

High-Field/High-Frequency ESR Study of Metallofullerenes

Tatsuhisa Kato^{1,2}, Ko Furukawa¹, Namiki Toyama¹, Singo Okubo², Haruhito Kato³, and Hisanori Sinohara³

¹Institute for Molecular Science, Myodaiji, Okazaki 444-8585, JAPAN

²The Graduate University for Advanced Studies, Myodaiji, Okazaki 444-8585, JAPAN

³Department of Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, JAPAN

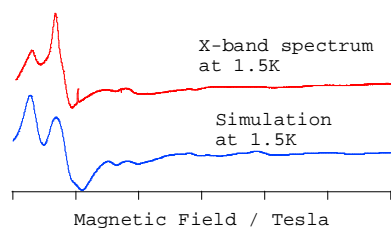
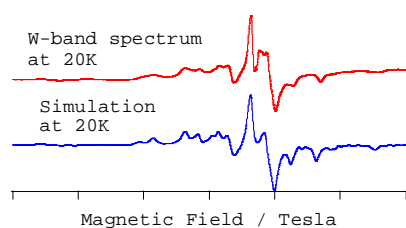
ABSTRACT

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@C_{82} , $\text{Gd@C}_{82}(\text{OH})_n$, and other metallofullerenes are reported here as examples.

A Gd metallofullerene has the electronic structure which is described by the electronic configuration of $\text{Gd}(4f^7)@C_n(\pi^1)$. The complicated electron spin state would be expected because of eight radical electrons. A Gd metallofullerenol $\text{Gd@C}_{82}(\text{OH})_n$ has been synthesized by the Nagoya group of authors. The effect of the addition of OH on the spin state can be deduced by the ESR analysis of the Gd metallofullerenol.

The measurements by X- and W-band ESR spectrometers were performed for Gd@C_{82} powder at low temperature, see Figure. The spectrum by the X-band ESR spectrometer exhibited the specific pattern for the high spin system with large fine structure. The unsymmetrical spectral feature was given because of the large zero-field splitting parameter D and E. The high-field measurement by the W-band ESR spectrometer made the spectrum simplified. The combination of the $S=1/2$ spin state on the fullerene cage with the $S=7/2$ high spin state on Gd ion was determined by the parallel simulation of spectra obtained by X- and W-band ESR spectrometers.

The spectra of $\text{Gd@C}_{82}(\text{OH})_n$ in water solution were also analyzed by the parallel simulation. The 0.06cm^{-1} of D and 0.02cm^{-1} of E were determined. The addition of OH results in the smaller zero-field splitting parameter.



Simulation Parameters
S = 7/2
g = (1.99, 1.99, 2.00)
D = 0.210 cm⁻¹
E = 0.018 cm⁻¹

Figure. X- and W-band ESR spectra of Gd@C_{82} powder.