

II-I Molecular and Electronic Structures of Metallofullerenes

The continued interest in radical ions of fullerenes and metallofullerenes has resulted from the discovery of superconductivity in the CT complexes of alkali metals with fullerenes. Spectroscopic information concerning the electronic and spin states of the metallofullerenes has been obtained by ESR measurements.

II-I-1 Spin Dynamics of Lanthanum Metallofullerenes

OKUBO, Shingo; KATO, Tatsuhisa

Full separation of topological isomers of each La@C_n component ($n = 76$ to 90) was attempted by 2-stage HPLC separation with chlorobenzene eluent, and all species of La@C_n with even number n from 76 to 90 were detected. Their Electron Spin Resonance (ESR) spectra were recorded at various temperatures. The line width of the ESR spectrum in CS_2 solution was analyzed by the theory on the basis of hydrodynamics. Enormous variety of ESR spectra of La@C_n s was obtained in terms of g factor, hyperfine coupling constant, and line width. The feature of the temperature dependence of the line width was almost interpreted by the hydrodynamics, and the electronic structure of La@C_n was deduced from the ESR parameters. However in the cases of the isomer I of La@C_{80} and isomer II of La@C_{84} abnormally large line width was measured, as shown in Figure. The topological cage structure of La@C_{80} and La@C_{84} reflected on the specific spin dynamics.

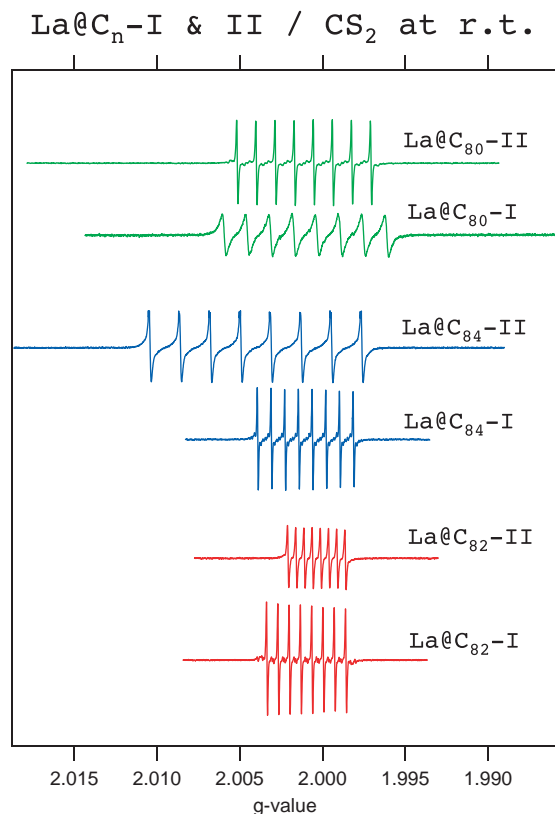


Figure 1. X-band ESR spectra of both isomers I and II of La@C_{80} , La@C_{82} , and La@C_{84} in CS_2 solution.

II-I-2 Electronic State of Scandium Trimer Encapsulated in C₈₂ Cage

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The ESR spectrum of $\text{Sc}_3\text{@C}_{82}$ in toluene and CS_2 solutions exhibits the symmetric hyperfine splitting of the 22 lines with a line width of 0.5 gauss at room temperature, which was consistent with the structure of $\text{Sc}_3\text{@C}_{82}$ having the C_{3v} symmetry. The line widths of the 22 lines were much broader than that for Sc@C_{82} . The broader line width of the scandium trimer in C_{82} could reflect the intra-molecular dynamics that averaged among three Sc metals' environments in the Jahn-Teller distorted structure of the whole molecule. The intra-molecular dynamics is the inherent nature of the Sc trimer encapsulated in the C_{82} cage with the symmetry of C_{3v} . The intra-molecular charge transfer from the central metal to the fullerene cage would give the stable electronic structure of an endo-metallofullerene. The X-ray diffraction study reported that there was no bonding electron between the cage and the trimer, and that the charge state of the Sc_3 was $3+$ leading to the electronic structure of $(\text{Sc}_3)^{3+}\text{@C}_{82}^{3-}$. Electron spin resonance (ESR) spectrum of the scandium trimer encapsulated in the C_{82} cage ($\text{Sc}_3\text{@C}_{82}$) was measured at the low temperature. The spectrum exhibited the specific pattern due to the strongly an-isotropic hyperfine tensor of the scandium trimer. The electronic state of the $\text{Sc}_3\text{@C}_{82}$ was given from the analysis of the hyperfine tensor, as shown in Figure 1.

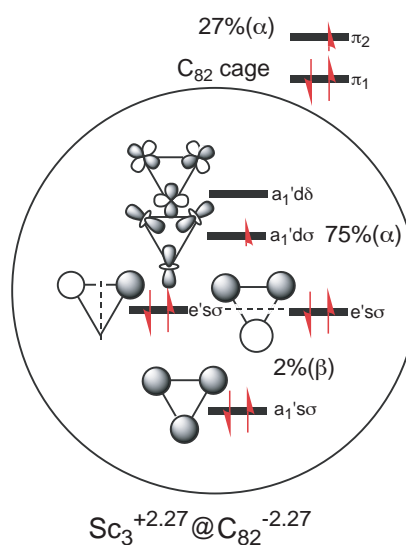


Figure 1. The Electronic structure of $\text{Sc}_3\text{@C}_{82}$ molecule deduced from the analysis of the hyperfine tensor of Sc metal.

II-I-3 Efficient Reduction of Metallofullerenes by Solvation of Pyridine and Dimethylformamide

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Various solvents have been used in the extraction of endohedral metallofullerenes from the raw soot produced by the arc-discharge method. Toluene, CS₂, and chlorinated benzenes have been used generally as solvent. On the other hand, pyridine and dimethylformamide (DMF) are known to give effective enrichment of metallofullerenes in the extraction, and aniline is especially effective for endohedral metallo-C₆₀. The specific affinity of these solvents with metallofullerenes would be attributed to the electronic interaction of the lone pair electron on nitrogen of the solvent with the π orbital of the metallofullerene's cage. However the exact nature of the interaction has not been clarified as yet. We recently presented the evidence that anions of La@C₈₂-I and Gd@C₈₂-I are easily produced with almost 100% yield by the solvation of pyridine and DMF. The formation of the La@C₈₂-I anion was confirmed by Vis-NIR and ¹³C-NMR measurements, which gave identical spectra with those of the La@C₈₂-I anion reported before. The ¹³⁹La-NMR and ¹³C-NMR spectra of La@C₈₂-I anion are respectively shown in Figure. The chemical shift of the ¹³⁹La-NMR line corresponded with that reported before. For assignment the anion generated in DMF, ¹³C-NMR spectrum was measured under same condition of electrochemically method in literature. After addition of electrolyte (TBAP) and removed DMF, the anion of La@C₈₂ generated in DMF

was dissolved in a mixture of CS₂ and acetone (1:1). The spectrum is in good agreement with that prepared by electrochemical method. The electron spin resonance (ESR) and Vis-NIR spectra of Gd@C₈₂-I dissolved in pyridine and DMF also give good agreements with those of the anion produced by electrochemical reduction. It could be generally concluded that the solvation of pyridine, and DMF, and aniline leads to the efficient reduction of endohedral metallofullerenes.

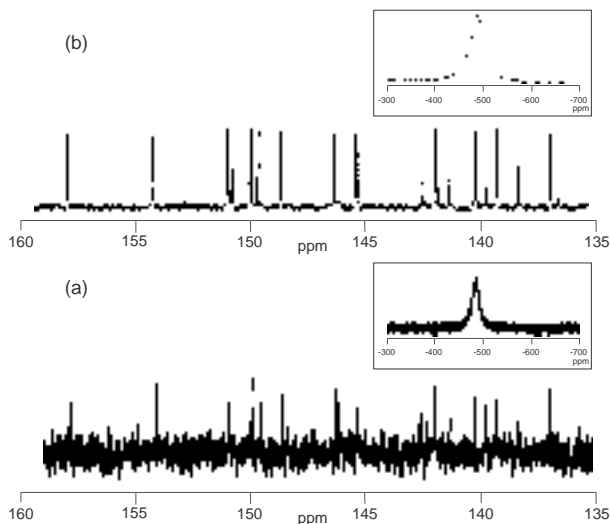


Figure 1. ¹³⁹La-NMR spectrum of La@C₈₂-I recorded in the DMF-d7 solution (a) and that of the La@C₈₂-I anion produced by electrochemistry (b), as shown in the inset of Figure. ¹³C-NMR spectrum of La@C₈₂-I in DMF (a) was measured under same condition of electrochemically method (b) in literature.

II-J High Field and Pulsed Electron Spin Resonance Spectroscopy

Electron spin resonance (ESR) spectroscopy has been a powerful technique for the characterization of radical species. The modern development of EPR spectroscopy enables us to investigate the heterogeneous and disordered system in detail. Especially the high frequency and pulsed EPR methods achieve the substantial resolution enhancement of spectrum. The advanced EPR spectroscopy is applied to study on the reaction mechanism in the heterogeneous system and the detection of the multi-cation species.

II-J-1 High-Field/High-Frequency ESR Study of Gadolinium Metallofullerenes

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A high-field/high-frequency ESR spectrometer is a powerful means to determine the complicated spin state of metallofullerenes. The analysis of the spin states of Gd@C₈₂-I and related species are reported here. The electronic structure of a gadolinium metallofullerene is stabilized by the intra-molecular charge transfer, and is described by the electronic configuration of Gd(4f⁷)-

@C₈₂(π^1), as shown in the Figure 1. The complicated electron spin state would be expected because of the combination of the octet spin site of gadolinium with the π spin of the fullerene cage. If the exchange interaction of J between the π spin and the octet spin is negative, these spins couple in anti-ferromagnetic manner and the resultant spin quantum number S will be 3. If the π spin on the cage is cancelled by adding an extra spin on the π orbital, S will be 7/2. This cancellation would be attained in the case of Gd@C₈₂ anion, or in the case of the dimerization of two Gd@C₈₂s. The π spin on the cage has the key function for the determination of the total spin state, and we confirmed the spin

state of $\text{Gd@C}_{82}\text{-I}$ in its monomer form, dimer form, and anion form by the high-field/high-frequency ESR measurement as shown in Figure 1.

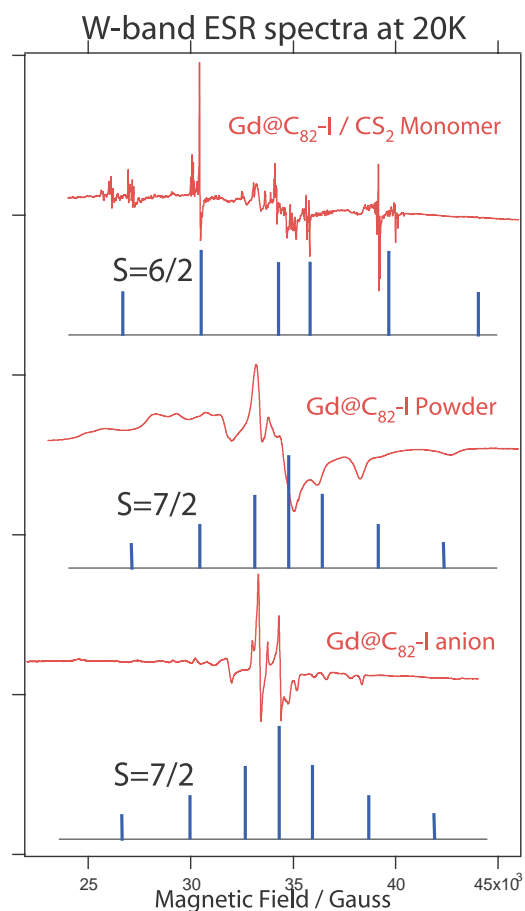


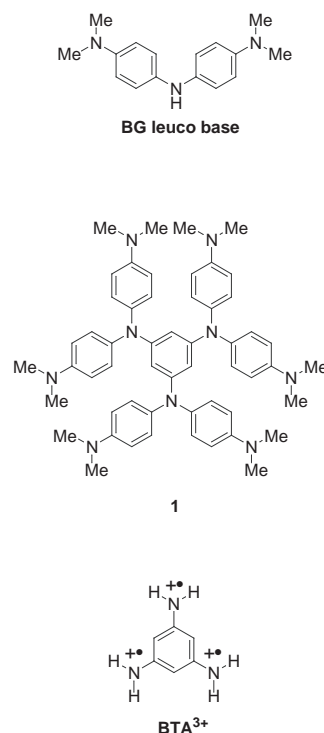
Figure 1. The high-field/high-frequency ESR (95 GHz) spectra of $\text{Gd@C}_{82}\text{-I}$ in its monomer form, dimer form, and anion form produced by the electrochemical method.

II-J-2 A Bindschedler's Green-Based Arylamine: Its Polycations with High-Spin Multiplicity

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Intramolecular high-spin correlation in a series of the successively generated polycationic species of Bindschedler's green-based arylamine, N,N,N',N',N'',N'' -hexakis[4-(dimethylamino)phenyl]-1,3,5-benzenetriamine (**1**) have been investigated by continuous and pulsed EPR spectroscopy. Cyclic voltammetry shows multi-redox behavior of **1** that can be reversibly oxidized from monocation to hexacation. Depending on quantity of the added oxidant, the characteristic EPR spectra are observed for polycations of **1** in frozen solution. Unequivocal determination of the spin state at each oxidation stage of **1** is given by a pulse EPR technique, that is, electron spin transient nutation spectroscopy as shown in Figure 1. Observation of the unusual spin state after annealing of the highly charged poly-

cations of **1** is also reported.



Scheme 1. (1): Molecular structures of N,N,N',N',N'',N'' -hexakis[4-(dimethylamino)phenyl]-1,3,5-benzenetriamine.

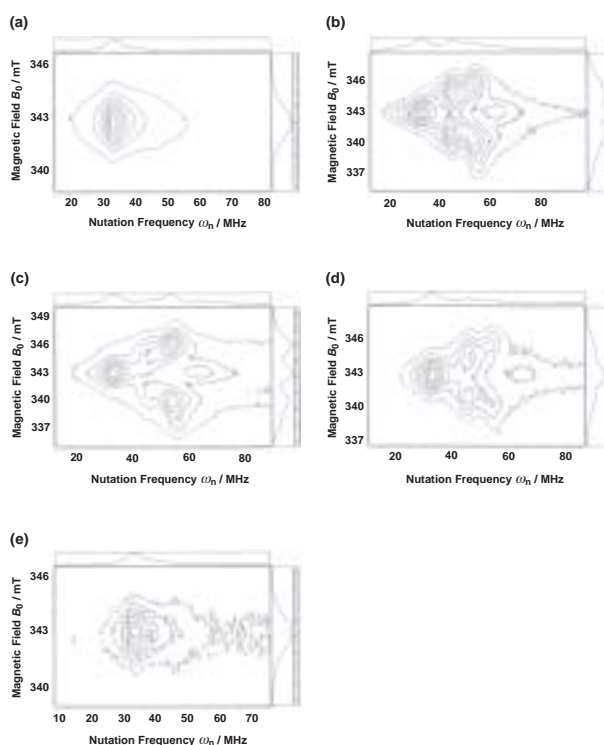


Figure 1. Field-swept electron spin transient nutation spectra of **1** oxidized by (a) 1 molar equiv, (b) 2 molar equiv, (c) 3 molar equiv, (d) 4 molar equiv, and (e) 5 molar equiv of $\text{TBA}\cdot\text{SbCl}_6$ in *n*butyronitrile at 5 K. ω_1 corresponds to about 30 MHz.

II-K State Correlated Raman Spectroscopy

The vibrational Raman polarizability tensor responds to molecular reorientational relaxation process, and the structural environment in condensed media. The measurement of Raman scattering is a powerful technique for the study of molecular motion and of the mechanism of phase transition. We've built up the system of multichannel type detection of Raman scattering combined with the temperature controlled cell.

II-K-1 Molecular Ordering Deformation Induced by Externally Applied Electric Field in an Antiferroelectric Liquid Crystal

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[*Jpn. J. Appl. Phys.* **41**, 5292 (2002)]

Molecular orientational ordering in an antiferroelectric liquid crystal was studied by observing polarized Raman scattering in a homogeneously aligned thin sample exposed to static electric field. The apparent orientational order parameters gradually increased with the applied electric field strength even in the pretransitional regime from antiferro- to ferroelectric phase although the averaged molecular orientation was hardly changed. (See Figure 1) This change in the order parameters indicates the deformation of the *c*-director and is represented by the similar equation describing the nematic director deformation induced by an external electric field, in which the electric coherence length was inversely proportional to the applied electric field strength.

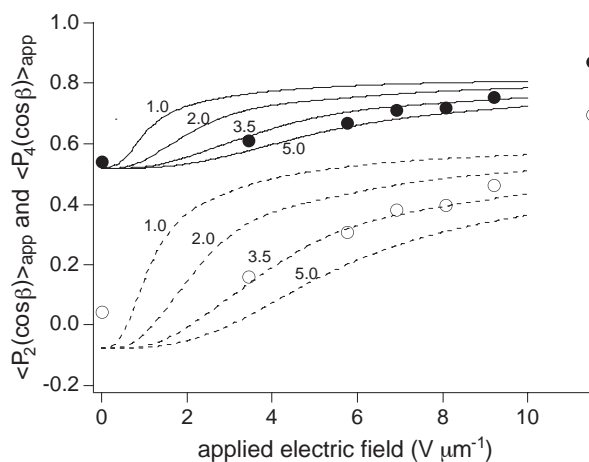


Figure 1. Apparent orientational order parameters under static electric field, solid circle: $\langle P_2(\cos\beta) \rangle_{\text{app}}$; open circle: $\langle P_4(\cos\beta) \rangle_{\text{app}}$. The solid and dotted lines are $\langle P_2(\cos\beta) \rangle_{\text{app}}$ and $\langle P_4(\cos\beta) \rangle_{\text{app}}$ given by the model calculation. The numbers beside the lines show the values of $\xi_b E$; 1.0, 2.0, 3.5 and 5.0 V. Here, ξ_b is the electric coherence length and E is the applied electric field strength.