First observation of the hyperfine structure of an excited quintet state in liquid solution†

Lorenzo Franco,[a] Martina Mazzoni,[a] Carlo Corvaja,*[a] Valentina P. Gubskaya,[b] Lucia Sh. Berezhnaya[b] and Ildus A. Nuretdinov[b]

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After pulsed photoexcitation of a new fullerene-linked bisnitroxide, a well resolved transient EPR spectrum is detected which is assigned to an excited quintet spin state generated by spin coupling of the nitroxides and the fullerene excited triplet.

Photoinduced changes and switching of molecular magnetism in organic systems is a quite important process for future applications of molecular based magnetism.[1]

This phenomenon could be observed by time resolved electron paramagnetic resonance (TR-EPR), which is a powerful tool for investigating short lived paramagnetic intermediates, formed after laser excitation of organic molecules.[2] With nitroxide and nitronyl nitroxide spin labeled chromophores, like phenylanthracene,[3] porphyrins,[4] metallo phthalocyanines[5] and fullerenes,[6] excited states of high spin multiplicity as quartet (S = 3/2) and quintet (S = 2) have been observed and characterized. They arise from the coupling of the excited triplet spins of the chromophore with the spins of the radical labels. The quintet state multiplicity was determined unequivocally by the transient nutation frequency of the TR-EPR spectrum recorded in rigid glass matrices.[6c–d] Quartet state species have been observed not only in rigid glass matrices but also in liquid solutions,[6a] because their $-1/2 \Leftrightarrow 1/2$ EPR transition does not depend on the molecular orientation and it is not modulated by the molecular rotational diffusion. The quartet state nature was inferred by the values of the g factor and of the ^{14}N hyperfine coupling constants.

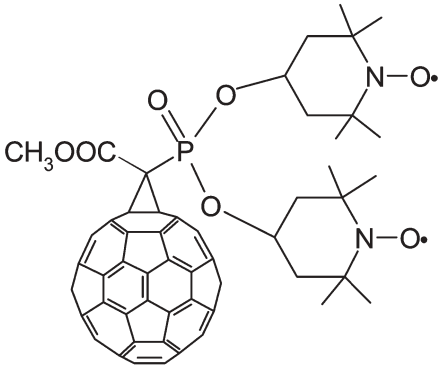
In this paper we report on the first observation *in liquid* solution of an excited quintet species with a completely resolved hyperfine pattern. It was obtained by photo-exciting at room temperature the doubly spin labeled methano-fullerene **1** (Scheme 1).[7]

The experimental TR-EPR spectrum[8] of **1** is shown in Fig. 1.

Fig. 2(A) shows the spectrum corresponding to a delay of 0.5 μs after the laser pulse. The conventional EPR spectrum of **1** recorded in the dark is displayed in Fig. 2(B). For comparison purposes the latter one is presented in the integrated form.

The spectrum recorded in the dark is typical of a nitroxide biradical species with electron exchange interaction of the same order as the ^{14}N hyperfine coupling.[9] It is accounted for by the spin Hamiltonian (1):

$$H = g\beta B\,\mathrm{S_z}(1) + g\beta B\,\mathrm{S_z}(2) + a_\mathrm{N}\,\mathrm{S_z}(1)\mathrm{I_z}(a) + a_\mathrm{N}\,\mathrm{S_z}(2)\mathrm{I_z}(b) - 2J\,\mathbf{S}(1)\mathbf{S}(2) \quad (1)$$



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Scheme 1 The fullerene-bisnitroxide system.

where 1 and 2 refer to the unpaired electrons and a and b to the two nitrogen nuclei, B is the magnetic field, a_N is the hyperfine coupling constant and J is the exchange integral. The other symbols have their usual meaning.

The spectrum shows three narrow lines due to biradicals having the two nitroxide ^{14}N spins with the same z components $m_\mathrm{I}(a) = m_\mathrm{I}(b)$, and other broader lines due to biradicals with $m_\mathrm{I}(a) \neq m_\mathrm{I}(b)$. These lines are split by the presence of the exchange interaction term in the Hamiltonian. The spectrum is well

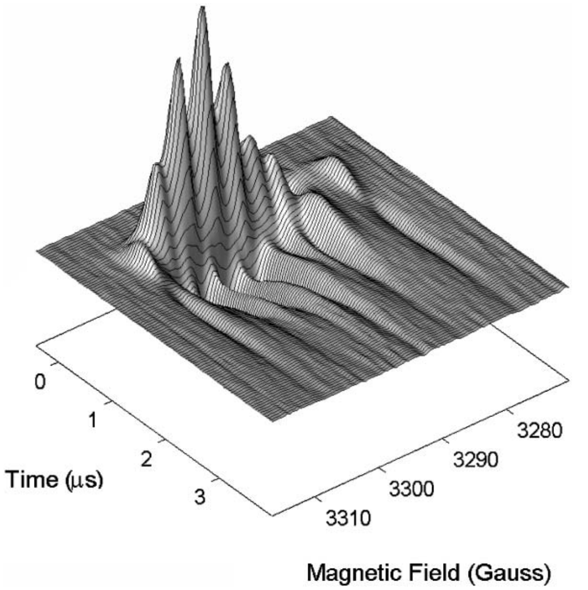

Fig. 1 TR-EPR spectrum of **1** recorded at 290 K in toluene solution.

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† Electronic supplementary information (ESI) available: details of EPR spectra simulations of the fullerene-bisnitroxide **1**. See http://www.rsc.org/suppdata/cc/b4/b417056c/

*carlo.corvaja@unipd.it

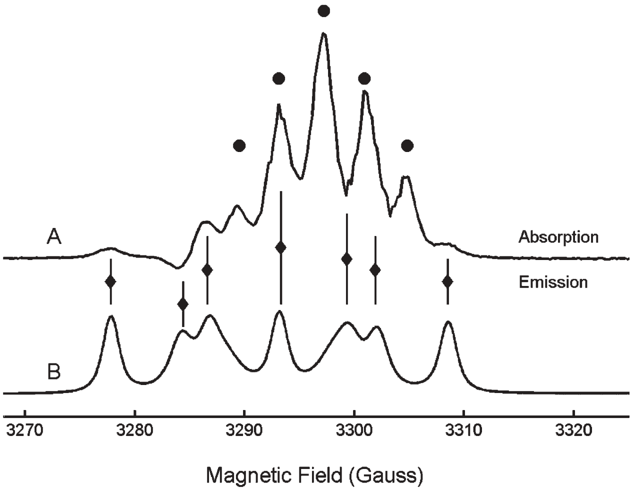

Fig. 2 (A) TR-EPR spectrum of **1** in toluene solution at 290 K, at 0.5 μs after the laser pulse. (B) Integrated form of the conventional steady state EPR spectrum of **1**. Biradical transitions are marked in both spectra with diamonds while quintet state transitions are marked with circles.

simulated by assuming $a_N = 15.4$ Gauss, $g = 2.0062$ and $J/g\beta = 45$ Gauss. The hyperfine coupling constant agrees with that of a TEMPO nitroxide radical in the same solvent.

The TR-EPR spectrum is more complex and asymmetric. Fig. 3 shows the simulation of the spectrum obtained by the superposition of the EPR lines of the biradical **1** in its ground state and of an additional five lines, indicated in Fig. 2A by circles, with intensity ratios 1 : 2 : 3 : 2 : 1, centred at $g = 2.0039 \pm 0.0005$ and separated by $a = 3.85$ Gauss.

The lines corresponding to the ground state show anomalous intensities and even occur in emission. The anomalous line intensity of the ground state lines can be explained by a selective spin population from the excited states.[10] We assign the additional lines in the TR-EPR spectrum to the hyperfine-resolved lines of the excited quintet state, on the basis of the following arguments.

Derivative **1** in its electronic ground state could be in a triplet (T_{NO}) or in a singlet (S_{NO}) spin configuration. Upon irradiation with a laser pulse, the fullerene chromophore undergoes a transition to the first excited triplet state T_1 whose spins can be coupled to the nitroxide spins, giving rise to a singlet (S), a quintet (Q) and two triplet states (T and T′). One of the triplets, say T′, corresponds to having the nitroxide spins in the singlet state S_{NO}. In liquid solution, it should give rise to a spectrum at a field position corresponding to $g \approx 2.0013$, typical of excited triplets of C_{60} mono-adducts[11] and consisting of a single line, since the nitroxide ^{14}N hyperfine coupling vanishes.

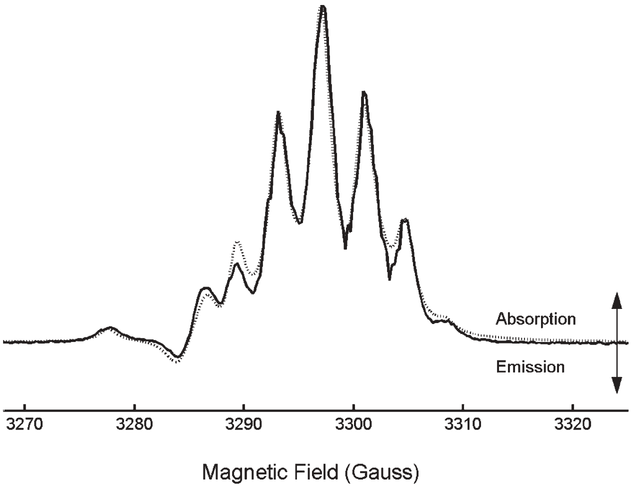

Fig. 3 Experimental TR-EPR spectrum of **1** (continuous line) and its computer simulation (dashed line).

The experimental g-factor and hyperfine coupling constant of the spectrum are therefore compatible only with the quintet or the second triplet (T) excited states: $g = (2.0062 + 2.0013)/2 = 2.0037$ and $a = 15.4/4 = 3.85$ Gauss.[12]

Because of the small width of the EPR lines ($\Delta B = 1$ Gauss) we can exclude that the five line spectrum derives from the triplet state T. In fact, for triplet and quintet states all EPR transitions depend strongly on the molecular orientation in the magnetic field, and in liquids the linewidth is determined by the rotational diffusion correlation time (τ) and the anisotropy of the EPR transition: $\Delta B \propto \tau\ D_{eff}$.[2] The latter is determined by the effective electron–electron spin dipolar interaction parameter D_{eff}, which for the quintet state is smaller by a factor of 3 than that of the triplet.[12]

To the best of our knowledge this is the first observation of a resolved hyperfine structure in a molecular excited quintet state in liquid solution.

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Lorenzo Franco,[a] Martina Mazzoni,[a] Carlo Corvaja,*[a]
Valentina P. Gubskaya,[b] Lucia Sh. Berezhnaya[b] and Ildus A. Nuretdinov[b]
[a] *Department of Chemical Sciences, University of Padova, via Marzolo, 1 35131, Padova, Italy. E-mail: carlo.corvaja@unipd.it; Fax: +39 49 8275239; Tel: +39 49 8275684*
[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences, Arbuzov Street, 8, 420088, Kazan, Russian Federation. E-mail: in@iopc.knc.ru*

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8 Toluene solutions (2×10^{-4} M) were sealed under vacuum (10^{-3} torr) in 4 mm o.d. quartz tubes. TR-EPR spectra were recorded with a Bruker ER200D spectrometer equipped with a LeCroyLT344 digital oscilloscope. Laser excitation was performed with the second harmonic of a N:Yag pulsed laser ($\lambda = 532$ nm; $\tau = 5$ ns; $E = 5$ mJ). A data-set matrix was obtained. Rows give EPR spectra at different time delays, while columns represent the EPR signal time evolution.

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