Time Resolved Magnetic Field Effects as a Probe for Geminate Recombination

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A theoretical description for the magnetic field dependence of geminate recombination as observed in transient spectroscopy of electron transfer reactions, is given and applications of this novel magnetic field effect are discussed.

It is now commonly accepted that chemically induced dynamic polarization of nuclei (CIDNP) and, in most cases, chemically induced dynamic polarization of electrons (CIDEP)[1] can be described by the radical pair model. In this model the spin precession of the two unpaired electrons in the external and internal magnetic fields is assumed to be responsible for the change of the total electronic spin, e. g. for the formation of a triplet from an initial singlet state.

Recently[2] we have shown that there is a direct experimental access to the observation of this spin precession based on a sensitive absorption measurement on the nsec time scale under the influence of a weak magnetic field ($H \lesssim 200$ Oe). Electron transfer between primarily excited pyrene molecules as electron donor and diethylaniline as electron acceptor species results in a short-lived radical ion pair when the experiment is performed in polar solution. Upon recombination of the pair of simultaneously generated radical ions (geminate recombination), singlet and triplet states can be formed, depending on the total spin of the ion pair state. Since the hyperfine interaction is not identical for the two unpaired electrons, their total spin precesses from an overall singlet to a triplet state. Thus, in the time interval between the generation and the recombination of these radical ions, the spin precession of the electrons can be influenced by a weak magnetic field. Consequently, the magnetic field controls the yield of singlet and triplet final products. We have indeed found that the absorption of pyrene triplets and pyrene radical anions can be modulated by a weak magnetic field ($H \lesssim 200$ Oe) by more than 10% when measuring immediately (with 8 nsec delay) after the end of the excitation pulse. With increasing delay between the excitation and the monitoring pulse, the contribution of triplets, generated in a non-geminate recombination process tends to predominate, thus reducing the observable magnetic field effect.

This magnetic field effect is not related to the magnetic field sensitive annihilation of triplet states[3] as can be concluded from its decrease at longer delay times and its saturation at field strength of 40 Oe.

In the following we give an outline of a theoretical description of our experiments[2] within the framework of Noyes' diffusion model[4]. Finally, further applications of such magnetic field effects will be discussed.

A qualitative understanding of our experiments[2] was obtained with a model in which the asymmetric hyperfine interaction of the two electrons is simulated by the interaction of only one of them with a single proton. Thus, the spin Hamiltonian of the electron pair, employing usual notations[5], is given by

$$\mathcal{H} = g\,\beta\,\boldsymbol{H}\cdot(\mathbf{S}_1+\mathbf{S}_2) + a\,\mathbf{S}_1\,\boldsymbol{I}\,. \qquad (1)$$

The spin precession has been described by the equation for the density matrix ϱ

$$\frac{\mathrm{d}\varrho}{\mathrm{d}t} = \frac{i}{\hbar}\,[\varrho,\mathcal{H}] - \tfrac{1}{2}(\Gamma\varrho + \varrho\,\Gamma) \qquad (2)$$

in which the matrix Γ describes spin selective reactions as well as the decay of the radical pair by diffusion. In this treatment it is implicitly assumed that the probability of a re-encounter of the two ions is decaying exponentially.

An alternative and probably more realistic treatment can be based on Noyes' diffusion model[4] which has been introduced into the CIDNP theory by Adrian[6]. In this model the probability of a first re-encounter after N diffusive steps of duration τ is given by

$$f(N) = 0.24/(N+0.44)^{3/2} \qquad (3)$$

thus exhibiting a rather slow decay. In order to calculate the magnetic field modulation in our experiment on the basis of Noyes' model, we solve Eq. (2), however with $\Gamma = 0$, in the basis, $l, m, \ldots$ which diagonalizes $\mathcal{H}$ of Equation (1). A singlet initial state is specified by $\varrho(t=0) = \frac{1}{2}P^{\mathrm{S}}$ where P^{S} is projecting onto the singlet subspace of the electron pair. The amount of triplet character of the pair at a time $t > 0$,

$$T(t) = \operatorname{tr}\{\varrho(t)\,(1-P^{\mathrm{S}})\}\,, \qquad (4)$$

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is then averaged over $f(N)$ of Eq. (3) which in an approximation analogous to Ref. [6] results in

$$\begin{aligned}\overline{T} &= \int_0^\infty T(N\tau)\, f(N)\, \mathrm{d}N \\ &= \sum_{l\,m} |P^{\mathrm{S}}_{lm}|^2 \int_0^\infty f(N)\, \sin^2 \frac{E_l - E_m}{2\hbar} N \tau\, \mathrm{d}N \qquad (5) \\ &= 0.42 \sum_{l\,m} |P^{\mathrm{S}}_{lm}|^2 \sqrt{|E_l - E_m|\,\tau/2\hbar}\end{aligned}$$

where E_l, E_m denote the eigenvalues of $\mathcal{H}$. From this the magnetic field modulation of the triplet yield

$$\begin{aligned} m_T &= (\overline{T}(H=\infty) - \overline{T}(H=0))/\overline{T}(H=0) \\ &= \tfrac{2}{3}\sqrt{2} - 1 \approx -5.7\% \qquad (6)\end{aligned}$$

can be obtained after some transformations which, together with the extension of the model to multiple re-encounters and to a more general Hamiltonian, will be given elsewhere [7]. We note that the negative sign of the modulation has actually been observed in our experiments, and that also the magnitude of the modulation is in reasonable agreement with the experimental data.

The slow decay of $f(N)$ results in the square root dependence of the triplet yield on the product $a \cdot \tau$ in Eq. (5), whereas a quadratic dependence is found for the case of exponential decay. Further experiments are expected to allow a clear discrimination between both assumptions. Thus, the magnetic field modulation of radical pair dynamics promises the possibility of a direct observation of "long time tails", i. e. $t^{-3/2}$ laws. These "long time tails" are of considerable interest in the transport theory of liquids [8] and have been observed recently [9] using photon correlation spectroscopy applied to the Brownian motion.

Another point of interest is concerning rotational diffusion. Picosecond experiments [10] have so far been discussed with an isotropic diffusion model which is probably not adequate for planar aromatic molecules. Since the electron transfer step seems to depend critically on the formation of a sandwich configuration of the two molecules [10], but less on rotations preserving this sandwich structure, the measurement of the magnetic field modulation of the transient singnals could provide information on the anisotropy of the rotational diffusion.

The magnetic field modulation of geminate recombination of unpaired electrons has also applications in the solid phase [11]. Here the spin precession is an internal clock of the electron pair in processes like thermalization, hopping and trapping of charge carriers in insulators.

Low magnetic fields as a novel tool in time-resolved spectroscopy allow the investigation of electron transfer processes in condensed phases, e. g. the mechanism of the recombination of initially formed radical pairs. An upper bound for the time scale interesting in liquids and solids is given by the time constant of the spin-lattice relaxation (μsec-range). With respect to short times, the time scale is limited by the minimum concentration of recombination products detectable and should reach into the subnanosecond range in agreement with other experiments on the picosecond time scale [12]. In contrast to this novel magnetic field effect described, the time resolution in spin resonance methods does not allow experiments within the lifetime of such radical pairs.

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