



## Multiple Quantum Coherence and Magic Angle in Solid NMR Spectroscopy

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**Abstract:** In this paper we discussed how multiple quantum coherences evolve in the presence of anisotropic distribution of dipolar couplings. The magnitude of dipolar couplings were varied by changing the tilt angle of crystal axis. The stronger was dipolar coupling, the higher was frequency of multiple quantum coherence. That is, the order of multiple quantum coherence varies in proportion to the magnitude of dipolar couplings. The theoretical prediction for the multiple quantum coherence at magic angle  $54.7^\circ$  in solid NMR spectroscopy was verified in this study. The excitation pattern of  $n$ -quantum coherence, which can induce the effective size to characterize spin system, is expected in a larger and more complicated spin system for understanding of the relation of dipolar coupling and multiple quantum coherence.

### INTRODUCTION

In the present study, a numerical simulation was used to examine how multiple quantum coherence occurs according to anisotropic distribution of dipolar coupling constant in single crystal material of two-spin and three-spin system composed of nuclei with spin quantum number  $I = 1/2$ . The fundamental problems in multiple quantum coherence are how anisotropic distribution of dipolar coupling constant influences the excited form of multiple quantum coherence and how to examine the characteristics of isolated nuclei.

These problems can be solved through 'computer simulation experiment' using numerical solution of the Liouville-von Neumann equation that was used to understand the detailed movement of composition material, and here, the size of nuclear system can be

calculated from maximum value of coherence or maximum distribution of multiple intensity.

With the usual process of recording multiple spectra on several excited time in appropriate non-secular dipolar Hamiltonian<sup>2</sup>, the internuclear interaction that is solved with normal techniques of dipolar Hamiltonian is making different states produced by n-Zeeman protons in spin  $I=1/2$  nuclear system to superposition the numbers,  $0 \leq |n| \leq 1$ , in other words, to allow coherence to occur. In order to create this coherence, infinite time is always needed, and as the dipolar coupling constant is smaller, more time is needed.

The computer experiment used in the present study was performed to explain how multiple quantum NMR dynamics change when the dipolar coupling constants according to random direction change in single crystal.

## METHOD AND EXPERIMENTAL

### *Multiple Quantum Coherence*

Nuclear magnetization process was observed in NMR Spectroscopy and NMR Imaging<sup>3</sup>, and this magnetization was single quantum coherence that corresponds to the change of total magnetic quantum number between the two states by  $\pm 1$ , *i.e.*, the coherence of  $\Delta M_T = \pm 1$ , whereas multiple quantum coherence<sup>3,4</sup> is characterized by  $\Delta M_T \neq \pm 1$ , 'forbidden transition', so that direct excitation or measurement is impossible. Fig. 1 is a diagram that shows the energy level of a two nuclear system of spin  $I = 1/2$ .

### *Density Operator Description of Multiple Quantum NMR Dynamics*

An isolated spin  $I=1/2$  particle in an external magnetic field has the two eigenstates  $|\frac{1}{2}\rangle$  and  $|\frac{-1}{2}\rangle$ , which represent the two allowed orientations of its angular momentum.<sup>6,7</sup> Since the behavior of a single spin or group of spins cannot in general

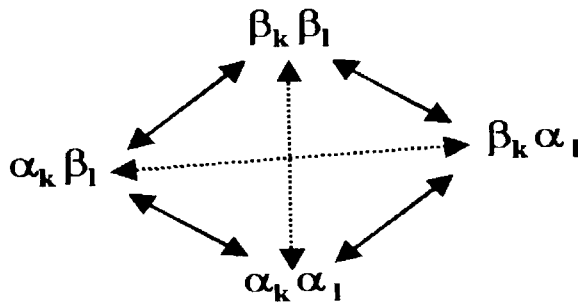


Fig. 1. Energy level diagram of a two spin system ( $k, l$ ). In addition to the four allowed single quantum transitions, there are two forbidden transitions, a zero quantum transition (diagonal dashed line) and a double quantum transition (vertical dashed line)

describe a macroscopic system, we introduce an ensemble of independent two-level subsystems. The term 'coherence' is defined as the presence of some degree of phase coherence between the basis states of the isolated subsystems throughout the ensemble.<sup>8</sup> An ensemble of spins can be described by the density operator,  $\rho$ , which is represented by

$$\rho = \sum p_i |\Psi_i\rangle\langle\Psi_i| = \overline{|\Psi\rangle\langle\Psi|} \quad (1)$$

where  $p_i$  is the probability of each state  $\Psi_i$  occurring in the superposition.<sup>9</sup> The equilibrium density operator can be represented by the  $|M_k\rangle\langle M_l|$  basis is given by

$$\rho_{eq} = \begin{pmatrix} \overline{C_{1/2}^* C_{1/2}} & \overline{C_{1/2}^* C_{-1/2}} \\ \overline{C_{1/2} C_{-1/2}^*} & \overline{C_{-1/2} C_{-1/2}^*} \end{pmatrix} \quad (2)$$

With the probabilities from the Boltzmann factor

$$P(M = \pm 1/2) = \exp(-M\hbar\omega_0 I_z / kT) / Z \quad (3)$$

the equilibrium density operator after averaging over the phase differences is given by

$$\rho_{eq} = \exp(-\hbar\omega_0 I_z / kT) / Z \quad (4)$$

From the high temperature approximation, the partition function  $Z$  is equal to  $2I+1$ . For the equilibrium density operator of a spin  $I = 1/2$  system, Eq. (2) can be rewritten as

$$[\rho_{eq}] = \begin{vmatrix} \exp(-\hbar\omega_0 / 2kT) / Z & 0 \\ 0 & \exp(+\hbar\omega_0 / 2kT) / Z \end{vmatrix} \quad (5)$$

The random phase among spins of different subsystems in the ensemble averages the off-diagonal elements to zero, but an application of an appropriate RF pulse to the ensemble results in non-zero off-diagonal elements in the matrix. The existence of the non-zero off-diagonal elements from a single pulse is described as single-quantum coherence. The order of a coherence between states  $|r\rangle$  and  $|s\rangle$  is defined as

$$n = \Delta M = |M_k - M_l| \quad (6)$$

where  $M_k$  and  $M_l$  are the total  $M_z$  values of all the spins in the states  $|k\rangle$  and  $|l\rangle$  respectively. The dimension of the density matrix increases as the size of the coupled spin system increases. The presence of phase coherences in large spin systems produced by a proper pulse sequence results in non-zero off-diagonal elements that represent the multiple quantum coherences between states.

### **Pulse Sequence for Multiple Quantum NMR**

Since multiple-quantum transitions are usually not directly observable with an NMR coil, they must be detected indirectly by two-dimensional spectroscopic methods. The typical scheme of a two-dimensional multiple-quantum NMR experiment is shown in Fig. 2. The pulse sequence creates a non-equilibrium condition of multiple quantum coherence during the preparation period  $\tau$ , allows the coherence to respond during the evolution period  $t_1$  and then transfers the coherence to  $z$  magnetization during the mixing time  $\tau'$ . The coherence is then detected after the detection pulse during the detection period  $t_2$  which creates observable  $M_x$  magnetization corresponding to a single-quantum coherence. The preparation period propagator arises from a combination of pulses and proper delays

$$U(\tau) = \exp(-iH\tau) \quad (7)$$

Under this propagator, the density operator,  $\rho(\tau)$ , becomes as follows by the end of the preparation period:

$$\rho(\tau) = U(\tau)\rho(0)U^{-1}(\tau) \quad (8)$$

The system is allowed to develop, freely or otherwise, for an evolution period of length  $t_1$ . During this time, the different modes of coherence oscillate at the eigen frequencies determined by the effective Hamiltonian  $H_1$  as defining in Fig. 2. No signal is recorded during this interval. After time development is halted at some time  $t_1$ , the coherences are transferred to detectable single-quantum modes during the mixing and detection periods and the density operator becomes as follows,

$$\rho(\tau, t_1, \tau') = V(\tau') \exp(-iH_1 t_1) \rho(\tau) \exp(iH_1 t_1) V^{-1}(\tau') \quad (9)$$

where  $V(\tau') = \exp(-iH'\tau')$  is the mixing period propagator. Transverse components of the total spin angular momentum  $M_x$  and  $M_y$  are obtained immediately after the mixing period.

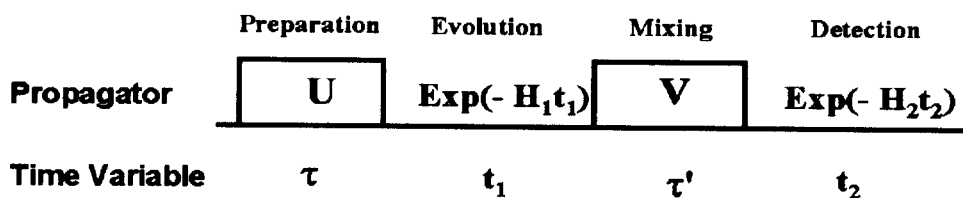


Fig. 2. General form of the pulse sequence of MQ NMR experiments

### Experiments

In the present study, as seen in Fig. 3, limited to  $^{19}\text{F}$ - $^{19}\text{F}$  two-spin system of spin 1/2 and single crystal that has  $^{19}\text{F}$ - $^{19}\text{F}$ - $^{19}\text{F}$  three-spin system, we performed a computer simulation to follow how the form of multiple quantum coherence changes according to the size of dipolar coupling constant.

The average dipolar Hamiltonian is determined by nuclear magnetogyric ratio  $\gamma$ , internuclear distance  $r$ , and oriented angle  $\theta$  on external magnetic field  $B_0$ . In case of two-spin system, the internuclear distance was fixed at 3.44 Å; in case of three spin system, by limiting to the shape to right-angled triangle with 45° with the diagonal line length at 1.414 Å, the direction angle according to the shape was selected randomly. The results of multiple quantum coherence were obtained by using ANTIOPE program that was made for simulation of nuclear spin dynamics. The notion 'n-spin system' is used for a group of  $n$  nuclei of spin quantum number  $I = 1/2$  that is characterized by no more than  $n$  resonance frequencies,  $\nu_k$  and  $n(n - 1)/2$  coupling constants,  $J_{kl}$ . In the present study, two-spin system of  $^{19}\text{F}$ - $^{19}\text{F}$  and three-spin system of  $^{19}\text{F}$ - $^{19}\text{F}$ - $^{19}\text{F}$  were used.

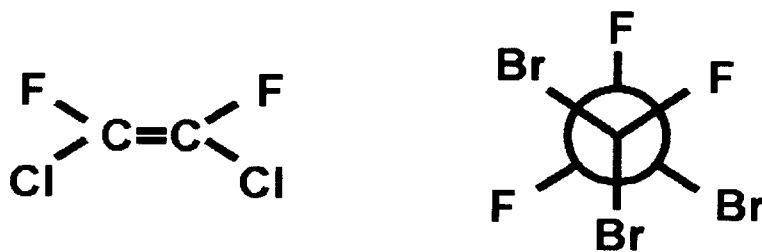


Fig. 3. Multiple quantum spin system

Dipolar coupling is an interaction between two nuclei within a molecule. In solid state where a molecule is in steady state(refer to Fig. 3), the total magnetic field of fluorine(<sup>19</sup>F) nucleus,  $\vec{B}_t$ , can be expressed as the sum of external magnetic field  $\vec{B}_0$  and local magnetic field of nucleus  $B_{loc}$  as seen in Eq. (10). The size of the interaction of two nuclei depends on nuclear magnetic moment  $\mu_F$ , internuclear distance  $r$ , and relative direction  $\theta$  on external magnetic field as in Eq. (11).

$$\vec{B}_t = \vec{B}_0 + \vec{B}_{loc} \tag{10}$$

$$\vec{B}_{loc} = \pm(\mu_F / r^3)(3 \cos^2 \theta - 1)(\vec{r} / r) \tag{11}$$

Here, the Hamiltonian of the even number multiple quantum coherence can be expressed as follows:

$$H_D = -\mu_k \cdot B_{Dl} = -\frac{1}{2} \sum_{l < k} D_{lk} (I_{l+} I_{k+} + I_{l-} I_{k-}) \tag{12}$$

The dipolar coupling constant  $D_{FF}$  of <sup>19</sup>F-<sup>19</sup>F system can be expressed as in Eq. (13).

$$D_{FF} = (\gamma_F^2 \hbar) / (1 - 3 \cos^2 \theta_{kl}) / 3r_{kl}^3 \tag{13}$$

Thus, in order to determine the form change according to anisotropic distribution of dipolar coupling in the <sup>19</sup>F-<sup>19</sup>F system, dipolar coupling constant was calculated on random  $\theta$ , and multiple quantum coherence was calculated on the <sup>19</sup>F-<sup>19</sup>F-<sup>19</sup>F 3-spin system that is the combination of 2-spin system.

In the present study, pulse sequence shown in Fig. 4 was used, and here, the pulse width

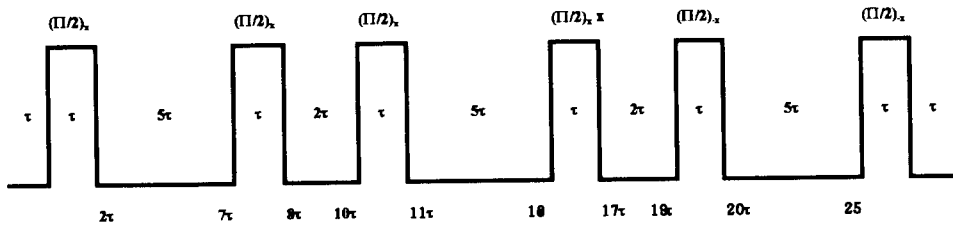


Fig. 4. Pulse sequence for the multiple quantum NMR

(PW) was set at 0.5  $\mu\text{sec}$ , and pulse delay(PD) between a pulse and another pulse,  $\Delta$ , was 1  $\mu\text{sec}$ . To make average dipolar Hamiltonian, the condition,  $\text{PD}(\Delta')=2 \cdot \text{PD}(\Delta)+\text{PW}$ , needs to be satisfied, so another PD( $\Delta'$ ) was set at 2.5  $\mu\text{sec}$ , and measured only those with the size of coherence transition are even number.

For the calculation of spin dynamics, pulse sequence was first inputted in ANTIOPE program, and after setting the internuclear distance of  $^{19}\text{F}$ - $^{19}\text{F}$  system at 3.44  $\text{\AA}$ , anisotropic Hamiltonian was made on each direction angle. Three-spin system of  $^{19}\text{F}$ - $^{19}\text{F}$ - $^{19}\text{F}$  was limited to the form of a right-angled triangle with the diagonal line length of 1.414  $\text{\AA}$  and with  $45^\circ$  and transitions included in zero coherence and double coherence were classified according to Table 1, 2, 3, and 4.

In table 1 and 3, among 4 and 8 spin states that are possible in each of 2-spin and 3-spin system, zero coherence transition was marked with  $\blacklozenge$  and  $\rightarrow$  indicates the direction of transition. For example,  $\alpha\beta \rightarrow \beta\alpha$  ( $\alpha = 1/2, \beta = -1/2$ ) means the spin transition from  $\alpha\beta$  to  $\beta\alpha$  state. On the other hand, Table 2 and 4 show double coherence transition. Thus, after this classification and obtaining the value of transition for each, by squaring of these value and summing, the size of zero coherence and double coherence according to time was calculated.

**Table 1.** Zero quantum transition in two-spin system

$\rightarrow$	$\alpha\alpha$	$\alpha\beta$	$\beta\alpha$	$\beta\beta$
$\alpha\alpha$	$\blacklozenge$			
$\alpha\beta$		$\blacklozenge$	$\blacklozenge$	
$\beta\alpha$		$\blacklozenge$	$\blacklozenge$	
$\beta\beta$				$\blacklozenge$

**Table 2.** Double quantum transition in two-spin system

$\rightarrow$	$\alpha\alpha$	$\alpha\beta$	$\beta\alpha$	$\beta\beta$
$\alpha\alpha$				$\blacklozenge$
$\alpha\beta$				
$\beta\alpha$				
$\beta\beta$	$\blacklozenge$			

**Table 3.** Zero quantum transition in three-spin system

$\rightarrow$	$\alpha\alpha\alpha$	$\alpha\alpha\beta$	$\alpha\beta\alpha$	$\beta\alpha\alpha$	$\alpha\beta\beta$	$\beta\alpha\beta$	$\beta\beta\alpha$	$\beta\beta\beta$
$\alpha\alpha\alpha$	◆							
$\alpha\alpha\beta$		◆	◆	◆				
$\alpha\beta\alpha$		◆	◆	◆				
$\beta\alpha\alpha$		◆	◆	◆				
$\alpha\beta\beta$					◆	◆	◆	
$\beta\alpha\beta$					◆	◆	◆	
$\beta\beta\alpha$					◆	◆	◆	
$\beta\beta\beta$								◆

**Table 4.** Double quantum transition in three-spin system

$\rightarrow$	$\alpha\alpha\alpha$	$\alpha\alpha\beta$	$\alpha\beta\alpha$	$\beta\alpha\alpha$	$\alpha\beta\beta$	$\beta\alpha\beta$	$\beta\beta\alpha$	$\beta\beta\beta$
$\alpha\alpha\alpha$					◆	◆	◆	
$\alpha\alpha\beta$								◆
$\alpha\beta\alpha$								◆
$\beta\alpha\alpha$								◆
$\alpha\beta\beta$	◆							
$\beta\alpha\beta$	◆							
$\beta\beta\alpha$	◆							
$\beta\beta\beta$		◆	◆	◆				

## RESULTS AND DISCUSSION

### *The size of dipolar coupling on direction angle*

In case of  $^{19}\text{F}$ - $^{19}\text{F}$  spin system, after setting random oriented angles  $0^\circ$ ,  $30^\circ$ ,  $54.7^\circ$ ,  $65^\circ$ ,  $90^\circ$ ,  $115^\circ$ ,  $125.3^\circ$ ,  $150^\circ$ ,  $180^\circ$  on external magnetic field, using Eq. (13), the value of dipolar coupling constant was obtained, and the results are shown in Table 5 and Fig. 5 and 6. Fig. 5 is a graph made based on the data in Table 5; the graph shows a similar



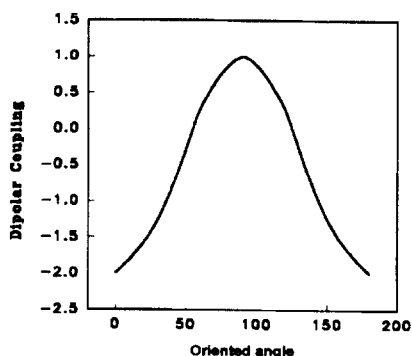


Fig. 5. The dipolar coupling constant in the oriented angle

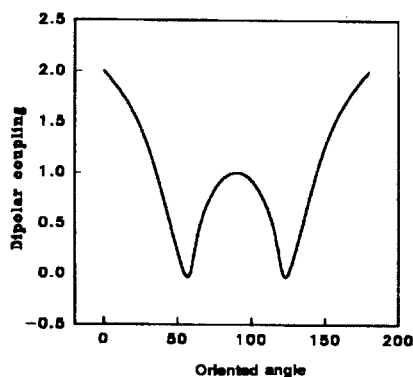


Fig. 6. The absolute value of dipolar coupling constant in the oriented angle

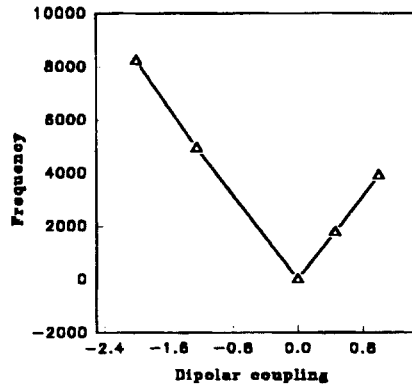
tendency as a Gaussian distribution with the size of dipolar constant symmetric at  $90^\circ$  on oriented angle and Fig. 6 is a graph constructed using the absolute value of dipolar coupling.

#### *Relationship between dipolar coupling and multiple quantum coherence*

When the magnitude of dipolar constant was measured by changing the tilt angle, the results showed that although the absolute value of dipolar coupling constant becomes larger, the amplitude did not attenuate and kept constant, but the frequency of multiple quantum coherence increased. Particularly at  $54.7^\circ$ , the frequency of dipolar coupling and multiple quantum coherence showed a straight line with '0' frequency. Thus, we determined that multiple quantum coherence did not occur at  $54.7^\circ$  so that the usefulness of magic angle that is used to eliminate dipolar coupling component in solid NMR. As shown in Table 5, the form of multiple quantum coherence changed proportional to the size of dipolar coupling, and the result of this change was verified to agree with the theory formula on multiple quantum coherence.

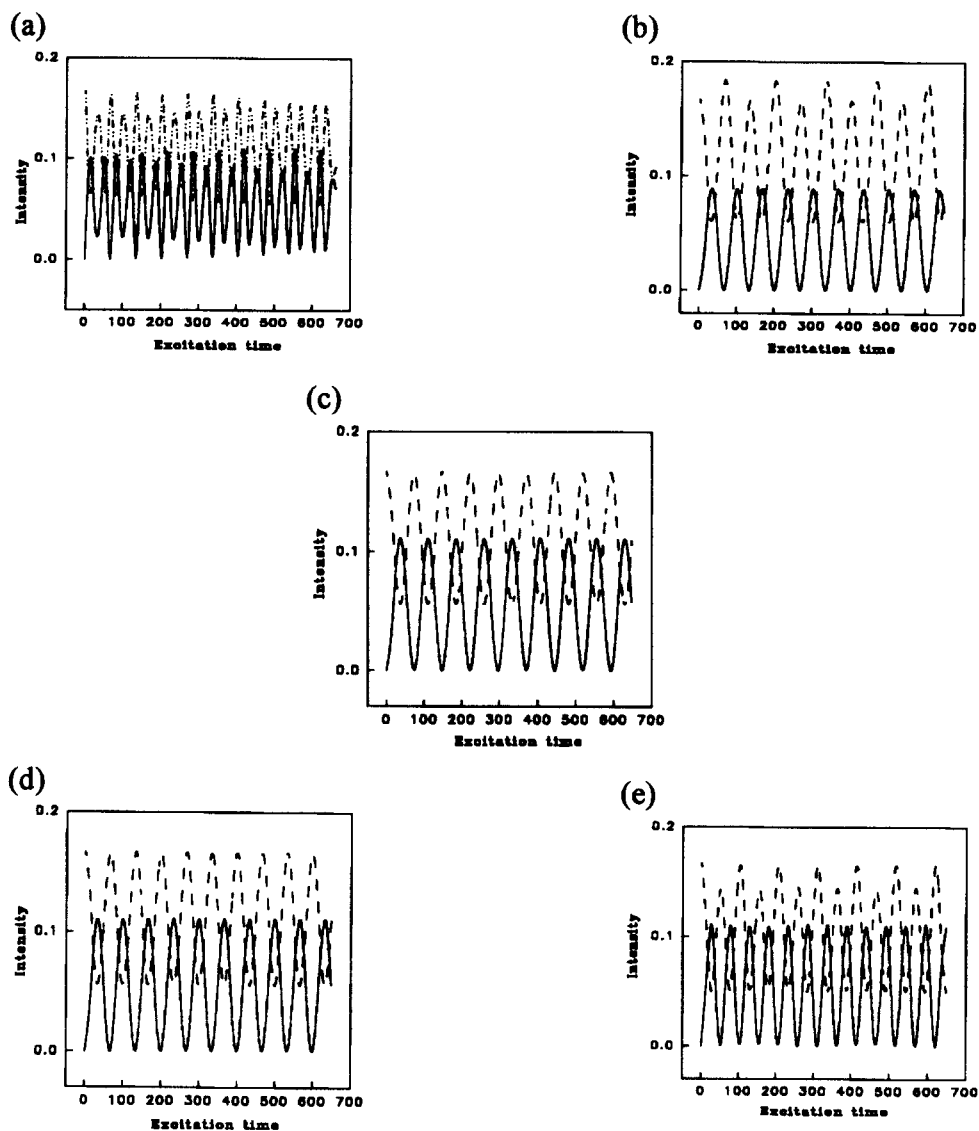
**Table 5.** The dipolar coupling constant and the frequency of MQ coherence in different oriented angle

$\theta$ (°)	Dipolar Coupling	Frequency(Hz)
0°	$-2 \cdot x$	7794.23
30°	$-1.25 \cdot x$	4938.27
54.7°	$-0.001758 \cdot x$	0
65°	$0.46 \cdot x$	1763.66
90°	$1 \cdot x$	3898.63
115°	$0.46 \cdot x$	1763.66
125.3°	$-0.001758 \cdot x$	0
150°	$-1.25 \cdot x$	4938.27
180°	$-2 \cdot x$	7794.23

**Fig. 7.** The frequency of zero and double coherence in different dipolar coupling constant

### *Multiple quantum coherence in $^{19}\text{F}$ - $^{19}\text{F}$ - $^{19}\text{F}$ Three-Spin System*

In case of three-spin system, we found out that multiple quantum coherence occurred by the combination of three components of dipolar coupling that make up three nuclei. Different from 2-spin system, irregular amplitude is shown, and the frequency on the same oriented angle also got bigger in 3-spin system. In the present study, the internuclear distance was fixed in both 2-spin and 3-spin systems and only the oriented angle on external magnetic field was changed, but since internuclear distance also affects on dipolar coupling so that form changes of multiple quantum coherence can be expected according to internuclear distance. Also, in case where nuclear spin system increased bigger than 3-spin system, not only severe frequency change but also decrease in attenuation occurs so that loss of the periodicity of harmonic oscillation can be found.



**Fig. 8.** Time development of zero and double quantum coherence in 3-spin system : (a) at  $0^\circ$  oriented angle, (b) at  $45^\circ$  oriented angle, (c) at  $54.7^\circ$  oriented angle, (d) at  $65^\circ$  oriented angle, (e) at  $90^\circ$  oriented angle

## CONCLUSIONS

In the present study, in single crystal that forms  $^{19}\text{F}$ - $^{19}\text{F}$  two-spin system and  $^{19}\text{F}$ - $^{19}\text{F}$ - $^{19}\text{F}$  three-spin system, the changes in the excited form of multiple quantum coherence according to anisotropic distribution was calculated using ANTIOPE program.

In  $^{19}\text{F}$ - $^{19}\text{F}$  two-spin system, the internuclear distance was set at 3.44 Å uniformly, and differing the oriented angle on external magnetic field randomly to ensure changes in dipolar coupling constant, and the form of dipolar quantum coherence according to the change changed proportionally with dipolar coupling constant. From this result, the agreement of the theoretical formula on multiple quantum coherence was verified, and as the absolute value of dipolar coupling constant got bigger, the frequency of multiple quantum coherence increased, but the amplitude had a fixed value from the lowest of 0 to the highest of '0.5'. Also at  $54.7^\circ$ , the dipolar coupling constant was shown to be 0; thus, we found out knew that multiple quantum coherence did not occur, and can verify directly that this process is the magic angle that used to eliminate the dipolar coupling component in solid NMR. Also, the period on random relative angle was 128.3  $\mu\text{sec}$   $\sim$  567  $\mu\text{sec}$ , and when using pulse sequence shown in Fig. 2, at least 128.3  $\mu\text{sec}$  pulse time was required to form one pulse in two spin system, and longer pulse time was needed as dipolar constant was smaller.

In case of the  $^{19}\text{F}$ - $^{19}\text{F}$ - $^{19}\text{F}$  three-spin system of an equilateral right-angled triangle with diagonal length of 1.414 Å, unlike the two-spin system, a little irregularity of amplitude was shown and the frequency on the same direction also got larger than that of two-spin system, by which the multiple quantum coherence was found to occur with the combination of the components of three dipolar coupling. Although the calculations were complex in the present study due to too many numbers of matrix component, based on the study results, multiple quantum coherence of n-spin system, where  $n \geq 4$  was larger than two or three spin system, could be inferred. In other words, as n gets bigger, the inter-spin interference proportion to pulse time gets bigger; thus, different from two-spin or three-spin system, the amplitude is more irregular and attenuate so that periodicity can be expected to be lost. Also, the results of the present study examined the characteristics of material from the biggest possible measurable size of multiple quantum coherence transition in n-spin system, thus, can be used as the basic method of determining actual size.

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