

LOCKING AND UNLOCKING THE SPIN CROSSOVER TRANSITION IN Fe(II)
COMPLEXES

by

Xin Zhang

A DISSERTATION

Presented to the Faculty of
The Graduate College at the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Doctor of Philosophy

Major: Physics and Astronomy

Under the Supervision of Professor Peter A. Dowben

Lincoln, Nebraska

July, 2016

ProQuest Number: 10151397

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 10151397

Published by ProQuest LLC (2016). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 - 1346

LOCKING AND UNLOCKING THE SPIN CROSSOVER TRANSITION IN FE(II) COMPLEXES

Xin Zhang, Ph.D.

University of Nebraska, 2016

Adviser: Peter A. Dowben

Spin crossover (SCO) molecules form a significant class of materials for which the magnetic structure can be altered at the atomic level by an external stimulus from low a spin diamagnetic state to paramagnetic high spin state. We find, however, that the transition is quite complex and the SCO molecular transition can be mediated by interactions at the substrate interface.

We have investigated the occupied and unoccupied electronic structure of thin films of the SCO $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ complex. The thermally induced spin crossover transition for molecules deposited on the organic ferroelectric copolymer PVDF-TrFE is suppressed. The choice of high spin or low state favored, over a wide of temperature, is seemingly influenced by the ferroelectric polarization direction of ferroelectric PVDF-TrFE substrate. We have also found that the molecule was locked in the low spin state also when deposited on a SiO_2/Si substrate, but can be excited to high spin state by X-ray irradiation in a temperature range from 15 K to 345 K. The locking of the spin state implies there is an activation barrier to the spin crossover transition, which is confirmed by time dependent X-ray absorption spectroscopy. The X-ray induced spin crossover transition is likely due to the surface charge that builds up at the interface during the X-ray photoemission process.

The isothermal spin state switching at room temperature, has been observed in SCO thin films grown on both magnetic NiCo_2O_4 and $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ thin film

substrate surfaces. The X-ray excited high spin state then can be isothermally relaxed back into low spin state by oscillating the direction of substrate magnetic moment. All of these effects point to a strong influence, by the interface, on the spin state changes on SCO molecules.

The mixture of SCO and dipolar zwitterion molecule is found suppressed in low spin state but can be excited into high spin state with X-ray radiation from 79 K to 340 K, leading to a possible new chemical path about spin states manipulation at the single molecule scale, and providing an exciting possibility for single molecule devices.

Acknowledgements

Before anything, I would like to express my very deep gratitude to my advisor, Professor Peter Dowben for his trust, guidance and unlimited support throughout my graduate program. I am truly thankful for the opportunity that he gave to work as a team member in his group. Without his help, this work would not have been possible. During those years in Lincoln, I am always supported and encouraged by him in both aspect of academic and life. I sincerely appreciate him for his help, patience, generous, kindness, and humor. I will never forget our uncountable coffee time, and summer soda time. I will keep all the funny T-shirts, the mug, and my “business card” as a memory of the precious time in lovely Lincoln.

I also would like to thank Professor Axel Enders, Professor Christian Binek, Professor Evgeny Tsymbal, and Professor Li Tan for serving as my supervisory committee. I am grateful to them for their careful and critical reading of this dissertation.

This work may not be remembered in the human being’s knowledge about the mysterious great nature, but I really appreciate the efforts made by all my collaborators. I am very thankful to Professor Bernard Doudin and Professor Jean-François Létard, Professor Patrick Rosa, Professor Takashi Komesu, Professor Luis Rosa, Dr. Sai Mu, Professor Axel Enders and Prof. Xiaoshan Xu. Their insightful guidance and kind help during my doctoral studies, as well as for collaborating with me on my thesis work. And I am very thankful to the scientists who work at Advanced Light Source at Lawrence Berkeley National Laboratory Dr. Alpha N'Diaye, Dr. Elke Arenholz and Dr. Padraic Shafer, who had mentored me when I was at their beamlines with an ALS fellowship. From Dr. Jing Liu. I have learned many valuable experience. Without their help, my synchrotron experiments would not have been able to be completed so smoothly.

My early mentors, Dr. Ning Wu and Dr. Zhengzheng Zhang, really taught me a lot and let me could start the research. Thank the machine shop and electronic shop for providing a really strong support for my projects. I also would like to thank my colleagues and peers, Dr. Ihor Ketsman, Dr. Juan Colon-Santana, Dr. Keisuke Fukutani, Dr. Lingmei Kong, Shi Cao, Iori Tanabe, Elena-Maria Echeverria, Yang Liu, Xuanyuan Jiang, Xiaozhe Zhang, Dr. Yuewei Yin, Dr. Xuegang Chen, George Peterson, Thomas Scott, Sumit Beniwal, and Paulo Costa who gave me a lot of help each in their own way, facilitating my experiments. Thanks to Professor Osman Bakr, Dr. Khabiboulakh Katsiev, Professor Hae Kyung Jeong, Dr. Tony Kelly, and Dr. David Turner, the collaboration with their groups with many different projects makes my research experience more rich and diversified. At last but not the least, I would like to thank my wife Yonghua Feng. Her love motivated me forward always. Her support and understanding during the whole doctoral studies was so important to keep me in peace. I am also very grateful to my parents and parents-in-law for their great support.

At the end, GO BIG RED! GO HUKERS!

Table of Contents

Chapter 1	Introduction.....	1
1.1	Spin crossover molecule and phenomenon.....	1
1.2	The advantages and challenges of spin crossover molecule.....	5
	References	9
Chapter2	Methods and techniques.....	13
2.1	Photoemission spectroscopy	14
2.1.1	Principle of photoemission spectroscopy.....	14
2.1.2	X-ray photoemission spectroscopy	19
2.1.3	Ultraviolet photoemission spectroscopy	21
2.2	Measuring the unoccupied bands.....	22
2.2.1	Inverse photoemission spectroscopy (IPES).....	23
2.2.2	X-ray absorption spectroscopy (XAS).....	24
2.3	Superconducting quantum interference devices (SQUID)	29
2.4	Molecule synthesis	29
	References	30
Chapter 3	The electronic structure of a spin crossover molecular adsorbate.....	32
3.1	Introduction.....	32
3.2	Experimental details of film preparation and characterization	34
3.3	The molecular orbital and molecular band offsets.....	39

3.4	Local charge occupation	43
3.5	Changes in the unoccupied electronic structure	46
3.6	Summary	49
	References	51
Chapter 4	Complexities of the molecular spin crossover transition.....	55
4.1	Introduction.....	56
4.2	Methods.....	59
4.3	Assignment of the unoccupied molecular orbitals	62
4.4	Concordance of the electronic and magnetic states?	66
4.5	More information for the calculated electronic structure	76
4.6	Summary	83
	References	84
Chapter 5	Local voltage controlled spin crossover	89
5.1	Introduction.....	89
5.2	Experimental: preparation of the poled P(VDF-TrFE 70:30).....	91
5.3	Spin state switch evidenced in unoccupied electronic structure	93
5.4	Spin state switch associated with magnetic property change	97
5.5	Summary	101
	References	103

Chapter 6	Room temperature switching of an Fe(II) spin crossover complex thin film.....	107
6.1	Introduction.....	107
6.2	Some additional experimental details	108
6.3	Reversible SCO transition around room temperature range	108
6.4	Toward room temperature isothermal switching	115
6.5	Summary	122
	References	123
Chapter 7	Future	125
	References	131
Publications	132

CHAPTER 1

INTRODUCTION

The goal here is to give the reader a general understanding of the topic of this thesis. The emphases of this thesis is characterization and spin state control of a variety of Fe(II) spin crossover molecules but the lessons learned may apply to other spin crossover molecules, with different metal center atoms. Aside from fundamental interests, there may be grand applications to be considered.

1.1 Spin crossover molecule and phenomenon

After the long success of the famous Moore's law in describing the fast development silicon based electronic components, for decades, the physical limitations from quantum effects are approaching. Alternative materials and new concepts are needed if basic device fabrication needs become significantly smaller, faster and cheaper. One possible direction is the organic electronics based on a single or "few" molecules in an assembly. Can this be combined with spintronics to add one more degree of freedom for the molecular electronics devices? There are still many challenges need to be addressed before large scale¹ organic spintronics is worthy of serious consideration but there is the promise a cheaper, lighter, and printable devices through molecular assemblies.²⁻⁴ The spin-orbit coupling is small in organic molecules, due to the typically light atoms used in composition, but new physical insights are needed before organic devices, such as organic spin valves,^{5,6} spin-injection,^{7,8} tunneling junctions⁹ (and so on) can be reliably realized, with operation at room temperature. Among all kinds of organic

molecules available, the prime candidates are the coordination complex or metal complex.

In nature, there are a vast classes of coordination complexes for which the magnetic structure can be altered at the atomic level by an external stimulus. These are spin-crossover (SCO) molecules which have bistable spin states: low spin (LS) and high spin (HS) states. The SCO phenomenon, occurring in various 3*d* transition metal compounds, is associated with changes to molecular electronic structure, as a consequence of the splitting of the energy of the transition metal *d* orbitals, for example into *t*_{2g} and *e*_g when set in octahedral ligand fields.^{10–17} There is a rich body of experimental work indicating that SCO transition can be induced by a change in temperature, pressure, light, magnetic and electric fields.^{18–22} Spin crossover induced by temperature is most frequently studied, typically with the transition identified by a change of magnetic moment and modification of structural properties and crystal packing of the spin crossover molecules. The key structure change during the SCO transition are the bond lengths and angles between center transition metal atom and the nearest six nitrogen atoms. Generally speaking, a shorter metal-ligand bond length results in a low spin state, while a high spin state has a longer metal-ligand bond length. In most cases, the metal-ligand bond length difference between in low spin and high spin states is about 0.2 Å.

Magnetic measurements are considered as the key experimental indicator of the SCO molecular state, typically making a transition from a diamagnetic low spin (LS) state at low temperatures to a paramagnetic high spin (HS) state at high temperatures for

the most studied class of complexes based on d^6 Fe(II) cation. Figure 1.1 gives an illustration of the SCO molecule.

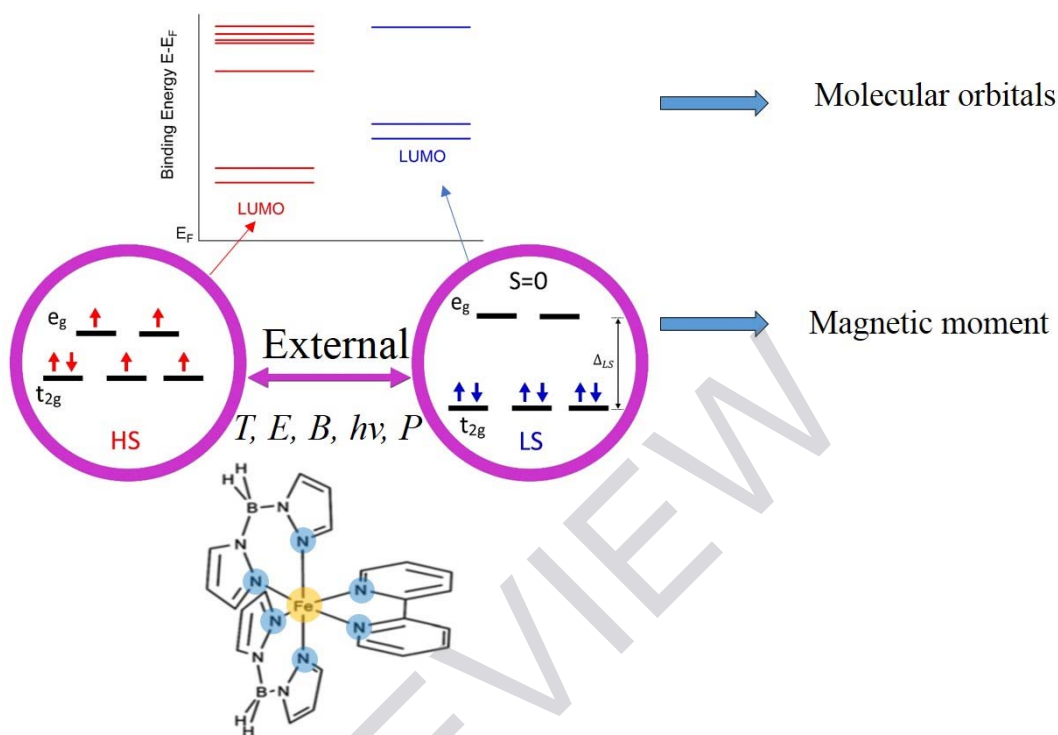


Figure 1.1 Bottom figure is the chemical scheme of one example of SCO molecule. The Fe 3d electrons configuration is switchable between high spin and low spin states under the influence of external stimuli, which directly affects the molecular magnetic moment. Different 3d electron configurations are associated with the molecular orbitals also, especially the lowest unoccupied molecular orbital (LUMO) position.

The two stable ground states (high spin and low spin states) are expected to be in similar energy levels with a small difference in the range of $k_B T$, where k_B is the Boltzmann's constant. Hence an external stimulus could provide enough energy to make it possible to switch the molecular spin states. The switching process could be very diverse and depends on the specific molecule, as shown in figure 1.2. The hysteresis loop in figure 1.2(c) is due to the lattice structure that changes with the associated SCO

transition and can also depend on the cooperative interactions between molecules so that intramolecular structure may also change. From figure 1.2(a) to (c), the cooperativity is increasing. In spin crossover molecules, the cooperative interaction has not been fully understood so far.²³ Phenomenologically, the cooperative interactions between molecules help to stabilize the spin state of the individual molecule, when temperature is changed. As cooperative interactions between molecules become stronger, the slow stabilization process in figure 1.2(a) become a steeper or more abrupt SCO transition process as in figure 1.2(b). When the cooperative interactions are very strong, the molecular spin state is more stable, meaning that the temperature has to be increased or decreased a lot to change the spin state, hence creating the hysteresis loop, as exists in figure 1.2(c). The two step transition, in figure 1.2(d), could happen in molecules with two lattice sites²⁴ or two transitional metal atoms (binuclear complex)^{25,26}. The imperfect spin crossover transition,²⁷ of in figure 1.2(e), is where the SCO system cannot reach a full or completely zero low spin state, because of either a kinetic barrier effect²⁸ or that some parts of the molecules are hard to convert due to the strong field strength at some lattice sites or a residual unpaired spin. It might sound like there would be huge differences in the molecule components, among SCO molecules, different types of SCO transitions, but actually only small modifications in the molecular components are necessary to achieve different SCO transitions.¹⁶

To simplify the investigation of the physics of the SCO transition, this thesis will emphasize the spin crossover molecules that exhibit no hysteresis loop, like what occurs in figure 1.2(a) and (b). In such cases, there are no complications where the molecular lattice sites matter significantly, and the transition temperature is easier to identify.

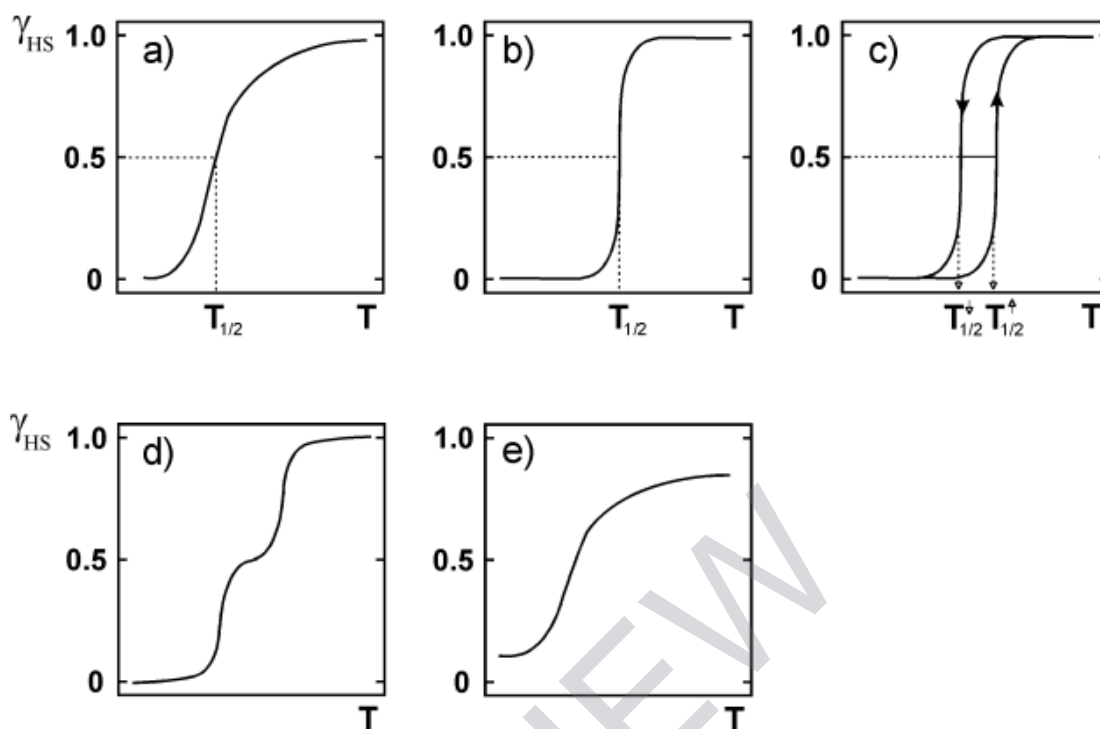


Figure 1.2 Representation of the principal types of spin transition curves by high spin fraction (γ_{HS}) (y axis) vs temperature (T) (x axis): a) gradual; b) abrupt; c) with hysteresis; d) two-step; e) incomplete. [Taken from ²³ with permission of Springer. Copyright (2004) Springer.]

1.2 The advantages and challenges of spin crossover molecule

After being discovered in 1931,²⁹ a lot of techniques have been applied to the study of the SCO transition, in order to measure and modify the spin states of SCO molecules.²³ Beside the temperature and pressure stimulated SCO transition, other stimuli have been used to change SCO molecules' spin states. Many stimuli only work at low temperature (usually below liquid nitrogen temperature) and require a change in temperature, which is typically done by increasing the temperature, to relax the excited spin state back to the low spin state. Although SCO films have been made by Langmuir-Blodgett techniques,^{30,31} only recently have a few typical SCO molecules been found to

be stable enough to survive thermal evaporation without decomposition, and then have been deposited on a substrate as an ultra-thin film.^{32–38} The physical vapor deposited thin films of SCO molecules make it possible to use surface spectroscopy techniques under high vacuum conditions to probe electronic (molecular orbital) properties.

Spin crossover (SCO) molecular thin films can be now made so as to measure changes in electrical conductivity when the transition occurs,³⁹ as in the case of the SCO $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ ($\text{pz} = 1H\text{-pyrazol-1-yl}$) complex sublimated on a surface.³² There is a growing interest in the electrical transport properties of SCO materials for switching molecular electronics studies,^{40,41} with photoconductivity effects also present in nanocrystals of polymeric SCO materials drop-casted on gold nanoelectrodes.^{42,43} One can expect that the electronic density of states differs in the HS and LS states, and has important consequences for the electronic transport properties.⁴⁴ Experimental insight into the density of states (DOS) of these materials is thus of paramount importance, and is a key aspect upon which this thesis work focuses. The HUMO-LUMO gap measurements,³⁷ show that the SCO molecular film is an organic semiconductor, and expected to have low conductivity. In the study of conduction for single molecules, the possibility to switch the spin states of the SCO molecule by a bias current or voltage has been illustrated on some low conductive substrates at a super low temperature.^{18,19,45} More discussion about the SCO thin films and possible applications can be found in references ⁴⁶ and ⁴⁷.

For developing novel spintronics devices, one of the promising approaches is to manipulate the magnetic states by electrical methods.⁴⁸ If the voltage controlled switching of magnetic states in device doesn't require large current densities, then there is

less power consumption. For a molecular spintronics device, low power consumption and low voltages for switching are likely. By way of comparison, novel spin valves for magnetic memory devices, not based on molecules, do need a relative large electrical current densities to operate.⁴⁹ It is proved in experiments that the SCO transition can be induced by a change in electric field.^{18,19,22,40,50} The successful SCO molecule thin film fabrication makes possible electronic device development based on SCO molecules. By using different substrates, more modification methods maybe added. Because of the different interactions possible from the substrate, the already rich SCO phenomena maybe modified further. As will be shown, the substrate interaction makes possible high temperature isothermal and reversible spin states switching. Further, once a heterostructure containing a spin crossover molecules layer and other functional organic molecule layers becomes possible, there is the possibility for exploring the organic molecule voltage-controlled multiferroic devices. For example, the SCO molecule to ferroelectric bilayer could provide a ferroelectric polarization leading to changes in HOMO and LUMO position of an SCO molecular complex, which can be, hopefully, controlled by voltage switching. The adjacent electronic structure changes induced in the SCO complex, due to the interaction with the ferroelectric layer, might make the voltage-controlled spin states or magnetic states switching device possible. This might lead to a device more favorable than novel spin valve magnetic memory devices that need relatively large electrical current densities to operate. There is the very real possibility that one might use molecular heterostructures to fabricate a room temperature device that operates at the nanoscale, and at low power extremely in the GHz frequency range. Such devices could provide alternative nonvolatile magneto-electric logic or memory devices,

only requiring current densities below 10^4 A*cm^{-2} , and coercive voltages less than 1 V.

All these advantages could lead to diminished latency time, significantly enhanced switchable magnetization, and reduce power consumption. Therefore, the voltage controlled spin states switching in SCO molecules could be a new direction for the organic spintronics.

PREVIEW

References

- (1) Boehme, C.; Lupton, J. M. Challenges for Organic Spintronics. *Nat Nano* **2013**, *8* (9), 612–615.
- (2) Sanvito, S. Molecular Spintronics. *Chem. Soc. Rev.* **2011**, *40* (6), 3336–3355.
- (3) Sanvito, S. Molecular Spintronics: The Rise of Spinterface Science. *Nat Phys* **2010**, *6* (8), 562–564.
- (4) Žutić, I.; Fabian, J.; Das Sarma, S. Spintronics: Fundamentals and Applications. *Rev. Mod. Phys.* **2004**, *76* (2), 323–410.
- (5) Tsukagoshi, K.; Alphenaar, B. W.; Ago, H. Coherent Transport of Electron Spin in a Ferromagnetically Contacted Carbon Nanotube. *Nature* **1999**, *401* (6753), 572–574.
- (6) Sun, D.; Fang, M.; Xu, X.; Jiang, L.; Guo, H.; Wang, Y.; Yang, W.; Yin, L.; Snijders, P. C.; Ward, T. Z.; et al. Active Control of Magnetoresistance of Organic Spin Valves Using Ferroelectricity. *Nat Commun* **2014**, *5*.
- (7) Xiong, Z. H.; Wu, D.; Valy Vardeny, Z.; Shi, J. Giant Magnetoresistance in Organic Spin-Valves. *Nature* **2004**, *427* (6977), 821–824.
- (8) Dediu, V.; Murgia, M.; Maticotta, F. C.; Taliani, C.; Barbanera, S. Room Temperature Spin Polarized Injection in Organic Semiconductor. *Solid State Communications* **2002**, *122* (3–4), 181–184.
- (9) Petta, J. R.; Slater, S. K.; Ralph, D. C. Spin-Dependent Transport in Molecular Tunnel Junctions. *Phys. Rev. Lett.* **2004**, *93* (13), 136601.
- (10) Long, G. J.; Grandjean, F.; Reger, D. L. Spin Crossover in Pyrazolylborate and Pyrazolylmethane Complexes. In *Spin Crossover in Transition Metal Compounds I*; Gütllich, P., Goodwin, H. A., Eds.; Topics in Current Chemistry; Springer Berlin Heidelberg, 2004; pp 91–122.
- (11) Bousseksou, A.; Molnár, G.; Salmon, L.; Nicolazzi, W. Molecular Spin Crossover Phenomenon: Recent Achievements and Prospects. *Chemical Society Reviews* **2011**, *40* (6), 3313–3335.
- (12) Gütllich, P.; Goodwin, H. A. *Spin Crossover in Transition Metal Compounds III*; Topics in Current Chemistry; Springer, 2004; Vol. 235.
- (13) Halcrow, M. A. Structure: function Relationships in Molecular Spin-Crossover Complexes. *Chem. Soc. Rev.* **2011**, *40* (7), 4119–4142.
- (14) *Spin Crossover in Transition Metal Compounds I*; Gütllich, P., Goodwin, H. A., Eds.; Springer, 2004.
- (15) Gütllich, P.; Garcia, Y.; Goodwin, H. A. Spin Crossover Phenomena in Fe(II) Complexes. *Chem. Soc. Rev.* **2000**, *29* (6), 419–427.
- (16) Guionneau, P.; Létard, J.-F.; Yufit, D. S.; Chasseau, D.; Bravic, G.; Goeta, A. E.; Howard, J. A. K.; Kahn, O. Structural Approach of the Features of the Spin Crossover Transition in Iron (II) Compounds. *J. Mater. Chem.* **1999**, *9* (4), 985–994.
- (17) Salmon, L.; Molnár, G.; Cobo, S.; Oulié, P.; Etienne, M.; Mahfoud, T.; Demont, P.; Eguchi, A.; Watanabe, H.; Tanaka, K.; et al. Re-Investigation of the Spin Crossover Phenomenon in the Ferrous Complex [Fe(HB(pz)₃)₂]. *New J. Chem.* **2009**, *33* (6), 1283–1289.

- (18) Gopakumar, T. G.; Matino, F.; Naggert, H.; Bannwarth, A.; Tuczek, F.; Berndt, R. Electron-Induced Spin Crossover of Single Molecules in a Bilayer on Gold. *Angewandte Chemie International Edition* **2012**, *51* (25), 6262–6266.
- (19) Miyamachi, T.; Gruber, M.; Davesne, V.; Bowen, M.; Boukari, S.; Joly, L.; Scheurer, F.; Rogez, G.; Yamada, T. K.; Ohresser, P.; et al. Robust Spin Crossover and Memristance across a Single Molecule. *Nat Commun* **2012**, *3*, 938.
- (20) Prins, F.; Monrabal-Capilla, M.; Osorio, E. A.; Coronado, E.; van der Zant, H. S. J. Room-Temperature Electrical Addressing of a Bistable Spin-Crossover Molecular System. *Advanced Materials* **2011**, *23* (13), 1545–1549.
- (21) Baadji, N.; Piacenza, M.; Tugsuz, T.; Sala, F. D.; Maruccio, G.; Sanvito, S. Electrostatic Spin Crossover Effect in Polar Magnetic Molecules. *Nature Materials* **2009**, *8* (10), 813–817.
- (22) Mahfoud, T.; Molnár, G.; Bonhommeau, S.; Cobo, S.; Salmon, L.; Demont, P.; Tokoro, H.; Ohkoshi, S.-I.; Boukheddaden, K.; Bousseksou, A. Electric-Field-Induced Charge-Transfer Phase Transition: A Promising Approach Toward Electrically Switchable Devices. *J. Am. Chem. Soc.* **2009**, *131* (41), 15049–15054.
- (23) Gütllich, P.; Goodwin, H. A. Spin Crossover—An Overall Perspective. In *Spin Crossover in Transition Metal Compounds I*; Gütllich, P., Goodwin, H. A., Eds.; Topics in Current Chemistry; Springer Berlin Heidelberg, 2004; pp 1–47.
- (24) Matouzenko, G. S.; Létard, J.-F.; Lecocq, S.; Bousseksou, A.; Capes, L.; Salmon, L.; Perrin, M.; Kahn, O.; Collet, A. Two-Step Spin Crossover in a Mononuclear Compound [Fe(DPEA)(bim)](ClO₄)₂·0.5 H₂O [DPEA = (2-Aminoethyl)bis(2-Pyridylmethyl)amine, Bim = 2,2-Bisimidazole] – Crystal Structure, Magnetic Properties, Mössbauer Spectroscopy, and Photomagnetic Effects. *Eur. J. Inorg. Chem.* **2001**, *2001* (11), 2935–2945.
- (25) Real, J. A.; Bolvin, H.; Bousseksou, A.; Dworkin, A.; Kahn, O.; Varret, F.; Zarembowitch, J. Two-Step Spin Crossover in the New Dinuclear Compound [Fe(bt)(NCS)₂]₂bpym, with Bt = 2,2'-bi-2-Thiazoline and Bpym = 2,2'-bipyrimidine: Experimental Investigation and Theoretical Approach. *J. Am. Chem. Soc.* **1992**, *114* (12), 4650–4658.
- (26) Palii, A.; Ostrovsky, S.; Reu, O.; Tsukerblat, B.; Decurtins, S.; Liu, S.-X.; Klokishner, S. Diversity of Spin Crossover Transitions in Binuclear Compounds: Simulation by Microscopic Vibronic Approach. *J. Phys. Chem. C* **2016**.
- (27) Zhang, X.; Mu, S.; Liu, Y.; Luo, J.; Zhang, J.; N'Diaye, A.; Enders, A.; Dowben, P. A. The Electronic Structure Signature of the Spin Crossover Transition of [Co(dpzca)₂]. *submitted*.
- (28) Moliner, N.; Gaspar, A. B.; Muñoz, M. C.; Niel, V.; Cano, J.; Real, J. A. Light- and Thermal-Induced Spin Crossover in {Fe(abpt)₂[N(CN)₂]₂}. Synthesis, Structure, Magnetic Properties, and High-Spin ↔ Low-Spin Relaxation Studies. *Inorg. Chem.* **2001**, *40* (16), 3986–3991.
- (29) Cambi, L.; Szegő, L. Über Die Magnetische Suszeptibilität Der Komplexen Verbindungen. *Ber. dtsh. Chem. Ges. A/B* **1931**, *64* (10), 2591–2598.
- (30) Ruauudel-Teixier, A.; Barraud, A.; Coronel, P.; Kahn, O. Spin Transition in a Magnetic Langmuir-Blodgett Film. *Thin Solid Films* **1988**, *160* (1), 107–115.

- (31) Létard, J. F.; Nguyen, O.; Soyer, H.; Mingotaud, C.; Delhaès, P.; Kahn, O. First Evidence of the LIESST Effect in a Langmuir–Blodgett Film. *Inorg. Chem.* **1999**, *38* (13), 3020–3021.
- (32) Mahfoud, T.; Molnár, G.; Cobo, S.; Salmon, L.; Thibault, C.; Vieu, C.; Demont, P.; Bousseksou, A. Electrical Properties and Non-Volatile Memory Effect of the [Fe(HB(pz)3)2] Spin Crossover Complex Integrated in a Microelectrode Device. *Applied Physics Letters* **2011**, *99* (5), 53307-053307–3.
- (33) Naggert, H.; Bannwarth, A.; Chemnitz, S.; Hofe, T. von; Quandt, E.; Tuczek, F. First Observation of Light-Induced Spin Change in Vacuum Deposited Thin Films of Iron Spin Crossover Complexes. *Dalton Trans.* **2011**, *40* (24), 6364–6366.
- (34) Zhang, X.; Wu, N.; Zhang, Z.; Létard, J.-F.; Guillaume, F.; Doudin, B.; Dowben, P. The Electronic Structure of a Local Charge-Transfer-Induced Spin Transition Molecular Adsorbate. **2011**, APS Meeting Abstract #V44.001.
- (35) Palamarciuc, T.; Oberg, J. C.; Hallak, F. E.; Hirjibehedin, C. F.; Serri, M.; Heutz, S.; Létard, J.-F.; Rosa, P. Spin Crossover Materials Evaporated under Clean High Vacuum and Ultra-High Vacuum Conditions: From Thin Films to Single Molecules. *J. Mater. Chem.* **2012**, *22* (19), 9690–9695.
- (36) Bernien, M.; Wiedemann, D.; Hermanns, C. F.; Krüger, A.; Rolf, D.; Kroener, W.; Müller, P.; Grohmann, A.; Kuch, W. Spin Crossover in a Vacuum-Deposited Submonolayer of a Molecular Iron(II) Complex. *J. Phys. Chem. Lett.* **2012**, *3* (23), 3431–3434.
- (37) Zhang, X.; Palamarciuc, T.; Rosa, P.; Létard, J.-F.; Doudin, B.; Zhang, Z.; Wang, J.; Dowben, P. A. Electronic Structure of a Spin Crossover Molecular Adsorbate. *The Journal of Physical Chemistry C* **2012**, *116* (44), 23291–23296.
- (38) Ellingsworth, E. C.; Turner, B.; Szulczewski, G. Thermal Conversion of [Fe(phen)3](SCN)2 Thin Films into the Spin Crossover Complex Fe(phen)2(NCS)2. *RSC Adv.* **2013**, *3* (11), 3745–3754.
- (39) Rotaru, A.; Gural'skiy, I. A.; Molnár, G.; Salmon, L.; Demont, P.; Bousseksou, A. Spin State Dependence of Electrical Conductivity of Spin Crossover Materials. *Chem. Commun.* **2012**, *48* (35), 4163–4165.
- (40) Prins, F.; Monrabal-Capilla, M.; Osorio, E. A.; Coronado, E.; van der Zant, H. S. J. Room-Temperature Electrical Addressing of a Bistable Spin-Crossover Molecular System. *Adv. Mater.* **2011**, *23* (13), 1545–1549.
- (41) Ruiz, E. Charge Transport Properties of Spin Crossover Systems. *Phys. Chem. Chem. Phys.* **2014**, *16* (1), 14–22.
- (42) Etrillard, C.; Faramarzi, V.; Dayen, J.-F.; Létard, J.-F.; Doudin, B. Photoconduction in [Fe(Htrz)2(trz)](BF4)·H2O Nanocrystals. *Chem. Commun.* **2011**, *47* (34), 9663–9665.
- (43) Létard, J.-F.; Etrillard, C.; Doudin, B.; Faramarzi, V.; Dayen, J.-F. Patent FR 2011/11 50949 (2011-02-07).
- (44) Aravena, D.; Ruiz, E. Coherent Transport through Spin-Crossover Single Molecules. *J. Am. Chem. Soc.* **2012**, *134* (2), 777–779.
- (45) Meded, V.; Bagrets, A.; Fink, K.; Chandrasekar, R.; Ruben, M.; Evers, F.; Bernand-Mantel, A.; Seldenthuis, J. S.; Beukman, A.; van der Zant, H. S. J. Electrical Control over the Fe(II) Spin Crossover in a Single Molecule: Theory and Experiment. *Phys. Rev. B* **2011**, *83* (24), 245415.

- (46) Cavallini, M. Status and Perspectives in Thin Films and Patterning of Spin Crossover Compounds. *Phys. Chem. Chem. Phys.* **2012**, *14* (34), 11867–11876.
- (47) *Spin-Crossover Materials: Properties and Applications*; Malcolm A. Halcrow, Ed.; Wiley:, 2013.
- (48) Tang, J.; Shao, Q.; Upadhyaya, P.; Amiri, P. K.; Wang, K. L. Electric Control of Magnetic Devices for Spintronic Computing. In *Spintronics-based Computing*; Zhao, W., Prenat, G., Eds.; Springer International Publishing, 2015; pp 53–112.
- (49) Grollier, J.; Boulenc, P.; Cros, V.; Hamzić, A.; Vaurès, A.; Fert, A.; Faini, G. Switching a Spin Valve Back and Forth by Current-Induced Domain Wall Motion. *Applied Physics Letters* **2003**, *83* (3), 509–511.
- (50) Zhang, X.; Palamarcu, T.; Létard, J.-F.; Rosa, P.; Lozada, E. V.; Torres, F.; Rosa, L. G.; Doudin, B.; Dowben, P. A. The Spin State of a Molecular Adsorbate Driven by the Ferroelectric Substrate Polarization. *Chem. Commun.* **2014**, *50* (18), 2255–2257.

CHAPTER 2

METHODS AND TECHNIQUES

This spin crossover project is motivated by constructing new devices with spin crossover molecules, taking advantage of the different spin states of the molecule. The electronic properties will directly affect the device performance, which is not only impacted by the molecular film quality, but also highly related with the molecular film's electronic structure (or band structure). The emphasis of this thesis is on the characterization of the electronic structure by photoemission, inverse photoemission spectroscopy and X-ray absorption spectroscopy, because these techniques give us a comprehensive and key information of the molecular thin film electronic structure. In this chapter, different electron spectroscopy and magnetometry techniques are introduced, although other techniques were also used in this project which will be explained when they are mentioned in later sections.

2.1 Photoemission spectroscopy

Photoemission spectroscopy (PES) has been developed for a long time and is a well established technique. Photoemission is used widely in academic research and has industrial application. This technique is also often called photoelectron spectroscopy. The photoemission was first explained theoretically by Albert Einstein as “photoelectric effect” in 1905,¹ for which he received the 1921 Nobel Prize in Physics. Experimentally, photoemission was discovered by Heinrich Hertz in 1887,² and its history is reviewed in references ^{3,4}. Depending on different light source, different aspects of the band structure can be probed. Here we introduce X-ray photoemission spectroscopy (XPS) and Ultra-violet photoemission spectroscopy (UPS).

2.1.1 Principle of photoemission spectroscopy

In a single atom, for example the hydrogen atom, the possible energy states of the electron are not continuous, but instead the electron can only be found in quantized energy levels. For hydrogen, this is described by the Bohr model,⁵ covered in all introduction to quantum mechanics class. Although the electron energy distribution is much more complicated in the case of crystalline materials, the concept of the quantized energy levels is still valid. Although there are nuclear (isotopic) perturbations possible, it is generally true that the electronic structure determines many of the electrical properties of materials. That is why we care about the electronic energy level structure. The question now is how we can obtain information on this energy levels structure. An electron could absorb a photon and gain the photon energy, then be excited to a higher energy level. When the absorbed energy is high enough, the electron could be emitted out

of the sample, resulting in the photoelectron process. The emitted electron can be collected and energy analyzed to get information about the energy levels that is to say electronic structure. By choosing different light sources, with different energies, electrons from different energy levels can be probed. It is like fishing, where the fisherman can use different lengths and types of fishing line to catch different fish that live at different water depths. With that said, there is no universal all-purpose photoemission technique like there is no true all-purpose fishing line. As one can image, the photoemission set up is simple: shoot the light on the sample and then collect the emitted electrons. Although, very sophisticated geometries can be used to extract considerable information about the initial state, as indicated later.

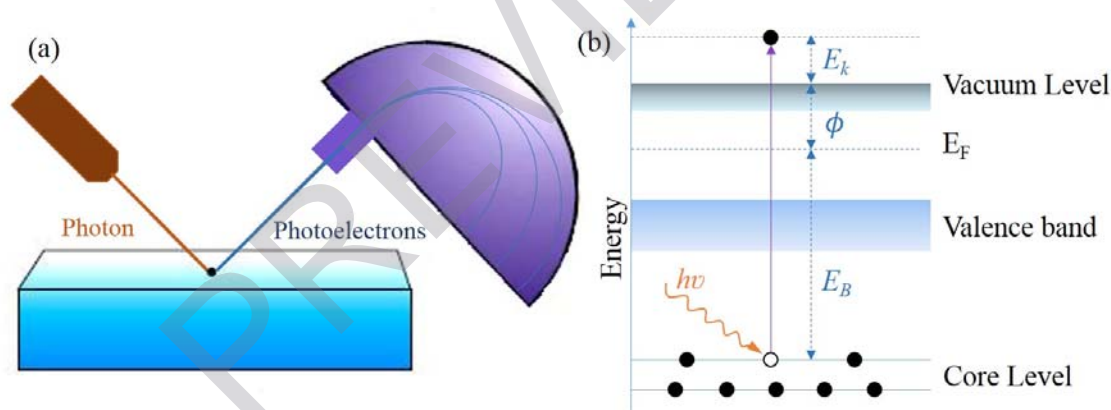


Figure 2.1 (a) Experiment set up geometry sketch for standard photoemission spectroscopy. (b) Energy level diagram illustrating the photoemission process.

The photoemission spectroscopy experiment geometry is schematically illustrated in Figure 2.1(a). There is the light source, providing photons on the sample, and then the emitted photoelectrons are analyzed by the energy analyzer. Figure 2.1(b) gives a basic idea how we use the energy conservation principle to obtain the original binding energy