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5. The Scientific Case

5. Chemistry

Panel:

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5.1 Introduction

In chemistry, the application of magnetic fields has a long tradition and has led to well established disciplines and techniques. Two main purposes in using high magnetic fields may be distinguished; the *probing* of structural and dynamical properties and the *controlling* of chemical processes and structures.

The ability of a magnetic field to function as a probe is usually based on the exploitation of the field dependence of some property of the chemical substance or system, including its interaction with radiation; i.e. various kinds of spectroscopies, of which NMR is the most vital and powerful one. Thereby detailed qualitative and quantitative information can be gained as to chemical composition (chemical analysis) as well as structural and dynamical properties. Structural aspects pertain to the characterization of the details of molecular geometry as well as of the energetics and spatial characteristics of the valence electrons, while dynamical aspects pertain to internal motions of the probed molecules as well as their molecular environment and to the rates at which elementary chemical processes take place.

At the molecular level, magnetic control of chemical processes is possible by the mechanisms of spin chemistry, applying in particular to chemical reactions with radical pair intermediates, whereas, including cooperative magnetic interactions, the modern field of molecular magnetism offers new possibilities for structural control by magnetic fields. In the following sections these several areas are discussed from the point of view of the likely impact of intense magnetic fields.

5.2 Molecular magnetism

Molecular magnetism is a rather new field of research which has emerged during the last decade or so. It deals with the physics and chemistry of open-shell molecules and of molecular assemblies involving open-shell units. What characterizes this field of research is its deeply *multidisciplinary* character. It brings together organic, inorganic, and organometallic synthetic chemists along with theoreticians, solid state physicists, materials and life scientists. The heart of the discipline nowadays concerns the design and the investigation of the physical properties of molecular assemblies exhibiting bulk properties such as long-range magnetic ordering or molecular bistability.

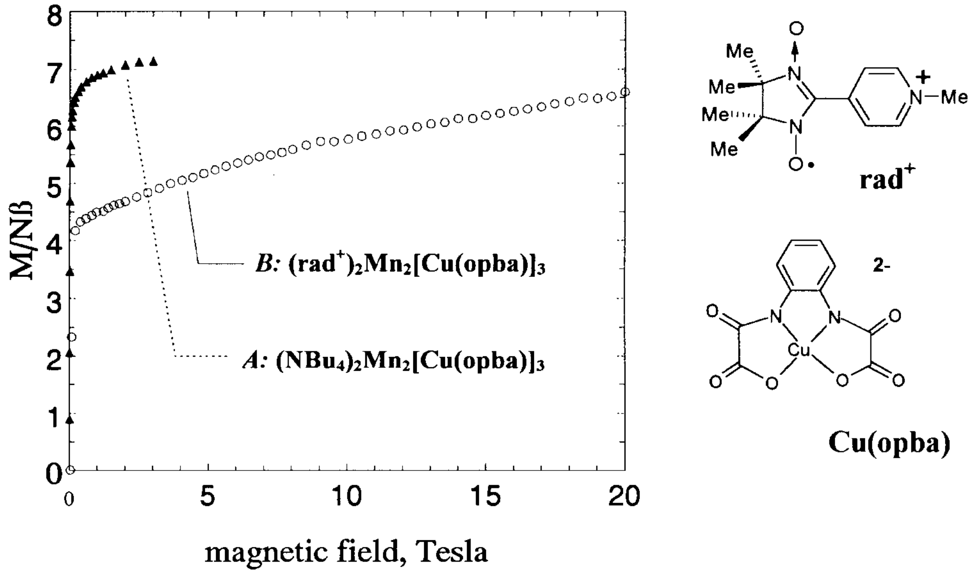
The first factor explaining the development of molecular magnetism, at the expense of the traditional field of magnetochemistry, is the shift of interest in molecular chemistry from isolated to collectively organized molecules (supramolecular chemistry). The initial successes in the synthesis of molecular conductors and superconductors prompted some scientists to try to synthesize molecular magnets, with a shift of interest from simple paramagnetic behavior to collective behavior. The development of supramolecular chemistry has some of its roots in the challenge of imitating biological molecules, in which properly organized building blocks form macromolecules capable of highly selective functions. Similarly, in the area of magnetism, nature sometimes uses molecular techniques to develop complex magnetic behavior patterns. Thus, the second important factor behind the emergence of molecular magnetism was the new understanding of the properties of complex biological systems ranging from heme proteins to iron-sulfur proteins, from superoxide dismutase to ferritin, and thus the mechanism of biomineralization. A third factor promoting renewed interest in molecular magnetism was the interest of solid state physicists in low-dimensional physics. During the last few years molecular magnetism has offered to the physicists quite a few exotic low-dimensional magnetic systems with unprecedented spin topologies. The final factor was the interest in new classes of advanced materials and the appearance of molecular electronics. One of the most exciting perspectives in molecular chemistry is the use of isolated molecules or assemblies of molecules in electronic circuits or devices. It is probably a rather long-term prospect, and the challenge is not to replace traditional (silicon) electronics, but to use molecule-based systems to perform functions that are not possible with silicon. Some ideas have already been proposed, with some advances made in switching, amplification, information storage, and signal processing.

5.2.1 Molecule-based magnets

For more than half a century it has been a dream for chemists to design molecule-based magnets. Today such exotic materials exist. The first ones were reported in 1986, both in America and in Europe. Ten years later, a few tens of molecule-based compounds exhibiting a spontaneous magnetization below a certain temperature are known. In contrast with the classical magnets which are opaque, the molecule-based magnets are usually weakly colored, so that one of the main issues concerns the synergy between magnetic and optical or photophysical properties. A very appealing perspective would be to design molecule-based magnets whose magnetic properties could be fine-tuned through light irradiation at given wavelengths.

The spin topology of most of the molecule-based magnets is rather complex, so that the effect of a high magnetic field is not as straightforward as for classical magnets. In many cases, even at 20 or 30 T, saturation is not reached. This situation is due to the fact that the compounds may present both ferromagnetic and antiferromagnetic interactions between uncompensated spins. At high enough fields, some decoupling of the antiferromagnetically coupled spins may occur, leading to unusual magnetization versus magnetic field curves (Fig. 1). In other respects, in purely molecule-based ferrimagnets, when the field is not too high, the temperature dependence of the product of the magnetic susceptibility exhibits a minimum at a certain temperature. This minimum is considered as the fingerprint of the ferrimagnetic regime. It has been suggested very recently from density matrix renormalization group (DMRG) calculations that this minimum should disappear in high fields somewhere between 30 and 80 T. There is a strong interest in the community about this prediction, and only a large field facility will allow confirmation or rejection of this conjecture.

Fig. 1: Magnetization (in Bohr magnetons per molecular unit) versus magnetic field curves for two molecular-based magnetic compounds showing long range magnetic ordering below 15 K (A) and 22.5 K (A). The magnetization curves were measured at 5 K (A) and 4.2 K (B), respectively. In compound A the ferrimagnetically coupled magnetic centers Mn^{II} and Cu^{II} are connected in a two-dimensional network whereas in compound B, where a third spin carrier rad^+ replaces the diamagnetic cation NBu_4^+ in A, the network becomes three-dimensionaly ordered. In A, full saturation of magnetization is attained within a few tesla, whilst in B, after a fast rise of magnetization at low fields, a slower rise follows which is not even saturated at 20T. This field dependence, the full analysis of which still needs measurements up to several times higher fields, bears important clues to the role of the magnetic coupling between the spin subsystems, the understanding of which is essential for developing new magnetic materials.



5.2.2 Molecular bistability and spin transition materials

The most spectacular example of molecular bistability is certainly provided by the phenomenon of spin crossover, or spin transition. Some transition metal molecular compounds can present a crossover between a low-spin (LS) and a high-spin (HS) state. This crossover may be induced by a variation of temperature, pressure, or by irradiation with light. In some cases, the thermally induced transition between LS and HS states is cooperative, occurring with well pronounced thermal hysteresis. In the family of Fe(II)-1,2,4-triazole compounds, for instance, the transitions occur around room temperature, with thermal hysteresis widths which may reach 50 K. Furthermore, the transitions are accompanied by a spectacular change of colour, from violet in the LS state to white in the HS state. Several of these compounds have already been used as active elements of display devices. Of course, the spin transition regime may be influenced by a magnetic field which shifts in energy the Zeeman components of the spin states. It would be very promising to investigate the response of such spin transition materials to an intense magnetic field. It has been suggested, but not verified to date, that this type of bistability could be induced by a very high field in materials which show no change of spin state in zero or weak field.

5.2.3 Nanoscale magnetic materials

A third exciting area in molecular magnetism, which was developed more recently, concerns molecular clusters of nanoscale dimensions. The interest here derives from the same ideas which result in the miniaturization of electronic devices. Matter on the nanoscopic scale has different properties, which could open up many new perspectives. One of these perspectives is to detect a transition from the quantum regime of microscopic particles to that of the thermodynamical regime, which applies to bulk magnets. Another appealing issue here is to demonstrate the effects of quantum tunnelling. Such effects have been found in a Mn_{12} molecular cluster. This cluster has a ground state with spin S=10 and a large magnetic anisotropy. When the cluster is in its ground state, the magnetization is preferentially oriented parallel to a tetragonal symmetry axis. It can be oriented either up or down, the two orientations having the same energy. For the system to reorient, it must overcome an energy barrier between the $M_S = +10$ and $M_S = -10$ states. Above about 60 K, the system easily passes over this energy barrier. On the other hand, at low temperature, reorientation becomes increasingly difficult, and at 2 K the time required for inverting the magnetization becomes of the order of one month. The cluster may be considered as a genuine molecular magnetic bistable device. Here again, the access to very high magnetic fields would be of the utmost importance to get new insights into the physics of this new class of compounds.

5.2.4 Chemical manipulation under very high magnetic fields

The last aspect of molecular magnetism covered here is the problem of knowing to what extent chemical manipulations under very high fields could provide new phases, or could preferentially yield a phase which is difficult to obtain under normal conditions. For example, the compound *para*-nitrophenyl-nitronyl-nitroxide, the first purely organic magnet, discovered by Kinoshita and coworkers [1], may exist in at least four phases, and only one of these phases, the β-phase , shows a long-range ferromagnetic ordering. This phase is difficult to obtain, and it has been suggested that a very high field would favor this magnetic phase during the crystal growing process. More generally, the use of very high magnetic fields to modify the output of chemical manipulations represents a virgin field, in which much can be expected (see also section 4).

The orientational ordering of large molecules is discussed in detail by section 6 in relation to Soft Condensed Matter. Here we want to add the interesting possibility that when using mesogenic magnetic metallopolymers the molecular ordering induced by the magnetic field due to the diamagnetic anisotropy of the mesogen would be accompanied by a very high magnetic anisotropy and it would be most interesting to study cooperative magnetic phenomena of such media in intense magnetic fields.

Finally we note that recent experiments in magnetic fields up to 8 T have demonstrated that the growth of crystals of diamagnetic compounds, even of low molecular weight, can be controlled by a magnetic field. The crystallization of proteins is one of the most difficult problems that must be solved to prepare samples suitable for structure determination by X-ray or neutron diffraction. The application of very high magnetic fields to promote the crystallization of large anisotropic macromolecules could make way for new break-throughs in the structure determination of biologically important macromolecules.

5.3 Magnetic resonance

In this section we will stress only the general chemical interest in developing magnetic resonance spectroscopy at higher magnetic fields. For more specific and more technological aspects we refer to the section 8 report below.

5.3.1 Nuclear magnetic resonance

One can hardly overemphasize the value of NMR as the chemist's most important analytical tool for molecular structure determination. The measurements of chemical shifts of various probe nuclei, their isotropic and anisotropic couplings and relaxation measurements have made detailed topological features of molecular structure accessible almost routinely. The main gain during the last two decades was achieved by increasing the resolution due to the use of higher fields, and hence frequencies, and the exploitation of more sophisticated pulse sequences in FT-NMR. The ultimate achievements in this respect represent the recent structure determinations of soluble proteins comprising as many as almost 300 amino acids. Indeed, expanding the limits in resolution and sensitivity requires the development of NMR technology beyond 18.8 T (800 MHz for ^{1}H-NMR). Pushing these limits forward would not only allow the analysis of larger molecules, with the use of the standard nuclei ^{1}H, ^{13}C, and ^{15}N but, due to the gain in sensitivity resulting from higher magnetic fields, would also expand the range of nuclei to less sensitive ones, so extending the range of chemical compounds amenable to this powerful analytical tool. Since, in higher fields, quadrupolar splittings become less significant relative to chemical shift differences, this will make the chemical shift of quadrupolar nuclei also more interesting as probes of their chemical environment.

Apart from the structural information regarding the average positions of nuclei within a molecular frame, which are encoded in NOE cross-peak intensities and the spectral positions and splittings, NMR relaxation times also hold a large information potential, illuminating dynamical aspects of intra- and inter-molecular motion (cf. section 5.3.4) and also of chemical reactions. The latter case shows up in spectral exchange processes between lines. The NMR time-resolution for such kinetics is determined by the chemical shift difference between the lines involved which will increase in proportion to the applied magnetic field.

Yet another kind of dynamical information, i.e. regarding kinetics and mechanisms of elementary chemical processes, may be encoded in the non-Boltzmann population of nuclear spin levels belonging to products formed during a chemical reaction with radical pair intermediates in a magnetic field (chemically induced nuclear polarization, CIDNP). For the exploitation of such effects, too, higher fields would open up new possibilities.

5.3.2 Electron paramagnetic resonance

Being restricted to molecular

species with unpaired electron spins, EPR does not have as wide a chemical scope as NMR, but it is, nevertheless, an invaluable spectroscopic technique in the study and characterization of paramagnetic chemical species.

The group of $S = 1/2$ systems comprises the important class of organic and inorganic radicals which usually occur as reactive intermediates in radical reactions and very often are involved in photochemical and radiation chemical reactions. On the other hand, a number of stable $S = 1/2$ systems are also known, e.g. stable organic and inorganic radicals of second row elements which are often utilized as spin probes, and numerous transition metal complexes, including metalloproteins. Structural information on $S = 1/2$ systems results from g-tensor and hyperfine-coupling (hfc) tensor parameters which allow chemical identification and electronic and conformation-related structural characterization, also with respect to the molecular environment of the spin probes. Here, as in NMR, an increase of field strength is tantamount to better spectral resolution and sensitivity.

It is sometimes possible in radical reactions for radical pairs to be trapped as they are generated. In closely coupled radical pairs the spin-spin interaction, in particular the exchange interaction, can be quite high due to an exponential increase of exchange energy with decreasing separation. Higher magnetic fields will move forward the frontiers of the study of such interactions by EPR. It is of interest that the detection of magnetic resonance in reactive radical pairs does not necessarily depend on a detection method which uses radiation in the frequency range of the resonance, but can utilize reaction yields to probe the field dependence of resonance absorption (that is, the reaction yield detected magnetic resonance, RYDMR, cf. section 5.4 on spin chemistry).

Molecular systems of interest, having more than one unpaired spin and $S > 1/2$, comprise excited molecular triplet states, organic polyradicals and mono- to poly-nuclear transition metal complexes, including many metalloproteins and building blocks of new magnetic materials. Also noteworthy are complexes of lanthanoid ions most of which belong to this class of $S>1/2$ compounds. For all these, EPR is an important tool when seeking to understand the relationship between electronic and geometric structure and for the identification of structure including, in particular, the molecular environment of active enzymatic centres. For $S>1/2$ systems, structure dependent interaction between the unpaired spins causes zero-field splittings which represent an important characteristic of the spin Hamiltonian of such systems and hence an important key to the structure. In fact, zero-field splittings can be much larger than the Zeeman splitting in available magnetic fields, in which case only incomplete information is available from magnetic resonance transitions. For this reason, as well as for the general argument concerning the improvement in sensitivity, a considerable increase in the scope of interesting molecular magnetic systems can be expected for EPR by increasing the range of accessible EPR fields.

Finally we mention that, as with nuclear spins, electron spin relaxation and chemically induced spin polarization effects are also highly informative phenomena which will benefit from the availability of higher magnetic fields.

5.3.3 Chemically induced magnetic polarization

The combination of magnetic interactions in radical pairs with spin conserving processes in the creation and recombination of such intermediates of radical reactions, can be a source of considerable deviation of spin level populations from thermal equilibrium. It gives rise to strongly enhanced absorption or emission lines detectable in the EPR spectra of paramagnetic intermediates or in the NMR spectra of diamagnetic products from radical reactions. These effects are known as chemically induced magnetic polarization (One should note the different usage of the term *spin polarization* here and in the context of molecular or metallic magnetism). From the polarization patterns and their dependence on various experimental parameters, including the magnetic field strength, detailed information can be obtained about the mechanism and dynamics of the underlying reactions. The application of high fields can be particularly useful in the case of radical pairs with strong exchange interaction, such as occur if the radical centres are closely connected by chemical links (small biradicals) or when the pairs are trapped in environments representing fairly rigid cages, i.e. in the solid state or in microheterogenous media.

In principle, chemically induced *nuclear* polarization (CIDNP) is easier to detect than electron polarization. Due to the long nuclear, T_1, spin relaxation times in diamagnetic compounds, which may be as long as several seconds, separate magnetic fields may be used to create the polarization, where the reaction is carried out, and then to measure the polarization by sample transfer in a flow line to a conventional NMR spectrometer. This technique has been successfully applied to investigate the field dependence of CIDNP in low fields and should be possible to employ with the very highest fields without the need to change the NMR technique.

In the case of chemically induced electron spin polarization (CIDEP), the polarization decays within microseconds or less and has to be measured in the field wherein it is created with time-resolved techniques. This represents a very direct observation method for paramagnetic reaction intermediates. It appears that as the applied fields and frequencies get higher, less microwave pulse energy is necessary to generate detectable signals, so that the pulses can be made shorter with a concomitant increase in time-resolution. Very high fields together with the corresponding high-field EPR technology are necessary to separate overlapping oppositely polarized (so compensating each other) spectral regions of two radical components in the case of radical pairs with *very small* difference in electronic g-factors.

5.3.4 Spin relaxation

While the spectral positions of magnetic resonance transitions yield information about time independent or time-averaged interactions of probe spins with their environment, other important information is encoded in dynamic observables, in particular in the spin lattice relaxation time, T_1. Energy exchange between a spin transition at some resonance frequency, ω_0, and the other intra- and inter-molecular degrees of ("lattice") motional freedom, requires a coupling of these lattice motions to the spin system and also that this coupling be modulated by stochastic lattice motions. The spectral power density of the stochastic perturbational force at the resonance frequency of the spin transition determines the spin-lattice energy exchange rate, T_1^{-1}. Thus, with this parameter measured as a function of magnetic resonance frequency (magnetic relaxation dispersion) it is possible to scan the power spectrum and thereby determine the dynamical characteristics of the lattice environment of the spin probe. Such modes of interest comprise molecular rotations and translational diffusion as well as conformational motions and other reversible chemical transformations. Different modes may be identified by their characteristic correlation times τ_c, leading to a characteristic drop of the power spectrum at $\omega_0=\tau_c^{-1}$. Thus it is clear that lattice modes of increasingly shorter correlation times may be probed through magnetic relaxation dispersion by increasingly higher magnetic fields.

The highest EPR frequencies in presently available *commercial* spectrometers allow the probing of lattice modes up to 90 GHz (3 cm^{-1}, 3 T). In commercial NMR spectrometers much higher magnetic fields (currently up to 18.8 T) are employed, but of course the corresponding NMR frequencies are lower (up to 800 MHz). There is however a way to utilize NMR fields and spectroscopy to probe EPR transitions indirectly through NMR in paramagnetic compounds, as in many transition metal complexes or metalloproteins. Here the relaxation time of the electron spin can be detected by its effect on the nuclear spin. Thus the highest NMR fields presently available can give access to electron spin lattice relaxation with energy quanta of 25 cm^{-1}. In an NMR field of 40 T, this range could be extended to 40 cm^{-1}. A further possibility to probe electron spin relaxation arises through spin chemical effects, as discussed in the next section, which, since they usually rely on optical probe techniques, could be measured even in pulsed fields of 100 T. Thereby, the effects of lattice motions could be assessed with 'formal' correlation times shorter than 10^{-13} s.

5.4 Spin chemistry

Spin chemistry denotes the area of chemical research devoted to the elucidation and exploitation of spin and magnetic field induced effects on chemical reactions. Although attempts to control chemical reactions by magnetic fields have a long history, the beginning of a systematic and successful evolution of the field dates back only about 30 years and depended largely on the discovery of some basic molecular mechanisms, involving spin control of reactivity in paramagnetic reaction intermediates, mostly radical pairs, with unpaired electron spins. These effects, which result in magnetic field dependent reaction yields and rates, or in non-equilibrium electron or nuclear spin polarization of products emerging from such reactions (cf. section 5.3.3), are essentially dynamical in nature and not a matter of thermodynamics, i.e. of chemical equilibrium. In spin chemistry one faces the remarkable situation that magnetic interactions that are small compared to thermal energies at usual reaction temperatures (> 200 K), and even much smaller than the reaction energies of the chemical transformations which they control, can be used to switch reaction probabilities and to control the flow into various reaction channels. These effects have a high potential for probing and acquiring an understanding of the dynamics of reaction intermediates.

The majority of spin chemical reaction effects are accounted for by the so-called radical pair mechanism. Important classes of reactions, among them many *photochemical* ones, including photosynthesis, proceed through radical pairs as reaction intermediates. These radical pairs can equilibrate between a set of nearly degenerate electron-nuclear spin states which, in spite of their near degeneracy, fall in two manifolds of states (electronic singlet and triplet) differing extremely in their chemical reactivity. Transitions between these manifolds can be induced by relatively weak interactions, e.g. hyperfine coupling, and are effective in modifying chemical reaction rates. External magnetic fields may have three different effects of spin chemical importance.

(i) The first is due to the Zeeman effect, causing level separations and crossings. Particular interest in using high external magnetic fields arises where radical pairs fixed at close distances are involved. Here the energy splitting between singlet and triplet (exchange interaction) may be too large to allow hyperfine induced singlet-triplet transitions in zero field, while such transitions may be feasible due to a singlet/triplet level crossing in a suitable external magnetic field. The present progress in the chemical synthesis of specially tailored supramolecular systems allows to make biradicals with well defined separation of radical centers for which high magnetic field spin chemistry as well as magnetic resonance spectroscopy can provide suitable methods of probing the electronic interaction between the two radical centers.

(ii) The second type of magnetic field effect is found in systems where the two radicals of a pair exhibit different spin-orbit coupling. This difference is reflected in different electronic g-factors and hence different coupling strength of the two radical spins to the external magnetic field. As a consequence, the external magnetic field disrupts the mutual alignment of the two radical spins which is equivalent to a field-induced mixing of triplet and singlet spin multiplicity. The transition rate, $\omega=\Delta g\gamma_e B/2$, is proportional to the magnetic field and to the difference in g-factors. Large effects will ensue if the spin transition rate can be tuned into the specific kinetic range of the chemical rate processes taking place within the radical pair. The highest magnetic fields applied so far to drive such transitions are still below 20 T. Recently it has been possible to probe fast electron transfer reactions with time constants of a few picoseconds in some reaction systems with high Δg involving transition metal complexes (Fig. 2). Other high field applications of this type of effect have been reported with the primary radical pair in photosynthetic reactions centers. The availability of higher magnetic fields, in the range 50-100 T, will allow the modification of the kinetics of many more systems in the nano- to femtosecond time domain and will be of particular interest in combination with detailed time-resolved studies of fast reactions in supramolecular entities.

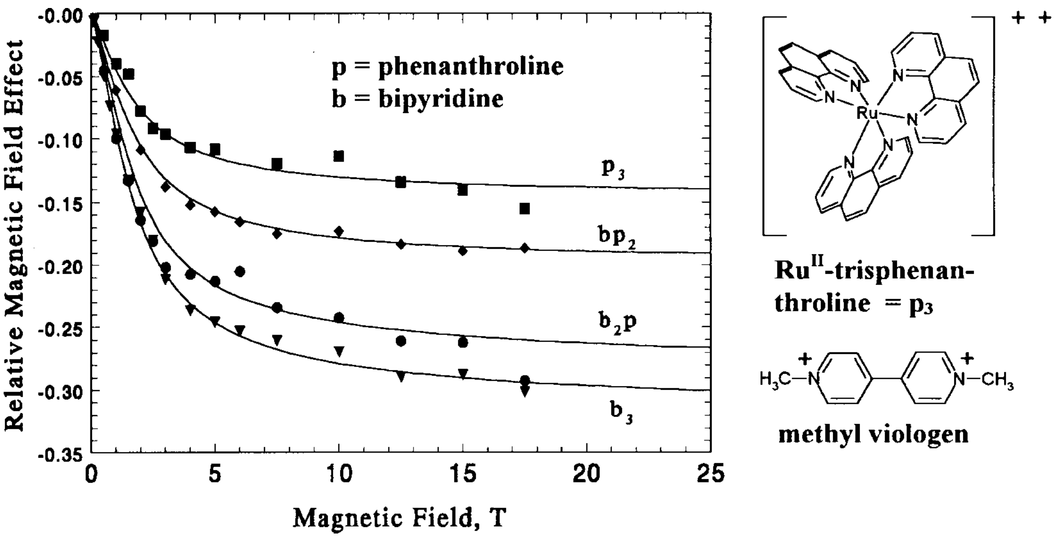


Fig. 2: Magnetic field dependence of the yield of separated electron transfer products in the photoinduced oxidation of various Ru^{II}-trisdiimine complexes by methylviologen. The yield decreases with increasing field due to a field-induced, Δg-dependent spin process, accelerating fast backward electron transfer prior to product separation in the primary pairs of electron transfer products. For these systems with their Δg~1 being exceptionally high, saturation of the effect could be reached at about 20 T, however for the great majority of systems of interest Δg is smaller and higher magnetic fields are necessary for attaining the full kinetic information inherent in this type of magnetic field effect.

(iii) As was already pointed out in section 5.3.4, a third type of spin chemical magnetic field effect results from the magnetic field dependence of spin lattice relaxation. In radical pairs chemical reaction rates are sensitive to spin transitions between the split Zeeman levels. Such transitions are brought about by the stochastic modulation of interactions with the lattice. Thus the magnetic relaxation dispersion can be probed through the magnetic field dependence of chemical reaction rates or yields. The advantage of this spin chemical method, as compared to the magnetic resonance one, is that, in contrast to the case of magnetic resonance spectroscopies, the optical methods usually applied for the detection of spin chemical effects do not require special technological adaptations when applied in high magnetic fields.

5.5 Optical spectroscopy

Whereas, in the optical spectroscopy of atoms, the study of magnetic level splittings, i.e. of the Zeeman effect, is of paramount importance for characterizing and assigning electronic states, such effects are less prominent in molecular spectroscopy. The reasons are twofold. First, the orbital contributions to the magnetic moment of electronic states is much reduced in molecules because usually they lack rotational symmetry. Thus orbital contributions to the Zeeman effect are small. Second, as a result of the greatly increased line widths in molecules, as compared to atoms, it is difficult to determine shifts and splittings. Because the Zeeman effect increases linearly with magnetic field, the availability of higher magnetic fields will extend the interest in, and the practical potential of, Zeeman effect studies in molecular spectroscopy. Of course, direct observations of molecular Zeeman effects will be most promising under conditions of high spectral resolution, i.e. in gas phase spectroscopy and low temperature spectroscopy of crystalline solids. But using special techniques, like spectral hole burning, less ordered systems can be investigated with narrow band resolution at low temperatures.

Besides energetic shifts displayed in the position of spectroscopic transitions, a second important effect of magnetic fields lies in the induction of dynamic effects, eventually observable in linewidths or excited state life times. This is a consequence first of changing energy separations, including level crossings, for close lying states with different magnetic moments. Intramolecular electronic relaxation is largely determined by the coupling between different state manifolds like singlet and triplet and is modified if the relative energies of these states change. Dynamic effects have been widely studied as magnetic field effects in gas phase luminescence spectroscopy. Extending the range of available magnetic fields will open up new ranges of level interactions. Such effects will very likely help to increase our understanding of the dynamics of intramolecular energy redistribution. A second aspect arises because the magnetic field itself can provide a coupling between different electronic states, thereby enhancing existing, or introducing new, channels of electronic relaxation, or allowing radiative transitions between states that are hidden in zero or low magnetic fields. The magnetic field induced predissociation of iodine is a famous historical example of such phenomena. Chemical effects of magnetic state mixing are of particular interest in the context of spin chemistry.

Finally, an important effect of the Zeeman separation of state energies in a magnetic field is to introduce chirality into optical transitions. This can be observed as magnetic circular dichroism (MCD), a phenomenon not restricted to high resolution spectroscopy. What circular dichroism spectroscopy achieves for chiral molecules or supermolecular systems with chiral properties (e.g. proteins of a regular secondary structure), namely the discrimination of small yet specific contributions of their optical absorption against a large absorption background of non-chiral contributions, is possible to exploit also for many molecular systems which do not have chiral chromophores or chirally ordered chromophores if one uses MCD spectroscopy.

MCD is an established spectroscopic technique with applications to molecules of high symmetry or at least derived from a parentage of high symmetry (aromatic molecules) and, furthermore, to many transition metal coordination compounds with degenerate or near degenerate ground states. Important representatives of the latter systems are found in metalloprotein enzymes. Here MCD is used as a structural investigation method offering an alternative and complementary approach to EPR. Significantly enhanced magnetic fields will inevitably widen the scope and potential of MCD for applications in structural investigation without requiring significant changes of the spectroscopic technique as in the case of EPR. For S>1/2 systems with large zero field splitting, high magnetic fields are particularly promising for extending the scope of possible applications.

5.6 Conclusion

Intense magnetic fields, beyond those currently available, are of wide application in many areas of Chemistry; molecular magnetism, magnetic resonance, spin chemistry and optical spectroscopy. In some cases, e.g. optical spectroscopy, the requirements on field homogeneity in space and constancy in time, are considerably less stringent than in magnetic resonance applications. Nevertheless, notwithstanding the interest in 100 T fields for exploring new forefront effects, for obtaining quantitative and precise data, steady fields of 50 T will be of wider application in this area than pulsed 100 T fields with a low repetition rate.

[1] Y. Nakazawa, K. Nozawa, D. Shiomi, K. Awagawa, T. Inabe, Y. Maruyama and M. Kinoshita, Phys. Rev. B 1992, 46, 8906,