

## 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 EPR and ENDOR measurements.

### II-I-1 Spin Chemistry of Metallofullerenes

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The consideration of crystal field effect due to the fullerene cage with the low symmetry was indispensable

for the analysis of the electronic and spin states for the metal ion encapsulated inside the fullerene cage. The ESR spectrum of Gd@C<sub>82</sub> could not be reproduced by the simulation without the assumption of the crystal field splitting of the ground electronic state. The ESR spectrum of Pr@C<sub>82</sub> exhibited no resolved band, this result could be also explained by the crystal field splitting.

## II-J Site Selective Spectroscopy in Solid Crystals

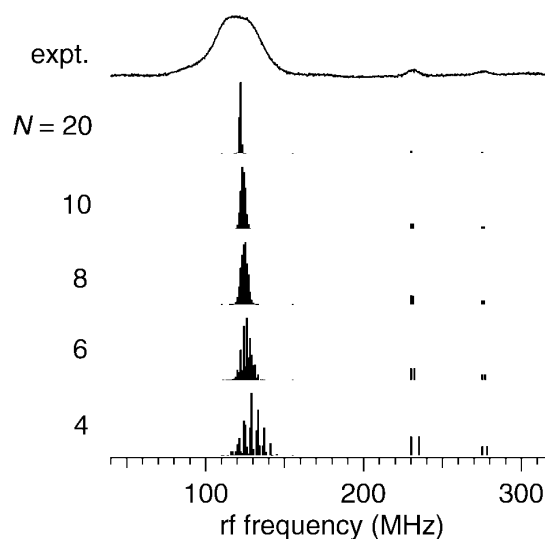
The line broadening due to the variation of the environment over the some sites in the crystal structure prevents from determining small energy splitting between pair of closely spaced levels with high accuracy. However the broadening effects give a nice prove to investigate the intermolecular interaction in the crystal structure. On the other hand some techniques of the site selective spectroscopy to eliminate the disturbance were proposed. We are applying the technique of the heterodyne detection of optical magnetic double-resonance to some systems of crystal.

### II-J-1 NQR by Coherent Raman Scattering of a Triplet Exciton in a Molecular Crystal

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Nuclear quadrupole resonance (NQR) of a linear triplet exciton in 1,4-dibromonaphthalene crystals has been observed as coherent Raman scattering. The Br NQR scattering originates from the hyperfine interaction between the electron spin and the Br spins. Since delocalization of the electron spin decreases the interaction, the intensity of the NQR scattering reflects the chain length of the exciton. The exciton is found to be delocalized over about 10 molecules, indicating the coherence length of the exciton is limited by scattering due to <sup>13</sup>C isomers.



**Figure 1.** Coherent Raman spectrum calculated for the exciton in 1,4-DBN delocalized over  $N$  molecules. The result is shown as histograms of the width of 1 MHz. The observation is shown on the top for the sake of comparison.

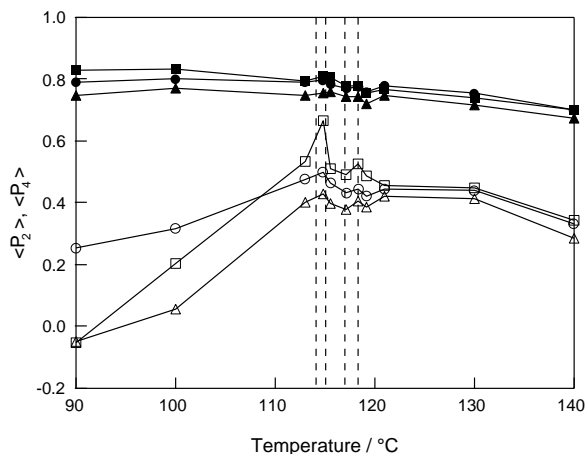
## II-K State Correlated Raman Spectroscopy

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 An Analysis of Polarized Raman Scattering Measurements for the Orientational Ordering of Ferro- and Antiferroelectric Liquid Crystal

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The orientational ordering of the ferro- and antiferroelectric liquid crystal molecule, MHPOBC was investigated in the series of the successive smectic phases by means of the polarized Raman scattering measurement. The improved equation of the polarized Raman intensity was derived as a function of the orientational order parameter and the incident laser polarization. According to the equation the second and the fourth orientational order parameters,  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$ , could be evaluated even in the chiral smectic phases. An unusual change of the orientational order parameter was observed with decreasing of temperature as shown in Figure 1. It was concluded that the irregular variation of the order parameter stemmed from the biaxiality of the molecular orientational distribution. It could be attributed to the difference of the angle between the optical axis and the center axis of the molecular orientational distribution as the increasing of biaxiality.



**Figure 1.** Temperature dependence of the orientational order parameter,  $\langle P_2 \rangle$  (solid circle: phenyl, solid square: chiral C=O, solid triangle: core C=O) and  $\langle P_4 \rangle$  (open circle: phenyl, open square: chiral C=O, open triangle: core C=O). The broken lines show the phase transition points. The phase sequence is as SmA-SmC $_{\alpha}^*$ -SmC $^*$ -SmC $_{\gamma}^*$ -SmC $_A^*$ .