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Time-Resolved Optical Detection of Coherent Spin Motion for Organic-Radical-Ion Pairs in Solution

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The evolution of the singlet character of correlated ion radical pairs, prepared by high-energy impact in alkane solutions, is monitored by nanosecond-time-resolved solute-recombination fluorescence. Results obtained in the presence and absence of magnetic fields ($B \leq 4$ kG) show evidence for damped periodic modulations ($\omega \approx 10$ MHz) of fluorescence intensity. They are explained in terms of hyperfine-interaction-induced coherent singlet-triplet mixing, and of field-dependent spin-lattice relaxation.

Direct observation of time-dependent quantum-interference effects, using optical detection, has been mainly limited to gaseous atomic systems, where pulse excitation of coherent superpositions of fine- or hyperfine-structure levels initiates quantum beats with modulations of fluorescence intensity.[1] In this Letter, we report the observation of coherent motion, together with relaxation, of nonstationary quantum states in *condensed* organic matter, by means of nanosecond-time-resolved fluorescence measurements. The systems considered are dilute solutions of a fluorescent organic compound, where high-energy impact excitation creates correlated solute-radical-ion pairs in a singlet electronic spin state.[2] By recombination, these ion pairs produce fluorescing solute excited states provided they are singlet at the neutralization time. Recombination luminescence may thus be used to monitor the time development of the singlet character of the solute-ion-pair states between initial sudden preparation and final recombination.

The principle of the experimental approach is based on the influence of a magnetic field on the slowly decaying component of the luminescence excited in dilute alkane solutions by fast electrons. This radioluminescence component is known to arise from geminate recombination of solute-ion pairs[3] which under nanosecond-resolution conditions may be regarded as impulsively formed in a singlet spin state.[2] The luminescence rate determining process is the migration of the correlated ions toward one another to form a closely spaced solute charge-transfer complex, which by spin-conserving recombination yields an excited solute molecule. Denoting by $n(t)$ the concentration of such recombination complexes and by $\rho_s(t)$ their probability to be singlet at time t after the $\delta(t)$ impact creation of the spatially separated ion pairs, we can express the recombination fluorescence intensity as $I(t) = q_f k_r n(t) \times \rho_s(t)$, if $t \gg \tau_f$. τ_f and q_f are the decay constant and quantum yield of solute fluorescence, and k_r is the recombination rate constant. The only magnetic-field-dependent factor in the expression of $I(t)$ is $\rho_s(t)$; the relative variation of luminescence intensity, $\Delta_B I / I = [I^B(t) - I^0(t)]/I^0(t)$, observed upon application of a field B, therefore measures the relative variation, $\Delta_B \rho_s / \rho_s = [\rho_s^B(t) - \rho_s^0(t)]/\rho_s^0(t)$, of the time-dependent singlet character of the ion-pair states.

The measurements were made at room temperature with degassed cyclohexane solutions of a scintillator solute denoted by 2b PPD [bis(butyl-4 phenyl)-2,5 oxadiazole-1,3,4 (cf. inset in Fig. 1)] with known fluorescence properties ($\tau_f = 1.5$
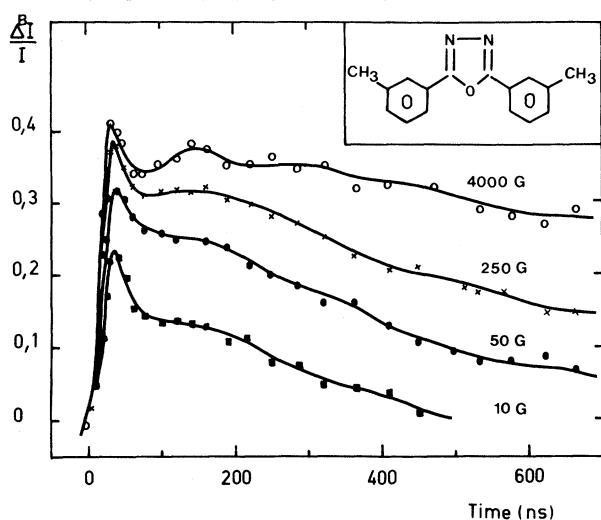
FIG. 1. Time dependence of relative-fluorescence-intensity increase, $\Delta_B I/I$, upon application of magnetic fields B, for a 1.5×10^{-3} M solution of 2b PPD (cf. inset) in cyclohexane solutions excited by β rays.
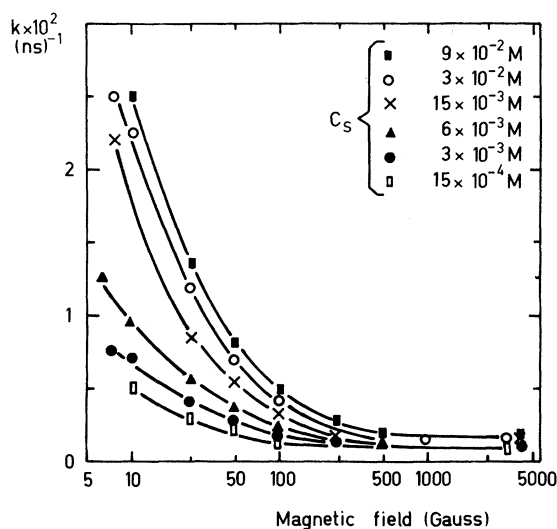

FIG. 2. Influence of field strength B and solute concentration C_s on the decay rate constant k of the exponentially decreasing component of $\Delta_B I/I$ for the 2b PPD solutions in cyclohexane at room temperature.

nsec, $q_f = 0.88$).[3] The radioluminescence decay curves, $I(t)$, of the solutions excited by the β rays of an immersed 0.1 μCi ^{90}Sr-^{90}Y source have been determined by a single photon counting technique for various applied magnetic field strengths. In Fig. 1, we show the observed variations of $\Delta_B I/I$ as a function of time ($t \leqslant 800$ nsec) for different fields ($B \leqslant 4$ kG) and a given solute concentration. Similar results were obtained for other concentrations. Inspection of these curves suggests that we consider the time dependence of $\Delta_B I/I = \Delta_B \rho_s/\rho_s$ as the sum of a damped oscillatory term and of a monotonically decreasing component: For 2b PPD, the former term is characterized by an oscillation period of the order of 120 nsec. Its observability depends on the nature of the solute since we could find no clear evidence for its occurrence with aromatic hydrocarbon solutes (anthracene, perylene). By contrast, the second component was observed in all cases investigated: Its decay is exponential with a rate constant k depending on the external field B and the solute concentration C_s as $k = k' + k''(B, C_s)$, where k' is constant, while $k''(B, C_s)$ increases with C_s but decreases for increasing fields around $B = 10^2$ G, and vanishes for $B \geqslant 1$ kG. The results for the 2b PPD solutions are represented in Fig. 2.

To discuss these experimental data, we must analyze in some detail the coherent and relaxation phenomena which determine electronic spin motion of the solute-ion pairs after the $\delta(t)$ ex-

citation in the singlet state. Following other work,[2,4-6] coherent motion of electronic spin in organic-radical pairs is controlled by the Zeeman and the hyperfine (hf) interactions within the radicals. For our purpose, it is convenient to write the Hamiltonian as the sum of two terms, $H = H_0 + H_1$, which are respectively symmetric and antisymmetric with respect to the interchange of the electronic spin indices on the radicals labeled $i = 1, 2$ ($\hbar = 1$)

$$H_0 = [g\mu_B \vec{B} + \tfrac{1}{2}\sum_i a(i)\vec{I}(i)][\vec{S}(1) + \vec{S}(2)],$$

$$H_1 = \tfrac{1}{2}[a(1)\vec{I}(1) - a(2)\vec{I}(2)][\vec{S}(1) - \vec{S}(2)]. \tag{1}$$

Nearly identical g values are assumed for the positive and negative ions. For simplicity, we consider only one set of magnetically equivalent nuclei in the radicals i, with total spin $\vec{I}(i)$ interacting with the electronic spin $\vec{S}(i)$ by isotropic contact hf coupling of constant $a(i)$. The symmetric part H_0 in (1) defines a representation in which the total electronic spin $\vec{S} = \vec{S}(1) + \vec{S}(2)$ of the ion pair is diagonal. The basis eigenvectors are written as the direct products $|SM_s; n\rangle$ of electronic- and nuclear-spin eigenvectors: The former (SM_s) include the singlet S_0 and the triplet (T_0, T_{+1}, T_{-1}) eigenstates of $\vec{S}$; the nuclear-spin states $|n\rangle$ are products of the eigenstates of $\vec{I}(1)$ and $\vec{I}(2)$, $|n\rangle = |I(1), M(1); I(2)M(2)\rangle$, and the total number is $N = [2I(1) + 1][2I(2) + 1]$. The cor-

responding energy spectrum is

$$E(S_0, n) = E(T_0, n) = 0;$$

$$E(T_\pm, n) = \pm \left[g\mu_B B + \tfrac{1}{2}\sum_i a(i)M(i) \right]. \tag{2}$$

The antisymmetric operator H_1 in (1) has only nondiagonal matrix elements coupling the different $\tilde{S}$ levels. For each nuclear spin $|n\rangle$, the two degenerate $|S_0 n\rangle$ and $|T_0 n\rangle$ states are then subject to resonance interaction, which gives rise to coherent oscillations between these $M_s = 0$ states, with the characteristic frequency

$$\Omega_n = \langle T_0 n | H_1 | S_0 n \rangle = \tfrac{1}{2}[a(1)M(1) - a(2)M(2)]. \tag{3}$$

Damping is introduced by the spin-flip transitions between the $(M_s = 0; n)$ states and the non-isoenergetic $(T_\pm, n \mp 1)$ levels, which are made possible by spin-lattice interaction. The corresponding rate constants are best discussed in the framework of the usual theory of relaxation by semiclassical random magnetic perturbations.[7,8] Here, two different perturbations contribute, so that the total rate is characterized by a constant of the form suggested by the experiments:

$$\Gamma = \Gamma' + \Gamma''(B, C_s). \tag{4}$$

The field- and concentration-independent term (Γ') is due to the rotational fluctuations of anisotropic magnetic interactions within the two radicals and may be expected to be of the order of the T_1^{-1} constants for the isolated radicals in solution ($T_1 \approx 10^{-6}$ sec).[8] The second relaxation mechanism is attributed to time modulations of the isotropic hf interactions by electron transfer from the radicals to neutral solute molecules encountered during diffusion in the liquid. The field and solute-concentration dependence of the corresponding rate constant Γ'' is justified with the help of the general expression[9] $\Gamma'' = \alpha\langle\delta\omega\rangle^2 \times J(\Delta\omega)$, where $\langle\delta\omega\rangle$ is the interaction-energy matrix element and $\Delta\omega$ the transition energy which, according to (2), increases linearly with B. $J(\omega)$ represents the power spectrum of the fluctuating perturbation with correlation time τ_c; $J(\Delta\omega) = 2\tau_c/[1+(\Delta\omega\tau_c)^2]$ decreases for increasing B in the 10^2 G range provided $\tau_c \approx 1$ nsec, which is reasonable for intermolecular electron transfer.[10] Finally α is the fraction of time during which the perturbation is operative. In terms of the mean times during (τ_1) and between (τ_2) the radical-neutral molecule encounters, α is of the form $\alpha = \tau_1/(\tau_1 + \tau_2)$, which shows that Γ'' increases with C_s since τ_2 is proportional to C_s^{-1}.

The experimentally significant temporal varia-

tions of $\rho_s(t)$, as they result from spin motion, may be expressed in terms of the reduced density operator ρ describing the charge-transfer pairs in the $(M_s = 0, n)$ states or, better, by the operators $\rho^{(n)} = \langle n|\rho|n\rangle$ in the electronic $M_s = 0$ subspace, for a fixed nuclear spin state:

$$\rho_s(t) = \sum_n \langle S_0 n | \rho(t) | S_0 n \rangle = \sum_n \langle S_0 | \rho^{(n)}(t) | S_0 \rangle. \tag{5}$$

The initial $\delta(t)$ excited singlet states are represented by $\rho(0) = N^{-1}\sum_n |S_0 n\rangle\langle S_0 n|$ or $\rho^{(n)}(0) = N^{-1}|S_0\rangle \times \langle S_0|$. Temporal evolution is given by

$$d\rho^{(n)}/dt = \rho^{(n)}(0)\delta(t) - i[H_1^{(n)}, \rho^{(n)}]$$
$$- 2\Gamma\rho^{(n)} + \Gamma(N^{-1} - \mathrm{Tr}\rho^{(n)}), \tag{6}$$

where the terms on the right successively account for initial excitation, coherent oscillation ($H_1^{(n)} = \langle n|H_1|n\rangle$), and decay and production of the $(M_s = 0, n)$ states by the transitions to and from the $(M_s = \pm 1, n \mp 1)$ levels; equal rates of the form (4) are assumed for these transitions. Solving Eq. (6), one determines $\langle S_0|\rho^{(n)}(t)|S_0\rangle$ to obtain after substitution in (5)

$$\rho_s{}^B(t) = (2N)^{-1}\sum_n \cos(2\Omega_n t)\exp(-2\Gamma t)$$
$$+ [1 + \exp(-4\Gamma t)]/4,$$

where Ω_n is given by Eq. (3). The field dependence is due to the previously discussed relaxation rate constants (4). For $B = 0$, Γ is maximum, and equilibrium is attained after relaxation times $\lesssim 10$ nsec. Under our experimental conditions, we can take $\rho_s{}^0(t) \sim \tfrac{1}{4}$, so that one gets the model expression

$$\Delta_B \rho_s / \rho_s = 2(N^{-1})\sum_n^N \cos(2\Omega_n t)\exp(-2\Gamma t)$$
$$+ \exp(-4\Gamma t), \tag{7}$$

which accounts for the principal features of the experimental data.

In Fig. 1, the above mentioned damped oscillatory component is interpreted by the first term in expression (7). The experimental time resolution does not permit a very precise frequency analysis, but a periodic behavior clearly appears, with a frequency of 8 MHz, which is of the order of the isotropic hf interactions in organic radicals, as expected from Eq. (3). Periodicity requires that the various Ω_n values in (7) are multiples of a common frequency which, following (3), implies that the hf coupling constants $a(1)$ and $a(2)$ on the positive and negative ions should be similar; our results suggest that this condition is better satisfied for 2b PPD than for anthracene and perylene.[11] The other, monotonical-

ly decreasing component of $\Delta_B \rho_s / \rho_s$ in Fig. 1 is described by the $\exp(-4\Gamma t)$ term of Eq. (7). The experimental quantities k are given by 4Γ, which according to the foregoing discussion of Eq. (4) accounts for the observed field and concentration dependences in Fig. 2.

To our knowledge, this is the first direct optical observation of time-dependent quantum-interference effects in the condensed phase.[12] The present experimental approach should also be a useful tool for spin-lattice relaxation measurements in the nanosecond range.

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Spherical Model of a Spin-Glass

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A spherical model of a spin-glass is solved in the limit of infinite-ranged interactions with a Gaussian probability distribution. We use the known properties of a large random matrix, and show that the results are identical to those obtained by the $n \to 0$ trick. We believe that the solution is exact.

Recently there has been much interest in the problem of magnetic systems with random exchange interactions—spin-glasses.[1-6] Experimentally such systems show definite anomalies similar to those associated with a second-order phase transition.[7, 8] Since a real spin-glass is a dilute system of magnetic ions in random but fixed positions interacting via a long-ranged oscillating interaction, we must treat a quenched system in which the free energy is calculated as an average over the interaction configurations of the free energy for a fixed configuration. To date, there have been two main approaches to the problem of which the most fruitful has been the trick of averaging the nth power of the partition function and taking the limit $n \to 0$ at the end.[1, 9] Very recently, Sherrington and Kirkpatrick[5] using this technique have investigated the Ising-like spin-glass analog of the Kac[10] model in which mean-field theory is exact and the statistical mechanics solvable. However, they obtain some odd results in the spin-glass phase, in particular a negative entropy at zero temperature. Otherwise, their results are physically very appealing.

More recently, Thouless et al.[11] have investigated this model by resumming the averaged high-