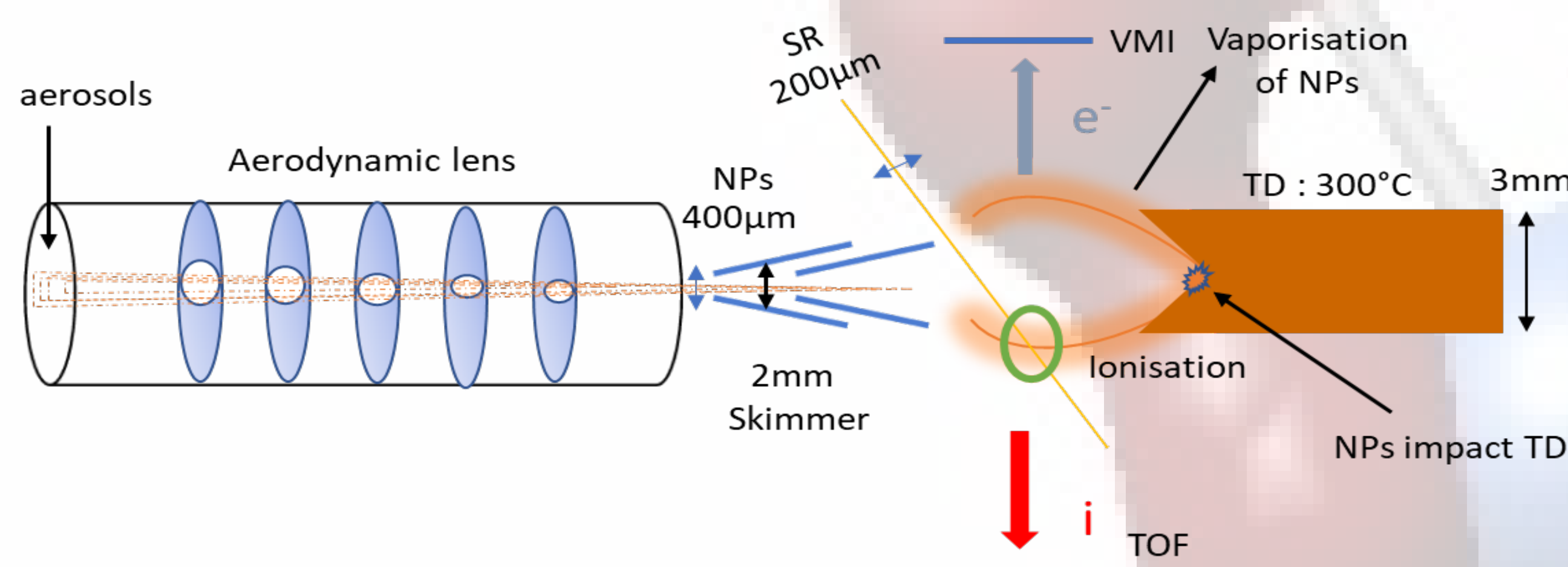
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## Introduction

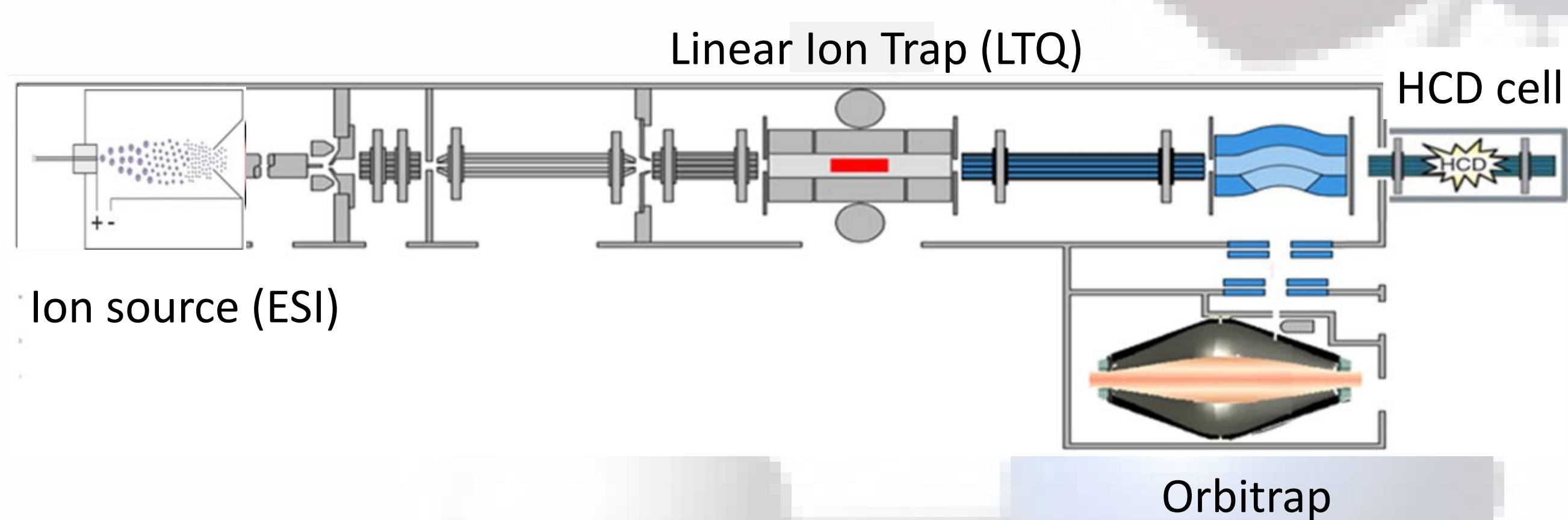
➤ This project aims to study the electronic effects of ligand on several organometallic complexes<sup>[1]</sup>. Ligands bound to the metal center are indeed known to be able to direct the reactivity of the complex through their steric and electronic effects<sup>[2]</sup>. This study was achieved using gas-phase approaches based on mass spectrometry and mass-selected photoelectron spectroscopy performed on the DESIRS<sup>[3]</sup> beamline at the SOLEIL synchrotron facility. The rationalization of the electronic effects of the ligand can then be obtained from the analysis of the ionization energies and the bond dissociation energies selected.

## Experiment

➤ Ionisation and dissociation of the gas-phase complexes using aerosols thermodesorption synchrotron radiation.



➤ Ionisation and dissociation of the gas-phase complexes using mass spectrometer.



## Theory

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

## Kinetic Modeling

- RRKM statistical model using MassKinetics software<sup>[6]</sup>
- Kinetic Shift (KS)<sup>[7]</sup>
  - $KS = AE - E_0$
  - Depends on DOF, Time,  $E_0$  &  $\Delta S$

$$E_0 \text{ (no RRKM)} = AE = 2.81 \text{ eV}$$

$$E_0 \text{ (RRKM)} = 0.99 \text{ eV}$$

$$\text{BDE (calculated)} = 0.96 \text{ eV}$$

$$KS = 1.82 \text{ eV}$$

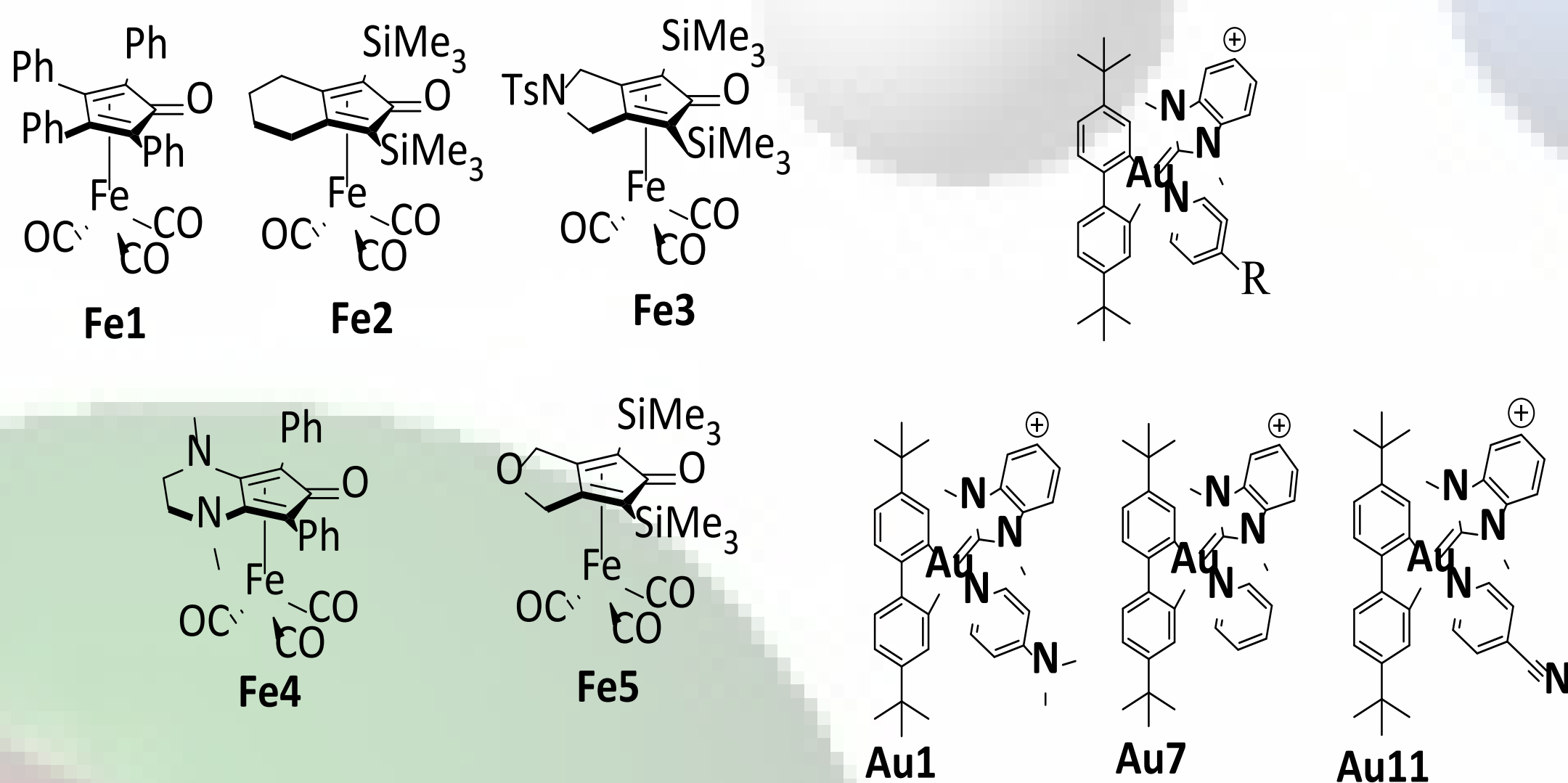
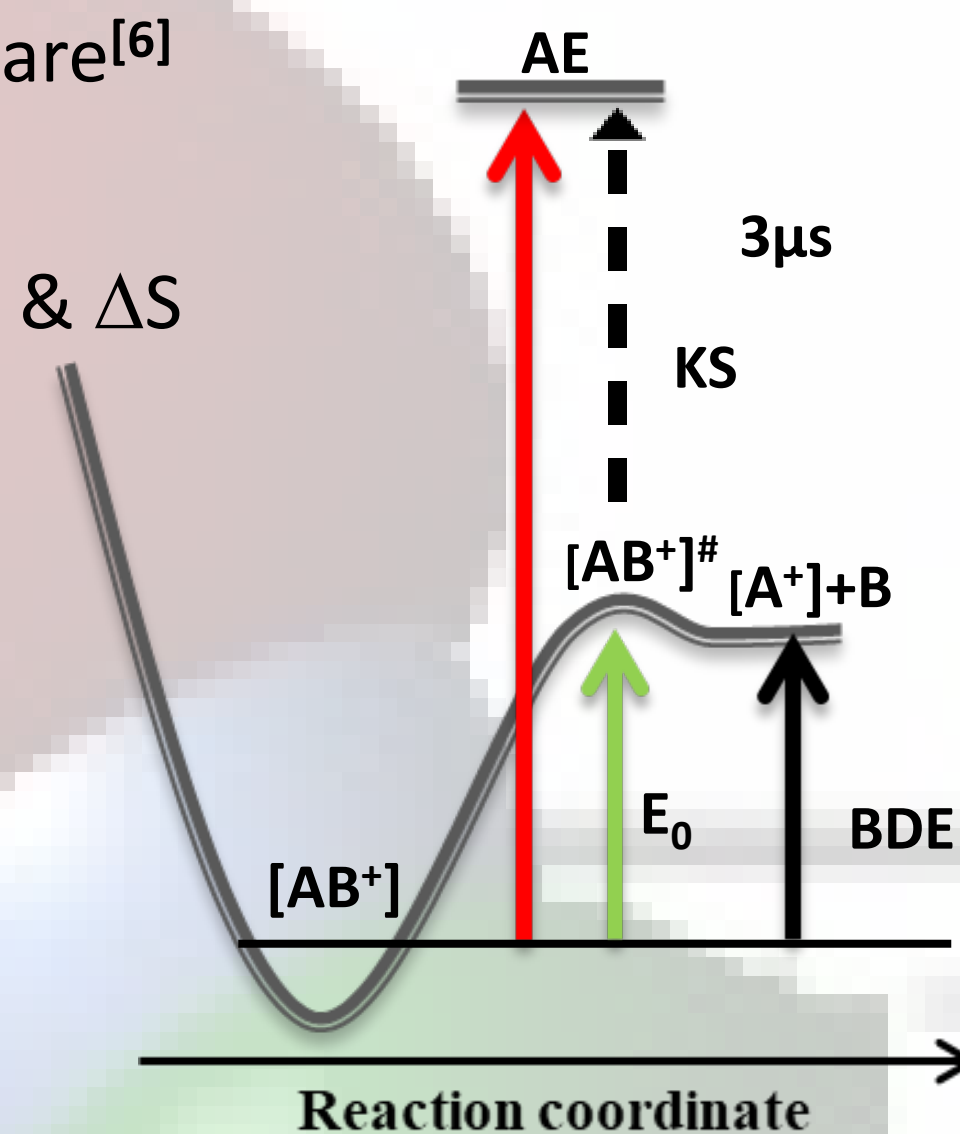


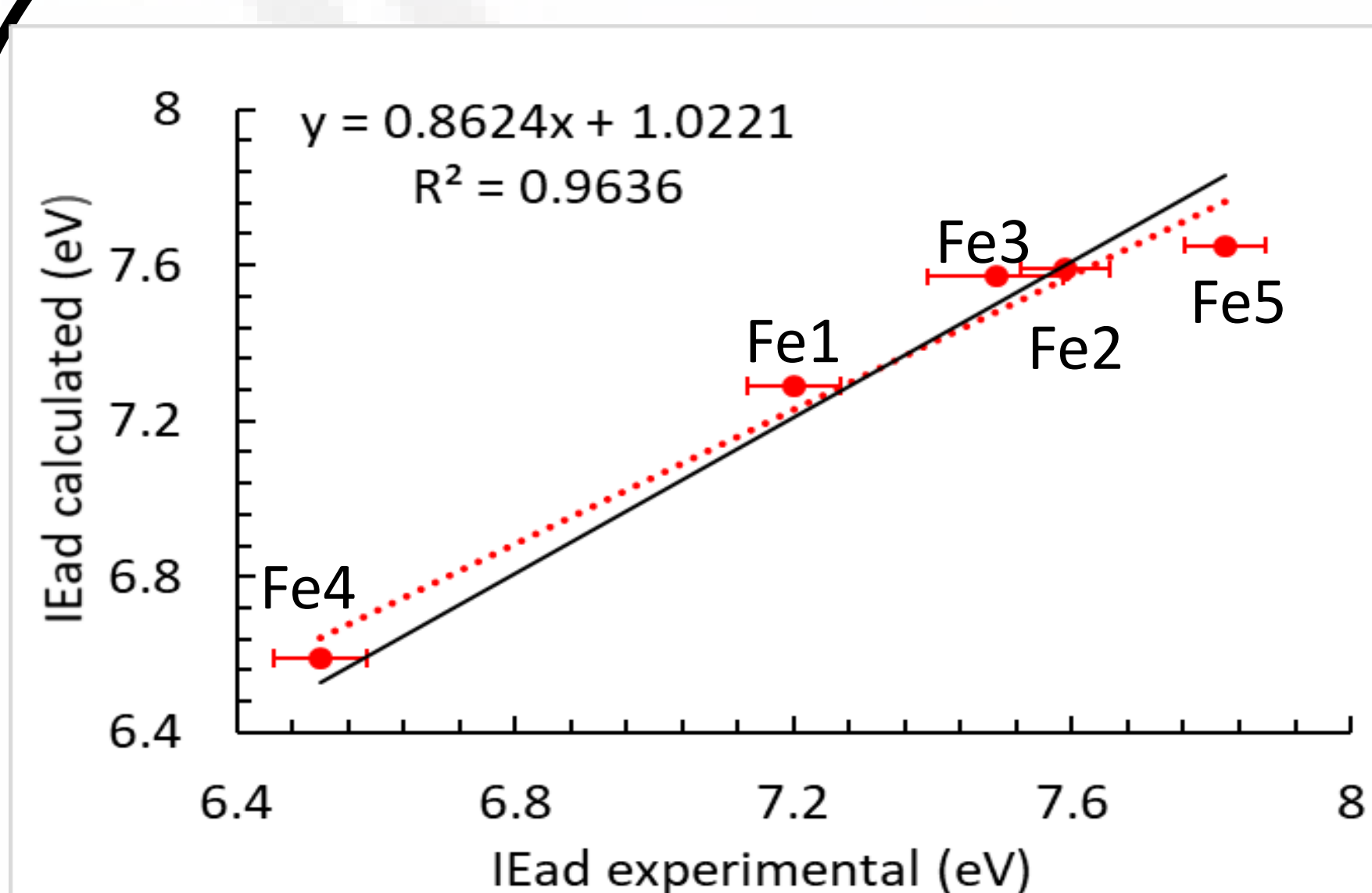
Figure 1. Structure of the studied organometallic complexes \*R varying

## Conclusion

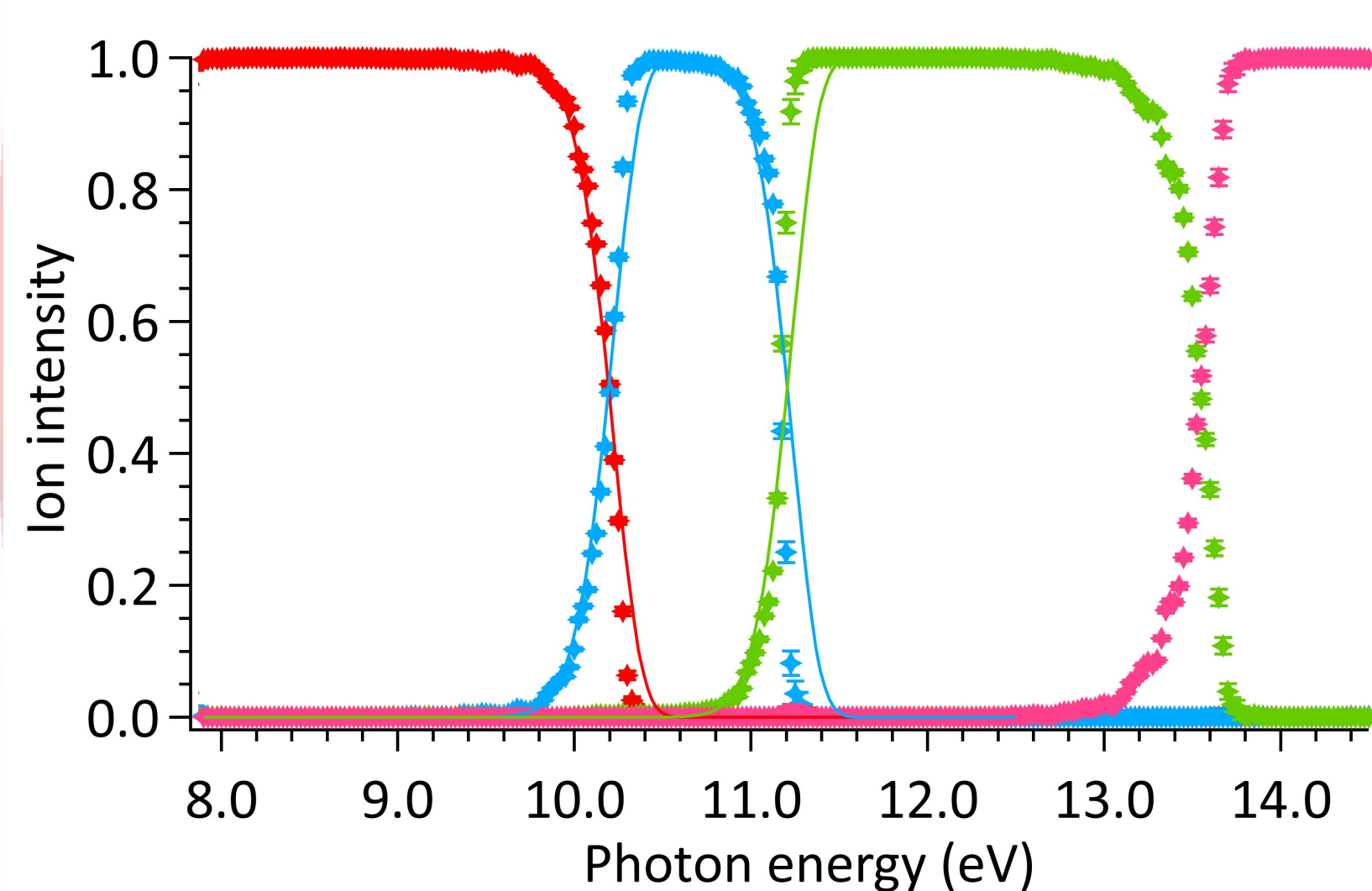
- Organometallic complexes that are thermally unstable can be vaporised using aerosol thermodesorption with very low quantities.
- SPES provide access to the electronic structure of the complexes which showed a good agreement with theory, considering the complexity of the system.
- The adiabatic ionisation energy of the Fe4 is noticeably lower than the other complexes, while its catalytic effect is highest.
- The first CO loss from the cationic complexes do not show any correlation with the measured yields in catalytic reactions.
- Electron-donor pyridines form stronger Au-pyridines bond.
- Good correlation between experimental dissociation energies and pKas

## Results

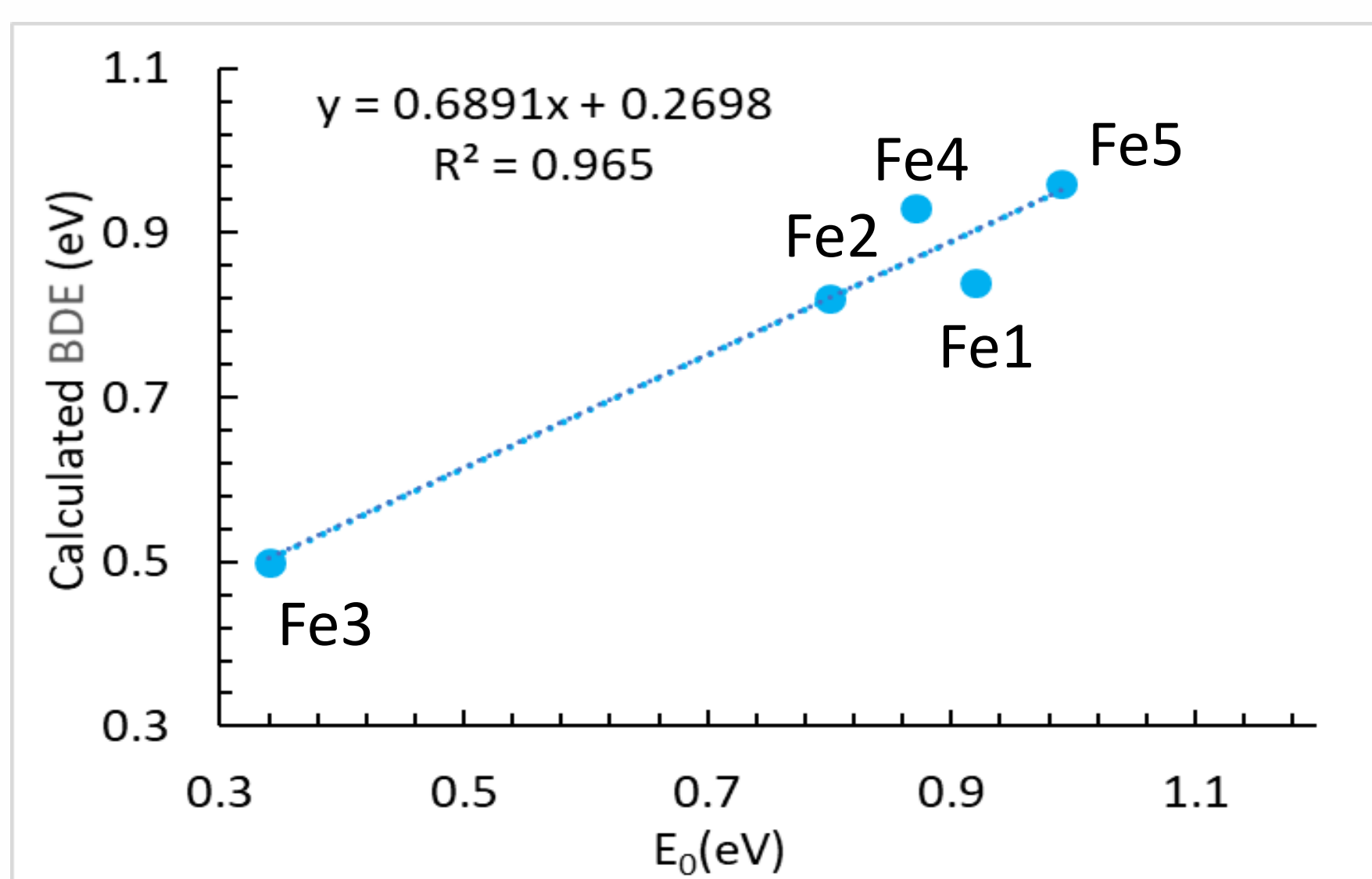
### Fe(II) complexes



Experimental and calculated adiabatic ionisation energy values of the studied complexes.

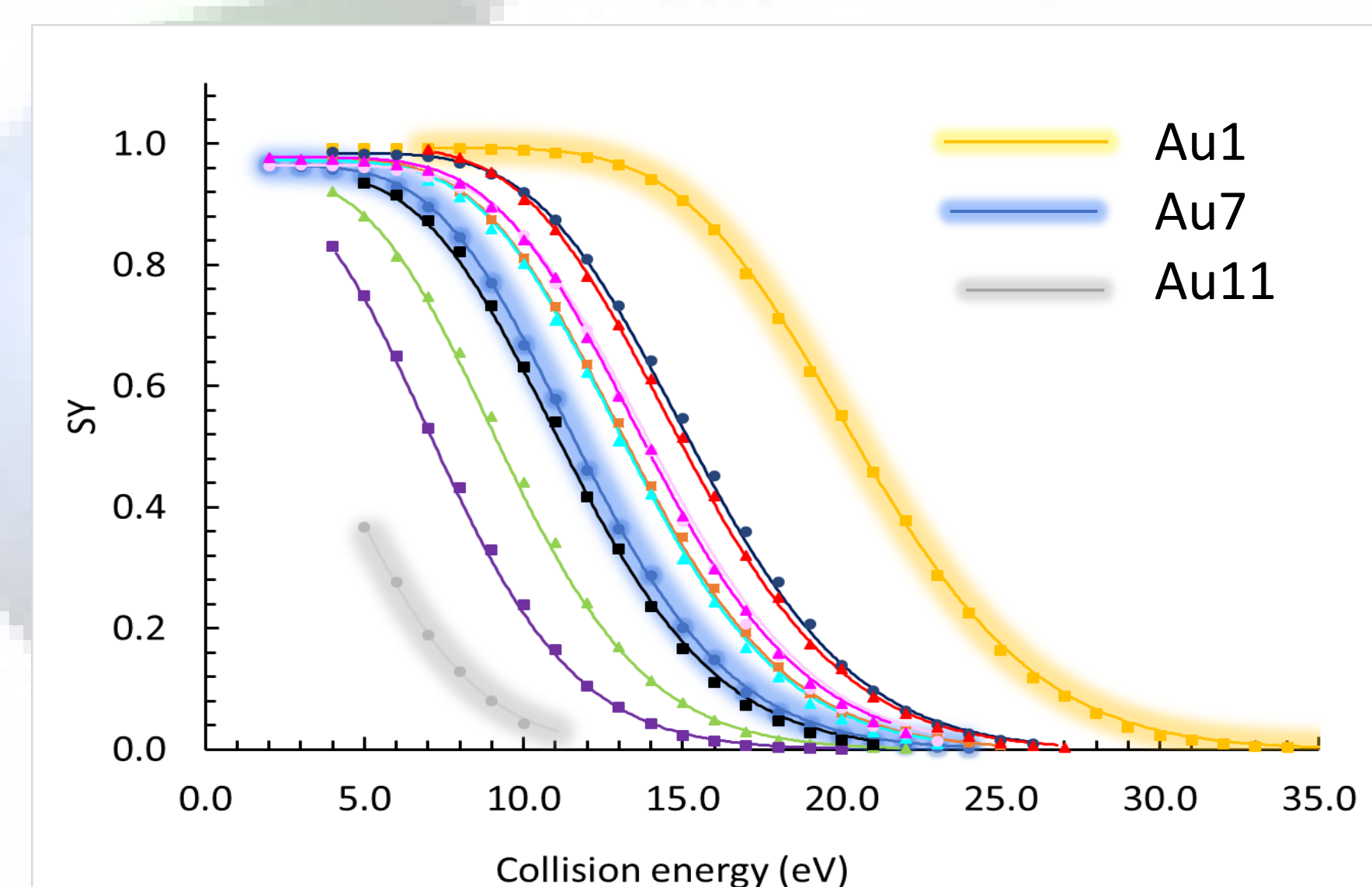


Breakdown diagram of Fe5 recorded in the 8.0 - 14.0 eV energy range with 100 meV energy resolution.

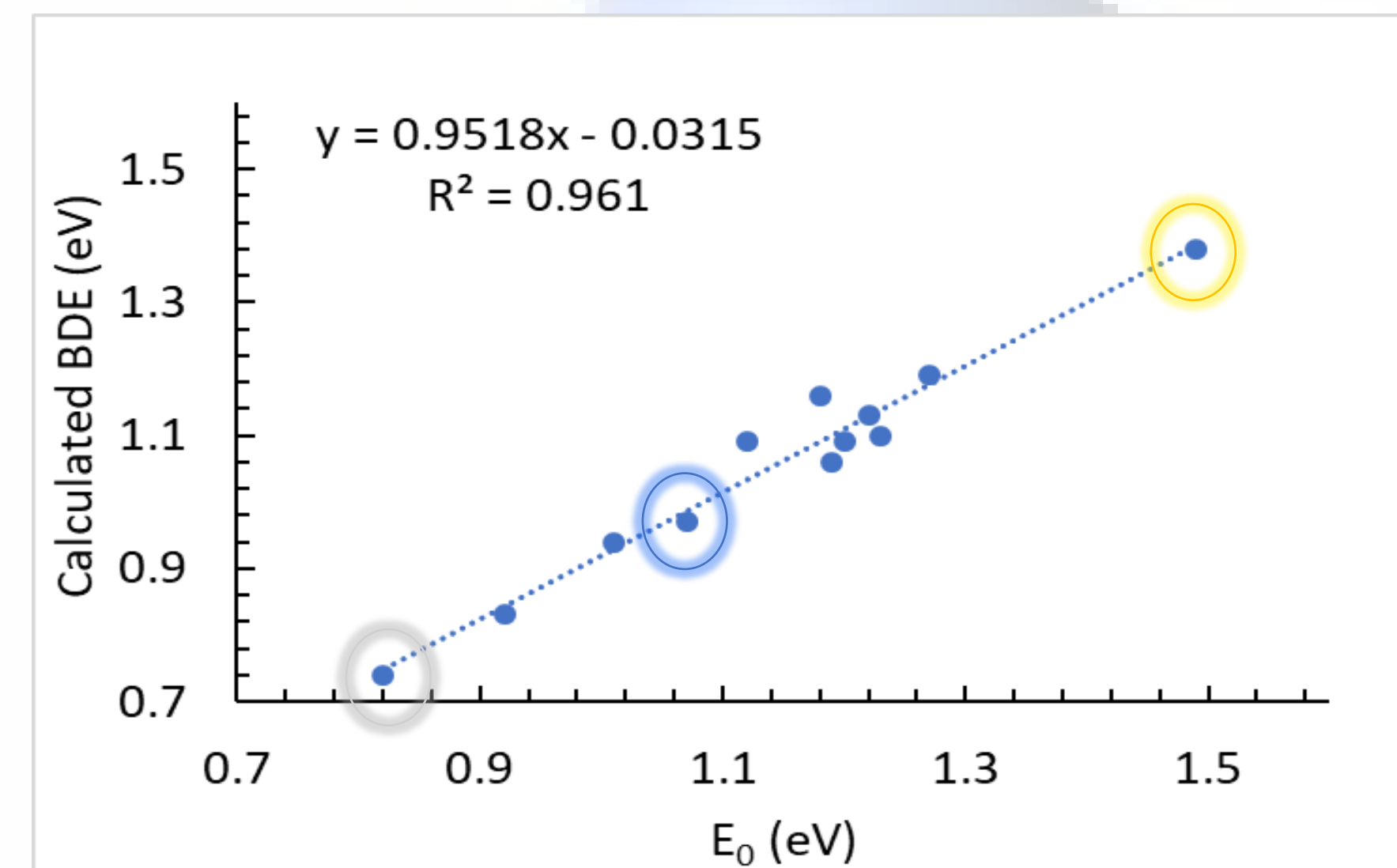


Experimental and calculated bond dissociation energies of the first CO loss fragment of the studied complexes.

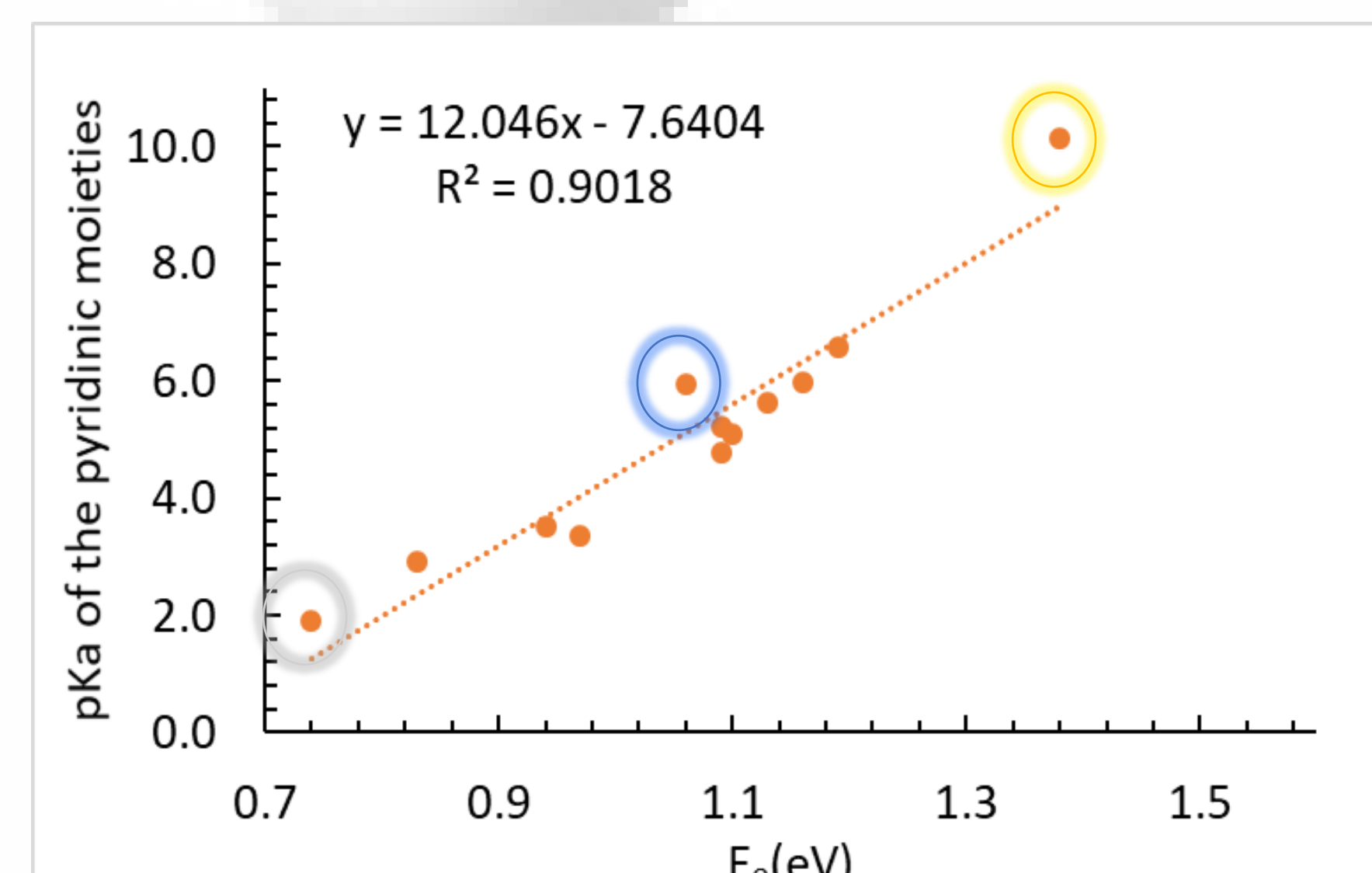
### Au(III) complexes



Parent ion intensity normalised as a function of photon energy for each studied complex.



Experimental and calculated bond dissociation energies of the studied complexes.



pKa of the pyridins as a function of the experimental bond dissociation energies of the studied complexes.

## References

- (a) Org. Lett., 2019, 21, 3057-3061. (b) Eur. J. Chem., 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) Chem. Phys., 1996, 105, 9982-9985. (c) Chem. Phys., 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.