The Journal of Physical Chemistry A

VOLUME 103, NUMBER 39, SEPTEMBER 30, 1999

# LETTERS

## First Observation of the Photoexcited Quintet State in Fullerene Linked with Two Nitroxide Radicals

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*Received: July 1, 1999; In Final Form: August 18, 1999*

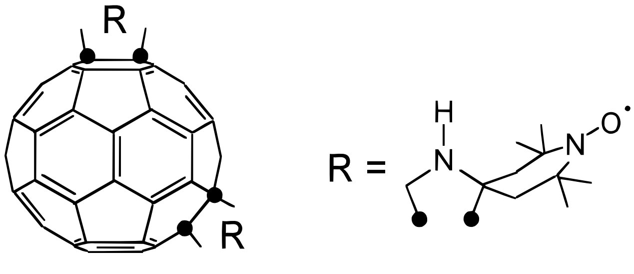
The bisadduct of fullerene (**1**) having two nitroxide radicals at the *trans*-3 position was newly synthesized. The ground and photoexcited states of **1** were studied by continuous-wave and pulsed two-dimensional electron paramagnetic resonance spectroscopy. An exchange interaction between the radicals was evaluated to be much smaller than an isotropic hyperfine splitting, showing a doublet ($S = 1/2$) character in the ground state. It was found from a 2D nutation spectrum that a photoexcited state has a quintet character ($S = 2$) which is generated via interactions between photoexcited triplet fullerene ($S = 1$) and the two nitroxide radicals ($S = 1/2$).

### Introduction

Many fullerene derivatives were synthesized[1] after a macroscopic production of fullerene was achieved.[2] They attract much attention as new materials and molecular devices because of their fascinating physical and chemical properties[3] based on a spherical structure and electron delocalization.

Recently, radical−triplet interactions have become of interest and have been investigated extensively,[4,5] as have also radical−triplet pairs from a viewpoint of a control of magnetization by a photon in organic compounds.[6−8] In these systems, photoexcited quartet and doublet states are generated via an interaction between the radical and the photoexcited triplet. When two or more paramagnetic species are linked to a $\pi$-conjugated triplet, higher spin states ($S > 3/2$) are expected to be realized. Furthermore in the case where the triplet molecule is so large that the radicals do not interact with each other, the ground state must be doublet ($S_G = 1/2$) and the excited state might be multiplet ($S_E > 3/2$) in nature. This is interesting because the excited state with $\Delta S (\equiv S_E - S_G) > 1$ is generated by a photon having an angular momentum of $l = 1$. To realize such an attractive system, we study a two-radicals−triplet system where the triplet moiety is fullerene.

We synthesized a new bisadduct of fullerene (**1**) having two nitroxide radicals at the *trans*-3 position



**1**

and investigated both the ground and photoexcited states of **1** by electron paramagnetic resonance (EPR). The black filled circles of **R** indicate positions of the corresponding carbons of $C_{60}$. In a previous paper, the photoexcited states of fullerene linked with a mono nitroxide radical were investigated.[8] A two-dimensional (2D) EPR nutation method was found to be very powerful for assignment and separation of the EPR signals in the radical−triplet pair system.[8] In this paper, the 2D nutation method together with EPR parameters is utilized to assign and

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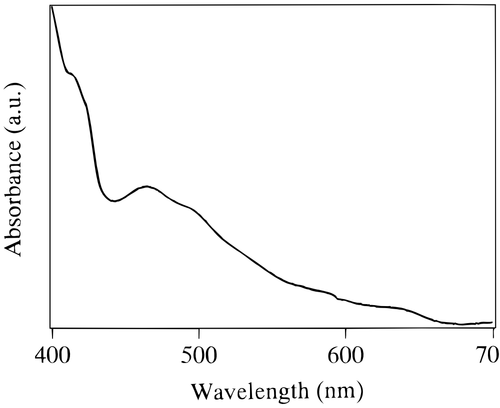

**Figure 1.** UV−vis spectrum of **1** in toluene at room temperature.

separate the ground and the photoexcited states. It is found for the first time that a photoexcited quintet state is realized in the radical−triplet system, where the ground state is doublet in nature.

## Experiment

**Material.** Syntheses of fullerene bisadducts were carried out by following almost the same procedure which Corvaja et al. described in the literature.[7] A mixture of 4-amino-4-carboxy-2,2,6,6,-tetramethylpiperidine-1-oxyl (TOAC, 2 molar equiv) and paraformaldehyde (4 molar equiv) was heated at reflux with $C_{60}$ (1 molar equiv) in toluene. TOAC was synthesized by following the literature.[9] Several fractions of different bisadducts were obtained and the fraction of highest yield was carefully purified several times by silica gel column chromatography using toluene and ethyl acetate as eluants. The formation of the bisadduct of $C_{60}$ was confirmed with fast atom bombardment mass spectroscopy (FAB-MS) and the purity was checked by elementary analysis. For bisadducts of $C_{60}$, it is well-known that there are eight isomers with respect to the linked positions. Among these isomers, the *trans*-3 and *cis*-3 isomers give relatively high yields in the Prato bisaddition.[10] From the UV−visible spectrum (Figure 1) obtained by a Shimadzu UV-240 spectrometer, the bisadduct was assigned as the *trans*-3 isomer.[10] For EPR measurements, $1 \times 10^{-4}$ M toluene solution was deaerated by the freeze−pump−thaw method.

**EPR Measurements.** Continuous wave (CW) EPR was measured on a Varian E-112 spectrometer. Time-resolved (TR) EPR measurements were carried out at 10 K on a JEOL-FE2XG EPR spectrometer using an Oxford ESR 900 helium gas flow system. The sample was irradiated by the second harmonic (532 nm) of a Quanta-Ray GCR-230 Nd:YAG laser with a repetition rate of 10 Hz. Details of TREPR measurements have been reported previously.[11]

2D nutation experiments were carried out at 5 K on a pulsed EPR spectrometer of our own design[12] with a two-pulse sequence.[8] The interval between the first and second microwave (MW) pulses and the length of the second MW pulse were set to 250 and 80 ns, respectively. The first MW pulse of duration $t_1$ was incremented in 30 steps of 10 ns. The sample was irradiated by the second harmonic of a Continuum SL I-20 Nd:YAG laser with a repetition rate of 20 Hz at 100 ns ($= \tau_d$) before the first MW pulse. A field-swept electron-spin-echo (ESE) spectrum was observed at each $t_1$ with two-step phase cycling $[0, 0]-[0, \pi]$ to eliminate signals of free induction decay from the second MW pulse.[13] Nutation signals were extrapolated to 200 points in the $t_1$ dimension by the fast linear prediction procedure[14,15] and zero-filled to 1024 data points. 2D nutation spectra were obtained from the Fourier transformation (FT) of field-swept ESE spectra in the $t_1$ dimension. To determine a microwave strength $\omega_1$ in the 2D experiment, we obtained a nutation frequency of the ground state in the dark just before measurements of the laser excitation. ESE-FT spectra were observed with four-step phase cycling[12] at various $t_1$ by FT of the echo signals in the $t_2$ dimension. A 2D nutation spectrum was obtained by FT of the ESE-FT spectra in the $t_1$ dimension, giving the nutation frequency of the ground state.

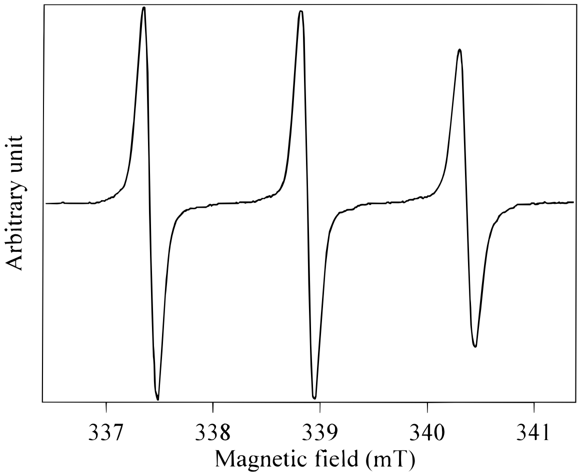

**Figure 2.** EPR spectrum of **1** at room temperature in the dark. The MW frequency and the power are 9.5137 GHz and 0.5 mW, respectively. The amplitude of 100 kHz field modulation is 5 $\mu$T.

## Results

A CW EPR spectrum of **1** was obtained at room temperature in toluene solution as shown in Figure 2. The spectrum shows three hyperfine lines of a typical mono nitroxide radical ($S = 1/2$). The isotropic *g*-value and hyperfine coupling constant ($a_{iso}$) were obtained as 2.0063 and 42.6 MHz, respectively. A 2D nutation spectrum of the ground state was obtained from field-swept ESE spectra at 5 K in the dark, where only one nutation frequency was observed in the spectrum as shown in Figure 3a.

Transient EPR signals were observed after the laser excitation in the solid phase. A TREPR spectrum at 10 K is shown in Figure 4a. The spectrum shows a field-dependent electron spin polarization which alternates from an absorption of microwave at the low field to an emission at the high field (A/E). In the central part of the spectrum, a little sharper and weaker signals are overlapping, having a similar polarization pattern (A/E). The EPR line shape of the spectrum was not temperature-dependent between 10 and 80 K.

To assign the signals, we observed a 2D nutation spectrum of the transient signals at 5 K as shown in Figure 3b. The transient signals are separated into three peaks with respect to the nutation frequency and indicated as D, Q, and Q′ in Figure 3b. The obtained nutation frequencies of D, Q, and Q′ were $\omega_D = 3.80 \pm 0.2$ MHz, $\omega_Q = 7.9 \pm 0.2$ MHz, and $\omega_{Q'} = 9-10$ MHz as summarized in Table 1. The spectra of D, Q, and Q′ are shown in Figure 4 by slicing the 2D spectrum at the corresponding nutation frequencies. The nutation frequency of the ground state, which was observed just before the 2D measurement with laser excitation, was obtained in the dark as $3.9 \pm 0.2$ MHz.

## Discussion

Assignments of the ground and the photoexcited states are made from the hyperfine coupling constant, the zero-field

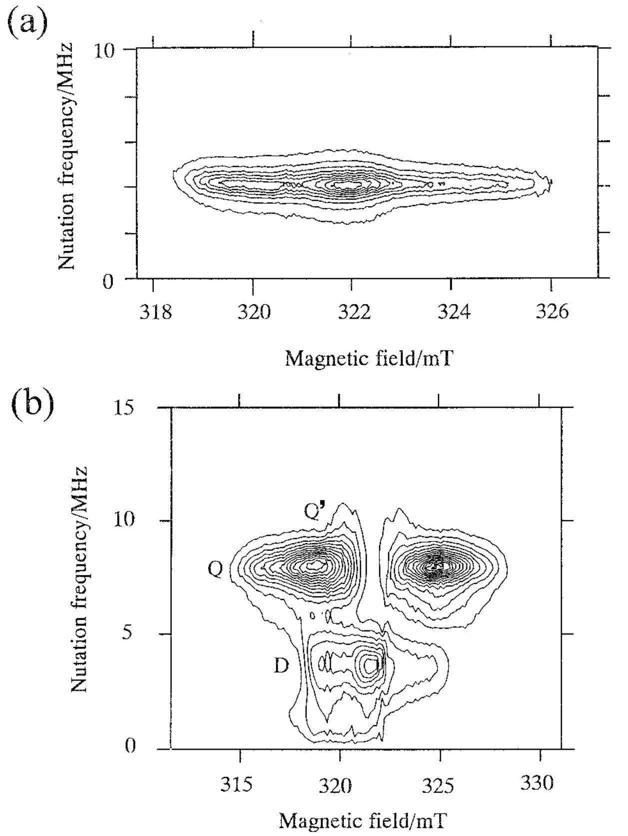

**Figure 3.** 2D EPR nutation spectra of **1** at 5 K for (a) the ground state in the dark and (b) the photoexcited state. The spectrum (b) was obtained under the condition that the first MW pulse was irradiated at 100 ns after the laser excitation. The MW frequencies are 9.0332 and 9.0240 GHz for (a) and (b), respectively.

splitting, and the nutation frequency. In the case that $S$ is a good quantum number and an EPR transition between the $|S,Ms - 1\rangle$ and $|S,Ms\rangle$ states is excited selectively by microwave, the nutation frequency $\omega_n$ of this transition is described as [8,16–19]

$$\omega_n = \sqrt{S(S + 1) - Ms(Ms - 1)}\omega_1 \tag{1}$$

Here $\omega_1$ ($= g\beta B_1/\hbar$) denotes the nutation frequency of a $S = 1/2$ system. The nutation frequencies $\omega_n$ which might be involved in our system are summarized in Table 1.

It is well-known for nitroxide biradicals that a spectrum is very complicated when the exchange interaction ($J_{RR}$) between the radicals is comparable to the isotropic hyperfine coupling constant ($a_{iso}$) and that five hyperfine lines emerge when $J_{RR} \gg a_{iso}$. The spectrum shows three hyperfine lines just like a typical nitroxide mono-radical in case of $J_{RR} \ll a_{iso}$. On the basis of these facts and the EPR spectrum in Figure 2, $J_{RR}$ is estimated to be much smaller than $a_{iso}$ ($J_{RR} \ll a_{iso}$) in the ground state of this molecule. This result is rationalized by the following discussion.

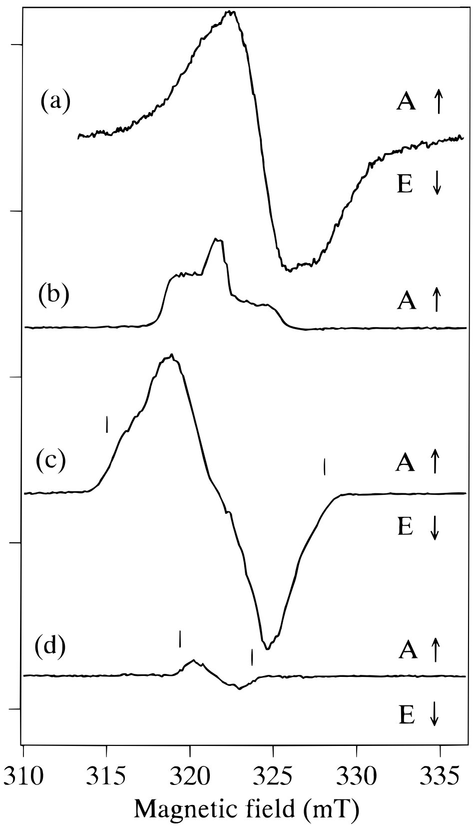

**Figure 4.** (a) TREPR spectrum of **1** at 10 K and 200 ns after the laser excitation. The microwave frequency is 9.0855 GHz. (b−d) Sliced EPR spectra of the 2D spectrum (Figure 3b) at the nutation frequencies of (a) 3.8, (b) 7.9, and (c) 10 MHz, respectively. A and E denote the phase of electron spin polarizations of absorption (A) and emission (E). The bars in (c) and (d) indicate a set of the outermost stationary fields in the quintet spectra.

**TABLE 1: Nutation Frequency for Each Transition**

| $\lvert S,Ms\rangle \Leftrightarrow \lvert S,Ms \pm 1\rangle$ | $\omega_n$[a] | $\omega$/MHz[b] | $\Delta B^{calc}$ | $\Delta B^{exp}$/mT[d] |
|---|---|---|---|---|
| $\lvert 2,\pm 2\rangle \Leftrightarrow \lvert 2,\pm 1\rangle$ | $2\omega_1$(7.8 MHz) | 7.9($\omega_Q$) | 6D | 13.0 |
| $\lvert 2,\pm 1\rangle \Leftrightarrow \lvert 2,0\rangle$ | $\sqrt{6}\omega_1$(9.6 MHz) | 9−10($\omega_{Q'}$) | 2D | 4.3 |
| $\lvert 1/2,1/2\rangle \Leftrightarrow \lvert 1/2,-1/2\rangle$ | $\omega_1$(3.9 MHz) | 3.8($\omega_D$) | | |
| $\lvert 1,\pm 1\rangle \Leftrightarrow \lvert 1,0\rangle$ | $\sqrt{2}\omega_1$ | | | |

[a] The nutation frequency obtained from eq 1; the values in parentheses are calculated $\omega_n$ from obtained $\omega_1$ (= 3.9 MHz). [b] The nutation frequency at the D, Q, and Q′ peaks from the 2D nutation experiment. [c] The calculated splitting between the two outermost stationary fields of each transition from the Hamiltonian[2] with $E = 0$. [d] The obtained splitting of the Q and Q′ peaks.

For the bisadducts of the *trans*-3 isomer, there are three isomers depending on the relative orientation of the nitroxide moiety. Their inter-radical distances between the centers of the N−O bonds are estimated to be 10.6, 14.2, and 16.3 Å from a geometrical calculation with the X-ray structural data of the nitroxide radical[20] and $C_{60}$.[21] In a nonconjugated nitroxide biradical, a magnitude of $J_{RR}$ mainly depends on direct overlap between orbitals of unpaired electrons and/or on spin polarization via $\sigma$ bonds.[22] $J_{RR}$ due to the direct overlap is approximated by an exponential function $J(r) = J_0 e^{-\alpha(r-d)}$,[22–25] where $r$ is the inter-radical distance and $J_0$ is the magnitude of the exchange interaction at distance $d$ of the closest approach with a characteristic length factor $\alpha^{-1}$. Although several kinds of parameter sets are reported in the literatures,[23–25] $J(r)$ is always calculated to be less than 1 MHz for $r = 10.6$ Å such that $J(r) = 0.19$ MHz for $r = 10.6$ Å, $J_0 = 10^{13}$ s$^{-1}$, $\alpha = 2.5$ Å$^{-1}$, and $d = 3.5$ Å.[25] As for a contribution via spin polarization of the $\sigma$ bonds, $J_{RR}$ is approximated roughly by the equation $J_{RR} = (-1)^n 3 \times 10^{6-n}$ MHz,[22] where n is a number of the $\sigma$ bonds. In compound **1** with $n = 12$, $J_{RR}$ is calculated as $3 \times 10^{-6}$ MHz. These quantitative considerations are consistent with the result that $J_{RR} \ll a_{iso}$(= 42.6 MHz) and that the ground state shows the doublet character. In such a case, the single nutation frequency is expected to be observed in the ground state, corresponding to $\omega_1$ as shown in Figure 3a. Then, $\omega_1$ in the 2D experiment with the laser excitation is determined as 3.9 ± 0.2 MHz from the nutation frequency of the ground state in the dark.

On the basis of the calculated and obtained nutation frequencies in Table 1, we can safely assign the peaks as those of the ground doublet (D) and quintet (Q and Q′) states in the 2D spectrum (Figure 3b). The sliced spectrum of D in Figure 4b is very similar to that of the typical mono-nitroxide radical. The Q and Q′ spectra are assigned as those of the transitions between $|S,Ms\rangle = |2,\pm 2\rangle \leftrightarrow |2,\pm 1\rangle$ and $|S,Ms\rangle = |2,\pm 1\rangle \leftrightarrow |2,0\rangle$ , respectively, in the quintet state. These assignments are also confirmed from the involved zero-field splitting and the exchange interaction parameter as the following. If a condition that $|D| \gg |E|$ is satisfied, the splittings between the two outermost stationary fields of the $|S,Ms\rangle = |2,\pm 2\rangle \leftrightarrow |2,\pm 1\rangle$ and $|2,\pm 1\rangle \leftrightarrow |2,0\rangle$ transitions correspond to $6|D|$ and $2|D|$, respectively.[26] Here $D$ and $E$ are defined by the spin Hamiltonian,

$$H = g\mu_B \mathbf{B}\cdot\mathbf{S} + hD\{S_Z^{\,2} - (1/3)S(S + 1)\} + (1/2)E(S_+^{\,2} + S_-^{\,2}) \quad (2)$$

The two outermost stationary fields of the $|2,\pm 2\rangle \leftrightarrow |2,\pm 1\rangle$ transitions (Q) are estimated as 315 and 328 mT from Figure 4c and those of Q′ are 319 and 324 mT (Figure 4d). These stationary fields are marked by bars in Figure 4. From these values, $|D|$ is approximately evaluated as 6 × 10 MHz (Q) and 6 × 10 MHz (Q′) from Q and Q′, respectively.[27] The coincidence of these values indicates that the two transitions are those of the quintet state.

The exchange interactions are briefly discussed here for the photoexcited state. The quintet state is considered to be generated via the interactions ($J_{RT}$) between photoexcited triplet $C_{60}$ and the nitroxide radicals, where the interaction ($J_{RR}$) between the radicals is very small. The condition for realizing the quintet state is that $|J_{RT}|$ is much larger than zfs parameter $|D_T|$ of the triplet moiety ($|J_{RT}| \gg |D_T|$), which is same for the quartet state in the mono-radical−triplet system.[29] This fact might be interpreted by the following model based on the direct overlap between R and T. The zfs parameters of the bisadduct of fullerene with *N*-methylpyrrolidine at the *trans*-3 position are reported as $|D_T| = 2.6 \times 10^2$ MHz and $|E_T| = 3.6 \times 10$ MHz,[30] that are considered to be similar for **1**. The distance between the radical and the closest carbon atom of $C_{60}$ is obtained as 4.9 Å from the geometrical calculation[20,21] and $J_{RT}$ is estimated to be $3.0 \times 10^2$ GHz from the exponential function $J(r) = J_0 e^{-\alpha(r-d)}$ with $J_0 = 10^{13}$ s$^{-1}$, $\alpha = 2.5$ Å$^{-1}$, and $d = 3.5$ Å at $r = 4.9$ Å. The second short distance is 5.2 Å, where $J_{RT}$ is calculated as $1.4 \times 10^2$ GHz by the same equation. Although we do not know exact spin densities $\rho_C(C_{60})$ at these positions, $\rho_C(C_{60})$ is not considered to be very far from the uniform distribution ($\rho_C(C_{60}) = 1/60$)[31] and $J_{RT}$ is considered to be large enough to fulfill the condition, $|J_{RT}| \gg |D_T|$.

## Conclusion

The bisadduct of fullerene with two nitroxide radicals at the *trans*-3 position was newly synthesized. The photoexcited quintet state in the radical−triplet system could be realized for the first time and assigned by the 2D EPR nutation method. It was also found that the exchange interaction between the radicals in the ground state is much smaller than the isotropic hyperfine interaction (42.6 MHz) due to the long inter-radical distance showing a doublet character. The photoexcited quintet is generated via the exchange interactions between triplet $C_{60}$ and the radicals. The EPR spectra of the $|S,Ms\rangle = |2,\pm 2\rangle \leftrightarrow |2,\pm 1\rangle$ and $|2,\pm 1\rangle \leftrightarrow |2,0\rangle$ transitions were separated by the 2D nutation method and the zfs of quintet state was evaluated approximately as $|D| = 6 \times 10$ MHz.

**Acknowledgment.** This work was supported by JSPS Research Fellowships for Young Scientists and a Grant-in-Aid for Scientific Research No. 08640630, 10044057, and 11640495 from the Ministry of Education, Science and Culture, Japan.

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