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STATIC AND DYNAMIC EFFECTS IN SPIN EQUILIBRIUM SYSTEMS

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CONTENTS

ABBREVIATIONS

bi	2,2′-bi-2-imidazoline
bipy	2,2′-bipyridine
BPh_4	tetraphenylborate anion
dppen	*cis*-1,2-bis(diphenylphosphino)ethylene
EPR	electron paramagnetic resonance
HS	high spin
IR	infrared
JT	Jahn–Teller
LF	ligand field
LS	low spin
$(6\text{-Mepy})_3$tren	tris[4-[(6-methyl)-2-pyridyl]-3-aza-3-butenyl]amine
NMR	nuclear magnetic resonance
nnp	*N*-(2-(diphenylphosphino)ethyl)-*N*′,*N*′-diethylethylenediamine
3-OEt-SalAPA	monoanion of the Schiff base condensate of 3-ethoxysalicylaldehyde and *N*-(3-aminopropyl)aziridine

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phen	1,10-phenanthroline
phy	1,10-phenanthroline-2-carbaldehyde phenylhydrazone
2-pic	2-picolylamine
P_4	hexaphenyl-1,4,7,10-tetraphosphadecane

> *"Nam nihil aegrius est quam res secernere*
> *apertas ab dubiis animus quas ab se protinus addit."*
>
> *Lucretius, De Rerum Natura, IV, 467–68.*

A. INTRODUCTION

More than fifty years have elapsed since Cambi and coworkers first reported the "anomalous" magnetic behavior of some ferric dithiocarbamates [1–4]. During this period a wealth of experimental data concerning the so-called "magnetically anomalous" compounds has accumulated and interest in this phenomenon has spread from inorganic chemistry to solid state physics and biochemistry. In the meantime numerous theoretical studies have been published beginning from the first quantitative analyses by Ewald et al. [5] on iron(III) complexes, by Barraclough [6] and Stoufer et al. [7] on cobalt(II) complexes and by König and Kremer [8–10] on iron(II) complexes. Indeed the proposal by Cambi et al. [3,4] of an equilibrium between different magneto-isomers can be considered substantially still valid if it is seen in the light of the LF theory. The real meaning to be attributed now to the term "magneto-isomer" is still a matter of discussion, as will be seen in the following sections.

We introduce nomenclature in order to avoid any misunderstanding.

The following terms concerning magnetically anomalous systems are encountered in the literature: intermediate spin state, spin transitions, spin equilibria and spin crossover systems.

Usually with the expression "intermediate spin state" one refers to a pure spin state, which has a spin multiplicity intermediate between those characteristic of a full LS or HS configuration, e.g. $S = 3/2$ for d^5 complexes. Since we are interested in mixed spin states and/or spin interconversion, this aspect will not be treated here.

Although the two expressions "spin transitions" and "spin equilibria" have often been used as synonyms, the former term should be reserved for abrupt transitions, which as a rule are accompanied by a crystallographic phase change, whereas the latter is more appropriate for continuous interconversions. "Spin crossover" is the most comprehensive term, in which the physical origin of the magnetic behavior is also inherent. In fact, looking at the Tanabe–Sugano energy level diagrams for d^4, d^5, d^6 and d^7 configurations in octahedral symmetry [11], it is evident that the ground level changes its spin multiplicity with increasing LF strength. When the LF splitting Δ ($= 10$ Dq) is comparable with the spin pairing energy, HS and LS states are nearly degenerate and the condition for mixed spin states is achieved. If the restriction of octahedral symmetry is released, ground states of different spin multiplicities are theoretically also allowed for d^2, d^3 and d^8 electronic configurations.

Besides the numerous examples so far reported for iron(II), iron(III) and cobalt(II), spin crossover has also been observed in other physical systems containing Mn(II) [12], Mn(III) [13–16], Co(III) [13,17–20], Ni(II) [21–23], Mo(II) [24] and finally in clusters of the type Nb_6I_{11} and HNb_6I_{11} [25].

Spin crossover systems have been reviewed many times recently so a thorough account of the phenomenon and its theoretical interpretation, particularly with respect to iron(II) complexes, can be found elsewhere [13,26–30]. In the present review we shall mainly consider systems showing spin equilibria, as defined above, by emphasizing some recent aspects such as (i) the role of vibronic coupling, (ii) the magnetic moment as a "marker" of conformational changes, chiefly in biomolecules, and finally (iii) the problem of distinguishing the simultaneous presence of HS and LS species.

B. SPIN EQUILIBRIUM PHENOMENA

(i) Solid state

Magnetic susceptibility measurements are most useful to demonstrate the occurrence of spin equilibria and, from a historical standpoint, it was just through this kind of measurement that the phenomenon was revealed [1–4]. However temperature affects not only the magnetic moment, but also other physical properties.

Since the first investigation of these systems, the relationship between magnetic moment and structural changes was a primary aspect to be clarified. Technical difficulties prevented X-ray crystal structure determinations at different temperatures until the seventies, when the first structures of iron(II) [31] and iron(III) [32] spin crossover complexes at room and liquid nitrogen temperature were reported. Some years later the crystal structure at 120 K of a typical cobalt(II) spin crossover system, $[Co(nnp)(NCS)_2]$, was reported [33] and compared to that at room temperature [34].

All the crystal structure studies performed so far (see refs. 28 and 30 for the most recent data at different temperatures) show a decrease of the metal–ligand bond length with decreasing temperature and, accordingly, LS states are stabilized at low temperature due to the larger LF strength. Using the complex $[Fe(bipy)_2(NCS)_2]$ it was shown that the LF splitting, 10 Dq, follows a R_{ML}^{-5} law to a good approximation [31]. However significant changes of the ligand–metal–ligand angles were also observed and they too contribute in stabilizing LS species at low temperature [35].

Using X-ray crystal structure data and other physical properties, two types of transition, discontinuous and continuous, can be distinguished in spin crossover systems [30]. In the former case there is evidence for a crystallographic phase change and, in general, the transition is thermodynamically first order. Different X-ray diffraction patterns are observed above and below the critical temperature T_c, corresponding to the HS and LS phases. It is very likely that strong cooperative interactions between the individual chromophores are effective to induce the growing of single domains of a particular spin state. The occurrence of such independent domains is actually considered as being closely related to the hysteresis, particle size and grinding effects, which are very often reported for this type of complex [30,36–38]. In the continuous case, to which most of the described spin crossover systems belong, no crystallographic phase change is observed and only a gradual modification of the bond lengths and angles occurs [33,35]. Moreover the coexistence of two spin isomers in the same lattice was revealed for $[Fe(2\text{-pic})_3]Cl_2 \cdot CH_3OH$ by a multiple-temperature crystallographic analysis [39]: both LS and HS species show smooth structural changes in the range 115–227 K. Finally, in this context, particular attention is paid to a very recent paper [40] on the ferric spin crossover complex $[Fe(3\text{-OEt-SalAPA})_2]ClO_4 \cdot C_6H_6$. Magnetic and spectroscopic investigations of this compound are in agreement with a continuous HS $\rightleftharpoons$ LS transition and no evidence for hysteresis was found from these measurements. However a multiple-temperature structural study at ca. 20, 128 and 175 K has revealed an order–disorder transformation with a change of space group from $C2/c$ (high temperature) to $P2_1/c$ (low temperature). The abrupt change of the intensity of the $(-5, -2, 1)$ reflection (and of the three symmetry related reflections) above 180 K and their marked hysteresis ($\Delta T = 15$ K) are characteristic of a first-order transition so that this is a typical case of mixed-order transformation [30]. Superposition of the room-temperature and low-temperature structures (Fig. 1) suggests that the high-temperature iron site is modeled as the superposition of the two low-temperature iron sites or, in other words, that a dynamic interconversion of two crystallographically distinct sites can occur besides a spin-state interconversion. This situation seems to be closely related to the $[Fe(2\text{-pic})_3]Cl_2 \cdot CH_3OH$ case [39], but here the spin isomers cannot be resolved due to the fast interconversion rate.

Indeed a very important role is played by the solvent molecules: for example, if we substitute methanol with ethanol in $[Fe(2\text{-pic})_3]Cl_2 \cdot CH_3OH$,

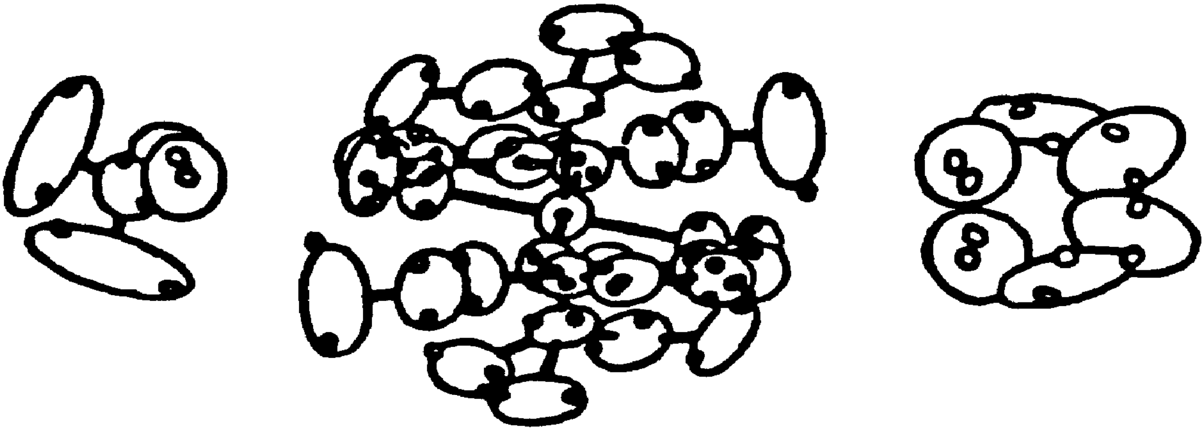

Fig. 1. The relationship between the room-temperature ($C2/c$) an the low-temperature ($P2_1/c$) structures. Thermal ellipsoids from the room-temperature structure are superimposed with small circles which indicate the atomic positions at low temperature and the low-temperature positions translated by $(a+b)/2$. This figure suggests that the refined room-temperature thermal parameters mask a disorder of the two independent orientations observed at low temperature. (Reprinted with permission from ref. 40.)

a cooperative spin transition is observed, accounted for in terms of a coupling with the order–disorder transition of the ethanol molecules [41]. An order–disorder transition was also suggested for $[Fe(dppen)_2Cl_2] \cdot 2(CH_3)_2CO$ [42], the X-ray crystal structure of which shows that the acetone molecule at 130 K is almost equally distributed between two different orientations [43] so as to induce two slightly different sites for the iron(II) ion. A quite analogous situation is found in $[Fe(bi)_3](ClO_4)_2$, where the presence of two inequivalent iron sites below 199 K is attributed to two possible configurations of the ClO_4^- ion [44]. Moreover the transition becomes very gradual when the solvent is removed from the above solvates. It seems likely that the solvent molecule can affect the intermolecular coupling by modifying the density of normal modes of lattice vibrations. Of course this reflects on the entropy change passing from the LS to the HS phase. It has been demonstrated by Sorai and Seki [45] that the largest contribution to the entropy change is vibrational, while a smaller contribution is due to the change in spin state. These last authors performed accurate heat capacity measurements on $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$ between 13 and 375 K and obtained evidence for the cooperative nature of the spin transition, achieved through electron–phonon coupling and the related formation of single domains.

In the case of abrupt transitions IR spectroscopy is one of the most suitable tools to demonstrate the coexistence of different spin states around the transition temperature. Figure 2 displays the far-IR spectra of

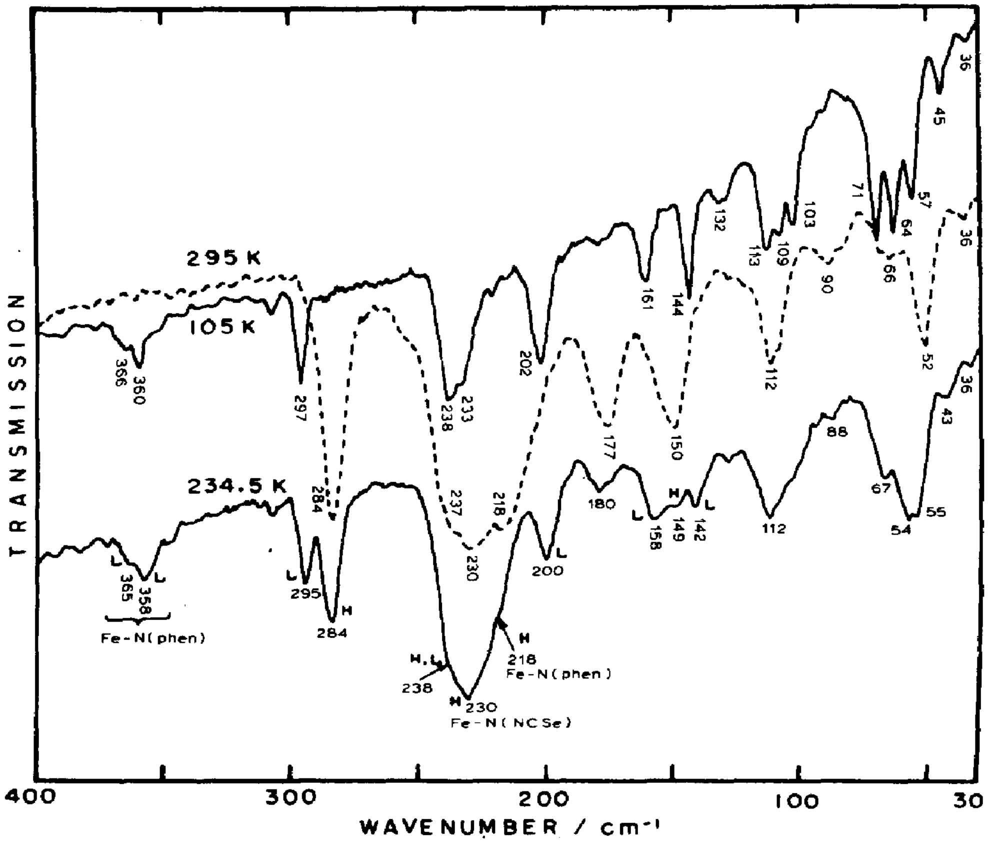

Fig. 2. Far IR spectra (400–30 cm^{-1}) of [Fe(phen)$_2$(NCSe)$_2$] at 295 K ($^5T_2$), at 105 K ($^1A_1$), and at 234.5 K (crossover region). (Reprinted with permission from ref. 45.)

[Fe(phen)$_2$(NCSe)$_2$] at different temperatures and clearly shows an overlap of the spectra of the LS and HS species in the crossover region [45]; similar evidence can also be obtained from temperature- dependent IR spectra in the C–N stretching region (see Fig. 3 [45]). A further result from these studies is that the frequencies of the two species are temperature independent so that variation of the energy separation between the two pure spin ground states as a function of temperature can be excluded. Hall and Hendrickson [46] were led to an analogous conclusion by analysing their IR data on ferric dithiocarbamates. This fact seems to be at variance with the results previously obtained for the complex [Co(nnp)(NCS)$_2$], for which a gradual shift of the N–H and C–N stretching frequencies was reported [47]: this different behavior could be accounted for by considering that in the last complex no phase transition is observed [33] and the conditions for a typical spin equilibrium are satisfied [48] (see also Section C).

Recently the first laser Raman spectroscopy study on a spin crossover system was reported in both the solid state and solution [49]. The chromophore $[Fe(6\text{-}Mepy)_3tren]^{2+}$ shows a metal-to-ligand charge transfer band at 568 nm. With laser radiation within this absorption band, two distinct imine stretching modes are observed at 1652 cm^{-1} and 1629 cm^{-1} for the HS and LS species, respectively. The results are interpreted to provide evidence against the domain hypothesis [36–38].

Very recent Mössbauer [50–52] and IR [53] measurements on $[Fe(phen)_2(NCS)_2]$ have revealed the existence of metastable HS species even at temperatures below the transition temperature T_c. The HS form is obtained from the LS form by optical pumping with white light or with the 632.8 nm radiation of a He/Ne laser and it reconverts into a new LS form on warming the samples above ca. 30 K. The phenomenon can be interpreted assuming a light-induced excited-spin-state trapping process [51,54]. Spin-singlet excited levels can be populated by optical pumping with light of suitable frequency within a metal-to-ligand charge-transfer band. They decay by intersystem crossing to a minimum of the potential energy surface corresponding to a spin-quintet state. At very low temperature such a new quintet species is "frozen" but it transforms into a LS species if sufficient energy is supplied to exceed the energy barrier. As demonstrated by variable-temperature Fourier transform IR spectra [53], the trapped HS species differ from the HS species, which are present at room temperature. Indeed, owing to greater occupancy of the antibonding orbitals in HS forms, the metastable HS form is expected to have a larger molecular volume than the LS form, which is stable at low temperature. Accordingly the HS complex is subject to a kind of internal pressure, because it is situated in the crystal lattice of the LS phase, and the observed shift [53] of the C–N stretching to higher frequencies in the metastable form supports this picture.

Since hydrostatic pressure is, in one sense, complementary to temperature, or, in other words, a decrease of temperature roughly acts on the crystal lattice like an increase of pressure, it seems obvious that a transition towards a LS species is favored by an increase of pressure. However a complete conversion does not occur, as has been shown by far-IR [55] and Mössbauer [56,57] spectroscopy under pressure. Quite recently Mössbauer measurements at different temperature and pressure [58] have been performed to investigate the effect of pressure on the thermal hysteresis in $[Fe(phy)_2]X_2$ ($X = BF_4$, ClO_4). An increase of the hysteresis width and of the residual fraction of the HS species is observed with increasing pressure. The theory of Landau and Lifshitz [59] can account for the hysteresis increment, but it is more difficult to explain the increase of the HS fraction. It is suggested that pressure strongly reduces the domain size and accordingly the cooperative region.

In the case of abrupt transitions, it is always possible to identify two different spin species even with rather slow spectroscopic methods, like

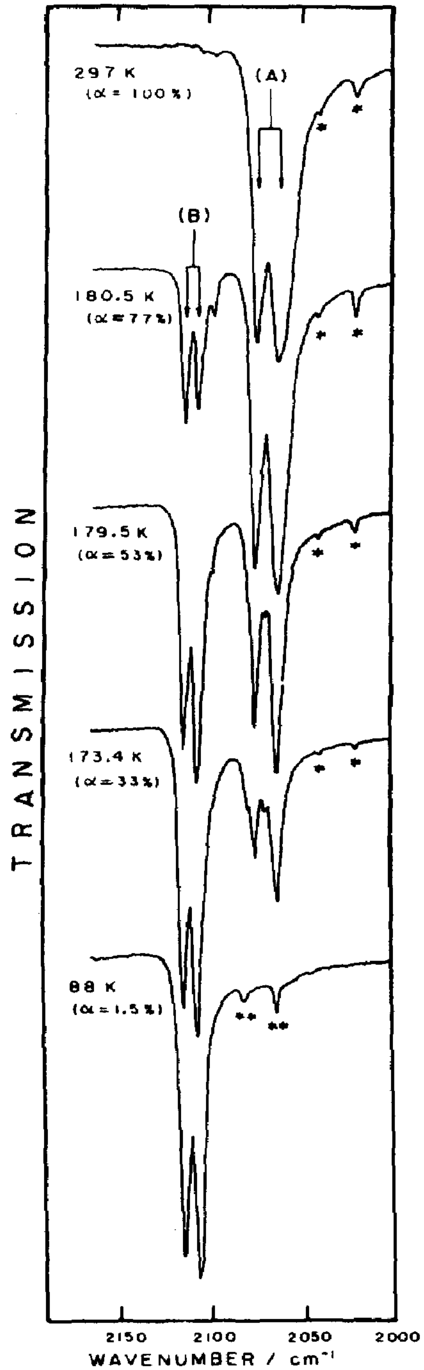

Fig. 3. Variation of the IR spectrum of $[Fe(phen)_2(NCS)_2]$ with temperature in the region of the C–N stretching frequency. Doublets (A) and (B) are assigned to $\nu_1(C^{12}-N)$ in the $^5T_2$ and the $^1A_1$ ground states, respectively. Weak bands marked with * and * * are due to ν_1 $(C^{13}-N)$ in the $^5T_2$ and the $^1A_1$ ground states, respectively. α indicates the HS content estimated from the peak areas. (Reprinted with permission from ref. 45.)

Mössbauer spectroscopy, so that the reconversion rate must be less than 10^7 s^{-1}, the precession time of the ^{57}Fe nucleus. With respect to continuous transitions, many complexes have been reported to have a single quadrupole doublet over the entire temperature range investigated [40,46,60–70]. In iron(III) coordination compounds the appearance of distinct EPR signals for the HS and LS species fixes a value of ca. 10^{10} s^{-1} for the upper limit of the transition rate. A slightly different situation is encountered in the complex $[Co(nnp)(NCS)_2]$ [33]: its EPR spectrum ($g_{\parallel} = 2.02$ and $g_{\perp} = 2.32$) from room temperature to 77 K is indicative of the presence of LS molecules and, accordingly, the intensities of the signals increase on cooling, but no signal due to the HS form has yet been recorded. HS cobalt(II) complexes give EPR signals too broad to be detected, except at liquid helium tempera-

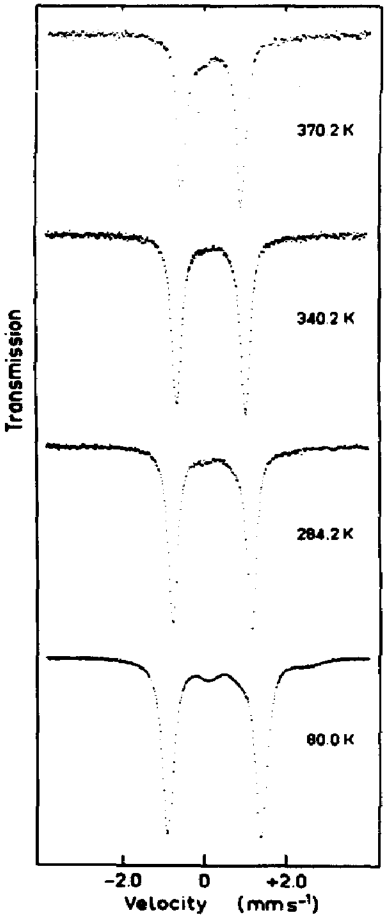

Fig. 4. Mössbauer spectra of $[Fe(P_4)I]BPh_4$ enriched to ca. 30% of the isotope ^{57}Fe at the temperatures of 80.0, 284.2, 340.2 and 370.2 K. The weak line at the center of the spectra is due to an unidentified impurity. (Reprinted with permission from ref. 70.)

ture, and on this basis Gatteschi et al. [33] attribute an interconversion rate slower than 10^{10} s^{-1}. However experimental data do not allow us to exclude a priori a more rapid intramolecular rearrangement. Indeed a similar fast rearrangement could be effective in the series of $[Fe(P_4)X]BPh_4$ complexes (X = Cl, Br, I) [35,71,72], which are one of the few examples of singlet–triplet spin crossover in iron(II) complexes. Closely related behavior is also shown by oxyhemoglobin, for which an analogous singlet–triplet spin equilibrium was assumed [73], while the Mössbauer spectra of $[Fe(1,10\text{-phenanthroline-2-carbothioamide})Cl_2] \cdot H_2O$ show two overlapping doublets, attributed to slowly interconverting singlet and triplet forms [74]. Instead the Mössbauer spectra of $[Fe(P_4)I]BPh_4$ show only one doublet from 4.2 K up to 370 K (Fig. 4) [70]. Moreover the electronic spectra exhibit a band at 7500–8500 cm^{-1}, which disappears at liquid nitrogen temperature [71,72]. By contrast, a very broad EPR signal can be recorded above room temperature [75]. These experimental data could be interpreted assuming a distribution of vibronic levels having different contributions from the pure triplet state [48] (see Section C).

(ii) Spin equilibria in solution and in biological systems

Usually the magnetic susceptibility of a solute molecule is measured using the Evans [76] NMR spectroscopy method. Alternatively a superconducting magnetometer, which is particularly suitable for metalloproteins, can be used in the whole temperature range between liquid helium and room temperature [77,78].

One may compare the experimental results obtained for spin crossover systems in the solid state and in solution; in the latter case, there are no abrupt transitions and no "anomalous phenomena", such as hysteresis. This can easily be understood if one admits that such effects originate in domains, which of course do not occur in solution.

Laser Raman temperature-jump [79–86] and ultrasonic absorption [87,88] techniques have allowed measurement of the conversion rate in solution. For all the systems investigated the conversion rates are in the range 10^5–10^9 s^{-1} and, as a rule, for the same complex, they are faster than in the solid state at comparable temperature. A theoretical treatment, which describes the spin transition process in terms of a non-adiabatic multiphonon radiationless transition, was able to account satisfactorily for the observed values [89]. Indeed the non-adiabaticity of the electron transfer process in the HS–LS conversion is justified by theoretical considerations [89] and supported by experimental data [88].

The dynamics of the spin change in a wide range of solvents has also been studied by pulsed-laser excitation in the ligand-to-metal charge transfer absorption band of iron(II) and iron(III) complexes [90,91]. Laser pulses excite LS species and a successive intersystem crossing, for which a rate of about 10^{11} s^{-1} is suggested, populates the potential energy surface of the HS state. This latter acts as a trap for the initially populated LS state and a further spin relaxation restores the equilibrium. The measured ground state recovery times are in agreement with the values obtained by the above mentioned laser Raman temperature-jump technique, while the high intersystem crossing rate probably implies strong coupling between charge transfer and LF states [90].

Electronic absorption spectroscopy, owing to its very short time of measurement ($\tau \approx 10^{-15}$ s), is usually able to differentiate the simultaneous presence of HS and LS species and often a thermochromic behavior of the solutions is observed because the bands characteristic of the HS chromophore tend to disappear at low temperature, while the bands of the LS one are strongly enhanced. However such a situation does not always occur and only minor changes in the absorption band shape can be revealed [83].

The spin conversion rate for $\Delta S = 1$ (ΔS is the variation in spin multiplicity) is comparable with the experimental data obtained for $\Delta S = 2$ [83] so that the spin change is not the main rate-determining process. Instead a pre-eminent role in affecting the conversion rate is played by ligand rearrangements. In fact the spin change is very likely accompanied by a substantial modification of the coordination geometry owing to greater occupancy of the antibonding orbitals in the HS form. Direct support for this hypothesis comes from the long conversion time measured for complexes with more sterically hindering ligands. In particular chromophores with two tridentate ligands reconvert more quickly than the similar chromophores with hexadentate ligands [84].

Often the conversion rate is strongly affected by the nature of the solvent. For example hydrogen bonds, i.e. with amino or imino groups of the ligands, are highly influential in determining the LS and HS distribution [80,82]. On the other hand ligand rearrangements can be hindered by the solvent–ligand hydrogen bond network.

These facts also reflect upon the entropy change associated with the spin transition. As a rule the observed values are larger than the electronic contribution due to the variation of the spin degeneracy and the excess entropy can be attributed mainly to ligand conformational changes and/or solvent–sphere reorganization [83,85].

The previous considerations suggest that in the case of metalloproteins the spin state change is accompanied by a rearrangement of the protein portion so as to imply a "functional role" of the spin equilibrium. Furthermore the occurrence of a spin crossover should help electron transfer in redox processes and actually many metalloproteins, in which spin equilibria are found, are involved in enzymatic oxidation/reduction reactions. Finally the spin state can represent a very good "probe" to investigate the microenvironment of the active site.

Spin equilibria in biomolecules were first reported in 1937, when Coryell et al. [92] observed that an increase of pH reduced the magnetic moment of ferric hemoproteins. Several years later the occurrence of a spin equilibrium in hemoglobin and myoglobin hydroxide was again suggested by Theorell and Ehrenberg [93,94]. Theoretical considerations [95] and further experiments [95–98] strongly supported the existence of a thermal equilibrium between HS and LS species. Hydrostatic pressure measurements [99–101], which showed a spectral shift in ferric hemoglobin and myoglobin complexes in agreement with the HS–LS transitions, gave a definitive positive answer to the problems of the existence of spin equilibria in hemoproteins.

Among the various metalloproteins only hemoproteins and their derivatives so far appear to possess all the requirements necessary for the occurrence of a spin crossover. In a series of papers [102–109] Kotani and coworkers laid the basis for subsequent work on the magnetic susceptibility of hemoproteins and since then the literature has flourished. Here I quote only a few of the papers appearing prior to the end of 1986 by including only those most relevant to this discussion [110–162].

The proteins containing an iron porphyrin (four pyrrole rings linked together by four methine bridges so as to form a 16-membered ring, inside which is situated an iron ion) as a prosthetic group are known collectively as hemoproteins. The prosthetic group is more properly called heme for iron(II) porphyrin and hemin for iron(III) porphyrin. In proteins axial ligation occurs giving five- or six-coordinated iron complexes. In some cases, as in hemoglobins or in myoglobins, the protein provides a single axial ligand and the vacant sixth position is protected by the tertiary protein structure for binding small molecules or ions (O_2, OH^-, H_2O). By contrast, other proteins, like some cytochromes, provide both fifth and sixth ligands. Usually spin equilibria are observed in ferric hemoproteins, where a delicate balance between LF strength and electronic repulsion is achieved, because only slight modifications of the stereochemistry or ligands are sufficient to induce a spin crossover. Indeed axial ligands have a large influence in determining spin equilibrium. For example, ligands such as azide form spin equilibrium ferric hemoprotein complexes, while F^- and CN^- form HS and LS species, respectively, when they are bound to the same proteins. Studies on catalase model systems and other ferric hemoproteins [144,145,151] have stressed the importance of the axial ligation at the sixth position. However the spin equilibrium can be further modulated by the stereochemical changes of the globin surrounding the hemin. Actually it was suggested [139–141] that axial ligation could be controlled by the quaternary structure of the protein. Anyway, conformational changes and spin equilibrium are undoubtedly related to each other and one could wonder whether such a link is significant for the enzymatic activity. An attractive hypothesis proposed [114] a coupling between electron transfer and oxidative phosphorylation through the conformational changes induced by the spin conversion. It may also be possible that there is control of the spin equilibrium by the substrate [112] or even by an organism, which could change the protein environment [148]. However high-pressure difference spectroscopy on camphor-bound cytochrome P-450 [161] has shown that global conformational changes linked to the spin equilibria are small. Instead further spectroscopic studies on camphor-bound cytochrome P-450 [156] and other methemoglobins [158] suggest that only a localized conformational change is involved in controlling the spin equilibrium. In the former case [156] a change in the microenvironment of a single tyrosine residue, which is probably an integral part of the active site or very close to it, accompanies the spin state change. In the latter case [158], resonance Raman, optical absorption and circular dichroism measurements were performed to examine the effect of the addition of inositol hexaphosphate. The results obtained seem to exclude the iron out-of-plane position or the iron–proximal histidine bond being involved in the spin state change due to the protein binding of inositol hexaphosphate. Rather, changes in the structure and electronic properties of the hemin induced by tertiary structural changes and orientation changes of the proximal histidine may heavily affect the spin equilibrium.

The addition of non-denaturing quantities of different alcohols to ferric hemoglobin has also been investigated using EPR spectroscopy [157]. The presence of alcohol molecules favors LS species, the EPR signals of which borrow intensity from the HS form; moreover a broadening of the HS resonance around the $g_\perp$ region can be detected. Ruling out the possibility that the alcohol molecules are directly bound to the iron at the sixth position (the results are independent of the type of alcohol used), it is likely that a direct alcohol–protein interaction can promote a rearrangement in the proximity of the hemin group like the binding of the distal histidine. Indeed the alcohol-induced broadening could be interpreted on the basis of a departure from tetragonal symmetry. Moreover, since two alcohol molecules per hemoglobin molecule are involved in the process, it is likely that only α or β subunits interact with alcohol molecules, while the other HS subunit is slightly modified through the intermolecular forces governing the quaternary structure of the protein.

As for the spin conversion rate in hemoproteins, the results are spread in a wide range from a few nanoseconds to 1000 s in a high viscosity medium [121,134,147,148,152]. Such differences can be understood by assuming that the spin equilibrium is linked to a simple rearrangement of the iron and ligands in the first coordination sphere (as in common coordination compounds) or to a much larger reorganization of the protein portion and the solvent, depending upon the boundary conditions in which the experiments are carried out. In any case, the spin conversion process is mainly intramolecular, as proven by spectroscopic measurements on frozen samples [151]: EPR and visible spectra are temperature dependent, although ligand exchange does not occur.

The only one spin equilibrium so far reported for a biomolecule containing iron(II) concerns oxyhemoglobin. For a long time this molecule was assumed to be diamagnetic, but magnetic susceptibility measurements of aqueous solutions of human oxyhemoglobin between 25 and 250 K [135] indicated a small paramagnetic contribution which was interpreted on the basis of a singlet–triplet spin equilibrium [73]. Actually spin triplet states can be stabilized by lowering the chromophore symmetry as shown by semi-empirical INDO-SCF-CI calculations [163]: moreover, the presence of low-lying triplet states could have a functional role by favoring the oxygen bond to the heme. However, very recently more accurate measurements [182] which suggest a full diamagnetism for oxyhemoglobin have been carried out. Accordingly, eventual low-lying triplet states should not be sufficiently stabilized to affect the magnetic susceptibility data.

C. VIBRONIC COUPLING

The experimental data for spin equilibria in solution agree well with an essentially intramolecular process, while interactions between two (or more) chromophores appear to be negligible. A quite different situation occurs for spin equilibria in the solid state. Indeed, although a clear cut distinction between inter- and intramolecular interactions is difficult, as shown by very recent experiments [40], many crystals are known where cooperative effects are indispensable for the understanding of their spin equilibrium, while for other systems the influence of such effects is not evident. However in both cases coupling with the vibrational modes plays a fundamental role and one could wonder whether, even in the most typical examples of cooperativity, local effects, acting as a trigger for successive transformations, are the main cause of the process. Actually there exists a close resemblance between the phenomena connected to a spin crossover situation and the JT effect [164–166]: in fact both the localized and cooperative JT effect can be observed, the latter occurring owing to interactions among JT centers near to one another. Finally, the JT coupling has been considered to be the most effective driving force for the spin transition [167–169].

(i) Intermolecular coupling

The first cooperative model for HS–LS transitions is due to Chestnut [170], who attempted to interpret the magnetic excitation spectra of tetracyanoquinodimethane-ion-radical salts. This model is a molecular field model involving a two-body interaction between HS and LS ions. The starting Hamiltonian is

$$H = NKQ^2 + \sum\nolimits_i (\Delta - VQ)n_i \tag{1}$$

where K is the elastic constant, Q is the displacement of the breathing mode from the equilibrium position in the pure LS form, Δ is the energy of the HS state at $Q = 0$, V is a coupling constant, which is taken to be positive, and finally n_i is the occupation number for the ith ion ($n_i = 0$, the ion is LS; $n_i = 1$, the ion is HS). The sum is extended over all the N ions.

The free energy per ion is given by

$$F = KQ^2 - k_B T \ln\left[1 + g \exp\left(-\frac{\Delta - VQ}{k_B T}\right)\right] \tag{2}$$

and accordingly the mean HS fraction can be calculated as

$$\bar{n} = \frac{g}{g + \exp[(\Delta - VQ)/k_B T]} \tag{3}$$

Here k_B is the Boltzmann constant and g is the overall degeneracy (spin + orbital degeneracy) of the HS state.

It is easily seen that at $Q = 0$ the system is LS, whereas the second term in eqn. (1) favors a HS state for large Q values. Depending upon the values of the parameters involved, three possibilities are found: (a) a continuous LS–HS transition; (b) a first-order LS–HS transition; and (c) thermal depletion of the HS ground state with increasing temperature. Moreover an applied magnetic field favors the HS state by lowering the transition temperature, which becomes 0 K at a critical field.

Chestnut's model is able to account qualitatively for the spin transitions in some transition metal complexes, but it fails in explaining residual paramagnetism, hysteresis effects or structural phase transitions accompanying spin-state transitions.

Later Wajnflasz and Pick [171,172] assumed that the metal ions may possess two stable equilibrium configurations with different ionic radii and a different LF energy level scheme. The interaction between the ions is represented by an Ising model still treated in the molecular field approximation.

Bari and Sivardière [173] extended Chestnut's model by including magnetic interactions between neighboring HS ions and also considered a two-sublattice model in which one sublattice is predominantly HS and the other LS. The Hamiltonian (1) is modified as follows:

$$H = NKQ^2 + \sum_{i\epsilon \mathrm{A}} (\Delta - VQ)n_i + \sum_{i\epsilon \mathrm{B}} (\Delta + VQ)n_i \tag{4}$$

where the summations are restricted to either sublattice A or sublattice B. The resulting interactions are of the form

$$-\frac{V^2}{4KN}\left(\sum_{\substack{i\epsilon \mathrm{A}\\ j\epsilon \mathrm{A}}} n_i n_j + \sum_{\substack{i\epsilon \mathrm{B}\\ j\epsilon \mathrm{B}}} n_i n_j - 2\sum_{\substack{i\epsilon \mathrm{A}\\ j\epsilon \mathrm{B}}} n_i n_j\right) \tag{5}$$

As can be seen from expression (5) the intra-sublattice interaction is attractive, while the inter-sublattice is repulsive. Depending on the parameter values used in the model, different kinds of behavior with a delicate balance between first- and second-order transitions are found.

Sorai and Seki [45] proposed an alternative model which closely follows the Frenkel theory of heterophase fluctuations in liquid [174]. It is based on the assumption that the phase transition is essentially first-order and that one phase contains embryos of a second phase in the transition region. Each embryo has a critical and uniform size.

Zimmermann and König [175] included the effect of low symmetry LFs and spin–orbit coupling. However the spin–orbit interaction is taken into account only within the quintet state $^5T_2$, while second-order interactions between $^1A_1$ and $^5T_2$ states through low-lying triplet states are neglected. An Ising-type interaction between the ith ion and the neighboring jth ions is also considered. This interaction only occurs between HS ions and does not depend upon the particular ionic pair or the spin state of the other neighboring ions. Accordingly the Hamiltonian is

$$H = \sum_i H^{(i)} = \sum_i \left[\sum_{m=1}^{15} E_m N_m^{(i)} - \epsilon \sum_{\substack{\text{neighbors}\\ jm,m'=1}}^{15} \sum N_m^{(i)} N_{m'}^{(j)}\right] \tag{6}$$

where 2ϵ is the interaction energy between HS states, and $N_m^{(i)}$ is the projection operator working on the mth state of the ith ion

$$N_m^{(i)} \,|\, m'\rangle = \delta_{mm'} \,|\, m'\rangle \tag{7}$$

and the energy of the LS state has been assumed to be zero.

By applying the Bragg–Williams approximation, the free energy per ion may be written as

$$F = (\Delta - k_\mathrm{B}T \ln \nu)\bar{n} - J\bar{n}^2 + k_\mathrm{B}T[\bar{n} \ln \bar{n} + (1 - \bar{n}) \ln(1 - \bar{n})] \tag{8}$$

with $J = \epsilon \cdot z$ and $\nu = \Sigma_{m=1}^{15} \exp[-(E_m - \Delta)/k_\mathrm{B}T]$, where z stands for the number of interacting neighbors. In eqn. (8) the first term corresponds to the free energy of the HS states, the second term results from the HS–LS interaction and the third term represents the entropy contribution due to the phase mixing, so that there is a close resemblance with the regular solution theory.

Instead, following the molecular field approximation, the free energy is written

$$F = J\bar{n}^2 - k_B T \ln\{1 + \nu \exp[-(\Delta - 2J\bar{n})/k_B T]\} \tag{9}$$

It is interesting to note the mathematical similarity between eqns. (2) and (9), in spite of the different physical approach.

Equations (8) and (9) provide the same minimum points

$$\bar{n} = \frac{\nu}{\nu + \exp[(\Delta - 2J\bar{n})/k_B T]} \tag{10}$$

Both discontinuous and continuous transitions are obtained from relationship (10).

A further advance in the Zimmermann–König theory is the inclusion of contributions from lattice vibrations within the approximation of the Debye model. Two different Debye temperatures are assumed for the HS (θ_h) and LS (θ_l) forms with $\theta_l > \theta_h$ owing to the weaker bonding of the iron in the HS state. By introducing a mean Debye temperature $\theta = [\theta_l^2 + (\theta_h^2 - \theta_l^2)\bar{n}]^{1/2}$, eqn. (8) is modified as

$$F = (\Delta - k_B T L_{tot})\bar{n} - J_{tot}\bar{n}^2 + k_B T[\bar{n} \ln \bar{n} + (1 - \bar{n}) \ln(1 - \bar{n})] \tag{11}$$

Here

$$L_{tot} = \ln \nu + aN\Delta\theta/T$$

and

$$J_{tot} = J + bNk_B(\Delta\theta)^2/\theta$$

where $\Delta\theta = (\theta_l^2 - \theta_h^2)/2\theta_l$, while a and b are functions of θ_l only.

Thermal hysteresis is taken into account in the paper by Zimmermann and König [175] and in a subsequent paper by Zimmermann [176]. Hysteresis effects are interpreted as a result of the existence of two minima for the free energy, as is yielded by eqn. (11) for temperatures in the neighborhood of the transition temperature. Nucleation processes are believed to be essential for the transition to occur and the nucleation rate is subject to strong variations due to the different surface energy for the different microcrystals. Accordingly, transitions will occur only for sufficiently large superheating or supercooling, though the transition temperature is the same for all microcrystals.

An improvement of the Bari–Sivardière model was made by Ramasesha et al. [177], who also took into account the kinetic energy term in the Hamiltonian

$$H = \left[\left(P_Q^2/2M\right) + \left(1/2M\omega_b^2Q^2\right)\right]\mathbf{I} + (\Delta + VQ)\sigma_z \tag{12}$$

where P_Q, M and ω_b are, respectively, the momentum conjugate, the effective mass and the fundamental angular frequency concerning the Q mode; $\mathbf{I}$ is the 2×2 unit matrix and σ_z is the Pauli spin matrix. It is shown that the dynamics of the lattice wash out any phase transition, which could arise from a static and linear coupling of the displacement to the spin states. The same authors also considered that the HS and LS states can be mixed by coupling to the lattice and the coupling is assumed to be quadratic in displacement since there is no reason for a directional dependence. The resulting Hamiltonian is

$$H = \left[\left(P_Q^2/2M\right) + \left(M\omega_0^2Q^2/2\right)\right]\mathbf{I} + \Delta\sigma_z + aQ^2\omega_0^2\sigma_x/2 \tag{13}$$

Starting from the above Hamiltonian, a non-zero population of the HS states at cryogenic temperatures is found, but no spin-state transition results. On the other hand the dynamic two-sublattice model does lead to a phase transition by means of coupling between the single octahedra. Moreover the coupling of the spin states to the cube of the lattice displacement can lead to a first-order phase transition. Therefore a two-phonon model was suggested in which an ion-cage mode mixes the spin states, while the linear coupling of the spin states to the breathing mode occurs without mixing.

Later, Kambara, in three papers [167–169], independently developed some of the above concepts by including JT interactions within the orbitally degenerate levels $^5T_{2g}$ or $^2T_{2g}$. The local JT distortion is considered the driving force for the transition, which can occur not only between HS and LS states, but also between the two HS states split by the distorting mode Q_θ, that is the θ component of the JT active vibrational mode ϵ_g. Indeed only ϵ_g vibrational modes are considered, while the other JT active vibrations of τ_{2g} symmetry are neglected. Thus the Hamiltonian of the system may be written

$$H = \sum_i h_i + NKQ_\theta^2/2 \tag{14}$$

where the Hamiltonian h_i for a single ion in the ith molecule is given by

$$h_i = h_0 + V_0 + V_{so} + (\delta V/\delta Q_\theta)_0 Q_\theta + \left(\delta^2 V/\delta Q_\theta^2\right)_0 Q_\theta^2/2 \tag{15}$$

Here h_0 is the Hamiltonian for the free ion, V_0 is the octahedral LF, V_{so} is the spin–orbit interaction and the derivatives are computed at the undistorted configuration.

Unlike previous models the phase transition can occur more than once over a certain range of coupling strength. The order parameter of the transition is the local displacement Q, which, for an ${}^1A_{1g}$–${}^5T_{2g}$ spin crossover problem, is given by

$$Q = M^{1/2}\omega Q_\theta = \frac{5a\exp(-\Delta/k_BT)[\exp(aQ/k_BT) - \exp(-1/2aQ/k_BT)]}{1 + 5\exp(-\Delta/k_BT)[\exp(aQ/k_BT) + 2\exp(-1/2aQ/k_BT)]} \tag{16}$$

the parameter a being the JT coupling constant to the tetragonal ϵ_g modes. For an intermediate energy separation Δ, the system changes from the undistorted phase ($Q_0 = 0$) to the tetragonally distorted phase ($Q_0 \neq 0$) and returns to the former undistorted phase as the temperature increases.

The first crude suggestion [167] was developed in two successive papers [168,169] by considering cooperative effects induced by molecular distortions. In particular the discontinuous HS–LS transitions may be induced by coupling with the uniaxial distortion, while the continuous transitions arise from the coupling with the breathing mode. Moreover the intramolecular distortions were treated as dynamic variables and the intermolecular coupling between the intramolecular distortions was also taken into account. Actually a weak local JT effect is expected for d^5 and d^6 ions in octahedral symmetry, since only π interactions are involved during deformation [178]. In spite of this it has been shown [169] that, even for intramolecular coupling too weak to induce singly the spin transition, lattice strain may play a fundamental role in inducing the spin transition.

(ii) Intramolecular coupling

In the above section much attention was paid to coupling with vibrational modes in order to explain cooperative effects. However it is our opinion that such coupling is also of primary importance from an intramolecular standpoint.

In 1981 a simple semiclassical model was proposed [179], which was able to account for spin transitions within a short range of temperatures by considering only intramolecular interactions. The model took into account two potential wells, one for each pure spin state, separated by an energy barrier. The transition rate w was computed in the semiclassical WKB approximation [180] and was expressed as

$$w = \frac{\sum_i D_i \nu_i \exp(-E_i/k_BT)}{\sum_i \exp(-E_i/k_BT)} \tag{17}$$

where ν_i is the vibrational frequency into the well for the ith level and D_i the transmission coefficient for the ith level with energy E_i.

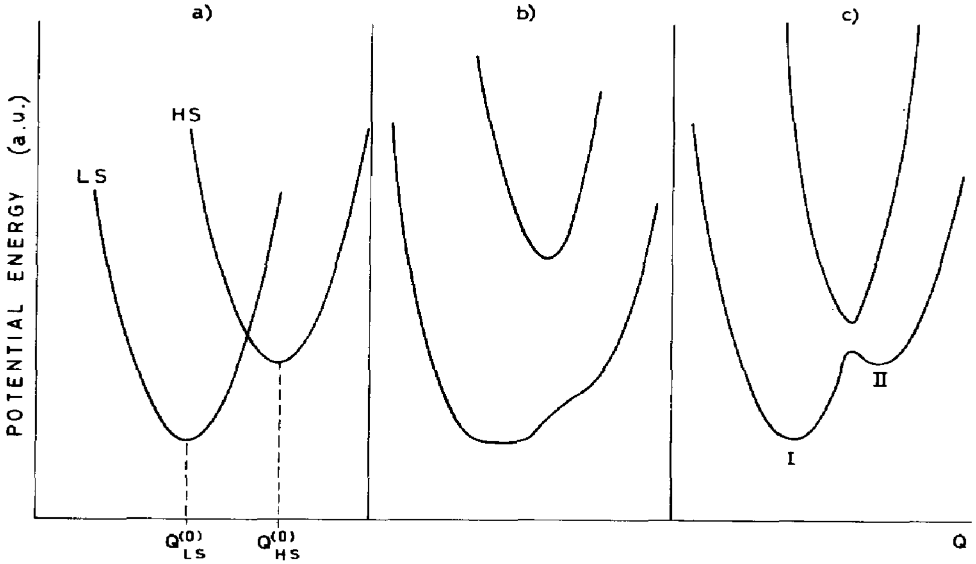

Fig. 5. Cross sections along the generic coordinate Q: (a) uncoupled LS and HS levels; (b) strong coupling; (c) weak coupling. (From ref. 48.)

The intramolecular transition process between two potential wells corresponding to two different spin states was then reconsidered qualitatively by Federer and Hendrickson [67] and very recently put on a more quantitative basis [48]. In these papers HS–LS interconversion is considered essentially as an intramolecular electron transfer, which involves a single chromophore, though the role of cooperativity in inducing phase transitions is not denied.

Another long debated problem consists in the possibility of identifying or not, single spin species and this is closely related to the interpretation of continuous or abrupt interconversions. An attempt to settle the problem has been made [48]. Actually pure spin states in a real physical system are an idealization, because they are not stationary states and are mixed to various degrees by spin–orbit coupling and other weaker perturbations. Depending upon the strength of the coupling, different situations are possible (Fig. 5). If the two energy surfaces of Fig. 5(b) are well separated, is it correct to speak about HS or LS states? Indeed the whole system will behave as if it were constituted of only one kind of molecule with an intermediate spin state. Accordingly, bond angles, distances and other physical properties will change gradually with temperature like "normal" molecules due to anharmonicity of the potential. The case depicted in Fig. 5(c) is quite different. Here states I and II can be differently populated mainly because of thermal activation even if, in some favorable cases, quantum tunneling across the barrier cannot be ruled out. Apart from the strength of the coupling, the magnitude of the displacement between the two pure spin states also plays a role in determining the final energy surfaces: large displacements do favor the situation in Fig. 5(c). Therefore this latter situation may more easily be encountered in complexes of Fe(II) and Fe(III) exhibiting singlet–quintet and doublet–sextet spin equilibria respectively, because spin–orbit coupling is effective only to second-order and a much larger displacement of the minima is expected [48]. Instead the situation in Fig. 5(b) is more typical of singlet–triplet and doublet–quartet spin equilibria in Fe(II) and Co(II) complexes, respectively.

However in real physical systems the situation is further complicated by the presence of those spin–orbit levels, which are not coupled by the spin–orbit Hamiltonian because of symmetry rules, and therefore the transition to these levels can be thought of as an intersystem crossing.

The problem of detecting pure spin species can be considered under two seemingly different theoretical points of view.

Let us assume we know the eigenvalues and eigenfunctions of the Hamiltonian of a given system. The various stationary states will be populated to a different extent depending on temperature, and each stationary state will be a mixture of spin states. Therefore, if we perform a measurement suitable to detect stationary states, we shall have information concerning an "intermediate" situation. In fact, because of the uncertainty principle ΔE, $\Delta t \geqslant \hbar/2$. The detection of stationary states requires slow measurements (large Δt) so that the associated uncertainty in energy (ΔE) is much less than the separation among stationary states. On the contrary fast spectroscopic techniques have an associated uncertainty of energy, which is larger than the separation of the stationary states and, as a consequence, non–stationary states, like pure spin states, can be "seen".

Alternatively we can get a better visualization by following the time evolution of a pure spin state. An initial pure spin state can be described by means of a function $\Psi(Q)$ (Q is a generic coordinate), which is expanded in terms of a complete set of stationary states Φ_i

$$\Psi(Q) = \sum_i c_i \Phi_i(Q) \qquad (18)$$

The time evolution is given by

$$\Psi(Q,\, t) = \sum_i c_i \Phi_i(Q) \exp[-(i/\hbar)\epsilon_i t] \qquad (19)$$

where $c_i = \langle \Phi_i \,|\, \Psi \rangle$.

If there is a potential well for each pure spin state, the probability of finding the system in the second well after a time t can be obtained by resolving the integral

$$P(t) = \int_{Q_{\text{crossing}}}^{\infty} |\Psi(Q,\, t)|^2 \mathrm{d}Q \qquad (20)$$

Otherwise one can follow a simpler approach [89], which is able, with some restrictions, to take into account the temperature effect. In such an approach the conversion rate is expressed according to Fermi's golden rule

$$w = (2\pi/\hbar) g \, |V|^2 G \qquad (21)$$

where g is the total degeneracy of the final state, V is the matrix element that couples the two pure electronic states and G is the thermally averaged nuclear Franck–Condon vibrational overlap factor.

The various terms in eqn. (21) can be evaluated by introducing suitable approximations and reasonable values for the conversion rate are obtained [48,89]. However this rate has probably to be slowed down by random perturbations [181]. In any way the spin conversion rates calculated for singlet–triplet equilibria in iron(II) complexes [48] are so high that, though slowed down by some order of magnitude, they still remain fast enough to hinder the detection of separate spin species.

D. CONCLUDING REMARKS

In the present review I have made an attempt to give a panoramic view of recent aspects of research on spin crossover systems. However spin crossover systems are nothing but a sub-ensemble of a much larger ensemble, which includes systems displaying electronic and/or stereochemical lability, such as mixed-valence or JT systems, for which, mutatis mutandi, many of the above considerations are still valid.

In the case of spin equilibria, magnetic measurements appear to be the most suitable to reveal the phenomenon. However many of the seeming incongruities, which were noted later on, when other physical measurements were performed, were just due to the magnetic susceptibility measurement. Indeed this is a measurement on stationary states, whereas other kinds of measurement may be so fast that they can detect non-stationary pure spin states.

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