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A Two-Dimensional EPR Nutation Study on Excited Multiplet States of Fullerene Linked to a Nitroxide Radical

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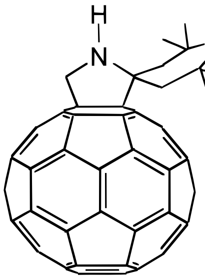
Photoexcited states of 3,4-fulleropyrrolidine-2-spiro-4′-[2′,2′,6′,6′-tetramethyl]piperidine-1′-oxyl (**1**) were studied by the two-dimensional (2D) EPR nutation method in toluene glass. 2D nutation spectra were observed by varying a pulse length of the first microwave pulse in the spin echo experiment. Three kinds of nutation frequencies were obtained from analyses of the 2D spectra and assigned to those of the excited quartet and doublet states on the basis of the fictitious spin-$^1/_2$ theory. The obtained EPR parameters such as *g*-values, hyperfine coupling constants, and zero-field splittings were discussed in terms of the spin Hamiltonian for doublet and quartet states.

Introduction

Transient nutation phenomena were first observed in NMR by Torrey[1] and applied to studies of the quadrupole interactions in disordered solids.[2−5] In EPR a nutation method has been used to investigate kinetics of photoinduced paramagnetic species[6,7] and determine electron-spin multiplicity of transition-metal ions.[8−10] Astashkin and Schweiger utilized this method to separate overlapping EPR signals of two different sites in a single crystal by choosing proper positions of two time gates.[10] Recently, a two-dimensional (2D) nutation technique has been reported for assignment and separation of a spin-correlated radical pair (SCRP) from free radicals[11] on the basis of different nutation frequencies of these species.[12] The 2D nutation method has more advantages in assigning and separating species of different multiplicities than the 1D method.

In this Letter, the 2D technique is applied to studies of the ground and excited states of compound **1**,[13]



fullerene linked to a nitroxide radical. For this molecule, a time-resolved EPR spectrum was reported in toluene solution and the EPR signal of the excited quartet state was assigned on the basis of hyperfine coupling constants and *g*-values.[13] A similar study has been reported for a system of tetraphenylporphinatozinc(II) coordinated by *p*-pyridyl nitronyl nitroxide in solid toluene. In this case, both doublet and quartet signals in excited states were assigned from their *g*-values and zero-field splittings.[14] Here we first try to observe a 2D nutation spectrum for our radical−triplet pair system, **1** in toluene solution, and then determine nutation frequencies of the signals and assign multiplicities of the involved states. Finally the spectrum of each state is separated on the basis of the nutation frequency. It is noted that this report is on the first 2D EPR nutation study of photoexcited multiplet states.

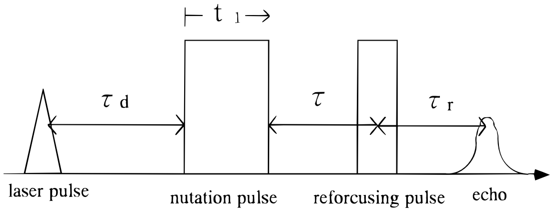


Figure 1. Pulse sequence for the 2D nutation experiment. τ_D and τ are delay times between the laser pulse and the first microwave pulse and between the first and second microwave pulses, respectively. The spin packets are reforcused at τ_r after the second pulse.

Experiment

Compound **1** was synthesized by following the method of Corvaja et al.,[13] and the quality was checked by elementary analysis, FABMS, UV−vis., steady-state EPR, and time-resolved (TR) EPR. For EPR measurements, 1×10^{-4} M toluene solution was deaerated by the freeze−pump−thaw method.

TREPR measurements were carried out at 80 K on a JEOL-FE2XG EPR spectrometer using an Oxford ESR 900 helium gas flow system. The samples were irradiated by the second harmonics (532 nm) of a Quanta-Ray GCR-230 Nd:YAG laser with a repetition rate of 10 Hz. Details of the TREPR measurements have been reported previously.[15]

2D nutation experiments were carried out on a pulsed EPR spectrometer of our own design[16,17] by utilizing the electron-spin-echo (ESE) technique as illustrated in Figure 1. In the ESE experiment a first microwave (MW) pulse of duration t_1 was applied after a laser pulse of the second harmonics (532 nm) of a Continuum SL I-20 Nd:YAG laser with 20 Hz, where t_1 was incremented in 34 steps of 4 ns. Nutated magnetization was refocused by a second MW pulse of ca. 20 ns, irradiated at 200 ns after the first MW pulse. ESE-detected EPR spectra were observed at various t_1 values by plotting integrated intensities of ESE signals with respect to the magnetic field (B_0), apodized in t_1 dimension with the cosine window and zero-filled to 1024 data points. 2D EPR nutation spectra were obtained from Fourier-transformation of the ESE spectra in the t_1 dimension.

Results and Discussion

The TREPR spectrum of compound **1** was obtained at 0.5 μs (τ_d) and 80 K as shown in Figure 2. The spectrum shows significant asymmetry of the peaks, involving field dependent

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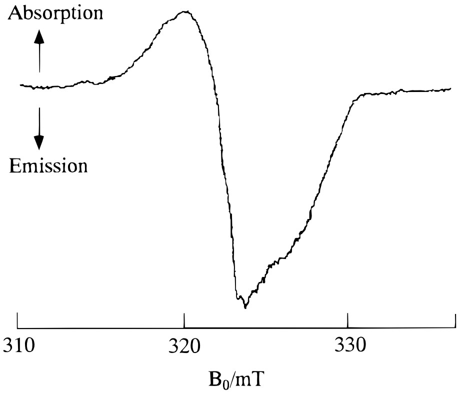

Figure 2. Time-resolved EPR spectrum of compound **1** in toluene at 80 K and 0.5 μs after the laser excitation. The microwave frequency is 9.0647 GHz.

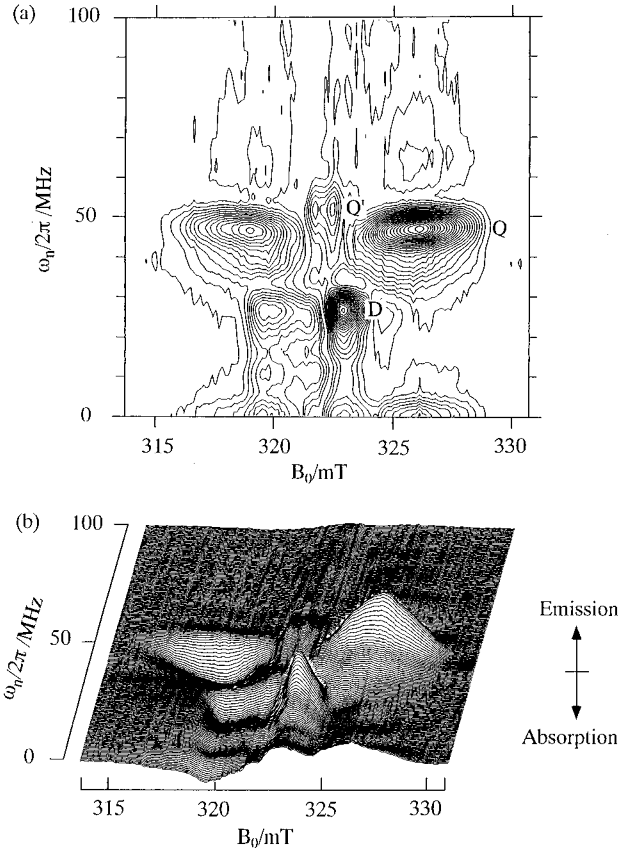

Figure 3. 2D nutation spectra observed in toluene at 1.5 μs and 80 K, where the microwave frequency is 9.0410 GHz. (a) and (b) show contour plots and stack plots of the spectra, respectively.

TABLE 1: Obtained Nutation Frequencies for 1

	$\omega_n/2\pi$/MHz[a]	ω_n/ω_1
D	27.5 (=ω_1)[b]	1
Q	47.5	1.73
Q′	54.2	1.97

[a] Nutation frequency. [b] Nutation frequency of a radical.

electron spin polarizations, absorption to emission from low to high fields. This result indicates an overlap of signals due to several origins. In order to assign the bands, the 2D nutation spectra were observed as shown in Figure 3a,b. From the contour plots of the signals, it is found that the EPR signals are separated into three groups with their different nutation frequencies, D, Q, Q′ as indicated in Figure 3b. The obtained nutation frequencies are summarized in Table 1.

As this system consists of spin packets having different nutation frequencies, the second pulse is not the complete π-pulse for all spin packets, giving echo signals at different time τ_r after the second MW pulse (Figure 1). It is also noted that the long (t_1) nutation pulse provides the complicated and prolonged echo signal.[18] We, therefore, selected a gate width that is wide enough to observe all the echo signals. Due to a difference in the pulse length of the second MW, a relative EPR intensity of a different spin state is generally different from that of a TREPR spectrum.

If an EPR transition between the $|S, M_s - 1\rangle$ and $|S, M_s\rangle$ states is excited selectively by microwave, the system can be described by the fictitious spin-$^1/_2$ formalism,[19] and the nutation frequency depends on spin multiplicity S and magnetic quantum number M_s. In solid phase, as this condition is usually satisfied due to large zero-field splittings ($S > {}^1/_2$), the nutation frequency ω_n of this transition is given by

$$\omega_n = \sqrt{S(S+1) - M_s(M_s - 1)}\,\omega_1 \qquad (1)$$

ω_1 ($=g\beta B_1/\hbar$) denotes a nutation frequency of a $S = {}^1/_2$ system, where B_1 is the field strength of a microwave in a rotating frame. On the basis of this equation, the nutation frequencies of the transitions, $|S = {}^3/_2, M_s = \pm{}^3/_2\rangle \leftrightarrow |{}^3/_2, \pm{}^1/_2\rangle$ and $|{}^3/_2, {}^1/_2\rangle \leftrightarrow |{}^3/_2, -{}^1/_2\rangle$, are predicted to be $3^{1/2}\omega_1$ and $2\omega_1$, respectively. From the comparison of these calculated and obtained values (Table 1), the peaks denoted by D, Q, and Q′ are assigned to those of the transitions between the doublet states, $|S, M_s\rangle = |{}^3/_2, \pm{}^3/_2\rangle \leftrightarrow |{}^3/_2, \pm{}^1/_2\rangle$ and $|{}^3/_2, {}^1/_2\rangle \leftrightarrow |{}^3/_2, -{}^1/_2\rangle$, respectively. These results provide the direct spectroscopic evidence for generations of the coupled quartet and doublet states in this system.

At the doublet nutation frequency ($\omega_1 = 27$ MHz), two types of spectra were observed, as shown in Figure 4b. These spectra consist of absorptive and emissive components. The absorptive part is assigned to the signal due to the ground (D_0) state of **1**, because the spectrum resembles closely the ESE spectrum (Figure 4a) of D_0 whose g-values and nitrogen hyperfine coupling constants are summarized in Table 2.

We next discuss EPR parameters of the excited states in terms of the spin Hamiltonians of coupled states. The effective Hamiltonians for an interacting radical (R; $S = {}^1/_2$)−triplet (T; $S = 1$) pair are given for quartet (Q; $S = {}^3/_2$) and doublet (D; $S = {}^1/_2$) states as[20]

$$\mathbf{H}_Q = \mu_B\mathbf{B}\cdot(\mathbf{g}_R/3 + 2\mathbf{g}_T/3)\cdot\mathbf{S} + ({}^1/_3)\mathbf{I}\cdot\mathbf{A}_R\cdot\mathbf{S} + \mathbf{S}\cdot(\mathbf{D}_T/3 + \mathbf{D}_{RT}/3)\cdot\mathbf{S} \qquad (2)$$

and

$$\mathbf{H}_D = \mu_B\mathbf{B}\cdot(-\mathbf{g}_R/3 + 4\mathbf{g}_T/3)\cdot\mathbf{S} - ({}^1/_3)\mathbf{I}\cdot\mathbf{A}_R\cdot\mathbf{S} \qquad (3)$$

respectively. Here $\mathbf{D}_{RT}$ denotes a dipolar−dipolar interaction tensor for R and T. $\mathbf{A}_R$ is a hyperfine coupling matrix for nitrogen nuclei of nitroxide, and other symbols have usual meanings. Using eqs 2 and 3, the EPR parameters of the excited D_1 and Q_1 states are estimated from the g and A values of the ground state of **1** and g_{iso} (=2.0012) of triplet fullerene.[21,22] These values are summarized in Table 2. The values for the excited doublet state are also shown in Figure 4b, where the estimated stationary fields are consistent with the observed ones of emissive polarity. It is concluded that the doublet peaks (ω_1) are superpositions of the emissive signal due to D_1 (T_1 + R) and the absorptive signal due to D_0 (S_0 + R). The D_2 (S_1 + R) signal is not considered to be observed due to a singlet character of constituent C_{60}, in contrast to a triplet character in D_1.

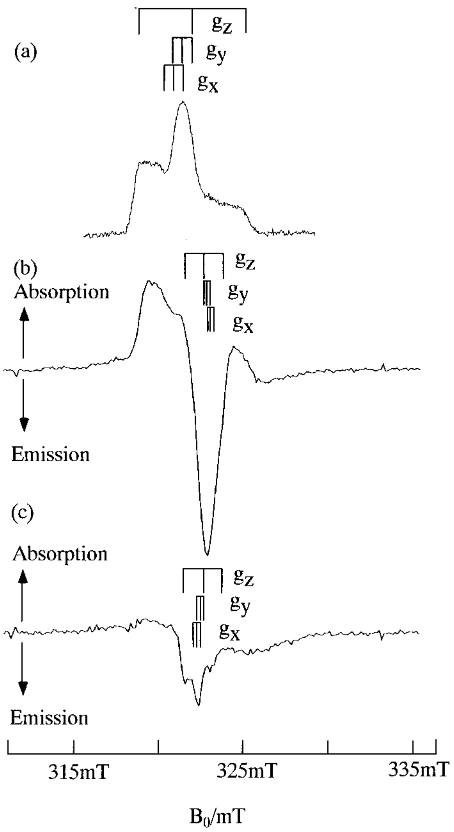

Figure 4. (a) ESE spectrum of compound **1** in the dark at 10 K, where the microwave frequency is 9.0277 GHz. (b) and (c) show sliced spectra of Figure 3a at nutation frequencies of 27 and 55 MHz, respectively, where the microwave frequency is 9.0410 GHz. Vertical sticks show estimated stationary fields based on the EPR parameters summarized in Table 2.

TABLE 2: Obtained and Estimated EPR Parameters of the Ground and Excited States for 1

	g_x	g_y	g_z	A_x/h/MHz	A_y/h/MHz	A_z/h/MHz
D_0 (S_0 + R)[a]	2.009	2.006	2.002	17	17	90
D_1 (T_1 + R)[b]	1.999	2.000	2.001	6	6	30
Q_1 (T_1 + R)[b]	2.004	2.003	2.002	6	6	30

[a] Obtained values. [b] Estimated from eq 1, values of D_0, and $g(T_1) = 2.0012$.

The spectrum spliced at 55 MHz is shown in Figure 4c. The *g*-values of this spectrum are consistent with those (Table 2) estimated for the excited quartet state as shown in the figure, where the spectrum is assigned to be due to the excited quartet state from the nutation frequency (55 MHz = 2 ω_1). The zero-field splitting parameter $|D|$ is estimated as 0.0028 cm^{-1} from the two outer most stationary fields (316 and 328 mT) in the quartet spectrum. This value is much smaller than that (0.0114 cm^{-1})[23] of triplet fullerene and is consistent with the spin Hamiltonian of the quartet state (eq 2).

Further investigations including analyses of time evolution and EPR parameters of the signals are now in progress.

Conclusions

The 2D nutation EPR spectrum of the radical−triplet pair was observed for the first time in frozen solution. From the observed nutation frequencies, the spin quantum numbers of $S = {}^3/_2$ and ${}^1/_2$ were found to be good quantum numbers for the coupled states, and generations of the photoexcited quartet and doublet states were proved directly. The EPR spectra of the quartet and doublet states were separated, and their EPR parameters were evaluated. A great ability of 2D nutation spectroscopy was demonstrated by a study of photoexcited multiplet states.

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