

II-I Molecular and Electronic Structures of Metallofullerenes and the Fullerene Radical Anions

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 cw- and pulsed-EPR measurements.

II-I-1 2D-HYSCORE Measurements of ^{13}C -La@C₈₂

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ESEEM (electron spin echo envelope modulation) was detected in the pulsed ESR (Electron Spin Resonance) measurements for two isomers of La@C₈₂. Especially the isomer I of La@C₈₂ showed the prominent modulation with the frequency of 3 MHz, which was originated from ^{139}La nuclear quadrupole coupling. The origine of the 3 MHz modulation was confirmed by HYSCORE (Hyperfine Sublevel Correlation Spectroscopy) 2D measurements. ^{139}La quadrupole coupling constant of La@C₈₂-I was directly determined.

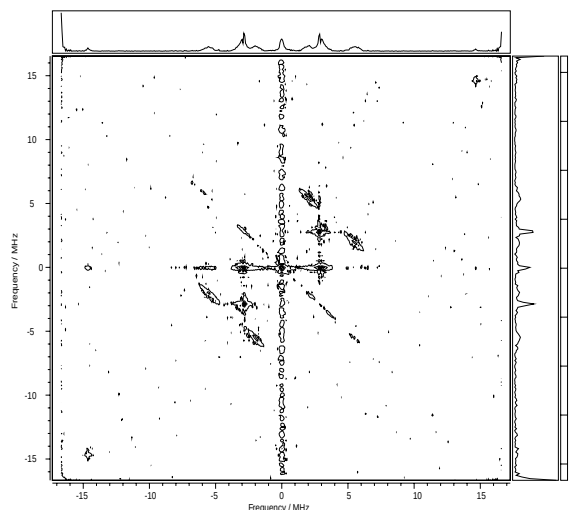


Figure 1. 2D-HYSCORE spectrum of the major isomer of ^{13}C -La@C₈₂ obtained at 80 K.

II-I-2 ESR Measurements of La@C_n

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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. Among them La@C₇₆, La@C₈₀-I, II, La@C₈₄-I, and II were newly purified, La@C₇₈, La@C₈₆, and La@C₈₈ were partially purified. Their ESR spectra were obtained, as shown in figure, and ESR parameters were determined. Enormous variety of ESR spectra of La@C_ns was obtained in terms of g factor, hyperfine coupling constant, and line width. The topological cage structure of La@C_n reflected on the specific values of the ESR parameter. The anisotropic components of g factor, hyperfine coupling constant, and quadrupole coupling constant were estimated from the temperature dependence of the line width of each La@C_n.

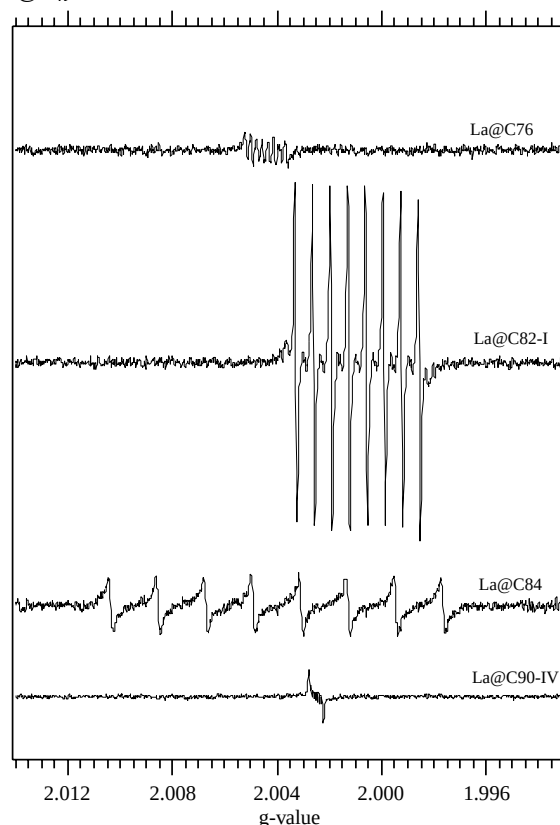


Figure 1. ESR spectra of La@C₇₆, La@C₈₂-I, La@C₈₄, and La@C₉₀-IV measured at room temperature in CS₂ solution.

II-J 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-J-1 Investigations of Orientational Order for an Antiferroelectric Liquid Crystal by Polarized Raman Scattering Measurements

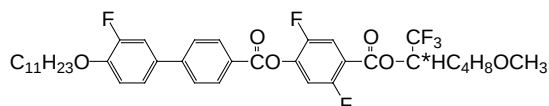
HAYASHI, Naoki; KATO, Tatsuhisa

The orientational ordering of the antiferroelectric liquid crystal molecules, MHPOBC was investigated in the series of the successive smectic phases by means of polarized Raman scattering measurement without any external field. An improved equation for the analysis of the polarized Raman intensity was derived as a function of an incident laser polarization and the orientational order parameters. Even in the chiral smectic phases, some apparent orientational order parameters could be defined by the proper corrections for the smectic layer structure and an optical disturbance. An unusual change of the orientational order parameters was observed with decrease in temperature. It was concluded that the irregular variation of the order parameter stemmed from the biaxiality of the molecular orientational distribution, which was attributed to the hindrance of molecular rotation around its long axis.

II-J-2 Polarized Raman Scattering Study for Frustoelectric Liquid Crystals

HAYASHI, Naoki; KATO, Tatsuhisa

Orientational ordering for two types of “V-shaped” switching liquid crystals was investigated by polarized Raman scattering measurements. One liquid crystal is based on the ferroelectric phase and the other on the antiferroelectric phase. The apparent orientational order parameters $\langle P_2(\cos\theta) \rangle_{app}$ and $\langle P_4(\cos\theta) \rangle_{app}$ obtained for the ferroelectric based liquid crystal,



are shown in Figure 1. Square marks show the order parameters obtained with the static electric field of 7 V/μm, circle marks show those without static electric field, and triangle marks show those at the tip of the V-shaped switching. The electric field at the tip of the V-shaped switching is effectively zero, however, the observed order parameters exhibit the similar values of those obtained with the static electric field of 7 V/μm, which are much larger than without static electric field. On the other hand, smaller order parameters were preliminarily obtained at the tip of the V-shaped switching for the other type of antiferroelectric based liquid crystals. The careful comparison of the apparent order parameters for two types of liquid crystal should be necessary for the realistic interpretation of the “V-shaped” switching mechanism.

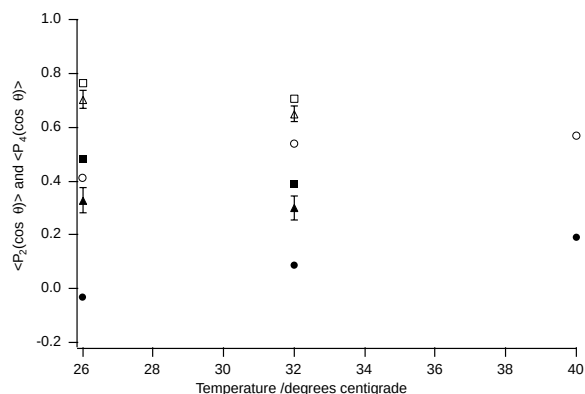


Figure 1. Temperature dependence of apparent orientational order parameters. Open marks show $\langle P_2(\cos\theta) \rangle$ and closed marks show $\langle P_4(\cos\theta) \rangle_{app}$. Square; with the static electric field of 7 V/μm, circle; without static electric field, triangle; at the tip of the V-shaped switching.