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Electronic state of scandium trimer encapsulated in C_{82} cage

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Electron spin resonance spectrum of the scandium trimer encapsulated in the C_{82} cage ($Sc_3@C_{82}$) was measured at low temperature. The spectrum exhibited the specific pattern due to the strongly anisotropic hyperfine tensor of the scandium trimer. The electronic state of the $Sc_3@C_{82}$ was taken from the analysis of the hyperfine tensor.

Since the success of laboratory synthesis of C_{60} and other fullerenes [1], a lot of papers on fullerenes and their chemical derivatives [2] have been reported within a decade. Especially metallofullerenes (fullerenes with metal(s) inside the hollow spherical carbon cage) have interested people because of their possibilities of the free tune of "outside chemistry", and have been prepared and characterized. In the beginning stage of the study, the trace amount of metallofullerenes has been detected by an electron spin resonance (ESR) spectrometer. The recent progress of the isolation and the purification of endohedral metallofullerenes [3–5] expanded the investigation of the characterization of the physical properties [6–9] and the chemical properties [10,11].

The scandium trimer encapsulated in the C_{82} cage ($Sc_3@C_{82}$) has been produced by Nagoya group [3, (a)], and also by IBM group [3, (c)]. Nagoya group succeeded in further separation and purification of $Sc_3@C_{82}$ from other metallofullerenes and empty fullerenes by the so-called two stages high performance liquid chromatography method. The ESR spectrum of $Sc_3@C_{82}$ in toluene and CS_2 solutions exhibits the symmetric hyperfine splitting of the 22 lines with a line width of 0.5 G at room temperature, which was consistent with the structure of $Sc_3@C_{82}$ 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 [3, (d)]. The intra-molecular dynamics is the inherent nature of the Sc trimer encapsulated in the C_{82} cage with the symmetry of C_{3v}.

Knight et al. [12] have obtained the scandium trimer matrix-isolated in solid neon, and reported the ESR spectrum of Sc_3. The electronic state of $^2A_1'$ and the molecular structure of D_{3h} for the Sc_3 were drawn from the analysis of the ESR spectrum. The scandium trimer isolated in solid neon matrix was a neutral radical, however, the scandium trimer encapsulated in C_{82} would be a cation radical. The intra-molecular charge transfer from the central metal to the fullerene cage would give the stable electronic structure of an endo-metallofullerene. Prof. Takata reported [13] 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 $(Sc_3)^{3+}@C_{82}^{3-}$.

1. Experimentals

The scandium-containing fullerenes was produced by are burning of a composite rod of graphite and Sc_2O_3 under $50-100$ Torr He pressure. The soot was extracted by carbon disulfide (CS_2) for 12 hours. The $Sc_3@C_{82}$ fullerene was separated and isolated from various empty and other types of scandium fullerenes (such as $Sc@C_{82}$ and $Sc_2@C_{84}$) by the two-stage High Performance Liquid Chromatography (HPLC) method. The two-stage HPLC method have been described in detail elsewhere [14]. The $Sc_3@C_{82}$ in CS_2, toluene, and liquid paraffin solutions were degassed using a freeze-pump-thaw cycle and sealed in quartz tubes. The ESR spectra were obtained with Bruker ESR 300E and E500 spectrometers in combination with a temperature control unit set for temperature between 290 and 80 K.

2. Results and discussions

The large temperature dependence of the ESR spectra of $Sc_3@C_{82}$ was obtained at the temperature range below 200 K in liquid paraffin solution [3, (d)], as shown in Fig. 1. The line width at the both wing of the hyperfine components of the spectrum became broader and this broadening effect was intensified at the lower temperature. And the spectrum exhibited the single line with the very broad wings at the temperature below freezing point of the solvent. One of the origins of the line width of ESR spectra in solution is an insufficient averaging of anisotropy of hyperfine and g tensors by a hydrodynamic rotation in solution. This type of the line width is proportional to the viscosity of solvent and to the reciprocal of temperature. We have reported that the ESR spectrum of $Sc@C_{82}$ in toluene and CS_2 solutions and showed the large temperature dependence of the line width [15]. In the case of $Sc_3@C_{82}$, the large temperature dependence of the line width was observed in the more viscous solvent of liquid paraffin. This type of line broadening is much enhanced in solvents with large viscosities such as liquid paraffin. Once the solution was frozen, the ESR spectrum exhibited a so-called powder pattern, which was totally broaden and an-isotropic. The line broadening at the both wing of the hyperfine components of the spectrum preceded that at the central part, and

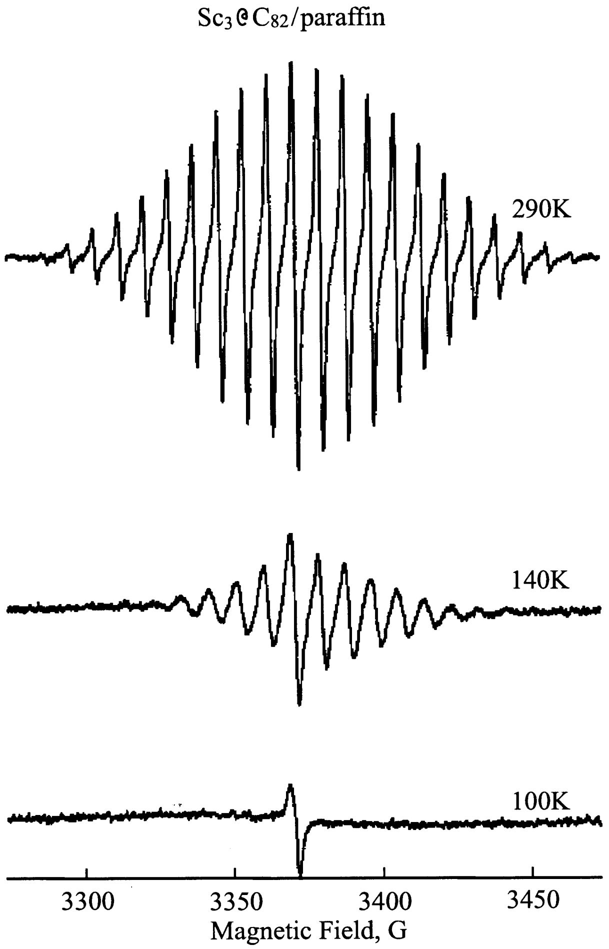

Figure 1. The ESR spectra of $Sc_3@C_{82}$ obtained at the temperature of 290, 140, and 100 K in liquid paraffin solution.

the central line remained at 100 K. The features of the temperature dependence and the spectrum at 100 K were due to the large an-isotropy of the hyperfine tensor of a scanium trimer, especially the central single line observed at 100 K was originated from the zero-valued perpendicular component of the an-isotropic hyperfine tensor. The ESR spectrum of $Sc_3@C_{82}$ in toluene solution observed at 80 K with a better signal to noise ratio is shown in the Fig. 2. There were two prominent features in the spectrum of the frozen solution of $Sc_3@C_{82}$. One was the central line with the broad spectra at the both wings. The other was the phase relationship in which the high-field spectra were of opposite phase to those at low field. The phase relationship in the broad spectra at the both wings suggested that the observed spectra were due to parallel components of the hyperfine structure of an axial molecule with $A_{\mathrm{perpendicular}} \ll A_{\mathrm{parallel}}$. The central line corresponded to the perpendicular component $A_{\mathrm{perpendicular}}$. Considering that the central line remained strong at the temperature below freezing point of the solvent, $A_{\mathrm{perpendicular}}$ would be nearly evaluated as zero. In addition an isotropic g value of 1.999 and an isotropic Sc hyperfine coupling constant of 6.25 G were obtained from the analysis of the solution spectrum at ambient temperature. Consequently $A_{\mathrm{iso}}(^{45}\mathrm{Sc}) = 6.25\,\mathrm{G}$, $A_{\mathrm{parallel}}(^{45}\mathrm{Sc}) = 18.8\,\mathrm{G}$, and $A_{\mathrm{perpendicular}}(^{45}\mathrm{Sc}) = 0\,\mathrm{G}$ were obtained. The isotropic hyperfine constant ($A_{\mathrm{iso}}(^{45}\mathrm{Sc}) = 6.25\,\mathrm{G}$) indicated that only 0.6% (totally about 2% for three Sc atoms) of the total unpaired spin density was due to 4*s* electron character. The magnetic dipole component A_{dip} of 6.25 G was given by the an-isotropic hyperfine components, and 25% (totally 75% for three Sc atom) of the total unpaired spin density sit on the 3*d* orbital of Sc.

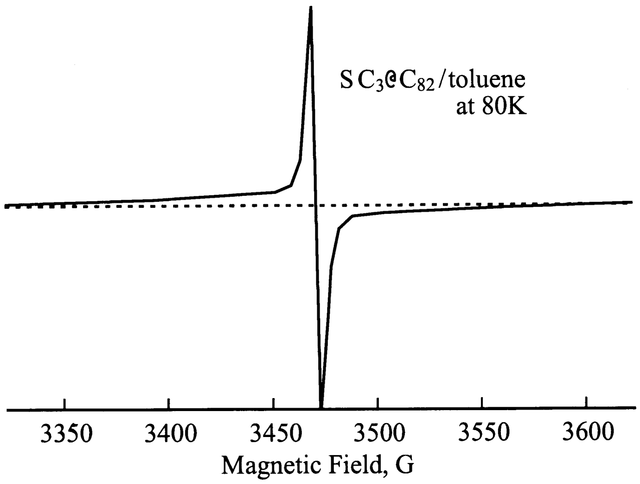

Figure 2. The ESR spectrum of $Sc_3@C_{82}$ in toluene solution observed at 80 K.

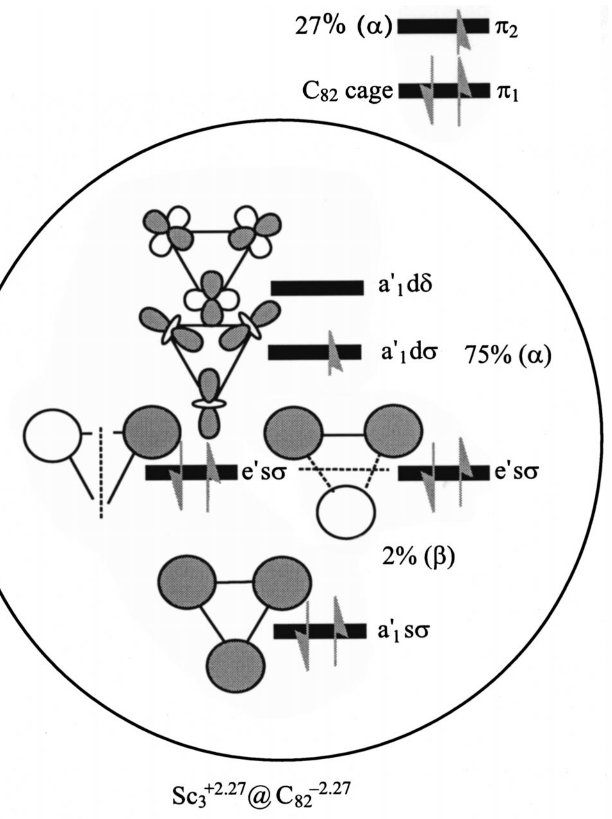

Figure 3. The distribution of the spin density on $Sc_3@C_{82}$ molecule.

For the electronic structure of the Sc trimer there were 18 ($4s$ and $3p$) molecular orbitals in which the nine valence electron could be placed. Assuming that the Sc trimer has D_{3h} symmetry with a theehold axis of symmetry perpendicular to the molecular plane, 5 orbitals out of 18 shown in Fig. 3 could be assigned as 5 lowest lying orbitals. From the analysis of the Sc hyperfine coupling constant mentioned above, the distribution of the spin density on $Sc_3@C_{82}$ molecule could be figured as in Fig. 3. The total spin density on the $Sc_3@C_{82}$ molecule was unit because of the spin state of $S = 1/2$ (the spin doublet state), so the density of an α spin and of a β spin was balanced to give the unit spin density. 75% density of an α-spin was on the $a'_1 d\sigma$ orbital of the Sc trimer, 2% density of a β spin was on the $e' s\sigma$ orbital of the Sc trimer, and 27% density of an α spin was on the π_2 orbital of the fullerene cage. As a result the charge state of Sc_3 was $+2.27$ describing the electronic state of $Sc_3^{+2.27}@C_{82}^{-2.27}$.

The ESR spectrum of $Sc_3@C_{82}$ solution observed at the low temperature exhibited the specific pattern given by the strongly an-isotropic hyperfine tensor of the scandium trimer. The electronic state of $Sc_3@C_{82}$ was deduced from the analysis of the hyperfine tensor. From the analysis, the distribution of the spin density on $Sc_3@C_{82}$ molecule was estimated, and the electronic state would be described as $Sc_3^{+2.27}@C_{82}^{-2.27}$.

References

[1] W. Kractschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman. Nature **347**, 354 (1990); W. Kractschmer, K. Fostiropoulos, D.R. Huffman. Chem. Phys. Lett. **170**, 167 (1990).

[2] J.M. Hawkins, T.A. Lewis, S.D. Loren, A. Meyer, J.R. Heath, Y. Shibata, R.J. Sakally. J. Org. Chem. **55**, 6250 (1990).

[3] (a) H. Shinohara, H. Sato, M. Ohchochi, Y. Ando, T. Kodama, T. Shida, T. Kato, Y. Saito. Nature **357**, 52 (1992); (b) H. Shinohara, H. Yamaguchi, N. Hayashi, H. Sato, M. Inagaki, Y. Saito, S. Bandow, H. Kitagawa, T. Mitani, H. Inokuchi. Mater. Sci. Eng. **B19**, 25 (1993); (c) C.S. Yannoni, M. Hoinkis, M.S. de Vries, D.S. Bethune, J.R. Salem, M.S. Crowder, R.D. Johnson. Science **256**, 1191 (1992); (d) T. Kato, S. Bandou, M. Inakuma, H. Shinohara. J. Phys. Chem. **99**, 856 (1995).

[4] J.H. Weaver, Y. Chai, G.H. Kroll, C. Jin, T.R. Ohno, R.E. Haufler, T. Guo, J.M. Alford, J. Conceicao, L.P.F. Chibante, A. Jain, G. Palmer, R.E. Smalley. Chem. Phys. Lett. **190**, 460 (1992); H. Shinohara, H. Sato, Y. Saito, M. Ohkohchi, Y. Ando. J. Phys. Chem. **96**, 3571 (1992).

[5] Y. Chai, T. Guo, C. Jin, R.E. Haufler, L.P.F. Chibante, J. Fure, L. Wang, J.M. Alford, R.E. Smalley. J. Phys. Chem. **95**, 7564 (1991); M.M. Alvarez, E.G. Gillan, K. Holczer, R.B. Kaner, K.S. Min, R.L. Whetten. J. Phys. Chem. **95**, 10 561 (1991); R.D. Johnson, M.S. de Vries, J. Salem, D.S. Bethune, C.S. Yannoni. Nature **355**, 239 (1992); K. Kikuchi, S. Suzuki, Y. Nakao, N. Nakahara, T. Wakabayashi, H. Shiromaru, I. Saito, I. Ikemoto, Y. Achiba. Chem. Phys. Lett. **216**, 67 (1993).

[6] T. Kato, S. Suzuki, K. Kikuchi, Y. Achiba. J. Phys. Chem. **97**, 13 425 (1993).

[7] E. Yamamoto, M. Tansho, T. Tomiyama, H. Shinohara, Y. Kobayashi. J. Am. Chem. Soc. **118**, 2293 (1996).

[8] T. Akasaka, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, H. Funasaka, M. Kako, T. Hoshino, T. Erata. Angew. Chem. Int. Ed. Engl. **36**, 1643 (1997).

[9] M. Takata, E. Nishibori, B. Umeda, M. Sakata, E. Yamamoto, H. Shinohara. Phys. Rev. Lett. **78**, 3330 (1997).

[10] T. Akasaka, T. Kato, K. Kobayashi, S. Nagase, K. Yamamoto, H. Funasaka, T. Takahashi. Nature **374**, 600 (1995).

[11] T. Akasaka, S. Nagase, K. Kobayashi, T. Suzuki, T. Kato, K. Yamamoto, H. Funasaka, T. Takahashi. J. Chem. Soc. Chem. Commun. 1343 (1995); T. Akasaka, T. Kato, S. Nagase, K. Kobayashi, K. Yamamoto, H. Funasaka, T. Takahashi. Tetrahedron **52**, 5015 (1996).

[12] L.B. Knight, Jr., R.W. Woodward, R.J. VanZee, W. Weltner, Jr. J. Chem. Phys. **79**, 5820 (1983).

[13] M. Takata, E. Nishibori, M. Sakata, M. Inakuma, E. Yamamoto, H. Shinohara. Phys. Rev. Lett. **83**, 2214 (1999).

[14] H. Shinohara, M. Inakuma, N. Hayashi, H. Sato, Y. Saito, T. Kato, S. Bandow. J. Phys. Chem. **98**, 8597 (1994).

[15] T. Kato, S. Suzuki, K. Kikuchi, Y. Achiba. J. Phys. Chem. **97**, 13 425 (1993).