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The Sign of the Exchange Interaction between Triplet Excited Fullerene and Nitroxide Free Radicals

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Abstract. The sign of the exchange interaction J in a series of radical triplet pairs (RTPs), formed by a nitroxide free radical and a triplet excited fullerene, has been determined from the spin polarization of time-resolved electron paramagnetic resonance spectra. Radical and fullerene are linked together by covalent bonds in different geometries. It is shown that the sign of J depends on the overlap between the orbital of nitroxide unpaired electron and the LUMO of fullerene, which is singly occupied in the excited triplet state. When the overlap does not vanish, a negative contribution to J arises from the admixing of a charge transfer structure in the wave function of the excited doublet state D^* of the RTP, which does not take place in the excited quartet state Q^*. The mixing of D^* and Q^* states lowers the energy of the former spin state and gives antiferromagnetic coupling.

1 Introduction

In the primary stages of several chemical and photochemical reactions radical pairs (RPs) are formed, which eventually evolve to reaction products [1–3]. Electron paramagnetic resonance (EPR) spectroscopy of these species is feasible, even if they are present in solution at low stationary concentration, in virtue of the spin polarization of the radical species in the early instants of their formation, which strongly enhances the EPR sensitivity. Time-resolved EPR (TR-EPR) technique, which combines EPR with laser photolysis, provides detailed information on these reactive species. The electron exchange interaction J in RP is an important parameter, whose value and sign determine the polarization pattern, the kinetic behavior, and the magnetic field effects on reactivity [1, 2, 4–7]. Similar pairs formed by a free radical and an excited triplet (RTP) were postulated as transient intermediate complexes in the quenching of triplet excitation by free radicals [8]. RTP are formed in doublet D^* or in quartet Q^* state depending on the relative orientations of the radical and the triplet spin angular momenta. Doublet RTP, ^{2}[RTP], has the same spin multiplicity as the ground state (singlet S and radical R). Therefore, ^{2}[RTP] decays fast by a spin conserving process, while ^{4}[RTP] is metastable. It was shown that triplet quenching is accompanied by spin polarization of the radical R; ^{4}[RTP] becomes polarized as well. The latter species can be observed if dissociation is prevented [5, 7]. Covalent link eliminates the dissociation of the pair into separated species. The first observation of an ^{4}[RTP] was accomplished upon photoexcitation of a fulleropyrrolidine nitroxide (FPNO), in which the triplet excited state T is localized on the fullerene core [9]. Recently an RTP in doublet excited state has been reported [10].

The EPR spectrum of ^{4}FPNO in liquid solution consists of the $-1/2$ to $1/2$ transition separated into three hyperfine components by the interaction of each unpaired electron with the nitroxide ^{14}N ($I = 1$) nuclear spin. The hyperfine separation in the excited quartet state is $a_N(Q^*) = 1/3\ a_N(D_G)$ where $a_N(D_G)$ is the nitroxide coupling constant of the ground doublet state. The quartet state nitrogen coupling constant $a_N(Q^*)$ is reduced to 1/3 because the exchange interaction J is much larger than $a_N(D_G)$. In liquid solution, the $-3/2$ to $-1/2$ and $1/2$ to $3/2$ transitions are too broad to be observed, but they can be detected in frozen samples at low temperature [10, 11]. The value of the exchange interaction cannot be measured from the EPR spectrum; however, its sign can be obtained from the polarization of the EPR lines. In fact, quartet and doublet states are mixed by the dipolar interaction between the unpaired electrons; since the energy of these two states is separated by the exchange interaction J, the mixing depends on the spin component along the magnetic field. Spin-selective doublet-quartet mixing gives rise to spin polarization of the transient EPR spectrum of ^{4}[RTP] and of the ground state R, recorded after pulsed light excitation. The polarization character (emission or enhanced absorption) depends on whether ^{4}[RTP] has lower or higher energy than ^{2}[RTP], i.e., on the sign of J.

In this paper we examine a series of fullerene-nitroxide conjugates where R (nitroxide radical) and T (functionalized fullerene in the triplet excited state) are covalently linked, through either a rigid or a flexible bridge. While for separated species the exchange interaction takes place through space possibly mediated by solvent molecules, in covalently linked systems exchange interaction could also occur by the polarization of the bonds separating the two-spin systems [12]. Discrimination between these exchange mechanisms is also discussed.

2 Experimental

The fullerene derivatives considered in this paper are shown in Fig. 1. In **1** the TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) unit is spiro-linked to the pyrrolidine ring. In **2** there is one C-C bond between the nitroxide TEMPO and the pyrrolidine ring. In **3** a tetramethylpyrrolidine-1-oxyl ring is fused to C_{60}, whereas in derivative **4** TEMPO and fulleropyrrolidine are connected through a peptide spacer. Note that the nitroxide structure is inserted in the peptide backbone; this makes the nitroxide position strongly dependent on the secondary structure of the peptide.

Details regarding the synthesis of compounds **1** [9], **2** [13] and **3** [14] have been previously reported.

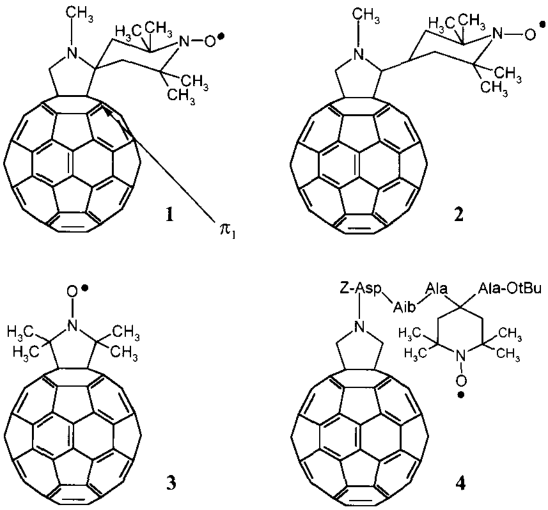


Fig. 1. Structures of the fullerene derivatives under study. Z – carbobenzoxy; Asp – aspartic acid; Aib – α-aminoisobutyric acid; Ala – alanine; tBu – *tert*-butyl.

The synthesis and characterization of derivative **4** will be reported elsewhere (A. Polese et al., unpubl.).

Toluene solutions of compounds **1**–**3** (ca. 10^{-4} M) were carefully deoxygenated by freeze-pump-thaw cycles, and sealed under vacuum in 4 mm outer diameter (o.d.) quartz tubes. The same procedure was used for compound **4** with chloroform as solvent. In this case 3 mm o.d. tubes were used, owing to the more microwave lossy solvent.

TR-EPR measurements were carried out on a Bruker ER 200D X-band EPR spectrometer equipped with a liquid nitrogen flow cryostat and with a LeCroy 9450A fast digital oscilloscope to collect and average the transient signals. No field modulation was used. A Lambda Physik FL 2000 dye laser (rhodamine 6G, $\lambda_{\text{peak}} = 581$ nm) pumped by a Lambda Physik LPX 100 excimer laser ($\lambda_{\text{peak}} = 308$ nm) was used for photoexcitation.

3 Results and Discussion

Laser excitation of derivatives **1**–**4** gives very strong spin polarized EPR signals due to the superposition of the spectra of ^{4}[RTP] and of R. The spectrum of R is characterized by three lines separated by about 15 G and centered at $g = 2.006$. The spectrum of ^{4}[RTP] consists of three lines as well (centered around $g = 2.003$) with hyperfine separation of about 5 G. The signals occur either in emission or in enhanced absorption and eventually change polarization as they evolve in timescale of the order of few microseconds.

The TR-EPR spectra of photoexcited **1** and **2** have been already described [11, 15].

Figure 2 shows the 2-D time-resolved EPR signal of derivative **3** in toluene solution recorded at 220 K. It represents the variation of the EPR signal intensity with respect to magnetic field and time axes. Both spectra and time evolution signals can be extracted from the surface as shown in Fig. 2 (inset A and B, respectively). Spectrum 1 in panel A corresponds to a time delay of 0.5 μs after the laser pulse, when the signal presents the best spectral resolution. As for **1** and **2**, two sets of three lines with intensity ratio 1:1:1 are clearly displayed. They are attributed to the excited quartet state Q* ($g = 2.0031$, $a_N = 4.62$ G) and to the ground doublet state D_G ($g = 2.0061$, $a_N = 14.96$ G).

The spin multiplicity of the quartet excited state is inferred from the nitrogen hyperfine coupling constant value that is reduced to 1/3 with respect to that of the ground doublet state. This is what is expected if the exchange interaction constant J separating the excited doublet D* and Q* is much larger than the hyperfine coupling.

Spectrum 2 in Fig. 2, inset A corresponds to a time delay of 0.9 μs when the signal presents the maximum emission. At this delay the excited quartet signal vanishes and only the ground doublet state radical contributes to the spectrum. Note that the high field $m_I = -1$ transition is broadened by the incomplete averaging of the magnetic anisotropies and furthermore it appears in absorption due to the multiplet polarization effect [16].

Inset B of Fig. 2 shows the time evolution signals taken at the field positions marked with solid and dotted vertical lines in inset A. The decay rate of the signal of Q* is larger than that of the ground doublet state D_G.

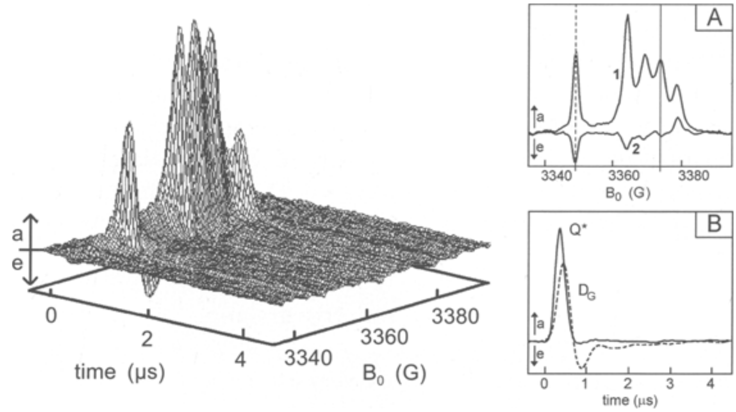


Fig. 2. Field-sweep TR-EPR spectrum of **3** in toluene solution at 220 K. The complete spectrum is in enhanced absorption immediately after the laser pulse and later in emission. Inset A: transient EPR spectra extracted at 0.5 μs (upper spectrum) and 0.9 μs (lower spectrum) after the laser pulse. The delay of 0.5 μs corresponds to the best spectral resolution for the absorptive signal, while the delay of 0.9 μs is chosen to display the maximum emissive signal. Vertical lines point out the field position corresponding to the time profiles shown in inset B. Inset B: time evolutions of the low-field line of the ground doublet state D_G signal (dotted line) and of the high-field line of the excited quartet state Q* signal (solid line).

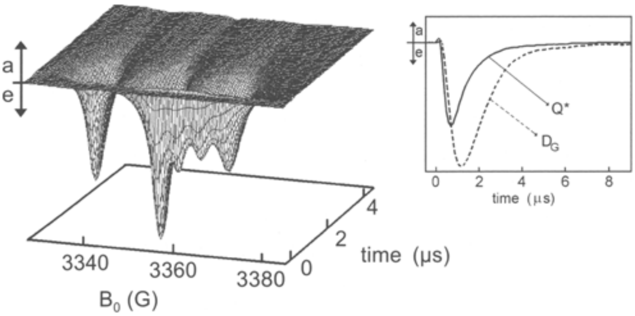


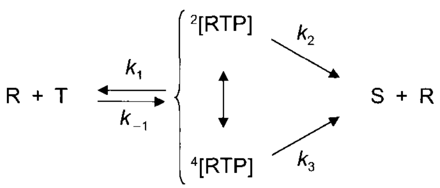
Fig. 3. Field-sweep TR-EPR spectrum of **4** in chloroform solution at 233 K. The complete spectrum shows a weak absorption after the laser pulse and immediately evolves in emission. Inset: time evolutions of the low-field line of the ground doublet state D_G signal (dotted line) and of the high-field line of the excited quartet state Q^* signal (solid line).

The 2-D TR-EPR signal of derivative **4** in chloroform at 233 K is reported in Fig. 3. Chloroform was used instead of toluene for solubility reasons. The inset of Fig. 3 shows the time evolution signals taken at the field position corresponding to the $m_I = +1$ component of D_G and $m_I = -1$ component of Q^*. In both cases a weak absorptive (a) signal after the laser pulse immediately evolves in strong emission (e). Note that again the signal corresponding to Q^* presents a decay rate larger than the one corresponding to D_G.

Before discussing the polarization pattern, the main aspects of the RTP polarization mechanism (RTPM) are briefly outlined in the following section.

3.1 Spin Polarization by RTP Formation

When a free radical R and an excited triplet species T are sufficiently close together, a RTP is formed according to the following reaction diagram:



^{2}[RTP] quenches the triplet excitation, by decaying fast to the singlet species S and the radical R, since this system has the same doublet total spin multiplicity. The process is spin-prohibited for ^{4}[RTP], whose decay to the same state S + R is slower ($k_3 \ll k_2$). Triplet quenching by ^{4}[RTP] becomes partially allowed because the quartet state is contaminated with doublet components by the electron dipolar interaction (zero-field splitting interaction, ZFS) within the triplet T and the one between the electron spin in R and those of T. Usually, for separated species, the latter one is not considered [17]. However, its contribution could be not negligible for covalently linked pairs.

The spin Hamiltonian of an RTP in the presence of magnetic field B is:

$$\mathscr{H} = \mathscr{H}_{\mathrm{Z}} + \mathscr{H}_{\mathrm{EX}} + \mathscr{H}_{\mathrm{ZFS}} \ , \tag{1}$$

where $\mathscr{H}_{\mathrm{Z}}$ is the Zeeman interaction, $\mathscr{H}_{\mathrm{EX}}$ the exchange interaction responsible for the energy splitting $3J$ between ^{2}[RTP] and ^{4}[RTP], and $\mathscr{H}_{\mathrm{ZFS}}$ is the ZFS interaction, described by the ZFS parameters D and E.

The wave functions which describe the doublet and quartet sublevels of an RTP in the uncoupled representation are:

$$|D_{1/2}\rangle = \frac{1}{\sqrt{3}}\left(|0,1/2\rangle - \sqrt{2}\,|1,-1/2\rangle\right) \ , \tag{2a}$$

$$|D_{-1/2}\rangle = \frac{1}{\sqrt{3}}\left(|0,-1/2\rangle - \sqrt{2}\,|-1,1/2\rangle\right) \ , \tag{2b}$$

and

$$|Q_{3/2}\rangle = |1,1/2\rangle \ , \tag{2c}$$

$$|Q_{1/2}\rangle = \frac{1}{\sqrt{3}}\left(\sqrt{2}|0,1/2\rangle + |1,-1/2\rangle\right) \ , \tag{2d}$$

$$|Q_{-1/2}\rangle = \frac{1}{\sqrt{3}}\left(\sqrt{2}|0,-1/2\rangle + |-1,1/2\rangle\right) \ , \tag{2e}$$

$$|Q_{-1/2}\rangle = |-1,-1/2\rangle \ . \tag{2f}$$

Equations (2a)–(2f) are eigenfunctions of the first two terms of the Hamiltonian Eq. (1), but not of $\mathscr{H}_{\mathrm{ZFS}}$ which can be considered as a perturbation, giving rise to mixing of the quartet Zeeman substates with the doublet components. The relevant mixing coefficients are:

$$c_{-3/2,1/2} = \frac{\langle T_{-1}|\mathscr{H}_{\mathrm{ZFS}}|T_1\rangle}{\sqrt{3/2}\,\left(3J + 1/3(5g_{\mathrm{T}} + g_{\mathrm{R}})\beta B_0\right)} \ , \tag{3a}$$

$$c_{3/2,-1/2} = \frac{\langle T_{-1}|\mathscr{H}_{\mathrm{ZFS}}|T_1\rangle^*}{\sqrt{3}\,\left(-3J + 1/3(5g_{\mathrm{T}} + g_{\mathrm{R}})\beta B_0\right)} \ , \tag{3b}$$

where the numerators of Eqs. (3a) and (3b) are complex conjugate matrix elements calculated on the triplet eigenstates. Note that the first subscript refers to quartet component and the second one to the doublet component. g_{R} and g_{T} are the isotropic g-factors of R and T. It should be noted that $c_{-3/2,1/2}$ and $c_{3/2,-1/2}$ are different because Zeeman energy and exchange energies occur with the same and respectively with different sign at the denominator. In the case of vanishing J they become equal.

Moreover [18]:

$$c_{\pm 1/2,\pm 1/2} = -\frac{\sqrt{2}}{2} \cdot \frac{\left[D(1/3 - n^2) + E(m^2 - l^2)\right]}{3J \pm 1/3(g_T - g_R)\beta B_0} , \tag{3c}$$

so that if $g_R = g_T$ then $c_{-1/2,-1/2} = c_{1/2,1/2}$ for any value of J. Therefore, only in the case of small J, the difference in g becomes important for the polarization.

Equations (3) show that for positive J (quartet state lower in energy than the doublet one) $|c_{3/2,-1/2}|^2 > |c_{-3/2,1/2}|^2$, while the reverse is true for negative J. It means that for $J > 0$ the quartet substate $(Q^*)_{3/2}$ is the one which has larger doublet character, while for $J < 0$ the larger mixing occurs between $(Q^*)_{-3/2}$ and $(D_G)_{1/2}$ states. Thus, in the case of $J > 0$, the rate constant of the process leading to $(D_G)_{-1/2}$ is larger than that leading to $(D_G)_{1/2}$, and the $-1/2$ to $1/2$ transition of both the excited quartet and the ground doublet state becomes polarized in enhanced absorption.

It should be noted that ^{4}[RTP] could be observed only if its dissociation into separated R and T is prevented. A covalent link between the triplet precursor (fullerene) and nitroxide ensures that dissociation does not take place.

Free radicals quench excited singlet states as well. The mechanism is similar to that illustrated for triplet states: formation of a radical singlet pair ^{2}[RSP] followed by its conversion by a spin conserving process into ^{2}[RTP], which is partially mixed with ^{4}[RTP].

As for triplet quenching, the spin selective mixing between the ^{2}[RTP] and ^{4}[RTP] substates produces spin polarization (A. Kawai, pers. commun.). For singlet quenching, the sign of polarization is opposite to that produced by triplet quenching. It should be noted that in order to observe singlet quenching the radical triplet interaction should be fast enough to be effective during the singlet lifetime. Covalent bond between the partners favors this process because diffusion of these latter is not necessary for their encounter.

The results of this discussion can be summarized as follows.

1. If $J > 0$ the $-1/2$ to $1/2$ transition of both ^{4}[RTP] and ground state radical R becomes polarized in emission (e) by singlet quenching, and in enhanced absorption (a) by triplet quenching. The reverse is true for $J < 0$.

2. Singlet quenching occurs immediately after the laser pulse and is responsible for the initial polarization (emission if $J > 0$).

3. Triplet sublevels are populated also by intersystem crossing due to spin-orbit coupling. At high field, $B \gg D/g\beta$, this population pathway does not polarize the $-1/2$ to $1/2$ transitions but contributes to the triplet population. The triplet species undergoes quenching by the interaction with the doublet radical and this process eventually reverses the sign of polarization from the initial value.

In conclusion, the exchange interaction determines the time evolution of the quartet and doublet signals: first emission and later absorption (e/a) for $J > 0$, and the reverse (a/e) for $J < 0$. Application of these rules shows that for derivatives **2**–**4**, J is negative. Derivative **1** is the only case where a positive J is observed.

3.2 The Exchange Interaction

The exchange interaction between two unpaired spins, which is responsible for the energy separation between states of different multiplicity, could take place through space and/or through bond.

The origin of through-bond interaction is spin polarization of electrons in the bonds separating the coupled spins. It was described by McConnell [12] who proposed the equation:

$$J(N) = (-1)^N 3 \cdot 10^{6-N} \ , \tag{4}$$

where N is the number of intervening σ bonds and J is expressed in megahertz.

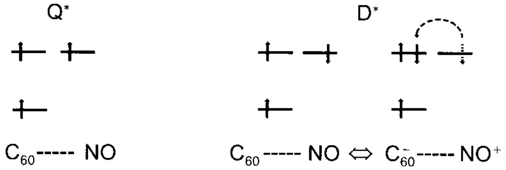
Although Eq. (4) does not reproduce correctly the measured values reported in literature [19], it takes into account the decrease of J with N and predicts a sign alternation with the bond number. This alternation could explain why J has opposite signs for derivatives **1** and **2**, but it does not give the correct result. In fact, if one considers that the number of σ bonds separating the nitrogen atom from the π system of fullerene is 5 in **1**, 6 in **2** and 18 in **4** the positive sign for **1** and the negative sign for **2** and **4** contrasts with the expected sign given by Eq. (4). The discrepancy could be overcome if at position π_1 (see Fig. 1) in the fullerene moiety the spin density would be negative. Nevertheless, on the basis of Eq. (4) one would expect **3** ($N = 3$) and **1** ($N = 5$) to have the same sign for J, contrary to the observation. This suggests that through-space interaction should dominate.

Through-space interaction has been investigated theoretically for the case of systems with two nitroxide radicals (spin $S = 1/2$) in different relative positions [20]. It contains two contributions having opposite sign [21]. The first one is negative and proportional to the square of the overlap integral S_{ab} between the wave functions of the singly occupied MOs (SOMOs) of the two nitroxide groups a and b. This term is associated to the formation of an "incipient" chemical bond and it is sometimes called "kinetic exchange" term since it is associated to the kinetic energy in the Hamiltonian $J_{\mathrm{KE}} = -CS_{\mathrm{ab}}$. The second contribution, called "potential exchange" and given by the exchange integral K_{ab}, is positive and associated to the intermolecular Coulombic potential energy between a and b, $J_{\mathrm{PE}} = K_{\mathrm{ab}}$. It prevails if the overlap vanishes or if it is small. This occurs for particular relative orientations of the two nitroxides.

RPs with positive J have been observed in very few cases [2, 22].

For RTP the origin of the exchange interaction is more complicated. In fact one should take into account three electrons in three different orbitals. We indicate with h and l the singly occupied molecular orbitals of the triplet moiety (HOMO and LUMO of fullerene in our case) and with n the molecular orbital which accepts the unpaired electron on the radical moiety. If higher-order contributions are neglected, the energy separation between quartet and doublet state depends on the exchange integrals $\langle h(i)n(j)|e^2/r_{ij}|n(i)h(j)\rangle$ and $\langle l(i)n(j)|e^2/r_{ij}|n(i)l(j)\rangle$. These terms give ferromagnetic coupling stabilizing the quartet state with respect to the doublet one. In addition, there are two kinetic exchange terms which depend on the charge transfer integrals β_{hn} and β_{ln} which give antiferromagnetic coupling. Their contribution is proportional to $\beta_{kn}^2/\Delta E_{kn}$ with $k = h, l$. Because of the energy difference in the denominator, the most important contribution involves the LUMO which has energy closer to that of the nitroxide unpaired electron orbital. β_{ln} is proportional to the overlap between l and n, and if this vanishes, only ferromagnetic coupling terms remain.

A negative contribution to J could be considered as arising from the admixing of a charge transfer structure in the wave function of the excited doublet state D* of the RTP, which does not take place in the excited quartet state Q*:



In the case of nonvanishing overlap the mixing of D* and Q* states lowers the energy of the former spin state giving antiferromagnetic coupling.

Therefore, we expect $J > 0$ when the nitroxide group -NO is placed on the nodal plane of the fullerene LUMO and is oriented in such a way that its wave function does not overlap with LUMO.

In Fig. 4 the position of the π orbital of the nitroxide radical and the LUMO of fullerene are drawn. Shaded and unshaded areas indicate the different phase of the wave functions. It is clearly shown that in **1** the overlap vanishes and a positive value of J is expected, while in all other cases, including **3**, the overlap be-

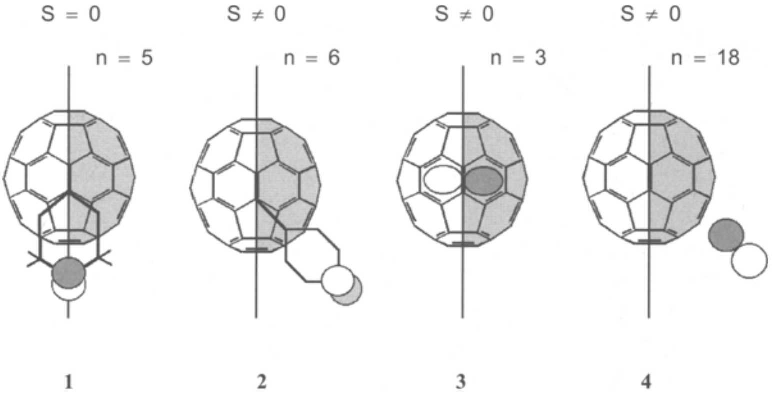


Fig. 4. Position of the π orbital of the nitroxide radical and LUMO symmetry of fullerene. Areas drawn with same grey level present same phase, while n represents the number of σ bonds separating the nitrogen atom from the π system of fullerene. In **1** the nodal plane of nitrogen π orbital is perpendicular to that of LUMO of fullerene and the resulting overlap is zero. In the case of **2–4** there is a nonzero overlap.

tween the fullerene and the nitroxide wave function is different from zero and the expected sign of J is negative, in complete agreement with the experiments.

With separate species, in the encounter with triplet excited fullerene the radical nitroxide approaches at different relative orientation. The averaging over all the orientations should result in $J < 0$.

Observation of positive value of J in RTPs are particularly rare (A. Kawai, pers. commun.).

3.3 Quartet-State Hyperfine Coupling Constant

We have observed a small, though significant, deviation of the quartet-state hyperfine coupling splitting $a_N(Q^*)$ from the expected value $a_N(D_G)/3$. The deviation is 0.36 G in **3**, corresponding to 7.35%.

One should consider that the nitrogen hyperfine coupling constant of the excited doublet state, represented in Eqs. (2a) and (2b), has the same value as that of the quartet state, but opposite sign. Therefore a contribution of D^* should lower the splitting constant.

Fast modulation of the ZFS interaction by the molecular tumbling can be considered as a stochastic perturbation which induces transitions between Q^* and D^*. Since the energy separation between these states is expected to be much lower than the thermal energy kT, the Q^* and D^* populations would be equal in the absence of a selective decay to the ground state. The latter occurs only for D^* which has the same spin multiplicity as the ground state.

Therefore, the Q^* and D^* population ratio depends on the relative magnitude of transition rate and decay rate. This affects the contribution of D^* to the hyperfine separation. The observed shift from the expected value of $a_N/3$ is consistent with a contribution of about 4% of doublet state.

A second possible explanation for the observed decrease could be a shift of charge density of the nitroxide N-O group towards the nitrogen atom and the corresponding shift of spin density toward the oxygen. This could be due to the increased electron-attracting property of the triplet excited fullerene compared with the ground state.

4 Conclusion

Fullerene derivatives covalently linked to a nitroxide free radical allow the investigation of RTPs where the radical and the triplet are bonded together at different distance and geometry. The sign of the exchange interaction value J separating the energy of the doublet and quartet states is easily obtained from the polarization of the TR-EPR spectra, measured after photoexcitation with laser pulses. It is found that the mechanism producing the exchange interaction occurs through space and that the sign of J is correlated with the overlap of the nitroxide unpaired electron orbital with the fullerene LUMO.

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