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# Magnetic field effect on the micellar $(C_{60})_n^{\bullet -}$–pyrene$^{\bullet +}$ radical-pair system

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## Abstract

We report for the first time a magnetic field effect on radical pair recombination involving fullerene clusters in a fluorinated micelle. It is found that the rate of decay of radicals increases with increasing external magnetic field strength. The effect at high field is attributed to the *g*-anisotropy-induced relaxation mechanism. ©1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Magnetic field effect; Spin chemistry; $C_{60}$ (fullerene) photophysics; Radical pair reactions

## 1. Introduction

The enthusiasm generated by the discovery of fullerenes [1–3] have led to extensive investigations of various aspects, photochemistry inclusive, of these new carbonaceous materials. Despite the stability of $C_{60}$ clusters, which is ascribed to the geodesic and electronic properties inherent in the truncated icosahedral cage structure [4], fullerenes can be made to undergo chemical reactions, especially in the electronically excited state. Upon photo-excitation $C_{60}$ goes first to the singlet excited state and then rapidly to the triplet state with efficiency almost unity. The triplet quantum yield has been measured by the sensitised formation of singlet oxygen [5]. In the ground state $C_{60}$ is a potential acceptor of electron, which is evident from its electron affinity of 2.6–2.8 eV [6]. Its electrochemical reduction occurs at a potential of $E_{\mathrm{red}} = 0.33$ V vs. Ag/AgCl, and 0.42 V vs. SCE in benzonitrile [7–9]. $C_{60}$ in its triplet state undergoes easier reduction because of its high triplet energy of 1.56 eV [10–12]. Photochemical reduction in the triplet state leading to $C_{60}^{\bullet -}$ has indeed been confirmed by EPR studies of reactions between $C_{60}$ and various aryl donors [13]. The laser-flash-photolytic studies with $C_{60}$ and various aromatic amine donors also demonstrate electron transfer to $C_{60}$ producing anion radicals [12].

The lifetime of radical pairs (RP) generated by such electron transfer as also the yield of escaped radicals ought to be magnetic field sensitive. The current understanding of magnetic field effect (MFE) on RP recombination [14–16] may be summarised as follows. Depending on the spin state of the precursor, the RP is born in either triplet or singlet state. The triplet-born RP has a long lifetime because it has to evolve into a singlet before recombination could occur. For such spin-evolution to the singlet, both hyperfine coupling with the internal field and Zeeman precession around the external field play their respective roles. The hyperfine coupling can cause transitions between the singlet (S) and all the three triplets ($T_0$, $T_+$, $T_-$) while the Zeeman interaction stops the $S \leftrightarrow T_\pm$ transitions by making the energy difference between the states more than the hyperfine splittings of levels. Thus, the ISC rate decreases and the lifetime increases significantly on application of a small field, reaching a saturation level at low fields [17]. At high fields, external field can increase precession rate between $T_0$ and S (i.e., $\Delta g$ effect). It can also open partially the blocked $S \leftrightarrow T_\pm$ channels, by speeding up relaxation caused by tumbling of an anisotropic molecule in an external field. The lifetime thus decreases again [18], albeit to a small extent.

From the point of MFE $C_{60}$ is an interesting system, because it does not contain any magnetic nuclei [19]. This should allow us to see $\Delta g$ and relaxation effects (caused by external field) unhindered by the internal field. Secondly, it is a highly symmetric molecule belonging to the $I_h$ point group [4], and hence, there is little possibility of anisotropy-induced relaxation. However, the possibility of electron hopping between C atoms leading to spin decoherence exists.

Surprisingly, the magneto-kinetic effect on the fullerene radical recombination is still to be reported in the literature.

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To observe the effect of external magnetic field on $C_{60}$ RP recombination, we have chosen a micellar environment so that the radical encounter time in solution, or the lifetime of the RP ($\tau_{RP}$) is comparable to the RP $S \leftrightarrow T$ evolution time [14] ($\tau_{ST}$). Since micelles provide micro-cages with suitable reflection boundary, the escape yield becomes lower leading to an amplification of MFE [20–26]. Here we report MFE on RP recombination in photo-induced electron transfer (PIET) from pyrene (Py) to $(C_{60})_n$ in aqueous sodium perfluorononanoate micelle (SPFNM). Our choice of the system has been dictated by following requirements: (a) In homogeneous benzonitrile PIET in this $C_{60}$-pyrene system has been found to be efficient [12] although no MFE could be detected. (b) Ordinary micelles, such as SDS, are of open type and thus not suitable for solubilisation of $C_{60}$; on the other hand, perfluorinated micelles, being strong water-repellant, are compact in nature, and might be expected to solubilise both fullerene and pyrene. Despite the fact there are many good electron donors, we have deliberately chosen pyrene, a poor donor, because as a non-polar hydrophobic molecule it prefers to stay inside the micellar core instead of at the surface.

## 2. Experimental

$C_{60}$ was initially received as a gift from Prof. C.N.R. Rao, I.I.Sc., Bangalore and later on purchased from fluka. Pyrene (Aldrich) was used after zone-refining. Sodium perfluorononanoate was received as a gift from Late Prof. S.R. Palit of our department and was further purified by washing with *n*-heptane followed by recrystallisation from water. All the solutions are deaerated by purging argon for 30 min and then transferred to micro-cells, specially designed for high field studies, under nitrogen atmosphere.

The experiments were carried out in conventional laser-flash-photolysis (LFP) setup (Laser Kinetic Spectrometer, Applied Photophysics) coupled with a synchronised pulsed electro-magnet. For high field studies we have employed a home-built air-core electro-magnet, the pulse current is provided by the discharge of a series of two capacitors (500 μF, 4 kV each, connected in parallel) through an ignitron, the latter is being triggered by the discharge of another capacitor bank by a synchronously triggered thyristor with the aid of a pulser unit. The pulse duration for the main capacitor bank is about 2 ms. We have ensured that in the time scale of our experiment the magnetic field remains flat. The basic circuitory of our high field set up is described elsewhere [27]. The magnetic field was calibrated by using surge-coil technique. For our LFP studies we have used the second harmonic (532 nm) of Nd-YAG (DCR-11, Spectra Physics) Laser as the pump source, and a 250 W pulsed Xenon lamp for probe source. The output signal from a photodiode (IR sensitive) was fed into a digital storage oscilloscope (Tektronix, TDS350), the subsequent signal processing was done by an IBM PC-AT. The transient signal at each wavelength was averaged over 10 shots. Each experiment was repeated for three times to ensure reproducibility.

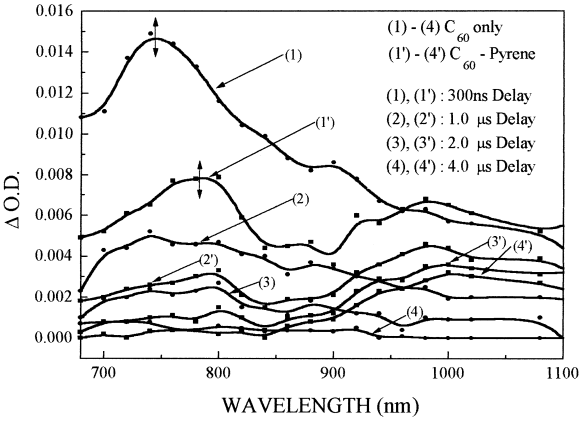


Fig. 1. Resolved absorption spectrum of excited colloidal $C_{60}$(without and with pyrene) in SPFNM (error bars are shown by double headed arrows for each set).

## 3. Results and discussion

### 3.1. The nature of the radical pair

Two separate degassed aqueous micellar solutions (0.11 M), one containing $C_{60}$ ($4 \times 10^{-5}$ M) only and the other containing $C_{60}$ ($4 \times 10^{-5}$ M) and pyrene ($4.1 \times 10^{-4}$ M), were separately employed in laser flash photolytic (LFP) study. The time-resolved spectra for both solutions are shown in Fig. 1. These time-resolved excited state absorption spectra of micellar $C_{60}$ are different from those obtained in a homogeneous medium such as benzonitrile. While in homogeneous solution of $C_{60}$ in neat solvents, a sharp T–T absorption band at 750 nm could be obtained, the corresponding band in our micellar solution is broad and diffuse. Similarly, the steady state $S_0 \rightarrow S_n$ absorption spectrum of $C_{60}$ in SPFNM (and other micelles such as SDS) consists of a very broad band between 400–700 nm. The large widths of $S_0 \rightarrow S_n$ and $T_1 \rightarrow T_n$ bands in micellar solution indicates that $C_{60}$ is attached to the micelles in clustered form of various sizes. A similar conclusion has been reached by Eastoe et. al. [28]. Their UV–VIS and small angle neutron scattering (SANS) studies provide evidence for the presence of monomeric and colloidal $C_{60}$ of various sizes in micellar solutions; the latter form is more stable and has very broad absorption bands. It may also be pointed out that the transient differential absorption of $C_{60}$ in thin films shows considerable difference from corresponding $C_{60}$ solution spectrum [29]. In the differential absorption spectra of the $C_{60}$ thin film, the absorption band due to intra-molecular triplet state could not be observed at the photon energy corresponding to that for $C_{60}$ in solution; however, an absorption bleaching due to the $^3$CT excitons ($\tau \sim 50$ ms) is observed. The suggestion of aggregation of the fullerene anion with other fullerene molecules has also been offered by Staško et. al., who ascribed a part of the contradictory EPR results to the tendency of fullerenes to aggregate [30]. A band structure calculation of fullerene polymer shows that the bands are considerably affected by intermolecular interaction [31].

At sufficiently long time delays (>2 μs) and in the absence of pyrene, the micellar $C_{60}$ solution does not show any residual absorption at 750 nm or other wavelengths, but in the presence of pyrene there is indeed a residual absorption. In view of the fact that earlier studies of $C_{60}$-pyrene system in homogeneous benzonitrile medium [12] have demonstrated the generation of $C_{60}{}^{\bullet-}$ radicals, we ascribe this residual absorption of the micellar solution to the clustered $(C_{60})_n{}^{\bullet-}$ radical. Production of negative fullerene radicals in micellar solutions in the presence of suitable donors has also been suggested by others; the monomeric one has long lifetime, but the colloidal one's lifetime has not been measured [28]. We noted, the residual absorption at long time delays plotted against wavelength, gave only a very broad flat band (Fig. 1). instead of the usual narrow-band of $C_{60}{}^{\bullet-}$ at 1080 nm [12]. On the basis of discussions made in the last paragraph, we ascribe this spectral diffuseness to the clustering effect of $C_{60}$ molecules.

We discuss our results in the framework of the following general mechanistic scheme:

Although in most organic RP the hyperfine coupling mechanism (HFC) dominates the ISC process and as a result, lifetime and free radical yield increase with field for RP with triplet precursor [32], here the case is opposite (Fig. 2(b)). Absence of magnetic nuclei in $C_{60}$ only partially explains this observation, because the other partner of the RP, namely $Py^{\bullet+}$, contains magnetic nuclei. Presumably the effect of HFC in $Py^{\bullet+}$ spin relaxation is small. Also, the proximity of the two radicals due to small micellar and large host size might play a role for suppression of HFC.

A comprehensive kinetic framework was proposed by Hayashi et. al. [18] for the geminate recombination of RP in the absence and in the presence of a field and includes almost all the important rate processes.

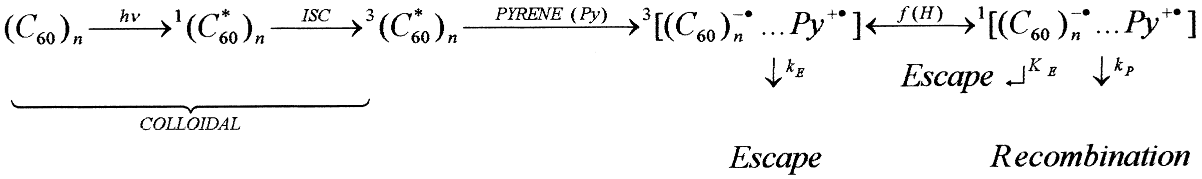
It has been deduced that for triplet precursor the rates could be expressed as follows:

$$B = 0T, \quad [\mathrm{R}] = I_0 \exp(-k_0 t) \tag{1}$$

$$B \gg 0T, \quad B \approx B_{\mathrm{L}}, \quad [\mathrm{R}] = I_{\mathrm{f}} \exp(-k_{\mathrm{f}} t) + I_{\mathrm{s}} \exp(-k_{\mathrm{s}} t) \tag{2}$$

where [R] is the total radical pair concentration in all the four sublevels, i.e.

$$[\mathrm{R}] = [\mathrm{S}] + [\mathrm{T}_+] + [\mathrm{T}_-] + [\mathrm{T}_0]$$



The micellar colloidal $(C_{60})_n$ is excited to the singlet excited state from which it rapidly slides down to the triplet exciton state which has been observed to exist below the $^1$CT exciton state in thin film [29]. In the presence of pyrene a triplet radical pair is generated by electron transfer from pyrene to $(C_{60})_n$ in its $^3$CT state. The triplet parentage of the radical pair is evident from the time scale of observation and is quite consistent with other studies [12]. The caged triplet radical pair decays essentially by two competing channels – cage-escape which generates free radicals, and intersystem crossing which generates singlet RP where fast recombination (back-electron transfer) competes with escape.

### 3.2. Magnetic field effect

The decay curves (Fig. 2(a)) for deaerated micellized $C_{60}$ at about 980 nm were chosen for our MFE studies. It contains a fast component in addition to a slow component, the former being insensitive to field. However, a MFE has been noted on the slower decay process at delays greater than 1 μs. The plot of the slower decay rate as a function of the external field is shown in Fig. 2(b).

For $k_{\mathrm{B}} \gg k_{\mathrm{P}} \gg$ other rates, $k_{\mathrm{f}}$ and $k_{\mathrm{S}}$ can be represented as follows,

$$k_{\mathrm{f}} = \frac{k_{\mathrm{P}}}{2} + k_{\mathrm{s}}$$

$$k_{\mathrm{S}} = k_{\mathrm{R}} + k'_{\mathrm{R}} + k_{\mathrm{E}} \tag{3}$$

If $k_{\mathrm{P}} \gg k_{\mathrm{B}} \gg$ other rates, the expressions changes to,

$$k_{\mathrm{f}} = k_{\mathrm{B}} + k_{\mathrm{s}}$$

$$k_{\mathrm{S}} = k_{\mathrm{R}} + k'_{\mathrm{R}} + k_{\mathrm{E}} \tag{4}$$

In our case we obtained a bi-exponential fit both in presence and in absence of field. This is due to the fact that RP decay has got mixed up with the $^3C_{60}$ decay, as is often the case. The influence of field on the faster decay process, therefore, could not be studied. We, therefore, discuss only the influence of field on $k_{\mathrm{S}}\left(= k_{\mathrm{R}} + k'_{\mathrm{R}} + k_{\mathrm{E}}\right)$. Observed variation of $k_{\mathrm{s}}$ for our system is shown in Fig. 2(b).

The question we first address to is: Is the $\Delta g$-mechanism relevant for the observed field induced changes? The $\Delta g$ mechanism affects the $T_0 \leftrightarrow S$ transition rate, $k_{\mathrm{B}}$ at all

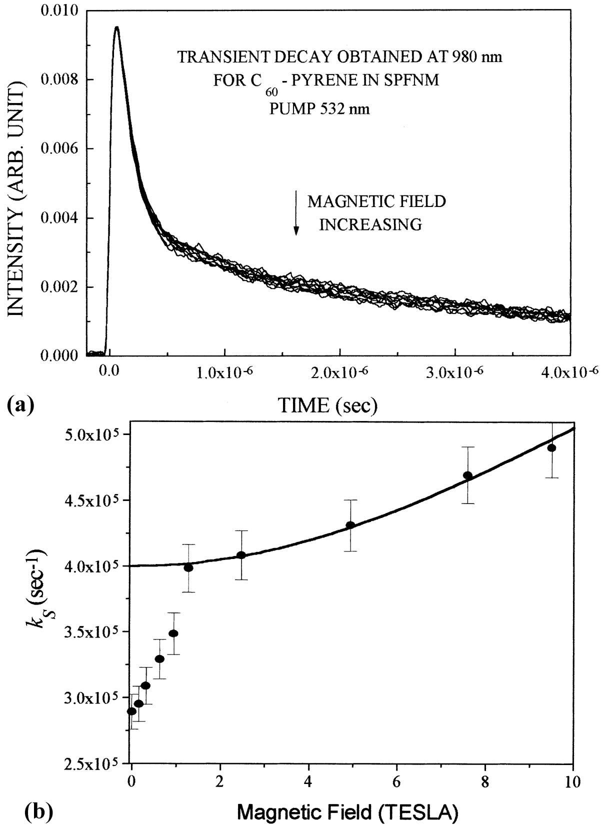
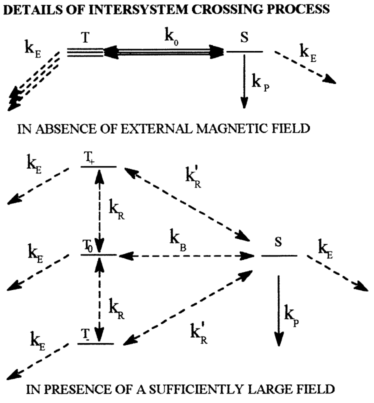


Fig. 2. (a) Decay of the transient species obtained at 980 nm in presence of varying external fields (b) Plot of RP decay rate ($k_S$) vs. various external magnetic fields. Solid line corresponds to simulated curve.



Scheme 1.

fields. The $\Delta g$-induced ISC rate constant $k_{\mathrm{ISC}}$ ($\Delta g$) can be estimated as $k_{\mathrm{ISC}}(\Delta g) = \Delta g \beta H_{\mathrm{ex}}/\hbar$ (where $\beta$ is Bohr magneton, $H_{\mathrm{ex}}$ the external magnetic field, $\Delta g$, the $g$ value difference between the two radical partners, which is 0.0025 in our case, assuming $g$(aggregate of $C_{60}$-monoanion) = 2.0006 [33], and $g$(pyrene cation) = 2.0031 [34]. At $H_{\mathrm{ex}} = 2$ T, $k_{\mathrm{ISC}}(\Delta g)$ is estimated to be $4.2 \times 10^8$ s$^{-1}$. Since the observed slow decay rate of the RP at $\sim$2 T is about $4 \times 10^5$ s$^{-1}$, it is obvious that the $\Delta g$-induced ISC process cannot have a role to play in inducing changes in $k_S$ except at very low fields ($<$2 T) when the components of the RP decays via $T_0$ and $T_\pm$ are not well separated.

Since isotropic HFC and $\Delta g$ parameters cannot provide explanations for changes observed in high fields, we turn our attention to the spin-lattice relaxation (SLR) mechanism which becomes significant in magnetic fields above 1.5 T. The slow rate determining steps for ISC are considered to be $T_\pm \rightarrow T_0$ and $T_\pm \rightarrow S$ transitions or $k_R$ and $k_R'$ in Scheme 1. In very high fields the tumbling of a molecule with anisotropic characteristics may induce a relaxation process between the components of triplet ($T_+$, $T_0$, $T_-$) or between $T_\pm$ and S. Thus, the observed changes might be related to the increase in $k_R$ and $k_R'$ (Scheme 1) in high magnetic fields.

Confusion exists in the literature regarding the spin relaxation time of $C_{60}$ monoanion. Depending on the mode of generation of the radical, the line-widths (which are inversely related to the SLR times) differ by orders of magnitude. While a large solvent-dependent line-width (pp $\approx$ 5 mT) has been observed [35–37] and ascribed to the degeneracy of electronic states, narrow-line spectra (pp $\approx$ 0.1 mT) with more-or-less the same $g$-factor have also been observed [30,38] and attributed to the same mono-anion and its consecutive reaction products. The main point of difference in the two groups is that in the first group EPR spectra are studied after the generation of radicals and at low temperatures, whereas the second group measured the EPR spectrum in-situ at room temperature. In the case of photo-induced electron transfer, sub-microsecond time-resolved FT-EPR was measured by Bennati et. al. [39], who reported a narrow line spectrum. Stasko et. al., made a direct steady-state EPR study of the radical generated by laser flash and by cathodic reduction (with and without added $TiO_2$) in 1 : 1 toluene/methanol solvent at room temperature, and could identify two radicals both with narrow line-widths (pp $\approx$ 0.09 and 0.042 mT, respectively) [30]. One has been ascribed to the $C_{60}{}^{\bullet -}$ mono-anion and the other was speculated to be a mono-anion aggregate.

In the absence of an unambiguous verdict from EPR-spectroscopists regarding the relaxation time, we toyed with both ideas. However, the observed shape of the time decay curve does not indicate fast nanosecond relaxation. If the spin-equilibrium is achieved within several nanoseconds (as indicated by broad EPR spectrum), the yield of long-lived radical ($\tau \sim 30$ s) would have remained steady with time after the initial decay of $^3C_{60}$ and fast recombination of RP. Our observation (Fig. 2(a)) apparently does not conform to this pattern. Even after 1 $\mu$s, there is a slow decay of the absorption signal. We, therefore, try the other alternative possibility, namely, that the spin-relaxation rates in our radicals are slow. This hypothesis is consistent with the idea that the lack of anisotropy in the spherical $C_{60}{}^{\bullet -}$ mono-anion (or in its likely spherical aggregate) would cause the relaxation to be slow.

The properties which might contribute to SLR are (a) anisotropic hyperfine interaction ($\delta hf$), (b) inter-radical dipole–dipole (*dd*) interaction, and (c) anisotropic Zeeman interaction ($\delta g$). These are discussed below.

*(a) Anisotropic hyperfine interaction:*

SLR rate ($k_{\rm rel}(\delta hf)$) due to hyperfine anisotropy is given as follows [40–44].

$$\frac{1}{k_{\rm rel}(\delta hf)} = \frac{1}{\gamma^2 H_{\rm loc}^2 \tau_{\rm c}(\delta hf)} + \frac{\tau_{\rm c}(\delta hf)}{H_{\rm loc}^2} H_{\rm ex}^2 \qquad (5)$$

where γ is the magnetogyric ratio of the electron, $H_{\rm loc}$ the locally fluctuating field for the electron, and $\tau_{\rm c}(\delta hf)$ the correlation time due to $\delta hf$ interaction. It is obvious from Eq. (5) that the SLR rate ($k_{\rm rel}(\delta {\rm hf})$) decreases in proportion to the square of the applied magnetic field.

*(b) Inter-radical dipole–dipole interaction*

SLR rate due to dipole–dipole interaction of biradicals is given as follows [41],

$$\frac{1}{k_{\rm rel}({\rm dd})} = \frac{1}{\gamma^2 H_{\rm dd}^2 \tau_{\rm c}'} + \frac{H_{\rm ex}^2 \tau_{\rm c}'}{H_{\rm dd}} \qquad (6)$$

where $H_{\rm dd}$ is the locally fluctuating magnetic field due to *dd* interaction between the two radicals, and $\tau_c'$ the rotational correlation time for the same. Here too, with increase of magnetic field SLR rate ($k_{\rm rel}({\rm dd})$) induced by dipole–dipole interaction decreases.

*(c) Anisotropic Zeeman ($\delta g$) interaction*

SLR rate ($k_{\rm rel}(\delta g)$) induced by $g$ anisotropy is expressed as [40–44],

$$\frac{1}{k_{\rm rel}(\delta g)} = \frac{10\hbar^2 \gamma^2 \tau_{\rm c}(\delta g)}{\delta g^2 \beta^2} + \frac{10\hbar^2}{\delta g^2 \beta^2 \tau_{\rm c}(\delta g) H_{\rm ex}^2} \qquad (7)$$

where $\delta g^2 = g_1^2 + g_2^2 + g_3^2 - 3\,[(g_1 + g_2 + g_3)/3]^2$ ($g_1, g_2, g_3$ are $g$ values for the principal axis of the $g$ tensor of a radical), $\beta$ the electron Bohr magneton and $\tau_{\rm c}(\delta g)$ the correlation time due to $\delta g$ interaction. From Eq. (7) it follows that the SLR rate ($k_{\rm rel}(\delta g)$) increases as the external field increases.

It is instructive to examine in a qualitative way the magnetic field dependence of the SLR rates due to above three causes. The SLR rate due to hyperfine anisotropy or due to *dd*-interaction vanishes when $\omega$ (the resonance angular frequency, $\gamma H_{\rm ex}$) approaches infinity, whereas the SLR rate due to $g$ tensor anisotropy converges to a certain value $\left(\delta g^2 \beta^2 / 10\hbar^2 \gamma^2 \tau_{\rm c}(\delta g)\right)$ when the field strength (i.e., $\omega$) approaches infinity. Our observed results are in qualitative agreement with the behaviour predicted on the basis of $T_1$ relaxation due to $g$-tensor anisotropy [45]. On going from a low field to a very high field, the dominant contribution to MFE is switched from the relaxation rate due to hyperfine anisotropy and dipole–dipole interaction to that due to $g$-tensor anisotropy.

We have simulated our results assuming that the anisotropic $\delta g$-mechanism is solely responsible for variation of MFE at high fields. Fig. 2(b) shows the curve simulated by using following equation [40], obtained from Eq. (7) after addition of $K_{\rm T}$, a term for magnetic field-independent decay rate constant from the triplet state,

$$k_{\rm RP} = k_{\rm S} \left\{ \frac{\tau_{\rm c} \beta^2 (\delta g)^2 H^2}{10\hbar (1 + \gamma^2 \tau_{\rm c}^2 H^2)} \right\} + K_{\rm T} \qquad (8)$$

and with following parameters, $K_{\rm T} = (4 \pm 0.5) \times 10^5\ {\rm s}^{-1}$ and $\tau_{\rm c} = (2.6 \pm 0.7) \times 10^{-13}$ s and $\delta g^2 = (6.4 \pm 1) \times 10^{-6}$. Only data for fields greater than 2 T are included in the fit to avoid contaminations from other contributions such as $\Delta g$-effect, HFC, $\delta(hfc)$, etc. The $\tau_{\rm c}$ and $\delta g$-value should principally relate to the pyrene radical if we assume that the fullerene radical to be spherically symmetric. The obtained $\tau_{\rm c}$ values may not represent the correlation time for rotation of the whole molecule, which are normally much larger, but rather correspond to local motions, as pointed out in [40]. It has been shown by Fujiwara et. al. [46] that the $k_{\rm s}$ vs. field curve is very sensitive to the value of $\tau_{\rm c}$; the higher the $\tau_{\rm c}$ value, the less prominent is the effect of relaxation on MFE.

## 4. Conclusion

We have noted a MFE on the decay of the RP generated from micellar solution of fullerene and pyrene by laser flash. The RP has been identified as fullerene cluster anion and pyrene cation. The SLR mechanism induced by $g$-anisotropy of pyrene cation ($\mathrm{Py}^{\bullet +}$) seems to be a possible explanation of the observed high field MFE. Further works with similar systems are needed to substantiate the explanation offered by us.

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## References

[1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, Nature (London) 318 (1985) 162.
[2] F. Diederich, R.L. Whetten, Acc. Chem. Res. 25 (1992) 119.
[3] W. Krätschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman, Nature 347 (1990) 354.
[4] H.W. Kroto, A.W. Allaf, S.P. Balm, Chem. Rev. 91 (1991) 1213.
[5] J.W. Arbogast, A.P. Darmanyan, C.S. Foote, Y. Rubin, F.N. Diederich, M.M. Alvarez, S.J. Anz, R.L. Whetten, J. Phys. Chem. 95 (1991) 11.
[6] S.H. Yang, C.L. Pettiette, J. Conceicao, O. Cheshnovsky, R.E. Smalley, Chem. Phys. Letts. 139 (1987) 233.
[7] P.M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M.M. Alvarez, S.J. Anz, R.L. Whetten, J. Am. Chem. Soc. 113 (1991) 1050.
[8] D. Dubois, K.M. Kadish, S. Flanagan, R.E. Haufler, L.P.F. Chibante, L.J. Wilson, J. Am. Chem. Soc. 113 (1991) 4364.

[9] D. Dubois, K.M. Kadish, S. Flanagan, L.J. Wilson, J. Am. Chem. Soc. 113 (1991) 7773.

[10] R.R. Hung, J.J. Grabowski, J. Phys. Chem. 95 (1991) 6073.

[11] Y. Zeng, L. Biczok, H. Linschitz, J. Phys. Chem. 96 (1992) 5237.

[12] J.W. Arabogast, C.S. Foote, M. Kao, J. Am. Chem. Soc. 114 (1992) 2277.

[13] P.J. Krusic, E. Wasserman, B.A. Parkinson, B. Malone, E.R. Holler, P.N. Keizer, J.R. Morton, K.F. Preston, J. Am. Chem. Soc. 113 (1991) 6274.

[14] K.M. Salikov, Yu.N. Molin, R.Z. Sagdeev, A.L. Buchachenko, Spin Polarization and Magnetic Effects in Radical Reactions, Akademiai Kiado, Budapest. Hungary, Elsevier, Amsterdam, 1984.

[15] U.E. Steiner, T. Ulrich, Chem. Rev. 89 (1989) 51.

[16] K. Bhattacharya, M. Chowdhury, Chem. Rev. 93 (1993) 507.

[17] M. Chowdhury, R. Dutta, S. Basu, D. Nath, J. Mol. Liquids 57 (1993) 195.

[18] H. Hayashi, S. Nagakura, Bull. Chem. Soc., Jpn. 57 (1984) 322.

[19] L. Biczok, H. Linschitz, R.I. Walter, Chem. Phys. Letts. 195 (1992) 339.

[20] N.J. Turro, G.C. Weed, J. Am. Chem. Soc. 105 (1983) 1861.

[21] J.S. Scaiano, E.B. Abuin, L.C. Stewart, J. Am. Chem. Soc. 104 (1982) 5673.

[22] J.S. Scaiano, D.J. Laugnot, J. Phys. Chem. 88 (1984) 3379.

[23] Y. Tanimoto, K. Shimizu, M. Itoh, Photochem. Photobiol. 39 (1984) 511.

[24] Y. Tanimoto, K. Shimizu, M. Itoh, J. Am. Chem. Soc. 106 (1984) 7257.

[25] Y. Tanimoto, K. Shimizu, M. Itoh, J. Phys. Chem. 88 (1984) 6053.

[26] I.R. Gould, N.J. Turro, M.B. Zimmt, Adv. Phys. Org. Chem. 1 (1984) 20.

[27] A. Misra, R. Dutta, D. Nath, S. Sinha, M. Chowdhury, J. Photochem. Photobiol. A 96 (1996) 155.

[28] J. Eastoe, E.R. Crooks, A. Beeby, R.K. Heenan, Chem. Phys. Letts. 245 (1995) 571.

[29] M. Ichida, A. Nakamura, H. Shinohara, Y. Saitho, Chem. Phys. Letts. 289 (1998) 579.

[30] A. Staško, V. Brezová, S. Biskupic’, K.P. Dinse, P. Schweitzer, M. Baumgarten, J. Phys. Chem. 99 (1995) 8782.

[31] P.R. Surjan, Int. J. Quant. Chem. 63 (1997) 425.

[32] S. Nagakura, H. Hayashi, T. Azumi (Eds.), Dynamic Spin Chemistry, Kodansha, Tokyo, Wiley, New York, Fig. 2.4(b), p. 17, 1998.

[33] V. Brezová, A. Staško, P. Rupta, G. Domschke, A. Bartl, L. Dunsch, J. Phys. Chem. 99 (1995) 16234.

[34] M. Morita, K. Hirosawa, T. Sato, K. Ouchi, Bull. Chem. Soc. Jpn. 53 (1980) 3013.

[35] M.M. Khaled, R.T. Carlin, P.C. Trulove, G.R. Eaton, S.S. Eaton, J. Am. Chem. Soc. 116 (1994) 3465.

[36] T. Kato, T. Kodama, M. Oyama, S. Okazaki, T. Shida, T. Nakagawa, Y. Matsui, S. Suzuki, H. Shiromaru, K. Yamauchi, Y. Achiba, Chem. Phys. Letts. 186 (1991) 35.

[37] D. Dubois, M.T. Jones, K.M. Kadish, J. Am. Chem. Soc. 114 (1992) 6446.

[38] L. Dunsch, Fullerenes: recent advances in chemistry and physics of fullerenes and related materials, in: K.M. Kadish, R.S. Ruoff (Eds.), The Electrochemical Society, Pennington, NJ, 1994, p. 1068.

[39] M. Bennati, A. Grupp, P. Baeuerle, M. Mehring, Chem. Phys. 185 (1994) 221.

[40] S. Nagakura, H. Hayashi, T. Azumi (Eds.), Dynamic Spin Chemistry, Kodansha, Tokyo, Wiley, New York, Sec. 3.4.2, pp. 73–76, 1998.

[41] U.E. Steiner, H.S. Wolff, Photochemistry and Photophysics, CRC Press, Boca Raton, 1991.

[42] A. Abragam, The Principles of Nuclear Magnetism, Ch. 8, Claredon Press, Oxford, 1961.

[43] C.P. Slichter, Principles of Magnetic Resonance, Ch. 5, Harper & Row, New York, 1963.

[44] A. Carrington, A.D. McLachlan, Introduction to Magnetic Resonance with Application to Chemistry and Chemical Physics, Ch. 11, Harper & Row, New York, 1967.

[45] K. Lüders, K.M. Shalikhov, Chem. Phys. 117 (1987) 113.

[46] Y. Fujiwara, T. Aoki, K. Yoda, H. Cao, M. Mukai, T. Haino, Y. Fukazawa, Y. Tanimoto, H. Yonemura, T. Matsuo, M. Okazaki, Chem. Phys. Letts. 259 (1996) 361.