

Review

Ultrafast photophysics and photochemistry of iron hexacyanides in solution: Infrared to X-ray spectroscopic studies

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ABSTRACT

We review recent results from the literature and from our work on ferrous and ferric hexacyanides in solution using a combination ultrafast spectroscopic tools, spanning from the infrared to the hard X-ray domain: transient infrared and visible spectroscopy, 2-dimensional deep-ultraviolet spectroscopy, vacuum ultraviolet photoelectron spectroscopy of solutions and hard X-ray absorption spectroscopy. The photoinduced dynamics in the case of the ferrous complex includes photoionization and photoaquation processes. The latter shows a sequence of events that includes: ultrafast intramolecular relaxation, dissociation with geminate recombination and solvent cage escape, formation of a penta-coordinated photo-product, conformational changes of the latter, binding of a water solvent molecule. The case of the ferric complex is different where upon excitation of the lowest LMCT state, a prompt change from Fe^{3+} to Fe^{2+} occurs followed by a back electron transfer, whose time scale is solvent-dependent. Furthermore, an electronic-to-vibrational energy transfer occurs as the molecule is found with a population reaching $\nu = 3$ of the CN stretch mode vibrational level. A weak photochemical channel is identified by IR and X-ray spectroscopy, showing formation of the same aquated species as in the ferrous case.

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1. Introduction

Iron is one of the most abundant metals in Nature and in molecular edifices, it gives rise to remarkable properties that have attracted the interest of physical chemists for decades. The Spin Cross-over (SCO) phenomenon [1,2] in Fe complexes in solution and the light-induced excited state spin trapping (LIESST) in cryogenic crystals [3], are typical examples of such properties. SCO corresponds to an electron spin flip from a low spin (LS) ground state to a high spin (HS) excited state in molecular complexes containing metal atoms of the first transition series [4]. The reverse process also takes place if the ground state is the HS and the excited state is LS. The interest for SCO is stirred by the potential applications in data storage by optical writing and read-out by magnetic means [5] but also for fundamental interest. In recent years, the SCO process in Fe-polypyridine complexes has intensely been investigated by ultrafast optical [6–12] and X-ray [13–18] spectroscopy, to the point that the smallest member of the family of SCO complexes, $[\text{Fe}(\text{bpy})_3]^{2+}$, is now competing with its ruthenium counterpart as the “H-atom of coordination chemistry”.

As a matter of fact, because iron is much more abundant and cheaper than ruthenium, iron(II) polypyridine complexes are also increasingly being explored as candidates in photovoltaics by means of dye-sensitized solar cells [11], so far mainly successful with ruthenium-based complexes [19]. The main limitation for such applications of Fe-complexes is the SCO and the focus of such studies is to increase the lifetime of the metal-to-ligand-charge-transfer (MLCT) states [20–23], which are extremely short-lived due to a non-radiative relaxation channels to lower, high spin, ligand-field (LF) or metal-centred (MC) states during the SCO process [7,8]. Among the candidates for such sensitizers are Iron complexes containing N-heterocyclic carbene (NHC) ligands, as superior σ -donors, to minimize the depopulation of MLCT states [24–27] or iron-cyano-polypyridine ones, such as *cis*-Fe(*dc*bpy)₂(CN)₂ and Na₂[Fe(bpy)(CN)₄] (bpy = 2,2'-bipyridine) [28–34]. The latter complexes are intermediates between the polypyridine and the hexacyanide ones. Although of a simpler molecular structure, with an octahedral symmetry, the ultrafast dynamics of ferrous and ferric iron hexacyanides have paradoxically been less studied than their polypyridine counterparts. Just as the detailed ultrafast dynamics studies of Fe-polypyridine complexes [6–10,12–15,35], have helped to devise alternative strategies for lengthening their MLCT lifetimes [20–23], so should similar studies of the ultrafast photophysics and photochemistry of iron-hexacyanides also help in this respect. There is an additional interest for Fe-cyano complexes: i.e. the process of electron transfer in donor-bridge-acceptor molecular assemblies as recently reported by Khalil and co-workers, who investigated the ultrafast metal-to-metal (Fe²⁺–Pt⁴⁺) charge transfer in a system with two ferrous Fe(CN)₆ linked via a CN–[Pt⁴⁺(NH₃)₄]–NC bridge [36].

Here, after presenting some of the electronic, structural and vibrational properties of Fe-hexacyanide complexes in solution, we will review recent studies of their ultrafast dynamics, from our work and that of others, using a combination of ultrafast deep-ultraviolet (deep-UV) to infrared transient absorption (TA)

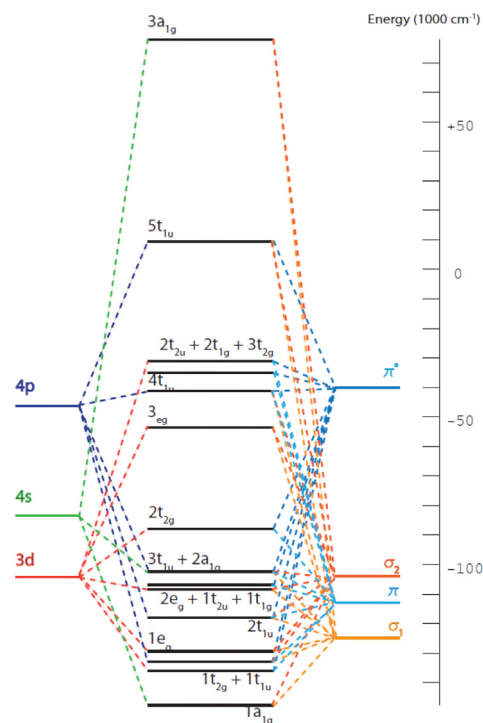


Fig. 1. Molecular orbital diagram of iron hexacyanide. The t_{2g} -subset of the Fe-3d orbitals mixes with ligand π/π^* orbitals, the e_g -subset of the Fe-3d orbitals and the Fe-4s orbital mix with ligand σ_1/σ_2 orbitals and the Fe-4p orbitals mix with ligand $\sigma_1/\sigma_2/\pi$ and π^* orbitals. Figure redrawn from Ref. [37]

spectroscopy, ultrafast X-ray spectroscopy and ultrafast vacuum ultraviolet (VUV) photoelectron spectroscopy of liquid solutions. These unravel details of the structural dynamics and electronic relaxation pathways upon photoexcitation of the complexes in solution, eventually leading to chemical reactions with solvent molecules. Because of their largely different electronic structure and dynamics, the results on the ferric and ferrous species are presented separately.

2. Properties of Fe-hexacyanides

2.1. Electronic structure

In these molecules the central Fe atom has an octahedral (O_h) coordination, with the Fe²⁺ (Fe³⁺) having a 3d⁶ (3d⁵) configuration. The 3d orbitals are split into subsets the irreducible representation t_{2g} and e_g . The former consist of non-bonding d_{xy} , d_{yz} and d_{zx} orbitals while the latter of the anti-bonding d_z^2 and $d_{x^2-y^2}$ orbitals (Fig. 1). The t_{2g} orbitals are engaged in π -bonding with the ligands, being stabilized and destabilized by π -back and -forward donation, respectively, and they lie at lower energies than the e_g orbitals. The splitting between the two sets is referred to as ligand field splitting and it changes only little between the two forms [37]. Yet despite

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