

Radio Frequency Magnetic Field Effects on Electron-Hole Recombination

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(Received 8 December 2000; published 26 July 2001)

We present measurements of the spectrum (1–80 MHz) of the effect of a weak ($\sim 500 \mu\text{T}$) radio frequency magnetic field on the electron-hole recombination of radical ion pairs in solution. Distinct spectra are observed for the pyrene anion/dimethylaniline cation radical pair in which one or both of the radicals are perdeuterated. The radical pair mechanism is developed theoretically and shown to account satisfactorily for both the magnetic field effect and the associated magnetic isotope effect.

DOI: 10.1103/PhysRevLett.87.077602

PACS numbers: 76.30.Rn, 33.20.Bx, 87.50.Jk

The radical pair mechanism (RPM) is well established as the basis of the magnetic field dependence of radical recombination rates in solution and in modified photosynthetic reaction centers [1]. Conventionally used to explain the effects of static fields in the range 1–100 mT, the RPM has recently been extended to describe behavior down to $\sim 100 \mu\text{T}$, the so-called low field effect [2–4]. A largely unexplored implication of this mechanism is that weak radio frequency fields should also modify reaction yields, and that the effect should be frequency dependent [5–7]. We report here experimental measurements of the spectrum (1–80 MHz) of the radio frequency field effect on a photochemical electron transfer reaction. Using isotopomers of the reactants, we demonstrate the influence of $\sim 100 \mu\text{T}$ magnetic fields in a much more convincing manner than is possible with time-independent (or 50–60 Hz) fields. Possible applications of the technique include studies of the magnetic field sensitivity of electron-hole recombination in light emitting polymers, and discrimination between mass and magnetic isotope effects on free radical kinetics. It could also be used to distinguish a magnetite-based mechanism for the magnetic sense in animals from a solid state radical pair process.

The RPM describes how relatively weak magnetic interactions influence the yields and rates of chemical reactions that have radical pairs as transient paramagnetic intermediates [8,9]. It may be summarized as follows. (i) Radical pairs are created, for example, by intermolecular electron transfer, in a spin-correlated electronic state, which can either be singlet ($S = 0$) or triplet ($S = 1$) depending on the multiplicity of the molecular precursor. (S is the total electronic spin angular momentum quantum number.) This initial state is *not* usually a stationary state of the combined electron-nuclear spin system. (ii) Magnetic interactions within the radicals—principally electron-nuclear hyperfine interactions—drive coherent intersystem crossing of the radical pair between singlet and triplet states, on a nanosecond time scale. (iii) The efficiency and extent of this process is affected by the Zeeman interaction of the electron spins with an applied magnetic field. (iv) The radicals react spin selectively from the singlet and triplet states, with different rates and to form chemically distinct prod-

ucts. (v) The probability that a radical pair reacts through (say) the singlet channel at a given time after its formation depends on the details of the magnetic interactions that control the singlet \leftrightarrow triplet mixing. (vi) If the radical pairs are sufficiently long-lived (≥ 100 ns), a weak magnetic field ($\sim 100 \mu\text{T}$) can enhance the singlet \leftrightarrow triplet interconversion and so significantly alter the fractions of radical pairs that react via the singlet and triplet channels. This can take place even though the applied field may be much smaller than the hyperfine couplings, *and* all magnetic interactions are much weaker than the thermal energy per molecule, $\sim kT$ [3].

Not only static, but also radio frequency (rf) magnetic fields can modify the spin evolution of a radical pair. In principle, one can expect a response whenever the frequency, ω_{rf} , satisfies a magnetic resonance condition in either radical. The magnitude of such a resonant change in the product yield will depend on the extent to which the singlet probability of the system is changed, which in turn is determined by the hyperfine interactions, the properties of the applied field, and the kinetics of the radical pair reactions.

We have studied the photochemical reaction of pyrene (Py) and *N,N*-dimethylaniline (DMA) in solution. Continuous UV irradiation of pyrene in the presence of DMA, using a 300 W xenon lamp, produces the transient radical ion pair $\text{Py}^{\bullet-}\text{DMA}^{\bullet+}$ in a spin-correlated singlet state that interconverts with the corresponding triplet state on a nanosecond time scale. Electron-hole recombination of the *singlet* radical pair produces an exciplex (electronically excited complex of $\text{Py}^{\bullet-}$ and $\text{DMA}^{\bullet+}$ [10]) whose fluorescence, detected with a photomultiplier, was used to monitor the concentration of singlet pairs under steady state conditions, as the rf is swept slowly through the range 1–80 MHz. The field was generated by applying a rf signal (amplified to 200 W) to an 8 mm diameter coil surrounding the sample contained in a 3×3 mm flow cuvette. Most of the power was dissipated in a 50Ω load connected in series with the low inductance coil. The rf field was 100% amplitude modulated at an audio frequency (381 Hz), and the photomultiplier output demodulated in a phase sensitive detector at the same frequency. In this way

the experiment detects only the magnetic field-sensitive component of the fluorescence, arising from the exciplex. The sample and coil were enclosed in a mu-metal box to reduce the Earth's magnetic field to a negligible level. All experiments were performed at room temperature. The samples, comprising 0.1 mM Py and 10 mM DMA in 9:1 cyclohexanol:acetonitrile (by volume), were deoxygenated by extensive argon bubbling and flowed through the cuvette to prevent photochemical degradation. No magnetic field effects were observed in the absence of DMA, indicating that fluorescence from pyrene and from pyrene excimers does not interfere with the measurements. A more detailed description of the spectrometer is given in Ref. [11].

Four isotopomers of the $\text{Py}^{\bullet-}\text{DMA}^{\bullet+}$ radical pair have been studied. Perdeuteration of one or both radicals produces a magnetic isotope effect [12] on the evolution of the radical pair via the ~ 6.5 fold reduction in the proton hyperfine couplings, and the change in nuclear spin quantum number, from $I = \frac{1}{2}$ to $I = 1$. The experimental spectra, shown in Fig. 1, are strongly dependent on whether the radicals are protonated or deuterated. For a proper understanding of the origin of these differences we turn to theory.

An exact calculation of the time-dependent singlet probability of the multinuclear $\text{Py}^{\bullet-}\text{DMA}^{\bullet+}$ radical pairs would be prohibitively time-consuming, even if radical diffusion and spin relaxation were ignored. We therefore develop here a novel and much faster, approximate method for simulating the spectra, which also gives considerable insight into their form. In the limit that the radio frequency field, B_1 , is weak enough that it excites only transitions that are exactly on-resonance (at ω_{rf}), one can use time-dependent perturbation theory to estimate the spectrum as a collection of delta functions whose frequencies are the spacings between the energy levels of the spin system, and whose heights are proportional to the change in singlet product yield induced by the field. This calculation is conveniently constructed in terms of the density operator of the radical pair, $\sigma(t)$, and the spin Hamiltonians that describe the hyperfine couplings (H_0) and the Zeeman interaction of the two electron spins with the radio frequency field [$H_1(t)$]. The rf field is taken to be circularly polarized, with strength B_1 . Both Hamiltonians are first transformed into a coordinate system rotating at ω_{rf} . Iterative expansion of the Liouville-von Neumann equation for the system, in the eigenbasis of H_0 , gives

$$e^{iH_0t}\sigma(t)e^{-iH_0t} = \sigma(0) + it[\sigma(0), \tilde{H}_1] - \frac{1}{2}t^2[[\sigma(0), \tilde{H}_1], \tilde{H}_1] + \dots, \quad (1)$$

where the tilde indicates that matrix elements of H_1 connecting nondegenerate eigenstates of H_0 in the rotating frame must be set to zero. This is equivalent to retaining only those transitions for which the radio frequency field is exactly on-resonance. The initial density operator, $\sigma(0)$, of a radical pair created as a pure singlet, and the probability, $\rho_S(t)$, that it is in a singlet state at time t , are given by

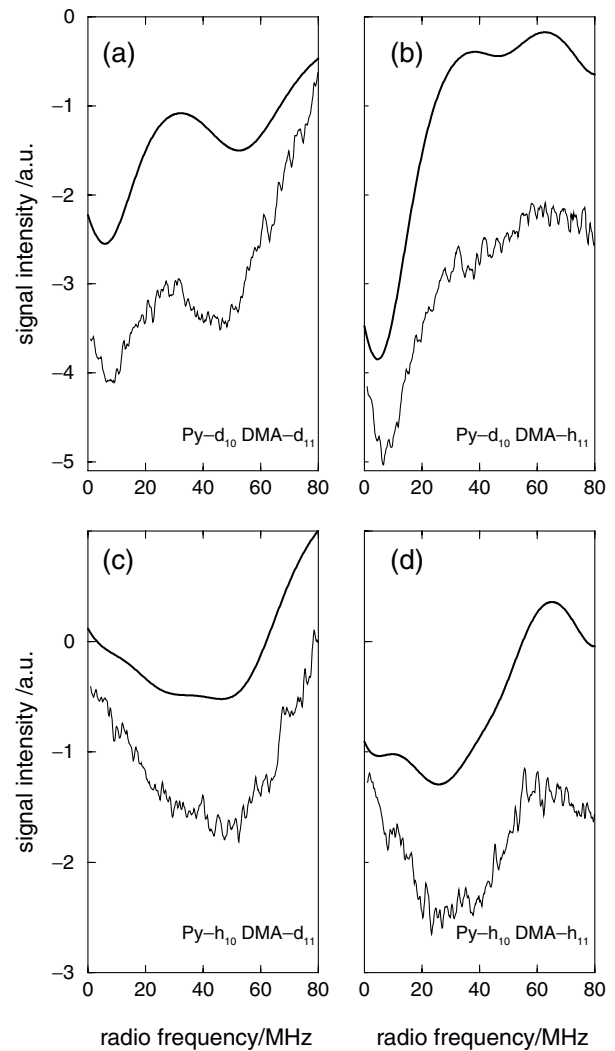


FIG. 1. Experimental and calculated (smooth lines) magnetic field effect spectra of isotopomeric $\text{Py}^{\bullet-}\text{DMA}^{\bullet+}$ radical pairs. The relative amplitudes of the four spectra and the four simulations have been preserved. The simulations in (b), (c), and (d) have been shifted vertically by +1.0, +1.6, and +2.0 units, respectively, for clarity.

$$\sigma(0) = P^S/M, \quad \rho_S(t) = \text{Tr}[\sigma(t)P^S], \quad (2)$$

where M is the number of nuclear spin configurations (e.g., $M = 2^N$ for N spin- $\frac{1}{2}$ nuclei), and P^S is the singlet projection operator.

The ultimate yield of products formed by reaction of singlet radical pairs is [3]

$$\Phi_S = k \int_0^\infty \rho_S(t) e^{-kt} dt, \quad (3)$$

where k is the recombination rate constant. The change in Φ_S produced by the radio frequency field is found to be simply

$$\Delta\Phi_S \propto -\text{Tr}[\tilde{P}^S \tilde{H}_1 \tilde{H}_1 \tilde{P}^S - \tilde{P}^S \tilde{H}_1 \tilde{P}^S \tilde{H}_1], \quad (4)$$

where the trace is evaluated in the eigenbasis of H_0 , retaining only matrix elements of H_1 and P^S that connect

degenerate eigenstates of H_0 . The Hamiltonians used to evaluate Eq. (4) are

$$H_0 = \sum_K \sum_j a_{Kj} \mathbf{S}_K \cdot \mathbf{I}_j - \omega_{\text{rf}} \sum_K S_{Kz} - \omega_{\text{rf}} \sum_j I_{jz}, \quad (5)$$

$$H_1 = \omega_1 \sum_K S_{Kx}, \quad (6)$$

in which a_{Kj} is the intramolecular hyperfine coupling of electron K with nucleus j , and \mathbf{I}_j and \mathbf{S}_K are nuclear and electron spin angular momentum operators. The radicals are assumed to be far enough apart in solution that, on average, the interrational exchange and dipolar interactions are negligible. Electron spin relaxation, caused by the modulation of local magnetic interactions by molecular motions, is also neglected: typical relaxation times ($\sim 1.0 \mu\text{s}$) are considerably longer than the time required for singlet-triplet interconversion. Equation (4) is strictly valid in the limit that the radio frequency field, $\gamma_e B_1$, is much smaller than the average rate of disappearance of the radical pairs, which is itself much smaller than the hyperfine interactions. The spectral intensities, $\Delta\Phi_S$, are expected to be negative for an initially singlet pair because the applied field increases the conversion to triplet, so reducing the probability of recombination via the singlet channel [2].

Figure 2 shows the “stick spectra” for the four isotopomeric radical pairs, calculated using the hyperfine coupling constants in Table I. Each spectrum has distinct features characteristic of the individual radicals, centered at frequencies approximately equal to the effective hyperfine coupling of each of the four radicals (Table I), defined as

$$\langle a_K \rangle = \sqrt{\sum_j a_{Kj}^2 I_j(I_j + 1)}, \quad (7)$$

where I_j is the spin quantum number of nucleus j in radical K . Py-d₁₀^{•-}, for example, has resonances exclusively below 10 MHz, consistent with all its hyperfine couplings being less than 0.1 mT [spectra (a) and (b)], while DMA-h₁₁^{•+} has a broad spectrum centered on ~ 80 MHz arising from couplings larger than 1 mT for both the ¹⁴N and the six equivalent methyl protons [spectra (b) and (d)]. As the radicals are assumed to have no interaction, the resonance frequencies of each radical are independent of the identity of its partner. However, it is clear that both the relative and absolute intensities do differ somewhat, because the spin correlation at the heart of the field effect is a property of both radicals.

One can see from Fig. 2 the origin of the more prominent features in the experimental spectra in Fig. 1 (e.g., the minimum near 5 MHz in (a) and (b) arising from Py-d₁₀^{•-}). A clearer comparison of theory with experiment can be obtained by convolving the stick spectra with a Lorentzian line shape to mimic the broadening caused by off-resonance rf excitation. Spectral simulations for one-proton radical pairs show that the linewidth is approximately equal to *twice* the field strength, B_1 , and indepen-

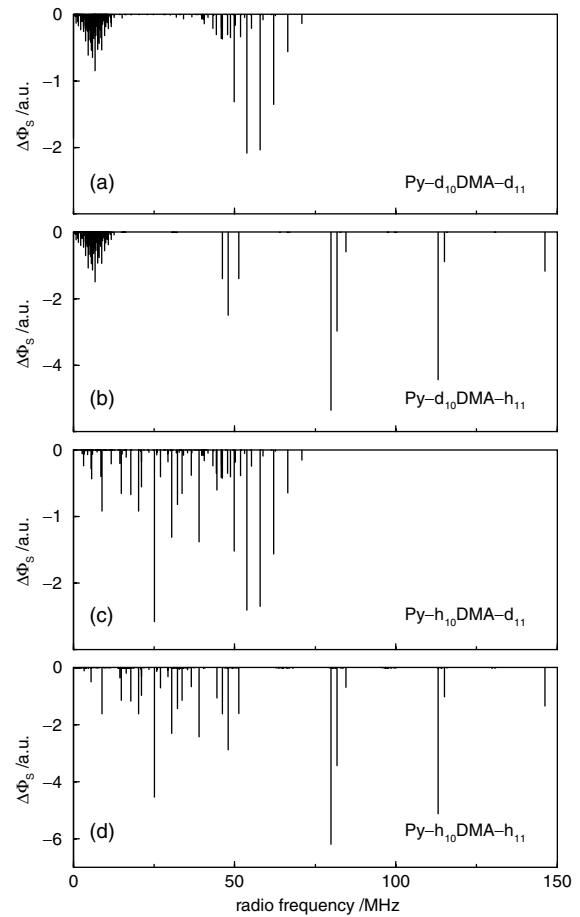


FIG. 2. Calculated magnetic field effect spectra of isotopomeric Py^{•-}DMA^{•+} radical pairs. Each “stick” represents a magnetic resonance among the electron-nuclear spin states of the radical pair, which produces a change in the yield of the product formed by recombination of singlet radical pairs.

dent of the diffusion coefficients of the radicals. Based on the coil dimensions and the circuit design, we estimate $B_1 \approx 500 \mu\text{T}$: consequently a line broadening of 1.0 mT was used. There will undoubtedly be some lifetime broadening of the spectra ($\Delta\nu = 1/\pi\tau$), but since the effect of a weak field will be dominated by radical pairs with

TABLE I. Hyperfine coupling constants (in mT) of radical ions derived from pyrene [13], *N,N*-dimethylaniline [14], and their perdeuterated forms.

	n_1 ^a a_1 /mT	n_2 a_2 /mT	$\langle a \rangle$ /MHz ^b
Py-d ₁₀ ^{•-}	4D 0.073	4D 0.032	6.3
Py-h ₁₀ ^{•-}	4H 0.481	4H 0.212	25.5
DMA-d ₁₁ ^{•+}	6D 0.181	1N 1.10	47.0
DMA-h ₁₁ ^{•+}	6H 1.18	1N 1.10	82.5

^a n_i and a_i are, respectively, the numbers of equivalent protons (H) or deuterons (D), and their hyperfine coupling constants (in mT). ^b $\langle a \rangle$ is the effective hyperfine coupling (in MHz) as defined in Eq. (7). The remaining H/D hyperfine couplings are all smaller than ~ 0.5 mT. Their inclusion would have increased $\langle a \rangle$ by 1.5%, at most.

relatively long lifetimes ($\tau \gtrsim 100$ ns), this is unlikely to be important.

Figure 1 compares simulated and experimental spectra. The important features of the latter are a minimum near 5 MHz in (a) and (b), due to Py-d₁₀^{•-}; the negative slope above ~60 MHz in (b) and (d), arising from DMA-h₁₁^{•+}; resonances, noticeable as local minima, at the following approximate frequencies: 45 MHz in (a) and (b); 50 MHz in (c); 30 MHz in (d). These are all reproduced in the simulations, which, though approximate, evidently provide an excellent guide to the appearance of the experimental spectra.

These experiments show exceptionally clearly how a weak rf magnetic field can influence a chemical reaction via the radical pair mechanism. Less intense, but better resolved, spectra can be anticipated for still weaker rf fields. In principle, the change in reaction yield can be up to 25% for radical pairs with sufficiently long-lived spin correlation [5]. If spin relaxation and diffusive separation of the radicals are slow enough, effects approaching this size might even be seen for fields as weak as the Earth's. In our experiments, probably only ~1% of pairs live long enough ($\gtrsim 100$ ns) to be significantly influenced by the applied magnetic field. In general, larger effects are expected if the diffusion is restricted, e.g., in more viscous or micellar solutions, or in the solid state [3]. Methods for quantifying the observed intensities are being developed.

The technique and results described here are relevant to the debate on the health implications of weak electromagnetic fields [15–18]. There are radical pair reactions that occur thermolytically at physiological temperatures, including some enzyme reactions [19], which exhibit magnetic field effects *in vitro*. When the spin correlation is sufficiently long-lived, essentially any radical pair should have a 10%–20% low field effect, irrespective of the manner of its production and of the number and distribution of hyperfine couplings in the radicals [3].

The technique described here is a form of optically detected electron paramagnetic resonance (EPR) spectroscopy, with no requirement for the strong static magnetic field normally required to polarize the electron spins. It gives clear insight into the spectrum of frequencies of coherent singlet \leftrightarrow triplet interconversion of radical pairs in zero field. This information is crucial for efficient control of the quantum yield and lifetime of charge-separated states of the electron donor-acceptor complexes studied as model photosynthetic systems [20]. Indeed, Fourier transformation of the radio frequency spectrum would give a time-dependent signal closely related to the oscillating probability of finding the pair in a singlet configuration.

The spectra presented here reveal the individual contributions of the four radicals of which the isotopomeric pairs are comprised and give a much clearer picture of the radical pair physics than would static field measurements, whose outcome is largely controlled by the average hy-

perfine interaction of the two radicals [10]. The spectra provide both a nice illustration of the magnetic isotope effect [12] and an unequivocal way of distinguishing it from the more common mass isotope effect arising from differences in vibrational zero point energies. Magnetic field effect spectroscopy, as described here, opens the possibility of identifying and characterizing the paramagnetic species responsible for the field sensitivity of, for example, enzymatic reactions [19] and electron-hole recombination in light emitting polymers [21], conceivably at concentrations below the limit of detection of time-resolved EPR. It could also be used as a diagnostic for the recently developed radical pair model of photoreceptor-based magnetoreception in birds [22].

We are grateful to the Engineering and Physical Sciences Research Council and the Royal Society (London) for support and to A. F. Curtis for preliminary work on the simulations.

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