

Analysis of I-I Coupling Fine Structures in Nuclear Magnetic Resonance Spectra of Simple Organic Molecules I

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Analysis of I-I Coupling Fine Structures in Nuclear Magnetic Resonance Spectra of Simple Organic Molecules I

By

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1. Introduction

It has been well known that the interaction between i -th and j -th nuclear spin of the form $J_{ij}\mathbf{I}_i \cdot \mathbf{I}_j$ is responsible for the fine structures observed in the high resolution nuclear magnetic resonance spectra of liquids. And it was reported^{[1]–[4]} that the interaction is the second order effect of hyperfine interactions of the nuclear spins $\mathbf{I}_i$ and $\mathbf{I}_j$ with the bond electrons in molecules.

As increase the numbers of magnetic nuclei in molecules, the fine structures become to be more complicated, but under certain conditions those were able to interpret^[2] easily and lately some works which make an attempt to develop them to the complicated case are appeared.^{[5]–[9]}

We will take up the method for assignment of I-I coupling fine structures of simple organic compounds in papers of this series and will develop it to some complicated case.

In the present paper, spin groups expressed as the formula, A_2B_2C , are principally attacked, where A, B, and C are the nuclear spins of which spins are $\frac{1}{2}$ and the gyromagnetic ratios, γ 's, different, and the suffix indicates the spin numbers belonging to the same group.

The compounds included in this formula are $H_2^{13}C=CF_2$, $H_2C=^{13}CF_2$, and $^{13}CH_2F_2$, etc. The study of the nuclear magnetic resonance spectra of these ^{13}C compounds will be appeared elsewhere.

2. Simple Multiplet Fine Structures

The features of the high resolution nuclear magnetic resonance spectra of liquids are based on the spin Hamiltonian described as follows^{[3],[4]}:

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} \quad (1)$$

$$\mathcal{H}^{(0)} = \hbar H \sum_i \gamma_i I_{zi} \quad (2)$$

$$\mathcal{H}^{(1)} = \sum_{i < j} J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j, \quad (3)$$

in which H is the magnetic field externally applied along z direction and γ_i the

effective gyromagnetic ratio including the shielding effect of the electron for i -th nucleus. Classifying the magnetic nuclei to the groups of nuclei having the same γ_i or the chemical equivalent groups A, B, ..., Eqs. (2) and (3) are written

$$\mathcal{H}^{(0)} = \mathcal{H}_A^{(0)} + \mathcal{H}_B^{(0)} + \dots \quad (2a)$$

$$\mathcal{H}_A^{(0)} = \hbar H \gamma_A F_{zA} \quad (2b)$$

.....

$$\begin{aligned} \mathcal{H}^{(1)} = \mathcal{H}_{AA}^{(1)} + \mathcal{H}_{BB}^{(1)} + \dots \\ + \mathcal{H}_{AB}^{(1)} + \mathcal{H}_{AC}^{(1)} + \dots \end{aligned} \quad (3a)$$

$$\mathcal{H}_{AA}^{(1)} = \sum_{i < j} J_{AiAj} \mathbf{I}_{Ai} \cdot \mathbf{I}_{Aj} \quad (3b)$$

.....

$$\mathcal{H}_{AB}^{(1)} = \sum_{i,k} J_{AiBk} \mathbf{I}_{Ai} \cdot \mathbf{I}_{Bk} \quad (3c)$$

.....

where γ_A is the gyromagnetic ratio of group A, J_{AiAj} is the coupling constant of the two spins both of which belong to group A, and J_{AiBk} is that of the two spins which respectively belong to group A or group B, and so on. F_A is the total spin angular momentum

$$\mathbf{F}_A = \sum_i \mathbf{I}_{Ai} \quad (4)$$

and F_{zA} is its z component.

The simple multiplet structures which was studied by Gutowsky, McCall and Slichter^[3] are produced in the case of the interactions between two groups which satisfy the following conditions :

- (i) All the coupling constants between both groups of A and B are equal.
- (ii) The resonance frequencies of both groups of A and B are well separated compared with the multiplet separation.

According to the condition (i), Eq. (3c) is represented as

$$\mathcal{H}_{AB}^{(1)} = J_{AB} \mathbf{F}_A \cdot \mathbf{F}_B, \quad (5)$$

and the condition (ii) means

$$|J_{AB}| \ll \hbar H |\gamma_A - \gamma_B|. \quad (6)$$

In the present case, we write the total Hamiltonian as

$$\mathcal{H} = \mathcal{H}_A + \mathcal{H}_B + \mathcal{H}_{AB}^{(1)} \quad (7)$$

$$\mathcal{H}_A = \mathcal{H}_A^{(0)} + \mathcal{H}_{AA}^{(1)} \quad (7a)$$

$$\mathcal{H}_B = \mathcal{H}_B^{(0)} + \mathcal{H}_{BB}^{(1)}, \quad (7b)$$

and after finding the spin eigen-function of $\mathcal{H}_A$ and $\mathcal{H}_B$, we treat $\mathcal{H}_{AB}^{(1)}$ as a perturbation. M_A and M_B , the eigen-values of F_{zA} and F_{zB} , are constants of motion in the unperturbed system, since F_{zA} and F_{zB} commute with both $\mathcal{H}_A$ and $\mathcal{H}_B$. On the other hand, Eq. (5) can be written in the form of

$$\mathcal{H}_{AB}^{(1)} = J_{AB} \left(\frac{1}{2} F_A^+ F_B^- + \frac{1}{2} F_A^- F_B^+ + F_{zA} F_{zB} \right) \quad (5a)$$

of which the first and second term are the matrix elements of

$$\Delta M_A = \pm 1, \quad \Delta M_B = \mp 1,$$

in the matrix expressed in terms of the eigen-functions of the unperturbed system. According to the perturbation theory, these terms can be neglected in the first order perturbation, as the result of Eq. (6). Therefore M_A and M_B are the well defined quantum numbers again in the perturbed system, and then Eq. (5a) is expressed as

$$\mathcal{H}_{AB}^{(1)} \cong J_{AB} M_A M_B. \quad (5b)$$

Now, the selection rules are to be seen. The selection rules for the resonances of A- and B-nucleus are obtained from the matrix elements of F_{xA} and F_{xB} , respectively.

The selection rules for the unperturbed system are the following: If the eigen-values of $\mathcal{H}_A$ and $\mathcal{H}_B$ are written in the form of

$$\mathcal{H}_A = \hbar H \gamma_A M_A + \epsilon_{AA}^{(1)} \quad (8a)$$

$$\mathcal{H}_B = \hbar H \gamma_B M_B + \epsilon_{BB}^{(1)} \quad (8b)$$

respectively, the non-vanishing elements of the matrix represented by the eigen-functions of the unperturbed system for F_{xA} and F_{xB} , will appear in the positions which combine the two states having the relations:

$$\Delta M_A = \pm 1; \quad \Delta \epsilon_{AA}^{(1)} = \Delta \epsilon_{BB}^{(1)} = \Delta M_B = 0, \quad (9a)$$

$$\Delta M_B = \pm 1; \quad \Delta \epsilon_{BB}^{(1)} = \Delta \epsilon_{AA}^{(1)} = \Delta M_A = 0. \quad (9b)$$

That is, Eqs. (9a) and (9b) should be the selection rules for the resonances of A- and B-nucleus respectively.

In the first order, the eigen-functions of the unperturbed system are by themselves equal to those of the perturbed system for the non-degenerate states, so that the selection rules for the perturbed system can be also given by Eqs. (9a) and (9b).

As the results of Eqs. (5b), (9a) and (9b), the multiplets of the resonance spectra of A- and B-nucleus are given by

$$\hbar \nu_A = \hbar \gamma_A H + J_{AB} M_B \quad (10a)$$

$$\hbar \nu_B = \hbar \gamma_B H + J_{AB} M_A \quad (10b)$$

respectively, and the intensity ratios of multiplets are the ratios of the degeneracies of M_A levels for A-nucleus, and those of M_B levels for B-nucleus.

As to the groups of nuclei including more than three, the similar treatments are applied.

If the two conditions that:

(i) The interactions between the groups are given by

$$\begin{aligned} \mathcal{H}_{AB}^{(1)} &= J_{AB} \mathbf{F}_A \cdot \mathbf{F}_B \\ \mathcal{H}_{BC}^{(1)} &= J_{BC} \mathbf{F}_B \cdot \mathbf{F}_C \\ \mathcal{H}_{AC}^{(1)} &= J_{AC} \mathbf{F}_A \cdot \mathbf{F}_C \\ &\dots\dots\dots \end{aligned} \quad (11)$$

(ii) The following relations are valid

$$\begin{aligned} |J_{AB}| &\ll \hbar H |\gamma_A - \gamma_B| \\ |J_{BC}| &\ll \hbar H |\gamma_B - \gamma_C| \\ |J_{AC}| &\ll \hbar H |\gamma_A - \gamma_C| \\ &\dots\dots\dots \end{aligned} \quad (12)$$

are satisfied, it can be illustrated that the resonance spectra of A-nucleus, as a typical one, will have the multiplet structures of the type

$$h\nu = \hbar \gamma_A H + J_{AB} M_B + J_{AC} M_C + \dots\dots\dots (13)$$

3. Additional Multiplet Fine Structures

When all the coupling constants between both groups of A and B are not equal each other, the resonances of A- and B- nucleus exhibit not any simple multiplet structures. To interpret these spectra, it is required to obtain the spin eigen-functions for the total Hamiltonian including the interactions.^{[5],[9]}

Suppose that the solutions of Hamiltonian have been found for the interactions between both groups of A and B, we add the third spin group C to this system and consider the case that the interactions between groups A and C, and B and C are given by the unique coupling constants J_{AC} and J_{BC} , respectively. Then total spin Hamiltonian is

$$\mathcal{H} = \mathcal{H}_A + \mathcal{H}_B + \mathcal{H}_C + \mathcal{H}_{AB}^{(1)} + \mathcal{H}_{AC}^{(1)} + \mathcal{H}_{BC}^{(1)}, \quad (14)$$

$$\mathcal{H}_{AB}^{(1)} = \sum_{i,j} J_{AiBj} \mathbf{I}_{Ai} \cdot \mathbf{I}_{Bj} \quad (14a)$$

$$\mathcal{H}_{AC}^{(1)} = J_{AC} \mathbf{F}_A \cdot \mathbf{F}_C \quad (14b)$$

$$\mathcal{H}_{BC}^{(1)} = J_{BC} \mathbf{F}_B \cdot \mathbf{F}_C, \quad (14c)$$

where the definitions for $\mathcal{H}_A$, $\mathcal{H}_B$, and $\mathcal{H}_C$ are similar to that given by Eq. (7a).

In this case, suppose that the conditions of Eq. (6) are satisfied, i. e.,

$$|J_{AiBj}| \ll \hbar H |\gamma_A - \gamma_B|, \quad (i=1, 2, \dots, j=1, 2, \dots) \quad (15a)$$

$$|J_{AC}| \ll \hbar H |\gamma_A - \gamma_C| \quad (15b)$$

$$|J_{BC}| \ll \hbar H |\gamma_B - \gamma_C| \quad (15c)$$

then M_A , M_B , and M_C are the well defined quantum numbers for the eigen functions of Hamiltonian of Eq. (14).

Now, let us assume that the solutions of Hamiltonian for both groups of A and B are found and that the eigen-value is given by

$$\mathcal{H}_A + \mathcal{H}_B + \mathcal{H}_{AB}^{(1)} = \hbar H (\gamma_A M_A + \gamma_B M_B) + \epsilon_{AA}^{(1)} + \epsilon_{BB}^{(1)} + \epsilon_{AB}^{(1)}. \quad (16)$$

When we add the group C to the system, the quantity

$$\mathcal{H}_{AC}^{(1)} + \mathcal{H}_{BC}^{(1)} \simeq J_{AC} F_{zA} F_{zC} + J_{BC} F_{zB} F_{zC} \quad (17)$$

is added as a perturbation to the unperturbed Hamiltonian which is equal to Eq. (16) plus $\mathcal{H}_C$, however, since M_A , M_B , and M_C are constants of motion, the eigen-functions of the unperturbed system which is the direct products of the eigen-functions of $\mathcal{H}_C$ and

those of Eq. (16), are directly employed as the eigenfunction, and the eigen-value is given by

$$\mathcal{H} = \hbar H(M_A + M_B + M_C) + \epsilon_{AA}^{(1)} + \epsilon_{BB}^{(1)} + \epsilon_{CC}^{(1)} + \epsilon_{AB}^{(1)} + J_{AC} M_A M_C + J_{BC} M_B M_C. \quad (18)$$

The selection rules for resonances of A- and B-nucleus are obtained as follows, similarly to Section 2,

$$\left. \begin{aligned} \Delta M_A = \pm 1, \quad \Delta M_B = \Delta M_C = 0, \\ \Delta \epsilon_{AA}^{(1)} = \Delta \epsilon_{BB}^{(1)} = \Delta \epsilon_{CC}^{(1)} = 0, \end{aligned} \right\} \quad (19a)$$

$$\left. \begin{aligned} \Delta M_B = \pm 1, \quad \Delta M_A = \Delta M_C = 0, \\ \Delta \epsilon_{AA}^{(1)} = \Delta \epsilon_{BB}^{(1)} = \Delta \epsilon_{CC}^{(1)} = 0. \end{aligned} \right\} \quad (19b)$$

Furthermore, as to the resonance of C-nucleus, $\mathcal{H}_{AB}^{(1)}$ commutes with F_{x_C} , so that $\Delta \epsilon_{AB}^{(1)} = 0$ is required and

$$\left. \begin{aligned} \Delta M_C = \pm 1, \quad \Delta M_A = \Delta M_B = 0, \\ \Delta \epsilon_{AA}^{(1)} = \Delta \epsilon_{BB}^{(1)} = \Delta \epsilon_{CC}^{(1)} = \Delta \epsilon_{AB}^{(1)} = 0. \end{aligned} \right\} \quad (19c)$$

TABLE I. The transition energy shift and the relative intensity for the resonance of A-nucleus

Transition	Transition energy shift	Relative intensity
$ A_1; 1, 1, \pm \frac{1}{2}\rangle \longleftrightarrow A_1; 0, 1, \pm \frac{1}{2}\rangle$	$\frac{1}{2}N \pm \frac{1}{2}J_{AC}$	$\frac{1}{12}$
$ A_1; 0, 1, \pm \frac{1}{2}\rangle \longleftrightarrow A_1; -1, 1, \pm \frac{1}{2}\rangle$	$\frac{1}{2}N \pm \frac{1}{2}J_{AC}$	$\frac{1}{12}$
$ A_1; 1, 0, \pm \frac{1}{2}\rangle \longleftrightarrow 1A_1; 0, 0, \pm \frac{1}{2}\rangle$	$\frac{1}{2}K - \frac{1}{2}(K^2 + L^2)^{\frac{1}{2}} \pm \frac{1}{2}J_{AC}$	$\frac{1}{12}L^2[K^2 + L^2 - K(K^2 + L^2)^{\frac{1}{2}}]^{-1}$
$ A_1; 1, 0, \pm \frac{1}{2}\rangle \longleftrightarrow 2A_1; 0, 0, \pm \frac{1}{2}\rangle$	$\frac{1}{2}K + \frac{1}{2}(K^2 + L^2)^{\frac{1}{2}} \pm \frac{1}{2}J_{AC}$	$\frac{1}{12}L^2[K^2 + L^2 + K(K^2 + L^2)^{\frac{1}{2}}]^{-1}$
$ B_2; 1, 0, \pm \frac{1}{2}\rangle \longleftrightarrow 1B_2; 0, 0, \pm \frac{1}{2}\rangle$	$\frac{1}{2}M - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}} \pm \frac{1}{2}J_{AC}$	$\frac{1}{12}L^2[M^2 + L^2 - M(M^2 + L^2)^{\frac{1}{2}}]^{-1}$
$ B_2; 1, 0, \pm \frac{1}{2}\rangle \longleftrightarrow 2B_2; 0, 0, \pm \frac{1}{2}\rangle$	$\frac{1}{2}M + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}} \pm \frac{1}{2}J_{AC}$	$\frac{1}{12}L^2[M^2 + L^2 + M(M^2 + L^2)^{\frac{1}{2}}]^{-1}$
$ 1B_2; 0, 0, \pm \frac{1}{2}\rangle \longleftrightarrow B_2; -1, 0, \pm \frac{1}{2}\rangle$	$-\frac{1}{2}M + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}} \pm \frac{1}{2}J_{AC}$	$\frac{1}{12}L^2[M^2 + L^2 - M(M^2 + L^2)^{\frac{1}{2}}]^{-1}$
$ 2B_2; 0, 0, \pm \frac{1}{2}\rangle \longleftrightarrow B_2; -1, 0, \pm \frac{1}{2}\rangle$	$-\frac{1}{2}M - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}} \pm \frac{1}{2}J_{AC}$	$\frac{1}{12}L^2[M^2 + L^2 + M(M^2 + L^2)^{\frac{1}{2}}]^{-1}$
$ 1A_1; 0, 0, \pm \frac{1}{2}\rangle \longleftrightarrow A_1; -1, 0, \pm \frac{1}{2}\rangle$	$-\frac{1}{2}K + \frac{1}{2}(K^2 + L^2)^{\frac{1}{2}} \pm \frac{1}{2}J_{AC}$	$\frac{1}{12}L^2[K^2 + L^2 - K(K^2 + L^2)^{\frac{1}{2}}]^{-1}$
$ 2A_1; 0, 0, \pm \frac{1}{2}\rangle \longleftrightarrow A_1; -1, 0, \pm \frac{1}{2}\rangle$	$-\frac{1}{2}K - \frac{1}{2}(K^2 + L^2)^{\frac{1}{2}} \pm \frac{1}{2}J_{AC}$	$\frac{1}{12}L^2[K^2 + L^2 + K(K^2 + L^2)^{\frac{1}{2}}]^{-1}$
$ A_1; 1, -1, \pm \frac{1}{2}\rangle \longleftrightarrow A_1; 0, -1, \pm \frac{1}{2}\rangle$	$-\frac{1}{2}K \pm \frac{1}{2}J_{AC}$	$\frac{1}{12}$
$ A_1; 0, -1, \pm \frac{1}{2}\rangle \longleftrightarrow A_1; -1, -1, \pm \frac{1}{2}\rangle$	$-\frac{1}{2}K \pm \frac{1}{2}J_{AC}$	$\frac{1}{12}$

TABLE II. The transition energy shift and the relative intensity for the resonance of C-nucleus

Transition	Transition energy shift	Relative intensity
$ A_1; 1, 1, \frac{1}{2}\rangle \rightleftharpoons A_1; 1, 1, -\frac{1}{2}\rangle$	$J_{AC} + J_{BC}$	$\frac{1}{16}$
$ A_1; 1, -1, \frac{1}{2}\rangle \rightleftharpoons A_1; 1, -1, -\frac{1}{2}\rangle$	$J_{AC} - J_{BC}$	$\frac{1}{16}$
$ A_1; -1, 1, \frac{1}{2}\rangle \rightleftharpoons A_1; -1, 1, -\frac{1}{2}\rangle$	$-J_{AC} + J_{BC}$	$\frac{1}{16}$
$ A_1; -1, -1, \frac{1}{2}\rangle \rightleftharpoons A_1; -1, -1, -\frac{1}{2}\rangle$	$-J_{AC} - J_{BC}$	$\frac{1}{16}$
$ A_1; 1, 0, \frac{1}{2}\rangle \rightleftharpoons A_1; 1, 0, -\frac{1}{2}\rangle$	J_{AC}	$\frac{1}{16}$
$ A_1; -1, 0, \frac{1}{2}\rangle \rightleftharpoons A_1; -1, 0, -\frac{1}{2}\rangle$	$-J_{AC}$	$\frac{1}{16}$
$ A_1; 0, 1, \frac{1}{2}\rangle \rightleftharpoons A_1; 0, 1, -\frac{1}{2}\rangle$	J_{BC}	$\frac{1}{16}$
$ A_1; 0, -1, \frac{1}{2}\rangle \rightleftharpoons A_1; 0, -1, -\frac{1}{2}\rangle$	$-J_{BC}$	$\frac{1}{16}$
$ B_2; 1, 0, \frac{1}{2}\rangle \rightleftharpoons B_2; 1, 0, -\frac{1}{2}\rangle$	J_{AC}	$\frac{1}{16}$
$ B_2; -1, 0, \frac{1}{2}\rangle \rightleftharpoons B_2; -1, 0, -\frac{1}{2}\rangle$	$-J_{AC}$	$\frac{1}{16}$
$ B_2; 0, 1, \frac{1}{2}\rangle \rightleftharpoons B_2; 0, 1, -\frac{1}{2}\rangle$	J_{BC}	$\frac{1}{16}$
$ B_2; 0, -1, \frac{1}{2}\rangle \rightleftharpoons B_2; 0, -1, -\frac{1}{2}\rangle$	$-J_{BC}$	$\frac{1}{16}$
$ 1A_1; 0, 0, \frac{1}{2}\rangle \rightleftharpoons 1A_1; 0, 0, -\frac{1}{2}\rangle$	0	$\frac{1}{16}$
$ 2A_1; 0, 0, \frac{1}{2}\rangle \rightleftharpoons 2A_1; 0, 0, -\frac{1}{2}\rangle$	0	$\frac{1}{16}$
$ 1B_2; 0, 0, \frac{1}{2}\rangle \rightleftharpoons 1B_2; 0, 0, -\frac{1}{2}\rangle$	0	$\frac{1}{16}$
$ 2B_2; 0, 0, \frac{1}{2}\rangle \rightleftharpoons 2B_2; 0, 0, -\frac{1}{2}\rangle$	0	$\frac{1}{16}$

Consequently, the resonance spectra for A-, B-, and C-nucleus are given by the expressions, respectively

$$h\nu_A = \hbar \gamma_A H + \Delta \epsilon_{AB}^{(1)} + J_{AC} M_C, \quad (20a)$$

$$h\nu_B = \hbar \gamma_B H + \Delta \epsilon_{AB}^{(1)} + J_{BC} M_C, \quad (20b)$$

$$h\nu_C = \hbar \gamma_C H + J_{AC} M_C + J_{BC} M_C. \quad (20c)$$

This indicates that each spectral line for A- and B-nucleus which appear in the case without C-nucleus, splits to multiplets due to M_C , and that the simple multiplet structures of the resonance spectra of C-nucleus are observed, as in the previous section.

4. A_2B_2C Spin Group of C_{2v} Symmetry

The spectra of A_2B_2 spin group with C_{2v} symmetry are analysed by McConnell, McLean, and Reilly.^[5] When C-nucleus is located on the C_2 axis, axis which connects the center of gravity of group A with that of group B, each energy level of A_2B_2 spin group splits to the doublet, as will be seen from the results of the previous section. The transition energy shifts and the relative intensities for the resonances of A- and C-nucleus are tabulated in Table I and II, respectively, and the results for B-nucleus are obtained by putting J_{BC} 's in place of J_{AC} 's in Table I.

In the tables, the designation of the spin state means

$$|n, \text{ symmetry species ; } M_A, M_B, M_C\rangle$$

and n is the letter to distinguish the states belonging to the same symmetry species and M_A , M_B , and M_C . The notations of the symmetry species are the same as that of McConnell et al,^[5] and the parameters in the tables are given by

$$K = J_A + J_B \quad (21a)$$

$$M = J_A - J_B \quad (21b)$$

$$N = J_c + J_t \quad (21c)$$

$$L = J_c - J_t, \quad (21d)$$

where J_A and J_B are the coupling constants between two spins of the group A and B respectively, and J_c and J_t the coupling constants between nuclei in both groups of A and B which are located on the position of *cis* and *trans* with each other.

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