



Title	Solid State Chemical Exchange in Some Sodium Salts as Studied by 2D Nutation NMR
Author(s)	Ohki, Hiroshi
Citation	大阪大学, 1990, 博士論文
Version Type	VoR
URL	<a href="https://doi.org/10.11501/2964159">https://doi.org/10.11501/2964159</a>
rights	
Note	

*The University of Osaka Institutional Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

Solid State Chemical Exchange  
in Some Sodium Salts  
as Studied by 2D Nutation NMR

By  
Hiroshi Ohki

①

# SOLID STATE CHEMICAL EXCHANGE IN SOME SODIUM SALTS

## AS STUDIED BY 2D NUTATION NMR

BY

HIROSHI OHKI

DEPARTMENT OF CHEMISTRY

FACULTY OF SCIENCE

OSAKA UNIVERSITY

1990

## Contents

Abstract	1
1. Introduction	3
2. Theory	
2.1 Liouville Representation in NMR	6
2.2 2D nutation NMR	10
2.3 Chemical Exchange Effect	22
2.4 Chemical Exchange Effect on the 2D Nutation Spectrum	25
3. Simulation	
3.1 Principle	31
3.1.1 Diagonalization of the Liouvillians	31
3.1.2 Powder Averaging	37
3.1.3 Line Broadening	40
3.1.4 2D Fourier Transformation	40
3.2 Simulation Procedure	41
4. Sample	
4.1 $\text{NaNO}_2$ and $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$	45
4.2 $\text{Na}_2\text{SeO}_3$	45
4.3 $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$	45



5. Experiment	49
5.1 Sample Preparation	49
5.1.1 $\text{NaNO}_2$ and $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$	49
5.1.2 $\text{Na}_2\text{SeO}_3$	49
5.1.3 $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$	49
5.2 2D Nutation NMR	54
6. Data Analysis	57
6.1 Nutation Spectrum	57
6.2 Data Analysis	63
7. Discussion	89
7.1 Summary of the Present Work	89
7.2 2D Nutation NMR	91
7.3 Chemical Exchange Effect	97
8. Appendix	A-1

## Abstract

A new theoretical method which is based on the Liouville representation was established to describe the evolution of the quadrupolar spin system under the influence of strong rf field, which has been termed 'nutation'. The Liouville formalism was introduced to handle time development of the spin system and to construct the theoretical expression for the complex interactions between the rf field and the multilevel spin system. Although the dimension of the matrix to be determined becomes far larger than that based on standard density matrix or fictitious spin methods, the formalism with the Liouvillian can easily be coded for computation and therefore is much suitable for the calculation by big computers. Also the Liouville representation has a form which can incorporate effects other than spin interaction in a straightforward manner. This property makes it possible to apply the nutation method to chemically exchanging system.

The new method was coded by FORTRAN to prepare the general simulation program which is necessary for analyzing the experimental 2D nutation spectra. The program can be applied to quadrupolar nuclei with spin numbers  $3/2 \sim 9/2$  and to systems with and without chemical exchange.

The 2D nutation NMR experiments were conducted for  $^{23}\text{Na}$  in several compounds. The  $^{23}\text{Na}$  resonance in  $\text{NaNO}_2$  and in  $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$  was used to examine the optimal experimental conditions for the 2D nutation spectra and to evaluate the sensitivity of the spectra to the quadrupole coupling constant,  $e^2Qq/h$ , and the asymmetry parameter,  $\eta$ , of the electric field gradient at the site of the resonant nucleus.



The  $^{23}\text{Na}$  2D nutation NMR was applied to  $\text{Na}_2\text{SeO}_3$  to distinguish the three crystallographically nonequivalent Na sites in this compound. The quadrupole coupling constants at the individual sites could be determined and also  $\eta$  was estimated for two of the three sites in this material.

$\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$  has been known as a typical sodium ion conductor. The  $^{23}\text{Na}$  2D nutation NMR was used to obtain the direct information on the sodium transport in this material. The spectrum was remarkably temperature dependent and indicated unambiguously that the sodium ions are exchanging between the two nonequivalent sites. The spectrum was analyzed by the new theoretical method developed here and the rate of the Na ion exchange was estimated at each temperature. It was found that the activation energy deduced from the nutation spectra differs significantly from that determined by a previous conductivity measurement. The large discrepancy between the two values was interpreted qualitatively by the following model. In the 2D nutation NMR, the spectra are governed by the local exchange of the Na ion between two sites, whereas the net ionic conduction must accompany the long-range ion transport through the formation of vacancy in addition to the fluctuational exchange.

## 1. Introduction

Solid state nuclear magnetic resonance (NMR) can provide the information on the local static structure of the solid phase and molecular or ionic motions in the solid. The line splitting in single crystal and the line shape in powdered or polycrystalline material can now be routinely analyzed to determine the local structure of solid. Very often the line shape varies with temperature reflecting the onset of some molecular or ionic motion in solid. The measurements of line characteristics as well as the relaxation behavior of the spin system as a function of temperature (or pressure in some cases) give fruitful information on the molecular motion excited in the solid.

In the (solid) powdered samples, the spectra are broadened by several interactions such as dipole-dipole interaction, chemical shifts, and so on. For the quadrupolar nuclei which have the spins  $I$  greater than  $1/2$ , the structure of the spectrum is often determined by strong quadrupole interaction that is caused by the coupling between the nuclear electric quadrupole moment and the electric field gradient (EFG). The quadrupole interaction can be used to examine the local site symmetry of the resonant nucleus and the electronic structure of molecular and ionic species in the crystalline solid. The quadrupolar nuclei are also used as a powerful probe for the "slow" molecular motion in solid. In the case where the quadrupole interaction is sufficiently large, the usual pure nuclear quadrupole resonance can apply to determine the quadrupole coupling constant ( $e^2Qq/h$ ) and the asymmetry parameter of the electric field gradient ( $\eta$ ). If the  $e^2Qq/h$  is consider-



ably small, one observes the quadrupole interaction as a perturbation to the NMR. Sometimes the strength of the quadrupole interaction is comparable with those of other interactions. In such case the usual NMR on powdered specimen cannot separate the individual interactions.

Two- or multi-dimensional NMR methods evolve different interactions along different coordinate axes and examine the different interactions independently. 2D nutation NMR recently proposed is one of such methods. It separates the quadrupole interaction from chemical shift interaction and others by evolving these different interactions onto two directions. In this method one measures the central component of the spectrum which is perturbed by the second order quadrupole interaction for the half-integer spin system but, by evolving the spectrum onto different directions under a specific condition, one can pick up the quadrupole interaction in the form free from other interactions. An important character of the nutation NMR lies in that crystallographically nonequivalent sites can be distinguished and the quadrupole interaction parameters as well as the magnitude of the chemical shift at each site can be determined.

It seems promising to utilize the nutation NMR by making use of the most of its specific characters to examine the dynamic process, in other words, chemical exchange process between nonequivalent sites. Although the quadrupole interaction of deuterium has been widely used to trace the chemical exchange in solid state, there has not been developed any direct method to study the motion of the quadrupolar nuclei with half-integer spins in the solid state. Since in solid electrolytes and fast ionic conduc-



tors various ions play the main role and as many of these ions have half-integer spins, number of valuable information about the ionic motion can be obtained if the nutation NMR can be used to examine the motional process in solid.

In the present work, a theoretical formulation of the 2D nutation NMR method using a new technique based on the Liouville representation is given. Next a method to incorporate the chemical exchange into the theory of the nutation NMR will be developed. Then  $\text{NaNO}_2$  and  $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$  will be used to test the efficiency of this method for determination of the quadrupole interaction parameters.  $\text{Na}_2\text{SeO}_3$  is chosen to demonstrate how to separate and distinguish any crystallographically nonequivalent sites in crystal. Finally a model ionic conductor,  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ , is chosen to examine the effect of the chemical exchange on 2D nutation NMR spectrum, and the data were analyzed by the simulation method. The applicability of the 2D nutation NMR for chemically exchanging system will be discussed.

## 2. Theory

### 2.1. Liouville Representation in NMR

General treatment of pulsed NMR spectroscopy has been done using time dependent density matrix formalism. Throughout the text in this thesis, however, the Liouville (superoperator) formalism [1] will be used to describe the time evolution of the spin system. Since the Liouville representation is not familiar to the most of chemists, it seems to be the due course to give brief introduction of this special formalism. The Liouville representation is suitable for handling complicated time development of the density matrix and is well adopted to computer implementation, because it has a transparent presentation of the commutator which is by all means needed in the calculation of the evolution of density matrix. Hereafter, several important properties of the Liouville formalism are summarized in comparison with the usual Schrödinger representation.

a) In the Schrödinger representation, the density matrix  $\rho$  obeys the von Neumann equation of motion [2]

$$d\rho/dt = -i[H, \rho] , \quad (2.1.1)$$

where  $H$  is the total Hamiltonian of the system in the frequency units. In the Liouville formalism, the elements of the density matrix form density superkets (basis sets) and the time dependence of the density superkets is determined by the Liouvillian  $L$  :

$$d\mathbf{p}/dt = -iL\mathbf{p} , \quad (2.1.2)$$

where  $\mathbf{p}$  is the density superkets in the column form, i.e.,



$$\rho = {}^t(\rho_{11} \ \rho_{12} \ \rho_{13} \ \dots \ \rho_{1n} \ \rho_{21} \ \dots \ \dots \ \rho_{nn}) , \quad (2.1.3)$$

where  $n = 2I+1$  and  $I$  is the spin.  $L$  is defined through the relation

$$L = H \otimes E - E \otimes {}^tH , \quad (2.1.4)$$

where  $E$  is the unit operator which has the same dimension as  $H$ , and  ${}^tH$  represents the transposed matrix of  $H$  and  $\otimes$  stands for the direct product [3] of two matrices. (See appendix.)

When the Hamiltonian can be diagonalized by a Unitary matrix  $U$  through the similarity transformation :

$$H^d = U^{-1} H U , \quad (2.1.5)$$

( $H^d$  means diagonalized Hamiltonian,) then the Liouvillian can be diagonalized by the use of the same Unitary matrix :

$$\begin{aligned} L^d &= U^{-1} L U \\ &= (U^{-1} \otimes U^{-1})(H \otimes E - E \otimes {}^tH)(U \otimes U) \\ &= H^d \otimes E - E \otimes H^d , \end{aligned} \quad (2.1.6)$$

It should be noted that while the Hamiltonian plays the role of the operator characterizing the time evolution as well as that of operator specifying the energy of the system, the Liouvillian plays the former role only. This can be seen by the fact that, according to (2.1.6), the eigenvalues of Liouvillian consist of the differences of eigenvalues of the corresponding Hamiltonian.

b) When the Hamiltonian can be separated into a large time-independent interaction  $H_0$  and a much smaller term  $H_1$ , one often writes the equation of motion of the spin system

in the interaction representation which removes unnecessary term  $H_0$  from the Hamiltonian. In this case, the Liouvillian can be written

$$L = L_0 + L_1 , \quad (2.1.7)$$

where

$$L_0 = H_0 \otimes E - E \otimes {}^t H_0 , \quad (2.1.8a)$$

$$L_1 = H_1 \otimes E - E \otimes {}^t H_1 . \quad (2.1.8b)$$

Then the Liouville description of the interaction representation is expressed by

$$\rho^* = \exp(+iL_0 t) \rho , \quad (2.1.9)$$

$$L^* = \exp(+iL_0 t) L_1 \exp(-iL_0 t) , \quad (2.1.10)$$

where  $\rho^*$  and  $L^*$  are density superkets and Liouvillian in the interaction representation, respectively. Accordingly the equation of motion of the density superkets becomes

$$d\rho^*/dt = -iL^* \rho . \quad (2.1.11)$$

If the Liouvillian  $L^*$  is explicitly time-independent, Eq. (2.1.11) can be solved formally :

$$\rho^*(t) = \exp(-iL^* t) \rho(0) . \quad (2.1.12)$$

c) Another feature of the Liouville formalism is in its convenience in calculating the observables. For example, the magnetization along the x-axis is described in the Schrödinger representation as

$$M_x = \text{Tr}(I_x \rho) , \quad (2.1.13)$$

while in the Liouville formalism,

$$M_x = I_x p, \quad (2.1.14)$$

where  $I_x$  is the operator in the row form.

Thus one can write physical quantities simply as a product of matrices and vectors.

#### Appendix

The properties of direct product are summarized as follows. Direct product of two matrices  $A$  and  $B$  of  $n$  dimensions is defined by

$$A \times B = \begin{pmatrix} a_{11}B & a_{12}B & \dots & a_{1n}B \\ a_{21}B & a_{22}B & \dots & a_{2n}B \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ a_{n1}B & a_{n2}B & \dots & a_{nn}B \end{pmatrix}$$

Thus the resultant matrix has  $n^2$  dimension. And

$$(A + B) \otimes C = A \otimes C + B \otimes C,$$

$$(A \otimes B)(C \otimes D) = AC \otimes BD,$$

where  $+$  has usual meaning of matrix sum.



## 2.2. 2D Nutation NMR

In the high magnetic field, the NMR spectra of quadrupolar nuclei that have the spins  $I \geq 1$  consist generally of  $2I+1$  lines due to quadrupole interaction. In the powdered or polycrystalline samples the angles between the external magnetic field and the principal axes of the electric field gradient (EFG) are distributed at random in each microcrystal and therefore the spectra show characteristic powder patterns as exemplified in Fig. 2.1. The powder patterns shown in Fig. 2.1 are ideal ones and if such spectral patterns are observed one can analyze the spectra to determine the quadrupole interaction parameters. In many cases, however, powder spectrum gives indistinct structure owing to strong quadrupole interaction and/or dipolar interaction; sometimes the former makes the spectrum spread over several hundred kHz and as a result causes the signal to be buried under the noise.

For half-integer spins, the central peak, that corresponds to the transition between the spin states  $|+1/2\rangle \leftrightarrow |-1/2\rangle$ , can be almost always observed because it is not affected by quadrupole interaction in the first order perturbation. Therefore it is meaningful to search for a method or methods to determine the quadrupole interaction parameters from observed central transition only. One method widely used is the line shape analysis of the normal one dimensional (1D) spectrum, which is governed by the second order quadrupole interaction. But one weak point of this method lies in the fact that the interactions other than the quadrupole interaction cause the line broadening and/or line shift and it becomes difficult to determine the

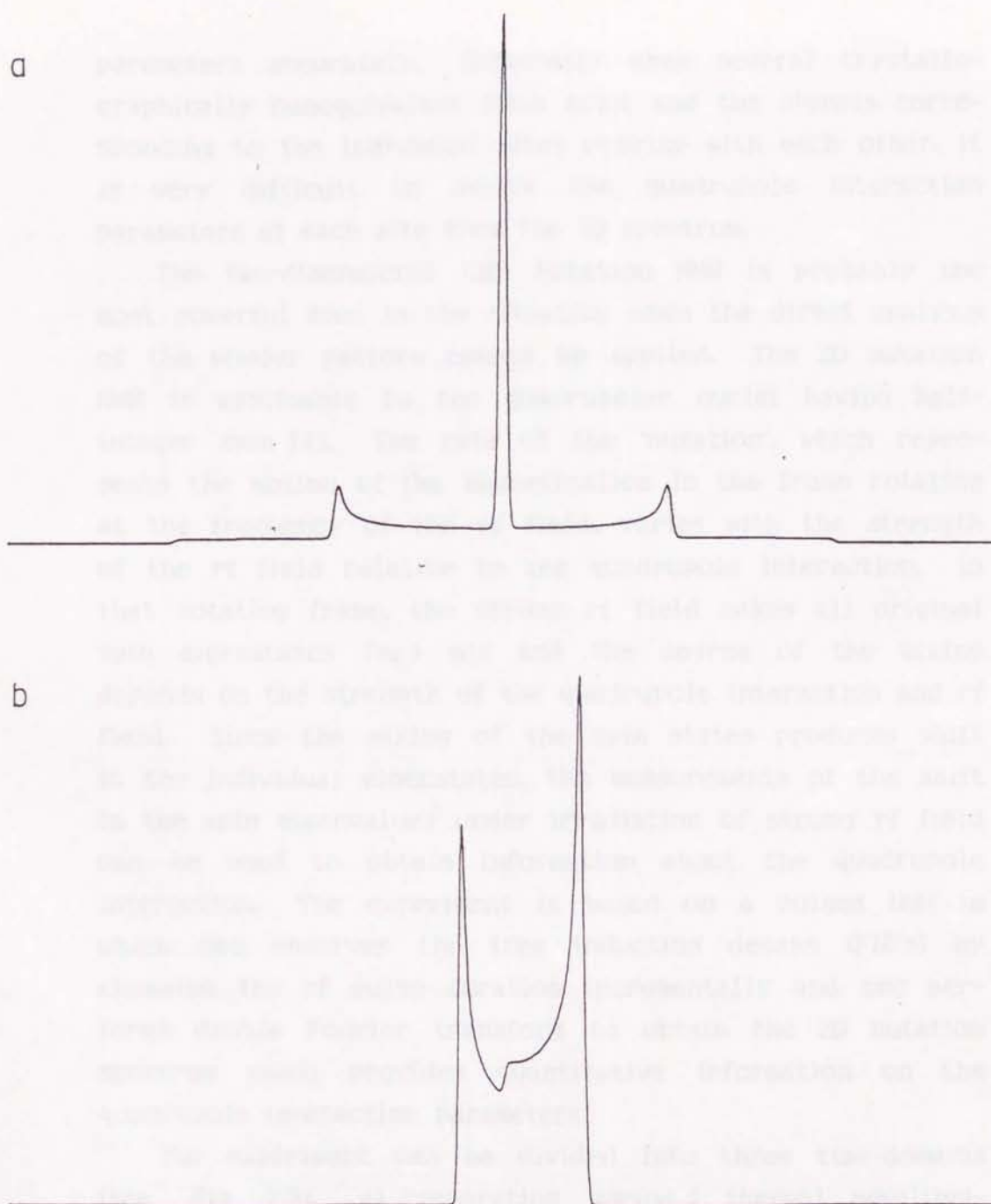


Figure 2.1

Simulated a) the first order and b) the second order powder lineshapes for  $I = 3/2$  ( $\eta = 0$ ).



parameters accurately. Especially when several crystallographically nonequivalent sites exist and the signals corresponding to the individual sites overlap with each other, it is very difficult to derive the quadrupole interaction parameters at each site from the 1D spectrum.

The two-dimensional (2D) nutation NMR is probably the most powerful tool in the situation when the direct analysis of the powder pattern cannot be applied. The 2D nutation NMR is applicable to the quadrupolar nuclei having half-integer spin [4]. The rate of the 'nutation', which represents the motion of the magnetization in the frame rotating at the frequency of the rf field, varies with the strength of the rf field relative to the quadrupole interaction. In that rotating frame, the strong rf field makes all original spin eigenstates  $|m_z\rangle$  mix and the degree of the mixing depends on the strength of the quadrupole interaction and rf field. Since the mixing of the spin states produces shift in the individual eigenstates, the measurements of the shift in the spin eigenvalues under irradiation of strong rf field can be used to obtain information about the quadrupole interaction. The experiment is based on a pulsed NMR in which one observes the free induction decays (FID's) by changing the rf pulse duration incrementally and one performs double Fourier transform to obtain the 2D nutation spectrum which provides quantitative information on the quadrupole interaction parameters.

The experiment can be divided into three time-domains (see Fig. 2.2). a) Preparation period : thermal equilibrium magnetization is established, b) Evolution period : the magnetization nutates around the rf field under the influ-

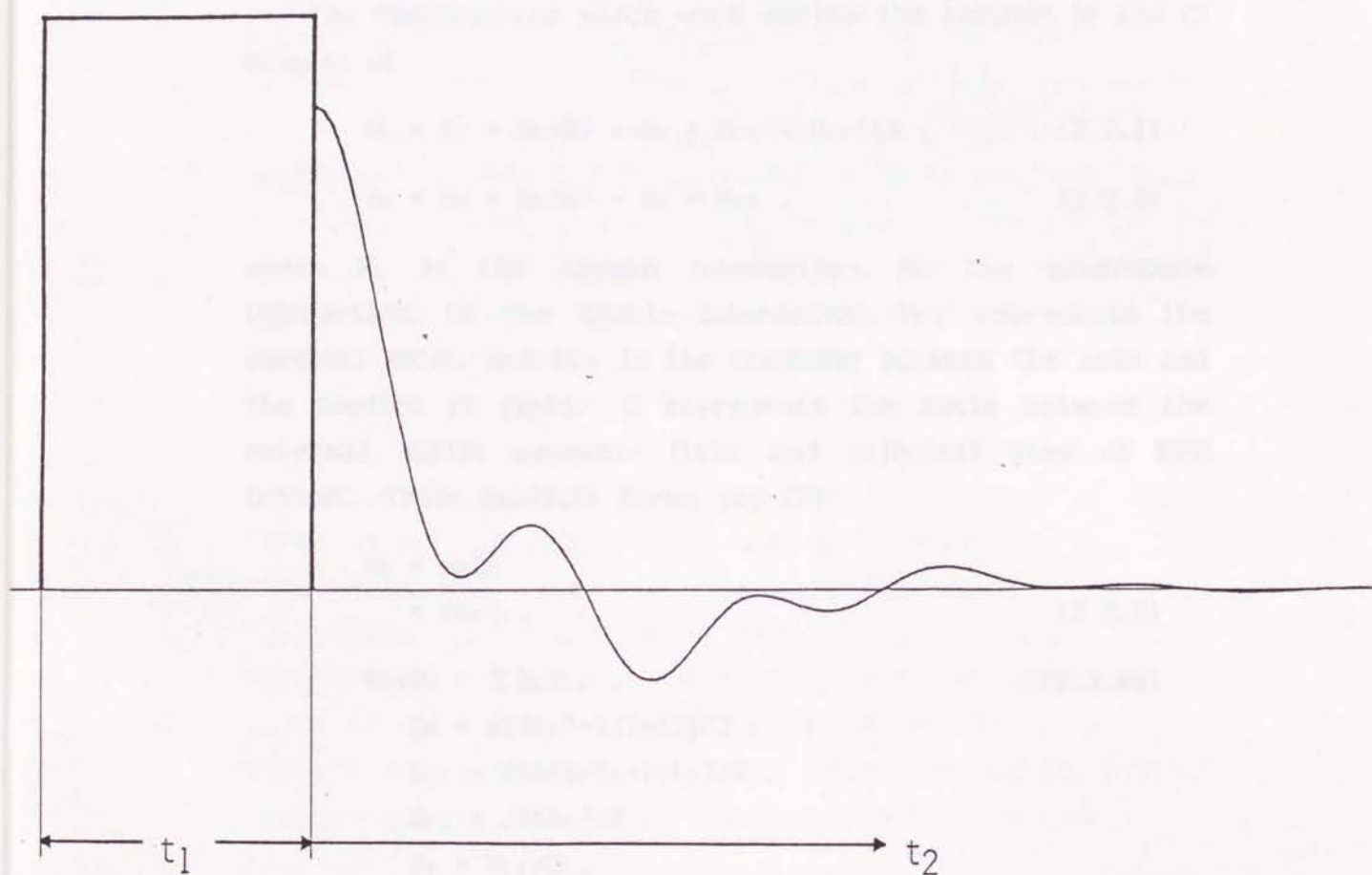


Figure 2.2  
Schematic representation of 2D nutation NMR experiment.

ence of an interaction Hamiltonian,  $H_1$ , during  $t_1$ , and  
c) Detection period : the magnetization along x-y plane in the laboratory frame is detected under the influence of another interaction,  $H_2$ , in the duration  $t_2$ .

The Hamiltonians which work during the periods b) and c) consist of

$$H_1 = H_z + H_Q(\Omega) + H_D + H_{CS} + H_{rf}(t) , \quad (2.2.1)$$

$$H_2 = H_z + H_Q(\Omega) + H_D + H_{CS} , \quad (2.2.2)$$

where  $H_z$  is the Zeeman interaction,  $H_Q$  the quadrupole interaction,  $H_D$  the dipole interaction,  $H_{CS}$  represents the chemical shift, and  $H_{rf}$  is the coupling between the spin and the applied rf field.  $\Omega$  represents the angle between the external static magnetic field and principal axes of EFG tensor. Their explicit forms are [2]

$$\begin{aligned} H_z &= \omega_0 I_z \\ &= \gamma H_0 I_z , \end{aligned} \quad (2.2.3)$$

$$H_Q(\Omega) = \sum Q_m V_{-m} , \quad (2.2.4a)$$

$$Q_0 = a[3I_z^2 - I(I+1)]/2 ,$$

$$Q_{\pm 1} = \sqrt{6}a[I_z I_{\pm} + I_{\pm} I_z]/4 ,$$

$$Q_{\pm 2} = \sqrt{6}a I_{\pm}^2/4 ,$$

$$V_0 = V_{zz}/2 ,$$

$$V_{\pm 1} = (V_{zx} \pm iV_{zy})/\sqrt{6} ,$$

$$V_{\pm 2} = (V_{xx} - V_{yy} \pm 2iV_{xy})/2\sqrt{6} ,$$

$$a = eQ/[I(2I-1)] , \quad (2.2.4b)$$

$$H_D = \sum I_i D I_j , \quad (2.2.5)$$

$$H_{CS} = H\sigma I , \quad (2.2.6)$$



and

$$H_{rf} = \omega_1 [I_x \cos(\omega_0 t) + i I_y \sin(\omega_0 t)] , \quad (2.2.7)$$

where  $\omega_0$  is the nuclear Larmor frequency,  $D$  and  $\sigma$  are the dipole interaction and the chemical shift tensors, respectively, and  $\omega_1$  is the strength of the rf field in the frequency units. Note that the Liouvillians in the absence of the chemical shift does not produce any net shift of the spectrum. (Although the quadrupole interaction leads to an asymmetric powder pattern, the center of gravity of its spectrum does not change. Also, the dipolar interaction makes the spectrum split but the center of gravity of the spectrum does not move.)

Henceforth, we will always assume that the relative strength of the different interactions is  $H_z \gg H_0 \approx H_{rf} \gg H_D, H_C$ . This situation is realized in the case of nuclei with fairly large quadrupole interaction such as  $^{23}\text{Na}$ ,  $^{39}\text{K}$ ,  $^{59}\text{Co}$ ,  $^{93}\text{Nb}$  etc. The most important condition is that the pulse apparatus can provide very strong rf field. Under above conditions one can treat the quadrupole interaction as well as the chemical shift as a perturbation and can neglect weaker dipole interaction. Then quadrupole interaction can be expanded up to the second order terms as

$$H_Q' = H_Q^{(1)} + H_Q^{(2)} , \quad (2.2.8)$$

where

$$\begin{aligned} H_Q^{(1)} &= e^2 q Q / 8 I (2I-1) (3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi) \\ &\quad \times [3 I_z^2 - I(I+1)] \\ &= \omega_Q [I_z^2 - I(I+1)/3] , \end{aligned} \quad (2.2.9)$$

and

$$\begin{aligned}
 H_Q^{(2)} = & (3e^2qQ/2I(2I-1))^2 I_z / 32\omega_0 \\
 & \times [ \{ 9(1-\cos^2\theta)^2 - 6\eta(1-\cos^4\theta)\cos 2\phi \\
 & + \eta^2(1+\cos^2\theta)^2\cos 2\phi + 4\eta^2\cos^2\theta(1-\cos^2 2\phi) \} \\
 & \times [2I_z^2 - 2I(I+1) + 1] \\
 & - \{ 9(1-\cos^2\theta)\cos^2\theta + 6\eta(1-\cos^2\theta)\cos^2\theta\cos 2\phi \\
 & + \eta^2(1-\cos^2\theta)\cos^2\theta\cos^2 2\phi \\
 & + \eta^2(1-\cos^2\theta)(1-\cos^2 2\phi) \} \\
 & \times 4[8I_z^2 - 4I(I+1) + 1] ] , \quad (2.2.10)
 \end{aligned}$$

where,  $\theta$  and  $\phi$  are the polar and the azimuthal angles of the direction of the static magnetic field with respect to the principal axes of the EFG, respectively, and others have usual meanings. The chemical shift interaction is represented by

$$H_{CS} = \sigma I_z , \quad (2.2.11)$$

Usually one can assume that the second order quadrupole interaction is negligible in the presence of a strong rf pulse, and the chemical shift term can be included in the Zeeman term, the Hamiltonians in Eqs. (2.2.1-2) can be redefined to be

$$H_1 = H_Q^{(1)} + H_{rf} , \quad (2.2.12)$$

and

$$H_2 = H_Q^{(1)} + H_Q^{(2)} . \quad (2.2.13)$$

The density superkets (Eq. (2.1.10)) at a time  $t_1+t_2$  becomes in the frame rotating at  $\omega_0$  (interaction representa-

tion),

$$\rho^*(t_1+t_2) = \exp(-iL_2^*t_2)\exp(-iL_1^*t_1)\rho(0), \quad (2.2.14)$$

and

$$L_1^* = H_1^* \otimes E - E \otimes H_1^*, \quad (2.2.15)$$

$$L_2^* = H_2^* \otimes E - E \otimes H_2^*, \quad (2.2.16)$$

where

$$H_1^* = H_0^* + H_{rf}^*, \quad (2.2.17)$$

$$H_2^* = H_0^*, \quad (2.2.18)$$

and

$$H_0^* = H_0^* = H_0^{(1)} + H_0^{(2)}, \quad (2.2.19)$$

$$H_{rf}^* = \omega_1 I_x, \quad (2.2.20)$$

In Eq. (2.2.14)  $\rho(0)$  is the density superkets at thermal equilibrium. In the high temperature approximation, it yields

$$\rho(0) = (1 - \hbar\omega_0 I_z/kT)/(2I+1), \quad (2.2.21)$$

assuming that the Zeeman coupling dominates other interactions. The unit ket 1 in Eq. (2.2.21) can be always disregarded in the calculation since it does not contribute to signal.

Hereafter, Eq. (2.2.14) is solved for  $I = 3/2$  as an example with respect to each period, i.e., evolution and detection periods.

a) Evolution period

Before examining the general feature of the nutation



NMR, two limiting cases will be studied as an illustration.

In the evolution period an rf pulse,  $H_1 = \omega_1/\gamma$ , is applied on the spin system. If the rf strength is much stronger than the quadrupole interaction, the spin system can be treated as if the quadrupole interaction is absent while the rf field is applied. Then the Hamiltonian becomes

$$H_1 = \begin{pmatrix} 0 & \sqrt{3}\omega_1/2 & 0 & 0 \\ \sqrt{3}\omega_1/2 & 0 & \omega_1 & 0 \\ 0 & \omega_1 & 0 & \sqrt{3}\omega_1/2 \\ 0 & 0 & \sqrt{3}\omega_1/2 & 0 \end{pmatrix}. \quad (2.2.22)$$

This Hamiltonian can be diagonalized through a similarity transformation by the orthogonal matrix :

$$R = \begin{pmatrix} \sqrt{3} & 1 & -1 & \sqrt{3} \\ -1 & \sqrt{3} & \sqrt{3} & 1 \\ -1 & \sqrt{3} & -\sqrt{3} & -1 \\ \sqrt{3} & 1 & 1 & -\sqrt{3} \end{pmatrix} / 2\sqrt{2}, \quad (2.2.23)$$

and the corresponding eigenvalues are  $-\omega_1/2$ ,  $3\omega_1/2$ ,  $\omega_1/2$ , and  $3\omega_1/2$ . Then one can immediately show that the magnetization nutates around the rf field at the characteristic frequency  $\omega_1$ .

In the opposite case when the rf pulse strength is much smaller than the quadrupole interaction, the rf pulse can merely excites the central transition when the rf frequency satisfies nearly the resonance condition, and so no effective mixing of the eigenstates occurs. This is because the energy difference of the adjacent levels is quite different from each other. Hence one can pick up the components concerning with the central transition from the Hamiltonian

$$H' = \begin{pmatrix} 0 & \omega_1 \\ \omega_1 & 0 \end{pmatrix}, \quad (2.2.24)$$

and this has the eigenvalues  $\pm\omega_1$ . Therefore the motion of the magnetization is represented by the rotation at frequency of  $2\omega_1$ . In general, it can be shown that the magnetization corresponding to the central transition rotates at  $(I+1/2)\omega_1$  [2].

In summary, when quadrupole interaction is weak enough compared with the strength of the rf field, then the magnetization nutates at  $\omega_1$ , and in the opposite case the magnetization nutates at  $(I+1/2)\omega_1$ .

If the quadrupole interaction and the rf field are comparable in magnitude, the nutational motion becomes complex. The equation of motion of the spin system in such complex cases has been solved using several different techniques [5]. In the present work a new technique based on the Liouville representation is introduced to solve the problem.

The matrix representation of the Hamiltonian in the period  $t_1$  can be written as

$$H_1 = \begin{pmatrix} \omega_0 & \sqrt{3}\omega_1/2 & 0 & 0 \\ \sqrt{3}\omega_1/2 & -\omega_0 & \omega_1 & 0 \\ 0 & \omega_1 & -\omega_0 & \sqrt{3}\omega_1/2 \\ 0 & 0 & \sqrt{3}\omega_1/2 & \omega_0 \end{pmatrix}, \quad (2.2.25)$$

where  $\omega_0$  is defined in Eq. (2.2.9). This Hamiltonian can be diagonalized through the similarity transformation by the orthogonal matrix [6]



$$Q = \begin{pmatrix} \cos\theta_- & -\sin\theta_- & -\sin\theta_+ & \cos\theta_+ \\ \sin\theta_- & \cos\theta_- & \cos\theta_+ & \sin\theta_+ \\ \sin\theta_- & \cos\theta_- & -\cos\theta_+ & -\sin\theta_+ \\ \cos\theta_- & -\sin\theta_- & \sin\theta_+ & -\cos\theta_+ \end{pmatrix} / \sqrt{2}, \quad (2.2.26a)$$

$$\tan 2\theta_{\pm} = (\sqrt{3}/2)\omega_1 / (\omega_0 \pm \omega_1/2), \quad (2.2.26b)$$

and the corresponding eigenvalues are

$$\begin{aligned} \lambda_1 &= \omega_1/2 + (\omega_1^2 + \omega_0^2 - \omega_1\omega_0)^{1/2}, \\ \lambda_2 &= \omega_1/2 - (\omega_1^2 + \omega_0^2 - \omega_1\omega_0)^{1/2}, \\ \lambda_3 &= -\omega_1/2 - (\omega_1^2 + \omega_0^2 + \omega_1\omega_0)^{1/2}, \\ \lambda_4 &= -\omega_1/2 + (\omega_1^2 + \omega_0^2 + \omega_1\omega_0)^{1/2}. \end{aligned} \quad (2.2.27)$$

The Liouvillian can be diagonalized by taking account of Eq. (2.1.6) and it leads to the density superkets at the end of the pulse as

$$\rho^*(t_1) = R \exp(-iL_d t_1) R^{-1} \rho(0), \quad (2.2.28a)$$

or

$$\rho_j^*(t_1) = \sum [R_{jk} R_{k1} \rho_1(0)] \exp(-i\lambda_l t_1), \quad (2.2.28b)$$

where  $\lambda_l$  is the  $l$ -th eigenvalue of the Liouvillian. In the above Eq. (2.2.28b),  $A_{j1} = \sum [R_{jk} R_{k1} \rho_1(0)]$  is called the 'transition amplitude' which represents the intensity of the component with the frequency  $\lambda_l$ .

b) Detection period

After the rf pulse field is switched off, the Hamiltonian (also the Liouvillian) is diagonal and the density superkets at a time  $t_1+t_2$  is given by

$$\rho^*(t_1+t_2) = \exp(-iL_2 t_2) \rho^*(t_1). \quad (2.2.29)$$

A lengthy manipulation yields the result that the signal corresponding to the central transition at a given orientation of the principal axes of the EFG with respect to  $H_0$  is proportional to

$$\begin{aligned}
 S(t_1+t_2) \propto & \{ [3\sin 2\theta - \sin 2\theta, -(1-\cos 2\theta)(1+\cos 2\theta)] \sin(\lambda_3 - \lambda_1) t_1 \\
 & - [3\sin 2\theta - \sin 2\theta, +(1-\cos 2\theta)(1-\cos 2\theta)] \sin(\lambda_4 - \lambda_1) t_1 \\
 & - [3\sin 2\theta - \sin 2\theta, +(1+\cos 2\theta)(1+\cos 2\theta)] \sin(\lambda_3 - \lambda_2) t_1 \\
 & + [3\sin 2\theta - \sin 2\theta, -(1+\cos 2\theta)(1-\cos 2\theta)] \sin(\lambda_4 - \lambda_2) t_1 \} \\
 & \times \exp(-i\omega_q^{(2)} t_2) ,
 \end{aligned}
 \tag{2.2.30}$$

where  $\omega_q^{(2)}$  is the second order quadrupole shift of the central transition expressed by [7]

$$\begin{aligned}
 \omega_q^{(2)} = & (e^2 q Q / h)^2 / 192 \omega_0 \\
 & \times \{ 9(1 - \cos^2 \theta)^2 - 6\eta(1 - \cos^4 \theta) \cos 2\phi \\
 & + \eta^2(1 + \cos^2 \theta)^2 \cos^2 2\phi + 4\eta^2 \cos^2 \theta (1 - \cos^2 2\phi) \\
 & - 72(1 - \cos^2 \theta) \cos^2 \theta - 48\eta(1 - \cos^2 \theta) \cos^2 \theta \cos 2\phi \\
 & - 8\eta^2(1 - \cos^2 \theta) \cos^2 \theta \cos^2 2\phi \\
 & - 8\eta^2(1 - \cos^2 \theta)(1 - \cos^2 2\phi) \} .
 \end{aligned}
 \tag{2.2.31}$$

Eq. (2.2.30) indicates that four of six transitions between the four eigenvalues contribute to the spectrum and their transition frequencies can be determined by numerical analysis of the spectrum. It should be noted that Eq. (2.2.30) consists of two parts; one is the nutation which is merely a superposition of sine functions of  $t_1$ , and the other depends on  $t_2$  and is governed by the second order quadrupole interaction.

### 2.3. Chemical Exchange Effect

Chemical exchange means that the nucleus jumps between the 'sites' whose environments are different from each other, i.e., crystallographically nonequivalent sites in solids.

The basic assumption of the chemical exchange is that the principle of detailed balance between the sites is satisfied, i.e.,

$$p_j k_{ji} = p_i k_{ij} , \quad (2.3.1)$$

where  $p_j$  stands for the thermal equilibrium population of the  $j$ -th site and  $k_{ji}$  represents the exchange rate from the  $j$ -th to  $i$ -th site. Then one can write the exchange matrix for  $m$  sites :

$$K = \begin{pmatrix} k_{11} & k_{12} & \dots & k_{1m} \\ k_{21} & k_{22} & \dots & k_{2m} \\ \cdot & \cdot & \dots & \cdot \\ k_{m1} & k_{m2} & \dots & k_{mm} \end{pmatrix} , \quad (2.3.2)$$

where the diagonal component  $k_{ii}$  is the rate of jump from  $i$ -th site to another, i.e., the reciprocal of the average life time at the  $i$ -th site. The sign of  $k_{ii}$  is taken to be negative (or zero). Each column must satisfy the following relation

$$k_{j1} + k_{j2} + \dots + k_{jm} = 0 . \quad (2.3.3)$$

Another assumption adopted here is that the spin-spin interaction between the sites is extremely small and can be neglected. This assumption makes possible to describe the Liouvillian and the density superkets in a simple form.



In principle, in the case where the chemical exchange occurs among the  $m$  sites, the density superkets  $\rho$  is defined by [8]

$$\rho = \rho^{(1)} \otimes \rho^{(2)} \otimes \dots \otimes \rho^{(m)} , \quad (2.3.4)$$

where  $\rho^{(j)}$  represents the density superkets at the  $j$ -th site and  $\otimes$  means the direct product of the kets. Eq. (2.3.4) tells that the cross terms between the density superkets at different sites should be calculated in order to describe the time evolution of the system. Since such cross terms appear mainly as a result of the interaction between spins at different sites, and fortunately, the spin-spin interaction between quadrupolar nuclei is usually very weak, one can ignore this type of interaction. Then, the total density superkets can be reduced as follows :

$$\rho = \rho^{(1)} \oplus \rho^{(2)} \oplus \dots \oplus \rho^{(m)} , \quad (2.3.5)$$

where  $\oplus$  means the direct sum of the density superkets. Similarly, the Liouvillian consists in principle of complex components if we take account of the interaction between the different sites. However, if we disregard the spin-spin interaction as mentioned above, the Liouvillian can be written in a simple form as

$$L = \begin{pmatrix} L^{(1)} & 0 & 0 & \dots & 0 \\ 0 & L^{(2)} & 0 & \dots & 0 \\ 0 & 0 & L^{(3)} & \dots & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots \\ 0 & 0 & 0 & \dots & L^{(m)} \end{pmatrix} , \quad (2.3.6)$$

where  $L^{(j)}$  is the Liouvillian corresponding to the  $j$ -th

site.

When the chemical exchange occurs, under the assumption that the exchange between the sites is instantaneous, the spin does not change its state during the jump. In other words no relaxation occurs in the course of the exchange process. Then

$$d\rho/dt = -(iL+K)\rho, \quad (2.3.7)$$

and

$$K = \begin{pmatrix} k_{11} & k_{12} & k_{13} & \dots & k_{1m} \\ k_{21} & k_{22} & k_{23} & \dots & k_{2m} \\ . & . & . & \dots & . \\ k_{m1} & k_{m2} & k_{m3} & \dots & k_{mm} \end{pmatrix} \otimes E_k, \quad (2.3.8)$$

where  $E_k$  is  $(2I+1)^2$  dimensional unit matrix.

#### 2.4. Chemical Exchange Effect on the Nutation Spectrum

In this section, two-site exchange is examined for simplicity but the extension to the general multisite case is straightforward.

In usual treatment of the chemical exchange, the effect of chemical exchange on the spin system is neglected during the short rf pulse so as to simplify the problem. But in this work, the exchange of spins should be taken into account because it has severe effect on the nutation spectrum.

The Liouvillians corresponding to the  $j$ -th site are

$$L^{(j)}_1 = L_0^{(j)} + L_{cs}^{(j)} , \quad (2.4.1a)$$

$$L^{(j)}_2 = L_0^{(j)} + L_{cs}^{(j)} + L_{rf} , \quad (2.4.1b)$$

where  $L_0^{(j)}$  and  $L_{cs}^{(j)}$  stand for quadrupole interaction and chemical shift at the  $j$ -th site, respectively. The exchange matrix becomes

$$K = \begin{pmatrix} k_1 & -k_2 \\ -k_1 & k_2 \end{pmatrix} \otimes E_k . \quad (2.4.2)$$

Thus the density superkets at a time  $t_1+t_2$  becomes

$$\rho(t_1+t_2) = \exp\{-(iL_2+K)t_2\} \exp\{-(iL_1+K)t_1\} \rho(0) , \quad (2.4.3)$$

where  $L_1$  and  $L_2$  are the Liouvillians in the presence and absence of the rf pulse, respectively.

Now two limiting cases are examined.

i) Slow motion regime :  $k_1, k_2 \ll H_0, H_{rf}$

In this case the chemical exchange effect can be treated as a perturbation because the effect on the spectrum from



the chemical exchange is small compared with that from the quadrupole and rf couplings. Then one can diagonalize the Liouvillian alone by means of the orthogonal matrix Eq. (2.2.26) :

$$\begin{aligned} L^d &= \begin{pmatrix} Q^{-1(1)} & 0 \\ 0 & Q^{-1(2)} \end{pmatrix} \begin{pmatrix} L^{(1)} & 0 \\ 0 & L^{(2)} \end{pmatrix} \begin{pmatrix} Q^{(1)} & 0 \\ 0 & Q^{(2)} \end{pmatrix} \\ &= \begin{pmatrix} L^{d(1)} & 0 \\ 0 & L^{d(2)} \end{pmatrix}. \end{aligned} \quad (2.4.4)$$

And the exchange matrix becomes

$$K^s = \begin{pmatrix} k_1 E_K & -Q^{(1)-1} k_2 Q^{(2)} \\ -Q^{(2)-1} k_1 Q^{(1)} & k_2 E_K \end{pmatrix}. \quad (2.4.5)$$

According to the perturbation theory, the diagonal terms of the exchange matrix should cause the change of the spectrum in the first order. Hence the line width of the peak corresponding to each site is determined by the exchange rate  $k_1$  and  $k_2$ , respectively.

ii) Fast Motion Regime :  $k_1, k_2 \gg H_0, H_{rf}$

In the opposite case, one must diagonalize the exchange matrix and treat the quadrupole and rf pulse as the perturbation. To diagonalize the exchange matrix, one must symmetrize the exchange matrix if it is not symmetric. This symmetrization can be done by the matrix  $P$ ,

$$P_{ij} = \sqrt{p_i} \delta_{ij} \quad (2.4.6)$$

through the similarity transformation, where  $\delta_{ij}$  stands for the Kronecker's delta. The Liouvillian is not altered and the exchange matrix becomes

$$\begin{aligned}
K^S &= \begin{pmatrix} 1/\sqrt{p_1} & 0 \\ 0 & 1/\sqrt{p_2} \end{pmatrix} \begin{pmatrix} -k_1 & k_2 \\ k_1 & -k_2 \end{pmatrix} \begin{pmatrix} \sqrt{p_1} & 0 \\ 0 & \sqrt{p_2} \end{pmatrix} \otimes E_k, \\
&= \begin{pmatrix} -k_1 & k' \\ k' & -k_2 \end{pmatrix} \otimes E_k.
\end{aligned} \tag{2.4.7}$$

This can be diagonalized by

$$\begin{aligned}
K^d &= \begin{pmatrix} \cos\Phi & -\sin\Phi \\ \sin\Phi & \cos\Phi \end{pmatrix} \begin{pmatrix} -k_1 & k' \\ k' & -k_2 \end{pmatrix} \begin{pmatrix} \cos\Phi & \sin\Phi \\ -\sin\Phi & \cos\Phi \end{pmatrix} \otimes E_k, \\
&= \begin{pmatrix} -(k_1+k_2) & 0 \\ 0 & 0 \end{pmatrix} \otimes E_k,
\end{aligned} \tag{2.4.8a}$$

$$\tan 2\Phi = 2k'/(k_1 - k_2), \tag{2.4.8b}$$

and so the Liouvillian is expressed as

$$\begin{aligned}
L^f &= \begin{pmatrix} L^{(1)} + L^{(2)} & 0 \\ 0 & L^{(1)} + L^{(2)} \end{pmatrix} \\
&\quad + (L^{(1)} - L^{(2)}) \begin{pmatrix} \cos 2\Phi & \sin 2\Phi \\ \sin 2\Phi & -\cos 2\Phi \end{pmatrix}.
\end{aligned} \tag{2.4.9}$$

Here the diagonal blocks of the Liouvillian determine predominantly the spectral appearance. However the components of the Liouvillian corresponding to  $-(k_1+k_2)$  decrease so fast that these can be neglected. Then the spectrum is characterized by :

$$\begin{aligned}
&(1 - \cos 2\Phi)L^{(1)} + (1 + \cos 2\Phi)L^{(2)} \\
&= p_1 L^{(1)} + p_2 L^{(2)}.
\end{aligned} \tag{2.4.10}$$

Thus the spectrum is described by the use of the weight-averaged Liouvillian. In the case of the two-site jump the time-averaged spectrum shows a characteristic pattern de-

pending on the relative orientation of the principal axes of the EFG tensor at the two sites. Hence the analysis of the spectrum at fast motion regime can determine the angle between the EFG principal axes at the two sites.

### iii) Intermediate cases

The spectrum will change its appearance drastically if the rate of chemical exchange becomes comparable to the difference of the nutation frequencies at different sites. Therefore the 2D nutation spectrum can be applied to chemically exchanging systems to determine the rate of exchange when it is of the comparable order with  $e^2Qq/h$  (and also with  $\omega_1$ ). For the analysis of the complicated spectrum in the above region one must simulate the nutation spectrum with the exchange rate as a variable parameter.



## References

- [1] See, for example,  
R.R. Ernst, G. Bodenhausen, and A. Wokaun,  
*Principles of Nuclear Magnetic Resonance  
in One and Two Dimensions*, Oxford Press, 1987.  
J. Jeener,  
*Superoperators in Magnetic Resonance*,  
Adv. Magn. Reson., Vol. 10, Academic Press, 1982.
- [2] A. Abragam,  
*Principle of Magnetic Resonance*,  
Oxford University Press, 1961.
- [3] G. Arfken,  
*Mathematical Methods for Physicists*,  
Academic Press, 1970.
- [4] A. Samoson and E. Lippmaa,  
*Chem. Phys. Lett.*, **100**(3), 205 (1983).  
A. Samoson and E. Lippmaa,  
*Phys. Rev.*, B **28**, 6567 (1983).
- [5] H. Ohki, N. Nakamura, and H. Chihara,  
*27th NMR touronkai yokousyuu*, Sapporo, 1988.  
R. Janssen, and W.S. Veeman,  
*J. Chem. Soc., Faraday Trans. I*, **84**, 3747 (1988).  
P.P. Man,  
*J. Magn. Reson.*, **67**, 78 (1986).

- [6] L. Pandey, S. Towta, and D.G. Hughes,  
*J. Chem. Phys.*, **85**, 6923 (1986).
- [7] D.R. Torgeson and R.G. Barnes,  
*J. Chem. Phys.*, **62**(10), 3968 (1975).
- [8] J. Sandström,  
*Dynamic NMR Spectroscopy*, Academic Press, 1982
- [9] T.E. Bull,  
*J. Magn. Reson.*, **8**, 344 (1972).

### 3. Simulation

#### 3.1. Principle

##### 3.1.1. Diagonalization of the Liouvillians

In the case when only one kind of site exists, the calculation is straightforward since the analytical expression given in Sec. 2.2 can be applied. Even when several nonequivalent sites exist in the crystal and when no chemical exchange occurs, the whole spectrum can be represented by the superposition of the spectrum corresponding to each site. In the case where the chemical exchange occurs, one should calculate the Eq. (2.4.3), or equivalent to say, one must diagonalize the matrices in each period numerically. Because the matrices  $L_1+K$  and  $L_2+K$  in Eq. (2.4.3) are complex and non-Hermitian and have very large dimension of  $(2I+1)^2 \times (\text{number of site})$ , they cannot be diagonalized directly by the usual methods. Then several modifications on the matrices must be made.

At first, the exchange matrix should be transformed by the matrix  $P$  so as to symmetrize the whole matrix. Then,

$$\begin{aligned} L^s_1 &= (P^{-1} \otimes E_k)(L_1 + K)(P \otimes E_k) \\ &= L_1 + K^s, \end{aligned} \quad (3.1.1a)$$

$$\begin{aligned} L^s_2 &= (P^{-1} \otimes E_k)(L_2 + K)(P \otimes E_k) \\ &= L_2 + K^s, \end{aligned} \quad (3.1.1b)$$

where

$$K^s = (P^{-1} \otimes E_k)K(P \otimes E_k), \quad (3.1.1c)$$

and  $P$  is defined by Eq. (2.4.6). Then it is proved that the matrix  $L^s_1$  (and also  $L^s_2$ ) can be diagonalized by a complex orthogonal matrix. (The complex orthogonal matrix means



that the multiplication of its transposed matrix and itself yields the unit matrix.) It should be noted that the exchange matrix is symmetrized by the above transformation which is however independent of the Liouvillian at each site.

In the evolution period when rf pulse is applied, another transformation is needed to reduce the dimension of the matrix to be diagonalized. This can be achieved by transforming the  $I_z$  basis\* to  $I_x$  basis [1]. When the rows and the columns are suitably interchanged, the Liouvillian at the  $j$ -th site  $L_j$  can be factorized so as to have a block-diagonal structure whose blocks have the dimension  $(2I+1)^2/4 = 4$ .

$$\begin{aligned} L_j^x &= (RT)^{-1} L_j (RT) \\ &= \begin{bmatrix} A_j & & & 0 \\ & B_j & & \\ & & B'_j & \\ 0 & & & A'_j \end{bmatrix}, \end{aligned} \quad (3.1.2)$$

and density superket at the site  $j$  becomes

$$\rho_j^x = (RT)^{-1} \rho_j, \quad (3.1.3)$$

where  $R = R \otimes R$  ( $R$  is defined in Eq. (2.2.23)) is an

---

\* ' $I_z$  basis' means that the axis parallel to the static external magnetic field is the quantization axis. Thus  $I_z$  becomes good quantum number. Also, ' $I_x$  basis' means that the axis parallel to the rf field is the quantization axis and in this choice of the basis,  $I_x$  is good quantum number.

orthogonal matrix which operates to transform the basis from  $I_z$  to  $I_x$ , and  $T$  the matrix to interchange the rows and the columns. By this transformation, the exchange matrix remains unchanged. The explicit matrix forms of the block matrices  $A$ ,  $A'$ ,  $B$ , and  $B'$  for  $I = 3/2$  are :

$$A_j = \begin{pmatrix} 0 & \sqrt{3}\omega_{Qj} & -\sqrt{3}\omega_{Qj} & 0 \\ \sqrt{3}\omega_{Qj} & -2\omega_{Qj} + 4\omega_1 & 0 & -\sqrt{3}\omega_{Qj} \\ -\sqrt{3}\omega_{Qj} & 0 & 2\omega_{Qj} - 4\omega_1 & \sqrt{3}\omega_{Qj} \\ 0 & -\sqrt{3}\omega_{Qj} & \sqrt{3}\omega_{Qj} & 0 \end{pmatrix} / 2 , \quad (3.1.4a)$$

$$B_j = \begin{pmatrix} 2\omega_{Qj} + 2\omega_1 & \sqrt{3}\omega_{Qj} & \sqrt{3}\omega_{Qj} & 0 \\ \sqrt{3}\omega_{Qj} & 6\omega_1 & 0 & \sqrt{3}\omega_{Qj} \\ \sqrt{3}\omega_{Qj} & 0 & -2\omega_1 & \sqrt{3}\omega_{Qj} \\ 0 & \sqrt{3}\omega_{Qj} & \sqrt{3}\omega_{Qj} & -2\omega_{Qj} + 2\omega_1 \end{pmatrix} / 2 , \quad (3.1.4b)$$

$$B'_j = \begin{pmatrix} -2\omega_{Qj} - 2\omega_1 & -\sqrt{3}\omega_{Qj} & -\sqrt{3}\omega_{Qj} & 0 \\ -\sqrt{3}\omega_{Qj} & -6\omega_1 & 0 & -\sqrt{3}\omega_{Qj} \\ \sqrt{3}\omega_{Qj} & 0 & -2\omega_1 & -\sqrt{3}\omega_{Qj} \\ 0 & -\sqrt{3}\omega_{Qj} & -\sqrt{3}\omega_{Qj} & 2\omega_{Qj} - 2\omega_1 \end{pmatrix} / 2 , \quad (3.1.4c)$$

$$A'_j = \begin{pmatrix} 0 & -\sqrt{3}\omega_{Qj} & \sqrt{3}\omega_{Qj} & 0 \\ -\sqrt{3}\omega_{Qj} & 2\omega_{Qj} + 4\omega_1 & 0 & \sqrt{3}\omega_{Qj} \\ \sqrt{3}\omega_{Qj} & 0 & -2\omega_{Qj} - 4\omega_1 & -\sqrt{3}\omega_{Qj} \\ 0 & \sqrt{3}\omega_{Qj} & -\sqrt{3}\omega_{Qj} & 0 \end{pmatrix} / 2 , \quad (3.1.4d)$$

where  $\omega_{Qj}$  represents the first order quadrupole interaction at the site  $j$ . The corresponding density superkets at  $j$ -th



site transformed as the Liouvillian are given by :

$$\rho^x_j = p_j^{-1} ( 0 \ 0 \ 0 \ 0 \ \sqrt{3} \ 3 \ 0 \ -\sqrt{3} \ \sqrt{3} \ 3 \ 0 \ -\sqrt{3} \ 0 \ 0 \ 0 \ 0 ), \quad (3.1.5)$$

Because the elements of the density superkets corresponding to the matrices A and A' on the basis  $I_x$  are zero at thermal equilibrium, these can be disregarded. Because the matrices B and B' are complex conjugates with each other and the density superkets corresponding to B and B' are identical at time zero, the matrix to be diagonalized is reduced to

$$L^{s_1'} = \begin{pmatrix} iB_1 - k_1 E_B & k'E_B \\ k'E_B & iB_2 - k_2 E_B \end{pmatrix}, \quad (3.1.6)$$

where  $B_j$  is given in Eq. (3.1.4b) and  $E_B$  is the unit matrix which has the same dimension as  $B_j$ 's.

Although the  $I_x$  basis is very convenient for diagonalizing the Liouvillian, it is not suitable for calculation of the FID's since the transition observed in the detection period is labelled by the transition between the quantum number  $m_z$ , which is the eigenvalues of  $I_z$ . Then it has to be put back to the  $I_z$  basis.

In the detection period, the Liouvillian is diagonal and exchange matrix merely couples the density superkets with the same labels belonging to different sites. Then one calculates a matrix which consists of the elements concerning only with the central transition. Because the dimension of its matrix,  $L^{s_2'}$ , is the number of the sites, this matrix can be easily diagonalized compared with that in the evolution period.

Then the FID signal at a time  $t_1+t_2$  becomes



$$\begin{aligned}
S(t_2, t_1) &\propto I_X \rho(t_2, t_1) \\
&= \sum P_{ij} Q_{2ij} \exp[-iL_2^d t_2] Q_2^{-1}{}_{jk} \\
&\quad \times R_{kl} Q_{1lm} \exp[-iL_1^d t_1] Q_1^{-1}{}_{mn} \rho_X(0)_n,
\end{aligned}
\tag{3.1.7}$$

where  $Q_1$  and  $Q_2$  are complex orthogonal matrices which diagonalize  $L_1^s$  and  $L_2^s$ , respectively.

The Liouvillians  $L_1^s$  and  $L_2^s$  have special properties : It is symmetric (or can be symmetrized by the method described in Sec. 3.1), and all their elements distant from the diagonal element by a certain fixed number, which denotes a band width, are zero. These properties can be fully utilized to perform the numerical diagonalization. There are many possible methods to do this but the present work adopts a method which consists of two stages [2]. First is to find a transformation which reduces the band width and gives the symmetric tridiagonal matrix but keeps the symmetric and bandform characters of the Liouvillians unchanged. This is accomplished by the successive Jacobi rotation in the plane of  $i$  and  $j = i+1$  which is the orthogonal transformation

$$J(i,j,\chi) = \begin{pmatrix} \dots & \cdot & \cdot & \cdot & \cdot & \dots \\ \dots & \cdot & \cdot & \cdot & \cdot & \dots \\ \dots & 1 & 0 & 0 & 0 & \dots \\ \dots & 0 & \cos\chi & \sin\chi & 0 & \dots \\ \dots & 0 & -\sin\chi & \cos\chi & 0 & \dots \\ \dots & 0 & 0 & 0 & 1 & \dots \\ \dots & \cdot & \cdot & \cdot & \cdot & \dots \\ \dots & \cdot & \cdot & \cdot & \cdot & \dots \end{pmatrix} \begin{matrix} \\ \\ i) \\ j) \\ \\ \end{matrix} \quad (3.1.8)$$

This procedure is for eliminating the matrix element at  $(i,i+1)$ . Although the Jacobi rotation creates a new non-zero element at  $(i+b,j+b)$ , where  $b$  is the band width of the matrix, a series of rotations gives rise to result that  $i+b$  or  $j+b$  is greater than the dimension of the matrix. Thus one can eliminate the element without creating another one. These transformations are continued until the matrix is tridiagonalized. Then the Liouvillian becomes

$$L^T = \Pi(J^{-1})L^S\Pi J, \quad (3.1.9)$$

where  $L^T$  has zero off-diagonal elements except those immediately adjacent to the diagonal one.

Secondly, the matrix is diagonalized by the QR method. Let  $A_0$  be a general symmetric  $n$ -dimensional matrix to be diagonalized. An origin-shift parameter  $s_j$  is suitably selected so as to realize the factorization  $A_j - s_j E = Q_j R_j$  where  $Q_j$  is a complex orthogonal matrix and  $R_j$  is an upper triangular matrix, then  $A_{j+1} = Q_j^{-1} A_j Q_j$  can be obtained. When this procedure is iterated it can be shown that this series of matrices similar to  $A_0$  generally tends to an upper



triangular matrix. Since  $A_0$  is a tridiagonal matrix, the resultant matrix is diagonal and its diagonal elements give the eigenvalues in this case.

In each step of iteration, the origin shift is chosen to be one of the two eigenvalues of  $2 \times 2$  submatrix at the bottom right-hand corner that has smaller modulus. The Jacobi rotations to effect the decomposition  $A_j - s_j E = Q_j R_j$  is used to triangularize  $A_j$ , i.e., in the rotations in the planes  $(i, r+1)$  where  $i=1, 2, \dots, r$ , rotation angle is determined such that the element  $(r+1, i)$  becomes zero.

The actual diagonalization subprogram is the modification of the one in the NUMPAC routine in the Nagoya University. First stage of the tridiagonalization is referred to [2]. And second stage is QR method modified by the use of complex orthogonal matrix instead of Unitary matrix.

### 3.1.2 Powder Averaging

In the powdered samples, the crystals are oriented at random with respect to the magnetic field. Thus one must designate the orientation of the principal axes of the EFG tensor with respect to the static magnetic field so as to perform the powder averaging [3] :

$$f(t_2, t_1) = \int d\phi \int \sin\theta d\theta S(t_2, t_1) . \quad (3.1.10)$$

The coordinate transformation from the laboratory frame to the crystalline frame (a coordinate fixed in the crystalline specimen) is represented by the rotation :



$$R_c = \begin{pmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\phi & \cos\phi & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{pmatrix}, \quad (3.1.11)$$

where  $\theta$  and  $\phi$  are the polar and the azimuthal angles of the crystalline frame referred to the direction of the static magnetic field, respectively. When the EFG principal axes at the site  $j$  are indicated by the Euler angles  $\alpha$ ,  $\beta$ , and  $\gamma$  in the crystalline frame by :

$$R_j = \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix} \begin{pmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (3.1.12)$$

then the matrix representing the rotation from the orientation of the magnetic field to the EFG principal axes is given by

$$R_j'(\theta_j, \phi_j) = R_j R_c. \quad (3.1.13)$$

Here, the terms needed in the actual calculation are

$$\begin{aligned} z_j^2 &= \cos^2\theta_j, \\ x_j^2 - y_j^2 &= \sin^2\theta_j \cos 2\phi_j, \end{aligned} \quad (3.1.14)$$

where

$$\begin{aligned} x_j &= [\cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma]x_c \\ &\quad + [\cos\alpha\cos\beta\sin\gamma + \sin\alpha\cos\gamma]y_c - \cos\alpha\sin\beta z_c, \\ y_j &= -[\sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma]x_c \\ &\quad - [\sin\alpha\cos\beta\sin\gamma - \cos\alpha\cos\gamma]y_c + \sin\alpha\sin\beta z_c, \\ z_j &= \sin\beta\cos\gamma x_c + \sin\beta\sin\gamma y_c + \cos\beta z_c, \end{aligned} \quad (3.1.15)$$

and

$$\begin{aligned}x_c &= \sin\theta\cos\phi, \\y_c &= \sin\theta\sin\phi, \\z_c &= \cos\theta,\end{aligned}\quad (3.1.16)$$

where  $\theta_j$  and  $\phi_j$  are the polar angles of the EFG principal axes with respect to the magnetic field at the site  $j$ . By the use of  $z_j^2$  and  $x_j^2 - y_j^2$ , the first and the second order quadrupole interactions are expressed by

$$\omega_Q^{(1)}{}_j = e^2qQ/8I(2I-1)\{3z_j^2 - 1 + \eta(x_j^2 - y_j^2)\}, \quad (3.1.17)$$

$$\begin{aligned}\omega_Q^{(2)}{}_j &= (e^2qQ/h)^2/192\omega_0 \\&\quad \{9(1-z_j^2)^2 - 6\eta(1+z_j^2)(x_j^2 - y_j^2) \\&\quad \quad + 4\eta^2z_j^2 + \eta^2(x_j^2 - y_j^2)^2 \\&\quad - 72z_j^2(1-z_j^2) - 48\eta z_j^2(x_j^2 - y_j^2) \\&\quad - 8\eta^2(1-z_j^2) + 8\eta^2(x_j^2 - y_j^2)^2\}.\end{aligned}\quad (3.1.18)$$

Then the calculation must be performed over the ranges  $0 < \theta < \pi$ , and  $-\pi < \phi \leq \pi$  in order to accomplish the powder averaging.

In the actual calculation,  $\cos\theta$  is used instead of  $\theta$  because the powder averaging (3.1.10) can be rewritten as

$$f(t_2, t_1) = \int d\phi \int d(\cos\theta) S(t_2, t_1). \quad (3.1.19)$$

Thus the region of the integration is divided into  $N$  with respect to  $\cos\theta$  ( $-1 < \cos\theta < +1$ ) and  $\phi$  ( $-\pi < \phi \leq \pi$ ).

In the case where only one kind of site exists, one can tentatively coincide the crystalline frame with the EFG

principal axes. Since  $S(t_2, t_1)$  is symmetric with respect to  $\cos\theta$  and  $\phi$ , the number of calculation can be reduced by a factor of 4 of the total division.

### 3.1.3 Line Broadening

The line broadening effect should be incorporated as the multiplication of the FID's Eq. (3.1.19) by the Gaussian (or Lorentzian) function. Since the origin of the line broadening is mainly due to dipole interaction in the detection period but the distribution of (static) quadrupole interaction and/or dipole interaction cause the line broadening in the evolution period, the broadening factors in each period may be different, and in practice they are used as adjustable parameters. Other reasons which bring about the line broadening are discussed later.

### 3.1.4 2D Fourier transformation

The FID's obtained by the above procedure should be Fourier-transformed to deduce the 2-dimensional spectrum.

$$g(\omega_2, \omega_1) = \int \exp(-i\omega_2 t_2) dt_2 \int \exp(-i\omega_1 t_1) dt_1 f(t_2, t_1), \quad (3.1.20)$$

where  $f(t_2, t_1)$  is given in Eq. (3.1.19).



### 3.2 Computational Procedure

Two simulation programs were constructed, one for the simulation of 2D nutation spectrum without chemical exchange and the other with chemical exchange.

Brief explanation of the former is given in the following. Although the analytical expression has been given, the diagonalization is performed numerically so as to be able to treat the general case in which spin  $I \geq 3/2$ .

#### 1) Parameter Input

Input the parameters necessary to simulate the spectrum.  
spin number  
Larmor frequency  
quadrupole coupling constant and asymmetry parameter  
rf pulse strength in the frequency unit  
number of experiments and increment of the pulse length  
number of sampling points and sampling interval  
number of division over the sphere for numerical integration

#### 2) Quadrupole Interaction

The first and the second order quadrupole interactions are determined at a given angle  $\theta$  and  $\phi$  with respect to the external magnetic field.

#### 3) Calculation of the FID

Diagonalize the Hamiltonian and calculate the evolution of the density matrix to evaluate the FID signal. These are accumulated in the range  $0 \leq \cos\theta < 1$ , and  $0 \leq \phi < \pi$ .

Short explanation of the simulation program with chemical exchange is given below.

1) Parameter Input

Input the parameters necessary to calculate the FID's.

Larmor frequency

number of site for exchange

$e^2qQ/h$ ,  $\eta$  and the Euler angles

which relate the crystalline frame

and the principal axes of the EFG at each site

relative population of each site

chemical exchange rate between any pair of the sites

rf pulse strength in the frequency unit

number of experiments and increment of the pulse length

number of sampling points and sampling interval

number of division over the sphere for numerical integration

2) Quadrupole interaction at a given orientation

The first and the second order quadrupole interactions are calculated at a given angle  $\theta$  and  $\phi$  with respect to the external magnetic field.

3) Calculation of FID

Diagonalize the Liouvillians corresponding to each dimension and calculate the FID.

These are summed over the sphere in the range  $-1 < \cos\theta < 1$  and  $-\pi < \phi \leq \pi$ .

In each case, the number of divisions over the sphere is chosen to be sufficient to produce the powder spectrum, i.e., 3000-10000. A set of data points  $128 \times 256$  are used to calculate the FID's. The program lists are given in

Appendix. The program is coded in FORTRAN and calculated by the ACOS-6 of the computer center of Osaka University and/or NEC PC-9801E/VM personal computer.

The Fourier transformation (Eq. (3.1.20)) was done by the use of the ASPECT-3000 minicomputer incorporated in the BRUKER MSL-200 NMR system. The ASPECT-3000 is equipped with an array processor which can execute the 2D Fourier transformation very efficiently and with the plotting routine to draw up the spectrum. The data conversion program provided by BRUKER Co. Ltd. was modified to convert the data format between the MS-DOS operating system on NEC PC-9801 personal computer and the ASPECT-3000 system. The line broadening parameters can also be defined in the ASPECT-3000 system.



## References

- [1] R. Janssen and W.S. Veeman,  
*J. Chem. Soc., Faraday Trans., I*, **84**, 3747 (1988).
- [2] R.G. Gordon and T. Messenger,  
in *Electron Spin Relaxation in Liquids*,  
Ed. by L.T. Muus and P.W. Atkins, Plenum Press, 1972.
- [3] See, for example,  
U. Haeberlen,  
*High Resolution NMR in Solids*,  
Adv. Magn. Reson., suppl. 1, Academic Press, 1976.

#### 4. Sample

##### 4.1. $\text{NaNO}_2$ and $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$

$\text{NaNO}_2$  crystallizes in an orthorhombic (space group  $\text{Im}2\text{m}$ ) crystal system with the unit cell dimension of  $a = 3.569 \text{ \AA}$ ,  $b = 5.563 \text{ \AA}$ , and  $c = 5.384 \text{ \AA}$ ,  $Z = 2$ . [1]

Crystal of  $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$  is orthorhombic (space group  $\text{Pnma}$ ) with four molecules in the unit cell [2]. The lattice parameters are :  $a = 9.372 \text{ \AA}$ ,  $b = 4.037 \text{ \AA}$ , and  $c = 18.71 \text{ \AA}$ . Sodium atoms are coordinated by two  $\text{H}_2\text{O}$  molecules and four chlorine atoms.

Both of the above compounds have only one kind of sodium site and can be used to preliminary test of 2D nutation NMR method.

##### 4.2 $\text{Na}_2\text{SeO}_3$

This crystal has three nonequivalent sodium sites [3]. This sample can be used to examine whether 2D nutation NMR method can be applied to determine the quadrupole interaction parameters at each site.

##### 4.3. $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$

The system  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$  has been known to be a fast alkali-ion conductor. [4] The crystal structure is shown in Fig. 4.1. [5] Complete solid solution exists for the composition between  $x = 0$  and 3 and the crystal structure varies between  $\text{R}3$  ( $0.0 \leq x < 1.8$ ,  $2.2 < x \leq 3.0$ ) and  $\text{C}2/c$  ( $1.8 \leq x \leq 2.2$ ). The latter is a slightly deformed structure of the former. The structure consists of a three-dimensional skeletal network of  $\text{PO}_4$  (and/or  $\text{SiO}_4$ ) tetrahedra which are corner-shared with  $\text{ZrO}_6$  octahedra. The  $\text{ZrO}_6$  octahedron is linked by three  $\text{PO}_4$  tetrahedra so as to form a ribbon along the hexagonal  $c$ -axis and also linked by six  $\text{PO}_4$

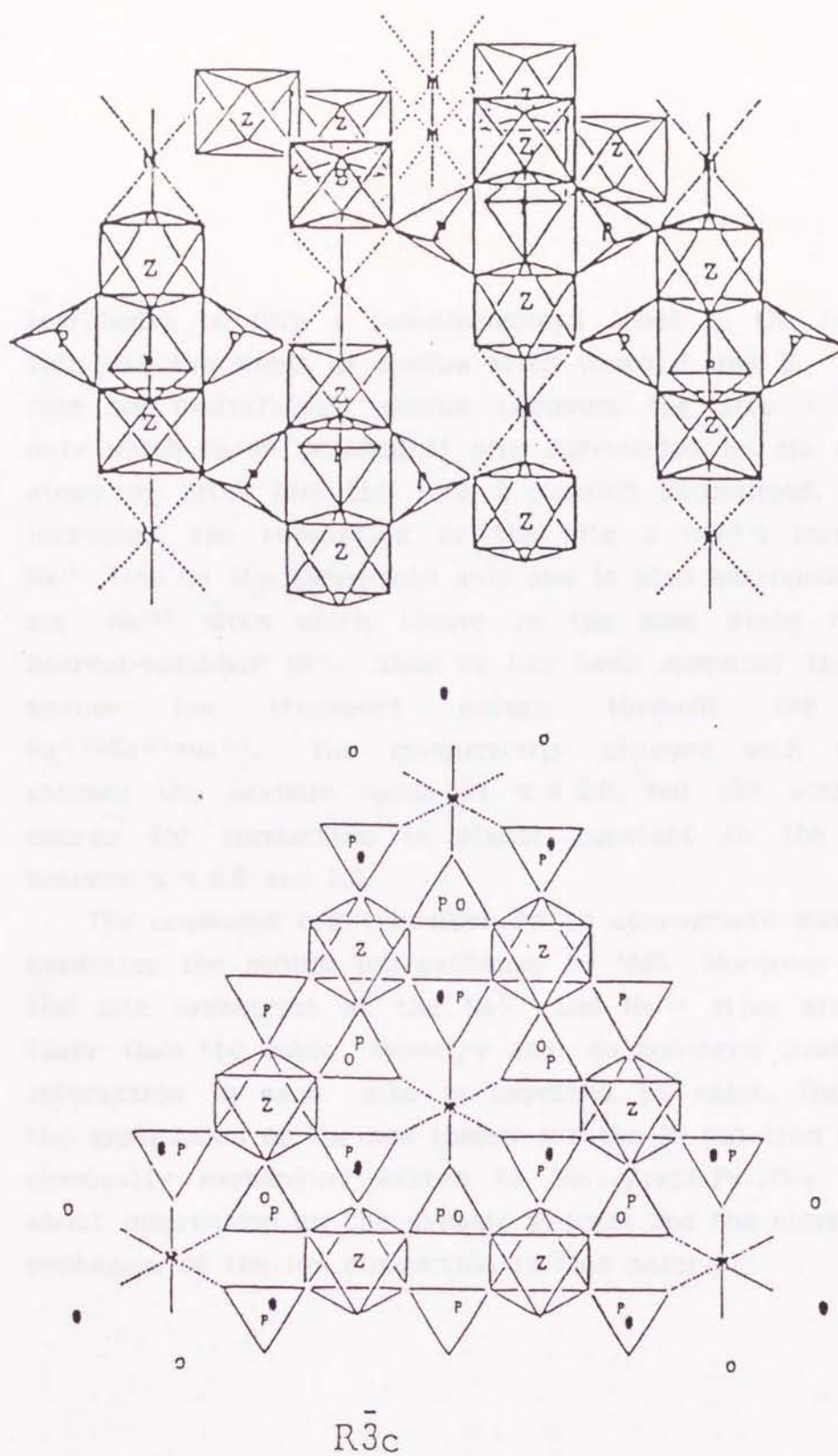


Figure 4.1

Crystal structure of  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ .



tetrahedra to form a two-dimensional sheet in the c-plane. This has two kinds of sodium sites named 1 and 2. In the case  $x=0$  ( $\text{NaZr}_2\text{P}_3\text{O}_{12}$ ), sodium occupies the site 1 ( $\text{Na}^{(1)}$ ) only which is an octahedral site surrounded by six oxygen atoms of  $\text{ZrO}_6$ , and the site 2 remains unoccupied. As  $x$  increases, the population of the site 2 ( $\text{Na}^{(2)}$ ) increases.  $\text{Na}^{(1)}$  lies on the three-fold axis and is also surrounded by six  $\text{Na}^{(2)}$  sites which locate in the same plane of the nearest-neighbor  $\text{O}^{2-}$ . Thus it has been supposed that the sodium ion transport occurs through the path  $\text{Na}^{(1)} \rightarrow \text{Na}^{(2)} \rightarrow \text{Na}^{(1)}$ . The conductivity changes with  $x$  and assumes the maximum value at  $x = 2.0$ , but the activation energy for conduction is almost constant in the range between  $x = 0.0$  and  $3.0$ .

The compound can therefore be an appropriate model for examining the sodium ion exchange by NMR. Moreover, since the site symmetries at the  $\text{Na}^{(1)}$  and  $\text{Na}^{(2)}$  sites are both lower than the cubic symmetry and so non-zero quadrupole interaction in each site is expected to exist. Therefore the application of the new theory for the 2D nutation NMR on chemically exchanging system to  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$  brings about information on the dynamic process and the microscopic mechanism of the ion conduction in this material.

## References

- [1] R.W.G. Wyckoff,  
*Crystal Structures*, 2nd Ed., Vol. 2,  
John Wiley & Sons, 1964
- [2] R.W.G. Wyckoff,  
*Crystal Structures*, 2nd Ed., Vol. 3,  
John Wiley & Sons, 1965
- [3] G. Perinet, P. Bianco, and R. Sabbah,  
*Bull. Soc. Fr. Mineral. Cristallogr.*, **91**(4), 396(1968).
- [4] J.B. Goodenough, H.Y-P. Hong, and J.A. Kafalas,  
*Mat. Res. Bull.*, **11**, 203 (1976).
- [5] H.Y-P. Hong,  
*Mat. Res. Bull.*, **11**, 173 (1976).

## 5. Experiment

### 5.1. Sample Preparation

#### 5.1.1. $\text{NaNO}_2$ and $\text{NaHgCl}_2 \cdot 2\text{H}_2\text{O}$

$\text{NaNO}_2$  is of commercial source (Nacalai Tesque, guaranteed reagent grade, purity 98.0%) and used without further purification.

$\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$  was prepared from aqueous solution of the appropriate mixture of  $\text{NaCl}$  (Tomita Seiyaku) and  $\text{HgCl}_2$  (Nacalai Tesque, guaranteed reagent grade, purity 99.5%). Colorless polycrystals were grown by slow evaporation of water. The X-ray powder diffraction pattern of this product (Fig. 5.1) was compared with that calculated with the lattice parameters given in the literature [1]. The result identified  $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$  but indicated at once the existence of small amount of  $\text{HgCl}_2$ . However, this  $\text{HgCl}_2$  impurity is supposed to have little influence on the NMR of  $^{23}\text{Na}$ .

#### 5.1.2. $\text{Na}_2\text{SeO}_3$

$\text{Na}_2\text{SeO}_3$  was prepared from aqueous solution of a stoichiometric mixture of  $\text{NaOH}$  (Nacalai Tesque, reagent grade, purity 93%) and selenious acid  $\text{H}_2\text{SeO}_3$ . [2]  $\text{H}_2\text{SeO}_3$  is prepared by dissolving  $\text{SeO}_2$  (Nacalai Tesque, guaranteed reagent grade, purity 98%) in water. Slow evaporation of the solution gave the white powder.

#### 5.1.3. $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$

The powdered specimen was synthesized from the stoichiometric mixture of  $\text{Na}_2\text{CO}_3 : \text{ZrO}_2 : \text{SiO}_2 : \text{NH}_4\text{H}_2\text{PO}_4 = 1+x : 4 : 2x : 2(3-x)$ ,  $x=0.0, 1.0$ , and  $2.0$ . [2] The reagents used here were :  $\text{Na}_2\text{CO}_3$ , Nacalai Tesque, guaranteed reagent grade, purity 99.5%;  $\text{ZrO}_2$ , Nacalai Tesque, reagent grade;



SAMPLE NAME: NAHGCL3  
 TARGET : Cu  
 VOL and CUR: 40KV 40mA  
 SLITS : 05 1 R5 .15 SS 1  
 SCAN SPEED: 4 DEG/MIN.  
 STEP/SAMPL.: .02 DEG  
 PRESET TIME: 0 SEC  
 FILE NAME : NAHG100  
 OPERATOR : YAMAMOTO  
 COMMENT :

DATE: 00.06.14  
 SHOOTING NO.: 9  
 THRESH. INTEN.: 355 CPS  
 2nd DERIV.: 2442 CPS/(DEG\*DEG)  
 WIDTH: .09 DEG  
 B.G. (SAMP.): 32  
 B.G. (CYCLE): 32  
 OUTPUT FILE :

Sample Name : NAHGCL3

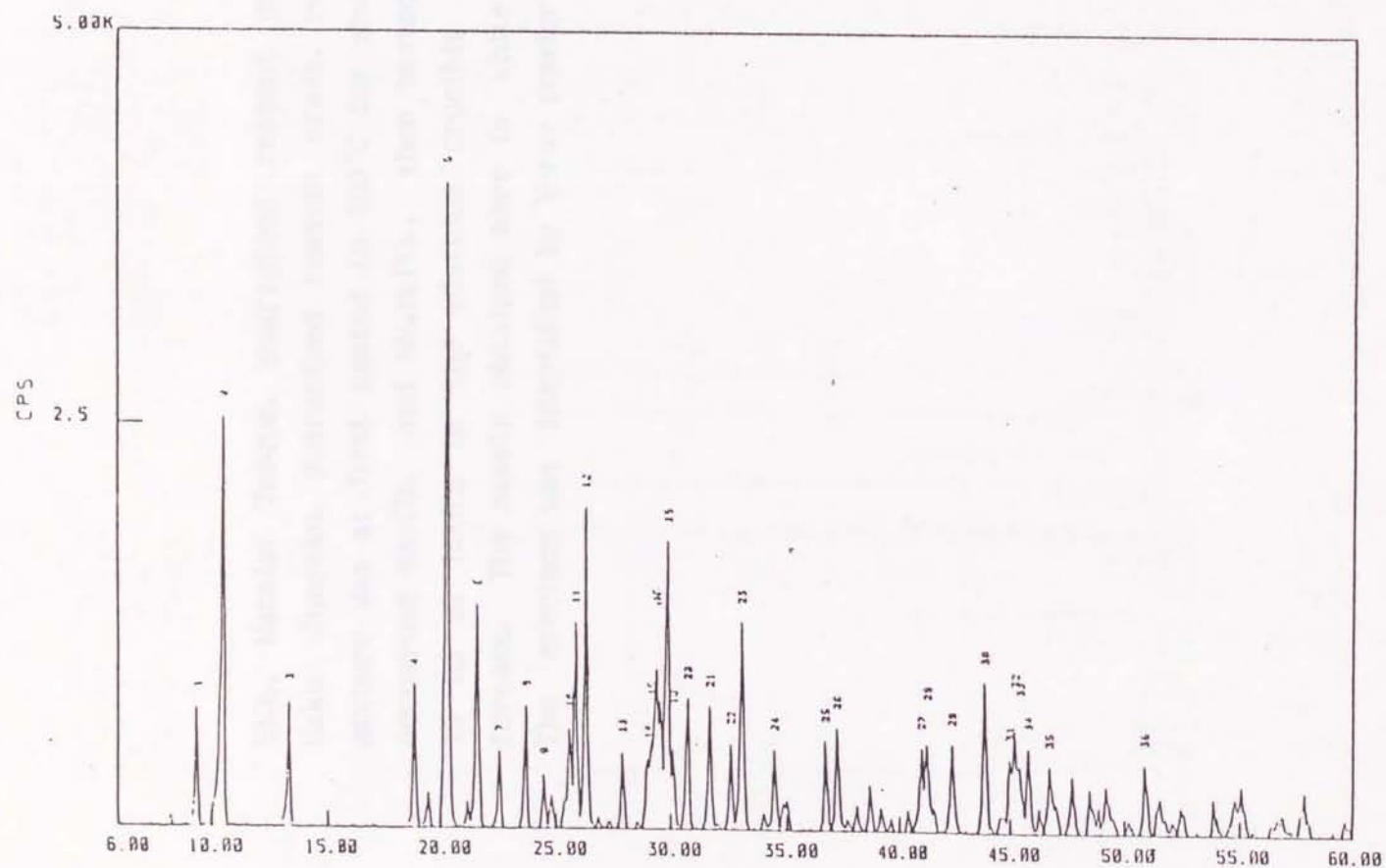


Figure 5.1  
 The X-ray powder diffraction pattern of  $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$ .

SiO<sub>2</sub>, Nacalai Tesque, guaranteed reagent grade; NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, Wako Junyaku, guaranteed reagent grade, purity 98%. The mixture was at first heated to 900°C for several hours to decompose Na<sub>2</sub>CO<sub>3</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, then heated to 1200°C for 10 to 20 hours in the platinum crucible in an electric furnace. The sample obtained here is white fine powders. The specimen was identified by X-ray powder diffraction.



Figure 12

after X-ray diffraction pattern of the sample

SAMPLE NAME: NaZr2P3O12  
 TARGET : Cu  
 VOL and CUR: 40KV 40mA  
 SLITS : OS 1 RS .3 SS 1  
 SCAN SPEED: 3 DEG/MIN.  
 STEP/SAMPL.: .02 DEG  
 PRESET TIME: 0 SEC  
 FILE NAME : 01100  
 OPERATOR : YAHAMOTO  
 COMMENT :

DATE: 89.10.20  
 SMOOTHING NO.: 11  
 THRESH. INTEN.: 157 CPS  
 2nd DERIV.: 263 CPS/(DEGxDEG)  
 WIDTH: .09 DEG  
 B.G. REDUCTION: NO EXECUTION  
 OUTPUT FILE :

Sample Name : NaZr2P3O12

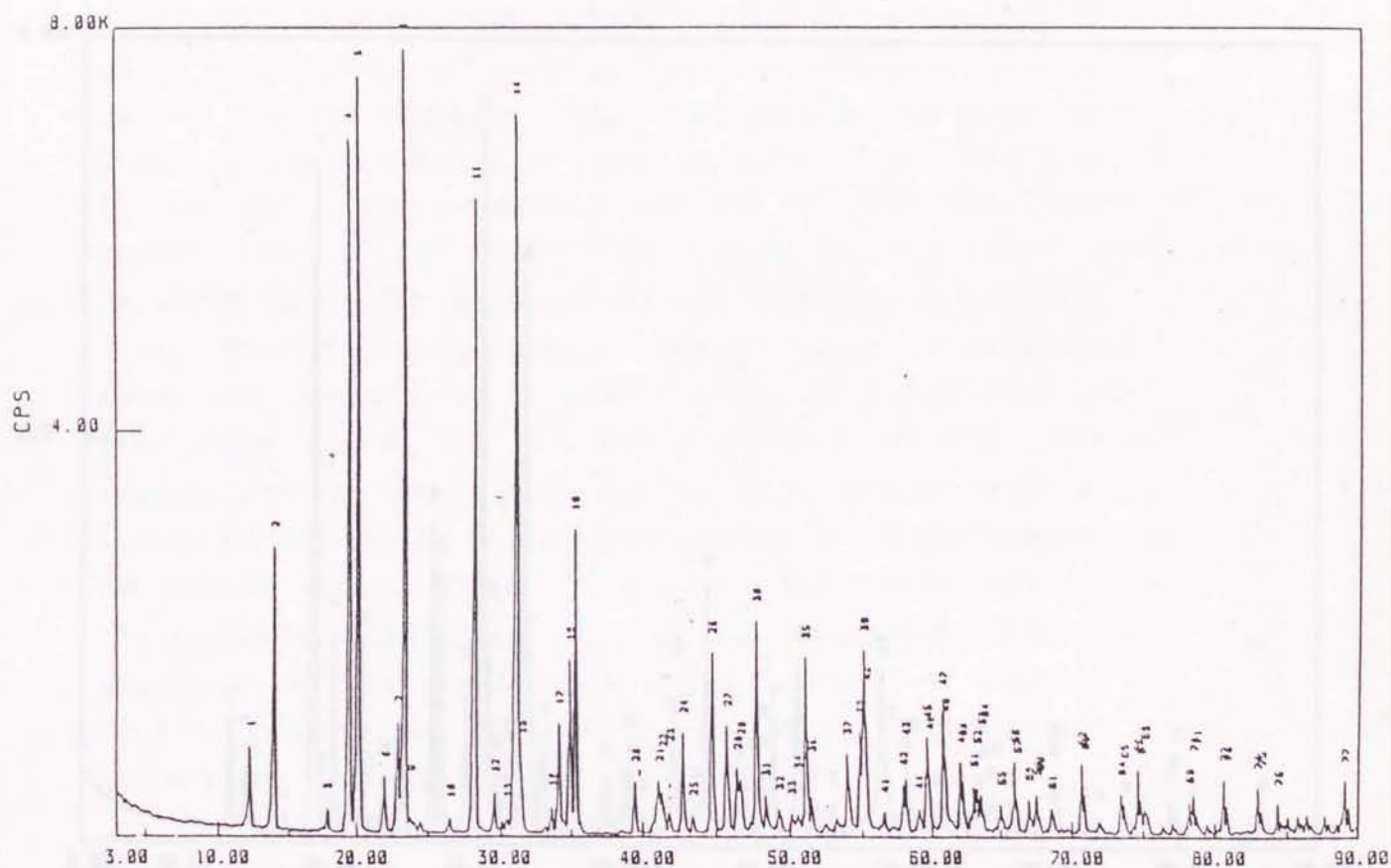


Figure 5.2

The X-ray powder diffraction pattern of NaZr<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>.



SAMPLE NAME: Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>P  
 TARGET : Cu  
 VOL and CUR: 40KV 40mA  
 SLITS : DS 1 RS .3 SS 1  
 SCAN SPEED: 3 DEG/MIN.  
 STEP/SAMPL.: .02 DEG  
 PRESET TIME: 0 SEC  
 FILE NAME : 03100  
 OPERATOR : YAMAMOTO  
 COMMENT :

DATE: 89.10.27  
 SMOOTHING NO.: 11  
 THRESH. INTEN.: 137 CPS  
 2nd DERIV.: 263 CPS/(DEGxDEG)  
 WIDTH: .09 DEG  
 B.G. REDUCTION: NO EXECUTION  
 OUTPUT FILE :

Sample Name : Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>P

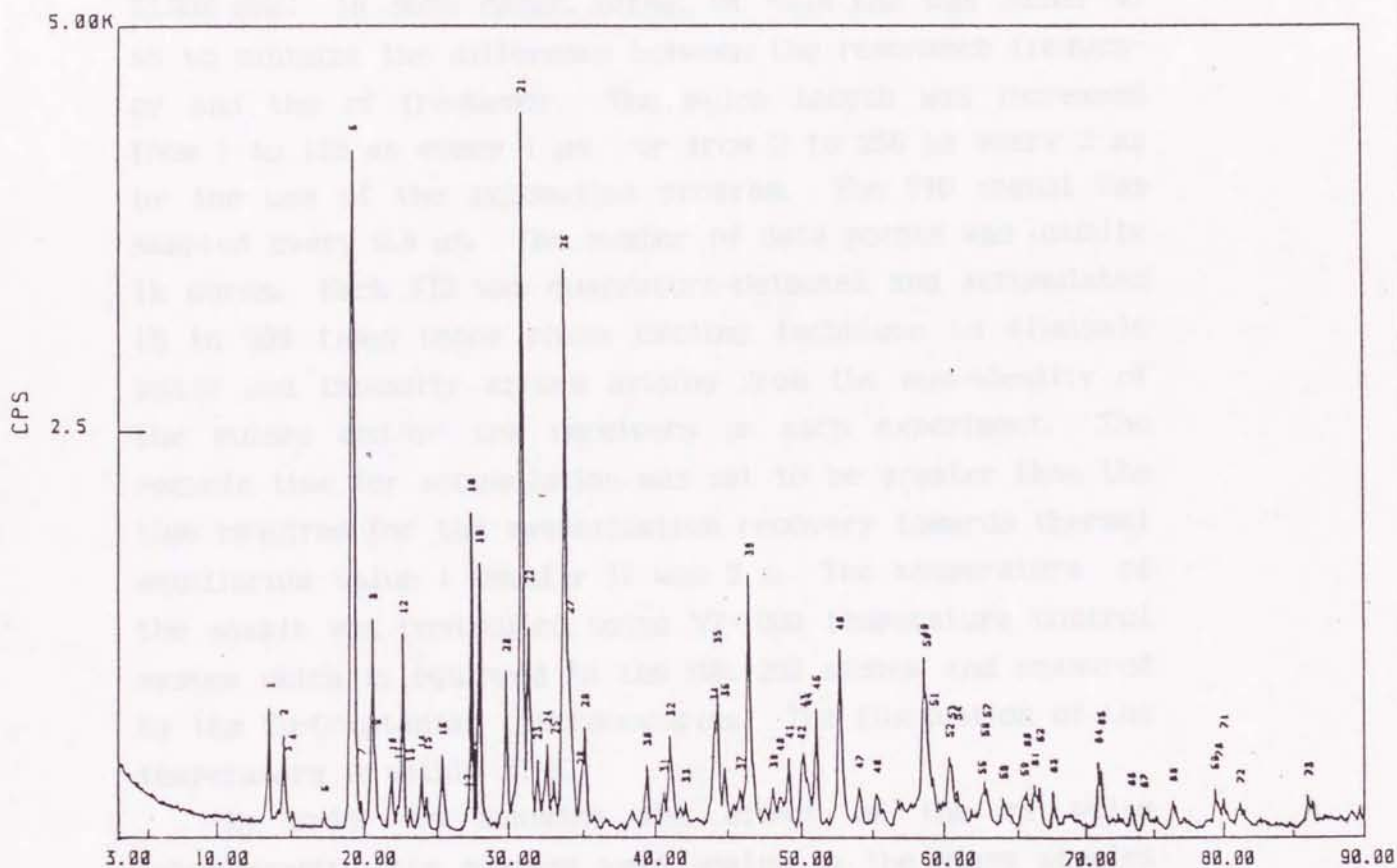


Figure 5.3

The X-ray powder diffraction pattern of Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>P<sub>2</sub>O<sub>12</sub>.

## 5.2 Nutation NMR

The  $^{23}\text{Na}$  NMR spectrum was measured by the use of the BRUKER MSL-200 NMR system at the Larmor frequency of 52.938 MHz. In some cases, offset of  $\sim \pm 10$  kHz was added so as to minimize the difference between the resonance frequency and the rf frequency. The pulse length was increased from 1 to 128  $\mu\text{s}$  every 1  $\mu\text{s}$ , or from 2 to 256  $\mu\text{s}$  every 2  $\mu\text{s}$  by the use of the automation program. The FID signal was sampled every 0.8  $\mu\text{s}$ . The number of data points was usually 1k words. Each FID was quadrature-detected and accumulated 16 to 500 times using phase cycling technique to eliminate phase and intensity errors arising from the non-ideality of the pulses and/or the receivers in each experiment. The recycle time for accumulation was set to be greater than the time required for the magnetization recovery towards thermal equilibrium value : Usually it was 5 s. The temperature of the sample was controlled using VT-1000 temperature control system which is equipped in the MSL-200 system and measured by the Cu-Constantan thermocouples. The fluctuation of the temperature is within  $\pm 1$  K.

In order to minimize the effect of the rf pulse inhomogeneity, the samples were sealed in the glass ampules with 10mm $\phi$  in ca. 10mm long. The signal of sodium from the ampule was negligible since the glass ampule used here was very thin and the amount of sodium in it was negligibly small compared with that in the sample.

The data acquired were 2D Fourier transformed by the use of ASPECT-3000 computer. Before 2D FT, zero filling up to 1k or 2k words in the  $F_1$  dimension was made in order to increase the digital resolution of the spectrum. In some





## References

- [1] R.W.G. Wyckoff,  
*Crystal Structures*, 2nd Ed., Vol. 3,  
John Wiley & Sons, 1965
- [2] The Merck Index, 8th Ed.,  
Merck & Co., Inc., 1968.
- [2] J.B. Goodenough, H.Y-P. Hong, and J.A. Kafalas,  
*Mat. Res. Bull.*, **11**, 203 (1976).
- [3] L-O. Hagman and P. Kierkegaard,  
*Acta Chem. Scand.*, **22**, 1822 (1968).
- [4] T.C. Farrar and E.D. Becker,  
*Pulse and Fourier Transform NMR*, Academic Press, 1971.
- A.G. Marshall and F.R. Verdun,  
*Fourier Transforms in NMR, Optical,  
and Mass Spectrometry*, Elsevier, 1990.

## 6. Data Analysis

### 6.1 Nutation Spectrum

Figs. 6.1 and 6.2 show stacked and contour plots of typical 2D nutation spectrum simulated with parameters  $e^2Qq/h = 0.2$  MHz,  $\eta = 0$ , and  $\omega_1/2\pi = 50$  kHz. The horizontal axis, which will be called  $F_2$  for brevity, is the conventional 1D NMR spectrum axis and the projection onto this axis gives the powder spectrum characterized by the second order quadrupole interaction. (See Fig. 6.2a.) The vertical axis,  $F_1$ , shows the nutation spectrum whose pattern varies with strength of the quadrupole interaction relative to the rf strength.

If the Hamiltonian in the evolution period,  $H_2$ , does not contain any useful information other than quadrupole interaction, an FT over  $t_1$  gives nutation spectrum which gives rise directly to the ratio  $\Omega_Q/\omega_1 = [3e^2Qq/2I(2I-1)\hbar]/\omega_1$ , where  $\Omega_Q$  is the lowest pure quadrupole resonance frequency.

Fig. 6.3 illustrates the simulated dependence of the nutation spectrum on the strength of the quadrupole interaction for  $I = 3/2$  ( $\eta = 0$  and  $\omega_1/2\pi = 50$  kHz). The numbers on the right-hand side of the spectrum represent  $e^2Qq/h$ . The bottom spectrum corresponds to the case when the quadrupole interaction is absent; only one sharp peak appears at around  $\omega_1$  as mentioned in Sec. 2.3. As the strength of the quadrupole interaction is increased, the spectrum splits into several peaks and they move away from  $\omega_1$ . In the top-most spectrum, the quadrupole interaction is so strong that only one peak is found at around  $2\omega_1$ . In this case, the intensity of the peak at  $2\omega_1$  is reduced to 1/4 of that of the peak at  $\omega_1$  in the case of  $e^2Qq/h = 0$ , indicating that



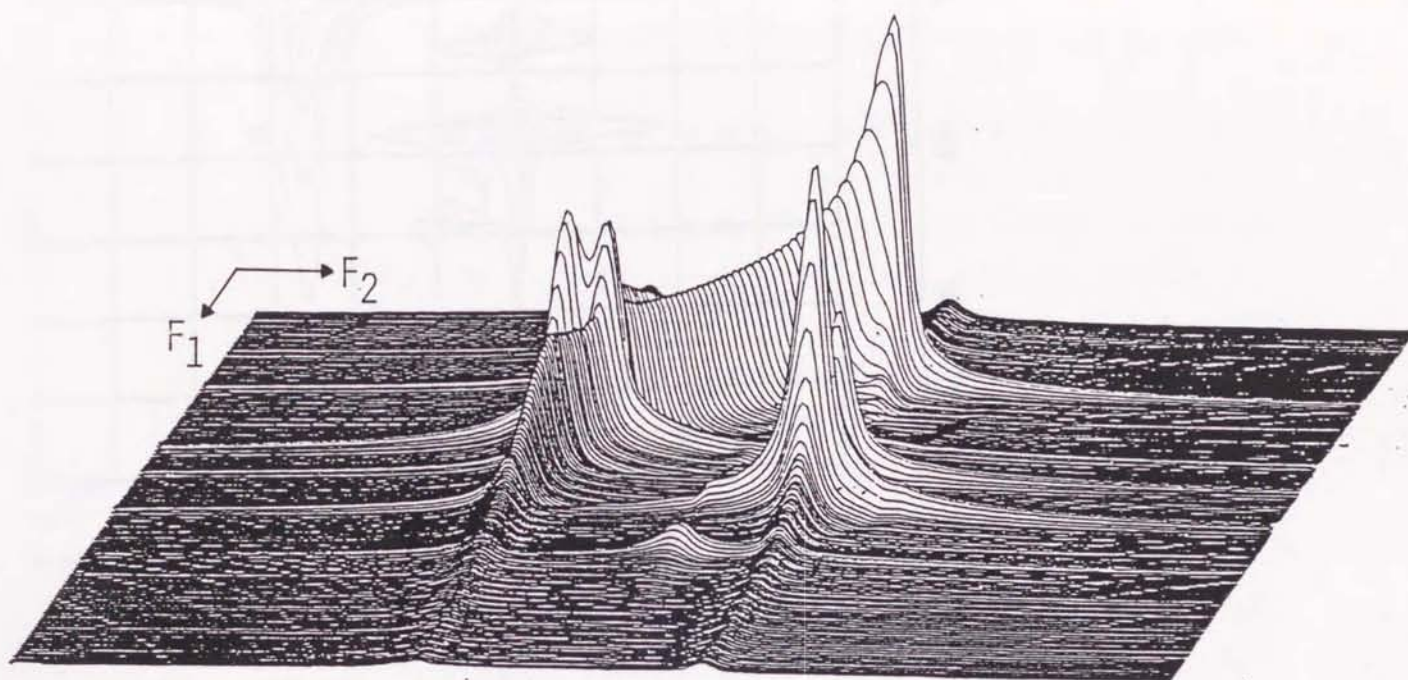


Figure 6.1

Stacked plot of 2D nutation spectrum simulated with parameters  $e^2 Qq/h = 0.2$  MHz,  $\eta = 0$ ,  $\omega_1/2\pi = 50$  kHz.



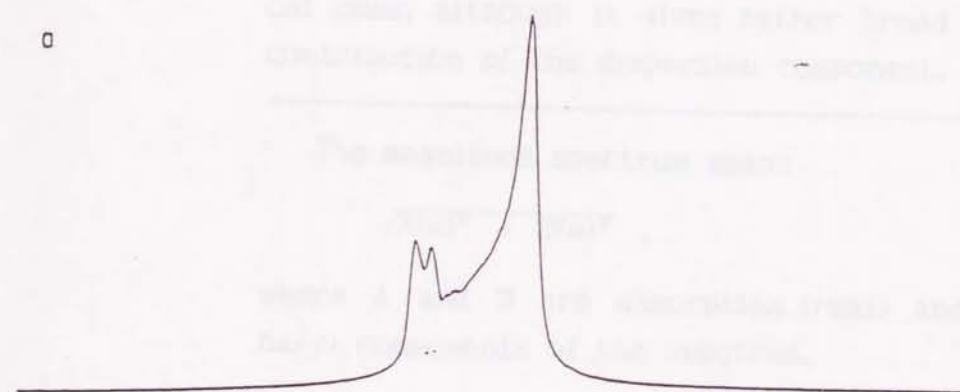
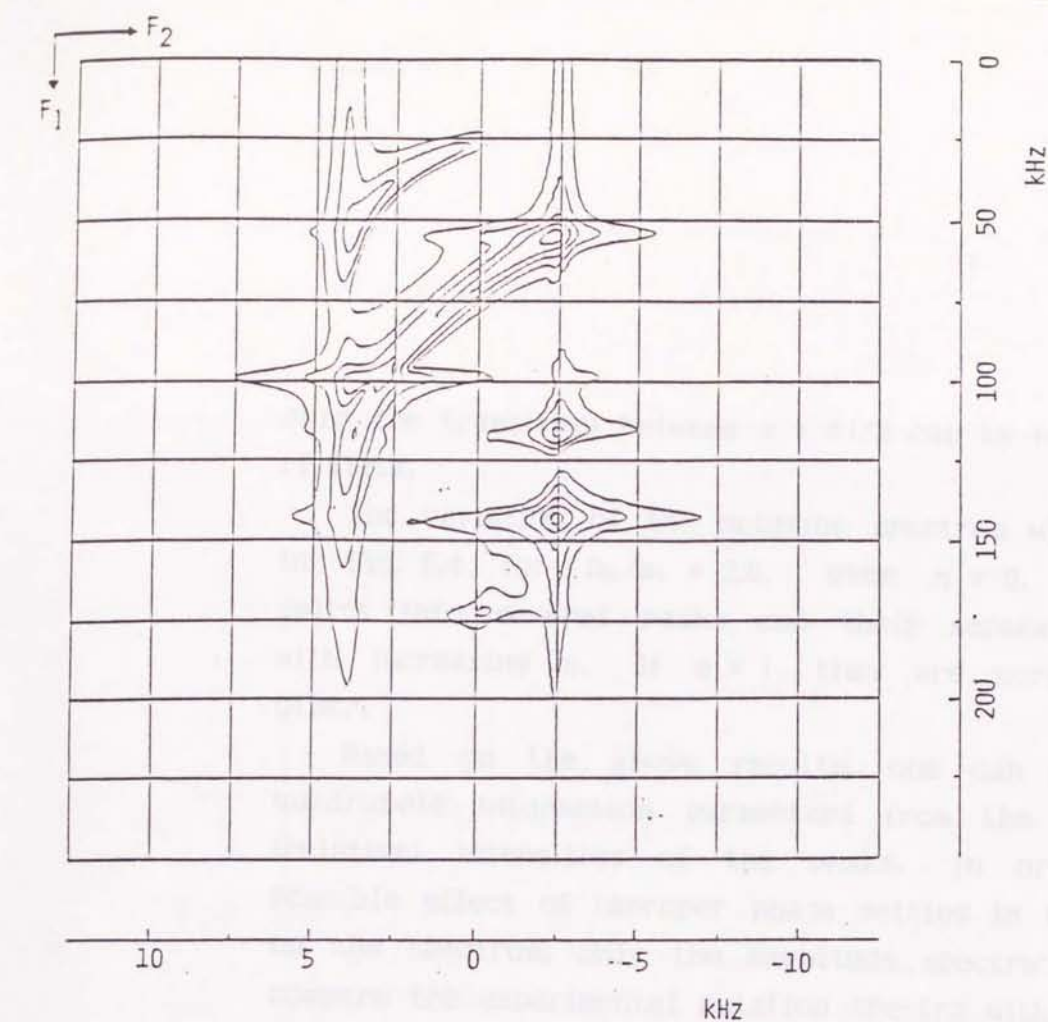


Figure 6.2

Contour plot of simulated 2D nutation spectrum. Calculated parameters are as in Fig. 6.1. a) Projections onto  $F_1$  and b)  $F_2$  axis, respectively.

only the transition between  $m = \pm 1/2$  can be excited by weak rf field.

The variation of the nutation spectrum with  $\eta$  is shown in Fig. 6.4 for  $\Omega_0/\omega_1 = 2.0$ . When  $\eta \neq 0$ , the spectrum splits into several peaks and their separations increase with increasing  $\eta$ . If  $\eta = 1$ , they are merged with each other.

Based on the above results, one can determine the quadrupole interaction parameters from the positions and (relative) intensities of the peaks. In order to avoid possible effect of improper phase setting in the experiment on the spectrum, only the magnitude spectra\* are used to compare the experimental nutation spectra with the theoretical ones, although it gives rather broad peaks owing to the contribution of the dispersion component.

- 
- \* The magnitude spectrum means

$$\sqrt{A(\omega)^2 + D(\omega)^2} ,$$

where A and D are absorption (real) and dispersion (imaginary) components of the spectrum.

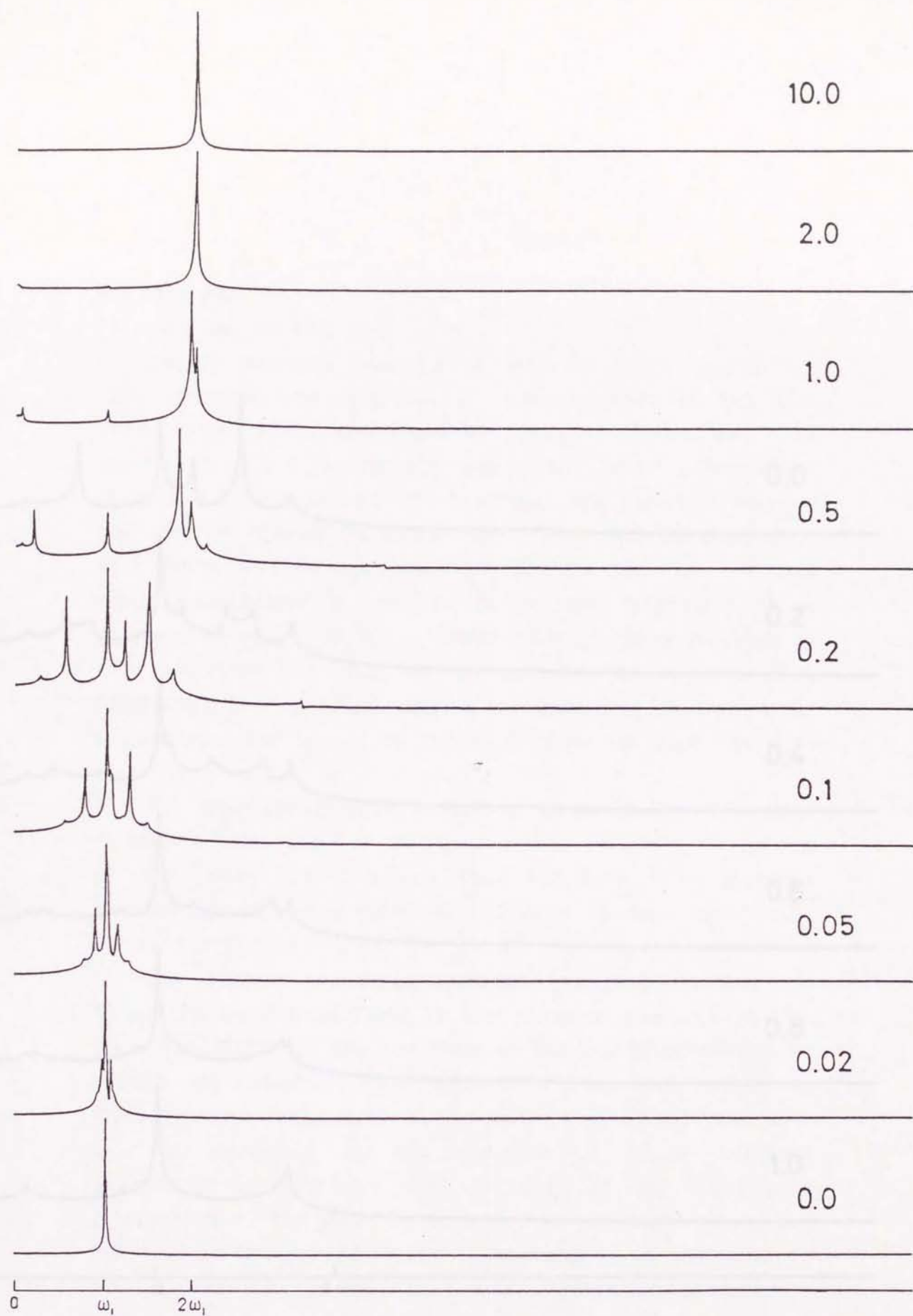


Figure 6.3

Dependence of nutation spectrum on the strength of quadrupole interaction.



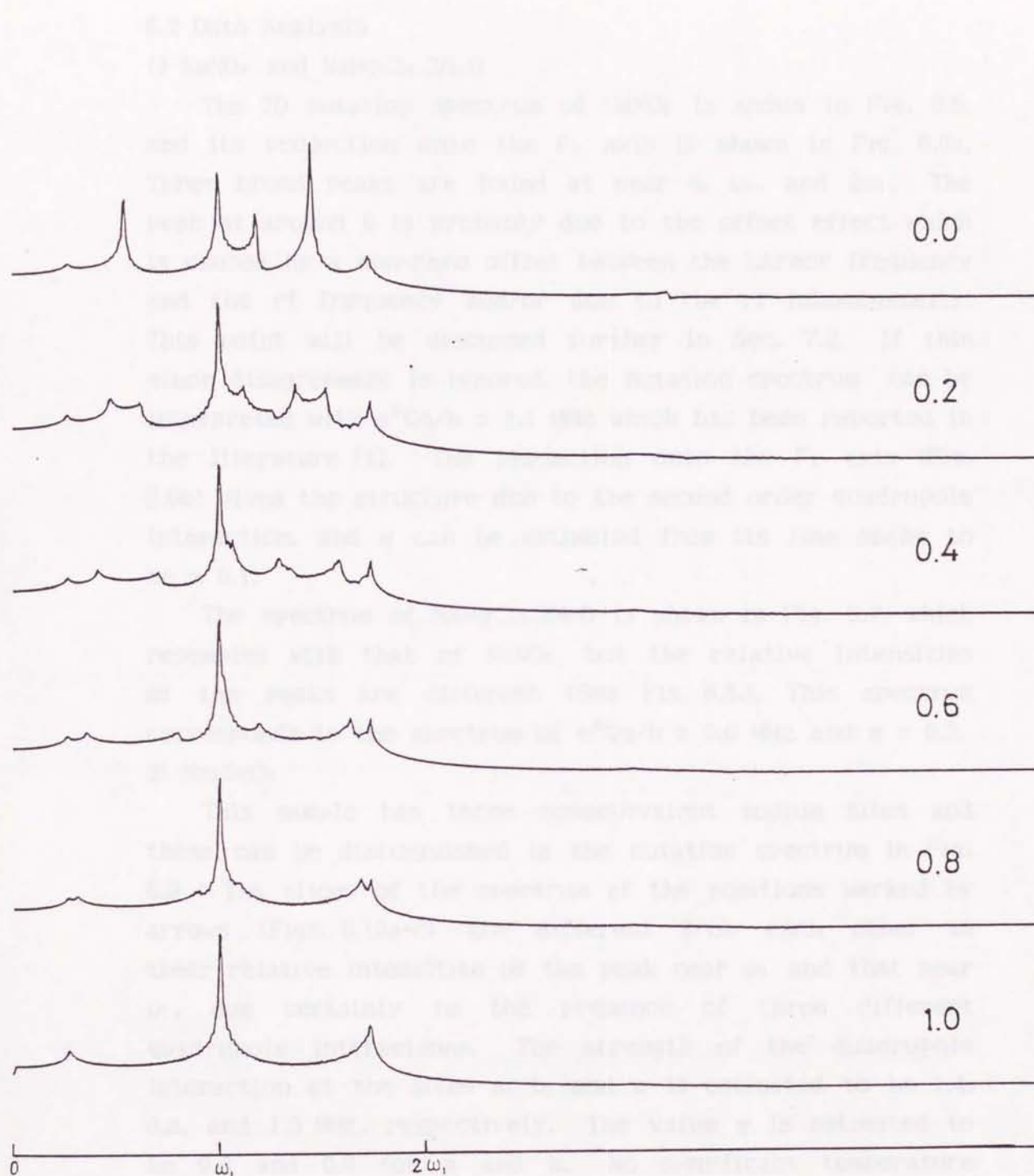


Figure 6.4

$\eta$  dependence of nutation spectrum.  $\Omega_0/\omega_1 = 2$ .

## 6.2 Data Analysis

### 1) $\text{NaNO}_2$ and $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$

The 2D nutation spectrum of  $\text{NaNO}_2$  is shown in Fig. 6.5, and its projection onto the  $F_1$  axis is shown in Fig. 6.6a. Three broad peaks are found at near 0,  $\omega_1$ , and  $2\omega_1$ . The peak at around 0 is probably due to the offset effect which is caused by a non-zero offset between the Larmor frequency and the rf frequency and/or due to the rf inhomogeneity. This point will be discussed further in Sec. 7.2. If this minor disagreement is ignored, the nutation spectrum can be interpreted with  $e^2Qq/h \simeq 1.1$  MHz which has been reported in the literature [1]. The projection onto the  $F_2$  axis (Fig. 6.6b) gives the structure due to the second order quadrupole interaction, and  $\eta$  can be estimated from its line shape to be  $\simeq 0.1$ .

The spectrum of  $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$  is shown in Fig. 6.7, which resembles with that of  $\text{NaNO}_2$ , but the relative intensities of the peaks are different (See Fig. 6.8.). This spectrum corresponds to the spectrum of  $e^2Qq/h \simeq 0.6$  MHz and  $\eta \simeq 0.2$ .

### 3) $\text{Na}_2\text{SeO}_3$

This sample has three nonequivalent sodium sites and these can be distinguished in the nutation spectrum in Fig. 6.9 : The slices of the spectrum at the positions marked by arrows (Figs. 6.10a-c) are different from each other in their relative intensities of the peak near  $\omega_1$  and that near  $2\omega_1$ , due certainly to the presence of three different quadrupole interactions. The strength of the quadrupole interaction at the sites a, b, and c is estimated to be 1.4, 0.8, and 1.3 MHz, respectively. The value  $\eta$  is estimated to be 0.8 and 0.0 for a and b. No significant temperature

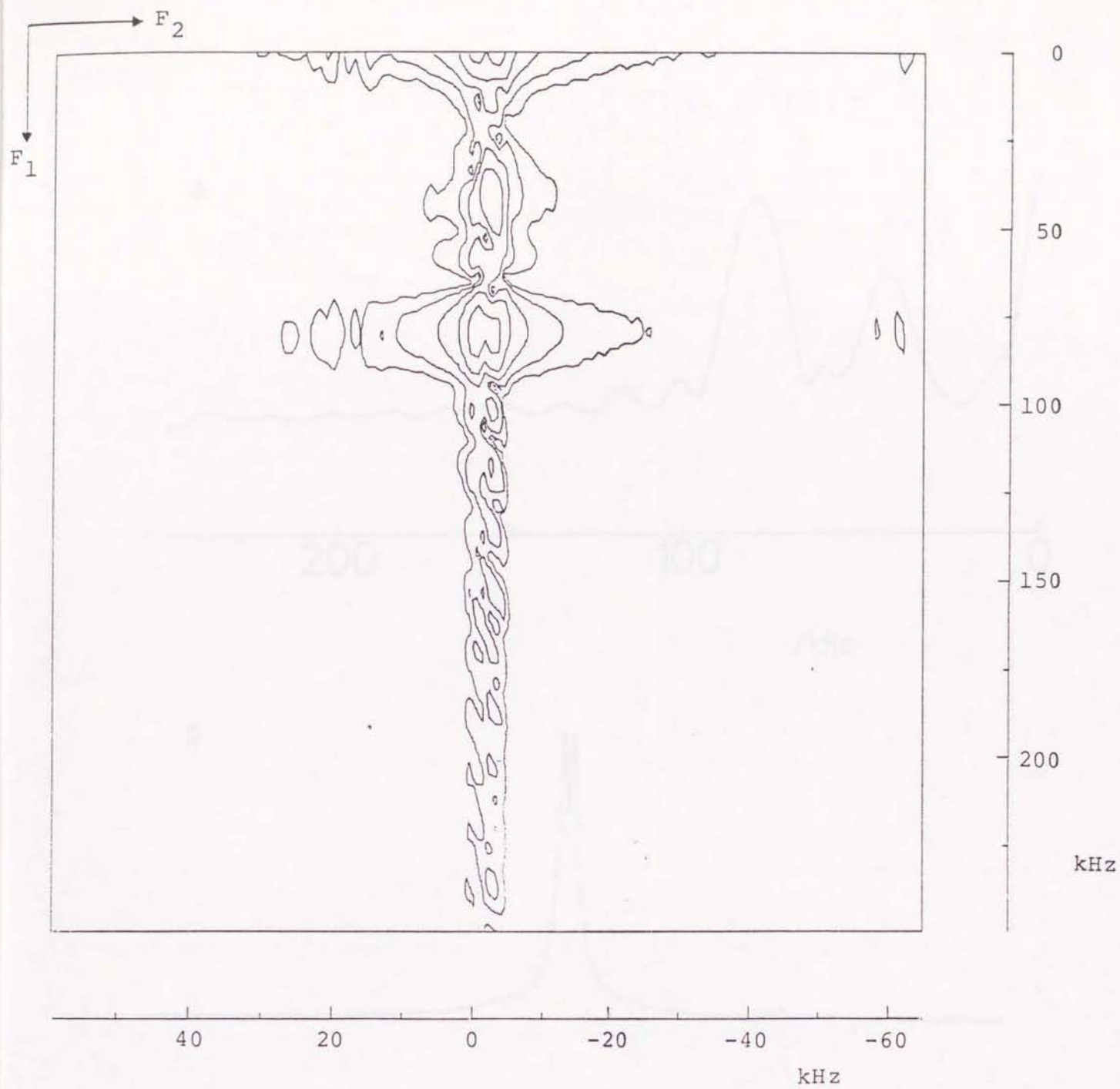


Figure 6.5

Contour plot of 2D nutation spectrum of  $\text{NaNO}_2$  at room temperature.



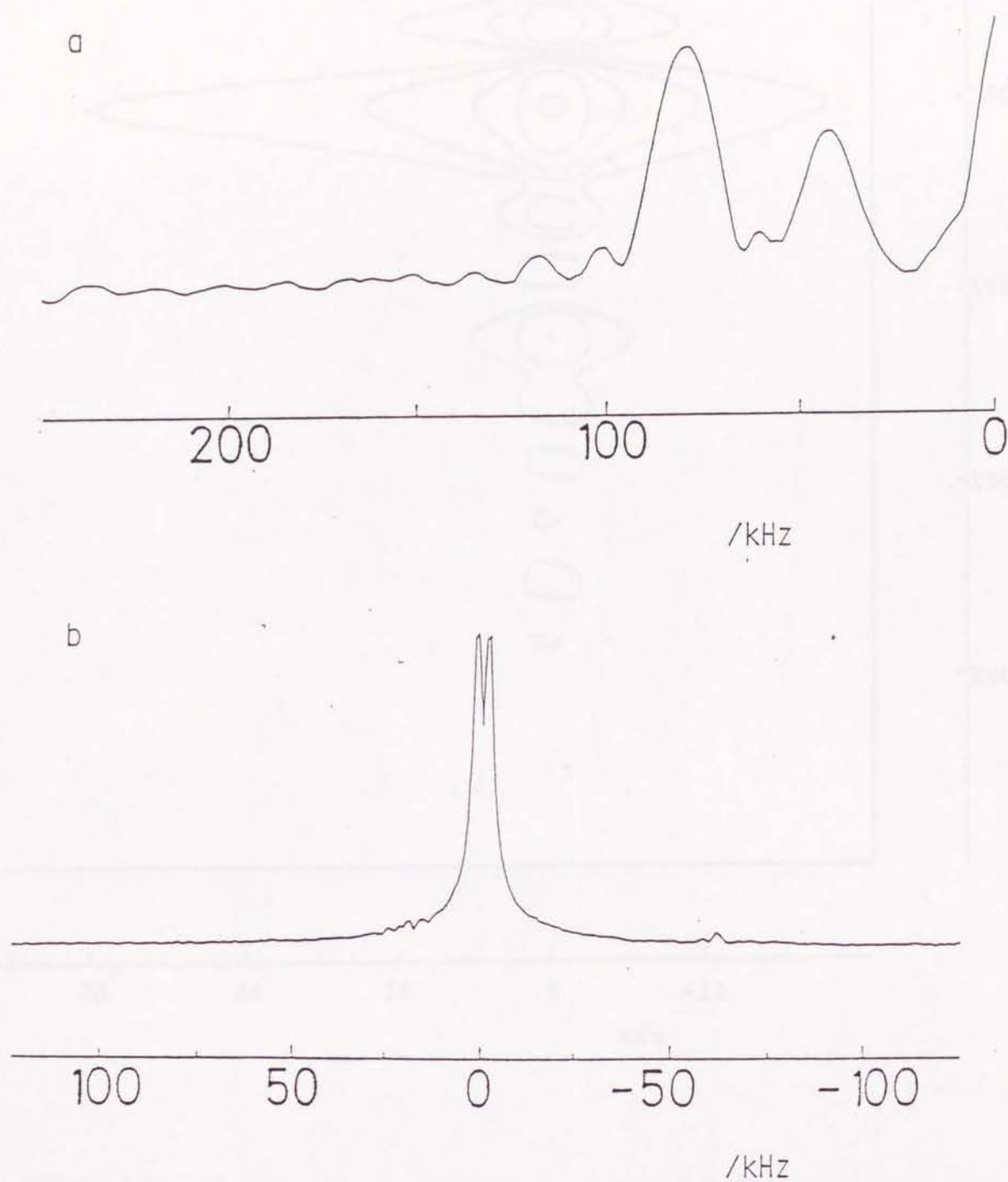


Figure 6.6  
2D nutation spectrum of  $\text{NaNO}_2$  at room temperature.  
a) Projection onto  $F_1$  axis. b) Projection onto  $F_2$  axis.

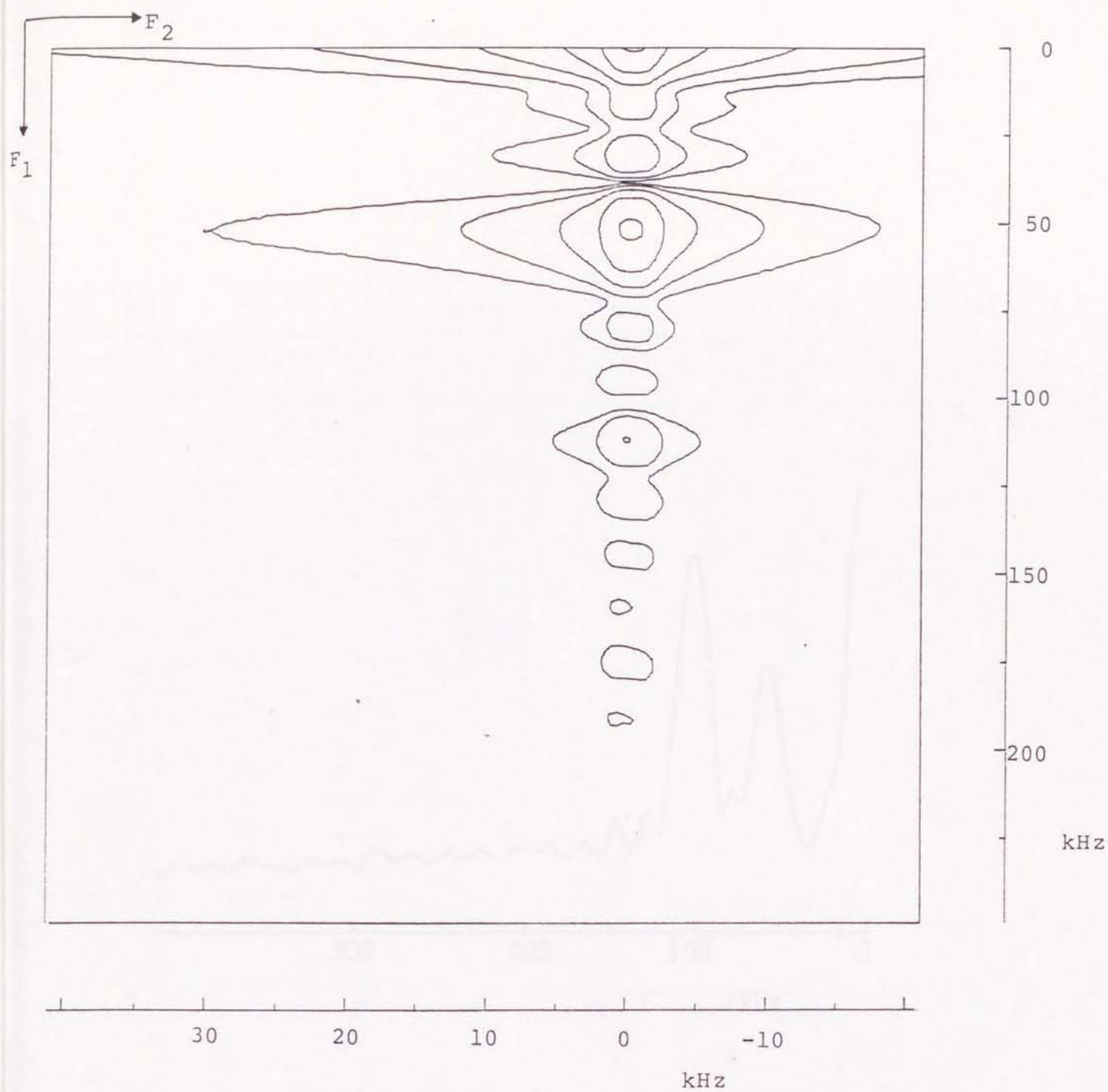


Figure 6.7

Contour plot of 2D nutation spectrum of  $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$  at room temperature.

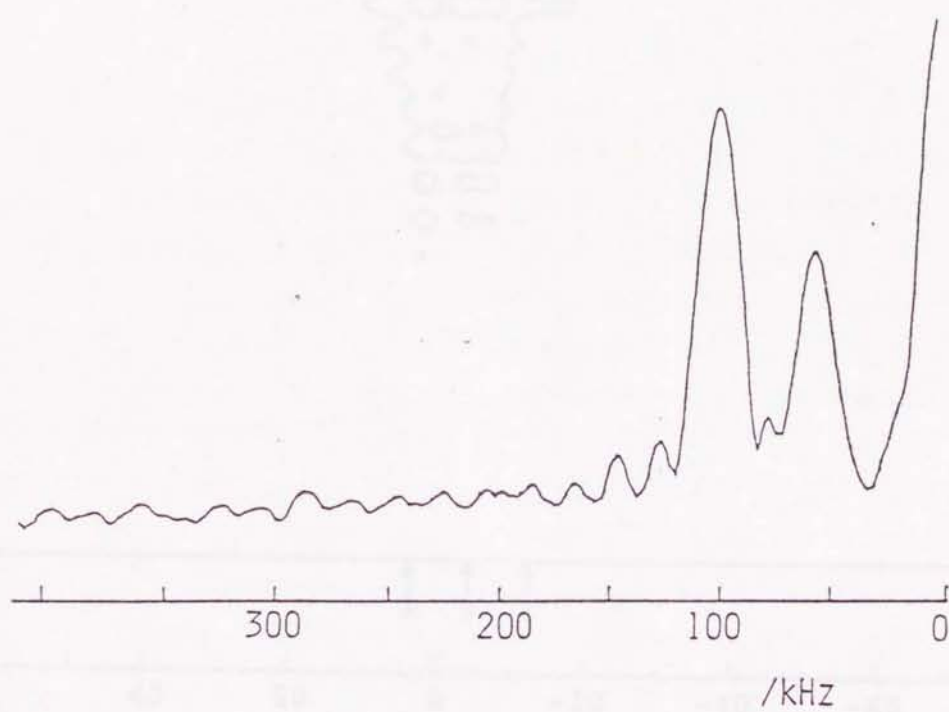


Figure 6.8

2D nutation spectrum of  $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$ . Projection onto  $F_1$  axis.



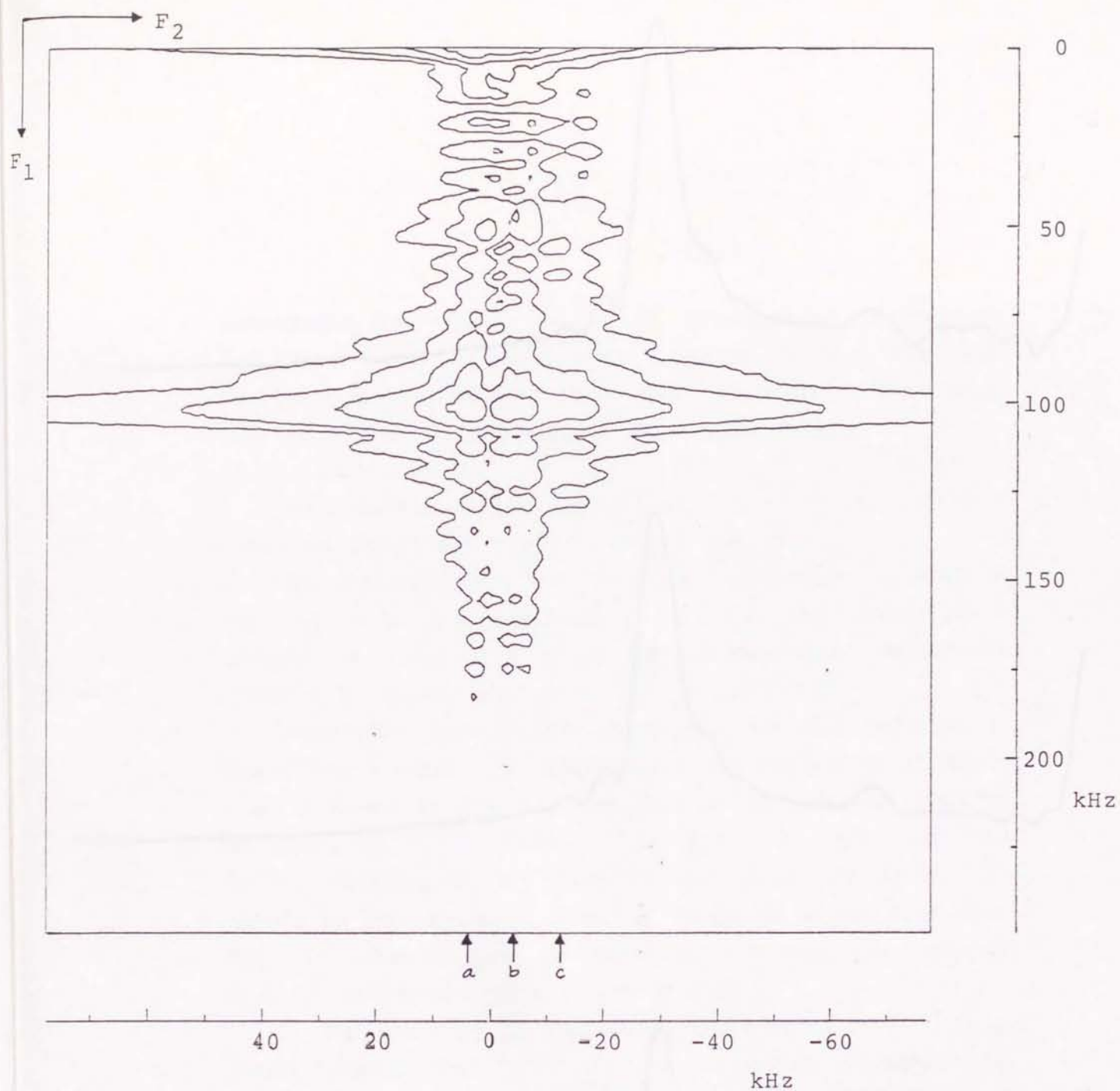


Figure 6.9

Contour plot of 2D nutation spectrum of  $\text{Na}_2\text{SeO}_3$  at room temperature.

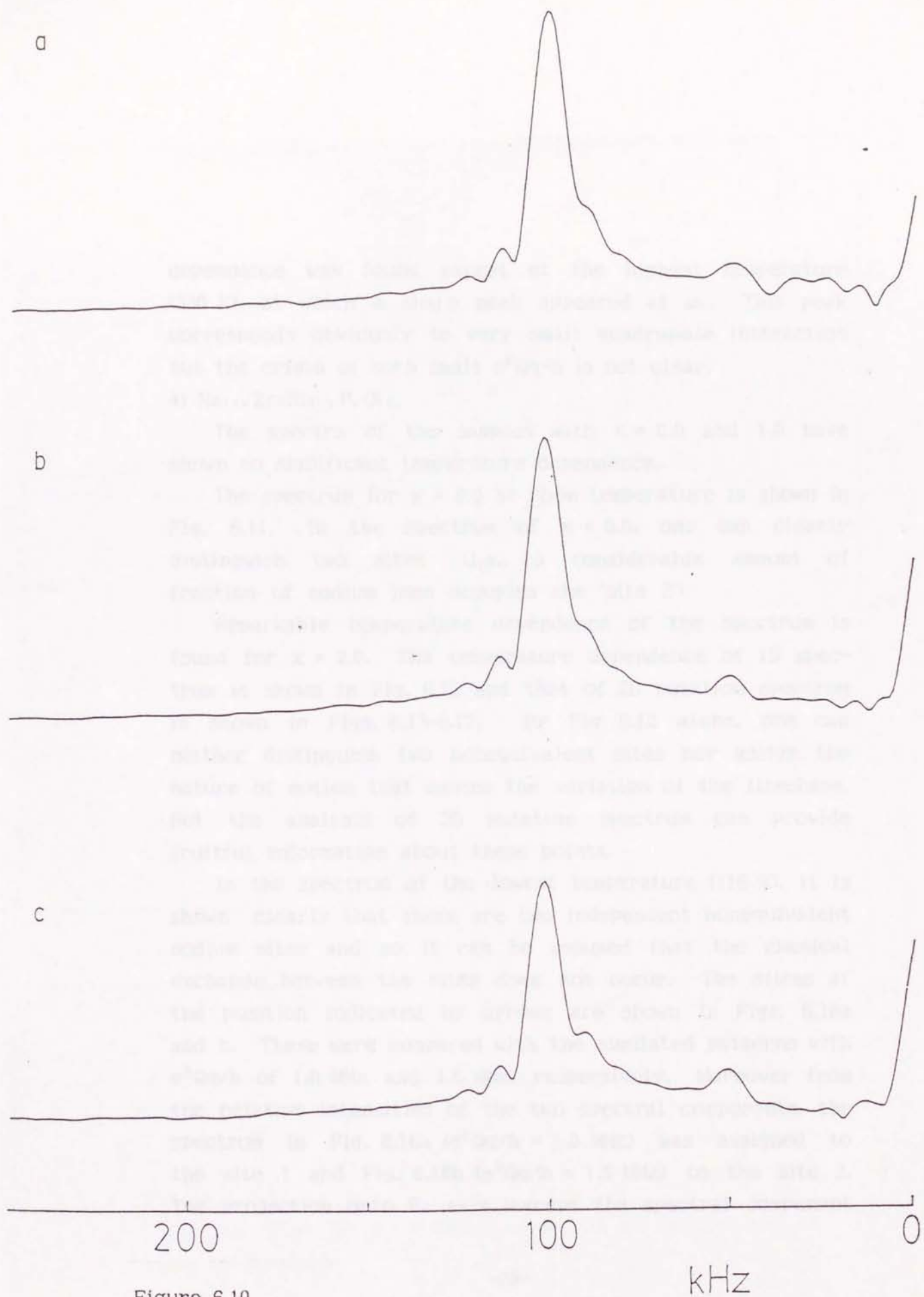


Figure 6.10

The slices of the spectrum at the positions marked by arrows in Fig. 6.9.

dependence was found except at the highest temperature (330 K), at which a sharp peak appeared at  $\omega_1$ . This peak corresponds obviously to very small quadrupole interaction but the origin of such small  $e^2Qq/h$  is not clear.

#### 4) $\text{Na}_{1+x}\text{Zr}_2\text{Si}_{3-x}\text{P}_x\text{O}_{12}$

The spectra of the samples with  $x = 0.0$  and  $1.0$  have shown no significant temperature dependence.

The spectrum for  $x = 0.0$  at room temperature is shown in Fig. 6.11. In the spectrum of  $x = 0.0$ , one can clearly distinguish two sites (i.e., a considerable amount of fraction of sodium ions occupies the 'site 2').

Remarkable temperature dependence of the spectrum is found for  $x = 2.0$ . The temperature dependence of 1D spectrum is shown in Fig. 6.12 and that of 2D nutation spectrum is shown in Figs. 6.13-6.17. By Fig. 6.12 alone, one can neither distinguish two nonequivalent sites nor assign the nature of motion that causes the variation of the lineshape. But the analysis of 2D nutation spectrum can provide fruitful information about these points.

In the spectrum of the lowest temperature (116 K), it is shown clearly that there are two independent nonequivalent sodium sites and so it can be assumed that the chemical exchange between the sites does not occur. The slices at the position indicated by arrows are shown in Figs. 6.18a and b. These were compared with the simulated patterns with  $e^2Qq/h$  of 1.0 MHz and 1.5 MHz, respectively. Moreover from the relative intensities of the two spectral components, the spectrum in Fig. 6.18a ( $e^2Qq/h = 1.0$  MHz) was assigned to the site 1 and Fig. 6.18b ( $e^2Qq/h = 1.5$  MHz) to the site 2. The projection onto  $F_2$  axis (except the spectral component



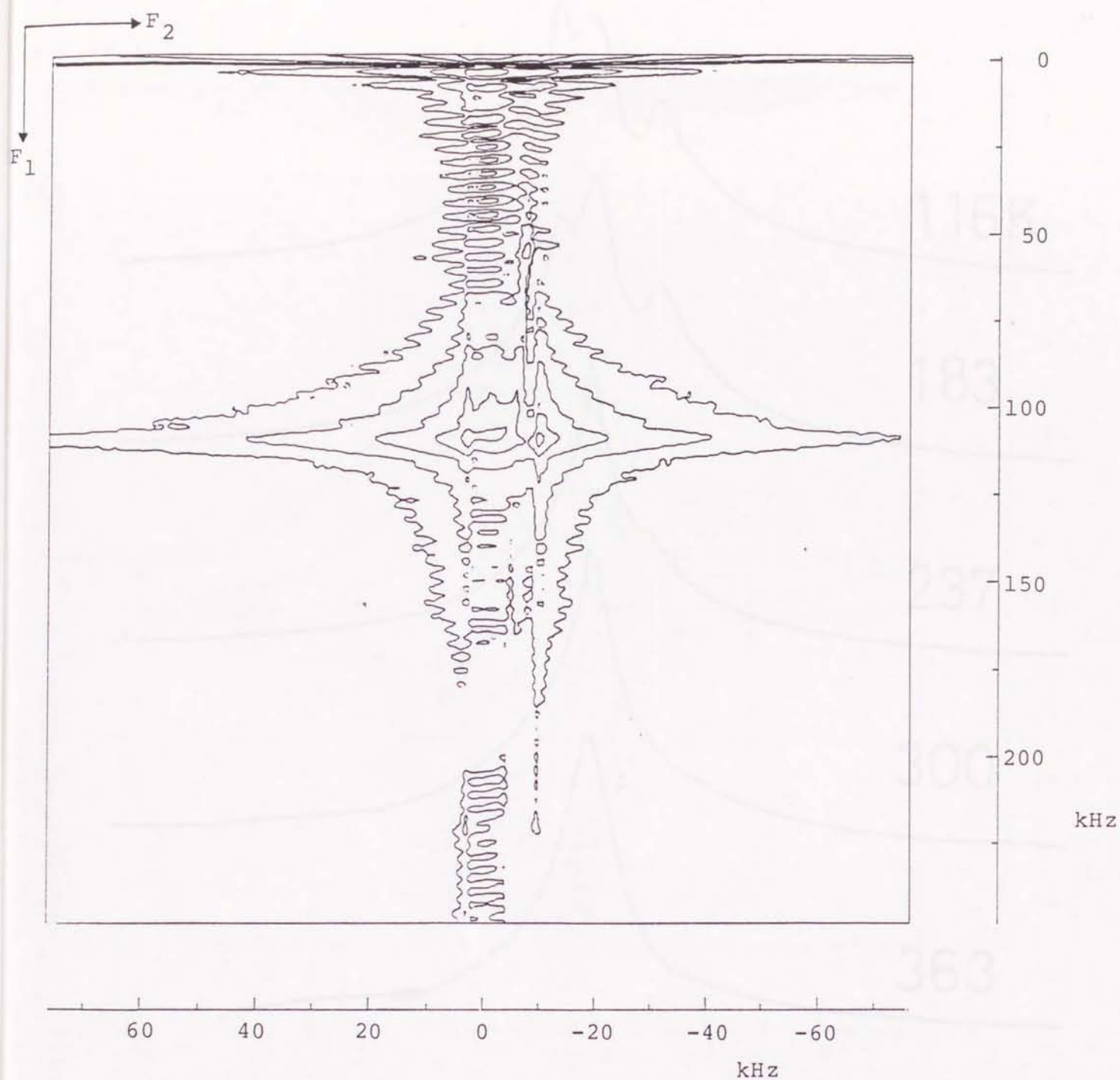


Figure 6.11

Contour plot of 2D nutation spectrum of  $\text{NaZr}_2\text{Si}_3\text{O}_{12}$  at room temperature.

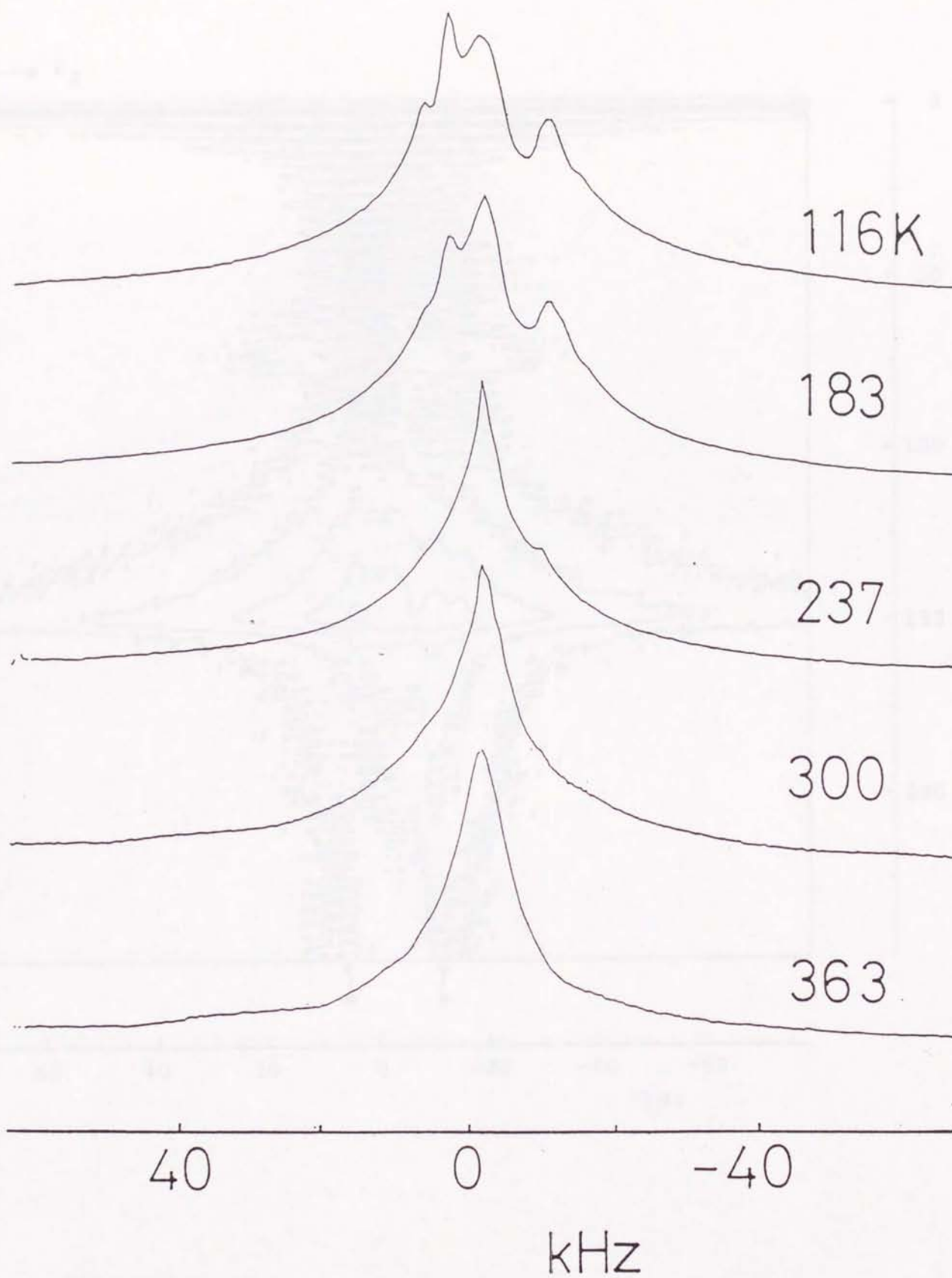


Figure 6.12

Temperature dependence of 1D spectrum of  $\text{Na}_3\text{Zr}_2\text{SiP}_2\text{O}_{12}$ .

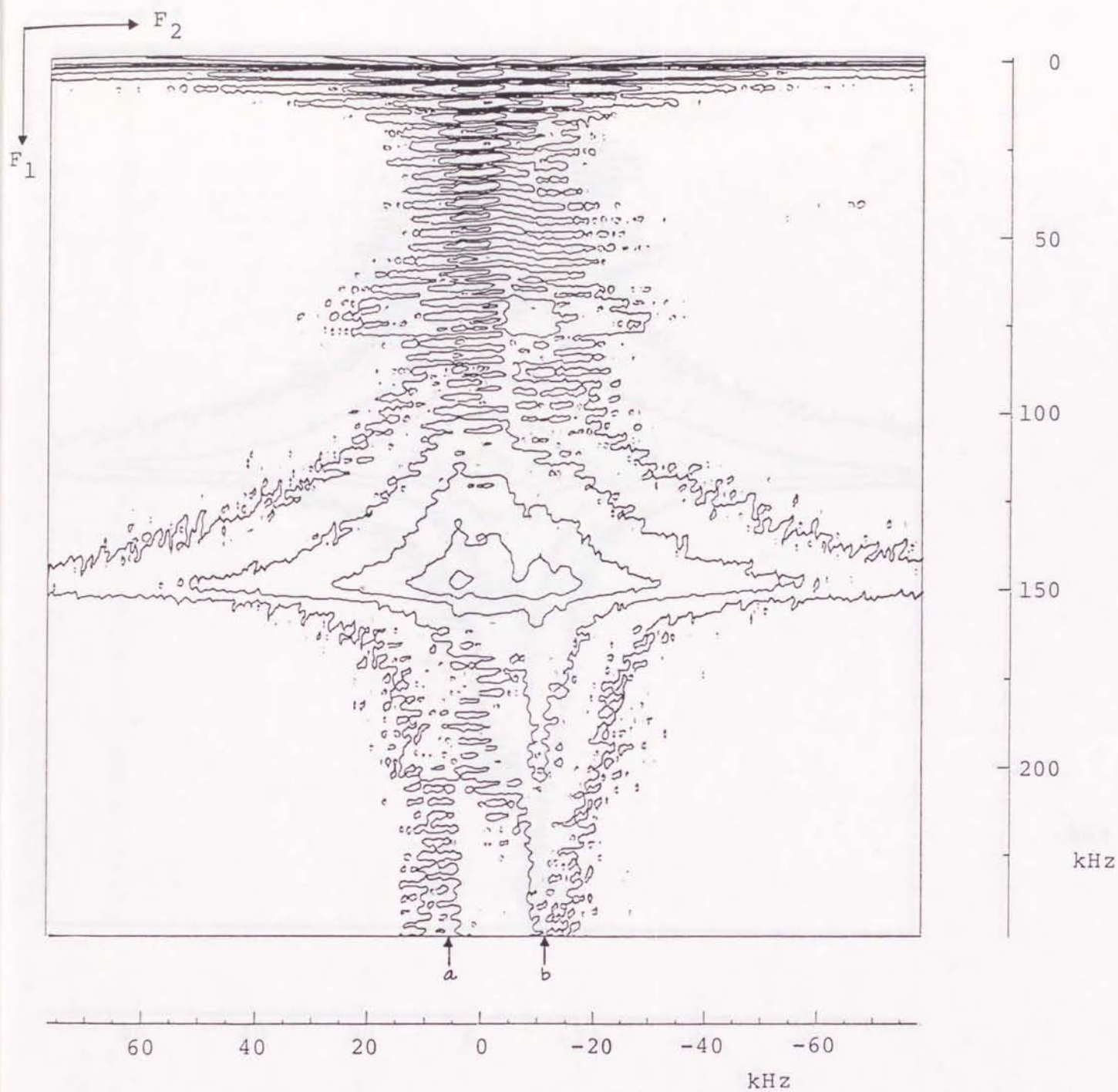


Figure 6.13

Contour plot of 2D nutation spectrum of  $\text{Na}_3\text{Zr}_2\text{SiP}_2\text{O}_{12}$  at 116 K.



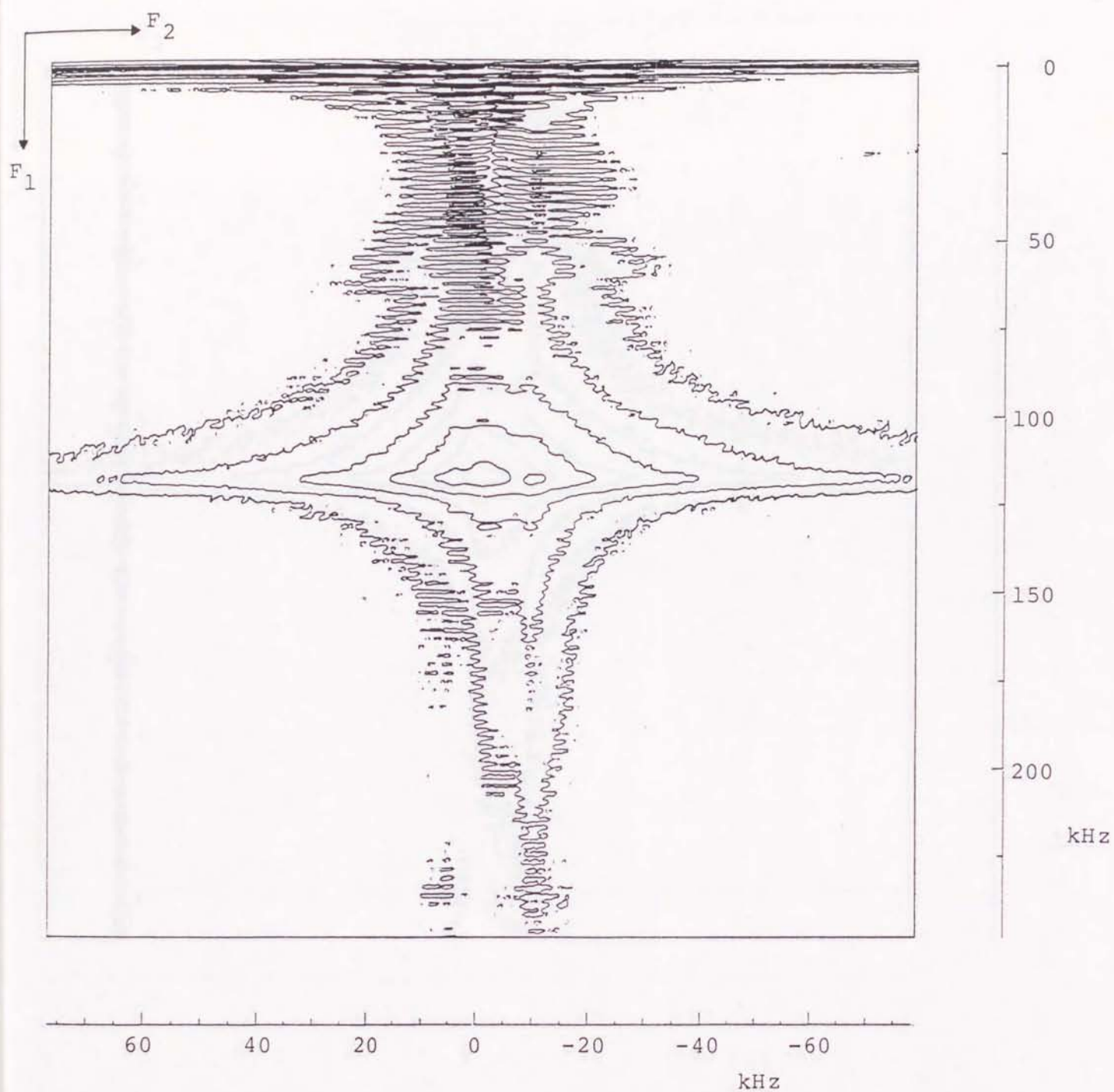


Figure 6.14

Contour plot of 2D nutation spectrum of  $\text{Na}_3\text{Zr}_2\text{SiP}_2\text{O}_{12}$  at 186 K.

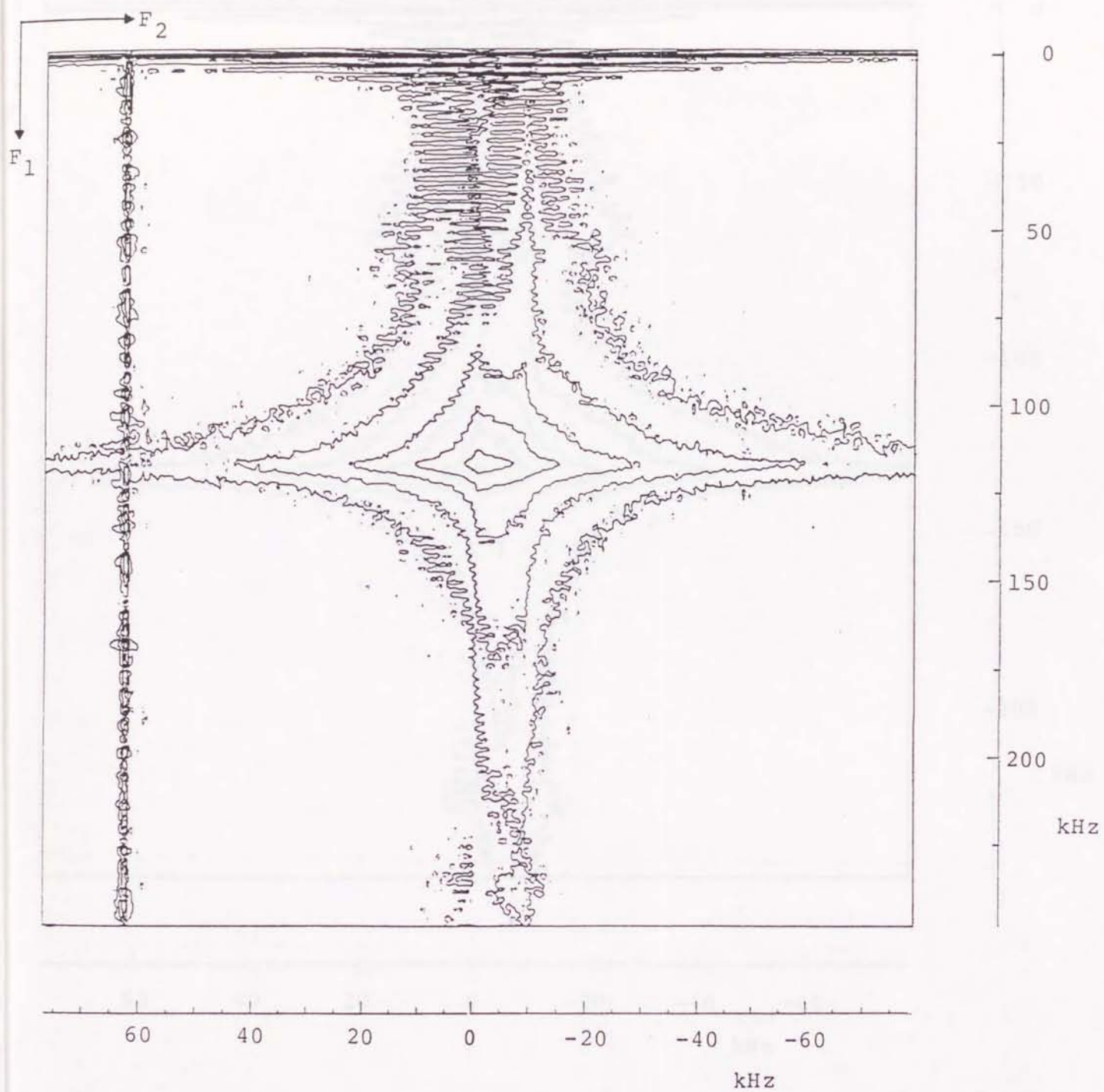


Figure 6.15

Contour plot of 2D nutation spectrum of  $\text{Na}_3\text{Zr}_2\text{SiP}_2\text{O}_{12}$  at 237 K.

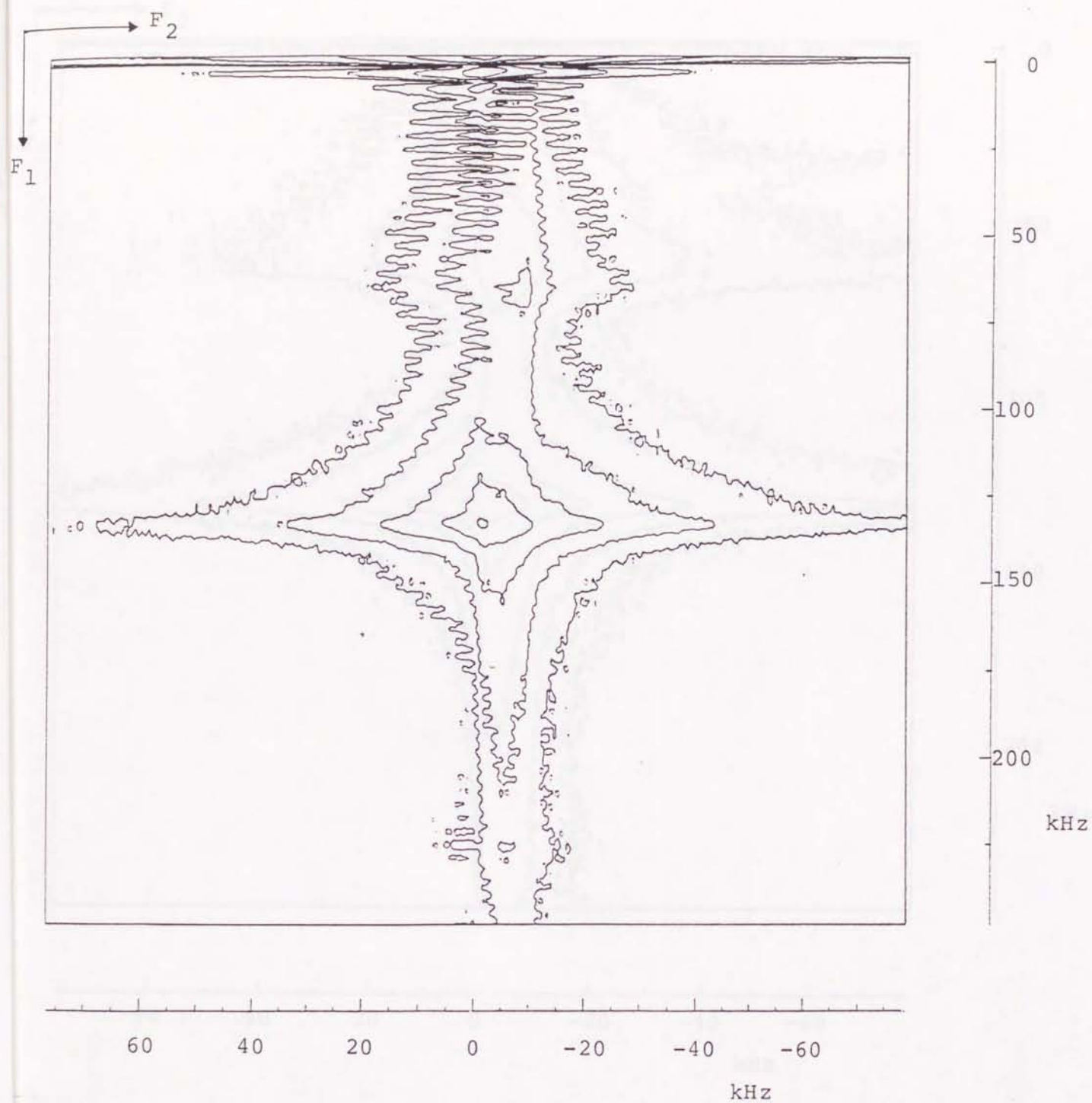


Figure 6.16

Contour plot of 2D nutation spectrum of  $\text{Na}_3\text{Zr}_2\text{SiP}_2\text{O}_{12}$  at 300 K.



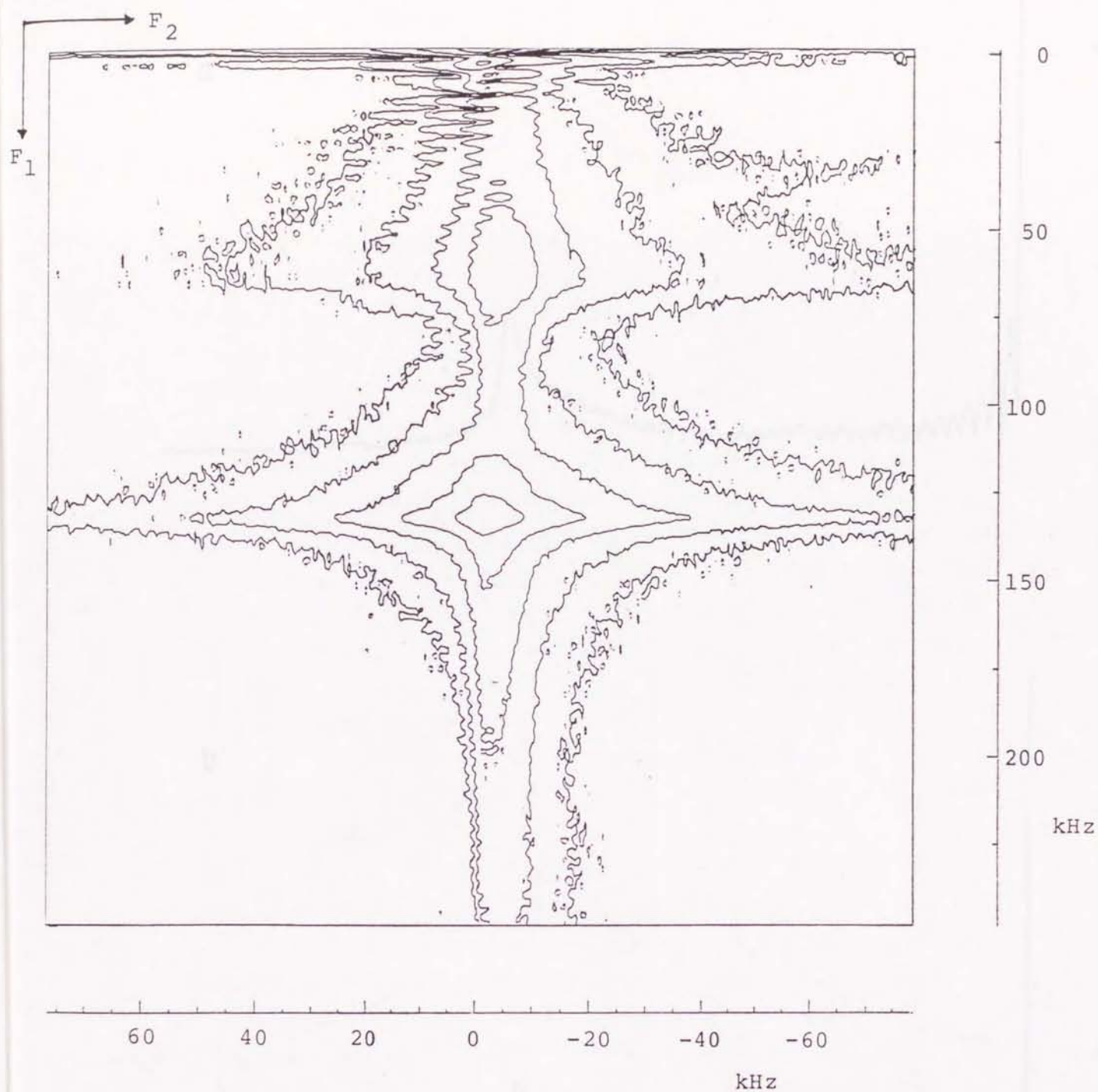


Figure 6.17

Contour plot of 2D nutation spectrum of  $\text{Na}_3\text{Zr}_2\text{SiP}_2\text{O}_{12}$  at 363 K.

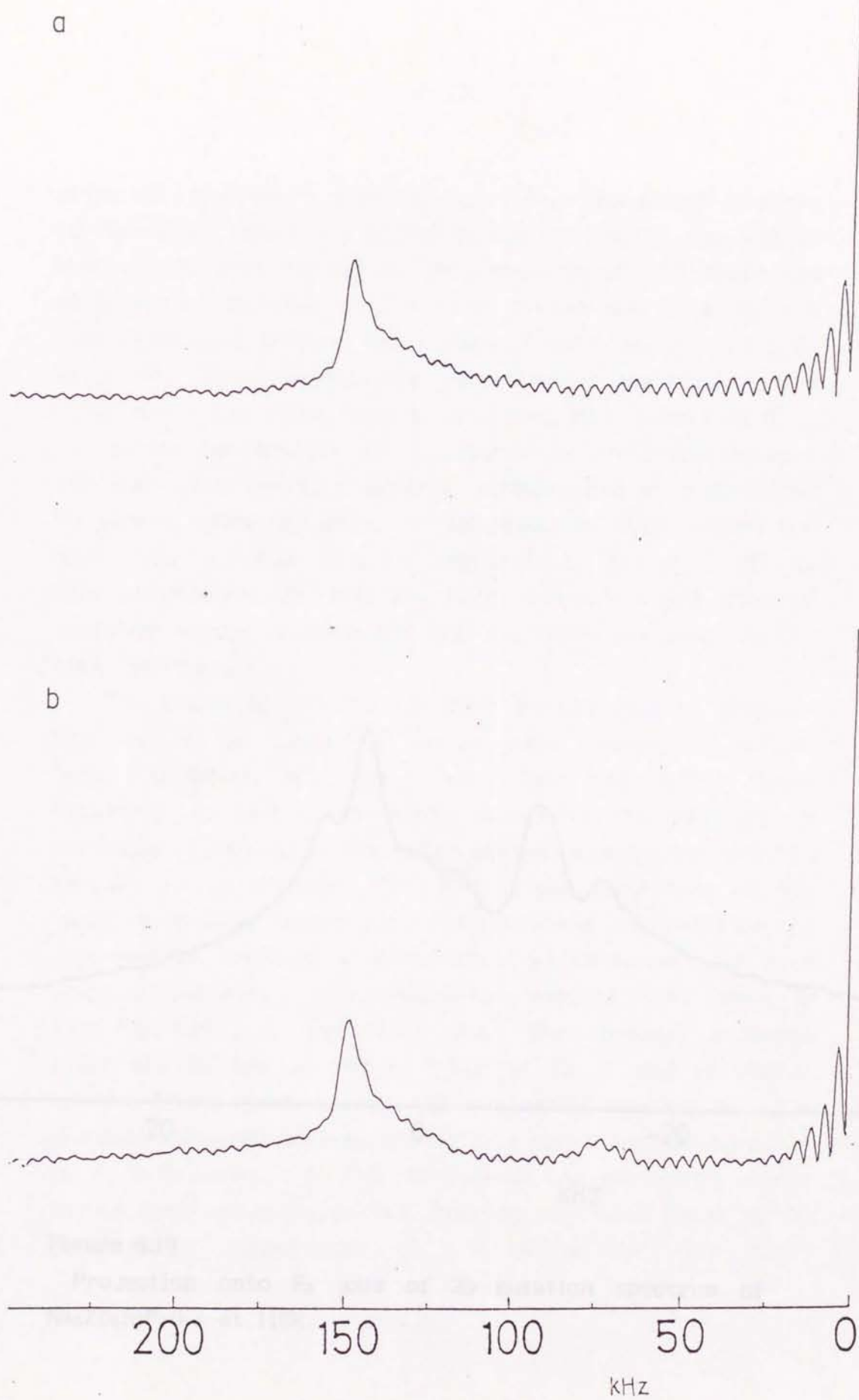


Figure 6.18

The slices at the positions marked by the arrows in Fig. 6.13.

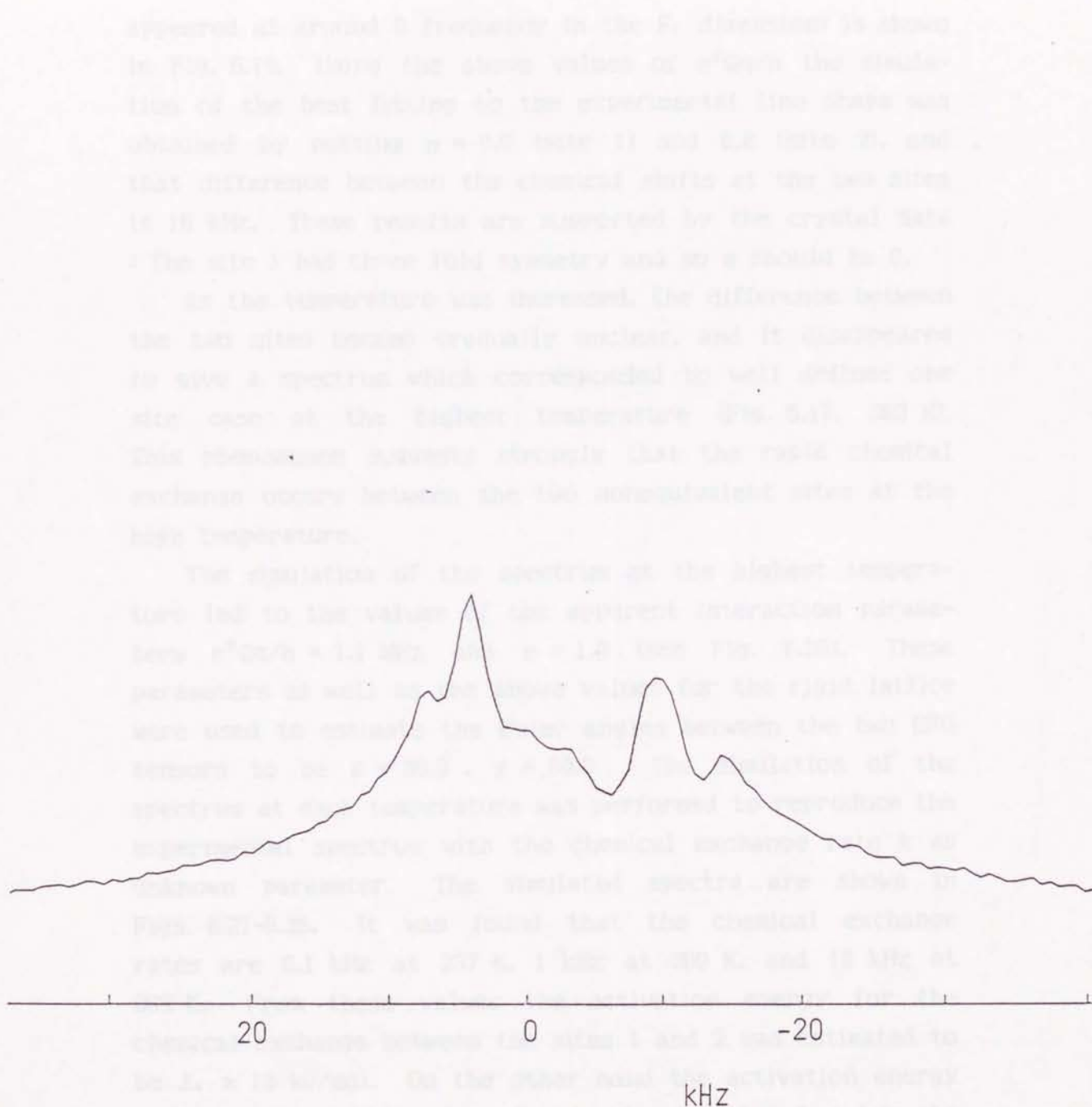


Figure 6.19

Projection onto  $F_2$  axis of 2D nutation spectrum of  $\text{Na}_3\text{Zr}_2\text{SiP}_2\text{O}_{12}$  at 116K.



appeared at around 0 frequency in the  $F_1$  dimension) is shown in Fig. 6.19. Using the above values of  $e^2Qq/h$  the simulation of the best fitting to the experimental line shape was obtained by putting  $\eta = 0.0$  (site 1) and 0.8 (site 2), and that difference between the chemical shifts at the two sites is 16 kHz. These results are supported by the crystal data : The site 1 has three fold symmetry and so  $\eta$  should be 0.

As the temperature was increased, the difference between the two sites became gradually unclear, and it disappeared to give a spectrum which corresponded to well defined one site case at the highest temperature (Fig. 6.17, 363 K). This phenomenon suggests strongly that the rapid chemical exchange occurs between the two nonequivalent sites at the high temperature.

The simulation of the spectrum at the highest temperature led to the values of the apparent interaction parameters  $e^2Qq/h = 1.1$  MHz and  $\eta = 1.0$  (see Fig. 6.20). These parameters as well as the above values for the rigid lattice were used to estimate the Euler angles between the two EFG tensors to be  $\beta = 30.0$  ,  $\gamma = 60.0$  . The simulation of the spectrum at each temperature was performed to reproduce the experimental spectrum with the chemical exchange rate  $k$  as unknown parameter. The simulated spectra are shown in Figs. 6.21-6.25. It was found that the chemical exchange rates are 0.1 kHz at 237 K, 1 kHz at 300 K, and 10 kHz at 363 K. From these values the activation energy for the chemical exchange between the sites 1 and 2 was estimated to be  $E_a \approx 13$  kJ/mol. On the other hand the activation energy values obtained above do not coincide with that found in the conductivity measurement ( $E_a \approx 31$  kJ/mol) [2]. The large

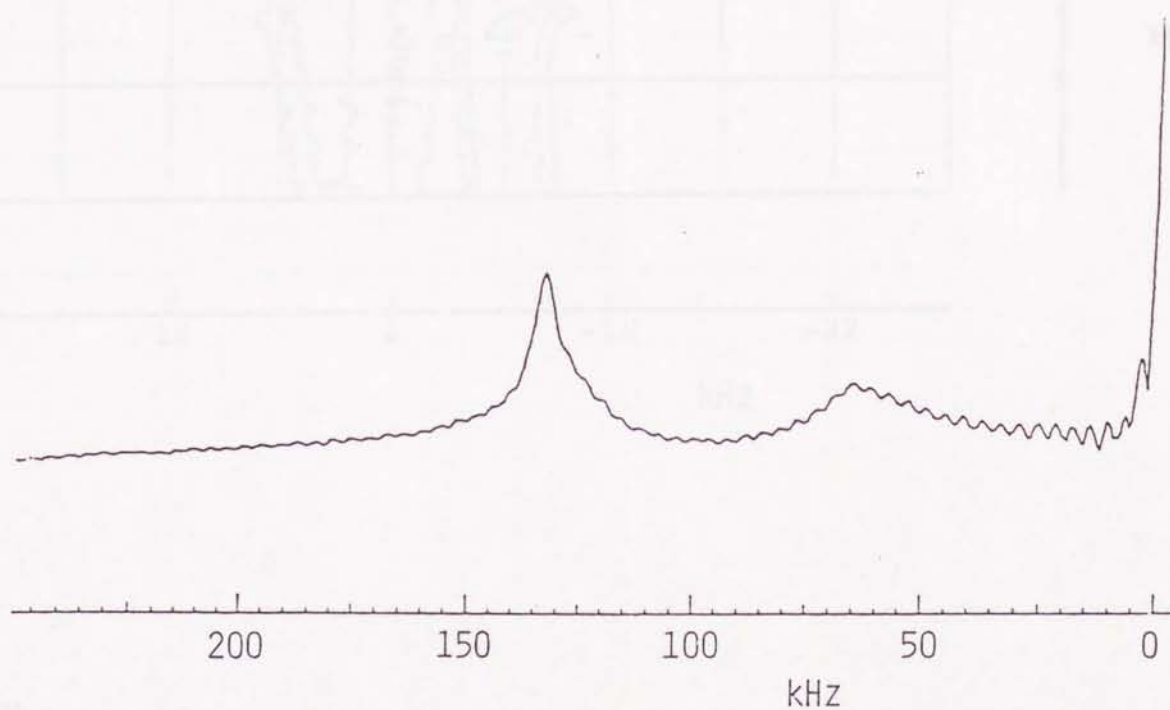


Figure 6.20  
 Projection onto  $F_1$  axis of 2D nutation spectrum of  
 $\text{Na}_3\text{Zr}_2\text{SiP}_2\text{O}_{12}$  at 363K.

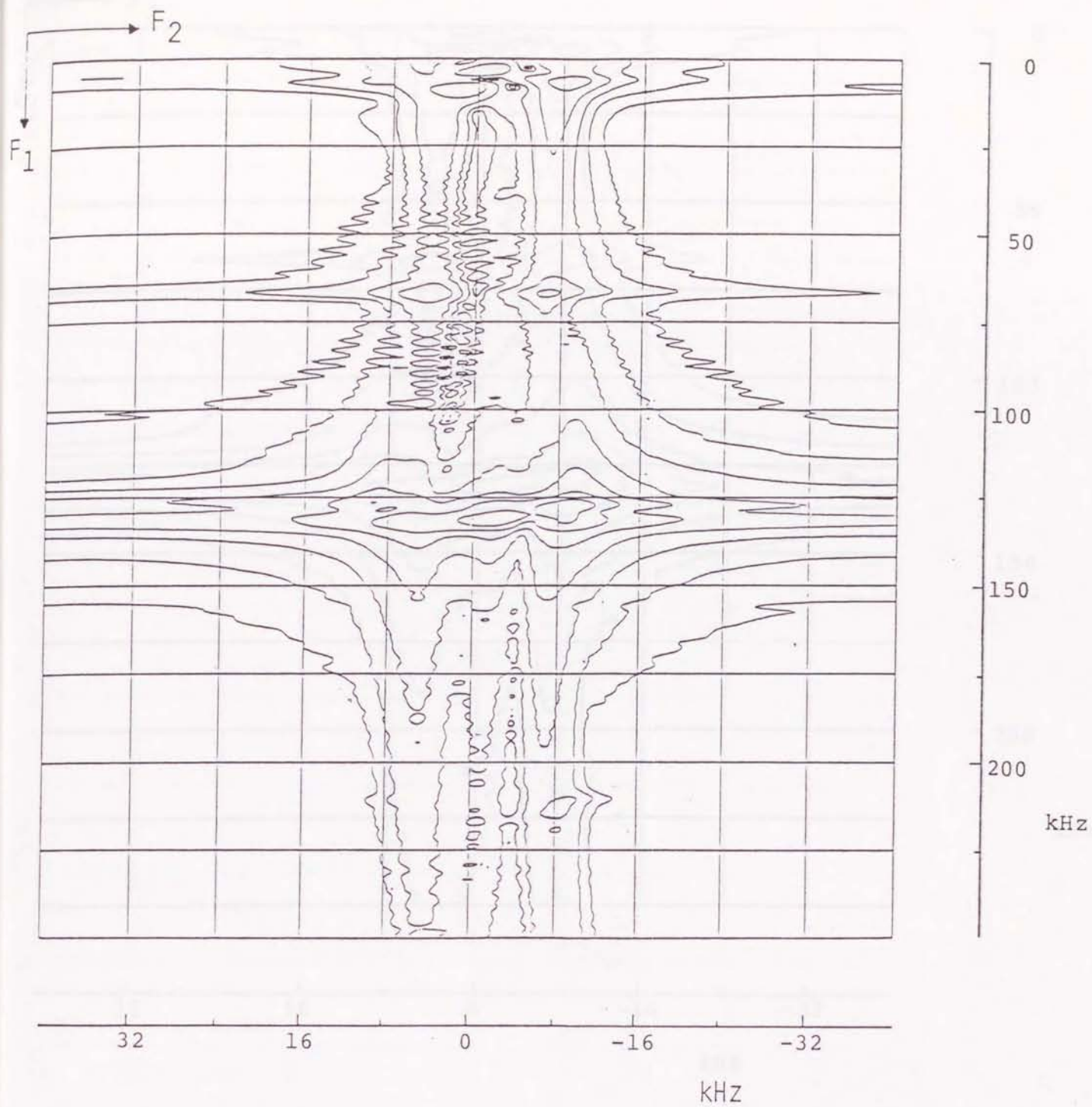


Figure 6.21

Contour plot of 2D nutation spectrum simulated with chemical exchange rate  $k = 0.001$  kHz. Other parameters are described in the text.



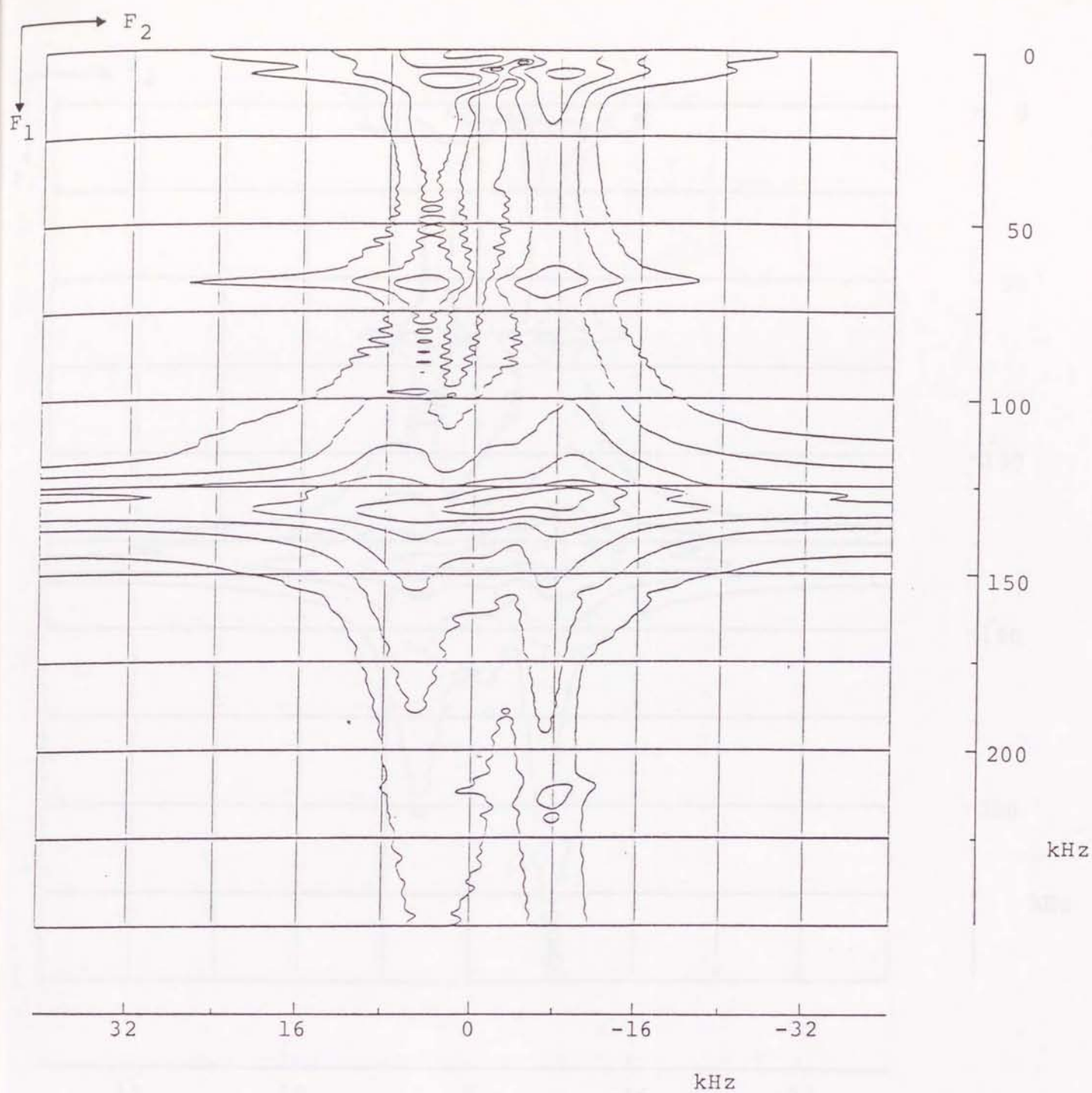


Figure 6.22

Contour plot of 2D nutation spectrum simulated with chemical exchange rate  $k = 0.01$  kHz.

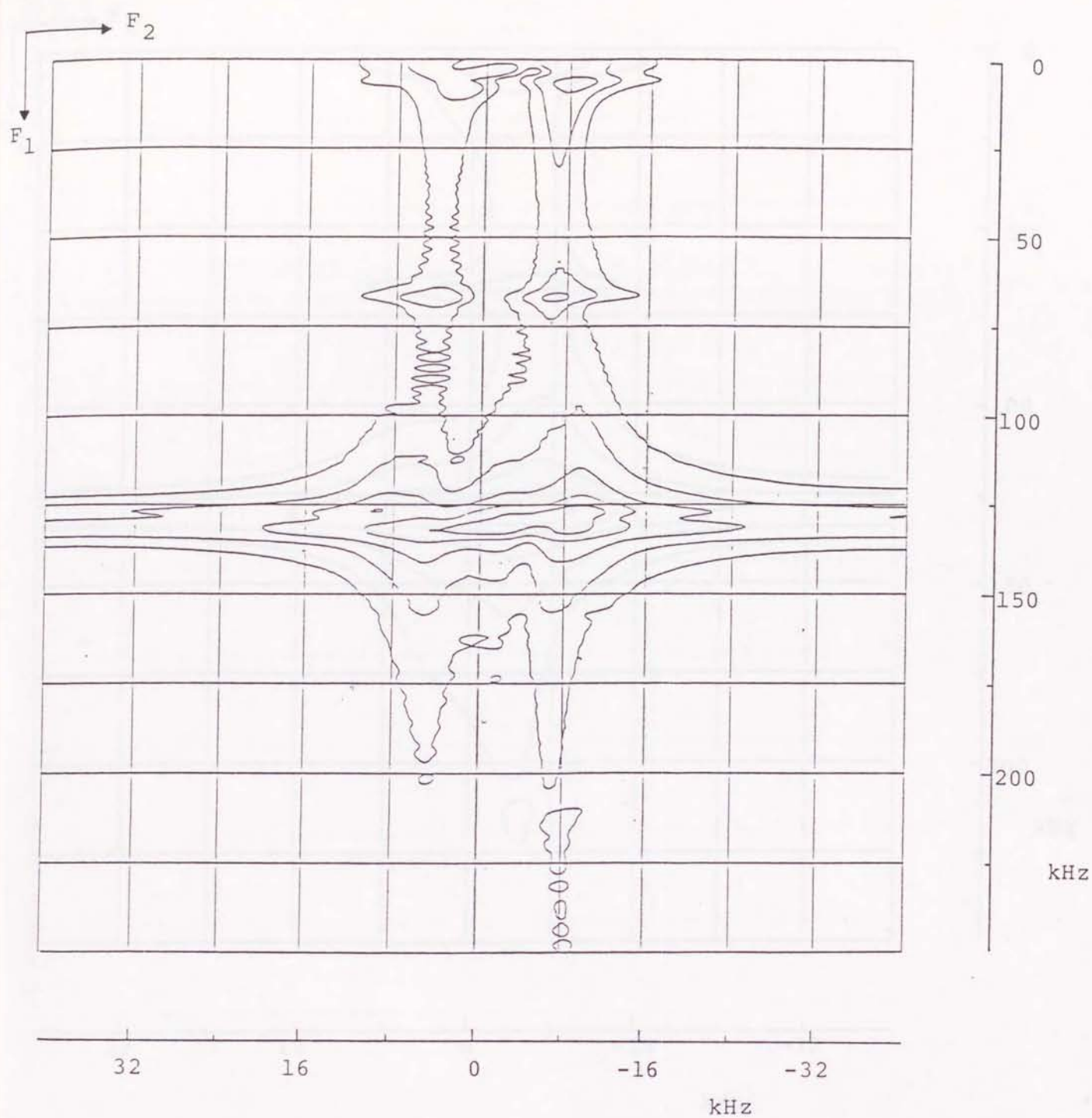


Figure 6.23

Contour plot of 2D nutation spectrum simulated with chemical exchange rate  $k = 0.1$  kHz.

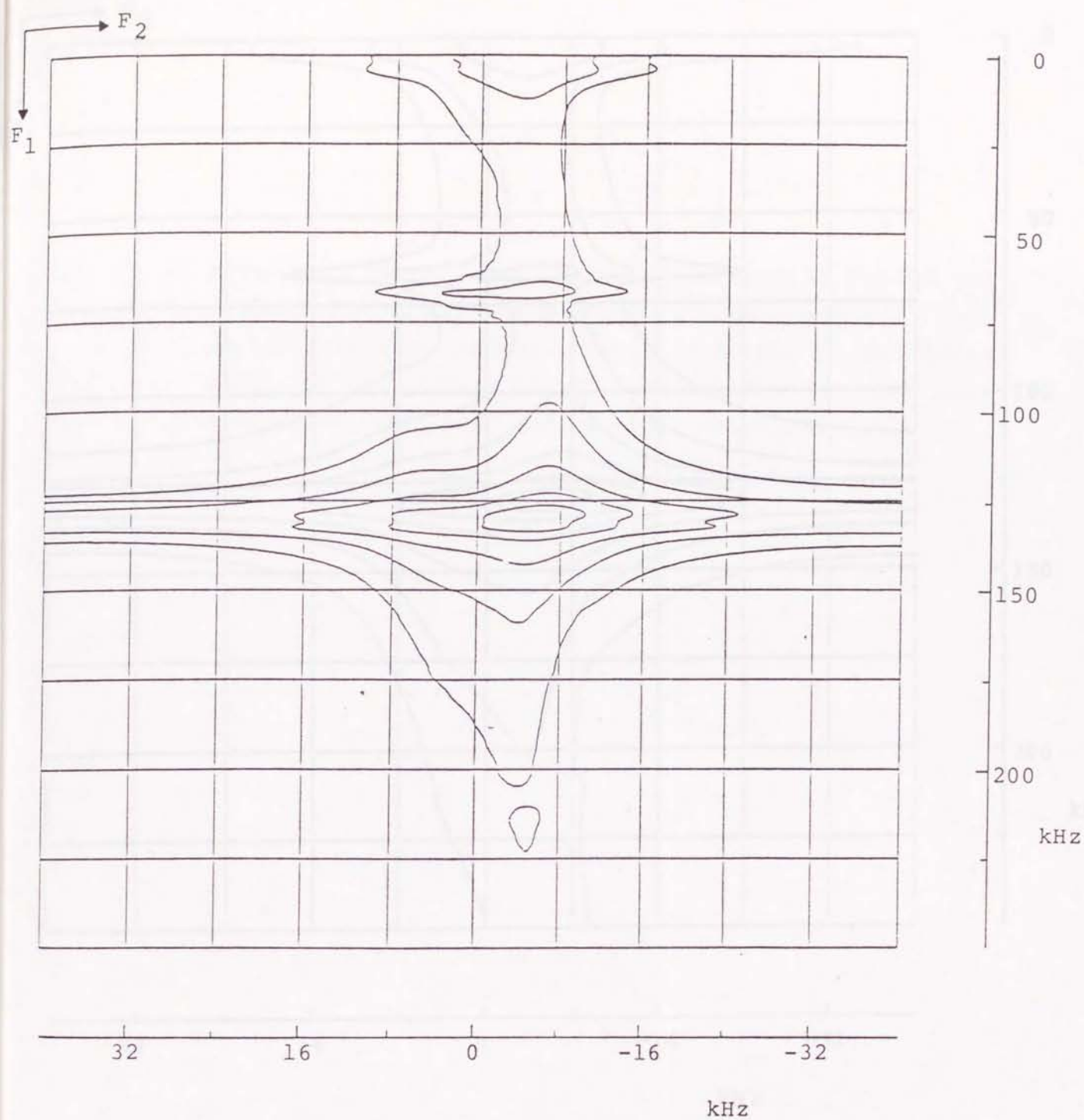


Figure 6.24

Contour plot of 2D nutation spectrum simulated with chemical exchange rate  $k = 1.0$  kHz.



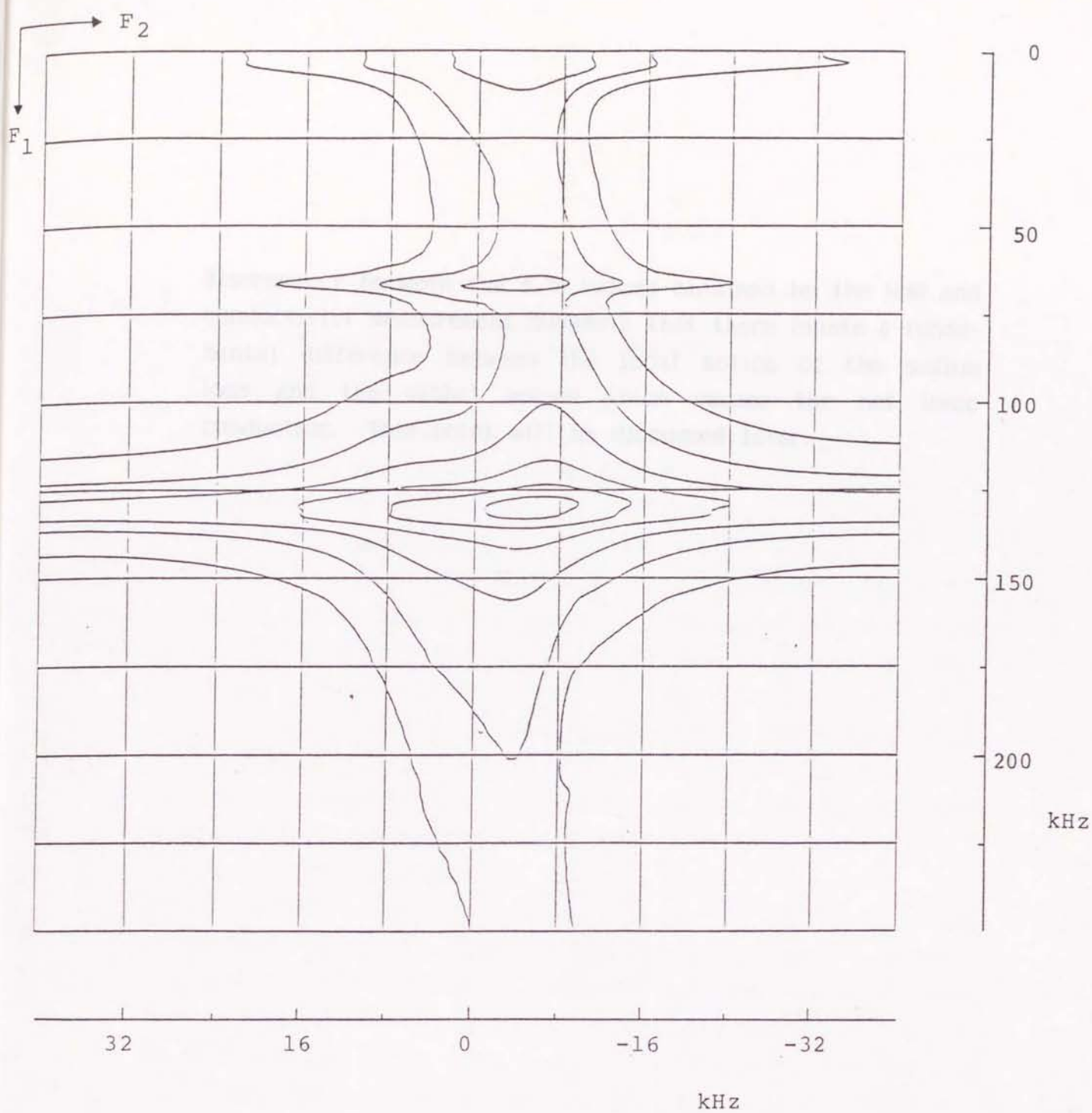


Figure 6.25

Contour plot of 2D nutation spectrum simulated with chemical exchange rate  $k = 10$  kHz.

discrepancy between the  $E_a$ 's values obtained by the NMR and conductivity measurement suggests that there exists a fundamental difference between the local motion of the sodium ions and the global motion which causes the net ionic conduction. This point will be discussed later.

## References

- [1] Landolt-Börnstein Tabellen, New Series,  
Group III, Vol 20a.
- [2] J.B. Goodenough, H.Y-P. Hong, and J.A. Kafalas,  
*Mat. Res. Bull.*, **11**, 203 (1976).



## 7. Discussion

### 7.1 Summary of the Present Work

So far in the previous Chapters a new theoretical method to describe the evolution of the quadrupolar spin system under the influence of strong rf field was established. This method is based on the Liouville representation and is superior in the following points to the other methods previously developed :

1. It is easy to construct the theoretical expression for the complex interaction between the spin system and the rf field and so can be easily extended to the system with spin higher than  $3/2$ .
2. Although the dimension of the matrix to be determined is far larger than that based on other standard methods, the formalism with the Liouvillian can be coded by computer language(s) and therefore is much suitable for the computation by a big computer.
3. Liouville representation has a form which can incorporate effects other than spin interaction in a straightforward manner. This property makes it possible to apply the nutation method to chemically exchanging system.

The new method was coded by FORTRAN to prepare the general simulation program which is necessary for analyzing the experimental 2D nutation spectra. The program can be applied to quadrupolar nuclei with spin numbers  $3/2 \sim 9/2$  and to systems with and without chemical exchange.

The 2D nutation NMR experiments were conducted for  $^{23}\text{Na}$  species involved in several compounds :

1. The  $^{23}\text{Na}$  resonances in  $\text{NaNO}_2$  and  $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$  were used to establish the optimal experimental conditions for the 2D

nutaton spectra and to evaluate the sensitivity of the spectra to the quadrupole interaction parameters,  $e^2Qq/h$  and  $\eta$ .

2. The  $^{23}\text{Na}$  nutaton NMR was applied to  $\text{Na}_2\text{SeO}_3$  to distinguish the three crystallographically nonequivalent Na sites in this compound. The value  $e^2Qq/h$  at the individual sites could be determined and also  $\eta$  was estimated for two of the three sites in this material.

3. The  $^{23}\text{Na}$  2D nutaton NMR was used to examine the dynamic process of  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ . The spectrum was remarkably temperature dependent and by applying the new theoretical method for the chemically exchanging system to it the chemical exchange rate of Na ions between two nonequivalent sites was estimated at each temperature. It was found that the activation energy deduced from the nutaton spectra differs significantly from that determined by a previous conductivity measurement.

In the course of this work a number of problems have been encountered concerning the practice of the 2D nutaton NMR. In what follows I will discuss the applicability, advantage and/or disadvantage of the 2D nutaton NMR newly developed in the present work.



## 7.2 2D Nutation NMR

Nuclear quadrupole interaction can provide a lot of useful information on the static and dynamic structures of crystalline materials. In the case that  $e^2Qq/h$  is larger than about 1 MHz, the pure quadrupole resonance can be applied to determine the quadrupole interaction parameters. When  $e^2Qq/h$  is much smaller than  $\sim 100$  kHz, the conventional NMR is used to detect the quadrupole-perturbed spectra either on single crystal or powdered specimen.

Many of chemically interesting nuclei such as  $^{23}\text{Na}$ ,  $^{27}\text{Al}$ ,  $^{39}\text{K}$ ,  $^{59}\text{Co}$ , etc. give often  $e^2Qq/h$  of the magnitude between ca. 100 kHz and a few MHz region. In such a frequency region it is extremely difficult to apply the above two methods because of the limitation on the sensitivity and/or band width of the radio-frequency spectrometers. Moreover when a number of crystallographically nonequivalent sites exist for the nuclei of interest, it is usually almost impossible to analyze the complex spectra even if the second order quadrupole interaction could be detected.

It was shown in a preceding Chapter that the 2D nutation NMR can successfully be applied to such cases. Since the strength of the rf pulse usually available is 100 kHz at most, it means that this method can be applied to determine the quadrupole coupling constant  $\Omega_q/2\pi$  up to about 1 MHz.

Most remarkable feature of the nutation NMR method lies in the fact that if a strong rf field can be used and if the condition  $H_D, H_{CS} \ll H_{rf}$  holds, undesirable line broadening effect due to  $H_D$  and  $H_{CS}$  along the  $F_1$  axis is dramatically reduced. (In the usual 1D spectrum which corresponds to the  $F_2$  direction, the line broadening due to other interactions



can not be eliminated.) In this way, detailed information on the quadrupole interaction can be derived from the nutation spectrum.

Another advantage of the nutation NMR is found in its simple setting of the experiment as having been demonstrated in Chap. 5.

A special use of the nutation method is, as pointed out [1], the determination of relative orientation between the EFG and the other interaction tensors. It is possible if the dominant interaction in the detection period,  $t_2$ , is other than the second order quadrupole interaction. For example, if the static magnetic field is considerably high the line width due to the chemical shift extends over wide frequency range and may dominate the second order quadrupole interaction. In such case, the spectra developed onto  $F_1$  and  $F_2$  axes contain the information mainly on the quadrupole and chemical shift interaction, respectively, and the correlation between them allows to determine the angles between tensors of both interactions.

However, several effects are found to deform the spectrum. These are discussed below.

a) Peak near 0 in  $F_1$

When an off-resonant rf pulse is applied, i.e. when Larmor frequency in the absence of quadrupole interaction does not coincide with the rf frequency, there must appear a peak at zero frequency. This can be explained as follows in the case of  $I = 1/2$  for simplicity. If the offset between the rf frequency and the Larmor frequency is  $\Delta\omega$ , the signal at the end of the pulse becomes

$$S(t) \propto [\alpha(1-\cos 2\Omega t) + i\beta \sin 2\Omega t] , \quad (7.2.1)$$

where

$$\begin{aligned} \Omega &= \sqrt{\Delta\omega^2 + \omega_1^2} , \\ \alpha &= \omega_1 \Delta\omega / \Omega^2 , \\ \beta &= \omega_1 / 2\Omega . \end{aligned} \quad (7.2.2)$$

Since  $\Delta\omega \neq 0$ ,  $\alpha$  does not vanish and the term independent of time generates the peak at 0 frequency. Also the cosine term survives and this results in the phase modulation along  $F_1$  which will cause the distortion of the spectrum. Then it is desirable to minimize the resonance offset as long as possible. But when the inhomogeneity of the external magnetic field and/or dipole interaction between the spins are significant, this effect cannot be eliminated perfectly.

Another cause of central peak is the effect of the second order quadrupole shift during the evolution period which has been neglected in the theoretical formulation. The nutation spectrum including these effects is shown in Fig. 7.1. The greater the quadrupole interaction, the greater the intensity of the central peak.

#### b) Line Broadening

Another undesirable effect in the nutation NMR is caused by the inhomogeneity of the rf field in space. This cannot be avoided in the use of the solenoid of the finite length : The rf magnetic field is strongest at the middle of the coil and decreases to some extent at the ends of it. [2] This brings about the distribution of the ratio  $\Omega_0/\omega_1$  and it causes the line broadening in  $F_1$  dimension. Also, if the shape of the rf pulse is not rectangular (although it is



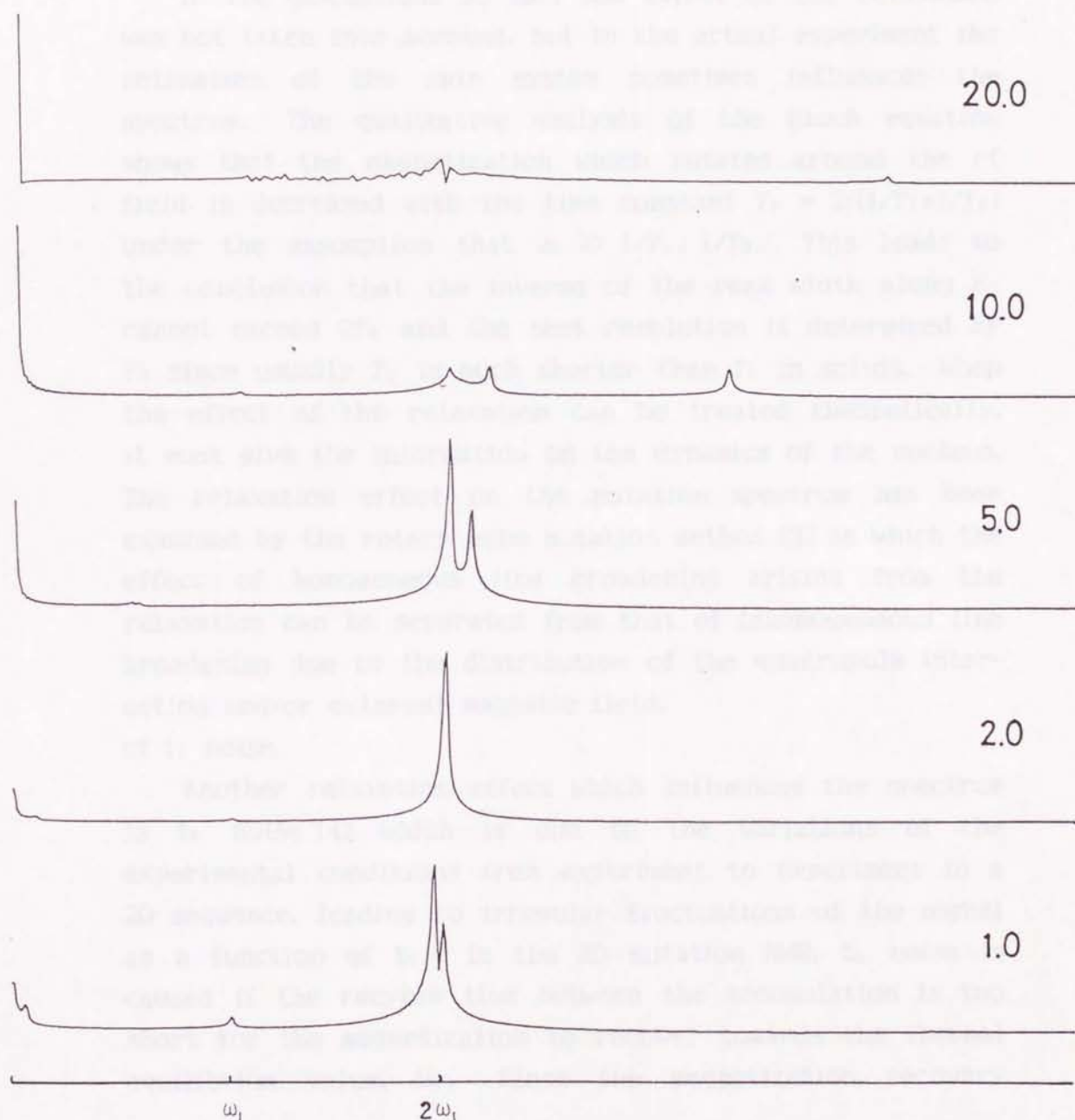


Figure 7.1

Dependence of nutation spectrum on the ratio  $\Omega_0/\omega_1$  including the second order quadrupole interaction as well as chemical shift.



assumed tacitly), it causes the spectrum to modify. The effect of the inhomogeneity in the rf field cannot be treated quantitatively.

In the discussions so far, the effect of the relaxation was not taken into account, but in the actual experiment the relaxation of the spin system sometimes influences the spectrum. The qualitative analysis of the Bloch equation shows that the magnetization which nutates around the rf field is decreased with the time constant  $T_n = 2/(1/T_1 + 1/T_2)$  under the assumption that  $\omega_1 \gg 1/T_1, 1/T_2$ . This leads to the conclusion that the inverse of the peak width along  $F_1$  cannot exceed  $2T_2$  and the best resolution is determined by  $T_2$  since usually  $T_2$  is much shorter than  $T_1$  in solids. When the effect of the relaxation can be treated theoretically, it must give the information on the dynamics of the nucleus. The relaxation effect on the nutation spectrum has been examined by the rotary echo nutation method [3] in which the effect of homogeneous line broadening arising from the relaxation can be separated from that of inhomogeneous line broadening due to the distribution of the quadrupole interaction and/or external magnetic field.

c)  $t_1$  noise

Another relaxation effect which influences the spectrum is  $t_1$  noise [4] which is due to the variations of the experimental conditions from experiment to experiment in a 2D sequence, leading to irregular fluctuations of the signal as a function of  $t_1$ . In the 2D nutation NMR,  $t_1$  noise is caused if the recycle time between the accumulation is too short for the magnetization to recover towards the thermal equilibrium value,  $M_0$ . Since the magnetization recovery

depends on  $t_1$  (and the recycle time) the peaks at  $2\omega_1$ ,  $3\omega_1$ ,  
... appears in the nutation spectrum.



### 7.3 Chemical Exchange Effect

As already demonstrated in a previous Chapter, the 2D nutation NMR gives its full ability in the situation where the spectrum arises from several nonequivalent sites. Often the signals corresponding to them overlap with each other and it is very difficult to decide which peak corresponds to each site. While by the use of 2D nutation NMR one can easily distinguish each site according to the difference of the strength of quadrupole interaction.

It was shown theoretically and experimentally that the nutation spectrum is drastically changed when the chemical exchange of the resonant nuclear species is excited. The detailed analysis of the spectrum brings about the quantitative information of the mechanism of the chemical exchange. Especially when slow and fast limits of the spectra can be obtained, one can determine the relative orientation of the EFG tensors as well as the rate constant of the exchange. Thus the method can be used to examine the mechanism of chemical exchange, ionic conduction, and/or solid state reaction from the microscopic point of view.

In Chap. 6 it was pointed out for  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$  that the activation energy for the sodium exchange was estimated from the 2D nutation NMR experiment to be 13 kJ/mol and that this value was very small compared with 31 kJ/mol deduced from a previous conductivity measurement. The most simple model for ionic conduction is based on the classical hopping mechanism through successive nearest-neighbor sites. In such a model conductivity measurement and NMR should give the same activation energy and jump rate. Serious discrepancies as was found above are often



encountered. [5] In the case that the ion transport occurs through the hopping between two or more nonequivalent ionic sites as was found in  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ , the discrepancy between the activation energies determined by different techniques can qualitatively be interpreted. Consider an ion transport through a potential shown in Fig. 7.2. As the potentials at sites 1 and 2 are largely different one ion can jump easily from 'site 2' to 'site 1' but the opposite is much difficult. If the neighboring 'site 1' is initially occupied, the ion will hop back and forth between the nearest sites until one of the other 'site 1' happens to become empty. The repetition of such local motion does not contribute to the net conductivity whereas it affects the NMR spectrum. The exchange and conduction of the sodium ions in  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$  are considered to apply to such a model. The 2D nutation NMR method looks at the rapid local motion with an average activation energy while the ion transport experiment measures an energy which is the sum of the activation energy for the jump and the energy for the vacancy formation at the 'site 1'. This idea enables one also to interpret the experimental results that the activation energy obtained from conductivity measurement is independent of the composition (x) while that from NMR is strongly dependent on x. (When  $x = 2$  the frequent jump between the sites 1 and 2 was observed as mentioned before but no sodium jump was recognized in the specimens with  $x = 0$  and 2. In the latter two samples the activation energies for the sodium exchange appear to be infinity.)

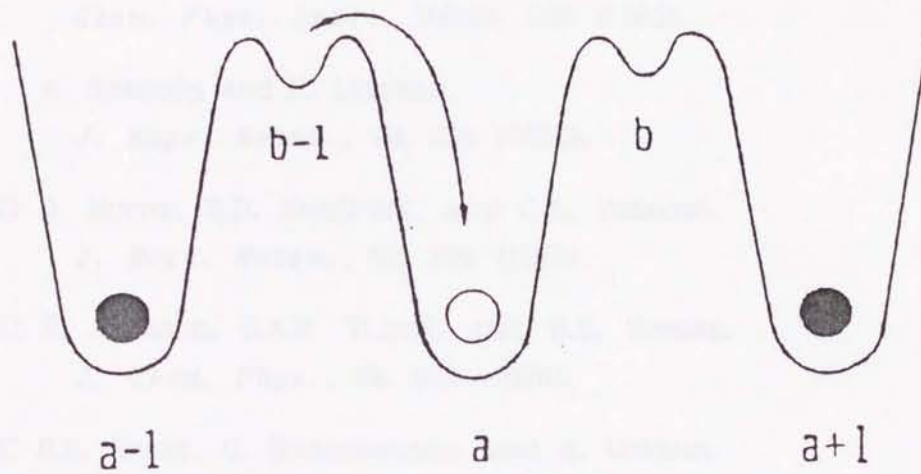


Figure 7.2

Nonequivalent site model with deep and shallow wells.

## References

- [1] A. Samoson and E. Lippmaa,  
*Chem. Phys. Lett.*, **100**(3), 205 (1983).  
  
A. Samoson and E. Lippmaa,  
*J. Magn. Reson.*, **79**, 255 (1988).
- [2] D. Horne, R.D. Kendrick, and C.S. Yannoni,  
*J. Magn. Reson.*, **52**, 299 (1983).
- [3] R. Janssen, G.A.H. Tijink, and W.S. Veeman,  
*J. Chem. Phys.*, **88**, 518 (1988).
- [4] R.R. Ernst, G. Bodenhausen, and A. Wokaun,  
*Principles of Nuclear Magnetic Resonance  
in One and Two Dimensions*, Oxford Press, 1987.
- [5] P.M. Richards,  
*Physics of Superionic Conductors*, Chap. 6,  
ed. by M.B. Salamon, Springer-Verlag, 1979.



```

Line# Source Line      Microsoft FORTRAN Optimizing Compiler Version 4.01

 1  $NOTRUNCATE
 2  $DECLARE
 3      PROGRAM NUTATION
 4  C
 5      COMPLEX*16 ARYDAT(1,1024),H1(100),R1(100),RDR(100)
 6      COMPLEX*16 E1(10),EE(10),REC(10),ERC(10),W(10)
 7      REAL*8      THD(10),QCC,ETA,QC2,W1,Q1F(10),W1F(10)
 8      REAL*8      AI,W0,PI2,T1(2),CT1,CT2(20000),CP1(900),H11(2,100),S,D
 9      INTEGER*4    DIM(2),MXD(2),NSP,NT,NP,MXT,I,J,K,L,N,ERS
10      CHARACTER*15 RGF,TDF
11  C
12      EQUIVALENCE (H1,H11),(CT2(901),CP1(1))
13      COMMON /ARYDAT/ARYDAT,DIM
14      COMMON /PARAMS/THD,QCC,ETA,QC2,Q1F,W1F
15      COMMON /WRKVAR/RDR,EE,REC,ERC,W
16  C      -----
17  C      Declarations of Constants
18  C      -----
19      PARAMETER(PI2=6.283185307179586D+00)
20      DATA MXD/1024,1/
21  C      -----
22  C      Spin Number
23  C      -----
24      WRITE(*,'(A11Y)') '0Spin *2 = '
25      READ(*,'(I2)') NSP
26      S=DBLE(NSP)/2.0D+00
27      AI=S*S+S
28  C      -----
29  C      Larmor Frequency
30  C      -----
31      WRITE(*,'(A20Y)') '0Lamor Freq / MHz = '
32      READ (*,'(F7.4)') W0
33  C      -----
34  C      Quadrupole Interaction Parameters
35  C      -----
36      WRITE(*,'(A17Y)') '0eqQ / MHz,  $\eta$  = '
37      READ (*,'(2F10.6)') QCC,ETA
38  C      -----
39  C      RF Strength in Frequency Units
40  C      -----
41      WRITE(*,'(A27Y)') '0RF Field Strength / kHz = '
42      READ (*,'(F6.3)') W1
43  C      -----
44  C      Sampling Points in each Dimension
45  C      -----
46      DO 300 I=1,2
47          WRITE(*,'(A13,I1)') '0Dimension : ', I
48          WRITE(*,'(A35,I4,A5Y)')
49      &      ' Number of Sampling Points ( Max. ',MXD(I),' ) = '
50          READ (*,'(I5)') DIM(I)
51          WRITE(*,'(A25Y)') ' Time Increment /  $\mu$ s = '
52          READ (*,'(F5.3)') TI(I)
53      300 CONTINUE

```

```

Line# Source Line      Microsoft FORTRAN Optimizing Compiler Version 4.01

54 C      -----
55 C      RGF : Stores Computational Condition
56 C      TDF : Saves FID Data
57 C      -----
58      WRITE(*,'(A25Y)') 'Registry File Name = '
59      READ(*,'(A15)') RGF
60      WRITE(*,'(A25Y)') 'Time Domain File Name = '
61      READ(*,'(A15)') TDF
62 C      -----
63 C      Get the Number to be calculated
64 C      -----
65      WRITE(*,'(A20)') 'Number of Division over  $\theta$  '
66      WRITE(*,'(A4Y)') ' [ Max. : 20000 (  $\eta$  = 0 ) 900 (  $\eta$  > 0 ) ] = '
67      READ(*,'(I5)') NT
68      DO 400 I=1,NT
69          CT1=DBLE(I)/DBLE(NT)
70          CT2(I)=CT1*CT1
71      400 CONTINUE
72      IF (ETA .EQ. 0.0D+00) THEN
73          NP=1
74          CP1(I)=0.0D+00
75      ELSE
76          NP=NT
77          DO 410 I=1,NP
78              CP1(I)=ETA*DCOS(PI2*DBLE(I)/DBLE(NT))
79      410 CONTINUE
80      END IF
81 C      -----
82 C      Store the Parameters
83 C      -----
84      OPEN (UNIT=50, FILE=RGF, ACCESS='SEQUENTIAL')
85      WRITE(50,'(A40)') '----- Computational Conditions ----- '
86      WRITE(50,'(A16)') '< Interactions >'
87      WRITE(50,'(A10,I2,A4)') ' Spin = ',NSP,' / 2'
88      WRITE(50,'(A22,F8.3)') ' Lamor Freq / MHz = ', W0
89      WRITE(50,'(A22,F7.3)') ' RF Field / kHz = ', W1
90      WRITE(50,'(A15,F10.6,A8,F10.6)')
91      & ' QCC / MHz = ',QCC,'; ETA = ',ETA
92      WRITE(50,'(A15)') '< Calculation >'
93      WRITE(50,'(A44)') ' Dimension Data Points Time Increments'
94      DO 500 I=1,2
95          WRITE(50,'(7X,I1,10X,I4,9X,F10.5)') I,DIM(I),TI(I)
96      500 CONTINUE
97      WRITE(50,'(/A28,I5)') ' Total Division over  $\theta$  = ',NT
98      WRITE(50,'(/A18,A15)') ' Data Stored in ',TDF
99      CLOSE (UNIT=50)

```



```

Line# Source Line      Microsoft FORTRAN Optimizing Compiler Version 4.01

100 C      -----
101 C      Determine the Parameters suitable to Calculation
102 C      -----
103      QCC=QCC/DBLE(NSP*NSP-NSP)*2.5D-01
104      QC2=QCC*QCC/W0*PI2*TI(2)*(AI-7.5D-01)
105      QCC=QCC*PI2*TI(1)
106      W1=W1*PI2*TI(1)*1.0D-03
107      D=DBLE(NSP)/2.0D+00
108      DO 600 I=1,NSP+1
109          THD(I)=D
110          Q1F(I)=D*D*3.0D+00-AI
111          W1F(I)=W1*DSQRT(AI-D*(D-1.0D+00))/2.0D+00
112          D=D-1.0D+00
113      600 CONTINUE
114          WRITE(*, '(A38,I5/)' )
115      & '      Total Division over THETA, PHI = ',NT*NP
116 C      -----
117 C      Powder Averaging Start here
118 C      -----
119      DO 710 I=1,NT
120          WRITE(*, '(A30,I5)' ) '+'      Powder Averaging Now : ',I*NP
121          DO 700 J=1,NP
122              CALL EVOLVE(NSP+1,H1,H11,R1,E1,CT2(I),CP1(J),ERS)
123              IF (ERS .NE. 0) GOTO 20000
124      700 CONTINUE
125      710 CONTINUE
126 C      -----
127 C      Normalize and Store the Data
128 C      -----
129      OPEN (UNIT=10, FILE=TDF)
130      D=1.0D+00/DBLE(NT*NP)
131      DO 810 I=1,DIM(1)
132          DO 800 J=1,DIM(2)
133              ARYDAT(J,I)=ARYDAT(J,I)*D
134              WRITE(10, FMT=9000, IOSTAT=ERS, ERR=10000) ARYDAT(J,I)
135      800 CONTINUE
136      810 CONTINUE
137      CLOSE (UNIT=10)
138      9000 FORMAT(D22.16,1X,D22.16)
139 C      -----
140 C      Normal End.
141 C      -----
142      GO TO 99999
143 C      -----
144 C      Error Exist in the Procedure.
145 C      -----
146      10000 WRITE(*, '(A18,I5)' ) ' File Write Error ',ERS
147      GO TO 99999
148      20000 WRITE(*, '(A23,I5)' ) ' Diagonalization Error ',ERS
149 C
150      99999 END
151      $PAGE

```



```

Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

152 SUBROUTINE EVOLVE(L,H1,H11,R1,E1,CT2,CP1,ERR)
153 C -----
154 C Calculate the Evolution of the Density Vectors
155 C -----
156 COMPLEX*16 ARYDAT(4,1024),H1(L,L),R1(L,L),E1(L),IC,Q2E
157 COMPLEX*16 RDR(10,10),EE(10),REC(10),ERC(10),W(10)
158 REAL*8 H11(2,L,L),Q1,Q2,D,CT2,CT4,ST2,ST4,CP1,CP2,SP2
159 REAL*8 THD(10),QCC,ETA,QC2,Q1F(10),W1F(10)
160 INTEGER*4 DIM(2),N1,N2,I,J,K,ERR
161 C
162 COMMON /ARYDAT/ARYDAT,DIM
163 COMMON /PARAMS/THD,QCC,ETA,QC2,Q1F,W1F
164 COMMON /WRKVAR/RDR,EE,REC,ERC,W
165 C -----
166 C Transformation of Coordinate to Molecular Frame
167 C -----
168 CT4=CT2*CT2
169 ST2=1.0D+00-CT2
170 ST4=ST2*ST2
171 CP2=CP1*CP1
172 SP2=ETA*ETA-CP2
173 C -----
174 C First Order Quadrupole Splitting
175 C -----
176 Q1=QCC*(3.0D+00*CT2-1.0D+00+ST2*CP1)
177 C -----
178 C Second Order Quadrupole Shift for the Central Transition
179 C -----
180 Q2=QC2*( ST4*9.0-(1.0-CT4)*CP1*6.0+(CT2*4.0+ST4)*CP2+CT2*SP2*4.0
181 C & -ST2*(CT2*(9.0+CP1*6.0+CP2)+SP2)*8.0 )
182 Q2E=DCMPLX(DCOS(Q2),DSIN(Q2))
183 C -----
184 C Set the Hamiltonian
185 C -----
186 DO 30 I=1,L
187 DO 20 J=1,L
188 H1(J,I)=0.0D+00
189 20 CONTINUE
190 H11(2,I,I)=Q1*Q1F(I)
191 IF (I .GT. 1) H11(2,I-1,I)=W1F(I-1)
192 IF (I .LT. L) H11(2,I+1,I)=W1F(I)
193 30 CONTINUE

```

```

Line# Source Line      Microsoft FORTRAN Optimizing Compiler Version 4.01
194 C      -----
195 C      Get the Eigenvalues and Eigenvectors to Calculate Exponentials
196 C      -----
197      CALL CHEQRD(L,H1,E1,R1,ERR)
198      IF (ERR.NE. 0) RETURN
199      DO 100 I=1,L
200          EE(I)=CDEXP(E1(I))
201      100 CONTINUE
202      DO 110 J=1,L
203          DO 110 I=1,L
204              RDR(I,J)=0.0D+00
205              DO 110 K=1,L
206                  RDR(I,J)=RDR(I,J)+R1(K,I)*THD(K)*R1(K,J)
207      110 CONTINUE
208      DO 120 I=1,L
209          REC(I)=R1(L/2,I)
210          ERC(I)=R1(L/2+1,I)
211      120 CONTINUE
212 C      -----
213 C      Calculate FID
214 C      -----
215      DO 300 N1=1,DIM(1)
216          DO 200 J=1,L
217              REC(J)=REC(J)*EE(J)
218              ERC(J)=ERC(J)*DCONJG(EE(J))
219      200 CONTINUE
220      DO 210 I=1,L
221          W(I)=0.0D+00
222          DO 210 J=1,L
223              W(I)=W(I)+REC(J)*RDR(J,I)
224      210 CONTINUE
225      DO 220 I=1,L
226          IC=0.0D+00
227          DO 220 J=1,L
228              IC=IC+W(J)*ERC(J)
229      220 CONTINUE
230      DO 300 N2=1,DIM(2)
231          ARYDAT(N2,N1)=ARYDAT(N2,N1)+IC
232          IC=IC*Q2E
233      300 CONTINUE
234 C
235      RETURN
236      END
237 C
238 $PAGE

```



```

Line# Source Line      Microsoft FORTRAN Optimizing Compiler Version 4.01

239      SUBROUTINE CHEQRD(N,LC,EC,VC,ERR)
240      C      -----
241      C      Calculate the Eigenvalues and Eigenvectors of Symmetric Matrix
242      C      -----
243      COMPLEX*16 LC(N,N),VC(N,N),EC(N),ZX,ZY,ZZ,ZR,ZC,ZS
244      REAL*8      CDABSP,DEL
245      INTEGER*4   I,J,IP1,LL,LU,ITR,ITRMAX,ERR
246      C
247      CDABSP(ZZ)=DABS(DREAL(ZZ))+DABS(DIMAG(ZZ))
248      DATA DEL,ITRMAX/5.0D-15,30/
249      C      -----
250      C      Set the Eigenvectors to Unit Matrix
251      C      -----
252      DO 110 I=1,N
253      DO 100 J=1,N
254      VC(J,I)=0.0D+00
255      100 CONTINUE
256      VC(I,I)=1.0D+00
257      110 CONTINUE
258      C      -----
259      C      Search for a Small Sub-diagonal Element.
260      C      -----
261      LU=N
262      300 ITR=0
263      310 LL=LU
264      320 IF (CDABSP(LC(LL,LL-1)) .GT. DEL) THEN
265      LL=LL-1
266      IF (LL .GT. 1) GO TO 320
267      END IF
268      IF (LL .NE. LU) THEN
269      C      -----
270      C      If Convergence is not Attained within 30 Iterations,
271      C      Truncate the Computation.
272      C      -----
273      IF (ITR .GT. ITRMAX) GO TO 10000
274      C      -----
275      C      Determine the Origin Shift as the Eigenvalue of the 2 by 2
276      C      Bottom Submatrix which is Nearer to the bottom Element.
277      C      -----
278      ZX=(LC(LU-1,LU-1)+LC(LU,LU))*0.5D+00
279      ZY=ZX-LC(LU,LU)
280      ZZ=CDSQRT(LC(LU-1,LU)*LC(LU,LU-1)+ZY*ZY)
281      ZZ=DSIGN(1.0D+00,CDABSP(ZY-ZZ)-CDABSP(ZY+ZZ))*ZZ+ZX
282      LC(LL,LL)=LC(LL,LL)-ZZ
283      ZC=1.0D+00

```



```

Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

284 C -----
285 C Left- and Right-hand Transformation.
286 C -----
287 DO 360 I=LL,LU-1
288 IP1=I+1
289 ZX=LC( I ,I)
290 ZY=LC(IP1,I)
291 ZR=CDSQRT(ZX*ZX+ZY*ZY)
292 IF (CDABSP(ZR) .LT. DEL) GOTO 20000
293 LC(I,I)=ZC*ZR
294 IF (I .GT. LL) LC(I,I-1)=ZS*ZR
295 LC(IP1,IP1)=LC(IP1,IP1)-ZZ
296 ZC=ZX/ZR
297 ZS=ZY/ZR
298 DO 330 J=IP1,N
299 ZY=LC(I,J)
300 LC( I ,J)=ZY*ZC+LC(IP1,J)*ZS
301 LC(IP1,J)=LC(IP1,J)*ZC-ZY*ZS
302 330 CONTINUE
303 DO 340 J=1,I
304 ZY=LC(J,I)
305 LC(J, I )=ZY*ZC+LC(J,IP1)*ZS
306 LC(J,IP1)=LC(J,IP1)*ZC-ZY*ZS
307 340 CONTINUE
308 LC(I,I)=LC(I,I)+ZZ
309 DO 350 J=1,N
310 ZY=VC(J,I)
311 VC(J, I )=ZY*ZC+VC(J,IP1)*ZS
312 VC(J,IP1)=VC(J,IP1)*ZC-ZY*ZS
313 350 CONTINUE
314 360 CONTINUE
315 LC(LU,LU-1)=LC(LU,LU)*ZS
316 LC(LU, LU )=LC(LU,LU)*ZC+ZZ
317 ITR=ITR+1
318 GO TO 310
319 END IF
320 LU=LU-1
321 IF (LU .GT. 1) GO TO 300
322 C -----
323 C QR-Transformation is Over.
324 C Eigenvalues are Given
325 C by the Diagonal Elements of the Resultant Matrix.
326 C -----
327 DO 400 I=1,N
328 EC(I)=LC(I,I)
329 400 CONTINUE

```

Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

```

330 C -----
331 C      Normal Exit.
332 C -----
333 C      ERR=0
334 C      RETURN
335 C -----
336 C      Error Exit.
337 C      10000 : Not Converged.
338 C      20000 : Devide by Zero.
339 C -----
340 10000 ERR=10000
341      RETURN
342 20000 ERR=20000
343      RETURN
344      END

```



Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

```

1 $DECLARE
2 PROGRAM EXCHANGE
3 C -----
4 C Simulation Program for 2D Nutation NMR with Chemical Exchange
5 C -----
6 COMPLEX*8 ARD(256,128)
7 REAL*8 QCC(2),ETA(2),QC2(2),ET2(2),CHS(2),RFS,EXC(2,2,2)
8 REAL*8 ALP(2),BET(2),GAM(2),TDX(8),THD(4,2),R(4),P(2)
9 REAL*8 X(-50:50,0:50),Y(-50:50,0:50),Z(-50:50)
10 REAL*8 SA(2),CA(2),SB(2),CB(2),SG(2),CG(2),TI(2)
11 REAL*8 W0,W1,D,PID,SNT,D2R,PI1,PI2,SQ3
12 INTEGER*4 DIM(2),MXD(2),NSP,NSI,MXS,NN,MXT,I,J,N,ERS
13 CHARACTER CHA
14 CHARACTER*15 RGF,TDF
15 C
16 EQUIVALENCE (TDX,THD),(CHA,RGF)
17 COMMON /ARD/ARD,DIM,TDX,R,P
18 COMMON /PAR/QCC,ETA,QC2,ET2,CHS,RFS,EXC
19 COMMON /ARG/SA,CA,SB,CB,SG,CG
20 C -----
21 C Declarations of Constants
22 C -----
23 PARAMETER(NSP=4,MXS=2,MXT=50)
24 PARAMETER(D2R=1.745329251994329D-02,SQ3=8.660254037844385D-01)
25 PARAMETER(PI1=3.141592653589793D+00,PI2=6.283185307179586D+00)
26 DATA MXD/128,256/
27 C -----
28 C Lamor Frequency
29 C -----
30 WRITE(*,'(A20Y)') '0Lamor Freq / MHz = '
31 READ (*,'(F7.4)') W0
32 C -----
33 C Number of Sites to be Considered
34 C -----
35 1 WRITE(*,'(A18Y)') '0Number of Site = '
36 READ (*,'(I1)') NSI
37 IF (NSI .GT. MXS) GOTO 1
38 C -----
39 C Quadrupole Interaction Parameters and Chemical Shifts
40 C -----
41 DO 100 I=1,NSI
42 WRITE(*,'(A7,I1)') ' Site : ',I
43 WRITE(*,'(A21Y)') ' eqQ / MHz, eta = '
44 READ (*,'(2F10.6)') QCC(I),ETA(I)
45 WRITE(*,'(A37Y)') ' Euler Angles of Principal Axis = '
46 READ(*,'(3F10.6)') ALP(I),BET(I),GAM(I)
47 D=ALP(I)*D2R
48 SA(I)=DSIN(D)
49 CA(I)=DCOS(D)
50 D=BET(I)*D2R
51 SB(I)=DSIN(D)
52 CB(I)=DCOS(D)
53 D=GAM(I)*D2R
54 SG(I)=DSIN(D)
55 CG(I)=DCOS(D)
56 WRITE(*,'(A27Y)') ' Chemical Shift / kHz = '
57 READ (*,'(F10.6)') CHS(I)
58 CHS(I)=CHS(I)*1.0D-03

```



```

Line# Source Line      Microsoft FORTRAN Optimizing Compiler Version 4.01

59      100 CONTINUE
60      C -----
61      C      Chemical Exchange
62      C -----
63      WRITE(*, '(A60Y)')
64      & '0Equilibrium Population of Each Site are Equal ( Y or N ) ? '
65      READ (*, '(A1)') CHA
66      IF ((ICHAR(CH A) .EQ. ICHAR('Y')) .OR.
67      & (ICHAR(CH A) .EQ. ICHAR('y')))) THEN
68      D=DBLE(NSI)
69      DO 200 I=1, NSI
70      P(I)=1.0D+00/D
71      200 CONTINUE
72      ELSE
73      D=0.0D+00
74      DO 210 I=1, NSI
75      WRITE(*, '(A30,I1,A3Y)')
76      & ' Relative Population of Site ', I, ' = '
77      READ (*, '(F6.4)') P(I)
78      D=D+P(I)
79      210 CONTINUE
80      DO 220 I=1, NSI
81      P(I)=P(I)/D
82      220 CONTINUE
83      END IF
84      DO 230 I=1, NSI
85      EXC(I, I, 1)=0.0D+00
86      DO 230 J=1, NSI
87      IF (J .GT. I) THEN
88      WRITE(*, '(A22,1X,I1,1X,A2,1X,I1,1X,A9Y)')
89      & ' Exchange Rate from ', I, ' to ', J, ' / MHz = '
90      READ (*, '(F10.8)') EXC(J, I, 1)
91      EXC(I, J, 1)=EXC(J, I, 1)*P(I)/P(J)
92      END IF
93      IF (I .NE. J) EXC(I, I, 1)=EXC(I, I, 1)-EXC(J, I, 1)
94      230 CONTINUE
95      C -----
96      C      RF Strength in Frequency Units
97      C -----
98      WRITE(*, '(A27Y)') '0RF Field Strength / kHz = '
99      READ (*, '(F6.3)') W1
100     C -----
101     C      DIM(1), DIM(2) : Sampling Points in each Dimension
102     C -----
103     DO 300 I=1, 2
104     WRITE(*, '(A13,I1)') '0Dimension : ', I
105     2 WRITE(*, '(A30Y)') ' Number of Sampling Points = '
106     READ (*, '(I5)') DIM(I)
107     IF (DIM(I) .GT. MXD(I)) THEN
108     WRITE(*, '(A14)') '0 Too Large !! '
109     GO TO 2
110     END IF
111     WRITE(*, '(A35Y)') ' Time Increment ( in microsec ) = '
112     READ (*, '(F5.3)') TI(I)
113     300 CONTINUE
114     C -----
115     C      RGF : Stores Computational Condition
116     C      TDF : Saves FID Data

```

```

Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

117 C -----
118 WRITE(*,'(A25Y)') '0Registry File Name = '
119 READ(*,'(A15)') RGF
120 WRITE(*,'(A25Y)') ' Time Domain File Name = '
121 READ(*,'(A15)') TDF
122 C -----
123 C Get the Number to be calculated
124 C -----
125 3 WRITE(*,'(A33Y)') '0Number of Division over THETA = '
126 READ(*,'(I3)') N
127 IF (N.GT. MXT) GOTO 3
128 D=DBLE(N)
129 PID=PI1/D
130 DO 400 I=0,N
131 Z(I)=DBLE(I)/D
132 Z(-I)=-Z(I)
133 SNT=DSQRT(1.0-Z(I)*Z(I))
134 DO 400 J=0,N
135 X(J,I)=SNT*DCOS(PID*DBLE(J))
136 Y(J,I)=SNT*DSIN(PID*DBLE(J))
137 X(-J,I)=X(J,I)
138 Y(-J,I)=-Y(J,I)
139 400 CONTINUE
140 WRITE(*,'(A38,I5/)')
141 & ' Total Division over THETA, PHI = ',N*N*4-N*2
142 C -----
143 C Store the Parameters
144 C -----
145 OPEN (UNIT=50, FILE=RGF, ACCESS='SEQUENTIAL')
146 WRITE(50,'(A40)') ' ----- Computational Conditions ----- '
147 WRITE(50,'(/A17)') ' < Interactions >'
148 WRITE(50,'(A22,F8.3)') ' Lamor Freq / MHz = ', W0
149 WRITE(50,'(A22,F7.3)') ' RF Field / kHz = ', W1
150 DO 500 I=1,NSI
151 WRITE(50,'(/A10,I1,A16,F10.8,A2)')
152 & ' Site : ',I,' ( Population = ',P(I),' )'
153 WRITE(50,'(A16,F6.4,A8,F6.4)')
154 & ' QCC / MHz = ',QCC(I),' ; ETA = ',ETA(I)
155 WRITE(50,'(A19,F5.2,A2,F5.2,A2,F5.2)')
156 & ' Euler Angles : ',ALP(I),' ',BET(I),' ',GAM(I)
157 WRITE(50,'(A27,F6.2)')
158 & ' Chemical Shift / kHz = ',CHS(I)*1.0D+03
159 500 CONTINUE
160 WRITE(50,'(/A25)') ' < Exchange Rates / MHz >'
161 DO 510 I=1,NSI
162 DO 510 J=1,NSI
163 WRITE(50,'(4X,I1,A5,I1,F16.12)') I,' --> ',J,EXC(I,J,1)
164 510 CONTINUE
165 WRITE(50,'(/A16)') ' < Calculation >'
166 WRITE(50,'(A45)') ' Dimension Data Points Time Increments'
167 DO 530 I=1,2
168 WRITE(50,'(8X,I1,10X,I3,10X,F10.5)') I,DIM(I),TI(I)
169 530 CONTINUE
170 WRITE(50,'(/A21, I3)') ' Total Division = ',N*N*4-N*2
171 WRITE(50,'(/A19,A15)') ' Data Stored in ',TDF
172 CLOSE (UNIT=50)
173 C -----
174 C Symmetrize the Exchange Matrix

```



```

Line# Source Line      Microsoft FORTRAN Optimizing Compiler Version 4.01

175 C      and Set the Spin Density Vectors at Thermal Equilibrium
176 C      -----
177      DO 600 I=1,NSI
178          P(I)=DSQRT(P(I))
179          THD(1,I)= SQ3*P(I)
180          THD(2,I)= -P(I)
181          THD(3,I)= 0.0D+00
182          THD(4,I)=-SQ3*P(I)
183      600 CONTINUE
184      DO 610 I=1,NSI
185          DO 610 J=1,NSI
186              IF (J .NE. I) EXC(J,I,1)=EXC(J,I,1)*P(I)/P(J)
187      610 CONTINUE
188 C      -----
189 C      Determine the Parameters suitable to Calculation
190 C      -----
191      DO 620 I=1,NSI
192          QC2(I)=PI2*QCC(I)*QCC(I)/W0*TI(2)/9.6D+01
193          QCC(I)=PI2*QCC(I)/8.0D+00*TI(1)
194          ET2(I)=ETA(I)*ETA(I)
195          CHS(I)=PI2*CHS(I)*TI(2)
196          DO 620 J=1,NSI
197              EXC(J,I,2)=EXC(J,I,1)*TI(2)
198              EXC(J,I,1)=EXC(J,I,1)*TI(1)
199      620 CONTINUE
200      RFS=PI2*W1*TI(1)*1.0D-03
201 C      -----
202 C      Powder Averaging Start here
203 C      -----
204      NN=0
205      DO 710 I=-N+1,N-1
206          WRITE(*,'(A30,I5)')
207      &      '+ Powder Averaging Now : ',NN+N*2
208          DO 700 J=-N+1,N
209              NN=NN+1
210              CALL EVOLVE(NSP,NSI,X(J,IABS(I)),Y(J,IABS(I)),Z(I),ERS)
211              IF (ERS .NE. 0) GOTO 20000
212      700 CONTINUE
213      710 CONTINUE
214 C      -----
215 C      Normalize and Store the Data
216 C      -----
217      OPEN(UNIT=10,FILE=TDF)
218      D=1.0D+00/DBLE(NN)
219      DO 800 I=1,DIM(1)
220          DO 800 J=1,DIM(2)
221              WRITE(10,'(E13.7,1X,E13.7)',Iostat=ERS,ERR=10000) ARD(J,I)*D
222      800 CONTINUE
223      CLOSE (UNIT=10)
224 C      -----
225 C      Normal End.
226 C      -----
227      GO TO 99999
228 C      -----
229 C      Error Exist in the Procedure.
230 C      -----
231      10000 WRITE(*,'(A18,I5)') ' File Write Error ',ERS
232      GO TO 99999

```



```

Line# Source Line      Microsoft FORTRAN Optimizing Compiler Version 4.01

233 20000 WRITE(*, '(A23,I5)') ' Diagonalization Error ',ERS
234 C
235 99999 END
236 C
237 BLOCK DATA IXTOIZ
238 COMPLEX*8 ARD(256,128)
239 REAL*8 TDX(8),R(4),P(2)
240 INTEGER*4 DIM(2)
241 COMMON /ARD/ARD,DIM,TDX,R,P
242 C -----
243 C Transformation Laws in Ix to Iz basis
244 C -----
245 DATA R/ 6.123724356957945D-01,
246 & 3.535533905932738D-01,
247 & -1.060660171779821D+00,
248 & -6.123724356957945D-01/
249 END
250 $PAGE

```

```

Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

251 SUBROUTINE EVOLVE(L,M,X,Y,Z,ERR)
252 C -----
253 C Calculate the Evolution of the Density Vectors
254 C -----
255 COMPLEX*8 ARD(256,128)
256 COMPLEX*16 LI(8,8),HI(4,2,4,2),Q1(8,8),E1(8),L2(2,2),Q2(2,2),E2(2)
257 COMPLEX*16 DZ1(2,128),RQ1(2,8),PQ2(2,2),C
258 REAL*8 QCC(2),ETA(2),QC2(2),ET2(2),CHS(2),RFS,EXC(2,2,2)
259 REAL*8 X,Y,Z,SA(2),CA(2),SB(2),CB(2),SG(2),CG(2)
260 REAL*8 XC(4,4,2),WQ1,WQ2,WQ3,SQ3,X2,Y2,Z2,CT2,ST2,CP1
261 REAL*8 TDX(8),R(4),P(2),CDABSP,EPS
262 INTEGER*4 DIM(2),I,J,K,S,S1,S2,SS,LM,ERR
263 C -----
264 EQUIVALENCE (LI,HI)
265 PARAMETER(SQ3=8.660254037844385D-01)
266 COMMON /PAR/QCC,ETA,QC2,ET2,CHS,RFS,EXC
267 COMMON /ARG/SA,CA,SB,CB,SG,CG /ARD/ARD,DIM,TDX,R,P
268 CDABSP(C)=DABS(DREAL(C))+DABS(DIMAG(C))
269 DATA EPS/1.0D-18/
270 C -----
271 C Set the Liouvillians correspond to F1 and F2 axis
272 C -----
273 DO 100 S=1,M
274 C -----
275 C Transformation of Coordinate to Molecular Frame
276 C -----
277 Z2=SB(S)*CG(S)*X+SB(S)*SG(S)*Y+CB(S)*Z
278 X2= (CA(S)*CB(S)*CG(S)-SA(S)*SG(S))*X
279 & +(CA(S)*CB(S)*SG(S)+SA(S)*CG(S))*Y-CA(S)*SB(S)*Z
280 Y2=- (SA(S)*CB(S)*CG(S)+CA(S)*SG(S))*X
281 & -(SA(S)*CB(S)*SG(S)-CA(S)*CG(S))*Y+SA(S)*SB(S)*Z
282 CT2=Z2*Z2
283 ST2=1.0D+00-CT2
284 CP1=(X2*X2-Y2*Y2)*ETA(S)
285 C -----
286 C First Order Quadrupole Splitting
287 C -----
288 WQ1=QCC(S)*(CT2*3.0+CP1-1.0)
289 C -----
290 C Second Order Quadrupole Shift + Chemical Shift
291 C -----
292 WQ2=CHS(S)+QC2(S)
293 & *( ST2*ST2*9.-(1.+CT2)*CP1*6.+CP1*CP1+ET2(S)*CT2*4.
294 & -(ST2*CT2*9.+CT2*CP1*6.0-CP1*CP1+ET2(S)*ST2)*8.0 )
295 L2(S,S)=DCMPLX(EXC(S,S,2),WQ2)
296 C -----
297 C Set the Hamiltonian in the basis Ix
298 C -----
299 WQ3=WQ1*SQ3
300 XC(1,1,S)= WQ1+RFS
301 XC(1,2,S)= WQ3
302 XC(1,3,S)= WQ3
303 XC(1,4,S)= 0.0
304 XC(2,2,S)= -RFS
305 XC(2,3,S)= 0.0
306 XC(2,4,S)= WQ3
307 XC(3,3,S)= RFS*3.0D+00
308 XC(3,4,S)= WQ3

```



```

Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

309      XC(4,4,S)=-WQ1+RFS
310      100 CONTINUE
311      C -----
312      C      Set the Liouvillian
313      C -----
314      DO 220 S=1,M
315      DO 200 I=1,L
316      H1(I,S,I,S)=DCMLPX(EXC(S,S,I),XC(I,I,S))
317      DO 200 J=1+1,L
318      H1(I,S,J,S)=DCMLPX(0.0D+00,XC(I,J,S))
319      H1(J,S,I,S)=H1(I,S,J,S)
320      200 CONTINUE
321      DO 210 SS=S+1,M
322      DO 210 I=1,L
323      DO 210 J=1,L
324      IF (I.EQ. J) THEN
325      H1(I,S,I,SS)=EXC(S,SS,I)
326      H1(I,SS,I,S)=EXC(S,SS,I)
327      ELSE
328      H1(I,S,J,SS)=0.0D+00
329      H1(J,S,I,SS)=0.0D+00
330      H1(I,SS,J,S)=0.0D+00
331      H1(J,SS,I,S)=0.0D+00
332      END IF
333      210 CONTINUE
334      220 CONTINUE
335      C
336      DO 300 S=1,M
337      DO 300 SS=S+1,M
338      L2(S,SS)=EXC(S,SS,2)
339      L2(SS,S)=EXC(S,SS,2)
340      300 CONTINUE
341      C -----
342      C      Get the Eigenvalues and Eigenvectors to Calculate Exponentials
343      C -----
344      LM=L*M
345      CALL CHEQRD(LM,L1,4,E1,Q1,ERR)
346      IF (ERR.NE. 0) RETURN
347      DO 400 I=1,LM
348      E1(I)=CDEXP(E1(I))
349      400 CONTINUE
350      SS=0
351      DO 420 S=1,2
352      DO 410 K=1,LM
353      RQ1(S,K)=0.0D+00
354      DO 410 J=1,L
355      DO 410 I=1,LM
356      RQ1(S,K)=RQ1(S,K)+R(J)*Q1(J+SS,K)*Q1(I,K)*TDX(I)
357      410 CONTINUE
358      SS=SS+L
359      420 CONTINUE
360      CALL CHEQRD(M,L2,1,E2,Q2,ERR)
361      IF (ERR.NE. 0) RETURN
362      DO 500 I=1,M
363      E2(I)=CDEXP(E2(I))
364      500 CONTINUE
365      DO 510 S2=1,M
366      DO 510 S1=1,M

```



```

Line# Source Line      Microsoft FORTRAN Optimizing Compiler Version 4.01
367      PQ2(S1,S2)=0.0D+00
368      DO 510 S=1,M
369          PQ2(S1,S2)=PQ2(S1,S2)+P(S1)*Q2(S1,S2)*Q2(S,S2)
370 510 CONTINUE
371 C -----
372 C      Calculate Density Vectors at the end of rf Pulse
373 C -----
374      DO 600 I=1,DIM(1)
375          DO 600 S=1,M
376              DZ1(S,I)=0.0D+00
377              DO 600 J=1,LM
378                  RQ1(S,J)=RQ1(S,J)*E1(J)
379                  DZ1(S,I)=DZ1(S,I)+(RQ1(S,J)-DCONJG(RQ1(S,J)))
380 600 CONTINUE
381 C -----
382 C      Calculate FID's
383 C -----
384      DO 710 J=1,DIM(2)
385          DO 700 I=1,DIM(1)
386              DO 700 S1=1,M
387                  DO 700 S2=1,M
388                      ARD(J,I)=ARD(J,I)+PQ2(S1,S2)*DZ1(S2,I)
389 700 CONTINUE
390              DO 710 S2=1,M
391                  DO 710 S1=1,M
392                      PQ2(S1,S2)=PQ2(S1,S2)*E2(S2)
393 710 CONTINUE
394 C -----
395      RETURN
396      END
397 C -----
398 $PAGE

```

```

Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

399 SUBROUTINE CHEQRD(N,LC,NBW,EC,VC,ERR)
400 C -----
401 C Calculate the Eigenvalues and Eigenvectors of Symmetric Matrix
402 C -----
403 COMPLEX*16 LC(N,N),VC(N,N),EC(N),ZX,ZY,ZZ,ZR,ZQ,ZC,ZS
404 REAL*8 CDABSP,DEL
405 INTEGER*4 I,J,K,IP1,IPM,IM1,JPM,JM1,LL,LU,M,ITR,ITRMAX,ERR
406 C
407 CDABSP(ZZ)=DABS(DREAL(ZZ))+DABS(DIMAG(ZZ))
408 DATA DEL,ITRMAX/1.0D-15,30/
409 C -----
410 C Parameter Error Check
411 C -----
412 IF ((N .LE. 1) .OR. (NBW .GT. N)) GO TO 20000
413 C -----
414 C Set the Eigenvectors to Unit Matrix
415 C and Determines the Band Width of the Matrix under Treatment.
416 C -----
417 DO 110 I=1,N
418 DO 100 J=1,N
419 VC(J,I)=0.0D+00
420 100 CONTINUE
421 VC(I,I)=1.0D+00
422 110 CONTINUE
423 IF (NBW .LE. 0) THEN
424 DO 130 I=1,N
425 DO 120 J=I+1,N
426 IF (CDABSP(LC(J,I)) .GT. DEL) K=J-1
427 120 CONTINUE
428 NBW=MAX0(NBW,K)
429 130 CONTINUE
430 END IF
431 C -----
432 C Reduction of Band Width to Tridiagonal Matrix
433 C by Jacobi Rotations.
434 C -----
435 DO 270 M=NBW,2,-1
436 DO 270 I=1,N-M
437 IPM=I+M
438 IM1=IPM-1
439 IF (CDABSP(LC(I,IPM)) .GT. DEL) THEN
440 ZR=-LC(I,IM1)/LC(I,IPM)
441 ZQ=CDSQRT(1.0D+00+ZR*ZR)
442 IF (CDABSP(ZQ) .LT. DEL) GOTO 30000
443 ZS=1.0D0/ZQ
444 ZC=-ZS*ZR
445 DO 200 J=1,N
446 ZZ=LC(IM1,J)
447 LC(IM1,J)=ZZ*ZC+LC(IPM,J)*ZS
448 LC(IPM,J)=LC(IPM,J)*ZC-ZZ*ZS
449 200 CONTINUE
450 DO 210 J=1,N
451 ZZ=LC(J,IM1)
452 LC(J,IM1)=ZZ*ZC+LC(J,IPM)*ZS
453 LC(J,IPM)=LC(J,IPM)*ZC-ZZ*ZS
454 210 CONTINUE
455 DO 220 J=1,N
456 ZZ=VC(J,IM1)

```



Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

```

457          VC(J,IM1)=ZZ*ZC+VC(J,IPM)*ZS
458          VC(J,IPM)=VC(J,IPM)*ZC-ZZ*ZS
459      220      CONTINUE
460          DO 260 J=IM1,N-M-1,M
461              JPM=J+M
462              JM1=JPM+1
463              IF (CDABSP(LC(J,JM1)) .GT. DEL) THEN
464                  ZR=-LC(J,JPM)/LC(J,JM1)
465                  ZQ=CDSQRT(1.0D0+ZR*ZR)
466                  IF (CDABSP(ZQ) .LT. DEL) GOTO 30000
467                  ZS=1.0D0/ZQ
468                  ZC=-ZS*ZR
469                  DO 230 K=1,N
470                      ZZ=LC(JPM,K)
471                      LC(JPM,K)=ZZ*ZC+LC(JM1,K)*ZS
472                      LC(JM1,K)=LC(JM1,K)*ZC-ZZ*ZS
473      230      CONTINUE
474                  DO 240 K=1,N
475                      ZZ=LC(K,JPM)
476                      LC(K,JPM)=ZZ*ZC+LC(K,JM1)*ZS
477                      LC(K,JM1)=LC(K,JM1)*ZC-ZZ*ZS
478      240      CONTINUE
479                  DO 250 K=1,N
480                      ZZ=VC(K,J+M)
481                      VC(K,JPM)=ZZ*ZC+VC(K,JM1)*ZS
482                      VC(K,JM1)=VC(K,JM1)*ZC-ZZ*ZS
483      250      CONTINUE
484                  END IF
485      260      CONTINUE
486      END IF
487      270      CONTINUE
488      C -----
489      C      Search for a Small Sub-diagonal Element.
490      C -----
491          LU=N
492      300      ITR=0
493      310      LL=LU
494      320      IF (CDABSP(LC(LL,LL-1)) .GT. DEL) THEN
495          LL=LL-1
496          IF (LL .GT. 1) GO TO 320
497      END IF
498      IF (LL .NE. LU) THEN
499      C -----
500      C      If Convergence is not Attained within 30 Iterations,
501      C      Truncate the Computation.
502      C -----
503          IF (ITR .GT. ITRMAX) GO TO 10000
504      C -----
505      C      Determine the Origin Shift as the Eigenvalue of the 2 by 2
506      C      Bottom Submatrix which is Nearer to the bottom Element.
507      C -----
508          ZX=(LC(LU-1,LU-1)+LC(LU,LU))*0.5D+00
509          ZY=ZX-LC(LU,LU)
510          ZZ=CDSQRT(LC(LU-1,LU)*LC(LU,LU-1)+ZY*ZY)
511          ZZ=DSIGN(1.0D+00,CDABSP(ZY-ZZ)-CDABSP(ZY+ZZ))*ZZ+ZX
512          LC(LL,LL)=LC(LL,LL)-ZZ
513          ZC=1.0D+00
514          DO 360 I=LL,LU-1

```



```

Line#   Source Line      Microsoft FORTRAN Optimizing Compiler Version 4.01

515      IPI=I+1
516 C      -----
517 C      Left- and Right-hand Transformation.
518 C      -----
519      ZX=LC( I ,I)
520      ZY=LC(IP1,I)
521      ZR=CDSQRT(ZX*ZX+ZY*ZY)
522      IF (CDABSP(ZR) .LT. DEL) GOTO 30000
523      LC(I,I)=ZC*ZR
524      IF (I .GT. LL) LC(I,I-1)=ZS*ZR
525      LC(IP1,IP1)=LC(IP1,IP1)-ZZ
526      ZC=ZX/ZR
527      ZS=ZY/ZR
528      DO 330 J=IP1,N
529          ZY=LC(I,J)
530          LC( I ,J)=ZY*ZC+LC(IP1,J)*ZS
531          LC(IP1,J)=LC(IP1,J)*ZC-ZY*ZS
532 330     CONTINUE
533      DO 340 J=1,I
534          ZY=LC(J,I)
535          LC(J, I )=ZY*ZC+LC(J,IP1)*ZS
536          LC(J,IP1)=LC(J,IP1)*ZC-ZY*ZS
537 340     CONTINUE
538      LC(I,I)=LC(I,I)+ZZ
539      DO 350 J=1,N
540          ZY=VC(J,I)
541          VC(J, I )=ZY*ZC+VC(J,IP1)*ZS
542          VC(J,IP1)=VC(J,IP1)*ZC-ZY*ZS
543 350     CONTINUE
544 360     CONTINUE
545      LC(LU,LU-1)=LC(LU,LU)*ZS
546      LC(LU, LU )=LC(LU,LU)*ZC+ZZ
547      ITR=ITR+1
548      GO TO 310
549      END IF
550      LU=LU-1
551      IF (LU .GT. 1) GO TO 300
552 C      -----
553 C      QR-Transformation is Over.
554 C      Eigenvalues are Given
555 C      by the Diagonal Elements of the Resultant Matrix.
556 C      -----
557      DO 400 I=1,N
558          EC(I)=LC(I,I)
559 400     CONTINUE
560 C      -----
561 C      Normal Exit.
562 C      -----
563      ERR=0
564      RETURN
565 C      -----
566 C      Error Exit.
567 C      10000 : Not Converged.
568 C      20000 : Parameter Error.
569 C      30000 : Devide by Zero.
570 C      -----
571 10000 ERR=10000
572      RETURN

```

PAGE 12  
09-27-90  
19:36:47

Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

573 20000 ERR=20000  
574 RETURN  
575 30000 ERR=30000  
576 RETURN  
577 END

Global Symbols

Name	Class	Type	Size	Offset
------	-------	------	------	--------

Code size = 0000 (0)  
Data size = 0000 (0)  
Bss size = 0000 (0)

No errors detected

