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Spin oscillations as a new tool to study recombining radical ion pairs

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The singlet–triplet oscillations of radical pairs, which are fundamental for spin effects in chemistry, are a powerful tool to study short lived radical ions in solution. The detection of spin oscillations provides information on the ESR spectra, spin relaxation times and fast reactions of radical ions, which are not observable by ESR techniques.

After the discovery of chemically induced nuclear polarization in the late 1960s, it became clear that this phenomenon is due to dynamic singlet–triplet transitions between the spin states of recombining radical pairs. The transitions occur on a nanosecond time scale and are harmonic in nature, with the frequencies determined by the external magnetic field and the internal fields created by the magnetic nuclei of radicals (Figure 1). Singlet–triplet transitions in radical pairs are also responsible for such extraordinary phenomena as magnetic field effects in chemical reactions and magnetic isotopic effect.[1]

The question immediately emerged whether singlet–triplet oscillations could be observed directly in a time-resolved experiment rather than deduced from their manifestations in magnetic field and spin effects. Such a possibility would have opened an exciting way of both studying the partners of the recombining pairs and tracking fast reactions they are involved in.

The first successful observations of singlet–triplet oscillations were performed in the 1980s by Anisimov *et al*.[2,3] using specifically tailored model systems in a time-resolved experiment. The decay of recombination fluorescence from the sample induced by a short pulse of ionizing radiation was detected. The pulse creates an ensemble of radical ion pairs in a spin-correlated singlet state in solution with typical distances between the partners of the pair of about 100 Å. The pairs in such an ensemble synchronously oscillate between their singlet and triplet states, but they recombine with different delays after generation due to diffusion-controlled encounters of the oppositely charged ions. The moments when the pairs are predominantly in the singlet state are detected by an increase in fluorescence intensity, since more singlet excited molecules are formed upon their recombination.

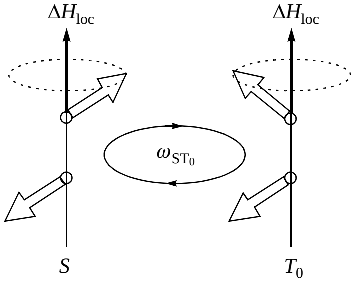
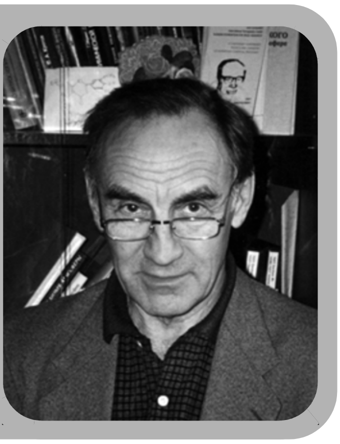


Figure 1 Vector diagram explaining the appearance of S–T_0 oscillations in a radical pair in a high external magnetic field. Oscillations arise if spins precess at different Larmor frequencies due to the difference ΔH_{loc} of local magnetic fields induced by hyperfine couplings and g-values difference.

Two simple model systems were chosen for demonstration experiments. In one system, the radical ions of the pair (p-terphenyl-d_{14})$^{\bullet-}$/$(C_6D_5)_2S^{\bullet+}$ had negligibly small hyperfine couplings (hfc) and substantially different g-values. As expected, the fluorescence decay curve for this system was modulated by harmonic singlet-triplet oscillations in the pair with modulation frequency increasing as the external magnetic field was increased (Figure 2). In the other pair, (p-terphenyl-d_{14})$^{\bullet-}$/ $Me_2C{=}CMe_2^{\bullet+}$, the g-values were nearly equal, but hyperfine couplings with 12 equivalent protons were present in the radical cation. In this case, the oscillations were shaped by internal hyperfine interactions in the pair, and experimental traces showed sharp periodically repeated maxima of the fluorescence intensity. This picture corresponded to the superposition of harmonic oscillations in radical ion pairs with different projections of the total nuclear spin on the direction of the external magnetic field, and the positions of the peaks were determined by the hyperfine coupling constant in the radical cation.

Bagryansky *et al*.[4] demonstrated that information on the spin dynamics of the pair is more conveniently extracted not from the original fluorescence decay curve but from the ratio of two such curves taken in strong and zero magnetic fields, that is, from a so-called time resolved magnetic field effect (TR MFE). Analysis of the TR MFE curves yields hfc constants, g-values and spin relaxation times of the test system[5] (Figure 3). Of course, these parameters could be obtained using ESR spectroscopy. However, because of their limited sensitivity and time resolution, conventional ESR techniques are in many cases inadequate for the detection of short-lived radical ions in solutions. For example, information on alkane radical cations is mainly provided by ESR studies at cryogenic temperatures. Significant progress in solution ESR was brought about with



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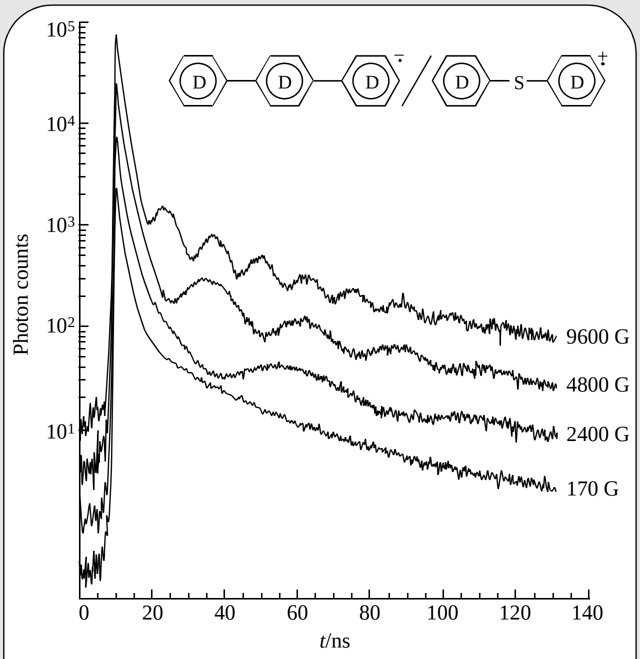

Figure 2 The decay of recombination fluorescence for a 10^{-3} M *p*-terphenyl-d_{14} and 3×10^{-2} M diphenylsulfide-d_{10} solution in isooctane in various magnetic fields. For convenience, the curves are displaced relative to each other.

the development of optically detected ESR (OD ESR) in stationary and time-resolved modes.[6,7] The inherently higher sensitivity of this method allowed, in certain cases, the detection of ESR signals in cooled liquid solutions. However, the ESR spectra of the radical cations of *n*-alkanes and cyclic alkanes still cannot be obtained.

The failure to detect the radical cations of *n*-alkanes can be attributed to the rather short lifetimes of radical cations, for which the values as short as nanoseconds to tens of nanoseconds had been reported.[8,9] OD ESR is not efficient under such circumstances due to its lower lifetime limit of several tens of nanoseconds. On the other hand, TR MFE allows one to expand the observable time range down to units of nanoseconds since it combines high sensitivity with time resolution as good as 1–2 ns in a working experimental installation.

Recently, Borovkov *et al.*[10] used the advantage of the TR MFE technique and for the first time obtained information on the ESR spectra of radical cations of C_8–C_{16} *n*-alkanes in solution.

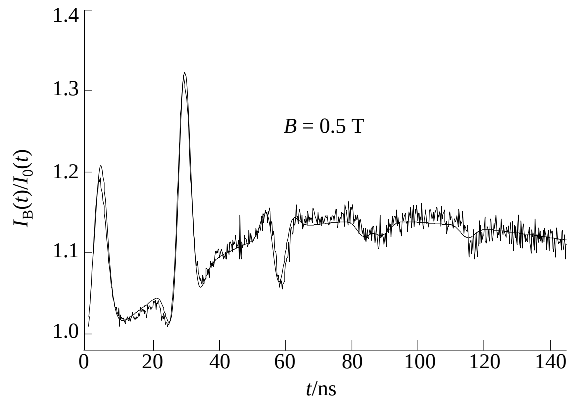

Figure 3 Experimental TR MFE curve for a 0.1 M hexamethylethane and 3×10^{-3} M *p*-terphenyl-d_{14} solution in *n*-hexane at 293 K in a magnetic field of 0.5 T. Smooth line is the approximation of experiment by the theoretical model. The peak positions are determined by the hfc constant with 12 equivalent protons in the hexamethylethane radical cation, the peak inversion is related to the *g*-value difference of radical cation and anion, the damping of peak amplitudes is caused by phase relaxation, and the long-time decay of the curve is a result of spin–lattice relaxation.

The test alkanes were added to liquid hexane together with small amounts of *p*-terphenyl-d_{14}. Under these conditions, the radical cations of hexane generated by ionization transferred their charge and spin to the molecules of the dissolved alkane, while excess electrons were captured by the molecules of *p*-terphenyl-d_{14}. Analysis of TR MFE curves demonstrated that the ESR spectra of radical cations were unresolved singlets with widths decreasing with lengthening of the *n*-alkane chain. Thus, the ESR spectra of the radical cations in solution differ substantially from their spectra in cryogenic matrices, which are known to be poorly resolved triplets. This difference has conformational nature: an *n*-alkane radical cation in a rigid matrix is usually frozen in a well-defined (normally all-*trans*) conformation, while in solution it undergoes rapid transitions between several conformers with different spin density delocalizations over the carbon chain. Fast conformational dynamics also results in substantially lower widths of solution ESR spectra as compared to spectra in frozen matrices.

As the concentration of the dissolved alkanes was increased, further narrowing of the ESR spectra was observed, which is characteristic of degenerate electron exchange. These experiments yielded the first estimations of the rate constant of exchange reactions involving alkane radical cations. It was found that in a hexane solution only approximately every hundredth encounter was effective for the charge transfer.

As opposed to normal alkanes, the radical cations of branched alkanes in solution, as follows from TR MFE results, often demonstrate broad ESR spectra with resolved structures.[5,11] This difference can be rationalised by noting that in the radical cations of branched alkanes the semioccupied orbital is usually localised at a single C–C bond adjacent to the branching point, and it is insensitive to conformational motion of the molecule. Another peculiarity of the branched alkanes is virtually blocked degenerate electron transfer even at high alkane concentrations. Most probably, the localization of the charge at the single C–C bond, which is substantially lengthened, creates a very high kinetic barrier for charge transfer because of an unfavourable Franck–Condon factor.

Another problem in radiation chemistry is the invariable failure to obtain OD ESR spectra from the radical cations of cyclohexane and other cyclic alkanes. Indeed, published data indicate that the lifetime of the cyclohexane radical cation in irradiated neat liquid cyclohexane is at least 100 ns. Furthermore, it is well known that the rate of degenerate charge transfer in cyclohexane is high so that the holes (solvent radical cations) of cyclohexane demonstrate unusually high mobility exceeding the normal molecular mobility by more than an order of magnitude.[12] At these high exchange rates, the OD ESR spectrum should be a strongly narrowed and thus easily observable unresolved singlet. However, this was never observed in practice.

The answer was provided by the TR MFE technique, which revealed unusually short spin-lattice relaxation times for this system.[13] The radical ion pairs $(c\text{-}C_6H_{12})^{+\cdot}/(C_6F_6)^{-\cdot}$ were created in a hexane solution. In this case, the TR MFE curve rapidly climbs up, passes through a maximum and then decays exponentially (Figure 4). A detailed study demonstrated that the decay was caused by fast spin–lattice relaxation in the radical cation with the time $T_1 \sim 9$ ns. Such short paramagnetic relaxation times have yet never been reported for organic radicals or radical ions. Given such a short longitudinal relaxation time, the microwave field of an ESR spectrometer cannot induce a noticeable change in the orientation of the electron spin, and thus the OD ESR signal does not develop.

Very short relaxation times were also found in the radical cations of other cyclic molecules with a high degree of symmetry, such as adamantane.[14] All these radical cations have electronically degenerate ground states and belong to the group of the so-called Jahn-Teller active species. Electronic degeneracy in these species is believed to lead to strong spin–orbit interaction, which is the immediate reason for the fast paramagnetic relaxation.

Thus, the technique of time-resolved magnetic field effect has opened to study a series of alkane radical cations in solution with either lifetimes or relaxation times as short as several nanoseconds, which cannot be detected by numerous ESR techniques. TR MFE has provided a wealth of data on their ESR spectra, spin relaxation times and the rates of degenerate electron transfer.

As opposed to alkane radical cations, for which the range of lifetimes was known beforehand from independent experiments, in many cases, it is believed that electron capture by a molecule or its ionization leads to instant fragmentation. Dissociative electron capture by alkyl or aryl halides provides a typical example. However, in all such cases, it is difficult to rule out an alternative possibility of the formation of short-lived radical ions that cannot be detected by available experimental techniques. The examples below illustrate the capabilities of TR MFE in solving problems of this type.

TR MFE curves for *n*-decane solutions of 1,2,3,4-tetraphenylcyclopenta-1,3-diene and its silicon and germanium analogues[15] showed clear oscillations induced by hyperfine interactions with CH_2 protons in radical anions of the dissolved molecules. Furthermore, similar oscillations were also recorded for Cl-substituted germoles. This unequivocally excludes the instantaneous dissociative electron capture with the elimination of Cl^- from consideration and implies that the lifetime of the corresponding radical anion is at least several tens of nanoseconds. This is the first observation of radical anions from halides of group 14 organoelements in solution. Simulation of experimental traces yielded the values of hfc constants with chlorine nuclei, which were later confirmed by the direct measurement of OD ESR spectra from these radical anions.[16]

Another example is provided by the radical cations $R_4E^{+\cdot}$ and $R_3EER_3^{+\cdot}$ with R = Me and E = Si, Ge or Sn.[17] It was generally believed that these radical cations undergo very fast fragmentation

$$R_4E^{+\cdot} \longrightarrow R_3E^+ + R^\cdot;$$
$$R_3EER_3^{+\cdot} \longrightarrow R_3E^+ + R_3E^\cdot.$$

Thus, they can be detected only in cryogenic matrices. The traces of fluorescence decay kinetics from hexane solutions containing 0.1 mol dm^{-3} of an organoelement compound and 3×10^{-5} mol dm^{-3} of *p*-terphenyl-d_{14} suggested the fast decay of Ge- and Sn-containing cations. Nevertheless, TR MFE curves were successfully registered on a nanosecond time scale and provided information on the ESR spectra of the short-lived radical cations.

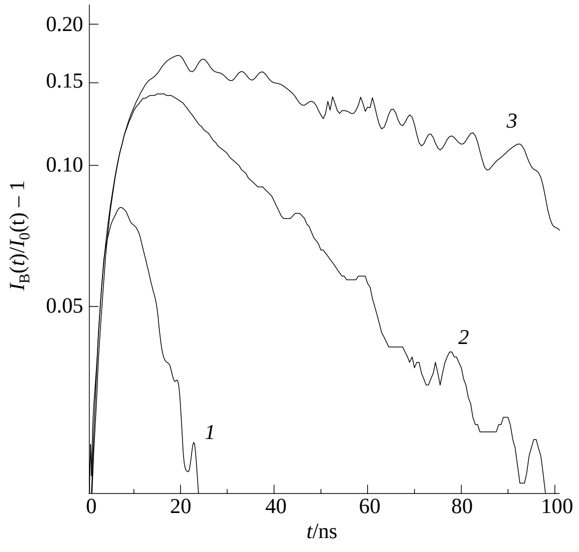

Figure 4 Semilogarithmic plots of TR MFE curves obtained for *n*-hexane solutions of 10^{-2} mol dm^{-3} C_6F_6 with the addition of 0.1 mol dm^{-3} cyclohexane (curve *1*), 0.1 mol dm^{-3} methylcyclohexane (curve *2*) and 0.1 mol dm^{-3} *cis*-decaline (curve *3*) in a magnetic field of 1 T. The decay rates are determined by the rates of spin–lattice relaxation.

It was found that in solution, similar to cryogenic matrices, these radical cations had substantially shifted *g*-values, and the shift increased with the atomic number of the element. As for hfc constants in the cations, the couplings in the $R_4E^{+\cdot}$ cations in the test solutions were completely averaged by fast electron exchange, and charge transfer occurred at nearly every encounter. However, for the $R_3EER_3^{+\cdot}$ cations, no indications of degenerate electron exchange and the ensuing averaging of the hfc were found. Most probably, in this case, the charge localization at the EE bond leads to its significant lengthening, which effectively blocks degenerate electron exchange, similar to branched alkanes.

In addition to the reaction of degenerate electron exchange, TR MFE is promising for measuring the rates of other reactions that involve short-lived radical ions. Any delay in the formation of the tracked radical ions desynchronises spin dynamics resulting in a certain phase shift of the oscillations and a decrease of their amplitude. This effect was employed by Grigoryants *et al.*[18] to determine the reaction rate of charge transfer from an isooctane radical cation to a diphenylsulfide molecule. Under the experimental conditions, the reaction completed in several nanoseconds, and the phase shift of the oscillations yielded a rate constant close to the diffusion-controlled limit of the solvent.

For another reaction, charge transfer from the *n*-alkane radical cations to 9,10-octaline molecules, the amplitude of oscillations was found unexpectedly larger than that predicted by a simple model of diffusion-controlled reactions.[19] The authors then inferred that the tunneling radius in this case exceeded the geometric radius by a factor of 2–3, which led to a significant contribution of the fast non-stationary portion of the reaction kinetics to the observed traces.

In summary, it can be stated that at present the experimental and theoretical basis of a new technique has been worked out, and several ways for its practical application have been paved. The method will surely enjoy further applications for obtaining spectroscopic information on radical ions that have not yet been studied in liquid solutions by ESR techniques because of their prohibitively short lifetimes. TR MFE opens exciting prospects for investigations into the mechanisms and rates of fast reactions, in which radical ions participate, in solutions. The method also offers new and interesting opportunities for the determination of relaxation times of short-lived radical species. Relevant information is practically unavailable, but it is crucial for the interpretation of experimental results on spin polarization and magnetic field effects in chemical reactions.

The apparent limitation of the quoted experimental investigations is caused by an insufficient time resolution of the existing installations. An improvement in resolution will bring about the extension of spectral and kinetic studies onto radical ions with still shorter lifetimes and more complex sets of hyperfine couplings and is thus an urgent problem. Further development of theory is also highly welcome, since existing models cover the spin dynamics of only the simplest spin systems.

Up to now, TR MFE has only been applied to study radical ion pairs generated by high-energy ionising irradiation.[20] However, the technique can readily be applied to photogenerated radical ion pairs with possible simplification in the interpretation of experimental results due to the use of monochromatic sources of ionization. Such an extension of experimental studies would be very beneficial, since a much wider class of experimental systems could then be studied.

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