

Physical and chemical induced spin crossover

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Physical and chemical induced spin crossover

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Abstract. Physical spin crossover (spin transition), one of the most fascinating dynamic electronic structure phenomena occurring in coordination compounds of third row transition metal ions, mostly of iron(II), iron(III) and cobalt(II), has attracted increasing attention by many research groups. Some examples for physical and chemical induced spin crossover are discussed. Among the physical is the temperature and pressure induced switching. Novel effects observed by irradiation and magnetic and electric field will be discussed. Some chemical induced switching effects caused by solvation, ligand exchange, ligand isomerisation and bond breaking will be briefly outlined.

1. Introduction

Molecular switching is one of the major targets in various disciplines, such as technology, biology and medicine. One approach is to develop chemically and physically induced transitions between electronic states. In some transition metal complexes such a switching has been discovered and labelled spin crossover (SC) or spin transition phenomenon [13, 14] (see Figure 1). The phenomenon of thermal spin crossover, though already well known in inorganic chemistry for more than seven decades, has developed in recent years to one of the most actively studied subjects in coordination chemistry [8, 14, 10, 12, 11, 15].

2. Physical Induced

2.1. Thermal Induced SC (TISC)

The thermal spin crossover was first observed in an Fe(III) complexes by Cambi, et al. in 1931. After 60 years the first Fe(II)-spin crossover complex, the [Fe(II)(phen)₂(NCS)₂], was found by Baker, et al. in 1963. The Mössbauer effect was very important for the understanding of the nature of this switching phenomenon. The essential condition for TISC is that the zero-point-energy gap, the difference in zero-point vibrational energy between high-spin and low-spin state, is at the order of thermal energy kT [13, 14].

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2.2. Pressure Induced SC (PISC)

The application of pressure leads to a first order approximation to an increased zero-point-energy gap. This shifts the transition temperature in the TISC to higher values [16]. In case of structural changes due to the application of pressure the opposite may be the case [16].

2.3. Light Induced SC

2.3.1. Batch Light Induced SC

2.3.1.1. *Light Induced Excited Spin-State Trapping (LIESST)*: The phenomena of LIESST (Light-Induced Excited Spin State Trapping) and reverse LIESST are well reviewed in the literature [14, 15]. For LIESST: green light irradiation on the Fe(II)-low-spin (S=0) state leads to an excited singlet state and decays via triplet states (S=1) to a trapped meta-stable quintet state, the Fe(II)-high-spin state (S=2) [14].

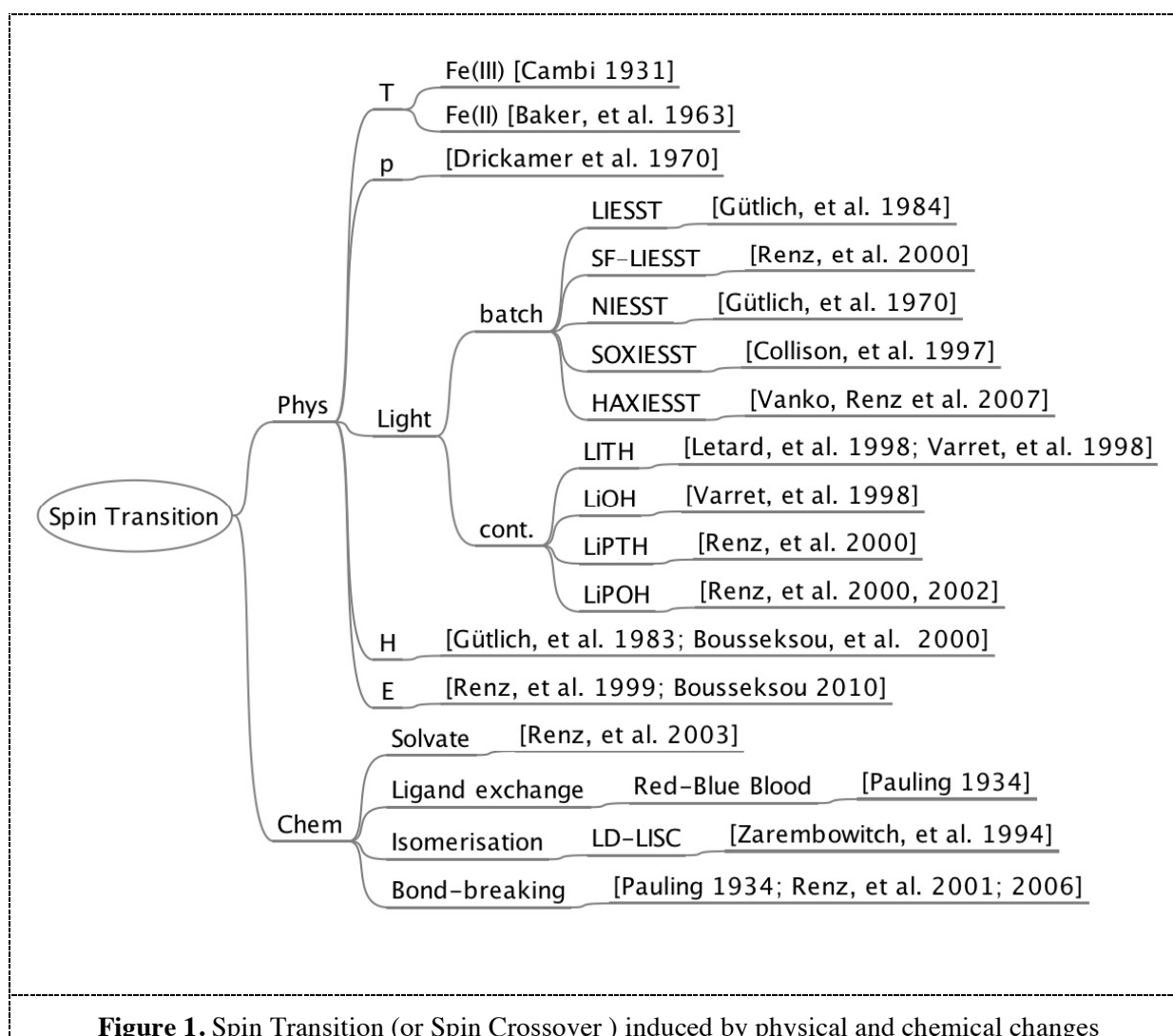


Figure 1. Spin Transition (or Spin Crossover) induced by physical and chemical changes

2.3.1.2. *Strong-Field- Light Induced Excited Spin-State Trapping (SF-LIESST)*[26]: Unexpected long life-time (mega-seconds) of the light-induced meta-stable state are observed for the strong-field

complexes $[\text{Fe(II)}_x\text{Mn(II)}_{1-x}(\text{terpy})_2](\text{ClO}_4)_2$, ($x < 0.1$). In opposite the non-diluted ($x = 1$) compound follows the expected LIESST mechanism at a life-time of sub-nanoseconds. The SF-LIESST effect seems to correlate with the tri-dentate inherent structure motive performing a double mode transition [22]. In comparison to that, usual mono-dentate perform single mode transitions. In such compounds the LIESST effect was first observed, e.g. $[\text{Fe(II)}(\text{ptz})_6]^{2+}$.

2.3.1.3. Nuclear Induced Excited Spin-State Trapping (NIESST)[14]: The nuclear decay of radioactive atoms embedded in a compound is known to lead to various chemical and physical "after effects" such as bond rupture, redox processes, formation of metastable states and others. One ways of investigating such effects is the "Mössbauer Emission Spectroscopy" (MES). Using this technique some metastable HS states of $^{57}\text{Fe(II)}$ in strong and intermediate ligand fields are observed. Many examples are described in a recent review article [9]. In analogy to the LIESST effect (generating and trapping of metastable HS states by irradiation with an external light source) the mechanism of the "Nuclear Decay Induced Excited Spin State Trapping (NIESST)" with its nuclear decay process $^{57}\text{Co(EC)}^{57}\text{Fe}$ may be regarded as an "internal" molecular excitation source.

2.3.1.4. Soft-X-ray Induced Excited Spin-State Trapping (SOXIESST)[5]: The soft X-ray electronic L-shell excitation in iron(II) coordination complexes leads to trapped metastable HS states. This is similar to the LIESST effect. Unfortunately further "after" effects such as bond rupture are also observed. This limits the application of this effect.

2.3.1.5. Hard-X-ray Induced Excited Spin-State Trapping (HAXIESST)[30]: The hard X-ray electronic K-shell excitation in iron(II) coordination complexes leads to trapped metastable HS states. This is similar to NIESST, SOXIESST and LIESST effect. In comparison to the SOXIESST and NIESST the HAXIESST has a much smaller probability for irreversible bond breaking. While L-shell experiments are performed under vacuum a K-shell measurement is done at ambient pressure under atmospheric conditions. A further advantage of the HAXIESST is its ability of single molecule addressing and switching, due to the atomistic spatial resolution of the short wavelength. In opposite the LIESST effects has a resolution of around 500 nm.

2.3.2. Continuous Light Induced SC

2.3.2.1. Light Induced Thermal Hysteresis (LITH)[17, 7]: Monitoring the HS fraction under constant-intensity continuous irradiation and variable temperature allows to observe a light induced thermal hysteresis. The LITH indicates a measure for cooperativity among the switching centers. If the cooperativity between the switching centers vanishes the thermal hysteresis width collapses to zero, so that the heating and cooling curve become identical.

2.3.2.2. Light Induced Optical Hysteresis (LIOH)[7]: Monitoring the HS fraction under variable-intensity continuous irradiation and constant temperature allows to observe a light induced optical hysteresis. LITH and LIOH can be interpreted in mean approximation with a master equation including a non-linear relaxation term[7].

2.3.2.3. Light Perturbed Thermal Hysteresis (LiPTH)[27]: Monitoring the HS fraction under constant-intensity continuous irradiation and variable temperature within a thermal hysteresis

allows to Light-perturb the thermal hysteresis (LiPTH). LiPTH allows to switch even at room temperature and in batch irradiations[28]. So far the maximum shift of a hysteresis was found to be around 50 K.

2.3.2.4. Light Perturbed Optical Hysteresis (LiPOH)[28, 27]: Monitoring the HS fraction under variable-intensity continuous irradiation and constant temperature within a thermal hysteresis allows to Light-perturb the thermal hysteresis seen as an optical hysteresis (LiPOH). LiPOH allows to switch even at room temperature and in batch irradiations[28].

2.4. Magnetic Field Induced SC (H)[4]

The effect of the magnetic field on the spin crossover transition temperature was weak and yielded a shift of ca. 2 K with a field of 5 Tesla as seen by Gütlich, et al. [21]. Almost two decades later Bousseksou, et al. used pulsed high-fields of up to 32 Tesla [3]. This turned out to be very effective[4].

2.5. Electric Field Induced SC (E)

The effect of the electric field on the spin crossover was seen on stretching a polar polymer matrix [25]. The matrix-incorporated spin crossover compound was exposed and affected by the electrostatic field of the polymer. More recent examples show the effect of the electrostatic field affects the bistability [6, 1, 19].

3. Chemical Induced

3.1. Solvate Induced SC

In solution the cooperativity is lowered and exhibit a Boltzmann-like behaviour. In opposite, non-coordinated solvates or adsorbats induce molecular switching (AIMS)[24] with potential room for applications.

3.2. Ligand Exchange Induced SC

Many compounds change their spin state on ligand exchange. E.g. hemoglobine reversibly coordinates oxygen. This causes the blue and red blood-color. Along with that a spin state change was observed by Pauling and Corvell [20].

3.3. Ligand Isomerisation Induced SC[29]

Roux et al. [29] have reported a method to obtain ligand-driven light-induced spin changes (LD-LISC) in transition metal compounds. Photo-sensitive ligands, such as cis-trans photo-isomerizable ligands, can alter the ligand field strength on irradiation and induce a spin state conversion at the metal center. LD-LISC was first observed in $[\text{Fe(II)}\text{L}_4(\text{NCS})_2]$ with L = cis, trans 4-styrylpyridine. For further examples see[2].

3.4. Bond-Breaking Induced SC

A non-reversible spin state change after a coordination bond-breaking is quite normal for many such chemical reactions. However, reversibility of such a phenomena is rare. One example is a rod-type structure consisting of $[\text{Fe(II)}(\text{acetate})_2]$ bridged by terpy-R-terpy (spacer R). Such systems switches pressure/digest and light-reversible [18, 23].

4. Outlook

This paper is a short compromise on some representative examples in an egocentric attempt to cover the vast development in the field and is far from complete. The intended compromise is to give a broad overview on selected effects and is not focused to systematically cover all the beautiful new compounds. Several very recent appealing new effects have not been included due to space restrictions.

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