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Magnetic field effects on recombination fluorescence in liquid iso-octane

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The 123.6 nm photoionization of deuterated isooctane at -10 °C in the presence of hexafluorobenzene has been studied by examining the effect of a magnetic field to alter the quantum yield of recombination fluorescence. This fluorescence results from geminate recombination of hexafluorobenzene anions with isooctane positive ions. The use of a deuterated as contrasted to a protonated alkane makes the intensity of the recombination fluorescence much more sensitive to the magnetic field and permits observation of two maxima in the fluorescence yield at field strengths of 0 and 411 G and a possible third maximum at 822 G. The theory of the hyperfine induced spin evolution predicts these resonances at selected multiples of the $C_6F_6^-$ hyperfine constant of 137 G. Utilizing the diffusion theory of geminate recombination in a Coulomb field, the experimental magnetic field spectrum is found to be well predicted over most of the range of magnetic field strengths studied (up to 2.5 kG) by a simple, one parameter, exponential radial probability density of initial scavenged geminate pair separation distances. © 1995 American Institute of Physics.

I. INTRODUCTION

Saturated hydrocarbon liquids when excited above their liquid phase ionization thresholds, eject electrons into quasifree states of the liquid which then rapidly localize at some distance, r_0 , from the positive ion.^{1–3} From studies on the electric field dependence of the photocurrent,² it has been deduced that the radial probability density of these separation distances is of an exponential or Gaussian form with an average distance which depends on the nature of the hydrocarbon but is usually well within the Onsager radius, $r_c (=e^2/\epsilon kT)$ of ~280 Å that is characteristic of these liquids (with optical dielectric constant, ϵ =2 at 25 °C). Since the probability for escape is the negative exponential of r_c/r_0 , only a relatively small population of electrons escape the Coulomb field of their parent positive ion and the majority recombine to generate excited states of the neutral hydrocarbon.

The time for recombination can be estimated from measurements of the mobilities of excess electrons in these fluids to be of the order of 1-10 ps.⁴⁻⁶ This is sufficiently rapid that the ion-pair retains the singlet spin multiplicity with which it is initially formed. Accordingly, geminate recombination generates low-lying excited singlet states of the neutral whose fluorescence, when of sufficient intensity, has also been utilized to determine features of the ionization process.^{3,7}

As was first pointed out by Brocklehurst,⁸ scavenging of the ejected electron by added electroaffinic materials lengthens the recombination time scale to times sufficiently long (ca. ns) to cause noticeable loss in initial singlet spin multiplicity due to hyperfine interactions on either or both molecular ions. Thus any fluorescence generated by virtue of geminate ion recombination has its magnitude reduced from what would have been expected had their been retention of singlet spin. Also, since the application of a magnetic field leads to some mixing of the hyperfine levels, the intensity of recombination fluorescence becomes also sensitive to the strength of this field.9

Magnetic field effects on the recombination of geminate ion pairs have been the subject of extensive study and have had a variety of applications.¹⁰⁻¹⁹ However, there has not been, as yet, any significant attempt to utilize these effects to extract information on the nature of the liquid phase photoionization transition. Our interest in this regard was stimulated by early reports that the steady-state recombination fluorescence of perfluorobenzene in a variety of saturated hydrocarbon solvents excited with beta particles was reduced on application of a small magnetic field but then increased at higher fields.²⁰ Theoretical analysis showed that this minimum in the field effect was an expected consequence of the recombination kinetics.

In the present investigation we have essentially repeated these experiments but using 123.6 nm light rather than beta particles and have somewhat altered the analysis of the field effect to accommodate Noolandi's analytical solution to the geminate ion pair diffusion problem.^{21,22} The solvent we have used is 2,2,4-trimethylpentane (isooctane) with a liquid phase ionization threshold $\sim 1.5 \text{ eV}$ below² our excitation energy of 10.03 eV. Although the liquid phase ionization potential of hexafluorobenzene is not known, its adiabatic and vertical gas phase values are 9.91 and 10.1 eV, respectively,²³ whereas the adiabatic gas phase ionization potential of isooctane is 9.8 eV.²⁴ If these differences between iso-octane and hexafluorobenzene are maintained in the liquid phase, the positive charge transfer rate constant from iso-octane to hexafluorobenzene is expected to be ~ 2 to 3 orders of magnitude less than diffusion controlled. Indeed for diffusion control of the charge transfer rate constant, exoergicities of the order of 1 eV appear to be required.²⁵ Accordingly, the geminate recombination of the hexafluorobenzne anion is expected to be almost exclusively with an isooctane cation.

There has been no reported fluorescence from neat iso-octane.²⁶ The implication is that the lowest excited sin-

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glet state of this solvent (that would be generated via internal conversions from upper excited states that do not eject an electron) is expected to live too short a time^{27,28} for any appreciable electronic energy transfer to hexafluorobenzene at concentrations below 1 M. Accordingly, any observed hexafluorobenzene fluorescence can be attributed to geminate recombination of hexafluorobenzene anion with the solvent positive ion.^{29,30} By using deuterated iso-octane, essentially the entire hyperfine interaction becomes centered on the hexafluorobenzene anion. This considerably simplifies the analysis of the field effect and permits us to more reliably extract information on the ionization and recombination process from the observed magnetic field effects. Additionally, the use of deuterated isooctane sufficiently sharpens the magnetic field spectrum to reveal the presence of high field resonances, previously predicted by Anisimov et al.²⁰ and very recently observed by Molin and co-workers using x-ray irradiation.³¹ The analysis of these resonances is also of assistance in studying the ionization process.

II. EXPERIMENT

The 123.6 nm line from a microwave powered krypton resonance lamp was utilized for sample ionization. The lamp was constructed of Pyrex to which was attached a 1 mm thick LiF window. The exciting light was passed through a 0.3 m McPherson 218 monochromator, operating at a bandpass of ~13 nm. A LiF lens was used to focus the excitation light to a spot of about 1 mm radius on the front surface of the sample cell. A 2.54 cm diam, 1 mm thick entrance LiF window was attached to the cell body via an indium wire gasket. The cell was made from nonmagnetic materials. The cell construction permitted evacuation to a vacuum better then 10^{-5} Torr. The sample fluorescence was collected at an angle of 60 °C from the excitation axis using a pair of Suprasil quartz lenses and directed onto the entrance slit of a 0.5 m Bausch and Lomb monochromator, operating at maximal bandpass of 44 nm. The emission was usually monitored at the maximum of the spectral distribution at 355 nm. A thermoelectrically cooled photomultiplier (Hamamatsu R943-02) was used for photon counting. Experimental spectra were recorded by the use of a DATA TRANSLATION DT2801 board of an IBM PC computer and stored for subsequent analysis. All experimental data were smoothed using a three-channel averaging procedure. The contribution from stray light to the measured fluorescence intensity was determined by measurements made with and without a Suprasil quartz flat placed in the excitation light path. Corrections for this stray light were generally, however, quite small by virtue of the spectral purity of the resonance lamp. The absolute yield of fluorescing states of hexafluorobenzene was determined by comparison of its fluorescence intensity using the 123.6 nm excitation with the intensity obtained using light directly absorbed by the hexafluorobenzene at 254 nm. The longer wavelength light was obtained from a 30 W Hamamatsu L879 D₂-lamp. A sodium salicylate screen was used to determine the ratio of lamp intensities at the two wavelengths.3

The sample cell was located between the poles of a Varian electromagnet. The magnetic field strength was mea-

sured using an Applied Magnetics Laboratory AML-PT71-30 (10×) hall effect probe with an accuracy of about 0.5 G. The entire cell compartment was maintained oxygen-free during the experiment via continuous purging with nitrogen gas. The temperature of the sample was controlled by a flow of cooled nitrogen gas through the sample cell chamber. A copper–constantan thermocouple was attached to the cell. The gas flow rate was regulated by an Omega CN9000A temperature controller and maintained at a constant temperature to within ± 0.5 °C.

Isooctane (Aldrich, spectrophotometric grade) was purified by two percolations through a one meter long column of activated silica gel. The sample that was used was determined to have an absorption coefficient of 20 cm⁻¹ at 178 nm and showed no evidence for aromatic impurity. Deuterated isooctane (Isotec, Inc., 98% isotopic enrichment) was used as received. Its absorption spectrum was similar but indicated the presence of a small ($\sim 2 \times 10^{-5}$ M) aromatic impurity. No attempt was made to remove this. Benzene- d_6 (Stohler Isotope Chemicals 99.5% D), hexafluorobenzene (Aldrich, 99.9%), and 1,4-difluorobenzene (PCR, Inc., 97%) were used without additional purification. Samples were deaerated by repeated freeze-pump-thaw cycles and then transferred to the sample cell under vacuum.

III. THEORY

Equations describing the spin evolution of a pair of electrons, that begin as singlet but experience isotropic hyperfine interactions with magnetic nuclei and, simultaneously, Zeeman interactions with an externally applied magnetic field have been presented elsewhere.^{13,32} However, previous formulations were found to be more general than was required for this investigation and, accordingly, rather difficult to apply. In the Appendix 2, we offer a brief derivation which provides an alternative but equivalent and more tractable form for the probability that the two electrons remain singlet at time t in a magnetic field, x, when only one of the electrons is bound to a center containing N equivalent nuclei. Equation (A17) gives our result for this probability, $P_s(x,t)$, in the case that the N magnetic nuclei each have spin 1/2. Equations (A18) show particularly simple forms for this probability in the limits of zero and infinite magnetic field strength.

Equation (A17) is to be applied to the prediction of the quantum yield for recombination fluorescence of the negative ion of hexafluorobenzene with its parent positive ion (assumed for the moment, and we return to this point later, to remain intact on the time scale of the recombination). For this purpose, we require the integral over all time of the product $-P_s(x,t)d\Omega(r_0,t)$ where $-d\Omega(r_0,t)$ is the probability that the geminate pair having been generated at t=0at a separation distance, r_0 , will have survived to time t and decayed by recombination between t and t+dt. This itself must then be integrated over a probability density for initial geminate pair separation distances. For this latter purpose we assume that the distribution is spherically symmetrical and let $f(r_0)$ be the pertinent radial probability density. To simplify our notation we first compute for a specified field strength x, a partial quantum yield of singlet recombinations per geminate ion pair for a given M and I, i.e., $\phi_M(I,x)$, and then subsequently average this over all M and I. Accordingly, we write

$$\phi_M = -\int_0^\infty \int_0^\infty p_M(I, x, t) \, \frac{d\Omega(r_0, t)}{dt} f(r_0) r_0^2 dr_0 dt, \quad (1)$$

where $p_M(I,x,t)$ is the probability that the system which began as singlet with a given I and M has remained singlet at time, t, in the magnetic field of strength x [see Eq. (A14)].

The geminate ion-pair survival probability $-d\Omega(r_0,t)$ for two charges diffusing in their mutual Coulomb field has been obtained as an analytical solution of the diffusion equation by Hong and Noolandi.²¹ The form of this solution is, however, sufficiently complicated that using it in Eq. (1) permits only numerical evaluation of the partial recombination quantum yield. In order to obtain an analytical form for $\phi_M(I,x)$, we have adopted the following procedure. We first integrate Eq. (1) by parts to give

$$\phi_M(I,x) = 1 - c_0 \Omega_{\rm esc} + \int_0^\infty \int_0^\infty \left[\frac{dp_M(I,x,t)}{dt} \right] \Omega(r_0,t)$$
$$\cdot f(r_0) r_0^2 dr_0 dt, \qquad (2)$$

where c_0 is the time independent term in $p_M(I,x,t)$ [see Eq. (A14)] and Ω_{esc} , is the so-called escape probability, i.e, the integral over r_0 of the product of the radial probability density with the infinite time limit of $\Omega(r_0,t)$,²¹

$$\Omega_{\rm esc} = \int_0^\infty f(r_0) r_0^2 \, \exp\left(-\frac{r_c}{r_0}\right) dr_0,\tag{3}$$

where r_c is the Onsager distance. Next the integral on the right-hand side of Eq. (2) is transformed using the time derivative of Eq. (A14) and introducing a dimensionless time, $\tau = 4Dt/r_c^2$, where D is the geminate ion-pair mutual diffusion constant. This permits us to re-express the recombination yield in terms of what Hong and Noolandi refer to as the scavenging function, $h_{sc}(s)$. Thus, we obtain

$$\phi_{M}(I,x) = 1 - c_{0}\Omega_{\rm esc} - \sum_{i \neq j} c_{ij} \operatorname{Re}[h_{\rm sc}(s_{ij})], \qquad (4)$$

where

$$h_{\rm sc} = \int_0^\infty \int_0^\infty s e^{-s\tau} d\tau \Omega(r_0\tau) f(r_0) r_0^2 dr_0 \tag{5}$$

and s_{ij} , for our application, is an imaginary dimensionless frequency defined as

$$s_{ij} = -i|\omega_{ij}|r_c^2/4D.$$
 (6)

The advantage of this formulation is that Hong and Noolandi's scavenging function, although still a rather complicated function of *s*, has been shown [for certain forms of the radial distribution function $f(r_0)$] to be well represented over a rather wide range in *s* by the much simpler function

$$h_{\rm sc}(s) = 1 - (1 - \Omega_{\rm esc})/(A' + B's^n), \tag{7}$$

where A', B', and n (and also Ω_{esc}) are all determined by $f(r_0)$.³³ Substituting Eq. (7) into Eq. (4) then gives us after some algebra,

$$\phi_M(I,x) = 1 - c_0 \Omega_{\rm esc} - \sum_{i \neq j} c_{ij} Z_{ij}, \qquad (8)$$

where c_{ij} is defined as in Eqs. (A13)–(A15) and

$$Z_{ij} = \frac{\gamma + z_{ij} [(1 + \gamma) \cos(n\pi/2) + z_{ij}]}{1 + z_{ij} [2 \cos(n\pi/2) + z_{ij}]}$$
(9)

with

$$\gamma = 1 - (1 - \Omega_{esc})/A',$$

$$z_{ij} = C' |\omega_{ij}|^n,$$
(10)

and

$$C' = (B'/A')(r_c^2/4D)^n$$

The total singlet recombination quantum yield $\Phi(x)$ is now obtained by summing Eq. (8) over all *M* and *I* [see Eqs. (A16) and (A17)]. This gives finally for the quantum yield at a field strength *x*,

$$\Phi(x) = \left(\frac{N+k}{2}\right)! \left(\frac{N-k}{2}\right)! \times \sum_{I=k/2}^{I=N/2} \sum_{M=-I}^{M=I} \frac{\phi_M(I,x)}{\left(\frac{N}{2}+I+1\right)! \left(\frac{N}{2}-I\right)!}, \quad (11)$$

where k=0 or 1 for N even or odd, respectively.

In the case that $\Omega_{esc}=1$, Eq. (10) shows that $\gamma=1$ and therefore, from Eq. (9) that $Z_{ij}=1$. Since, as is clear from Eq. (A14), $c_0 + \sum c_{ij}=1$, it follows from Eq. (8) that when $\Omega_{esc}=1$, the partial recombination quantum yield vanishes. This, of course, is physically expected for a single geminate pair. However, in typical experimental situations where there exists possibilities for recombination of ions from nonrelated geminate pairs there should be expected a singlet recombination in 1/4 of such encounters. The resulting fluorescence, however, would be insensitive to a magnetic field and, therefore subtractable as a background. For iso-octane, Ω_{esc} is sufficiently small that this background was of negligible importance.

IV. RESULTS AND DISCUSSION

The basic model that we employ here involves ionization of iso-octane at 123.6 nm, scavenging of the ejected electron by hexafluorobenzene, and then return of the hexafluorobenzene anion to the parent isooctane ion with charge transfer to generate a neutral, excited hexafluorobenzene of the same electron spin multiplicity as the precursor geminate pair. If this spin multiplicity is singlet, the hexafluorobenzene will emit its characteristic fluorescence. Any effect of a magnetic field to alter the electron singlet population of the geminate pair, results in a magnetic field effect on the intensity of the recombination fluorescence.

Figure 1 shows our results at -10 °C for deuterated isooctane containing 0.086 M hexafluorobenzene. The ordinate is the ratio of the fluorescence intensity induced by absorption of 123.6 nm light to the fluorescence intensity obtained by direct excitation of the hexafluorobenzene in its first absorption system at 254 nm. Since the ratio has been corrected



FIG. 1. The ratio, Ψ , of the fluorescence quantum yield of 0.086 M hexafluorobenzene in deuterated isooctane for excitation of the iso-octane at 123.6 nm to the fluorescence quantum yield for excitation of the hexafluorobenzene at 254 nm as a function of magnetic field strength, *H* in Gauss. Insert shows results at higher fields.

for the difference in incident fluxes at 123.6 and 254 nm it can be interpreted as the quantum yield for singlet recombinations per absorbed photon, hereafter referred to as Ψ . The abscissa is the magnetic field strength, H, in units of Gauss. Deuterating the isooctane appreciably "sharpens" the spectrum over what has been previously reported by Anisimov *et al.*²⁰ The minimum at $H=110\pm 6$ G is significantly more pronounced, a resonance appears clearly at $H=411\pm 6$ G and a possible second resonance at ca $H=820\pm 6$ G. Using the reported isotropic hyperfine constant of hexafluorobenzene in squalane at 25 °C of a=137 G,³⁴⁻³⁶ we find that the two resonances occur very close to magnetic field strengths of 3aand 6a.

Both the minimum and the higher field resonances are predicted by the general theory of spin evolution dynamics even without a detailed description of the diffusion process. Indeed, as has been previously noted by Sukhenko, Purtov, and Salikhov,³⁷ the physical origins of these structures are already implicit in the magnetic field dependence of the eigenvalues in Eq. (A10) of the Hamiltonian of Eq. (A3). This assertion follows from the following simple considerations. From Eq. (A14) it is clear that at sufficiently long times, the singlet probability, $p_M(I,x,t)$, when averaged over some small time interval, will, in general, at arbitrary field strength, x, approach c_0 . However, if there exists a field strength, x_r , at which some pair of eigenvalues λ_k and λ_l become degenerate, then the relevant cosine term of argument $\omega_{kl}t$ is unity for all time, and the singlet probability c_0 becomes augmented by the amount c_{kl} . The range in x over which this augmentation occurs will depend importantly on the time, but on the time scale of the geminate recombination in iso-octane this range is apparently sufficiently narrow to manifest the augmentation as an abrupt increase in fluorescence intensity. As noted in the Appendix [see paragraph following Eq. (A11)], for x > 0, only the eigenvalues that we have labeled as λ_2 and λ_3 can become degenerate and only at values of x_r provided by Eq. (A12). From this equation, and its subsequent discussion, we see that the degeneracy requires a negative value for M (the quantum number for the

projection of K on the field axis) but with the constraint that |M| be less than I. In the case of hexafluorobenzene which has six equivalent nuclei, $^{34-46}$ (N=6), total nuclear spin quantum numbers of I=0, 1, 2, and 3 are allowed and, accordingly, resonances are predicted only in the I=2, M=-1and I=3, M=-2 and -1 channels at values of $x_r=6$, 6, and 12, respectively. Since the recombination fluorescence utilizes all allowed channels of which there are five, with I=2and one with I=3, the resonance at $x_r=6$ is expected to be considerably more prominent than the resonance at $x_r = 12$. On the other hand, the degeneracies that appear at x=0 (with λ_1 and λ_2 both becoming equal to -I-1 and λ_3 and λ_4 both becoming equal to +I) are manifested at all possible values of I and M. Therefore, if we imagine the magnetic field to sweep from positive to negative (i.e., field reversed) values [in which case Eq. (A12) continues to be valid with M now positive], it follows that one can expect an even more prominent resonance at x=0.

Figure 1 confirms these predictions. The deep minimum that is observed is simply a consequence of the resonance at x=0 and the structure that is observed at a field strength of 411 G is positioned at exactly the predicted 3.0 hyperfine constants (i.e., $x_r=6.0$). The possible structure in Fig. 1 at 820 G, would, of course, correspond in position to the predicted $x_r=12$ resonance, but signal to noise is inadequate to establish this with certainty. However, if there is structure here, it is, as expected from our considerations of the previous paragraph, much less pronounced than that at the position $x_r=6.0$. An interesting consequence of this discussion is that the observation of the resonance at the predicted position provides an alternative to the usual ESR technique for measurement of the hyperfine constant of selected anions in hydrocarbon solutions.

As discussed in Sec. III, the yield of singlet recombinations, $\Phi(x)$, is determined from the radial probability density of separation distances. From Eqs. (3) and (5) the escape probability $\Omega_{\rm esc}$ and the function $h_{\rm sc}(s)$ are extracted using some assumed form for $f(r_0)$. The function, $h_{sc}(s)$ is then least square fit to Eq. (7) and the parameters A', B', and nobtained. This fitting is most simply accomplished by making a linear regression of $(1-\Omega_{esc})/[1-h_{sc}(s)]$ on s^n and extracting therefrom the intercept, A', and the slope, B'.³³ This procedure provides all of the parameters required for the evaluation of the partial singlet recombination yield, $\phi_M(I,x)$, in Eq. (8), and summing this over all pertinent I and M gives the total yield of singlet recombinations, $\Phi(x)$, via Eq. (11). The connection between $\Phi(x)$, which is a yield per scavenged geminate pair and the experimental yield $\Psi(x)$, a yield per absorbed photon, is simply a proportionality constant equal to the product of the photoionization ejection probability at 123.6 nm and the scavenging efficiency at 0.086 M hexafluorobenzene. We will attempt to evaluate this constant later. For the present, we simply determine the form of $f(r_0)$ that best fits the general shape of the spectrum in Fig. 1.

Two radial density probability functions an exponential and a Gaussian have been commonly considered in attempts to fit to Onsager's theory of geminate ion escape the dependence on electric field strength of the photocurrent from neat

TABLE I. Least-square diffusion parameters, n, A', and B' for exponential and Gaussian radial probability distributions for various values of γr_c and their corresponding escape probabilities, $\Omega_{\rm esc}$.

		Exponential		
γr_c	$\Omega_{ m esc}$	n	Α'	В′
17.0	0.013 20	0.660	1.000	0.048 1
18.0	0.011 01	0.660	1.000	0.042 6
19.0	0.009 23	0.655	0.996	0.039 4
20.0	0.007 76	0.654	0.995	0.035 6
		Gaussian		
γr_c	$\Omega_{ m sec}$	n	Α'	В′
7.0	0.006 35	0.800	1.011	0.023 4
8.0	0.003 60	0.790	1.004	0.017 8
8.5	0.003 20	0.785	1.001	0.015 5
9.0	0.002 07	0.780	0.999	0.014 1

isooctane or of ionizable solutes dissolved in isooctane.^{2,38,39} They are both functions of one variable γ and can be expressed in normalized form as

$$f(r_0) = \gamma_1^3 / 2 \exp(-\gamma_1 r_0),$$

$$f(r_0) = (4 \gamma_2^3 / \sqrt{\pi}) \exp(-\gamma_2^2 r_0^2),$$
(12)

where the average separation distance $\langle r_0 \rangle_i$ is connected to γ_i as

$$\langle r_0 \rangle_1 = 3/\gamma_1, \langle r_0 \rangle_2 = 2/\sqrt{\pi\gamma_2}.$$
 (13)

Although these distribution functions describe well the separation distances of the thermalized electron population that results from photoionization, we assume here that the same form of distribution function can be used to describe the population of scavenged electrons, albeit with possibly different parameters γ_i . We will return to this and other assumptions implicit in the use of these functions later.

In Table I we show for each of these functions, and at selected values of γ_i , the parameters A', B', and n that provide the best least square fits to the Noolandi scavenging function, $h_{sc}(s)$ over a range of s from 0.1 to 1000. Also shown in Table I are the escape probabilities predicted by Eq. (3) for each choice of $f(r_0)$ and for the selected values of γ_i . Figure 2 shows the quality of the fit for representative entries in Table I. The points in Fig. 2 are the ratios, Q, $\{=(1-\Omega_{esc})/[1-h_{sc}(s)]\}$. These points were obtained via Eqs. (3) and (5) using the radial density function and numerical values of the Noolandi-Hong function $\Omega(\tau, r_0)$ at selected τ and r_0 ²² The solid lines are nonweighted least square fits of Q to the linear regression $A' + B's^n$. As expected from previous reports,³³ the fits are very good (and over a much larger range in s than previously studied) with standard deviations on A' and B' of the order of 0.1% - 0.2%.

Figures 3 and 4 show some predictions of Eq. (11) using the parameters of Table I for the exponential and Gaussian functions at values of $\gamma r_c = 17.5$ and 7.8, respectively. The experimental data, from Fig. 1, are shown plotted in Figs. 3 and 4 as the ratio $[\Psi(x) - \Psi(x_0)]/\Psi(x_0)$ with $x_0 = 14.8$ cor-



FIG. 2. The parameter Q as a function s^n for (a) an exponential radial probability density with $\gamma r_c = 18$, (b) for a Gaussian radial probability density with $\gamma r_c = 8.0$.

responding to a field strength of 1.01 kG. Equation (11) is similarly displayed as $[\Phi(x) - \Phi(x_0)]/\Phi(x_0)$. For the geminate pair mutual diffusion constant, *D*, and Onsager radius $(r_c = e^{2}/\epsilon kT)$ in Eq. 10, we have used the values $3.1_8 \times 10^{-5}$ cm²/s and 321 Å, respectively.⁴⁰⁻⁴³ In Figs. 5 and 6 we explore the sensitivity of the predictions to some other values of γr_c albeit close to those in Figs. 2 and 3. In Figs. 7(a) and 7(b) we show predictions for the exponential and Gaussian distributions, respectively, using significantly smaller



FIG. 3. The 123.6 nm yield of recombination fluorescence (Ψ) at a field strength, *x*, minus the yield (Ψ_0) at a field strength $x_0=14.8$ (=1.01 kG) divided by Ψ_0 for the system 0.086 M hexafluorobenzene in deuterated iso-octane at -10 °C. Experimental data are shown as filled circles. The solid line is the corresponding theoretical prediction, ($\Phi-\Phi_0$)/ Φ_0 , using an exponential radial probability density with $\gamma r_c=17.5$. The theoretical prediction for the quantum yield of singlet recombinations at the normalization field of $x_0=14.8$ is $\Phi_0=0.716$. Insert shows results at higher fields.



FIG. 4. The 123.6 nm yield of recombination fluorescence (Ψ) at a field strength, *x*, minus the yield (Ψ_0) at a field strength $x_0=14.8$ (=1.01 kG) divided by Ψ_0 for the system 0.086 M hexafluorobenzene in deuterated iso-octane at -10 °C. Experimental data are shown as filled circles. The solid line is the corresponding theoretical prediction, ($\Phi-\Phi_0$)/ Φ_0 , using a Gaussian radial probability density with $\gamma r_c = 7.8$. The theoretical prediction field of $x_0=14.8$ is $\Phi_0=0.749$. Insert shows results at higher fields.



FIG. 6. Theoretical predictions for the yield of singlet recombinations (Φ) at a field strength, x, minus the yield (Φ_0) at a field strength $x_0=14.8$ (=1.01 kG) divided by Φ_0 for the system hexafluorobenzene in deuterated isooctane at -10 °C as a function of x assuming a Gaussian probability density of initial geminate ion separation distances with range parameters of $\gamma r_c = 7$ (a), 8 (b), 8.5 (c), and 9 (d). For each of these range parameters, the theoretical predictions for the quantum yield of singlet recombinations at the normalization field of $x_0=14.8$ are 0.711, 0.757, 0.781, and 0.798, respectively.

values of γr_c of 7.0 (for which B'/A' = 0.168, n = 0.750, and $\Omega_{\rm esc} = 0.107$) and 2.0 (for which B'/A' = 0.31, n = 0.908, and $\Omega_{\rm esc} = 0.168$). For these more diffuse distributions, the resonances become displayed more prominently. For all of the theoretical curves in Figs. 3–7, the absolute singlet recombination probabilities can be calculated using the values of $\Phi(x_0)$ at the normalization field of $x_0 = 14.8$ that are provided in the figure captions.

As will be briefly discussed later, the magnitude of the zero field resonance is expected to be very sensitive to small perturbations. These have the effect of removing some of the degeneracies at x=0, and, accordingly act to lower the yield of singlet recombinations below that predicted by Eq. (11). It was for this reason that we chose to normalize all spectra in Figs. 3-7 at a field strength (i.e., 1.01 kG) at which the sensitivity to such perturbations is much reduced. As will be





FIG. 5. Theoretical predictions for the yield of singlet recombinations (Φ) at a field strength, x, minus the yield (Φ_0) at a field strength x_0 =14.8 (=1.01 kG) divided by Φ_0 for the system hexafluorobenzene in deuterated isooctane at -10 °C as a function of x assuming an exponential probability density of initial geminate ion separation distances with range parameters of γr_c =17 (a), 18 (b), 19 (c), and 20 (d). For each of these range parameters, the theoretical predictions for the quantum yield of singlet recombinations at the normalization field of x_0 =14.8 are 0.710, 0.727, 0.742, and 0.757, respectively.

FIG. 7. Theoretical predictions for the yield of singlet recombinations (Φ) at a field strength, x, minus the yield (Φ_0) at a field strength $x_0=14.8$ (=1.01 kG) divided by Φ_0 for the system hexafluorobenzene in deuterated isooctane at -10 °C as a function of x assuming (a) an exponential probability density of initial geminate ion separation distances with range parameter of $\gamma r_c=7$, (b) a Gaussian probability density of initial geminate ion separation distances with range parameter $\gamma r_c=2$. For (a) and (b), respectively, the theoretical predictions for the quantum yield of singlet recombinations at the normalization field of $x_0=14.8$ are 0.492 and 0.461.

observed from Figs. 2 and 3, this appears to work very well. For both the exponential and Gaussian distribution functions, a single value of γr_c permits close matching of the experimental and theoretical curves over most of the spectrum. As can be seen from Figs. 4 and 5, the theoretical curves are very sensitive to the parameter, γr_c and permit us to fix its value to within ca. ± 0.2 unit.

Our best values for γr_c for the two distributions are 17.5 (exponential) and 7.8 (Gaussian) corresponding to an average separation distance of the scavenged electron from its geminate positive ion of $\langle r_0 \rangle = 55$ and 46 Å, respectively. Except at x=0, both distributions fit rather well over most of the range in magnetic field strength. However, it will be noted that the Gaussian does not predict the position of the minimum as closely as does the exponential and also underestimates the magnitude of the resonance peak at x=6. An analysis of the theory shows the magnitude of the x=6 peak to be very sensitive to the time available for spin evolution, increasing as this time increases (see Fig. 7). Apparently, the much faster fall-off of the Gaussian at large separation distances alters this time sufficiently to generate the observed effect. The propriety of using this criterion for distinguishing the two distribution functions is discussed later.

The values of $\gamma r_c = 17.5$ and 7.8 for the exponential and Gaussian distributions of scavenged pairs are significantly larger than those reported by Casanovas et al.² of 6.2 and 2.1 for the distribution of thermalized electrons as deduced from the electric field dependence of photocurrent from neat isooctane excited at 123.6 nm. The direction of the disparity is such as to suggest that the distribution of scavenged pairs is significantly more compact than that of the thermalized electrons in the absence of scavenger. Consistent with this we have found that the steady-state photocurrent from iso-octane (at 2 kV/cm) is strongly reduced on addition of C_6F_6 . Measurements at 20 kV/cm of the photocurrent from iso-octane at several concentrations of C_6F_6 indicate that the ratio of photocurrent with scavenger added to that without, i.e., J_0/J , is linearly increased up to 0.1 M with a slope of 17±1 $M^{-1.44}$

Similar effects of scavengers have been previously reported in photoionization studies of TMPD in saturated hydrocarbon solvents excited at 5.80 eV and attributed to a prethermalization of the electron, most plausibly via electron capture by the scavenger.45 In the case of iso-octane solvent containing *n*-perfluoheptane, J_0/J was found to be linear on scavenger concentration up to 0.2 M with a slope also of 17 M^{-1} . Subsequent studies of the electric field dependence of the TMPD photocurrent⁴⁶ directly confirmed the effect of the C₇F₁₆ to make more compact the distribution function. It was observed that the exponential distribution function while continuing to fit the Onsager theory over the entire range of scavenger concentration up to 0.13 M, required $\gamma_1 r_c$ to increase from 11.9 at zero concentration to 18.5 at 0.13 M (with an interpolated value of 16.5 at 0.086 M).⁴⁷ Unfortunately, we do not have the electric field dependence of the photocurrent from isooctane in the presence of C₆F₆, but the similarity of the effects of C_6F_6 and C_7F_{16} to reduce the steady state photocurrent from isooctane and the similarity in the values of $\gamma_1 r_c$ required to fit the data to the relevant magnetic and electric field theories, is clearly suggestive of a common mechanism operating.^{48,49}

Returning to the comparison of the exponential and Gaussian distribution functions, we note from Table I, at the relevant values of γr_c of 17.5 and 7.8, respectively, that the escape probabilities are predicted to differ by a factor of \sim 3.0 (= $\Omega_{esc1}/\Omega_{esc2}$ =.0121/.00402). Similarly large differences have been predicted in photoionization measurements of TMPD in iso-octane. This large disparity, however, has not usually provided a means for distinguishing the two distribution functions. Absolute photoionization current measurements provide only a quantum yield for escaped charge which is the product of $\Omega_{\rm esc}$ with an unknown molecular photoejection probability, ϕ_{\pm} . Although ϕ_{\pm} must be less than unity, this upper bound, by itself, is not always adequate for reliable distinction. On the other hand, as discussed above, the sensitivity of the x=6 resonance to the form of the tail of the distribution function appears to more definitively provide a discriminating criterion. Since any perturbations in the real system will always have the effect to make less pronounced the appearance of this resonance, we can safely conclude that its theoretical underestimation using either the Gaussian or the exponential distribution is a clear indication of the inadequacy of both distributions. Of course, of the two, the exponential seems somewhat superior, based on its predictions with regard to the position of the minimum and the shape of the x=3 resonance. But clearly, a distribution function which falls off more slowly with increasing r_0 is required. A similar need has been reported to develop from attempts to explain the yields of escaped electrons from high energy x-ray irradiated iso-octane.⁴ In this case it has been suggested that to a Gaussian distribution function at small r_0 (i.e., $\langle 2.4\gamma r_c \rangle$) be appended, at larger distances, an $r_0^$ power law tail. We have not yet made any quantitative attempts to fit the magnetic field dependence to multiparameter distribution functions. More highly resolved spectra will be required for this purpose.

Unlike the x=6 resonance, the magnitude of the resonance at x=0 is always *overestimated* by the theory. This, as indicated earlier, is most plausibly due to a higher sensitivity of the x=0 resonance to a variety of perturbations^{50,51} that act to remove the pertinent degeneracies. Depending on the nature of the perturbation, this additional sensitivity may be a simple consequence of the field dependence of the eigenvalues in Eq. (A10), namely, that the lower field degeneracies are more sensitive to change in field strength than are those at higher fields. Thus, in the case of hexafluorobenzene with N=6, we find that at x=0 where $\omega_{12}=\omega_{34}=0$, that $(d\omega_{12}/dx)$ and $(d\omega_{34}/dx)$ are both larger than $(d\omega_{23}/dx)$ at x=6 and 12 (where $\omega_{23}=0$) by factors of about 3 and 10, respectively. The effect of this is to make the x=0 significantly sharper than the two other resonances (see Fig. 7).

Measurement of the recombination fluorescence provides us, as noted earlier, with the quantum yield, $\Psi(x)$ for singlet recombinations per absorbed photon whereas the theory of the magnetic field effect provides us with the quantum yield for singlet recombinations per scavenged electron. Their ratio is simply the product of ϕ_{\pm} with the scavenging probability, p_{sc} . Although the latter is unknown for C₆F₆ in



FIG. 8. The ratio, Ψ , of the fluorescence quantum yield of (a) 0.086 M hexafluorobenzene and (b) 0.097 M 1,4-difluorobenzene in nondeuterated iso-octane for excitation of the iso-octane at 123.6 nm to the fluorescence quantum yield for excitation of the fluorocarbon at 254 nm as a function of magnetic field strength, *H* in Gauss.

iso-octane, it can be estimated using the equation,³³

$$p_{\rm sc} = Bc^n / (1 + Bc^n)$$

where

$$B = B' (k_s r_c^2 / 4D)^n, (14)$$

with k_s being the electron attachment rate constant, D, the diffusion constant of the electron and B' and n determined by the distribution function for geminate pair radial separation distances. Taking $\gamma_1 r_c = 12$ for neat iso-octane^{48,49} gives n=0.7 and B'=0.1. For k_s we have used the reported value $5.6 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$ for hexafluorobenzene in iso-octane.⁵² Substitution of this k_s into Eq. (14) together with $r_c=321 \text{ Å}$ and $D=0.1 \text{ cm}^2/\text{s}$ (from an electron mobility in iso-octane of 4.6 cm²/V s) (Ref. 53) gives $p_{sc}=0.75$ at 0.086 M. Using this, together with both the experimental $\Psi=0.20$ at 1 kG (see Fig. 1) and with the theoretical quantum yield for singlet recombination of 0.72 also at 1 kG (see caption to Fig. 3), we obtain finally an estimate of ϕ_{\pm} of 0.3 ± 0.1 , in approximate agreement with an earlier reported photoelectric value of 0.4_7 .²

A few preliminary measurements were made using 1,4difluorobenzene and 1,3,5-trifluorobenzene in nondeuterated iso-octane. The 1,3,5-trifluorobenzene had been reported to have a fluorescence quantum yield of 0.018 (Ref. 54) which is about 1/2 of that from hexafluorobenzene,^{30,54} but our measurements indicate a quantum yield at least $2.5 \times$ lower than this and, accordingly, too low for the sensitivity of our magnetic field measurements. The 1,4-difluorobenzene gave results shown in Fig. 8(b). For comparison we also show in Fig. 8(a) results for hexafluorobenzene in nondeuterated isooctane. As can be seen, only rather weak zero field resonances are observed and no indication for any higher field resonances. Perturbations via hyperfine interactions on the isooctane cation, in the case of the C_6F_6 and, additionally, for the 1,4-difluorobenzene on nonequivalent centers of the anion (with isotropic hyperfine constants of 5.30 and 1.75 G for the protons and fluorines, respectively³⁵) are most plausibly important contributors to the loss of the resonance structures.⁵¹

Charge transfer between the $C_6F_6^-$ anion and neutral C_6F_6 can reduce the anion–cation spin correlation and make less pronounced the magnetic field effects. Such charge transfer has been detected by monitoring the concentration dependence of the linewidth of the optically detected ESR spectrum of x-ray irradiated C_6F_6 in squalane and reported to be diffusion limited.⁵⁰ Although we have not yet made careful studies of the concentration dependence of the agenetic field effects in deuterated isooctane, preliminary measurements show no evidence for significant contribution from such charge transfer processes at least in the photoionization process at 123.6 nm and at concentrations up to 0.1 M.

Irradiation of saturated hydrocarbon liquids with 2 MeV electron pulses has yielded no evidence from fluorescence detected magnetic resonance (FDMR) for the existence of stable parent hydrocarbon ions (RH_2^+) on time scales greater than ~1 ns. Instead, only parent minus H_2 olefin radical cations (i.e., $R^+)$ are observed. 15,55 If the olefin radical cation retains the spin polarization of the parent ion (and the observation of FDMR suggests this to be the case in at least some of the decays), then such fragmentation, even were it occurring under our photoexcitation conditions, would have no effect on the magnetic field spectra so long as this fragmentation were the *exclusive* decay channel of RH_2^+ . However, there is also reported indirect evidence for the existence of an additional decay channel involving a bimolecular proton transfer reaction to form a neutral radical (RH), and a nonmagnetic cation (RH₃⁺).^{15,55} The effect of such a transformation would be to cause a loss of recombination fluorescence (since the proton affinities of RH₂ are generally too large for excitation of the hexafluorobenzene anion on recombination).

In order to seek evidence for transformations of RH₂⁺ to nonfluorescent species and/or to species which provide nonmagnetically sensitive recombination fluorescence, we have studied the effect of the addition of 1 M deuterated benzene on the magnetic field spectra and on the quantum yield of fluorescence. The benzene, with a $\sim 0.6 \text{ eV}$ lower ionization potential than isooctane, should effectively capture the isooctane positive charge to form the benzene radical cation (the thermoneutral proton transfer to benzene under these conditions is unlikely), converting thereby any intercepted decay channel to one with magnetically sensitive light. However there was observed no effect. The yield of recombination fluorescence, as well as its magnetic field dependence were both essentially unaffected (within $\sim 10\%$) upon addition of the benzene, implying thereby the absence of any significant decay of isooctane radical cation via channels other than that which provide magnetically sensitive light (at least under our photoexcitation conditions at -10 °C). The alternative, that the other channels (e.g., proton transfer) are too rapid for 1

M benzene to intrude, would require a decay constant of the isooctane so large, that we would be unable to explain reasonably either the yield of recombination fluorescence, or the magnitude of the observed magnetic field effect. A more complete analysis of the influence of multichannel ion decay on the magnetic field effect in other solvents (wherein we have indeed observed benzene to exert a significant influence), will be presented elsewhere.

V. CONCLUSIONS

The general theory of hyperfine-driven spin evolution of a geminate pair of ions diffusively recombining in their mutual Coulomb field predicts well the experimental effect of a magnetic field on the recombination fluorescence of deuterated iso-octane cations with hexafluorobenzene anions generated by the absorption of 123.6 nm light by the iso-octane. In the case that the entire hyperfine interaction is confined to a single ion containing N equivalent nuclei, (as is the case in the system studied here with N=6 for the fluorines of the C_6F_6 anion), resonances in the dependence of fluorescence quantum yield on magnetic field strength are predicted and observed at magnetic field strengths of H=0, 3a, and 6a, where a is the anion hyperfine constant. Although for C_6F_6 anion, a is known from ESR measurements to be 137 G, the resonance at 3a is sufficiently well defined to permit an independent determination of a exclusively from its magnetic field position in a simple measurement of the recombination fluorescence.

The magnitudes and shapes of the resonances are predicted and observed to be very sensitive to the detailed behavior of the radial probability density of initial geminate pair separation distances, and, most importantly, to their behavior at large distances. Although one parameter exponential, and one parameter Gaussian probability densities both fit extremely well the experimental field dependence of the quantum yield of recombination fluorescence over most of the range in H, they both tend to considerably overestimate the yield at H=0 and to slightly underestimate it at H=3a. The resonance at 6a was too weak for quantitative study. The overestimation at H=0 is largely contributed to by the theory's neglect of perturbations in the real system that tend to remove the degeneracies responsible for the resonance. However, the prediction of the magnitude of the H=3aresonance, which is much less sensitive to these perturbations, is considered to be underestimated by virtue of too rapid a decline in both exponential and Gaussian distribution functions at large values of the initial geminate pair separation distances. A power law tail appended to either of these distributions would be sufficient to accommodate the experimental results.

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APPENDIX

We consider first the case of two electrons, 1 and 2, both moving in a homogeneous magnetic field of strength H but with only one of the electrons bound to a nucleus of spin I. For basis vectors we choose a direct product of spin and spatial functions, i.e.,

$$|\Psi\rangle = |ISKM\rangle |u(1,2)\rangle,\tag{A1}$$

where I, S, K, and M label quantum numbers of the nuclear spin, the electron spin, the total spin, and its projection on the direction of the magnetic field.

For two electrons, we need only consider the following four spin functions for each possible M:

$$|X_1\rangle = |I0IM\rangle,$$

$$|X_2\rangle = |I1IM\rangle,$$

$$|X_3\rangle = |I1I+1M\rangle,$$

(A2)

and

$$|X_4\rangle = |I1I - 1M\rangle$$

The only constraint on the spatial function is that it be symmetrical or antisymmetrical in exchange of the positions of the two electrons depending on whether it is linked to a spin function with S=0 or S=1, respectively.

The conventional Hamiltonian for this problem expresses the isotropic hyperfine interactions of the two electrons with the one nucleus and the Zeeman interaction of the two electrons with the magnetic field, H. We ignore the nuclear Zeeman interaction (which is anyhow quite small at the fields we employ) and any difference in g value for the two electrons. Thus,

$$\mathcal{H} = \alpha [\delta(1)\mathbf{I} \cdot \mathbf{S}_1 + \delta(2)\mathbf{I} \cdot \mathbf{S}_2] + \beta \mathbf{H} \cdot (\mathbf{S}_1 + \mathbf{S}_2), \qquad (A3)$$

where α and β are expressed in terms of the bohr and nuclear magnetrons, μ_B and μ_N , the electron and nuclear *g* values, g_e and g_n [i.e., $\alpha = (8\pi/3)(\mu_B \mu_N g_e g_n)$ and $\beta = g_e \mu_B$], and **I** and **S** are in units of \hbar .

By virtue of the constraint on the spatial function, and the assumption that only one of the electrons is bound, (i.e., experiences the hyperfine interaction), it follows directly that the hyperfine part of H may be re-expressed as

$$\mathcal{H}_{\rm hf} = \kappa \mathbf{I} \cdot (\mathbf{S}_1 \pm \mathbf{S}_2) \tag{A4}$$

for matrix elements which are diagonal (upper sign) or offdiagonal (lower sign) in the quantum number *S*. The parameter $\kappa [= \alpha \langle u(1,2) | \delta(1) | u(1,2) \rangle]$ is one-half of what is usually referred to as the isotropic hyperfine coupling constant, *a*.

The elements of \mathcal{H}_{hf} that are diagonal in all four spin quantum numbers are most easily obtained using the well-known identities for a coupled representation of two angular momenta,⁵⁸ i.e.,

$$\langle I, S, K, M | \mathbf{I} \cdot \mathbf{S} | I, S, K, M \rangle$$
$$= \frac{[K(K+1) - I(I+1) - S(S+1)]}{2}$$
(A5)

and

$$\langle I, S, K, M | S_z | I, S, K, M \rangle$$

= $\frac{[K(K+1) - I(I+1) + S(S+1)]M}{2K(K+1)}$, (A6)

where S_z is the projection of $(\mathbf{S}_1 + \mathbf{S}_2)$ on **H**.

The off-diagonal hyperfine Hamiltonian commutes with I^2 , K^2 , and K_z (i.e., the projection of **K** on **H**) and, therefore, can only link $|X_1\rangle$ with $|X_2\rangle$. The Zeeman Hamiltonian commutes with I^2 , S^2 , and K_z and links $|X_2\rangle$ with $|X_3\rangle$ and $|X_4\rangle$, but being a vector operator, cannot link $|X_3\rangle$ and $|X_4\rangle$ for which ΔK =2. The nonzero matrix elements of the total Hamiltonian are obtained from the identities⁵⁶

$$\langle I, 1, I, M | \mathbf{I} \cdot (\mathbf{S}_1 - \mathbf{S}_2) | I, 0, I, M \rangle = \sqrt{I(I+1)}$$
 (A7)

and

$$\langle I, S, K, M | S_z | I, S, K-1, M \rangle$$

= $\sqrt{\frac{[K^2 - (I-S)^2][(I+S+1)^2 - K^2][K^2 - M^2]}{4K^2(4K^2 - 1)}}$. (A8)

Using Eqs. (A5)–(A8), the nonvanishing matrix elements of *H* (in units of κ) in the $|X_i\rangle$ representation can be expressed in terms of a dimensionless magnetic field strength $x = \beta H/\kappa$ as

$$\begin{aligned} \mathscr{H}_{12} &= \sqrt{I(I+1)}, \\ \mathscr{H}_{22} &= -1 + \frac{Mx}{I(I+1)}, \\ \mathscr{H}_{23} &= \frac{x\sqrt{I}}{(I+1)} \sqrt{\frac{(I+1)^2 - M^2}{(2I+1)}}, \\ \mathscr{H}_{24} &= \frac{x}{I} \sqrt{\frac{(I+1)(I^2 - M^2)}{(2I+1)}}, \\ \mathscr{H}_{33} &= I + \frac{Mx}{(I+1)}, \\ \mathscr{H}_{44} &= -I - 1 - \frac{Mx}{I}. \end{aligned}$$
(A9)

Solving for the eigenvalues, λ_i (in units of κ) gives

$$2\lambda_{1} = -1 - x - [(x+1)^{2} + 4R]^{1/2},$$

$$2\lambda_{2} = -1 + x - [(x-1)^{2} + 4R]^{1/2},$$

$$2\lambda_{3} = -1 - x + [(x+1)^{2} + 4R]^{1/2},$$

$$2\lambda_{4} = -1 + x + [(x-1)^{2} + 4R]^{1/2},$$

(A10)

where

$$R = I(I+1) + Mx. \tag{A11}$$

It is important to recognize, at this point, that since M cannot exceed K, the eigenvector $|X_4\rangle$ does not exist for $M = \pm I$, and \mathcal{H} is reduced to only three eigenvalues. Examination of the secular determinant shows that it is either λ_1 or λ_2 that must be eliminated depending on whether M is +I or -I respectively. Similarly, when $M = \pm (I+1)$ there can be only one eigenvalue, i.e., \mathcal{H}_{44} .

From Eqs. (A10) and (A11) it follows that at x=0, and for any value of M, the eigenvalues λ_1 and λ_2 both become equal to -I-1 and the eigenvalues λ_3 and λ_4 both become equal to I. Although these degeneracies are split as the field is applied, it is important to note, as is developed in the text, that at a field x_r , such that R=0, i.e., at

$$x_r = \frac{-I(I+1)}{M},\tag{A12}$$

a new degeneracy appears with the eigenvalues λ_2 and λ_3 both becoming equal to zero. Since, as noted above, the eigenvalue λ_2 does not exist for M = -I, Eq. (A12) is only satisfied for 0 > M > -I.

The eigenvectors of \mathcal{H} , hereafter referred to as $|\lambda_i\rangle$, can now be displayed in terms of the basis set. However all that we require is the coefficient $\langle \lambda_i | X_1 \rangle$, since at t=0 the system starts out as singlet (i.e, the spin state $|X_1\rangle$ with some value of M), and, therefore, at any subsequent time t, the probability amplitude for the system to be still singlet is $|\langle \lambda_i | X_1 \rangle|^2 \exp(-i\kappa \lambda_i t/\hbar)$ summed over all i. A straightforward calculation shows that

$$\begin{split} |\langle \lambda_i | X_1 \rangle|^{-2} &= 1 + \frac{\lambda_i^2}{I(I+1)} \\ &+ \frac{x^2}{(2I+1)} \left[\frac{(I+1)^2 - M^2}{(I+1)(I-\lambda_i \mp x)^2} \right. \\ &+ \frac{(I^2 - M^2)}{I(I+1+\lambda_i \pm x)^2} \right], \end{split}$$
(A13)

where the upper sign is to be used for the eigenvalues λ_1 and λ_3 and the lower sign for λ_2 and λ_4 . Accordingly, the probability that the system which began in $|X_1\rangle = |I0IM\rangle$ at t=0, will remain with S=0 at time t is

$$p_M(I,x,t) = c_0 + \sum_{i \neq j} c_{ij} \cos \omega_{ij} t, \qquad (A14)$$

where

$$c_{0} = \sum_{i} |\langle \lambda_{i} | X_{1} \rangle|^{4},$$

$$c_{ij} = 2 |\langle \lambda_{i} | X_{1} \rangle|^{2} |\langle X_{1} | \lambda_{j} \rangle|^{2},$$
(A15)

and

$$\omega_{ij} = \kappa (\lambda_i - \lambda_j) / \hbar.$$

Since K_z commutes with \mathcal{H} , and the initial excitation, we presume, generates an incoherent superposition of Mstates with equal probabilities, the *total* singlet probability is simply obtained by averaging Eq. (A13) over all possible initial values of M from M = -I to +I. We refer to this probability as p(I,x,t),

$$p(I,x,t) = \sum_{M=-I}^{M=I} \frac{p_M(I,x,t)}{(2I+1)}.$$
 (A16)

In the case that the single nucleus is replaced by N equivalent magnetic nuclei each of spin 1/2, we can treat each of the possible values of total nuclear spin from I=0 to I=N/2 independently. This, of course too is a consequence of the commutation of I^2 with the hyperfine Hamiltonian.

Accordingly, the total singlet probability for arbitrary N, hereafter referred to as $P_s(x,t)$, can be written as

$$P_{s}(x,t) = \left(\frac{N+k}{2}\right)! \left(\frac{N-k}{2}\right)! \times \sum_{I=k/2}^{N/2} \frac{(2I+1)}{\left(\frac{N}{2}+I+1\right)! \left(\frac{N}{2}-I\right)!} p(I,x,t),$$
(A17)

where k is 0 or 1 depending on whether N is even or odd and where the coefficient of p(I,x,t) is simply the fraction of states with a specified value of I. (e.g., for N=6, this fraction is 1/20, 5/20, 9/20, and 5/20 for I=3,2,1, and 0 respectively). For even N, Eq. (A17) assumes a much simpler form in the two limiting cases of zero and infinite magnetic field strength. For these two cases we obtain

$$P_{s}(0,t) = \left[\frac{N+2}{2(N+1)}\right] - \frac{N}{2} \left[\cos^{N-1}(\kappa t/\hbar) - \left(\frac{N+2}{N+1}\right)\cos^{N+1}(\kappa t/\hbar)\right]$$
(A18)

and

$$\lim_{x\to\infty} P_s(x,t) = \frac{\left[1 + \cos^N(\kappa t/\hbar)\right]}{2}.$$

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