Electronic Quartet and Triplet States of Polyanionic C_{60} Fullerene and Their Anomalous Spin Relaxation As Studied by cw-ESR/2D-Electron Spin Transient Nutation Spectroscopy

M. Cândida B. L. Shohoji,*,† M. Luisa T. M. B. Franco,†
M. Celina R. L. R. Lazana,† Shigeaki Nakazawa,‡
Kazunobu Sato,‡ Daisuke Shiomi, and Takeji Takui*,‡

Department of Chemistry, Instituto Superior Técnico
Universidade Técnica de Lisboa, Av. Rovisco Pais
1096 Lisboa Codex, Portugal
Departments of Chemistry and Materials Science
Graduate School of Science, Osaka City University
Sumiyoshi-ku, Osaka 558-8585, Japan

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Great attention has been paid to C_{60} as an intriguing new material from both experimental and theoretical aspects.[1] C_{60} is easily reduced to form anionic species due to its great electron affinity. Molecular solids of alkali or alkali-earth doped C_{60} and TDAE−C_{60} complexes show a variety of intriguing physical properties.[2−4] The key to an understanding of the properties of anions derived from C_{60} is the elucidation of the electronic spin structures associated with charge fluctuation and the splitting of the t_{1u} LUMO and t_{1g} NLUMO by Jahn−Teller distortions for successive levels of reduction. There have been many studies describing the electron spin resonance spectroscopy of C_{60}^{2-} and C_{60}^{3-} in frozen solution and solid phases.[5] Despite the attention focused on these polyanionic C_{60} compounds, however, there is a great deal of apparent controversy in the literature as to the spin identification of C_{60}^{2-} and C_{60}^{3-} in the ground and nearby excited states by cw-ESR spectroscopy. Triplet-state C_{60}^{2-} fullerene has been well documented,[5d] but only spin-doublet C_{60}^{3-} fullerene has been reported. In this paper we report the first detection of C_{60}^{3-} fullerene in the quartet state by cw-ESR/2D Electron Spin Transient Nutation (2D-ESTN) spectroscopy and the observation of anomalous spin relaxation from the polyanionic high-spin C_{60} fullerene at low temperature. Particularly, 2D-ESTN spectroscopy is useful to discriminate between high-spin species among spin mixtures in non-oriented media.[6−8]

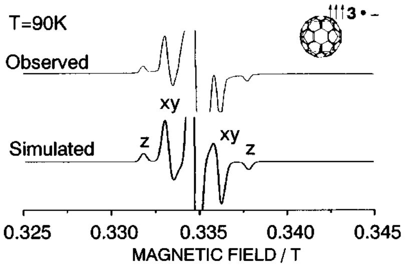

Figure 1. Observed and simulated quartet-state ESR fine-structure spectra from C_{60}^{3-} fullerene at 90 K; spin Hamiltonian parameters, $S = {}^3/_2$, $g = 2.0025$, $|D| = 0.0014$ cm^{-1}, and $E = 0$ cm^{-1}. X, Y, and Z denote the canonical absorption peaks. The microwave frequency used was 9.38250 GHz.

The polyanionic high-spin molecules were prepared by the chemical reduction of C_{60} fullerene with potassium metal at room temperature. The reduction was carried out in a sealed-off glass assembly with a cell for ESR measurements under high vacuum. The solvent used in the present work is 2-MTHF (2-methyltetrahydrofuran)/DG (diglyme) in the presence of dicyclohexano-18-crown-6-ether. Controlled experiments for generating the high-spin molecules were made under the following conditions: the volume ratio of 2-MTHF to DG was 2:1 to 3:2 with 1.5 mL of the total volume, and the weight ratio of C_{60} to 18-crown-6-ether was 2(mg):3(mg).

Pulsed ESR-based ESTN experiments were performed by a three-pulse sequence, which consists of a nutation pulse (for microwave excitation) and a pair of $\pi/2 - \pi$ pulses (for detection). Two-dimensional (2D) ESTN fine-structure spectra were constructed as a function of swept static magnetic field. Spin−lattice relaxation curves were observed by the echo-detected inversion recovery method.

Computer simulations of fine-structure cw-ESR spectra were carried out by the eigenfield method[9] to extract accurate spin Hamiltonian parameters, and all the forbidden transition intensities as well as the allowed ones were calculated.[10]

In the first reduction step, a superimposed ESR spectrum of the doublet state of C_{60}^{1-} fullerene and the triplet state of C_{60}^{2-} fullerene was observed, which was similar to the spectrum as reported earlier ($S = 1$, $g = 2.0025$, $|D| = 0.0025$ cm^{-1}, $E = 0$ cm^{-1}).[5d] Further reduction gave a mixed ESR spectrum of the dianionic triplet state and trianionic quartet state in addition to the doublet state spectrum. The continuing reduction yielded a quartet-state fine-structure ESR spectrum of C_{60}^{3-} fullerene dominating the triplet signal as shown in Figure 1(top). The quartet state spectrum was reproduced by spectral simulation with spin Hamiltonian parameters: $S = {}^3/_2$, $g = 2.0025$, $|D| = 0.0014$ cm^{-1}, $E = 0$ cm^{-1}.

Forbidden ESR transitions of $|\Delta m_s| \geq 2$ for the quartet state could not be detected in our ESR conditions, which was confirmed by the fact that their calculated intensities were six orders of magnitude smaller than those of the allowed ones.[10] To exclude any possibility that the observed fine structure spectrum is attributable to a triplet species with a larger $|D|$ value, 2D-ESTN spectroscopy was applied for the sample containing C_{60}^{1-}, C_{60}^{2-}, and C_{60}^{3-} fullerenes to determine the corresponding quantum number (S) unequivocally. In the extreme weak limit of the microwave irradiation field ($B_1 = \omega_1/\gamma$), the nutation frequency ω_n of spin magnetization is expressed as a function of S and m_s, as given by $\omega_n = \omega_1[S(S+1) - m_S(m_S - 1)]^{1/2}$ for an $|S, m_s\rangle \Leftrightarrow$

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† Universidade Técnica de Lisboa.

‡ Osaka City University.

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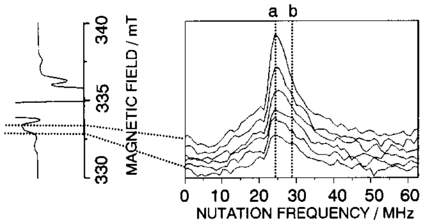

Figure 2. Slices of field-swept 2D-ESTN spectra observed for a mixture of monoanionic doublet, dianionic triplet, and trianionic quartet C_{60} fullerenes. Only the ESTN spectra corresponding to the low-field XY lines are depicted.

Table 1. Observed and Calculated Nutation Frequency Ratios ω_n/ω_1, and Assignment of Spin Quantum Numbers (S) and ESR Transitions

	ω_n/MHz	exptl ω_n/ω_1	theor ω_n/ω_1	S	$m_s \leftrightarrow m_s'$
a	24.1	1.32	1.4	1	$\pm1 \leftrightarrow 0$
b	29.0	1.59	1.73	$^3/_2$	$\pm^3/_2 \leftrightarrow \pm^1/_2$
c	18.2	1.00	1	$^1/_2$	$+^1/_2 \leftrightarrow -^1/_2$
d	35.0	1.92	2	$^3/_2$	$+^1/_2 \leftrightarrow -^1/_2$

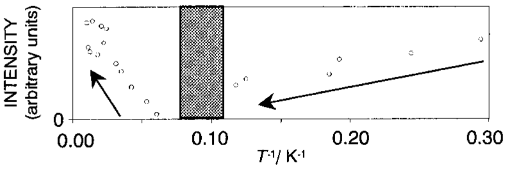

Figure 3. Temperature dependence of the signal intensity of the low-field Z line for the quartet state of annealed C_{60}^{3-} fullerene. Arrows indicate the annealing process from 3.4 K following rapid freezing of the sample down to 3.4 K from ambient temperature.

$|S, m_s - 1\rangle$ ESR allowed transition. The nutation frequency peaks **a** and **b** (see Figure 2(right)) were observed at the low-field XY line for the mixed fine-structure ESR spectrum (see Figure 2 (left)). **c** and **d** were observed at the central $g \sim 2$ field. ω_1 is 18.2 MHz because it belongs to the $S = ^1/_2$ species observed at $g \sim 2$ field. Table 1 gives the observed nutation frequency ratios ω_n/ω_1, which are compared with the theoretical values by the above expression, assuming the transition assignments given in the last two columns. It is unequivocally indicated that the sample contained the species with spin quartet, triplet, and doublet states.

Assuming similar molecular structures for both C_{60}^{2-} and C_{60}^{3-} since both have the vanishing E-value, a value of $(2S - 1)|D|$ represents a measure of spin−spin interactions and average inter-spin distances for the intramolecular triplet state and quartet state: the values are 0.0025 cm^{-1} for $S = 1$ and 0.0028 cm^{-1} for $S = ^3/_2$. This agreement shows that the observed quartet state originates in an intramolecular exchange interaction inherent in C_{60}^{3-} fullerene. The average distance between spins in C_{60}^{3-} derived from the spin dipolar approach for the quartet state is 7.8 Å, which can be compared with 7.1 Å for the mean atom-to-atom diameter of neutral C_{60} found by the X-ray diffraction method.[11] Excess charge fluctuation gives a rationale for the larger average distance observed for C_{60}^{3-}. The nonvanishing D value indicates the departure from I_h symmetry and the vanishing E value shows that the quartet state has axial symmetry. These findings are indicative of the occurrence of pseudo-Jahn−Teller interactions in the ^4A_u ground state of C_{60}^{3-} with I_h symmetry.

The temperature dependence of the signal intensities was closely examined to determine whether the quartet state of C_{60}^{3-} fullerene is a ground or thermally excited state, as the hysteretic dependence shown in Figure 3. Rapid quenching of C_{60}^{3-} fullerene in 2-MTHF/DG from ambient temperature to 3.4 K generates C_{60}^{3-} fullerene in its quartet ground state. Annealing the sample from 3.4 K catastrophically converts the quartet state to the doublet ground state at 10 K, as shown in Figure 3, where no quartet ESR signal was observed in the shadowed temperature range. In this particular range, a remarkable electric loss of microwave power was detected inside the ESR cavity, suggesting the occurrence of a phase transition of the solvent. The spin-state conversion observed for polyanionic C_{60} systems is attributable to a solvent-assisted change in surrounding polarity of the relaxed rigid-glass structure. Once the annealing process was complete, no quartet spectrum appeared below 10 K, showing that the conversion at 10 K is irreversible. C_{60}^{2-} fullerene in 2-MTHF/DG shows a similar behavior; after annealing, C_{60}^{2-} fullerene is singlet in the ground state. It should be noted that the entire process from ambient temperature is reversible for both C_{60}^{2-} and C_{60}^{3-}. A similar hysteretic temperature dependence and slow conversion from the singlet to triplet ground state during annealing following rapid cooling were reported for a neutral diradical in 2-MTHF at cryogenic temperatures.[12]

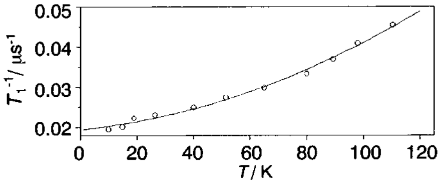

Figure 4. Temperature dependence of longitudinal spin relaxation rates for annealed C_{60}^{2-} fullerene. The static magnetic field was fixed at the XY line of the triplet-state spectrum.

The peculiar microwave-power saturation behavior associated with anomalous spin relaxation phenomena at low temperature was observed from the polyanionic high-spin C_{60} fullerene, as studied by an inversion recovery method. The anomalous longitudinal spin relaxation time observed for annealed C_{60}^{2-} follows a temperature dependence of T^2, as shown in Figure 4, indicating the possible occurrence of phonon bottleneck phenomena.[13] The spin relaxation curves were directly analyzed at all the observed temperatures by a phenomenological approach using modified Scott−Jeffries equations including the bottleneck factor σ, as well as the singlet−triplet energy gap ΔE_{ST}. ΔE_{ST} for the first time was able to be estimated by the modified Scott−Jeffries equations. Molecular hot phonon states are established before the energy exchange to thermal phonons in solid states in this model and σ stands for a ratio of the energy exchange rate between spins and phonons/the energy exchange rate between phonons and bath. σ was determined to be 6 at 12.9 K, which decreased as the temperature increased; $\sigma = 0.5$ at 65 K, clearly showing the occurrence of a strong phonon bottleneck ($\sigma \gg 1$) below ∼13 K. The anisotropy of σ was also found, suggesting the anisotropic reorientation process in the thermally accessible triplet state for annealed C_{60}^{2-}. ΔE_{ST} for annealed C_{60}^{2-} was found to be 30 cm^{-1} on the basis of the analysis at lower temperature. Bottleneck phenomena were also found in annealed C_{60}^{3-}. The high spin states of annealed C_{60}^{n-} fullerenes are possibly Jahn−Teller-effect mediated hot phonon states in the molecular solid state. To our knowledge, these findings are the first evidence of phonon bottleneck behavior from genuinely organic molecular systems. A complete analysis will be reported later.

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