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Direct observation of localized excitation in the lowest excited triplet state of fullerene dimers C_{120} and $C_{120}O$ by means of time-resolved electron paramagnetic resonance

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Abstract

Time-resolved EPR spectra were observed by means of the transient EPR technique for two kinds of fullerene dimers C_{120} and $C_{120}O$ in the lowest excited triplet (T_1) states and compared with those of mono-adducts of fullerene (C_{60}). It was found that zero-field splitting (zfs) parameters of both dimers are nearly the same as those of the monomers, indicating that the excitation is almost completely localized at one of the two fullerene units in the T_1 state. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Although electronic excited states of fullerene (C_{60}) have been extensively studied by means of various techniques, it is still very difficult to determine these structures mostly due to its high symmetry. Among the techniques, electron paramagnetic resonance (EPR) provides more reliable information on symmetry and electron distribution of paramagnetic species. In fact, several interesting results are reported for excited triplet (T_1) C_{60} by EPR; (1) the excitation is localized at some part (mostly near the equator) of whole moiety [1,2]. (2) The spin distribution varies slightly with addition of adduct depending on its position [3–5]. (3) The EPR spectrum changes dramatically with temperature even in solid reflecting averages over the states generated from the Jahn–Teller splitting [6,7]. (4) The T_1 structure is also evaluated from analysis of interactions with radical(s) in the radical adducts of C_{60}, where excited high spin states of quartet and/or quintet appear [8,9].

In this report, we study an electronic structure of T_1 fullerene dimers C_{120} and $C_{120}O$ (Fig. 1), especially focusing on localization and/or delocal-

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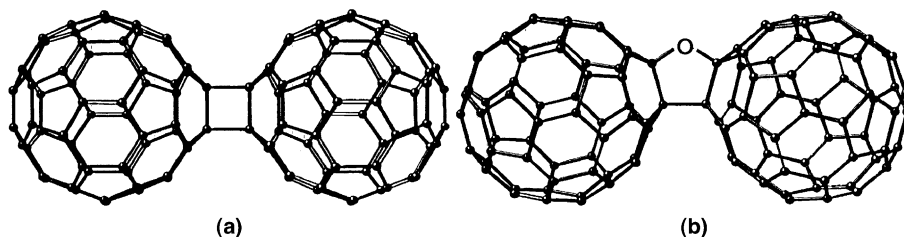*E-mail address:* yamauchi@tagen.tohoku.ac.jp (S. Yamauchi).

Fig. 1. Molecular structure of fullerene dimers (a) C_{120} and (b) $C_{120}O$.

ization of excitation by use of a time-resolved EPR (TREPR) technique.

A wavefunction of a dimer is described by a linear combination of those of localized exciton (EX) and delocalized charge resonance (CR) states in the valence bond method as the equation,

$$\Psi_{DM} = a\Psi_{EX} + b\Psi_{CR} \quad (a^2 + b^2 = 1). \quad (1)$$

The coefficients a and b of the two states are obtained from zero-field splitting (zfs) parameters $D \ (= -3/2 \cdot E_z)$ and $E \ (= 1/2(E_y - E_x))$ of the dimer (DM), EX, and CR states on the basis of the following equation [10,11]. $E_i \ (i = x, y, z)$ denotes energy of the triplet sublevel T_i under the zero-field

$$D_{DM} = a^2 D_{EX} + b^2 D_{CR}. \quad (2)$$

Although the analogous equation holds for the E value, E is not useful for quantitative evaluation of electron delocalization due to the Jahn–Teller distortion in this case. $D_{EX} = D_{MM}$ is realized, when the excitation is completely localized at one unit (monomer; MM) or transferred very fast between the two units of the dimer having parallel zfs axes. These coefficients have been analyzed and discussed quantitatively for metallo-porphyrins [10] and metallo-phthalocyanines [11] in terms of inter-planar (unit) interactions with parameters such as a distance, an orientation, and an inserting (metal) bridge. For the distance (d), $d = 3.5 \ \text{Å}$ was the measure of moderate inter-unit interactions [10,11]. Here we apply this method to the study of fullerene dimers, where a bond length of bridge is 1.575 Å in C_{120} [12], and examine whether the excitation is localized at one unit or delocalized over both units in the dimer. A mono-adduct of fullerene $C_{60}O$ was examined as reference of a localized model.

By means of several optical techniques, the electronic structure of C_{120} both in the excited S_1 [13] and T_1 [14] states was reported to be similar to the mono-adducts of C_{60} on the basis of the lifetime, transient absorption, quantum yield, and transition energy. A little different result was obtained for $C_{120}O$, indicating inter-sphere interactions [15]. In the di-anion $C_{120}O^{2-}$, although the spectrum showed triplet nature [16] and indicated significant interactions between the unpaired electrons, electron distribution has not been analyzed yet. Whether the properties of the dimers are similar to or different from the mono-adducts, it is very difficult to determine an extent of localization and/or delocalization of excitation by the optical methods.

2. Experimental

C_{120} was obtained by mechanochemical KCN catalyzed cycloaddition of C_{60} as described in the literature [12]. $C_{60}O$ was synthesized by ozonolysis of C_{60} in CS_2 solution [17]. $C_{120}O$ was prepared from heating the $C_{60}/C_{60}O$ mixture for 1 h at 200 °C in vacuo [17]. All the compounds were purified by the standard HPLC method. Toluene and α-chloro-naphthalene (CNP) were used as solvent in the EPR experiment. The solution of 0.4 mM C_{120} in CNP was diluted by a factor of 5 with toluene in order to make stable rigid glass solution of higher concentration. We have checked that the spectrum remains same in pure toluene. $C_{120}O$ and $C_{60}O$ were moderately soluble (0.2 mM) in toluene. TREPR spectra were observed at 5–170 K in solid. The experimental set-up for TREPR was already described in the literature [18].

3. Results and interpretation

Time-resolved EPR signals were observed for C_{120}, $C_{120}O$, and $C_{60}O$ in toluene at 6–180 K with respect to time and a magnetic field in a two-dimensional fashion. The spectrum had no change at all under laser irradiation for $C_{120}O$ and $C_{60}O$ but varied for C_{120} with prolonged irradiation as shown in Figs. 2a and b. An increased part in intensity is interpreted by generation of C_{60} based on its EPR spectrum (Figs. 2b and c). This fact is consistent with the reported photo-induced reaction of C_{120} [15], $C_{120}O$, and $C_{60}O$ [17]. All the observed spectra varied only slightly with temperature in solid (<175 K) as typically shown in Figs. 3 and 4. The spectra disappeared in solution (>180 K). The spectra remained also nearly the same with time as shown in Fig. 5. These results are very different from C_{60}, where electronic and molecular dynamics involve, providing remarkable spectral changes [6].

The typical EPR spectra in the T_1 state are shown at 30 K and 0.4 µs after the laser pulse in Fig. 2 together with that of C_{60}. It is easily found that the spectra are nearly the same for all these molecules including C_{60} both in polarization (absorption: Abs and emission: Emi of microwave at the low and high field sides, respectively) and spread (22.5–25 mT) of the spectrum. This result clearly indicates that the EPR parameters are nearly the same between the monomers and dimers. Simulations, calculated for random distribution of molecular orientations using the parameters summarized in Table 1, are shown in Fig. 2. Here the sign of D is assumed to be same with C_{60} ($D < 0$) [1] as already applied for the reported mono-adducts [4,5] based on similarity of the spectra. Here the T_z sublevel is populated least from S_1 both in the monomer and dimer. The EPR parameters obtained for $C_{60}O$ are similar to those reported previously [4].
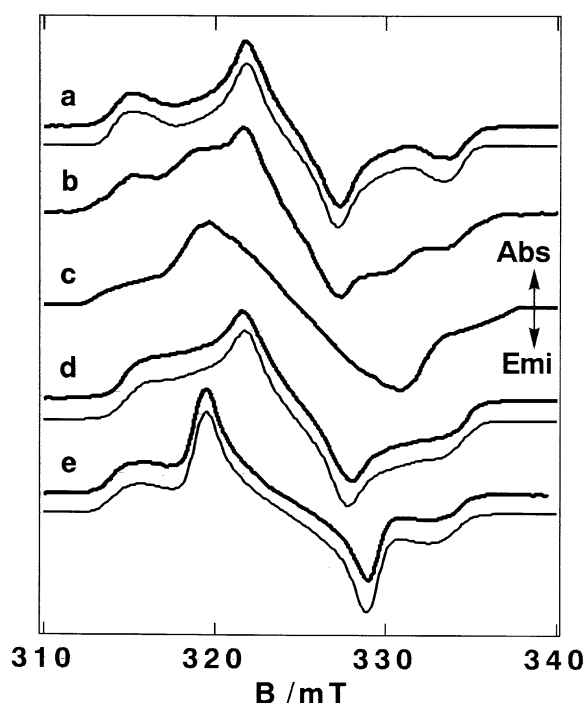

Fig. 2. Time-resolved EPR spectra in toluene for (a) fresh C_{120}, (b) irradiated C_{120}, (c) C_{60}, (d) $C_{120}O$, and (e) $C_{60}O$ observed at 30 K and 0.4 µs after the laser pulse.
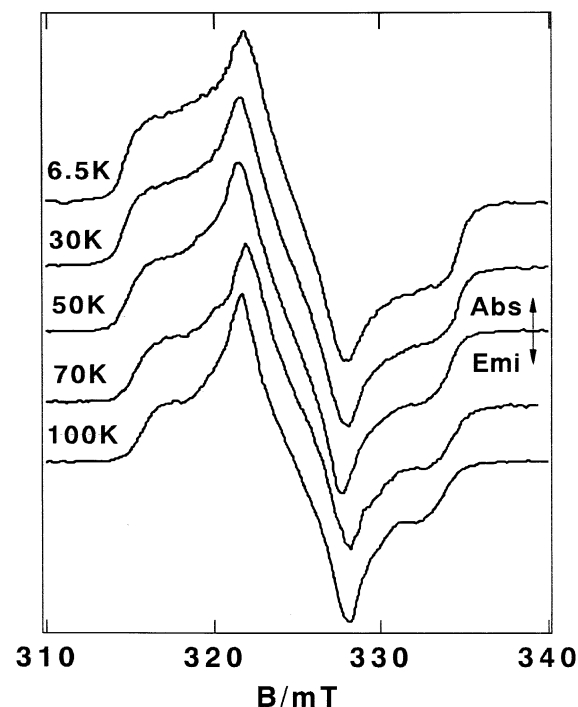

Fig. 3. Temperature dependence of the time-resolved EPR spectrum of $C_{120}O$ in toluene at 6.5–100 K and 0.4 µs after the laser pulse.
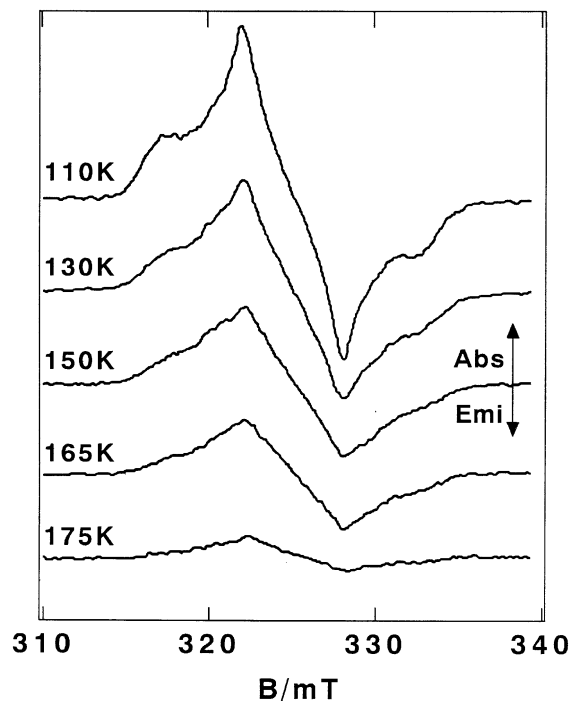
Fig. 4. Temperature dependence of the time-resolved EPR spectrum of $C_{120}O$ in toluene at 110–175 K and 0.4 μs after the laser pulse.

Fig. 5. Time profile of the EPR spectrum of C_{120} at (a) 1.3, (b) 1.9, and (c) 8.0 μs in toluene at 30 K.

4. Discussion

The results clearly indicate that the excitation mostly locates at one of the two fullerene units, namely in the EX state, for both the dimers. However, we calculate the zfs parameters of the CR state for C_{120} in order to support this conclusion quantitatively by evaluating the mixing coefficients of EX and CR states from Eq. (2). The point charge approximation [19] and spin density distribution of $\sin^2 \theta$ [20] in each unit are utilized for the C_{120} structure obtained from X-ray analysis [12]. Here θ denotes an angle between the principal z-axis of zfs for the mono-radical-adduct [21] and a radius vector of the particular C atom on the C_{120} surface. The calculated D and $|E|$ values are +0.12 and 0.028 GHz. The sign of D is different from those obtained from the experiment. Validity of this calculation was checked by comparing the calculated D value (-0.31 GHz) for T_1 of C_{60} with observed one (-0.34) [22].
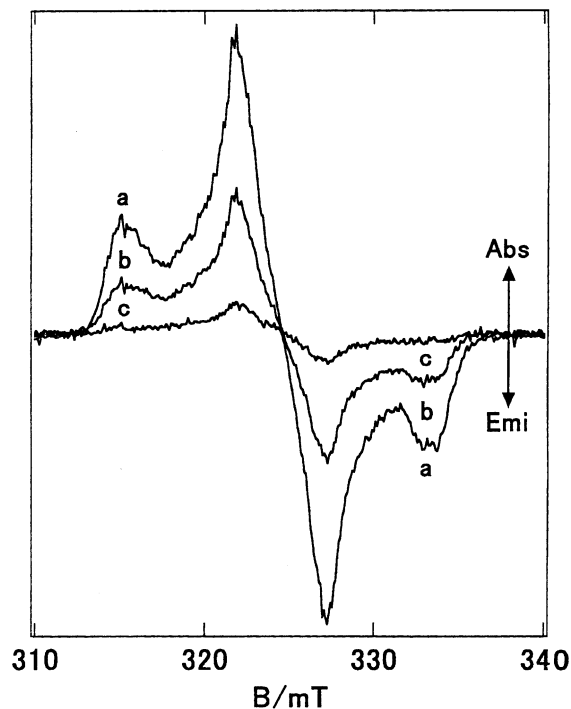
Table 1
Zero-field splitting parameters[a] and intersystem crossing ratio

	C_{120}	$C_{120}O$	$C_{60}O$
D (GHz)[b]	−0.287	−0.275	−0.281
$|E|$ (GHz)	0.047	0.037	0.002
P_x–P_z:P_y–P_z	0.74:0.26	0.62:0.38	0.85:0.15

[a] $g_{//}(B//z) = 2.001$ and $g_{\perp} = 2.000$.
[b] For the sign of D, see the text.

From the table and Eq. (2) with $D_{MM} = -0.281$ GHz (D of $C_{60}O$), the mixing coefficients of the EX and CR states are obtained as $a^2 = 1.02$ and $b^2 = -0.02$ for C_{120} and $a^2 = 0.98$ and $b^2 = 0.02$ for $C_{120}O$. The deviation from the values of $a^2 = 1$ and $b^2 = 0$ (a pure EX state) is within experimental errors (± 0.02) of the obtained D values. On the basis of these results it is concluded that the excitation is almost completely localized at one unit of the dimer. This conclusion remains the same even if the sign of D of the mono-adduct and dimer is different from C_{60} ($D < 0$). The excitation transfer

is slow as compared with the EPR time scale (ca. 100 ps). As the zfs principal axes of the two units are not parallel each other in the dimer [21], the fast transfer induces an average of D and fast spin relaxations, which is not a case.

Here we comment on the zfs parameters of the mono-adduct. From the reported data and ours, D and E seem to vary slightly depending on a size of an attached ring and a bridged atom (C, N or O) in the ring. The adducts of six- and three-membered >C-rings provide $D = -0.294$ [3] and -0.274 [5] GHZ, respectively. This seems to be consistent with expectation that the more stain in a ring induces the larger deviation from $D (= -0.344$ GHz) [22] of C_{60}. The hetero-atom also affects D such as $D = -0.281$ and -0.274 GHz for the three-membered >O and >C rings, respectively. Observed slight deviation from the monomer EX model might be due to size and hetero-atom dependence of the attached ring.

Acknowledgements

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