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

By
Hirosi Ohki

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SOLID STATE CHEMICAL EXCHANGE IN SOME SODIUM SALTS

AS STUDIED BY 2D NUTATION NMR

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1990

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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}Na in several compounds. The ^{23}Na resonance in 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, η , of the electric field gradient at the site of the resonant nucleus.

The ^{23}Na 2D nutation NMR was applied to Na_2SeO_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 η 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}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 $I > 1/2$, 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 (η). 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 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. Na_2SeO_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 ρ obeys the von Neumann equation of motion [2]

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

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 :

$$\frac{d\rho}{dt} = -iL\rho, \quad (2.1.2)$$

where ρ is the density superkets in the column form, i.e.,

$$\rho = {}^t (\rho_{1,1} \ \rho_{1,2} \ \rho_{1,3} \ \dots \ \rho_{1,n} \ \rho_{2,1} \ \dots \ \dots \ \rho_{n,n}) , \quad (2.1.3)$$

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

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

where E is the unit operator which has the same dimension as H , and ${}^t H$ 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 :

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

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 ρ^* 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,

$$M_x = I_x p ,$$

(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

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

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

a

b

With the exception of the first three, the other four are in the same order as the first three.

Figure 2.1. *Yield isotonics* illustrating the notion of *yield*.

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-

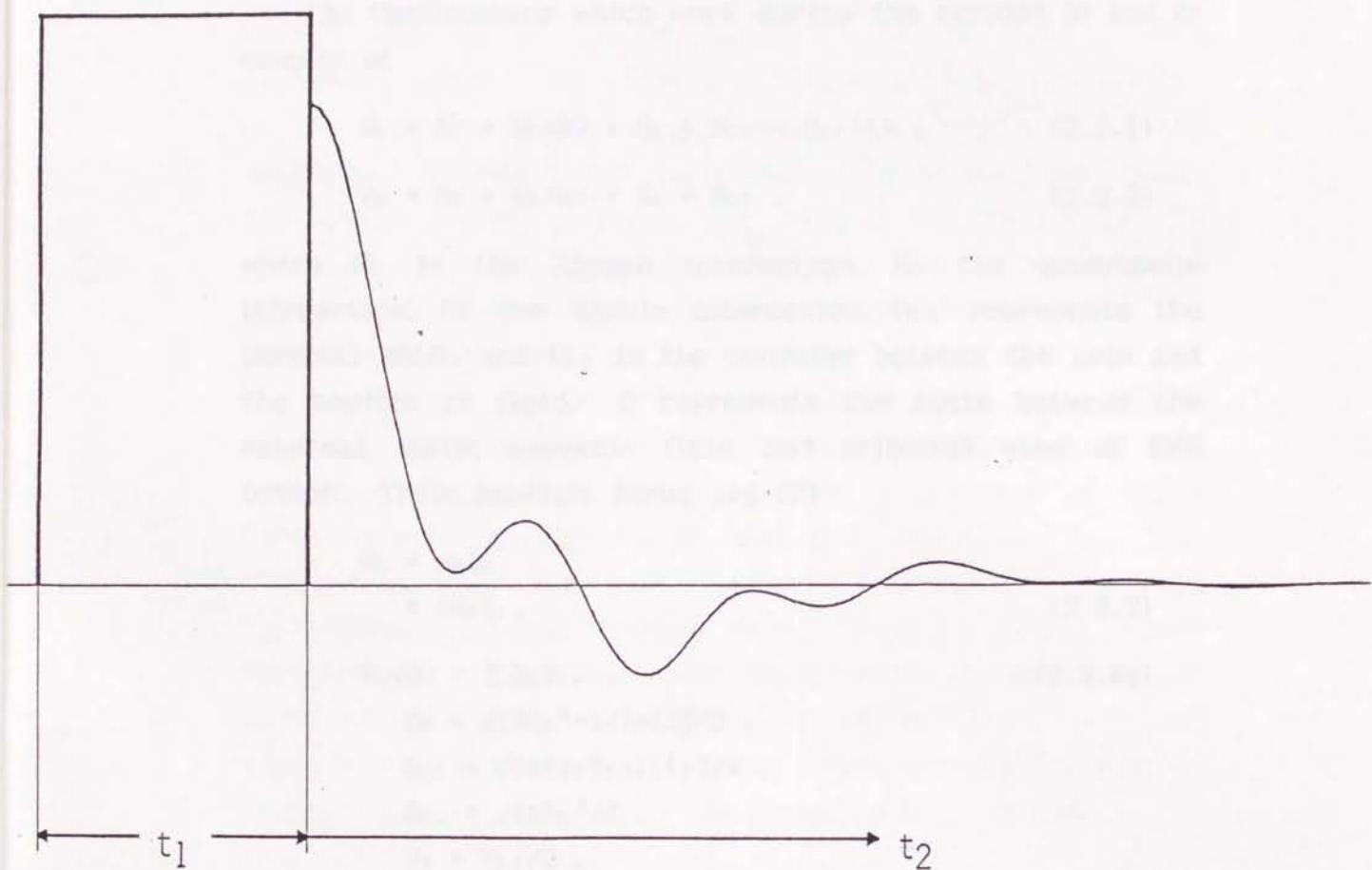


Figure 2.2
Schematic representation of 2D nutation NMR experiment.

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. Ω represents the angle between the external static magnetic field and principal axes of EFG tensor. Their explicit forms are [2]

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

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

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

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

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

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

$$V_{\pm 1} = (V_{ZX} \pm iV_{ZY})/\sqrt{6} ,$$

$$V_{\pm 2} = (V_{XX} - V_{YY} \pm 2iV_{XY})/2\sqrt{6} ,$$

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

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

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

and

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

where ω_0 is the nuclear Larmor frequency, D and σ are the dipole interaction and the chemical shift tensors, respectively, and ω_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 $H_z \gg H_0 \approx H_{rf} \gg H_D, H_{cs}$. This situation is realized in the case of nuclei with fairly large quadrupole interaction such as ^{23}Na , ^{39}K , ^{59}Co , ^{93}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

$$\begin{aligned} H_Q^{(1)} &= e^2 q Q / 8I(2I-1) (3\cos^2\theta - 1 + \eta \sin^2\theta \cos 2\phi) \\ &\quad \times [3I_z^2 - I(I+1)] \\ &= \omega_0 [I_z^2 - I(I+1)/3] , \end{aligned} \quad (2.2.9)$$

and

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

where, θ and ϕ 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 ω_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

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

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

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 ω_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 ω_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 ω_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

$$\rho^*(t_1) = R \exp(-iL^d_1 t_1) R^{-1} \rho(0), \quad (2.2.28a)$$

or

$$\rho^*_{jk}(t_1) = \sum [R_{jk} R_{kj} \rho_{kj}(0)] \exp(-i\lambda_j t_1), \quad (2.2.28b)$$

where λ_j is the j -th eigenvalue of the Liouvillian. In the above Eq. (2.2.28b), $A_{jj} = \sum [R_{jk} R_{kj} \rho_{kj}(0)]$ is called the 'transition amplitude' which represents the intensity of the component with the frequency λ_j .

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

$$\rho^*(t_1 + t_2) = \exp(-iL^d_2 t_2) \rho^*(t_1). \quad (2.2.29)$$

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

$$\begin{aligned}
 S(t_1 + t_2) \propto & \\
 & \{ [3\sin 2\theta_- \sin 2\theta_+ - (1 - \cos 2\theta_-)(1 + \cos 2\theta_+)] \sin(\lambda_3 - \lambda_1) t_1 \\
 & - [3\sin 2\theta_- \sin 2\theta_+ + (1 - \cos 2\theta_-)(1 - \cos 2\theta_+)] \sin(\lambda_4 - \lambda_1) t_1 \\
 & - [3\sin 2\theta_- \sin 2\theta_+ + (1 + \cos 2\theta_-)(1 + \cos 2\theta_+)] \sin(\lambda_3 - \lambda_2) t_1 \\
 & + [3\sin 2\theta_- \sin 2\theta_+ - (1 + \cos 2\theta_-)(1 - \cos 2\theta_+)] \sin(\lambda_4 - \lambda_2) t_1 \} \\
 & \times \exp(-i\omega_0^{(2)} t_2) , \\
 \end{aligned} \tag{2.2.30}$$

where $\omega_0^{(2)}$ is the second order quadrupole shift of the central transition expressed by [7]

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

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 :

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

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 ρ 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

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

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

$$K = \begin{bmatrix} k_{1,1} & k_{1,2} & k_{1,3} & \dots & k_{1,m} \\ k_{2,1} & k_{2,2} & k_{2,3} & \dots & k_{2,m} \\ \vdots & \ddots & \ddots & \dots & \vdots \\ k_{m,1} & k_{m,2} & k_{m,3} & \dots & k_{m,m} \end{bmatrix} \otimes E_K, \quad (2.3.8)$$

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

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

$$L^{(j)}_2 = L_Q^{(j)} + L_{CS}^{(j)} + L_{RF}, \quad (2.4.1b)$$

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

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

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 : $k_1, k_2 \ll H_Q, H_{RF}$

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 δ_{ij} stands for the Kronecker's delta. The Liouvillian is not altered and the exchange matrix becomes

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

This can be diagonalized by

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

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

and so the Liouvillian is expressed as

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

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 :

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

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 ω_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.

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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,

$$\begin{aligned} L^S_1 &= (P^{-1} \otimes E_K)(L_1 + K)(P \otimes E_K) \\ &= L_1 + K^S, \end{aligned} \tag{3.1.1a}$$

$$\begin{aligned} L^S_2 &= (P^{-1} \otimes E_K)(L_2 + K)(P \otimes E_K) \\ &= L_2 + K^S, \end{aligned} \tag{3.1.1b}$$

where

$$K^S = (P^{-1} \otimes E_K)K(P \otimes E_K), \tag{3.1.1c}$$

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 $(2I+1)^2/4 = 4$.

$$L^x_j = (RT)^{-1} L_j (RT)$$

$$= \begin{bmatrix} A_j & 0 \\ B_j & B'_j \\ 0 & A'_j \end{bmatrix}, \quad (3.1.2)$$

and density superket at the site j becomes

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

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 :

$$A_j = \begin{pmatrix} 0 & \sqrt{3}\omega_0 j & -\sqrt{3}\omega_0 j & 0 \\ \sqrt{3}\omega_0 j & -2\omega_0 j + 4\omega_1 & 0 & -\sqrt{3}\omega_0 j \\ -\sqrt{3}\omega_0 j & 0 & 2\omega_0 j - 4\omega_1 & \sqrt{3}\omega_0 j \\ 0 & -\sqrt{3}\omega_0 j & \sqrt{3}\omega_0 j & 0 \end{pmatrix} / \sqrt{2}, \quad (3.1.4a)$$

$$B_j = \begin{pmatrix} 2\omega_0 j + 2\omega_1 & \sqrt{3}\omega_0 j & \sqrt{3}\omega_0 j & 0 \\ \sqrt{3}\omega_0 j & 6\omega_1 & 0 & \sqrt{3}\omega_0 j \\ \sqrt{3}\omega_0 j & 0 & -2\omega_1 & \sqrt{3}\omega_0 j \\ 0 & \sqrt{3}\omega_0 j & \sqrt{3}\omega_0 j & -2\omega_0 j + 2\omega_1 \end{pmatrix} / \sqrt{2}, \quad (3.1.4b)$$

$$B'_j = \begin{pmatrix} -2\omega_0 j - 2\omega_1 & -\sqrt{3}\omega_0 j & -\sqrt{3}\omega_0 j & 0 \\ -\sqrt{3}\omega_0 j & -6\omega_1 & 0 & -\sqrt{3}\omega_0 j \\ \sqrt{3}\omega_0 j & 0 & -2\omega_1 & -\sqrt{3}\omega_0 j \\ 0 & -\sqrt{3}\omega_0 j & -\sqrt{3}\omega_0 j & 2\omega_0 j - 2\omega_1 \end{pmatrix} / \sqrt{2}, \quad (3.1.4c)$$

$$A'^j = \begin{pmatrix} 0 & -\sqrt{3}\omega_0 j & \sqrt{3}\omega_0 j & 0 \\ -\sqrt{3}\omega_0 j & 2\omega_0 j + 4\omega_1 & 0 & \sqrt{3}\omega_0 j \\ \sqrt{3}\omega_0 j & 0 & -2\omega_0 j - 4\omega_1 & -\sqrt{3}\omega_0 j \\ 0 & \sqrt{3}\omega_0 j & -\sqrt{3}\omega_0 j & 0 \end{pmatrix} / \sqrt{2}, \quad (3.1.4d)$$

where $\omega_0 j$ 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 :

$$\rho_{ij}^x = p_j^{-1} (0 \ 0 \ 0 \ 0 \ \sqrt{3} \ 3 \ 0 \ -\sqrt{3} \ \sqrt{3} \ 3 \ 0 \ -\sqrt{3} \ 0 \ 0 \ 0 \ 0). \quad (3.1.5)$$

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

$$L_{1'}^s = \begin{pmatrix} iB_1 - k_1 E_B & k'E_B \\ k'E_B & iB_2 - k_2 E_B \end{pmatrix}, \quad (3.1.6)$$

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, $L_{2'}^s$, 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

$$\begin{aligned}
 S(t_2, t_1) &\propto I \times \rho(t_2, t_1) \\
 &= \sum P_{i,j} Q_{2,i,j} \exp[-iL_2^d j t_2] Q_2^{-1} j,k \\
 &\quad \times R_{k,l} Q_{1,l,m} \exp[-iL_1^d m t_1] Q_1^{-1} m,n \rho_{x(0)} n,
 \end{aligned} \tag{3.1.7}$$

where Q_1 and Q_2 are complex orthogonal matrices which diagonalize L_{s1}' and L_{s2}' , respectively.

The Liouvillians L_{s1}' and L_{s2}' 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

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

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_θ 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 2×2 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 θ and ϕ 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 α , β , and γ 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 θ_j and ϕ_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

$$\omega_0^{(1)}_j = e^2 qQ/8I(2I-1)\{3z_j^2-1+\eta(x_j^2-y_j^2)\}, \quad (3.1.17)$$

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

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 θ 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 ϕ ($-\pi < \phi \leq \pi$).

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 ϕ , 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 θ and ϕ 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 , η 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 θ and ϕ 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 128×256 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

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4.2. NMR

The second line figure summarizes results of the NMR studies. The labels can be used to identify various spin relaxation paths leading from the initial to the final state. The spin-lattice relaxation parameters are summarized in Table 1.

4.3. Raman

The scheme for Raman scattering is also shown in the last figure. The labels are identical with the NMR. The crystal structure is shown in the last figure. Complex wave selection rules for the polarizations between $\sigma = 0$ and 3 and the crystal structure changes between $\alpha = 0$ and 3 are also shown. The polarizations of the Raman scattering are determined by the structure changes of the former. The structure changes of a three-dimensional physical system as the three cubic hyperboloids which are interconnected with three cylinders. The Raman selection rules used for wave pol. assignments are also shown. The labels along the physical σ -axis are also listed in Table 1.

4. Sample

4.1. NaNO_2 and $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$

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 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 H_2O 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 Na_2SeO_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 $\text{C}2/\text{c}$ ($1.8 \leq x \leq 2.2$). The latter is a slightly deformed structure of the former. The structure consists of a three-dimensional skeletal network of PO_4 (and/or SiO_4) tetrahedra which are corner-shared with ZrO_6 octahedra. The ZrO_6 octahedron is linked by three PO_4 tetrahedra so as to form a ribbon along the hexagonal c-axis and also linked by six PO_4

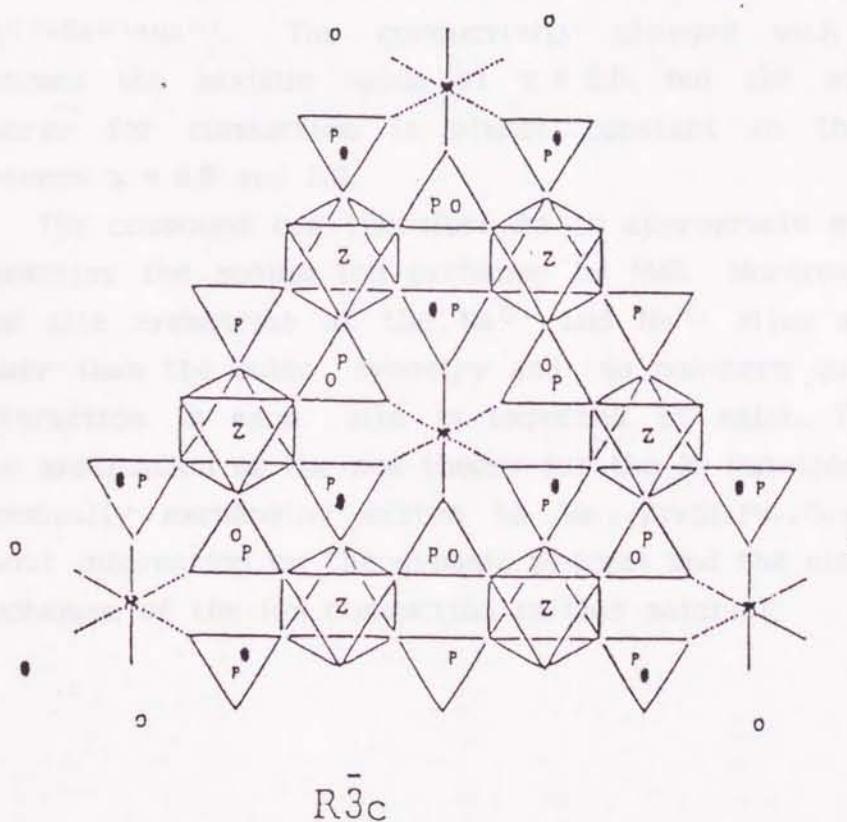
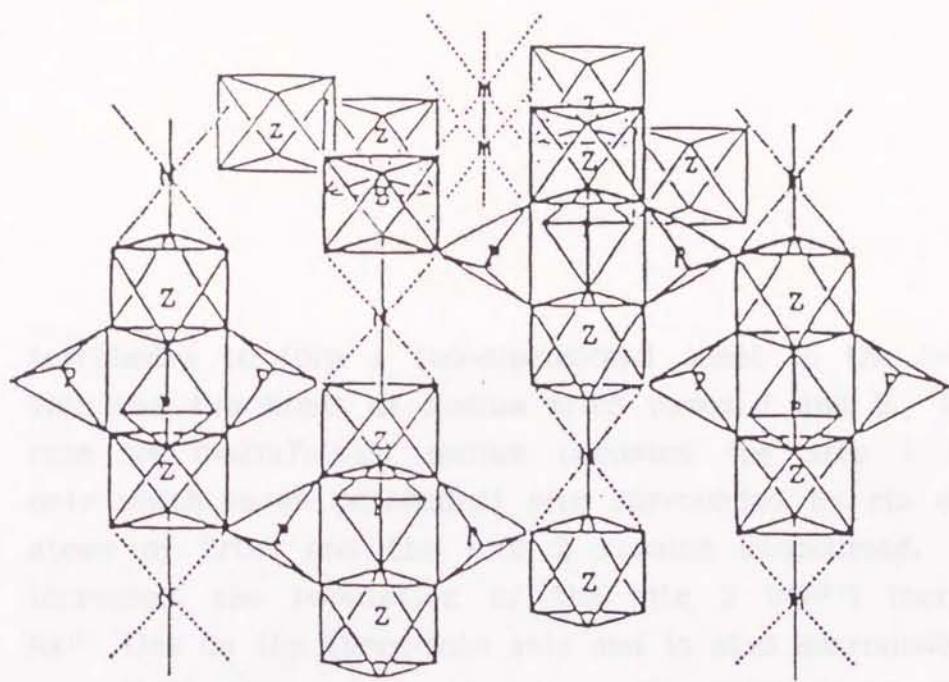


Figure 4.1
Crystal structure of $\text{Na}_{1+x} \text{Zr}_2 \text{Si}_x \text{P}_{3-x} \text{O}_{12}$.

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 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 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.

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Table I

Sample was prepared from solution mixture of a stoichiometric mixture of zinc nitrate, ferrous nitrate, zinc carbonate and aluminum oxide (MgO) 100 g each as prepared by University Paris-Dauphine. Zinc carbonate was zinc oxide powder 99% as stated. Zinc preparation of the solution was the zinc carbonate.

The composition mixture was dissolved and the mixture was heated at 100°C for 10 hours. The mixture was then cooled, and J.A. and H.Y-P. Hong prepared the sample. About 100 g of the sample was then dried at 100°C for 10 hours. Zinc carbonate was zinc oxide powder 99% as stated. Zinc preparation of the solution was the zinc carbonate.

5. Experiment

5.1. Sample Preparation

5.1.1. NaNO_2 and $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$

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 NaCl (Tomita Seiyaku) and 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 HgCl_2 . However, this HgCl_2 impurity is supposed to have little influence on the NMR of ^{23}Na .

5.1.2. Na_2SeO_3

Na_2SeO_3 was prepared from aqueous solution of a stoichiometric mixture of NaOH (Nacalai Tesque, reagent grade, purity 93%) and selenius acid H_2SeO_3 . [2] H_2SeO_3 is prepared by dissolving 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 : Na_2CO_3 , Nacalai Tesque, guaranteed reagent grade, purity 99.5%; ZrO_2 , Nacalai Tesque, reagent grade;

SAMPLE NAME: NAHgCl₃

TARGET : Cu

VOL and CUR: 40KV 40mA

SLITS : 0.5 1 RS .15 SS 1

SCAN SPEED: 4 DEG/MIN.

STEP/SAMPL.: .02 DEG

RESET TIME: 0 SEC

FILE NAME : NAHgCl₃

OPERATOR : YAMAMOTO

COMMENT :

DATE: 88.06.14

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

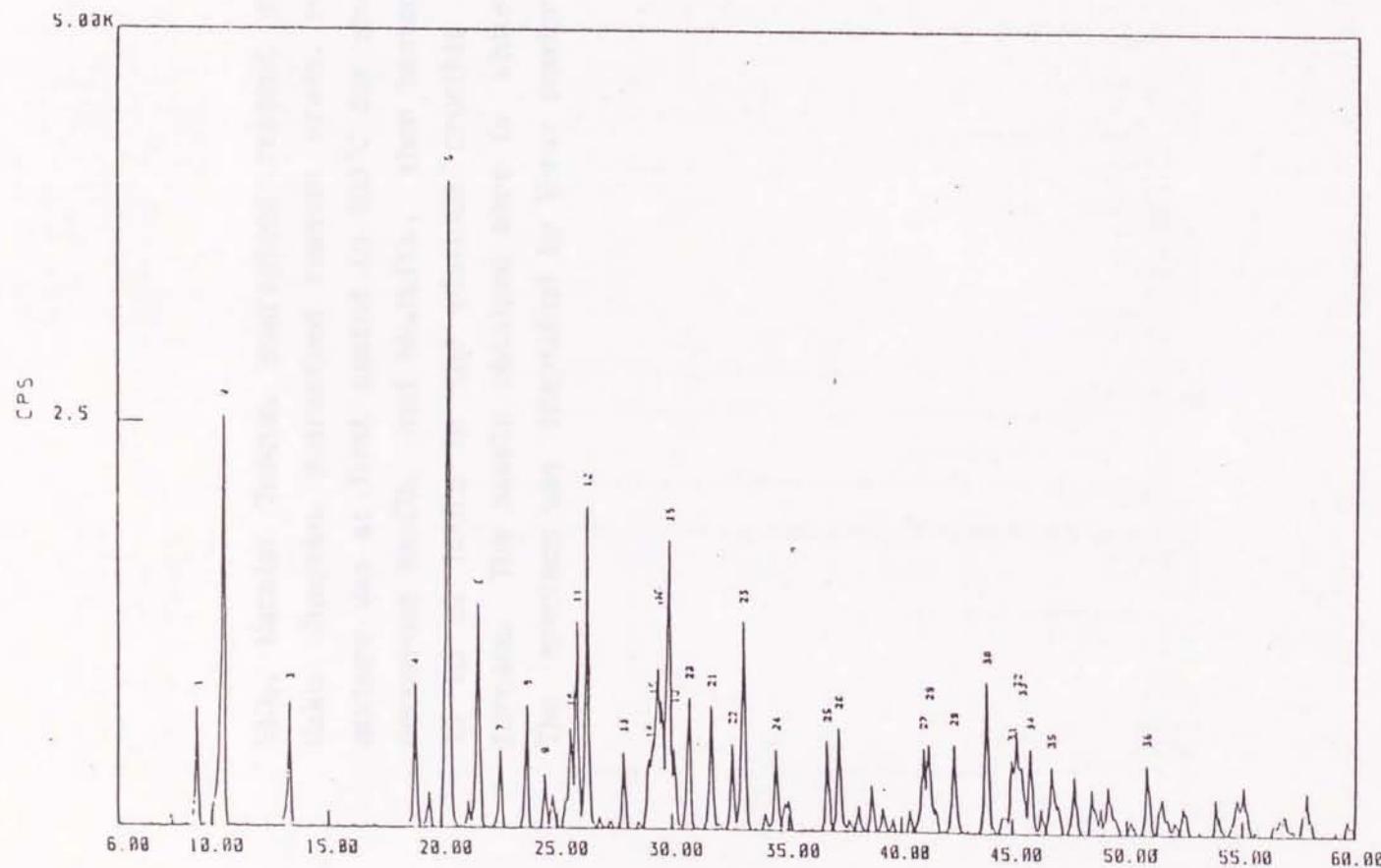


Figure 5.1
The X-ray powder diffraction pattern of NaHgCl₃·2H₂O.

SiO_2 , Nacalai Tesque, guaranteed reagent grade; $\text{NH}_4\text{H}_2\text{PO}_4$, Wako Junyaku, guaranteed reagent grade, purity 98%. The mixture was at first heated to 900°C for several hours to decompose Na_2CO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$, 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.

SAMPLE NAME:NaZr₂P3O₁₂
TARGET :Cu
VOL and CUR: 40KV 40mA
SLITS :05 1 RS .5 SS 1
SCAN SPEED: 3 DEG/MIN.
STEP/SAMPL.: .02 DEG
PRESET TIME: 0 SEC
FILE NAME :01108
OPERATOR :YAMAMOTO
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

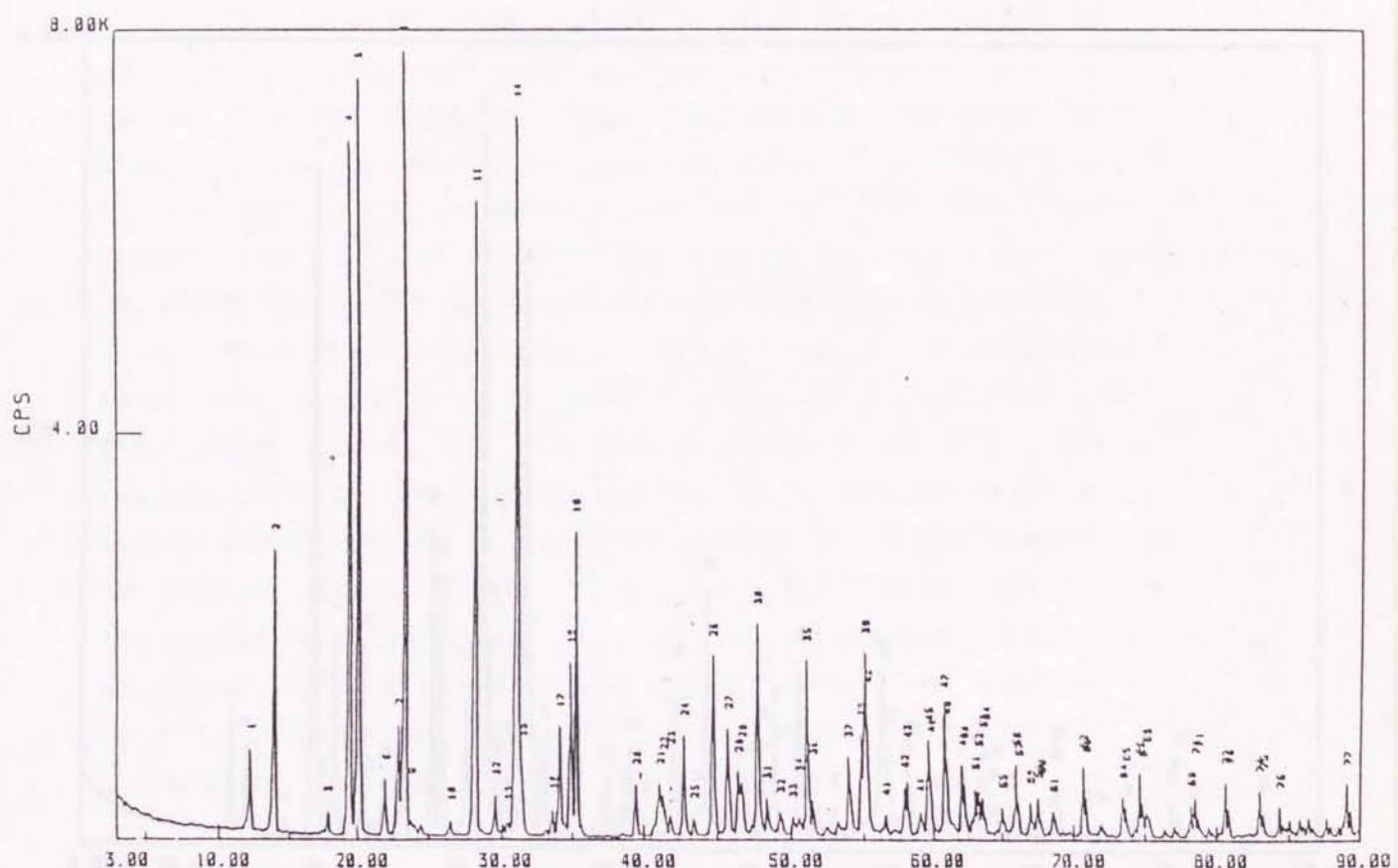


Figure 5.2

The X-ray powder diffraction pattern of NaZr₂Si₃O₁₂.

SAMPLE NAME: Na3Zr2Si2P
TARGET : Cu
VOL and CUR: 40KV 40mA
SLITS : 0.5 1.0 0.5 1.0
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 : Na3Zr2S12P

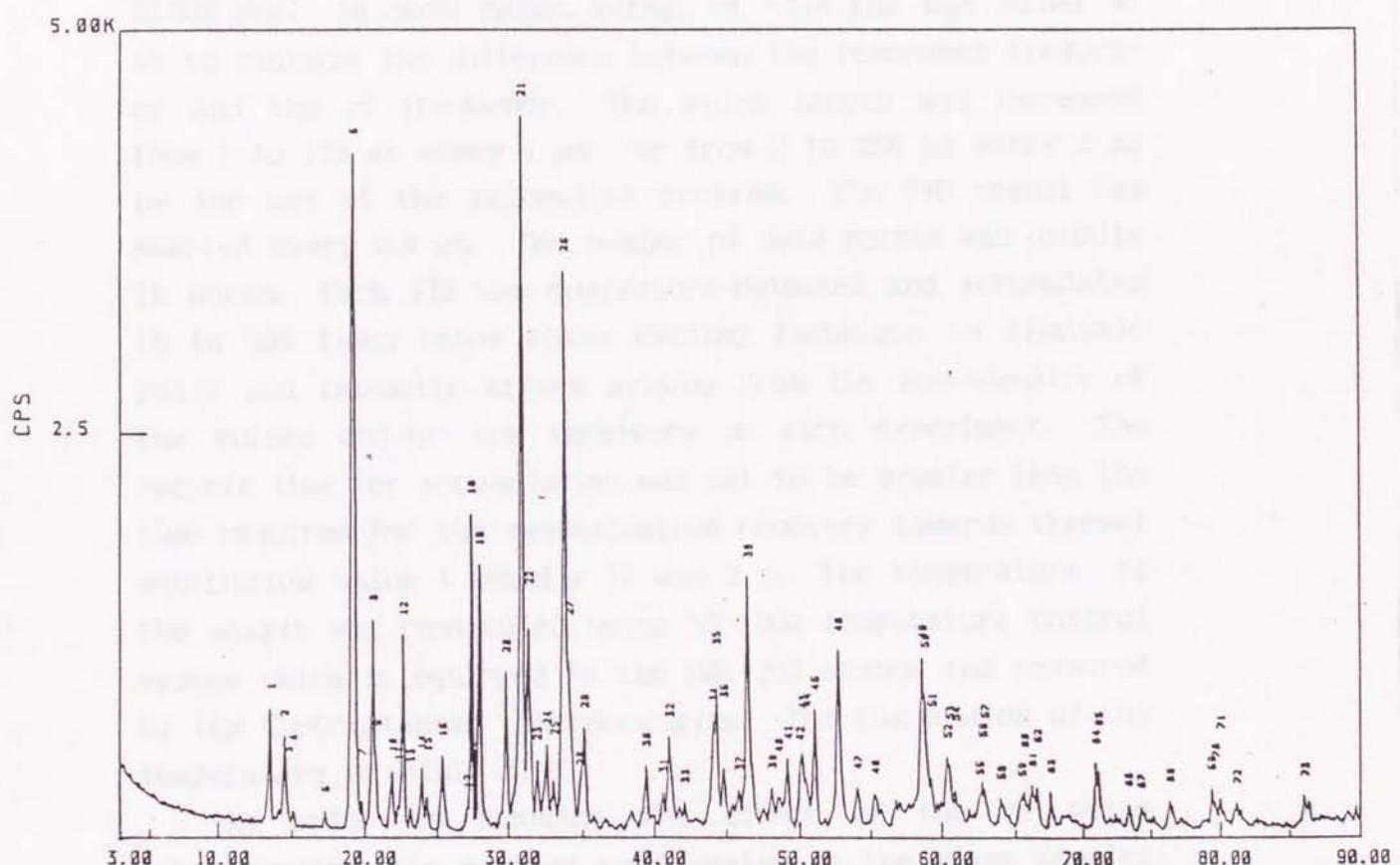


Figure 5.3

The X-ray powder diffraction pattern of $\text{Na}_3\text{Zr}_2\text{SiP}_2\text{O}_{12}$.

5.2 Nutation NMR

The ^{23}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 μs every 1 μs , or from 2 to 256 μs every 2 μs by the use of the automation program. The FID signal was sampled every 0.8 μs . 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 ± 1 K.

In order to minimize the effect of the rf pulse inhomogeneity, the samples were sealed in the glass ampules with 10mmφ 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

cases, the trapezoidal function was multiplied to the F_1 data to avoid the effect of cut-off of the tail that causes auxiliary wiggles on either side of the spectrum [4].

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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 $\Omega_0/\omega_1 = [3e^2Qq/2I(2I-1)\hbar]/\omega_1$, where Ω_0 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 ω_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 ω_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 ω_1 in the case of $e^2Qq/h = 0$, indicating that

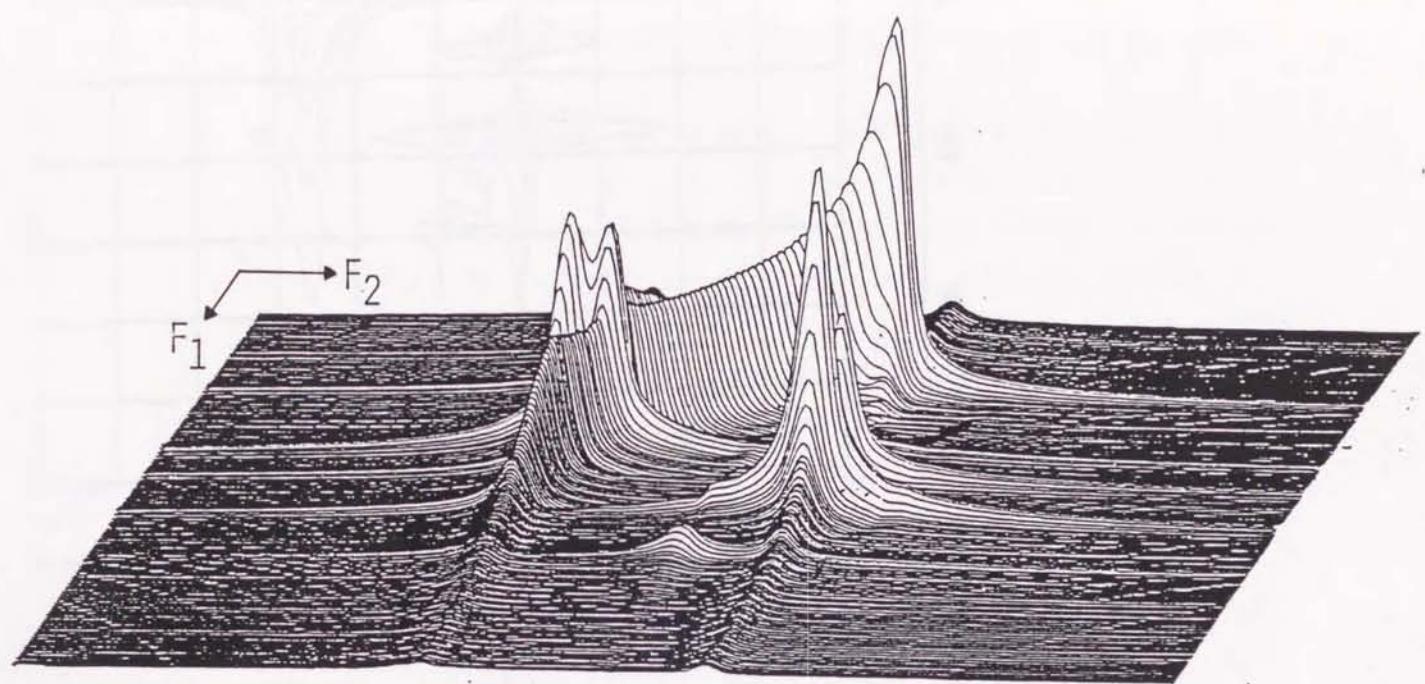


Figure 6.1

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

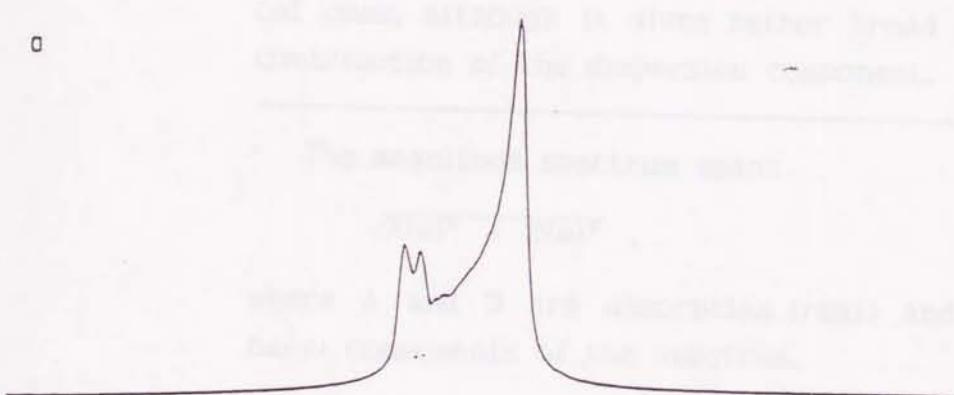
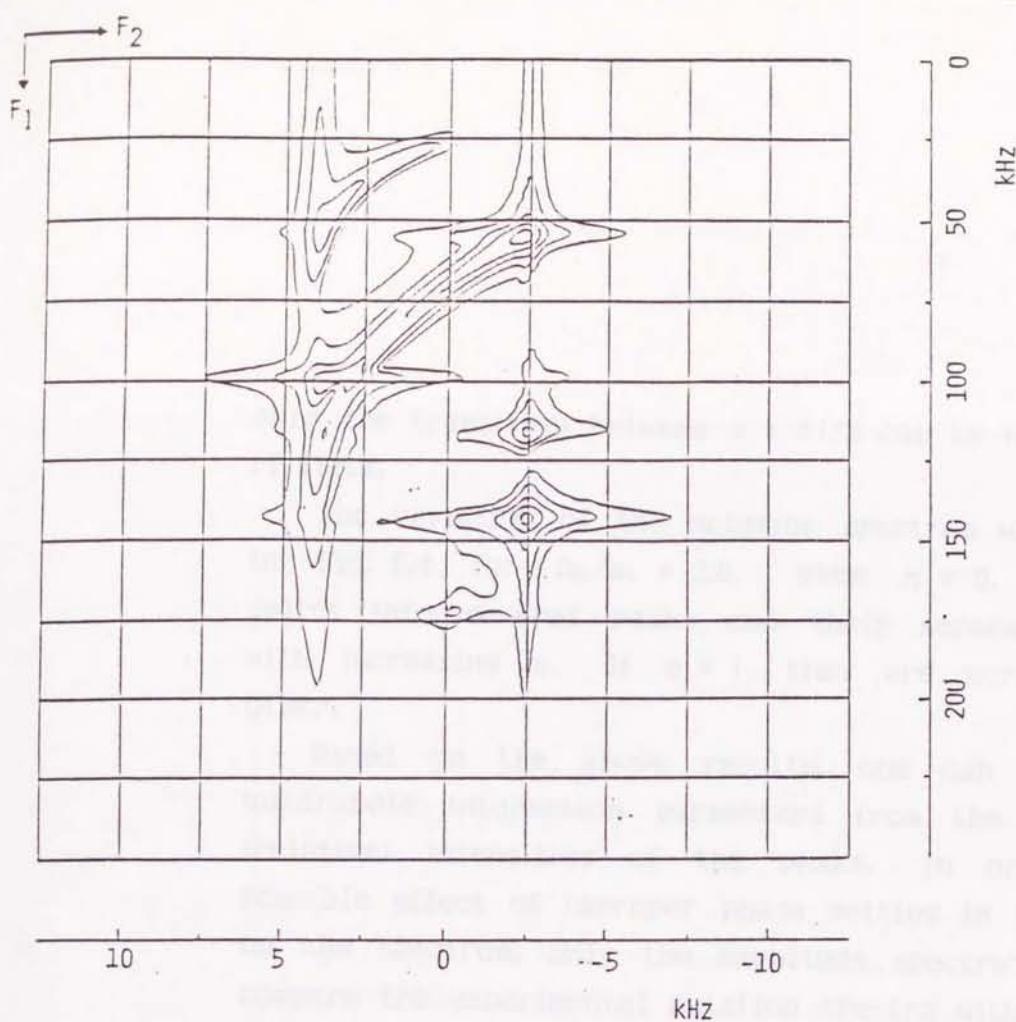


Figure 6.2

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 η 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 η . 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.

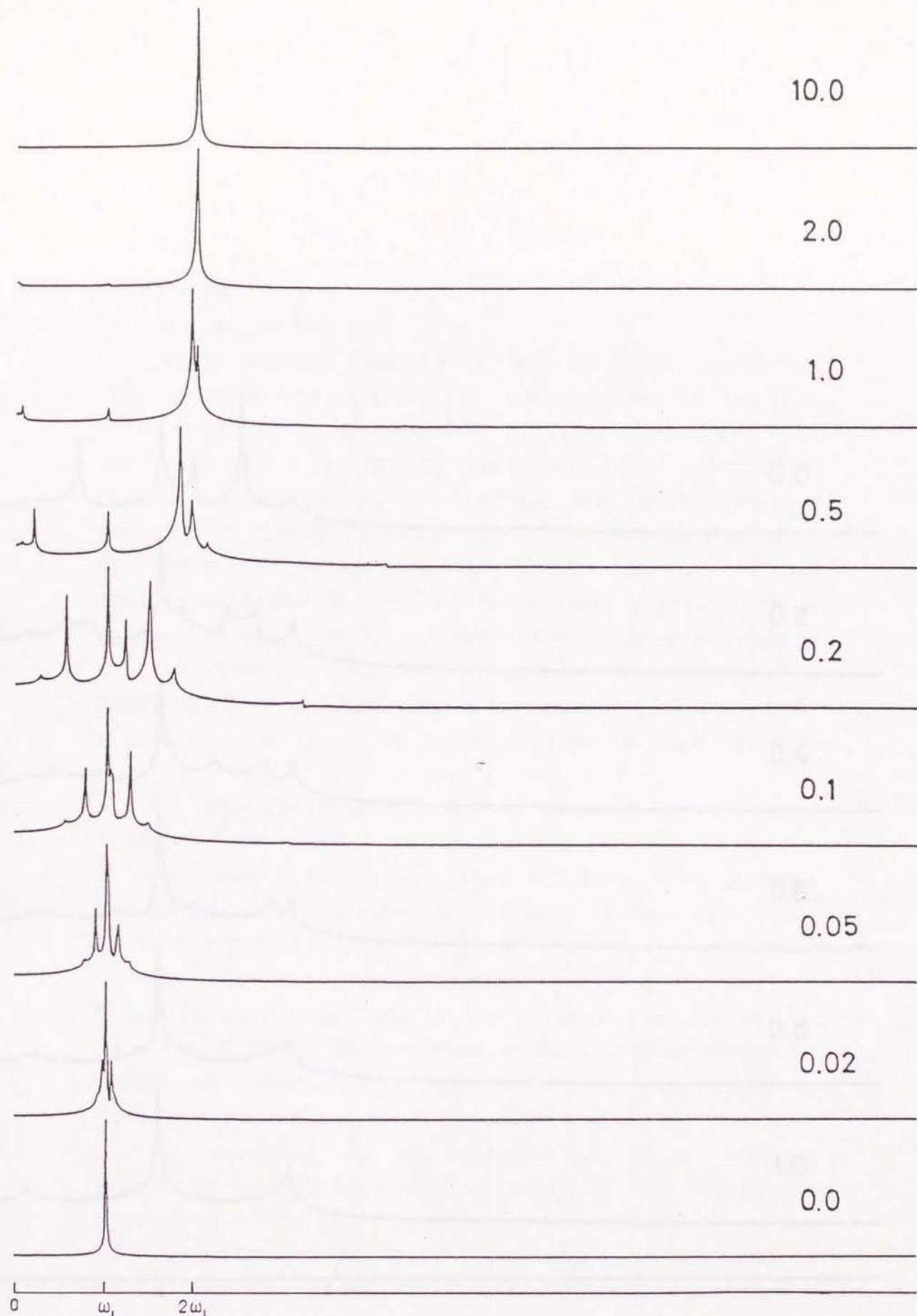


Figure 6.3

Dependence of nutation spectrum on the strength of quadrupole interaction.

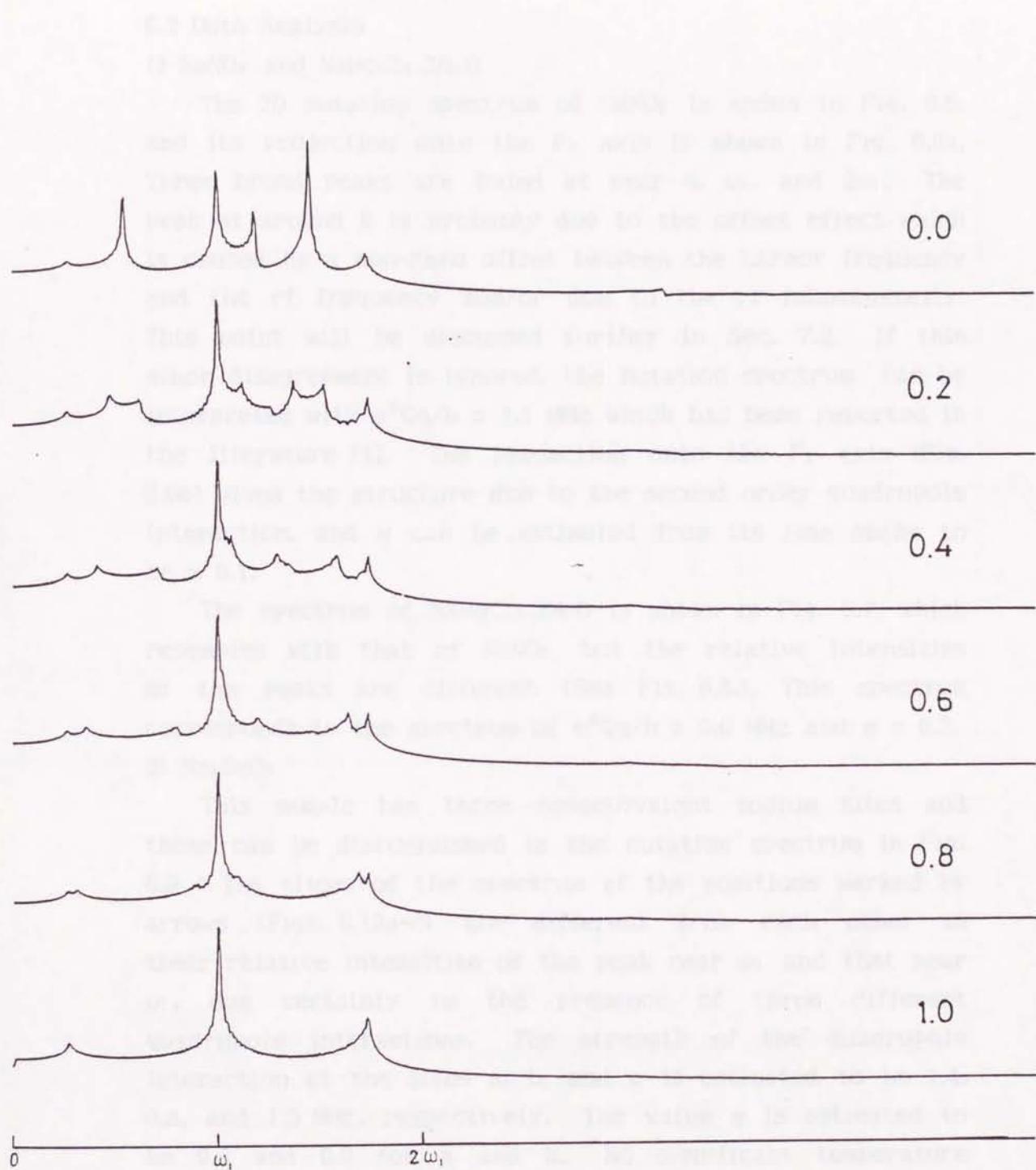


Figure 6.4
 η dependence of nutation spectrum. $\Omega_0/\omega_1 = 2$.

6.2 Data Analysis

1) NaNO_2 and $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$

The 2D nutation spectrum of 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, ω_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 $e^2Qq/h \approx 1.1$ 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 η can be estimated from its line shape to be ≈ 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 NaNO_2 , but the relative intensities of the peaks are different (See Fig. 6.8.). This spectrum corresponds to the spectrum of $e^2Qq/h \approx 0.6$ MHz and $\eta \approx 0.2$.

3) Na_2SeO_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 ω_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 η is estimated to be 0.8 and 0.0 for a and b. No significant temperature

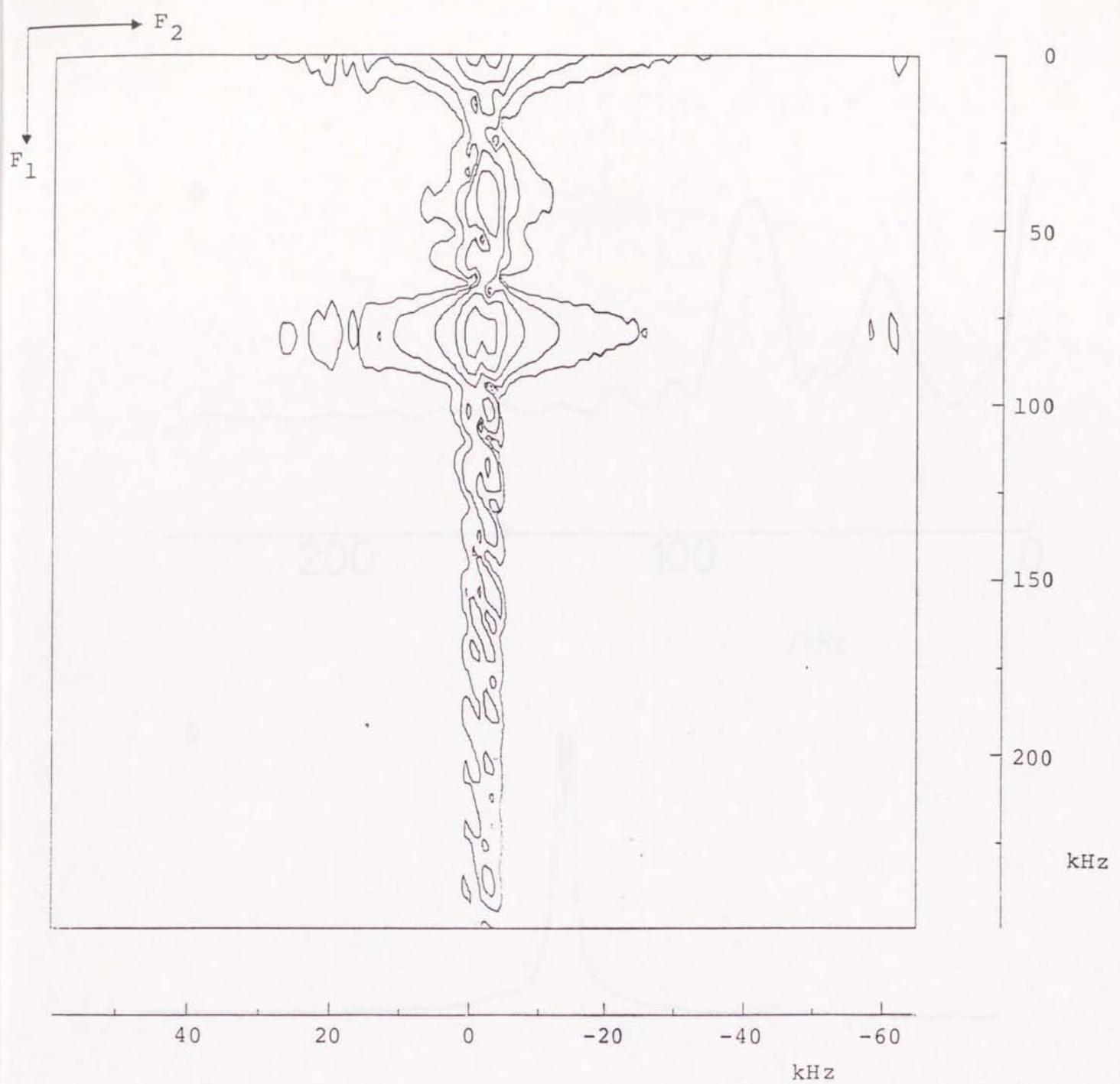


Figure 6.5

Contour plot of 2D nutation spectrum of NaNO_2 at room temperature.

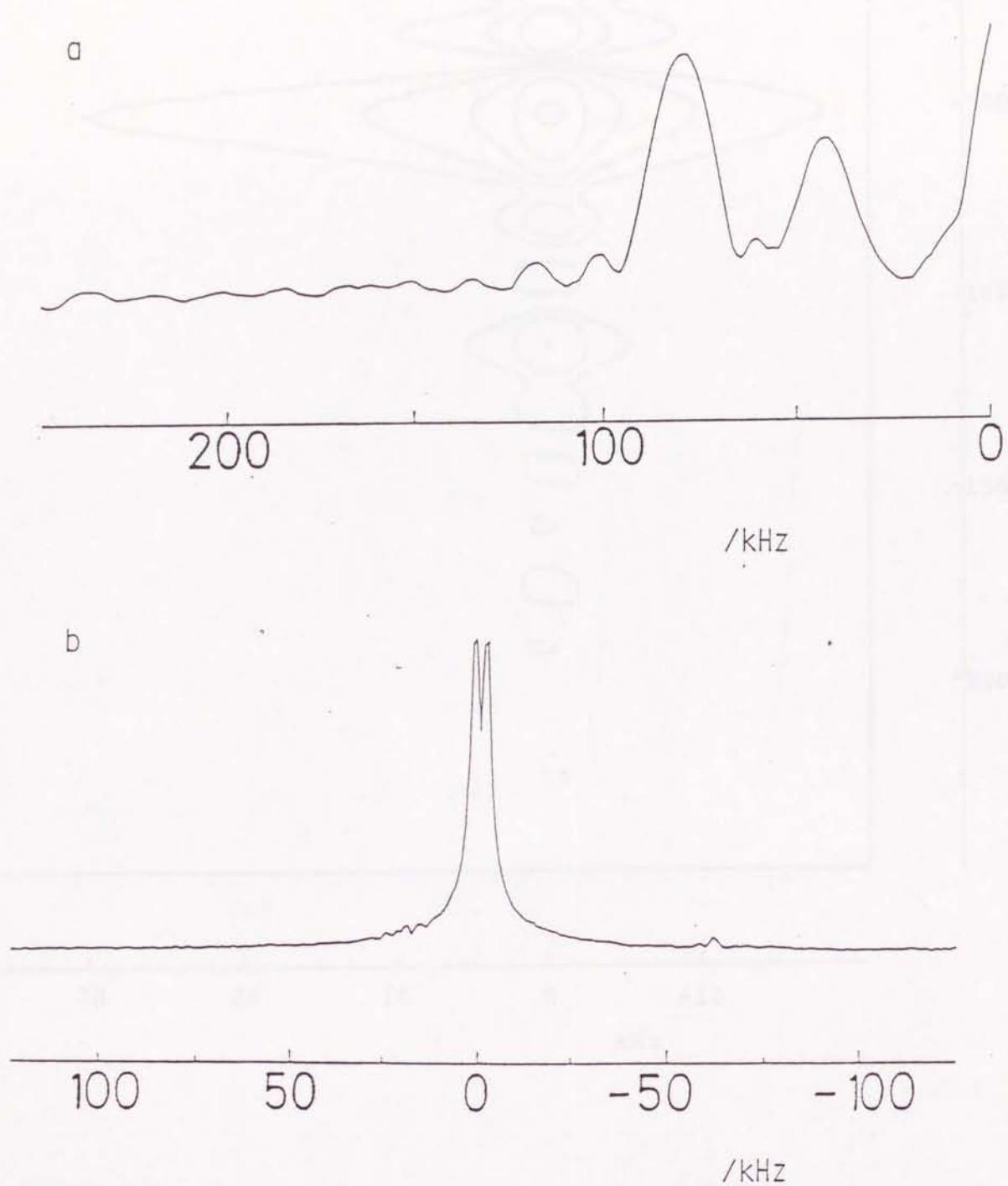


Figure 6.6

2D nutation spectrum of NaNO_2 at room temperature.
a) Projection onto F_1 axis. b) Projection onto F_2 axis.

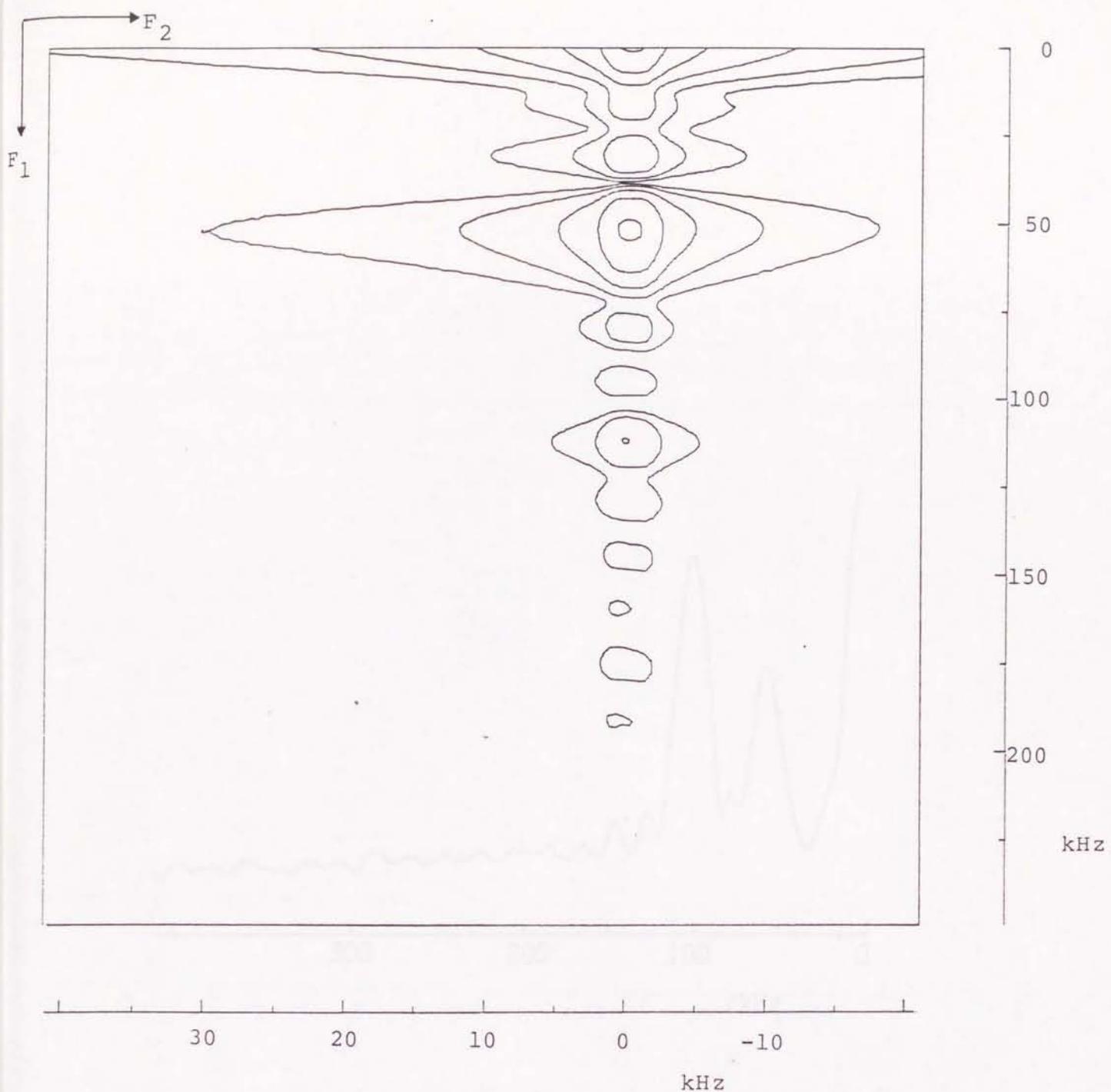


Figure 6.7

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

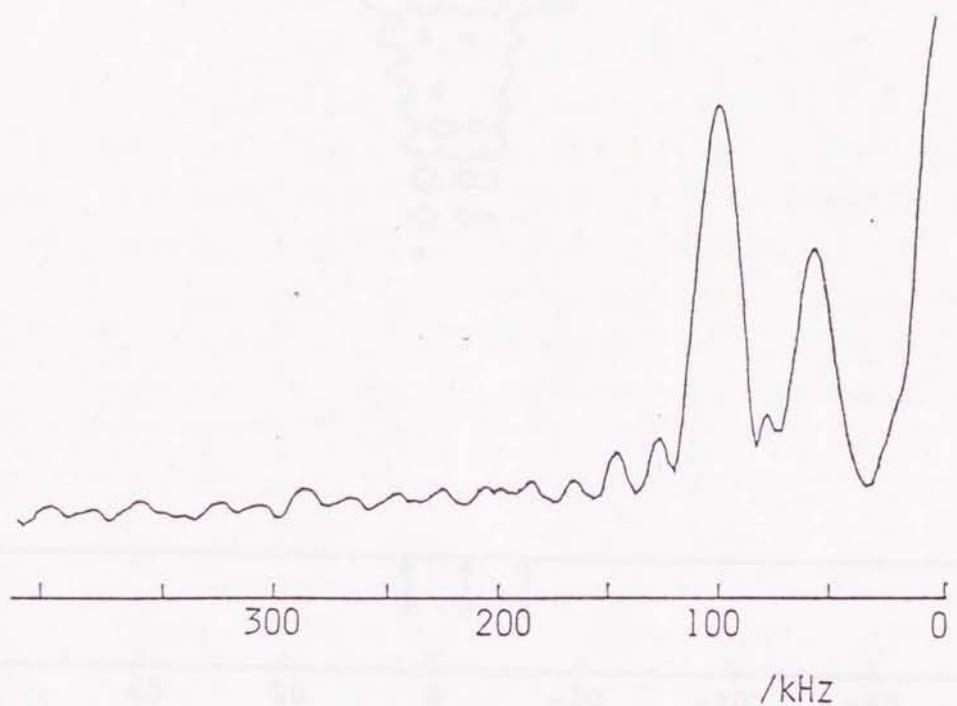


Figure 6.8

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

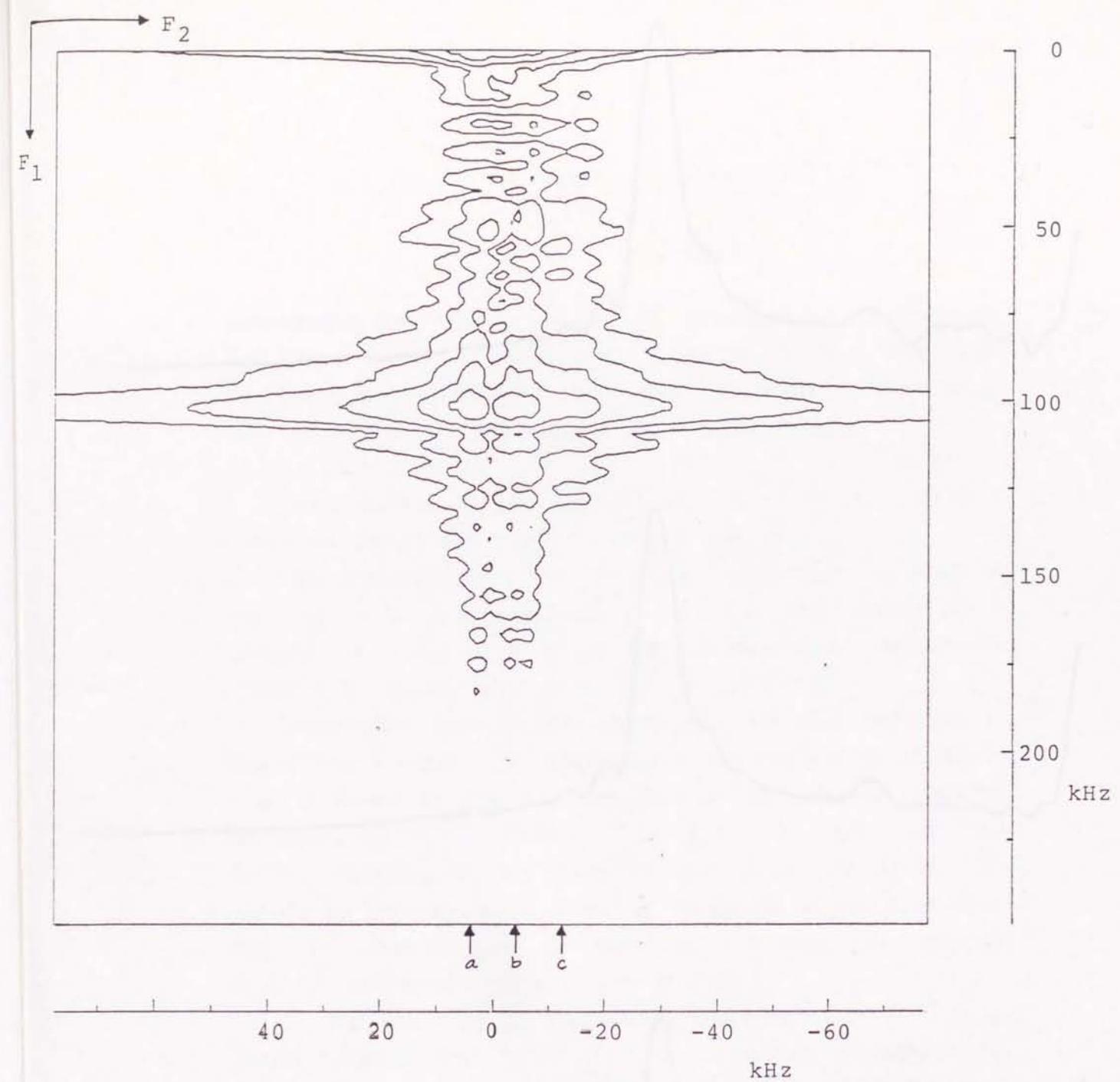
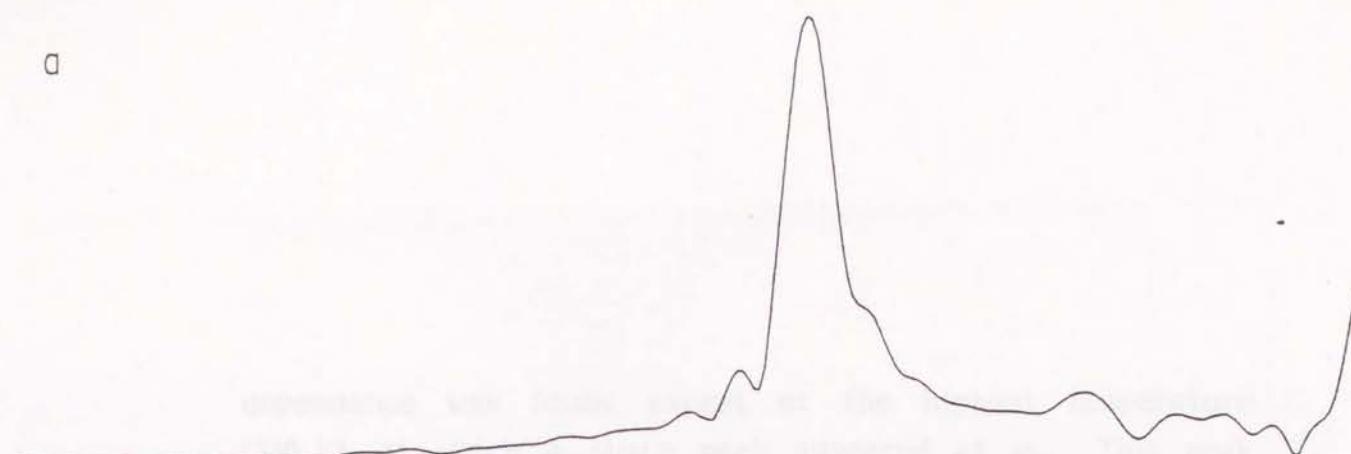


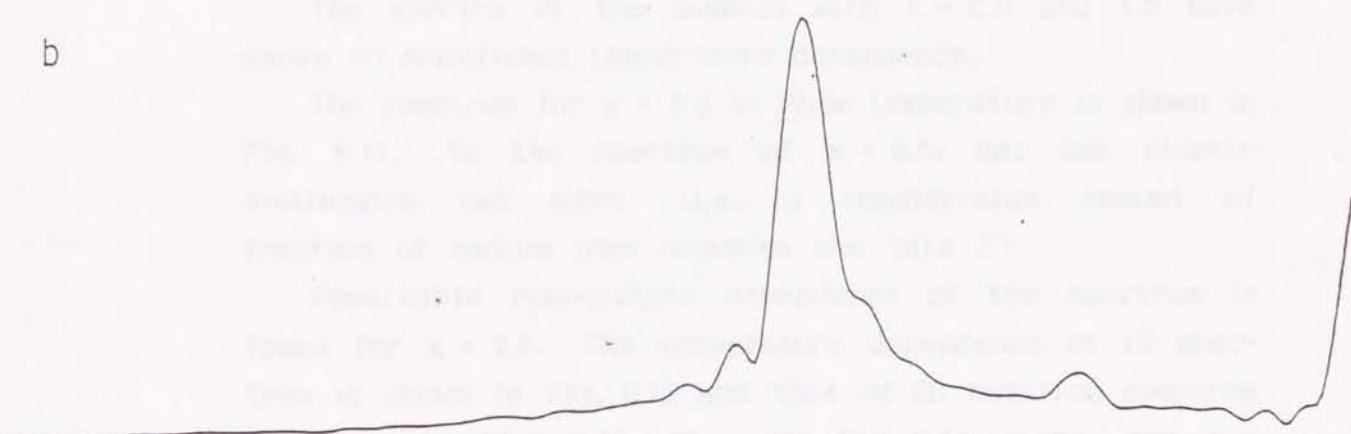
Figure 6.9

Contour plot of 2D nutation spectrum of Na_2SeO_3 at room temperature.

D



b



c

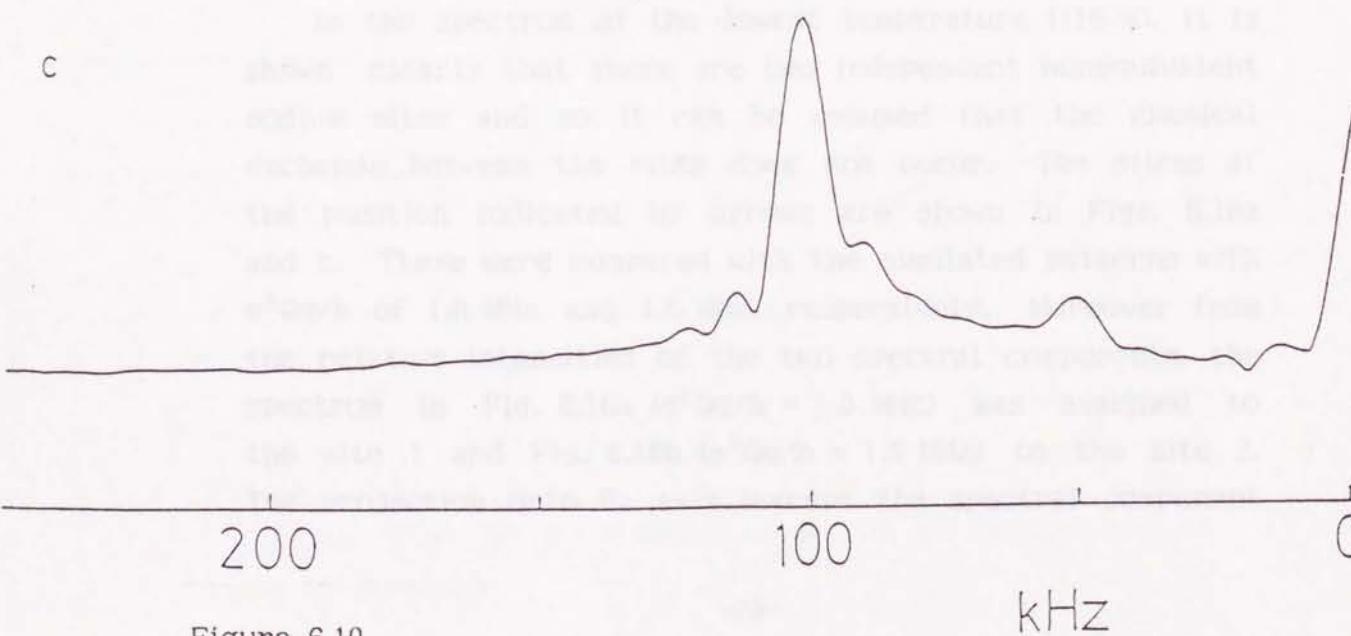


Figure 6.10

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 ω_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

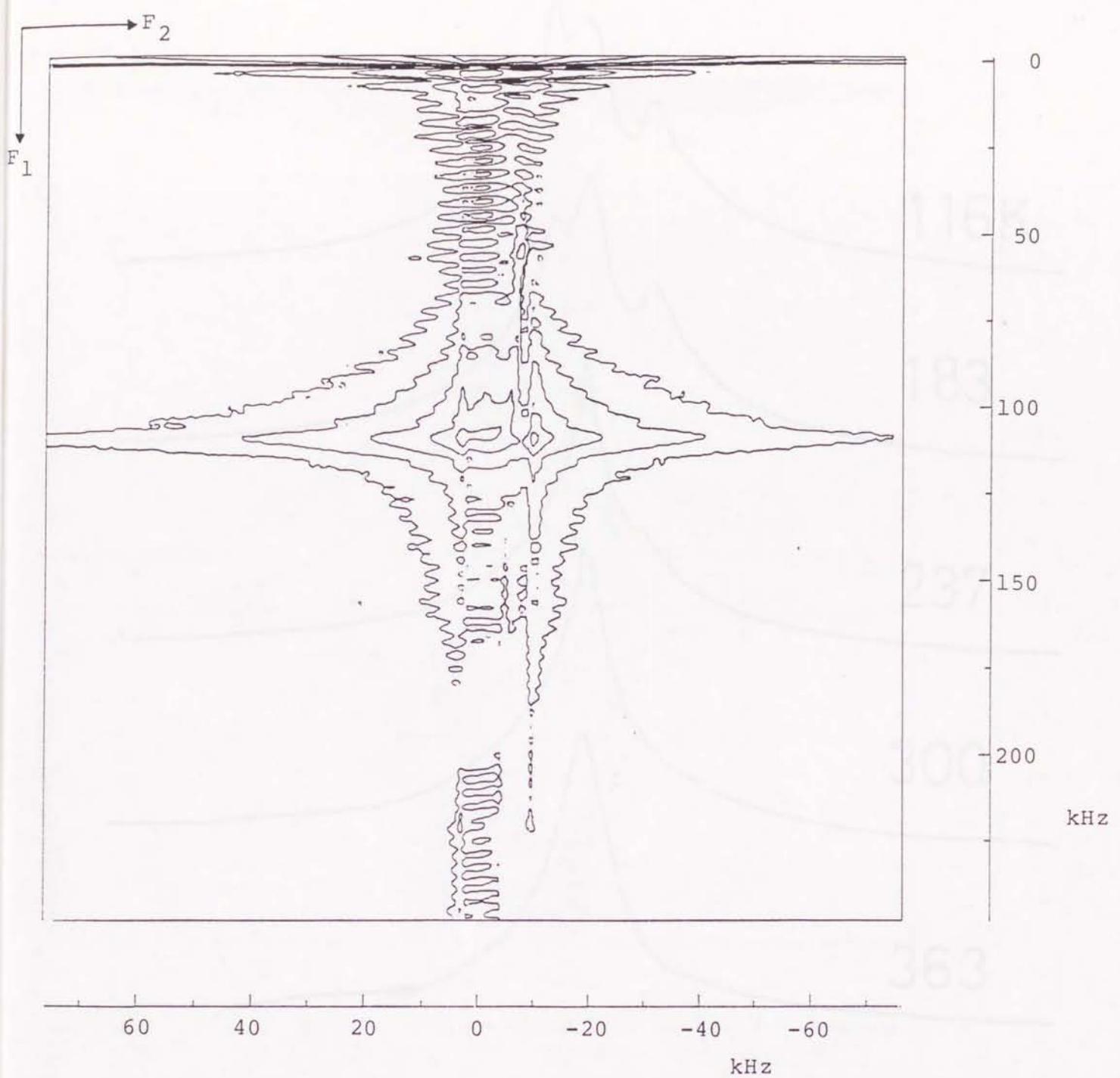


Figure 6.11

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

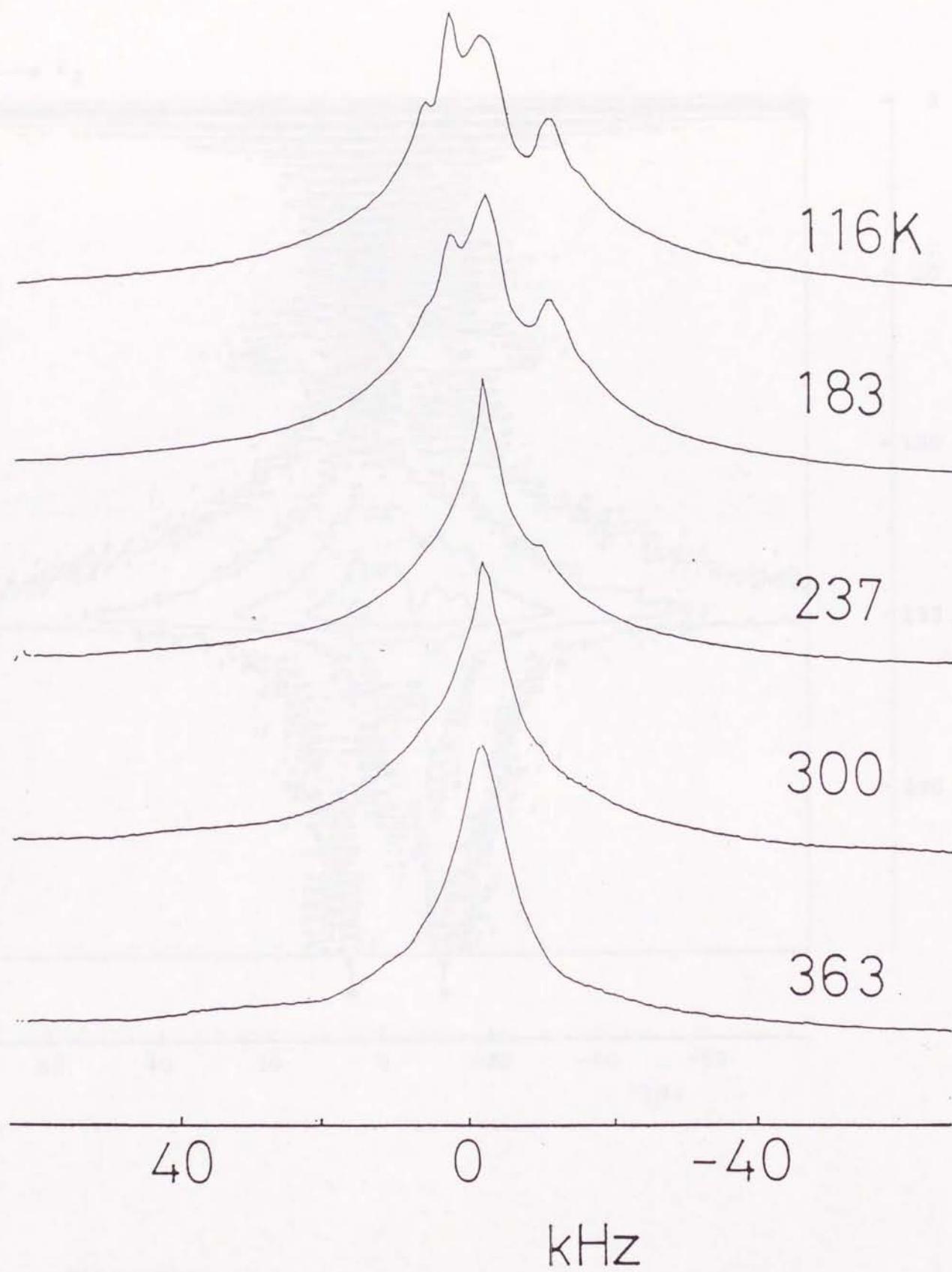


Figure 6.12

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

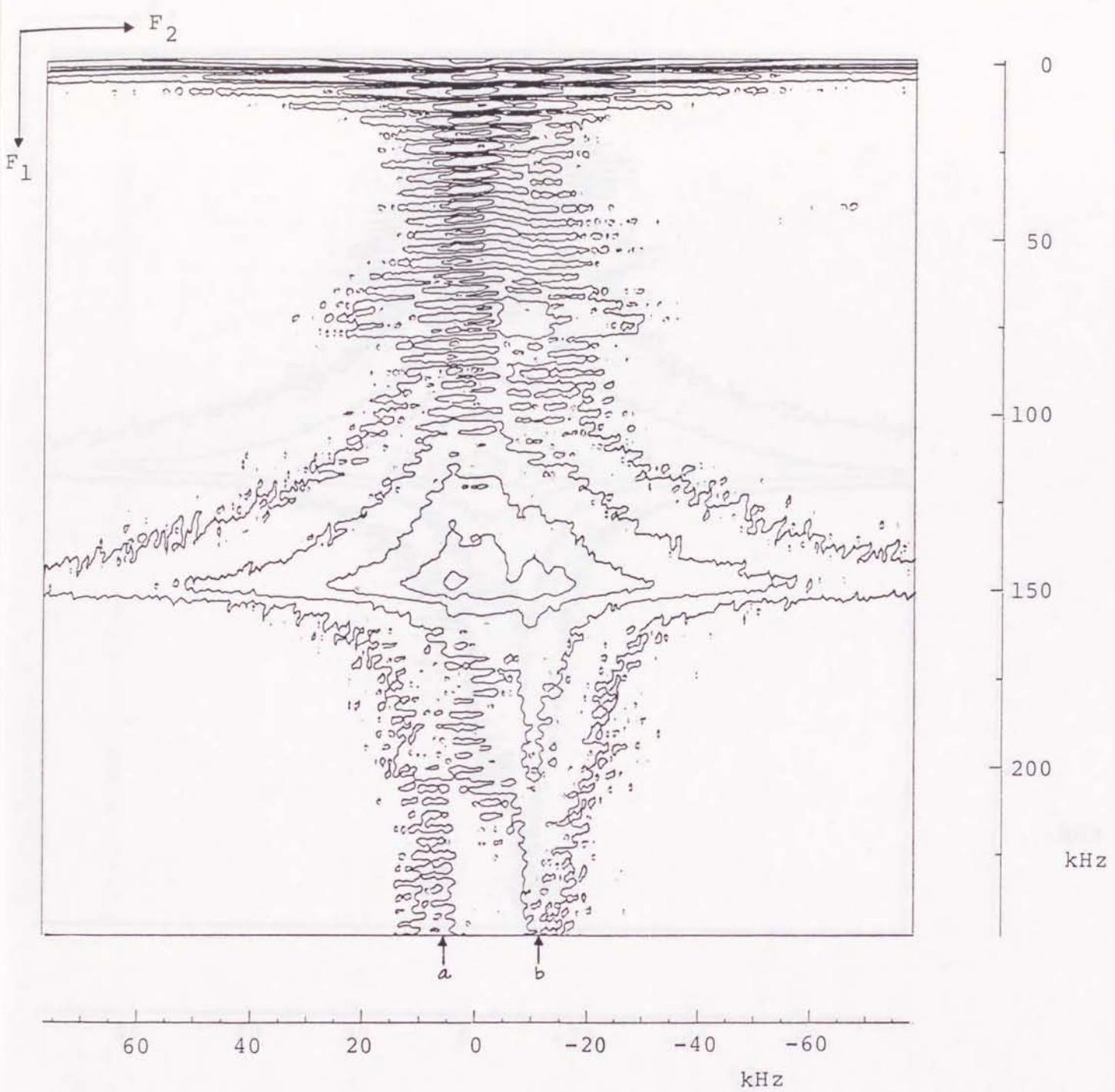


Figure 6.13

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

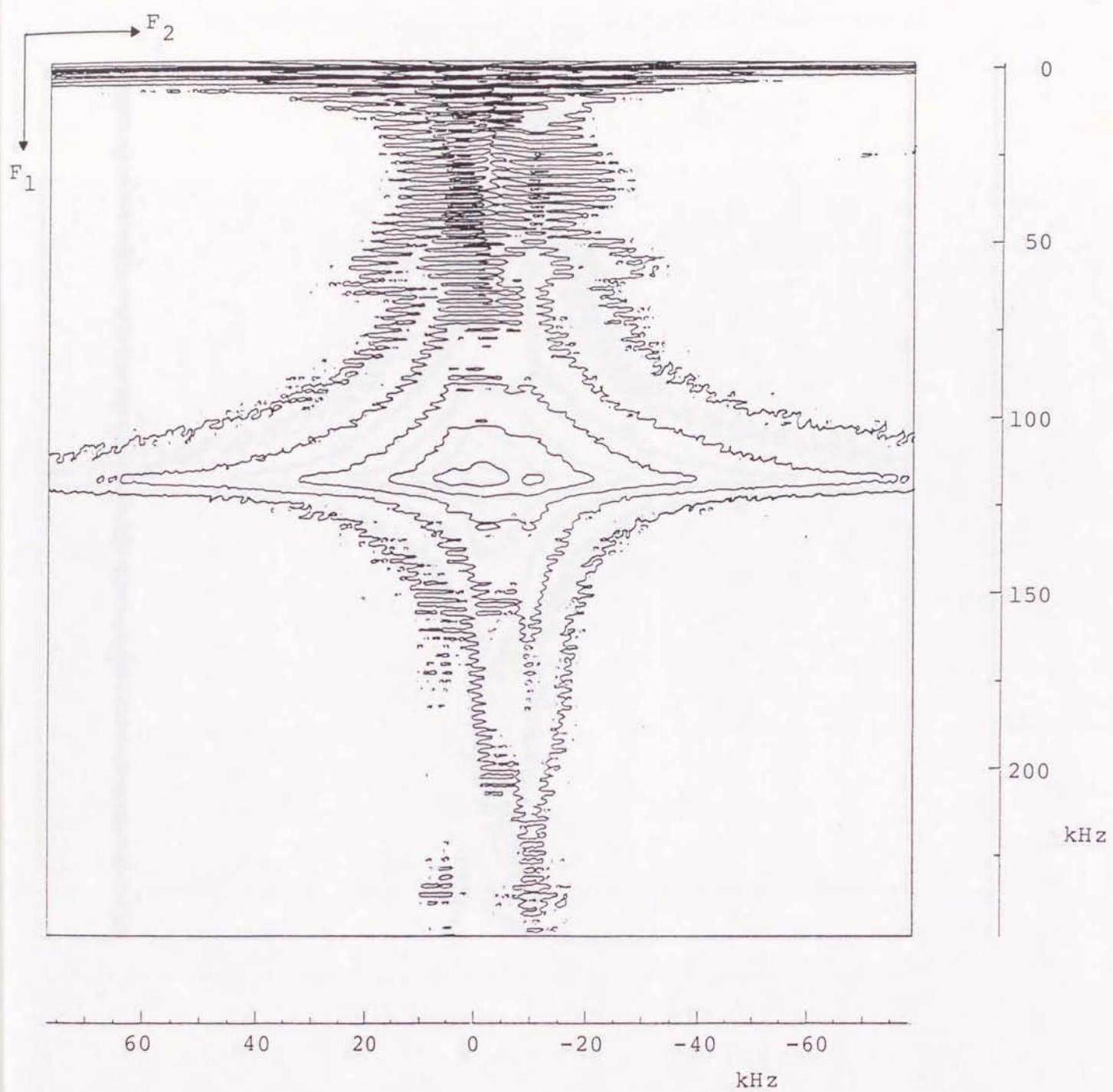


Figure 6.14

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

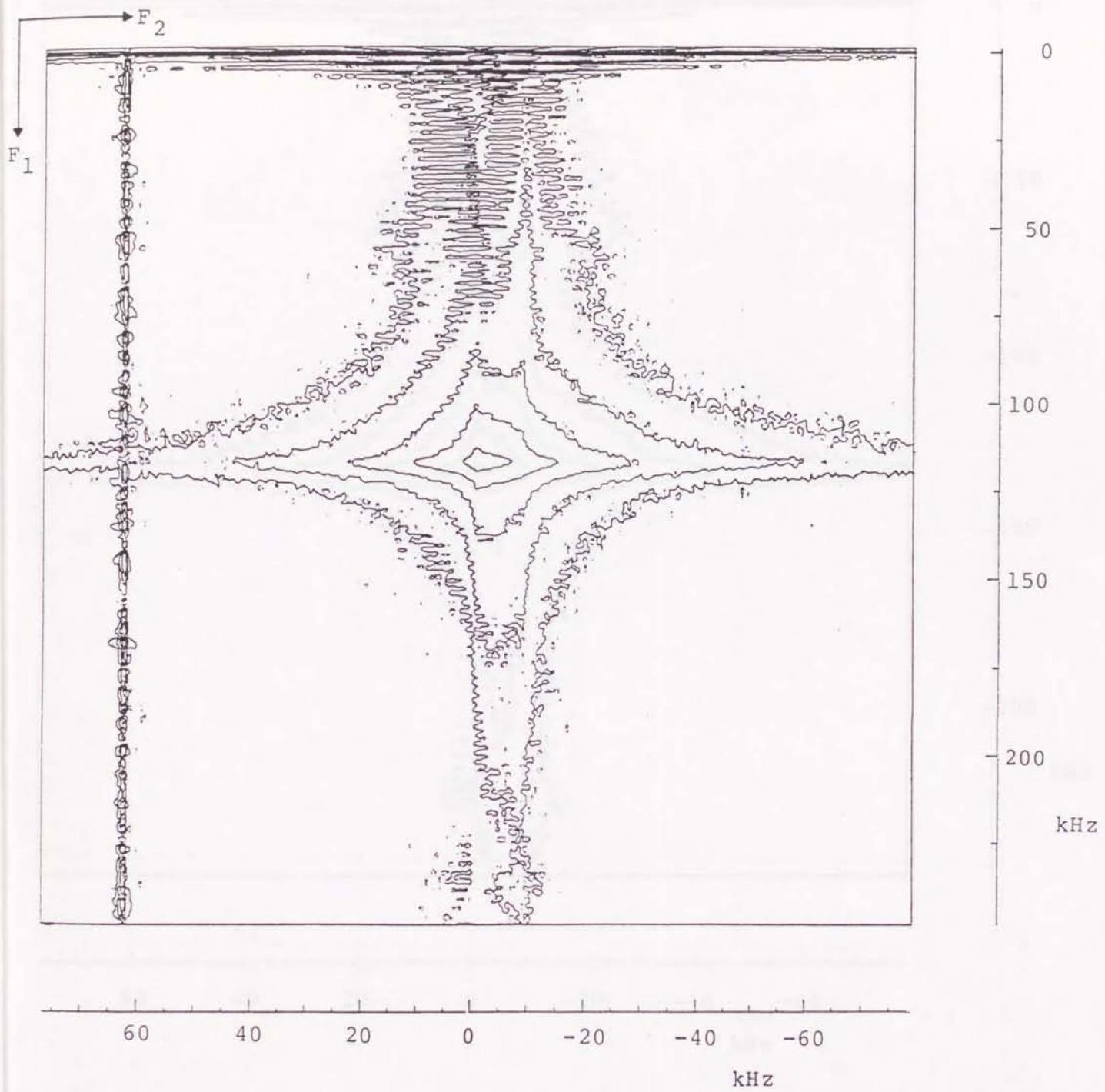


Figure 6.15

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

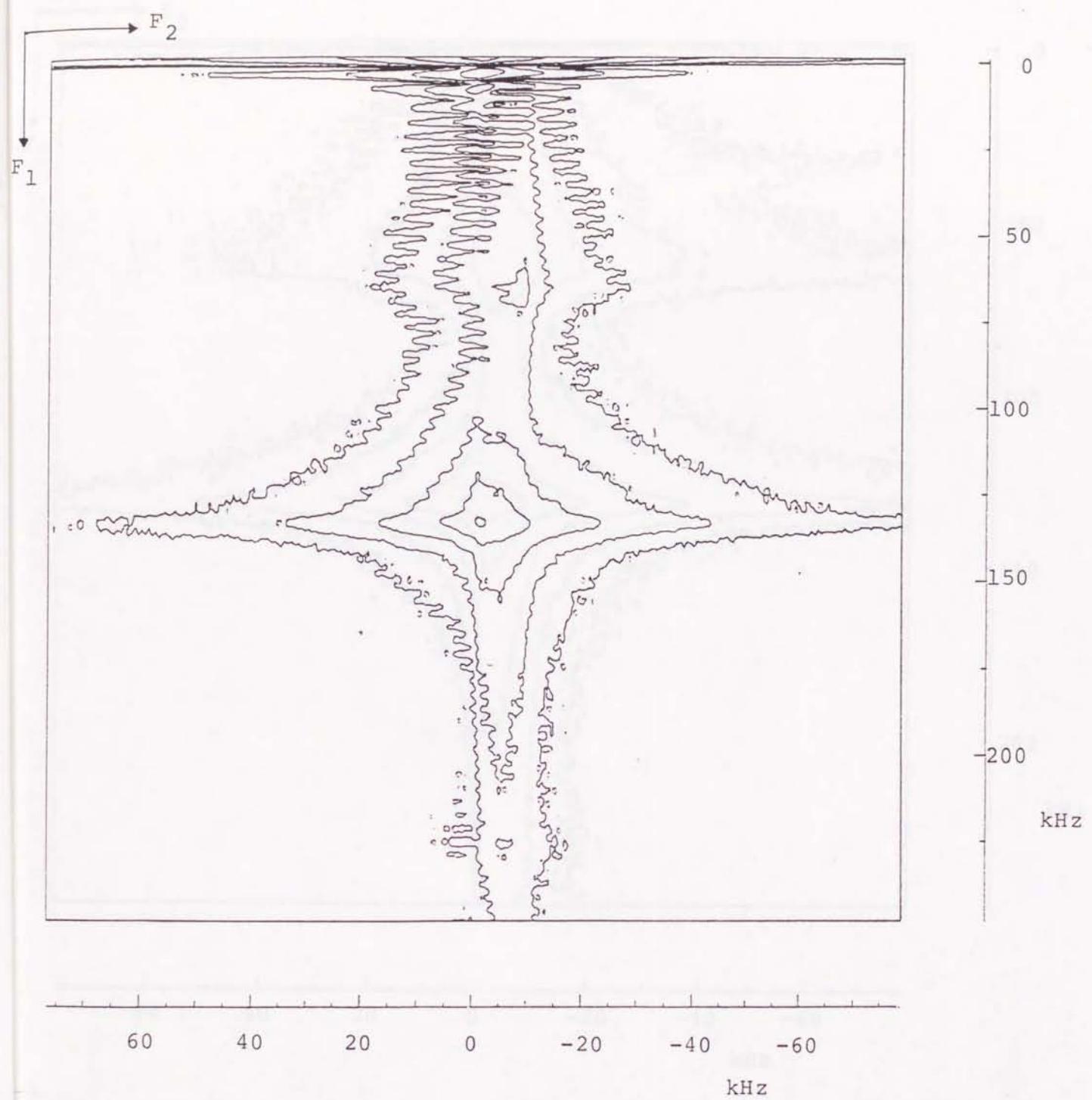


Figure 6.16

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

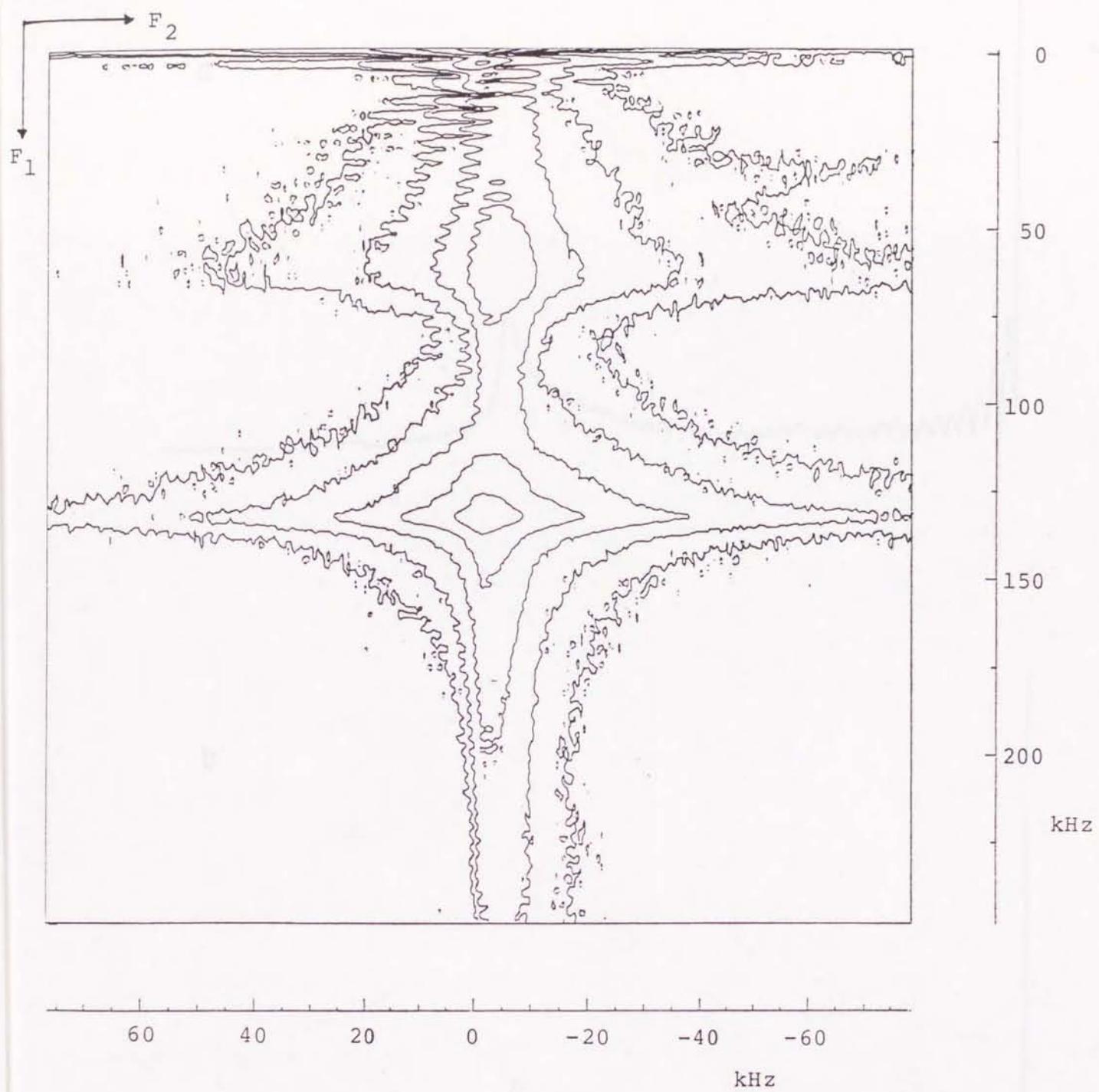


Figure 6.17

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

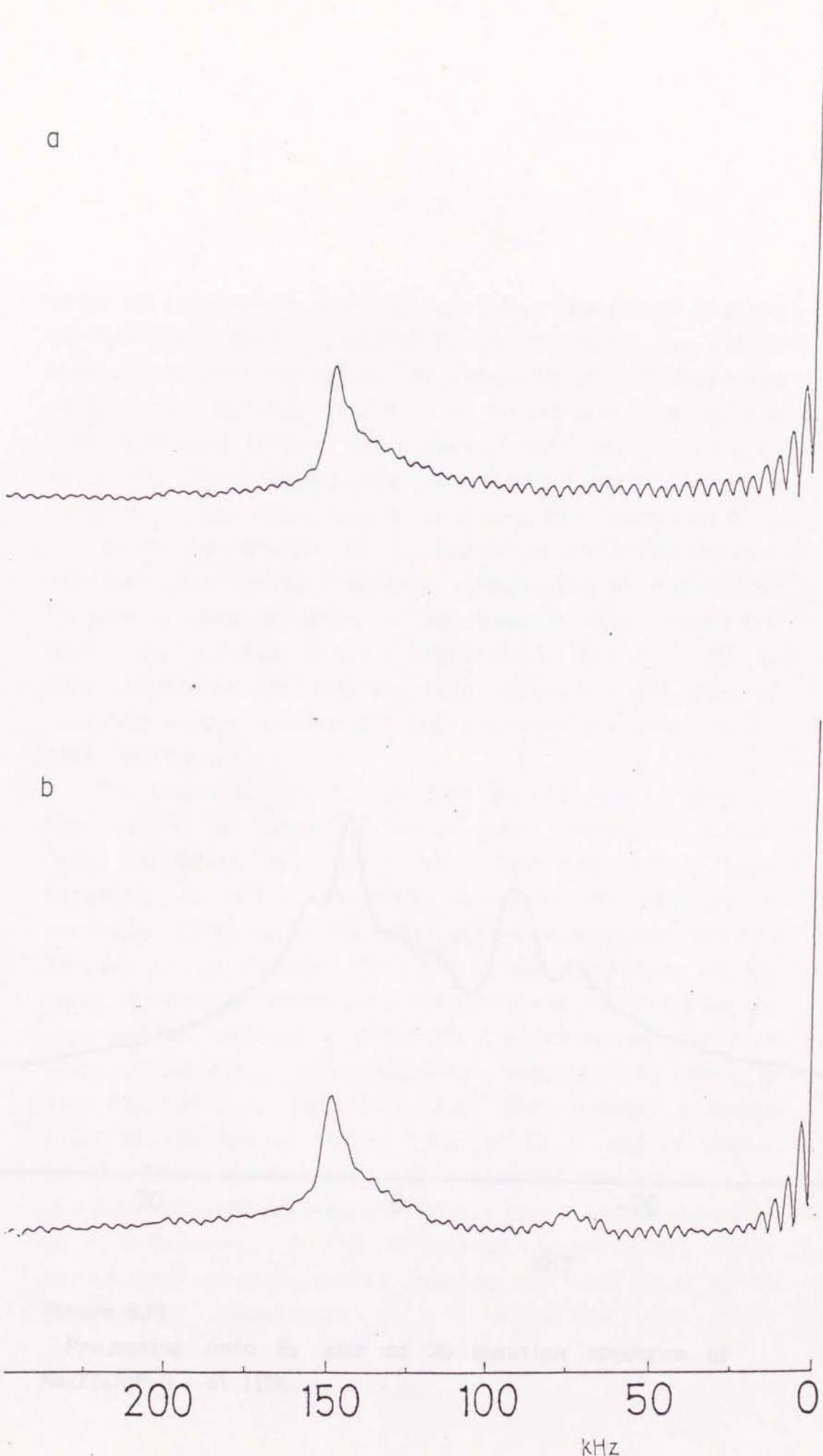


Figure 6.18

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

The simulation of the spectra of the oldest stars with the theoretical spectra of the different models shows that the spectra of the stars with the highest metallicity are in better agreement with the observed spectra than the spectra of the stars with the lowest metallicity. The agreement is not perfect, however, and the spectra of the stars with the lowest metallicity are not in perfect agreement with the theoretical spectra. The spectra of the stars with the highest metallicity are in better agreement with the theoretical spectra than the spectra of the stars with the lowest metallicity.

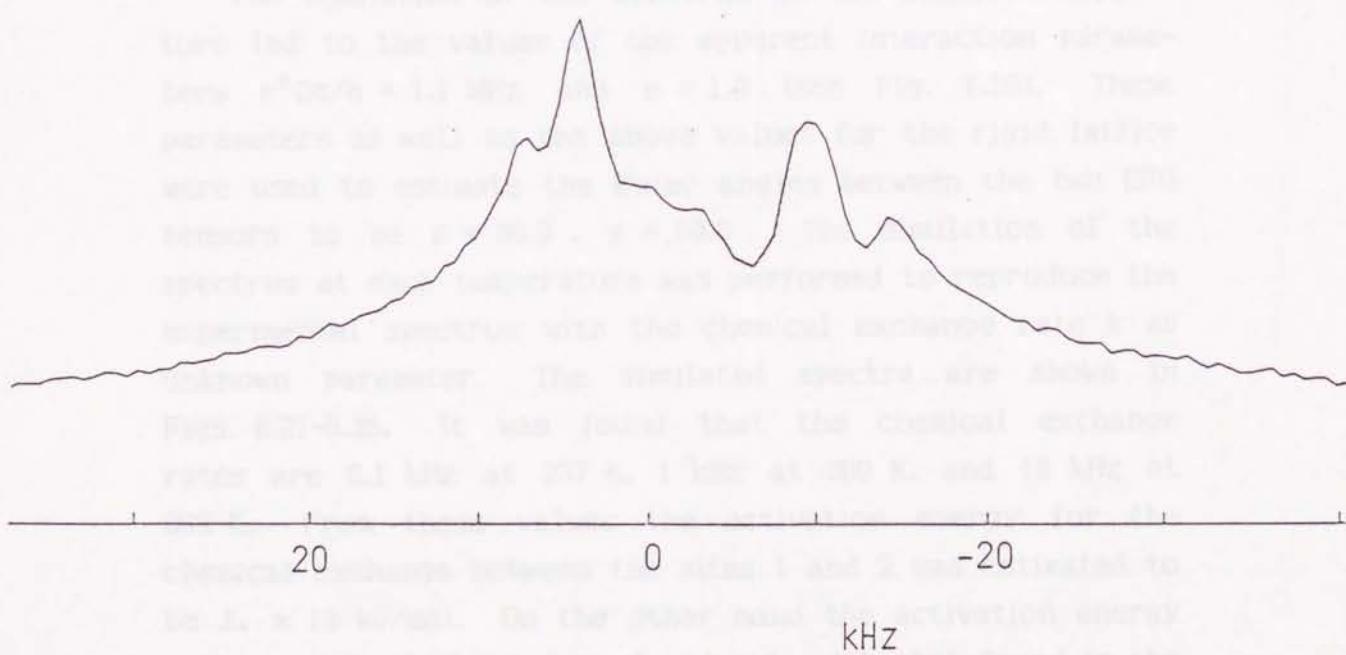


Figure 6.19

Projection onto F_2 axis of 2D nutation spectrum of $\text{Na}_3\text{Zr}_2\text{SiP}_2\text{O}_1\text{z}$ 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 η 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

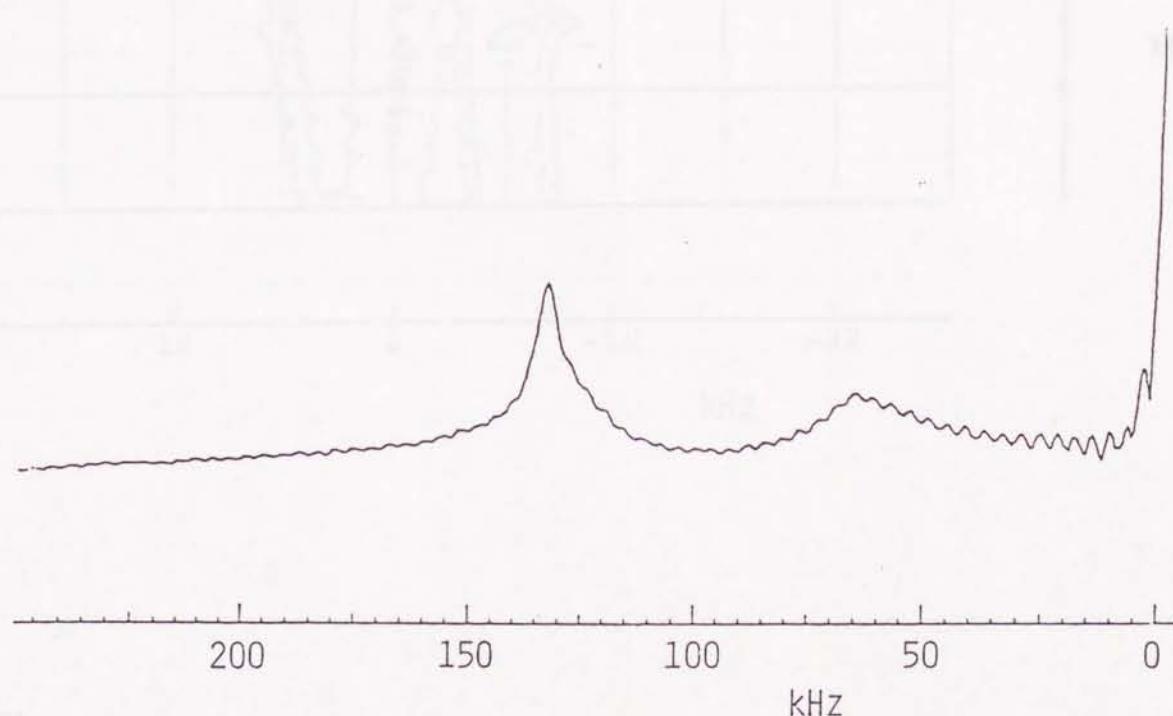


Figure 6.20

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

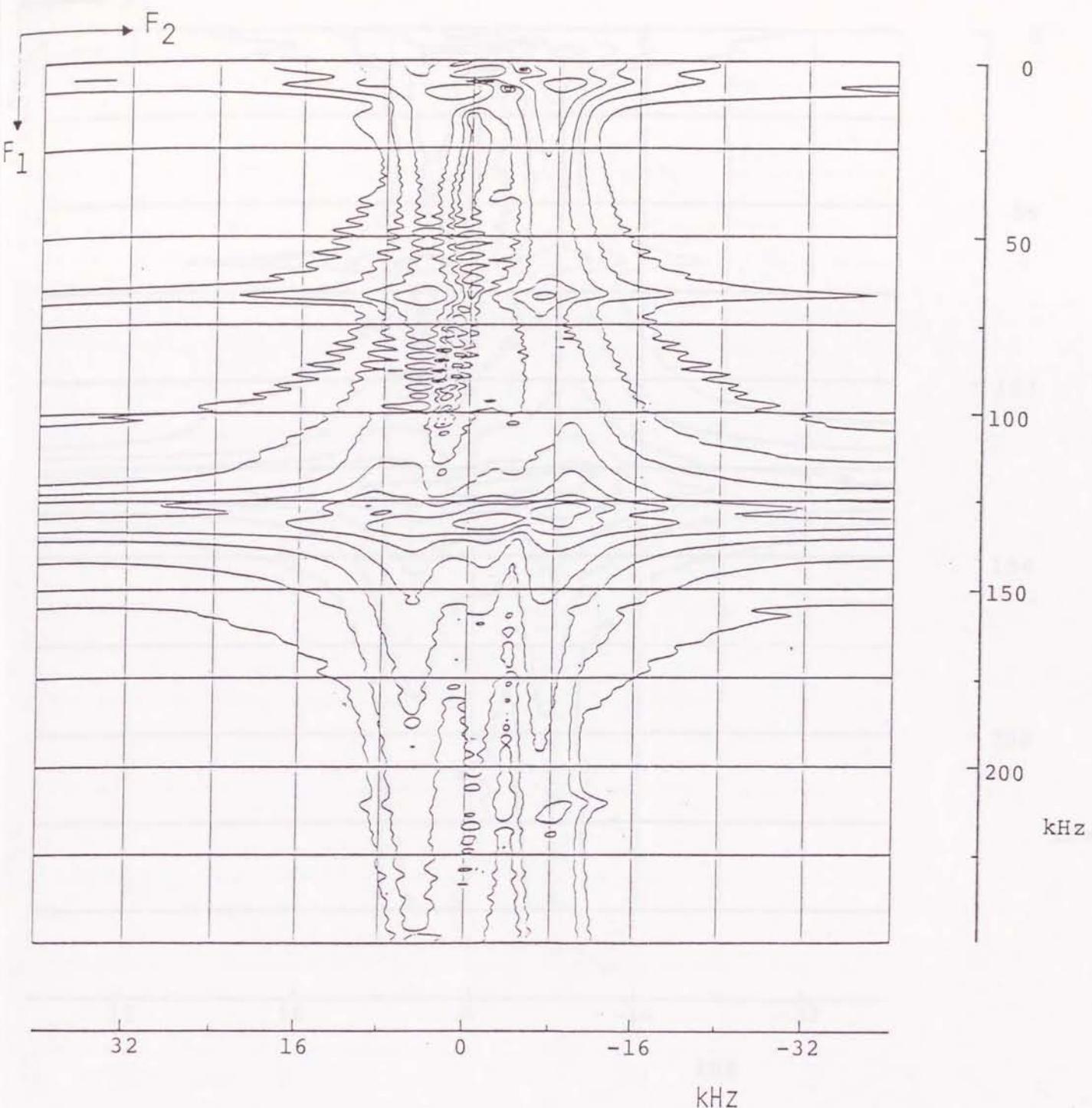


Figure 6.21

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

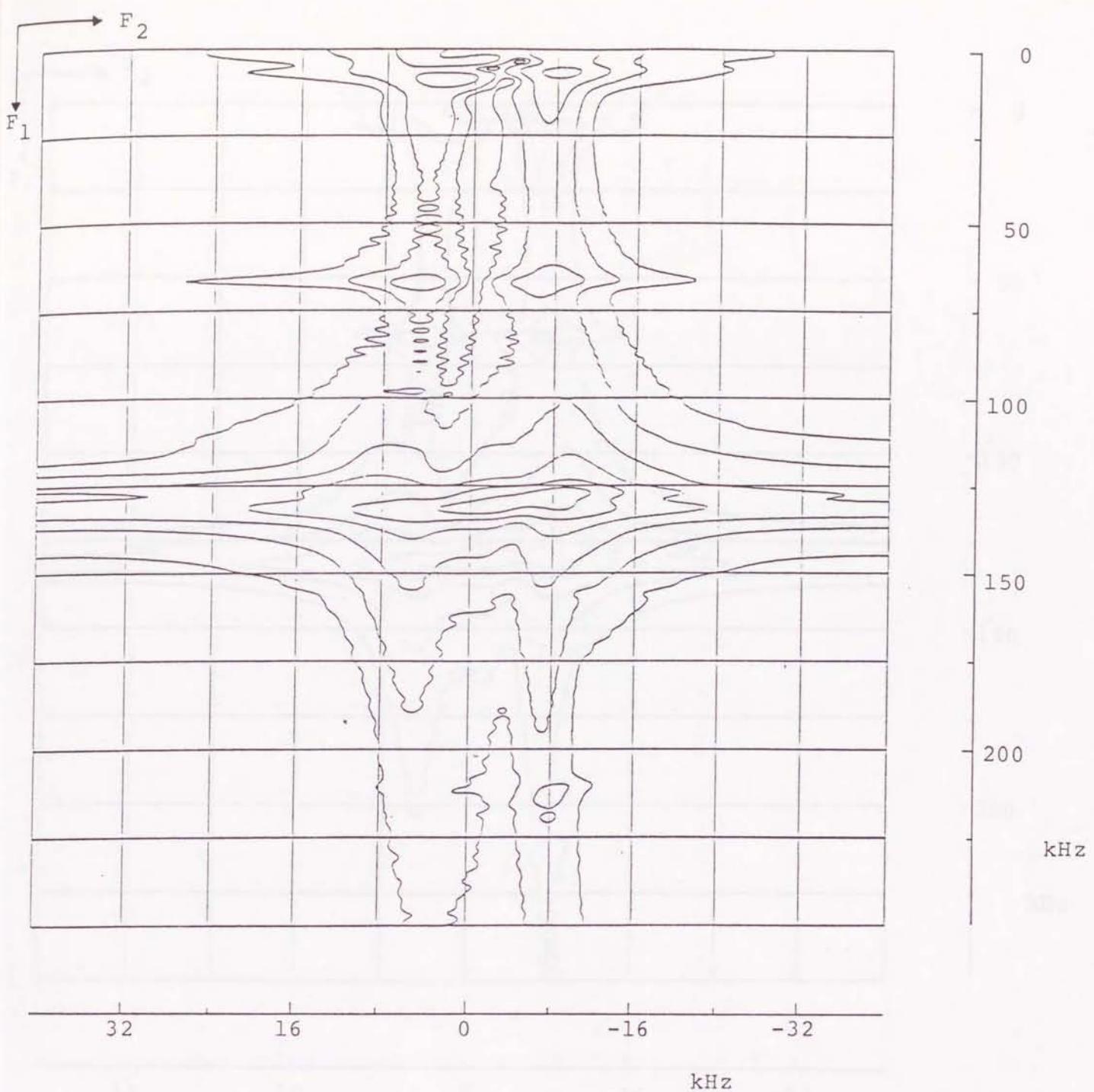


Figure 6.22

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

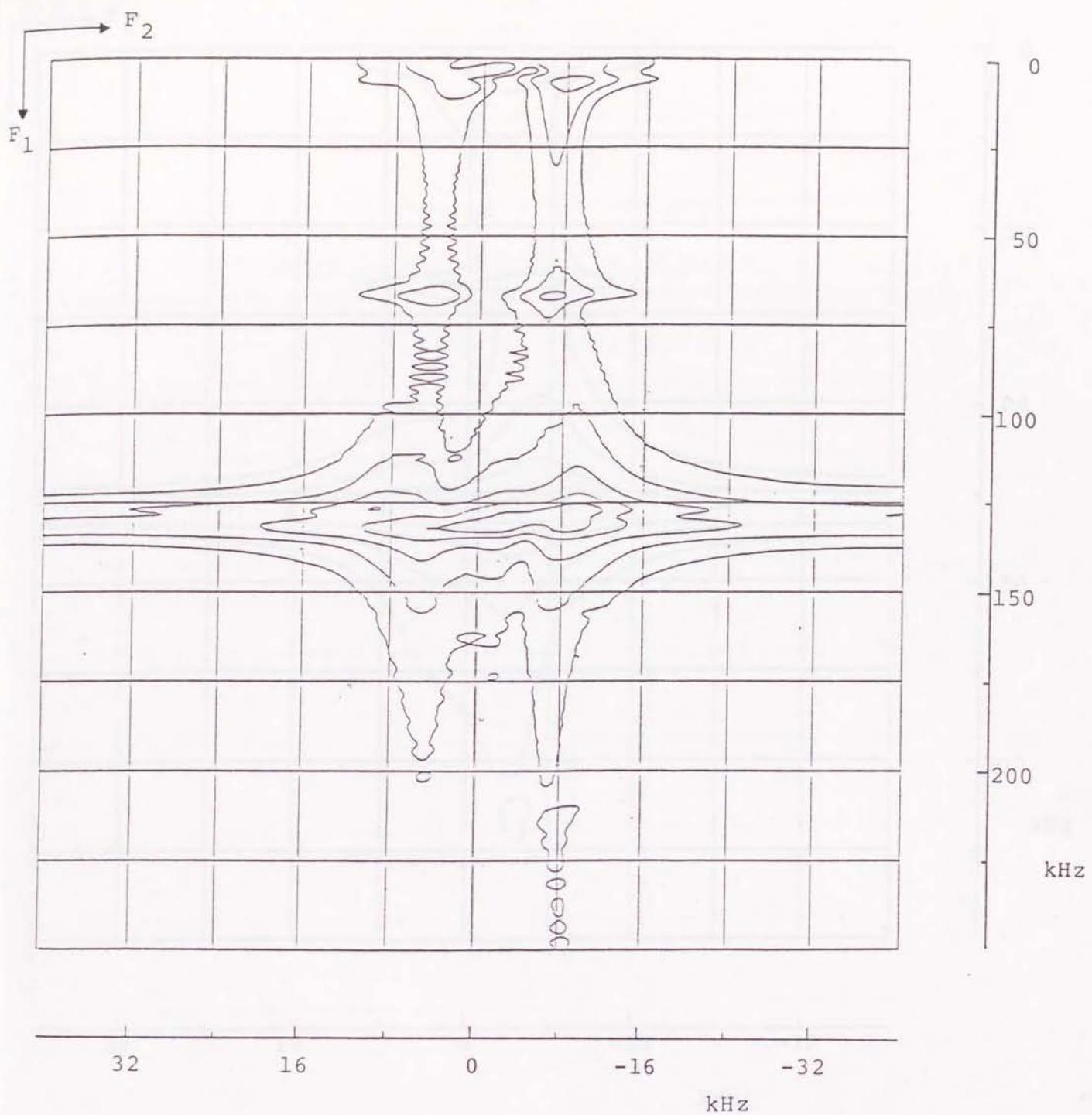


Figure 6.23

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

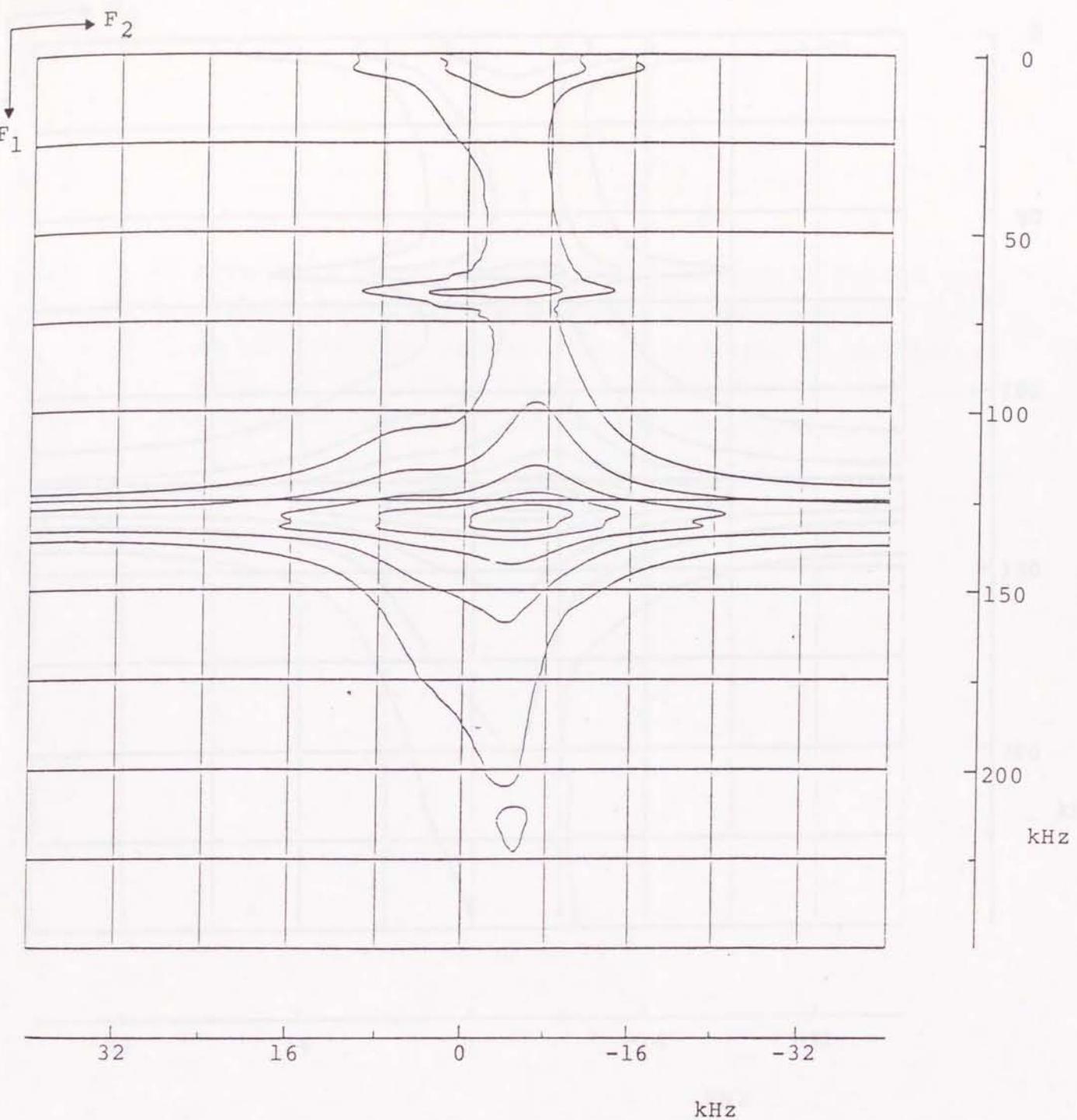


Figure 6.24

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

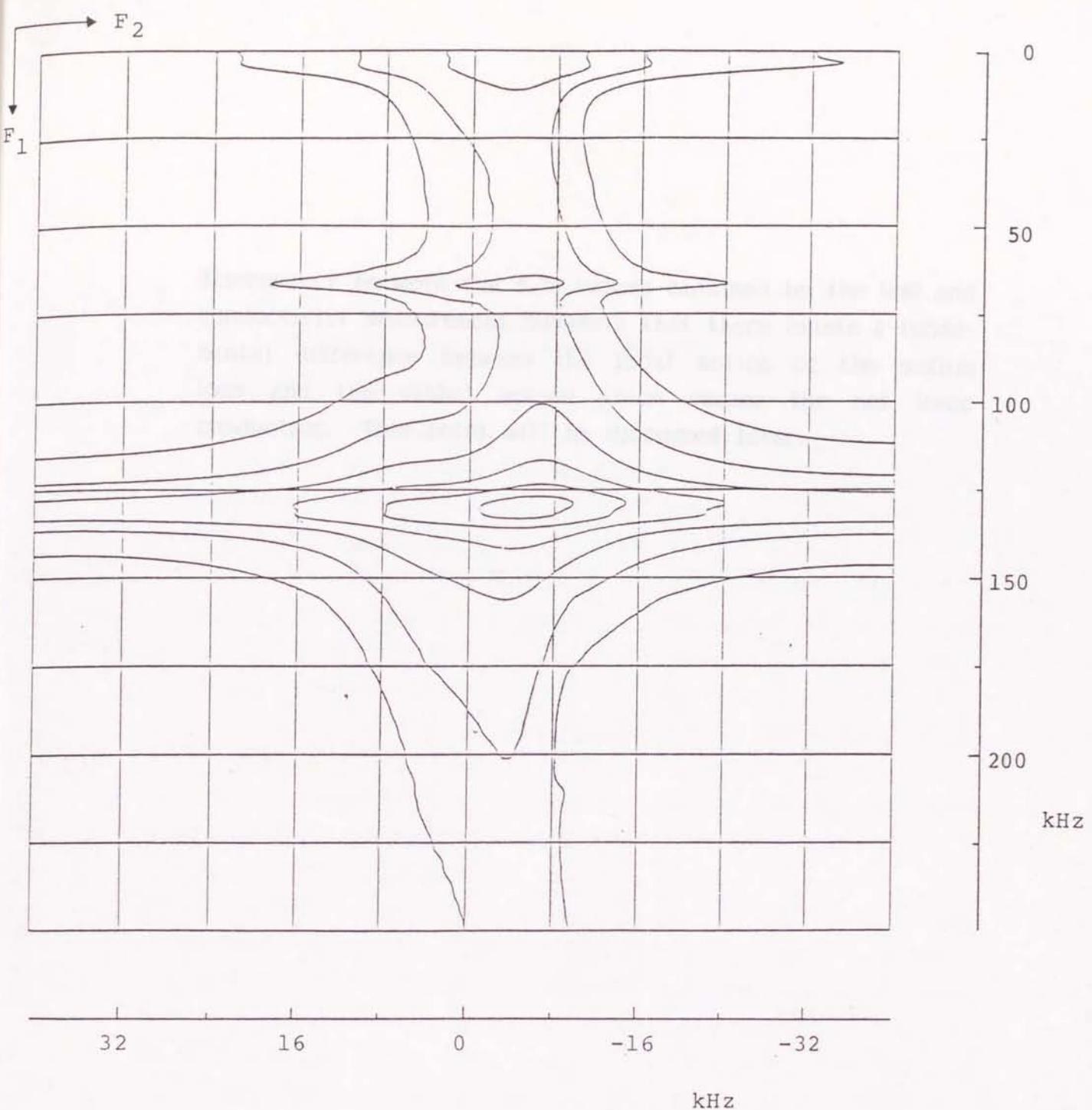


Figure 6.25

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.

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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}Na species involved in several compounds :

1. The ^{23}Na resonances in NaNO_2 and $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$ were used to establish the optimal experimental conditions for the 2D

nutation spectra and to evaluate the sensitivity of the spectra to the quadrupole interaction parameters, e^2Qq/h and η .

2. The ^{23}Na nutation NMR was applied to Na_2SeO_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 η was estimated for two of the three sites in this material.

3. The ^{23}Na 2D nutation 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 nutation 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 nutation NMR. In what follows I will discuss the applicability, advantage and/or disadvantage of the 2D nutation 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 ~ 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}Na , ^{27}Al , ^{39}K , ^{59}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 $\Omega_0/2\pi$ 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

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

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 $\Delta\omega \neq 0$, α 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 Ω_0/ω_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

different nutations to reduce the nutation motion. The effect on the intensity is the same as that due to quadrupole anisotropy.

Finally in the subsection on how the effect of the chemical shift and quadrupole anisotropy add in the actual spectrum, the dependence of the pure nutation patterns

20.0

is shown in the following figure. The figure shows the dependence of the pure nutation patterns

10.0

on the ratio Ω_0/ω_1 . The figure shows the dependence of the pure nutation patterns

5.0

on the ratio Ω_0/ω_1 . The figure shows the dependence of the pure nutation patterns

2.0

on the ratio Ω_0/ω_1 . The figure shows the dependence of the pure nutation patterns

1.0

on the ratio Ω_0/ω_1 . The figure shows the dependence of the pure nutation patterns

on the ratio Ω_0/ω_1 . The figure shows the dependence of the pure nutation patterns

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on the ratio Ω_0/ω_1 . The figure shows the dependence of the pure nutation patterns

on the ratio Ω_0/ω_1 . The figure shows the dependence of the pure nutation patterns

on the ratio Ω_0/ω_1 . The figure shows the dependence of the pure nutation patterns

ω_1 $2\omega_1$

Figure 7.1

Dependence of nutation spectrum on the ratio Ω_0/ω_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.

It is also possible to obtain the nutation spectrum in the situation where the two spins are coupled. In this situation, when both spins are coupled to each other and Ω is very different to ω_1 , which peak corresponds to each spin. This is because the two spin-pulses Π_{11} and Π_{22} are easily distinguished, even corresponding to the difference of the strength of the coupling interaction.

It was shown that it is not difficult to find out that the nutation spectrum can be directly checked when the chemical sequence of the resonant nuclear species is known. The detailed analysis of the spectrum brings about the quantitative information of the sequence of the nuclear moments. Especially when now, the two types of the spectra are being considered, one can determine the relative orientation of the two bonds as well as the rate-change of the coupling. Thus the method can be used to specify the structure of complex "systems." This conductivity, which could also be measured from the electrical polarizer of "viscous" solution, was studied by Chia et al. and was compared with the conductivity of the pure water. It was found that the "viscous" conductivity for the water solution was enhanced when the two spins are coupled. The value is 10% higher and this value was fully well measured with the electrical polarizer and a viscosity conductimeter measurement. The next sample used for "viscous" conductivity is based on the classical "hopping" mechanism through successive "interactions" sites. The result is more conductivity enhancement and this should give the new information about the "hopping" mechanism. Several discussions of the results found above are discussed.

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 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.)

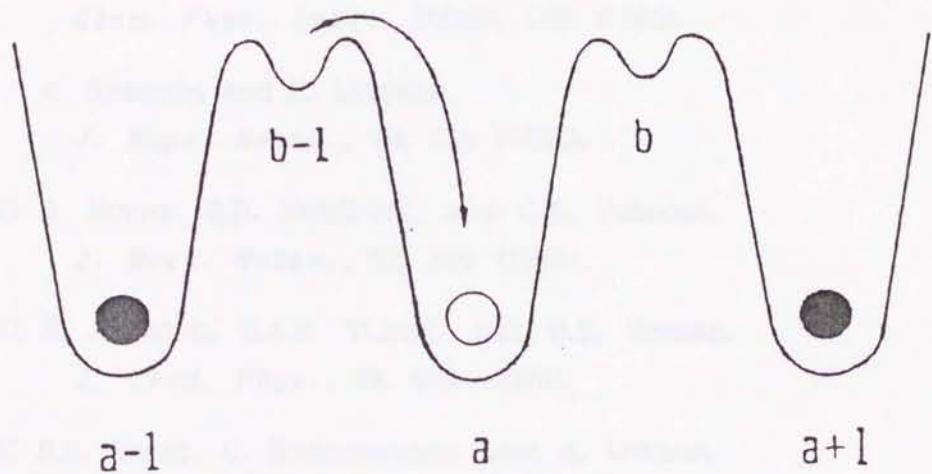


Figure 7.2

Nonequivalent site model with deep and shallow wells.

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2 $DECLARE
3     PROGRAM NUTATION
4 C
5     COMPLEX*16 ARYDAT(1,1024),H1(100),R1(100),RDR(100)
6     COMPLEX*16 E1(10),EE(10),REC(10),ERC(10),W(10)
7     REAL*8      THD(10),QCC,ETA,QC2,W1,QIF(10),WIF(10)
8     REAL*8      AI,W0,PI2,T1(2),CT1,CT2(20000),CP1(900),H1I(2,100),S,D
9     INTEGER*4   DIM(2),MXD(2),NSP,NT,NP,MXT,I,J,K,L,N,ERS
10    CHARACTER*15 RGF,TDF
11 C
12    EQUIVALENCE (H1,H1I),(CT2(901),CP1(1))
13    COMMON /ARYDAT/ARYDAT,DIM
14    COMMON /PARAMS/THD,QCC,ETA,QC2,QIF,WIF
15    COMMON /WRKVAR/RDR,EE,REC,ERC,W
16 C -----
17 C     Declarations of Constants
18 C -----
19     PARAMETER(PI2=6.283185307179586D+00)
20     DATA MXD/1024,1/
21 C -----
22 C     Spin Number
23 C -----
24     WRITE(*,'(A11$)') '0Spin *2 = '
25     READ(*,'(I2$)') NSP
26     S=DBLE(NSP)/2.0D+00
27     AI=S*S+S
28 C -----
29 C     Lamor Frequency
30 C -----
31     WRITE(*,'(A20$)') '0Lamor Freq / MHz = '
32     READ(*,'(F7.4$)') W0
33 C -----
34 C     Quadrupole Interaction Parameters
35 C -----
36     WRITE(*,'(A17$)') '0eqQ / MHz, η = '
37     READ(*,'(2F10.6$)') QCC,ETA
38 C -----
39 C     RF Strength in Frequency Units
40 C -----
41     WRITE(*,'(A27$)') '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,A5$)') 
49     & ' Number of Sampling Points ( Max. ',MXD(I),') = '
50     READ(*,'(I5$)') DIM(I)
51     WRITE(*,'(A25$)') ' Time Increment / μs = '
52     READ(*,'(F5.3$)') TI(I)
53     300 CONTINUE
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Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

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54 C -----  
55 C      RGF : Stores Computational Condition  
56 C      TDF : Saves FID Data  
57 C -----  
58      WRITE(*, '(A25$)') '0Registry File Name = '  
59      READ(*, '(A15$)') RGF  
60      WRITE(*, '(A25$)') ' Time Domain File Name = '  
61      READ(*, '(A15$)') TDF  
62 C -----  
63 C      Get the Number to be calculated  
64 C -----  
65      WRITE(*, '(A20$)') ' Number of Division over  $\theta$  '  
66      WRITE(*, '(A$)') ' [ Max. : 20000 ( $\eta = 0$ ) 900 ( $\eta > 0$ ) ] = '  
67      READ(*, '(I5$)') NT  
68      DO 400 I=1,NT  
69          CT1=DBLE(I)/DBLE(NT)  
70          CT2(I)=CT1*CT1  
71      400 CONTINUE  
72      IF (ETA .EQ. 0.0D+00) THEN  
73          NP=1  
74          CP1(I)=0.0D+00  
75      ELSE  
76          NP=NT  
77          DO 410 I=1,NP  
78              CP1(I)=ETA*DCOS(P12*DBLE(I)/DBLE(NT))  
79      410 CONTINUE  
80      END IF  
81 C -----  
82 C      Store the Parameters  
83 C -----  
84      OPEN (UNIT=50, FILE=RGF, ACCESS='SEQUENTIAL')  
85      WRITE(50, '(A40$)') ' ----- 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,RI,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,III,III1,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     III(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  C      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          H1I(2,I,I)=Q1*Q1F(I)
191          IF (I .GT. 1) H1I(2,I-1,I)=W1F(I-1)
192          IF (I .LT. L) H1I(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      RETURN  
235 C      END  
236 C  
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 $DECLARE
2     PROGRAM EXCHANGE
3 C -----
4 C     Simulation Program for 2D Nutation NMR with Chemical Exchange
5 C -----
6 COMPLEX*8  ARD(256,128)
7 REAL*8    QCC(2),ETA(2),QC2(2),ET2(2),CHS(2),RFS,EXC(2,2,2)
8 REAL*8    ALP(2),BET(2),GAM(2),TDX(8),THD(4,2),R(4),P(2)
9 REAL*8    X(-50:50,0:50),Y(-50:50,0:50),Z(-50:50)
10 REAL*8   SA(2),CA(2),SB(2),CB(2),SG(2),CG(2),TI(2)
11 REAL*8   W0,W1,D,PID,SNT,D2R,PI1,PI2,SQ3
12 INTEGER*4  DIM(2),MXD(2),NSP,NSI,MXS,NN,MXT,I,J,N,ERS
13 CHARACTER  CHA
14 CHARACTER*15 RGF,TDF
15 C -----
16 EQUIVALENCE (TDX,THD),(CHA,RGF)
17 COMMON /ARD/ARD,DIM,TDX,R,P
18 COMMON /PAR/QCC,ETA,QC2,ET2,CHS,RFS,EXC
19 COMMON /ARG/SA,CA,SB,CB,SG,CG
20 C -----
21 C     Declarations of Constants
22 C -----
23 PARAMETER(NSP=4,MXS=2,MXT=50)
24 PARAMETER(D2R=1.745329251994329D-02,SQ3=8.660254037844385D-01)
25 PARAMETER(PI1=3.141592653589793D+00,PI2=6.283185307179586D+00)
26 DATA MXD/128,256/
27 C -----
28 C     Lamor Frequency
29 C -----
30 WRITE(*,'(A20$)') '0Lamor Freq / MHz = '
31 READ (*,'(F7.4')') W0
32 C -----
33 C     Number of Sites to be Considered
34 C -----
35 1 WRITE(*,'(A18$)') '0Number of Site = '
36 READ (*,'(I1')') NSI
37 IF (NSI .GT. MXS) GOTO 1
38 C -----
39 C     Quadrupole Interaction Parameters and Chemical Shifts
40 C -----
41 DO 100 I=1,NSI
42     WRITE(*,'(A7,I1$)') ' Site : ',I
43     WRITE(*,'(A21$)') ' eqQ / MHz, eta = '
44     READ (*,'(2F10.6')') QCC(I),ETA(I)
45     WRITE(*,'(A37$)') ' Eular 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(*,'(A27$)') ' 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(*,'(A60$)')
64      & '0Equilibrium Population of Each Site are Equal ( Y or N ) ? '
65      READ (*,'(A1)') CHA
66      IF ((ICHAR(CHA) .EQ. ICHAR('Y')) .OR.
67      & (ICHAR(CHA) .EQ. ICHAR('y'))) THEN
68          D=DBLE(NSI)
69          DO 200 I=1,NSI
70              P(I)=1.0D+00/D
71      200 CONTINUE
72      ELSE
73          D=0.0D+00
74          DO 210 I=1,NSI
75              WRITE(*,'(A30,11,A3$)')
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,A9$)')
89                  & ' Exchange Rate from ',I,' to ',J,' / MHz = '
90                  READ (*,'(F10.8)') EXC(J,I,1)
91                  EXC(I,J,1)=EXC(J,I,1)*P(I)/P(J)
92              END IF
93              IF (I .NE. J) EXC(I,I,1)=EXC(I,I,1)-EXC(J,I,1)
94      230 CONTINUE
95  C -----
96  C      RF Strength in Frequency Units
97  C -----
98      WRITE(*,'(A27$)') '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(*,'(A30$)') ' Number of Sampling Points = '
106          READ (*,'(I5)') DIM(I)
107          IF (DIM(I) .GT. MXD(I)) THEN
108              WRITE(*,'(A14)') '0 Too Large !! '
109              GO TO 2
110          END IF
111          WRITE(*,'(A35$)') ' 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 C      WRITE(*, '(A25$)') '0Registry File Name = '  
119 C      READ(*, '(A15$)') RGF  
120 C      WRITE(*, '(A25$)') ' Time Domain File Name = '  
121 C      READ(*, '(A15$)') TDF  
122 C -----  
123 C      Get the Number to be calculated  
124 C -----  
125 3 WRITE(*, '(A33$)') '0Number of Division over THETA = '  
126 C      READ(*, '(I3$)') N  
127 C      IF (N .GT. MXT) GOTO 3  
128 C      D=DBLE(N)  
129 C      PID=PI1/D  
130 C      DO 400 I=0,N  
131 C          Z( I )=DBLE(I)/D  
132 C          Z(-I)=-Z( I )  
133 C          SNT=DSQRT(1.0-Z( I )*Z( I ))  
134 C          DO 400 J=0,N  
135 C              X( J, I )=SNT*DCOS(PID*DBLE(J))  
136 C              Y( J, I )=SNT*DSIN(PID*DBLE(J))  
137 C              X(-J, I )= X( J, I )  
138 C              Y(-J, I )=-Y( J, I )  
139 400 CONTINUE  
140 C      WRITE(*, '(A38,I5$)')  
141 C          & '      Total Division over THETA, PHI = ', N*N*4-N*2  
142 C -----  
143 C      Store the Parameters  
144 C -----  
145 OPEN (UNIT=50, FILE=RGF, ACCESS='SEQUENTIAL')  
146 C      ----- Computational Conditions ----- '  
147 C      WRITE(50, '(A40$)') ' < Interactions >'  
148 C      WRITE(50, '(A22,F8.3$)') ' Lamor Freq / MHz = ', W0  
149 C      WRITE(50, '(A22,F7.3$)') ' RF Field / kHz = ', W1  
150 C      DO 500 I=1,NSI  
151 C          WRITE(50, '(/A10,I1,A16,F10.8,A2$)')  
152 C          & ' Site : ', I, ' ( Population = ', P(I), ' )'  
153 C          WRITE(50, '(A16,F6.4,A8,F6.4$)')  
154 C          & ' QCC / MHz = ', QCC(I), '; ETA = ', ETA(I)  
155 C          WRITE(50, '(A19,F5.2,A2,F5.2,A2,F5.2$)')  
156 C          & ' Euler Angles : ', ALP(I), ', ', BET(I), ', ', GAM(I)  
157 C          WRITE(50, '(A27,F6.2$)')  
158 C          & ' Chemical Shift / kHz = ', CHS(I)*1.0D+03  
159 500 CONTINUE  
160 C      WRITE(50, '(/A25$)') ' < Exchange Rates / MHz >'  
161 C      DO 510 I=1,NSI  
162 C          DO 510 J=1,NSI  
163 C              WRITE(50, '(4X,I1,A5,I1,F16.12$)') I, ' --> ', J, EXC(I,J,1)  
164 510 CONTINUE  
165 C      WRITE(50, '(/A16$)') ' < Calculation >'  
166 C      WRITE(50, '(A45$)') ' Dimension Data Points Time Increments'  
167 C      DO 530 I=1,2  
168 C          WRITE(50, '(8X,I1,10X,I3,10X,F10.5$)') I, DIM(I), TI(I)  
169 530 CONTINUE  
170 C      WRITE(50, '(/A21, I3$)') ' Total Division = ', N*N*4-N*2  
171 C      WRITE(50, '(/A19,A15$)') ' Data Stored in ', TDF  
172 C      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,NS1
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,NS1
185      DO 610 J=1,NS1
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,NS1
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,NS1
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
```

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Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

```
233 20000 WRITE(*,'(A23,15)') ' 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
```

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```
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 L1(8,8),H1(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,CPI
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 (L1,H1)
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      CPI=(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
```

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```
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)=DCMPLX(EXC(S,S,1),XC(I,I,S))
317      DO 200 J=I+1,L
318      H1(I,S,J,S)=DCMPLX(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,1)
326          H1(I,SS,I,S)=EXC(S,SS,1)
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
```

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```
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,IPI,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=CDOSQRT(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)
```

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```
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=CDSSQRT(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=CDSSQRT(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
```

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```
515      IP1=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
```

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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

