

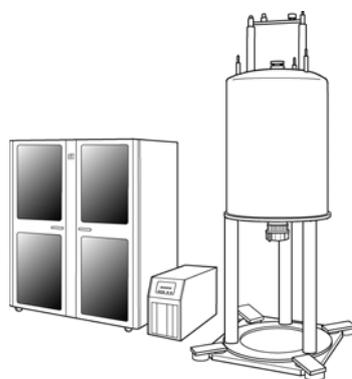
JNM-ECA Series JNM-ECX Series (Delta V5.0)

SOLID MEASUREMENT USER'S MANUAL

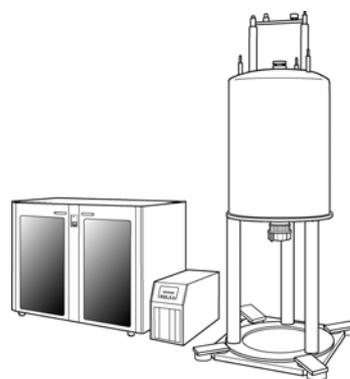
For the proper use of the instrument, be sure to read this instruction manual. Even after you read it, please keep the manual on hand so that you can consult it whenever necessary.

JNM-ECA Series JNM-ECX Series (Delta V5.0)

SOLID MEASUREMENT USER'S MANUAL



JNM-ECA Series



JNM-ECX Series

In the ECA or ECX NMR instrument, solid-state NMR measurement becomes possible when you add optional attachment, such as solid probe, to the standard composition.

This manual explains about cautions, measurement conditions, processing conditions, multi-nuclear measurement, relaxation-time measurement, and pulse sequence used in the solid experiment when solid NMR measurement will be carried out in JNM-ECA/ECX series.

Please be sure to read this instruction manual carefully, and fully understand its contents prior to the operation or maintenance for the proper use of the instrument.

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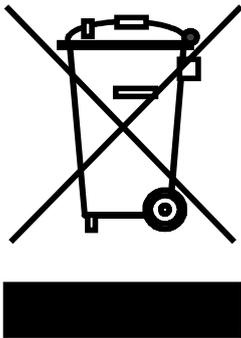
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NOTATIONAL CONVENTIONS AND GLOSSARY

■ Examples for general notations

- **CAUTION** – : Important precautions for use, which, if not followed, may result in damage to or problems with the device itself.
-  : Additional points to remember regarding the operation.
-  : A reference to another section, chapter or manual.
- 1, 2, 3** : Numbers indicate a series of operations that achieve a task.
- ◆ : A diamond indicates a single operation that achieves a task.
- File**: The names of menus, commands, or parameters displayed on the screen are denoted with **bold** letters.
- File–Exit** : Selecting a menu item from a pulldown menu is denoted by linking the menu and the item with a dash (–).
For example, **File–Exit** means selecting **Exit** from the **File** menu.
- Ctrl : Keys on the keyboard are denoted by enclosing their names in a box.

■ Examples for mouse terminology

- Mouse pointer: A mark, displayed on the screen, which moves following the movement of the mouse. It is used to specify a menu item, command, parameter value, and other items. Its shape changes according to the situation.
- Click: To press and release the left mouse button.
- Right-click: To press and release the right mouse button.
- Double-click: To press and release the left mouse button twice quickly.
- Drag: To hold down the left mouse button while moving the mouse.

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SAFETY PRECAUTIONS

Although this instrument is protected with safety device which prevents the occurrence of accident that could result in an injury, harm, and damage to the users or instrument itself, the safety feature may not work properly if you use the instrument for the purpose of use not intended or in an improper usage. For the proper use of the instrument, please be sure to read all of the instructions, descriptions, notices, and precautions contained in this manual carefully to understand them fully prior to the operation or maintenance. This section, "Safety Precautions," contains important information related to safety for using of the instrument.

The safety indications and their meanings are as follows:

	DANGER: An imminently hazardous situation which, if not avoided, will result in death or serious injury.
	WARNING: A potentially hazardous situation which, if not avoided, could result in death or serious injury.
	CAUTION: A potentially hazardous situation which, if not avoided, may result in minor or moderate injury, or a situation that could result in serious damage to facilities or acquired data.

Labels bearing the following symbols are attached to dangerous locations on the instrument. Do not touch any of these locations with your hands or anything else.



Examples of symbols

-  • Use the instrument properly within the scope of the purpose and usage described in its brochures and manuals.
-  • Never open/remove protective parts (exterior panels) and parts that can't be opened/removed without use of tool (including key), or disconnect/connect the cables/connectors that are not described in this manual.
-  • Never attempt to do any works of disassembling/assembling the instrument other than those described in this manual.
-  • Never make modifications that include installing substitute parts and disabling safety devices or other safety features.
-  • Never disconnect the grounding wire or move it from the prescribed position. Failure to follow this instruction could result in electric shock.
-  • To avoid falling, do not climb onto the operation table and console during daily operation or during maintenance or inspection.
-  • When you dispose of the instrument or liquid or other waste, follow all applicable laws and regulations, and dispose of it in a proper manner without polluting the environment.
-  • Be sure to read the "Safety Precautions" section of the manuals for the accessories attached to or built into the instrument.
-  • If anything is unclear, please contact your JEOL service office.



WARNING for Installation



- **Do not attempt to install the instruments by yourself.**

Installation work requires professional expertise and JEOL is responsible for the installation of the instruments and related attachments purchased from JEOL.

Consult your JEOL service office.



WARNING



- **When you use nitrogen gas, provide ventilation sufficient for the rate of gas usage.**

When ventilation is insufficient, the danger of asphyxiation will be present. Moreover, when using nitrogen gas, in order to avoid unexpected accidents, be sure to provide an oxygen alarm.

PRECAUTIONS FOR USE

Important precautions, which, if not followed, may result in damage to the device itself, are described below.

- **The probe may become damaged if the data-acquisition time is too long.**
- **Liquid samples, samples whose volume changes (such as between the solid and liquid states) when due to a change in temperature, and sublimating materials cannot be measured.**

Scattering the sample or bolts for the spinning cap occurs due to a change in volume caused by the expansion of the sample. Both of these events destroy the probe.

- **When you perform VT (Variable Temperature) measurement, be sure to flow bearing gas.**

If you do not flow the bearing gas, the heater produces anomalous heating then a fire might occur inside the probe.

- **When you set the measurement temperature to 150 °C or more, be sure to use nitrogen gas.**

If air is used, a flammable sample may ignite and fires might occur inside the probe. Moreover, the surface of the heater that is built into the probe would oxidize and the oxide would block a pipe, causing failure. The NMR detection coil would also oxidize and performance of the probe would deteriorate.

- **Carefully read the instruction manual then perform the magic angle spinning.**

There is a danger of destroying the probe.

- **When you first adjust the magic angle, receive instructions from an experienced person.**

An incorrect adjustment might damage the probe.

1

OUTLINE OF SOLID-STATE NMR MEASUREMENT

1.1	SOLID-STATE NMR SYSTEM	1-1
1.2	DIFFERENCE BETWEEN SOLID-STATE NMR AND SOLUTION NMR	1-2

1.1 SOLID-STATE NMR SYSTEM

High-Resolution solid-state NMR measurement by techniques such as cross-polarization magic-angle spinning (CPMAS) method becomes possible when you add optional attachments (such as a probe for the solid-state measurement) to the standard composition of JNM-ECA/ECX series. Moreover, multinuclear observation and the measurement under variable temperatures (VT) are also possible with this system.

If the Status cable is connected to the Status connector of the solid probe, the program and the spectrometer will enter the solid mode automatically. The instrument is in the solid mode if the LIQUID lamp of the INT CONT unit located behind the door on the right of the front of the spectrometer is turned off.

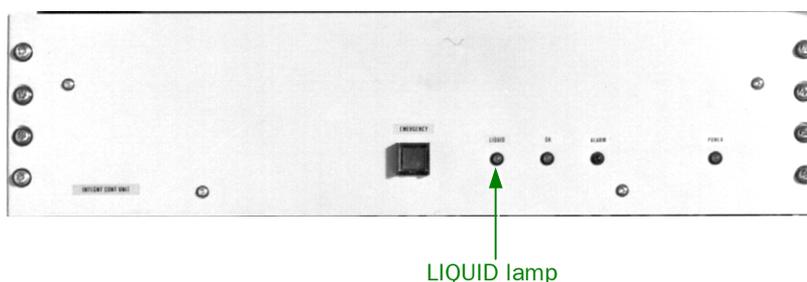


Fig. 1.1 INT CONT unit

The procedure for the measurement and processing in the solid mode are the same as those for the solution mode. In this manual, measuring methods peculiar to the solid-state NMR will be explained.

1.2 DIFFERENCE BETWEEN SOLID-STATE NMR AND SOLUTION NMR

The feature of solid high-resolution NMR that makes it different from solution NMR is the ability to measure a solid sample as it is. In solution NMR, since an observed molecule is dissolved in a solvent, almost all magnetic interactions except the spin-spin interaction can be eliminated by rapid molecular motion. Although the chemical bond structure of the molecule can be analyzed in detail by using high-resolution spectra in solution NMR, since it is dissolved in the solvent, the special features of the solid state will be lost. On the other hand, in solid-state NMR, the sample can be observed as it is.

However, analysis of the spectrum becomes difficult in solid-state NMR since the signal becomes broad due to the influence of various magnetic interactions (☞ Sect. 2.1), which have disappeared in solution NMR.

Usually, in solid-state NMR, in order to make a signal with a narrow line and to improve the signal-to-noise ratio, the measurement combines the following three methods.

- a. High-speed magic angle spinning
- b. High-power ^1H decoupling
- c. X-H cross polarization

Techniques **a** and **b** are methods for narrowing the line of a signal. Moreover, **c** is a method of improving the signal-to-noise ratio. Chapter 2 explains these techniques.

2

FUNDAMENTALS OF SOLID-STATE NMR MEASUREMENT

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2.1 INTERACTIONS INFLUENCING SOLID-STATE NMR SPECTRUM

Usually, the interactions in the NMR are expressed as the sum of the seven interactions shown below.

$$H = H_Z + H_o + H_J + H_{CSA} + H_{JA} + H_D + H_Q$$

H_Z :	Zeeman interaction
H_o :	Chemical shift isotropy
H_J :	Spin-spin interaction (J coupling) isotropy
H_{CSA} :	Chemical shift anisotropy
H_{JA} :	Spin-spin interaction anisotropy
H_D :	Magnetic dipole-dipole interaction
H_Q :	Quadrupole interaction

H_Z is the main interaction that determines the fundamental resonance frequency of the nucleus, and other interactions are expressed as perturbations of H_Z . On a spectrum, you can observe the perturbation terms. In the six perturbation terms, H_o and H_J are called isotropic terms, and H_{CSA} , H_{JA} , H_D , and H_Q are called anisotropic terms. The difference between anisotropic and isotropic terms is whether the interaction is dependent on the direction of the molecule or not.

Although anisotropic terms change greatly depending on the orientation of the molecule, they become 0 (zero) if the orientation of the molecule is changed uniformly and averaged. If the molecule is carrying out rotational Brownian motion, the anisotropic terms disappear and only the isotropic terms remain.

Spectroscopy of solution NMR is constructed under the assumption that the averaging is carried out by such molecular motion. However, in the solution NMR method, since anisotropic terms may affect a relaxation phenomenon, and anisotropic terms may appear in a spectrum by partial orientation of molecules in high-magnetic-field NMR, we cannot ignore it completely.

On the other hand, in solid NMR that treats a solid sample that has no molecular motion or is constructed from small molecules, anisotropic terms become rather dominant terms in the interaction.

How to deal with these anisotropic terms is the main subject of solid-state NMR.

Usually, in solid-state NMR, interactions are eliminated by the following two methods.

- a. Magic angle spinning(MAS)
- b. High-power decoupling

By using these techniques, H_{CSA} can be eliminated by magic angle spinning, and H_D can be eliminated by magic angle spinning and high-power decoupling. Moreover, H_Q exists only in a nucleus whose nuclear spin is larger than one half, and can be eliminated by the MQMAS (Multiple Quantum-Magic Angle Spinning) method (☞ Chap. 7).

Since H_{JA} can hardly be observed, we usually ignore it.

2.2 MAGIC ANGLE SPINNING

Magic Angle Spinning (MAS) is a spinning technique in which the sample rotates on an axis at 54.74 degree ($= \arccos \sqrt{1/3}$) with respect to the static magnetic field. MAS is the most fundamental and important technique in the solid-state NMR.

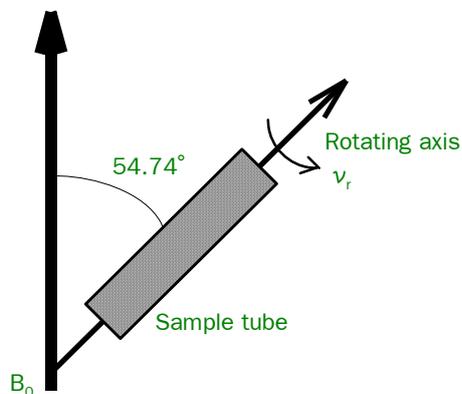


Fig. 2.1 Magic Angle Sample Spinning

MAS can eliminate all the anisotropic interactions expressed as second-rank tensors (H_D , H_{CSA} , H_Q). However, when the MAS frequency is smaller than the interaction, the interaction remains partially or the effect of MAS is not expressed fully. The partially remaining interaction appears as spinning sidebands or as a broadening of a main peak. Generally, since the H_D with ^1H cannot be completely eliminated by only using MAS, high-power decoupling (see Sect. 2.3) is used together with MAS.

2.3 HIGH POWER DECOUPLING

When ^1H and ^{13}C are directly coupled, the dipole interaction with ^1H is about 20 kHz. In order to completely eliminate the dipole interaction with the ^1H , ^1H high-power decoupling of about 60-80 kHz is usually required. Since there is a strong dipole interaction between the protons in an organic compound, you cannot use the technique of broad-band decoupling that is used in the solution NMR. Therefore, it is necessary to decouple with the high-power RF pulse. High-power decoupling peculiar to the solid-state NMR is called "Dipolar Decoupling."

Since RF pulses used for the high-power decoupling are very strong, decoupling is carried out only during data acquisition.

— CAUTION —

The probe may become damaged if the data-acquisition time is too long.

2.3.1 CW (Continuous Wave) Decoupling

The CW decoupling is a technique that has been used for many years. In solution NMR, various decoupling sequences other than CW decoupling have been proposed. However, the decoupling sequence of solution NMR has not demonstrated an effect in solid high-resolution NMR for the following two reasons.

- Since there is a strong homonuclear dipole interaction between the ^1H 's in a solid sample, a powerful artifact signal appears as a cycling sideband.
- In a pulse sequence having a long cycle, the decoupling effect is decreased by interference with MAS.

Moreover, CW decoupling has been a reliable decoupling technique because it is not influenced by imperfections in pulses.

2.3.2 TPPM (Two Pulse Phase Modulation) Decoupling

TPPM is a decoupling sequence proposed by A.E.Bennett et al.

Reference: A.E. Bennett et al., *J.Chem.Phys.*, 103, 6951-6958 (1995).

Although it is a very simple decoupling sequence that repeats two 180° pulses in which the phase only changed a small amount, the line-narrowing effect demonstrated in heteronuclear ^1H decoupling is more than in CW decoupling.

TPPM decoupling is not for canceling the wide range off-resonance effect by using weaker power like the decoupling sequence seen in solution NMR. Rather the decoupling effect becomes better with increasing decoupling power. Therefore, when TPPM decoupling is carried out, it uses the maximum decoupling power that can be used with the instrument the same as in CW decoupling.

The effect of TPPM decoupling depends on the flip angle ϕ of the phase and the pulse width τ_p . The TPPM decoupling with certain parameters cannot demonstrate an effect in comparison with CW decoupling. Moreover, since the decoupling effect depends on the pulse width, the effect decreases in a probe with poor uniformity of the RF magnetic field. In TPPM decoupling, the decoupling effect will decrease if the power is weaker.

In addition, since TPPM decoupling also decreases the interference between MAS speed and CW decoupling, it also prevents the line-width from increasing under high-speed MAS.

TPPM decoupling is especially effective in the following cases.

- High magnetic field (500 MHz or more)
- High-speed spinning
- ^{19}F decoupling
- System that has heteronuclear interactions other than ^1H such as ^{15}N or ^{14}N

2.4 SINGLE PULSE MEASUREMENT

One of the fundamental measuring methods of a solid-state NMR measurement is a single-pulse measurement. When you carry out a single-pulse measurement, you use MAS.

Usually, although the cross-polarization method (☞ Sect. 2.5) is used in the solid-state NMR of an organic compound, the single-pulse measurement is used for a sample which does not contain the ^1H nucleus or contains very few. Moreover, single-pulse measurement may also be used for a sample with rapid molecular motion like adamantane. When measuring a sample containing the ^1H nucleus, high-power decoupling is used in addition to MAS.

2.5 CROSS POLARIZATION

The Cross-Polarization (CP) method is the technique most generally used in solid-state NMR. The CP method is usually called the “CPMAS” method because it is used in combination with MAS.

Usually, CPMAS measurement has the following advantage when comparing it with the single-pulse measurement.

- Improvement of the SN ratio
- Shortening of repetition time (improvement in accumulation efficiency)

2.5.1 Principle of Cross Polarization

The ^1H nucleus and X nucleus are irradiated by RF simultaneously, and the spin lock is applied. The spin lock is a technique that irradiates a specific nucleus with a high-power radio frequency at the resonance frequency to arrange the magnetization of the nucleus in the direction of the B_1 magnetic field. When the B_1 magnetic field strengths of the spin-lock frequency of these two nuclei become equal, exchange between the magnetizations happens. This is called the “Hartmann-Hahn conditions.” If we denote the B_1 magnetic field strengths for I and S nucleus as B_1^I and B_1^S and γ ratio of I and S nucleus as γ^I and γ^S , respectively, the Hartmann-Hahn conditions can be expressed with the following formula.

$$|\gamma^I B_1^I| = |\gamma^S B_1^S|$$

Be aware of the direction of the spin lock and magnetization when the magnetization of the I and S nuclei reach equilibrium. When the signs of the γ ratio are the same, both magnetizations are turned in the same direction. When the signs of the γ ratio are opposite, the magnetizations are turned in opposite directions. For example, when observing the magnetization transfer from ^1H , the magnetizations of ^{13}C (γ ratio is positive) and ^{29}Si (γ ratio is negative) are observed in reverse phase.

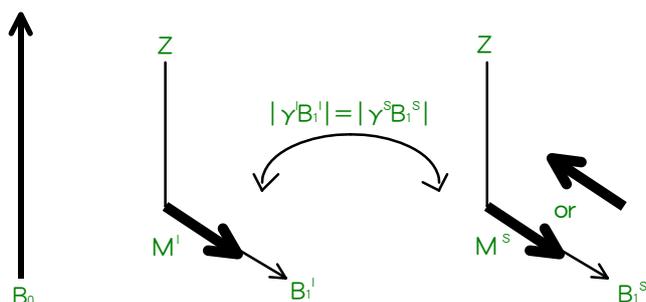


Fig. 2.2 Cross polarization of I and S nuclei

This method is often used for the magnetization transfer from ^1H to ^{13}C . Using this method improves the sensitivity of ^{13}C by $\gamma^{1\text{H}}/\gamma^{13\text{C}} = 4$ times. Furthermore, since a measurement can be repeated with approximately the relaxation time T_1 of ^1H , accumulation efficiency improves markedly.

The improvement of accumulation efficiency is $\sqrt{(T_1^{13\text{C}}/T_1^{1\text{H}})}$.

This method is applied for the rare spin system (^{15}N , ^{13}C , ^{29}Si and ^{31}P) of the spins 1/2 containing ^1H .

2.5.2 Notes of Cross Polarization

Since signal intensity depends on the contact time in the CPMAS method, it is necessary to search for the optimum conditions (see Sect. 4.3).

Moreover, the cross-polarization condition under high-speed MAS depends on the spinning speed. The Hartmann-Hahn condition, taking into account the spinning speed ω under high-speed MAS, is as follows.

$$|\gamma^I B_1^I| = |\gamma^S B_1^S| + n \cdot \omega \quad (n = \pm 1, \pm 2)$$

Thus, since the cross-polarization condition under high-speed spinning differs from the cross-polarization condition under low-speed spinning, it is necessary to take care during CPMAS measurement under high-speed spinning.

3

SETTING OF INSTRUMENT CONDITIONS

Chapter 3 explains the methods for setting the measurement conditions that are dependent on the instrument.

Basic measurement conditions are preset to suitable values at delivery time. However, if a long time passes and the state of the instrument changes, the preset values may shift and the signal and noise ratio may decrease. If this happens, it is necessary to adjust the instrument conditions.

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3.1 PRECAUTION FOR OPERATION

Read these general precautions before operating the instrument.

— CAUTION —

- **Liquid samples, samples whose volume changes (such as between the solid and liquid states) when due to a change in temperature, and sublimating materials cannot be measured.**

Scattering the sample or bolts for the spinning cap occurs due to a change in volume caused by the expansion of the sample. Both of these events destroy the probe.

- **When you perform VT (Variable Temperature) measurement, be sure to flow bearing gas.**

If you do not flow the bearing gas, the heater produces anomalous heating then a fire might occur inside the probe.

- **When you set the measurement temperature to 150 °C or more, be sure to use nitrogen gas.**

If air is used, a flammable sample may ignite and fires might occur inside the probe. Moreover, the surface of the heater that is built into the probe would oxidize and the oxide would block a pipe, causing failure. The NMR detection coil would also oxidize and performance of the probe would deteriorate.

- **Nitrogen gas**

When you use nitrogen gas, check that the specification of the source of nitrogen meets the needs of the probe.

 WARNING	
	<ul style="list-style-type: none"> • When you use nitrogen gas, provide ventilation sufficient for the rate of gas usage. When ventilation is insufficient, the danger of asphyxiation will be present. Moreover, when using nitrogen gas, in order to avoid unexpected accidents, be sure to provide an oxygen alarm.

- **Insertion and removal of a sample tube**

When you remove a sample tube from the probe, be sure to use the removal tool.

If stress is applied to the stator during sample exchange, the magic angle and the resolution will change.

- **Probe tuning**

After you change an observation nucleus or replace a sample, you must perform the probe tuning. If you do not, the signal and noise ratio might degrade because the observation condition might change. For details on tuning, refer to the manual of the individual probe.

- **Magic-angle spinning (MAS)**

When you perform a magic-angle spinning, use a MAS controller or High-precision regulator.

— CAUTION —

- Carefully read the instruction manual then perform the magic angle spinning.

There is a danger of destroying the probe.

- Heating the sample tube and its temperature calibration when in high-speed

When the sample rotates at a high speed, the rate of temperature increase is approximately the square of the spinning speed. The temperature increase depends on the individual sample tube. Moreover, depending on the temperature increase, a temperature gradient appears; therefore, you need to be aware of this factor.

If you need to estimate the temperature gradient precisely, perform the temperature calibration. The calibration should be on the individual sample tube with the bearing gas pressure that you routinely apply.

☞ Refer to the following literature for the temperature calibration.

A. Bielecki and D. P. Burum, *J. Magn. Reson. A* 116, 215–220 (1995).

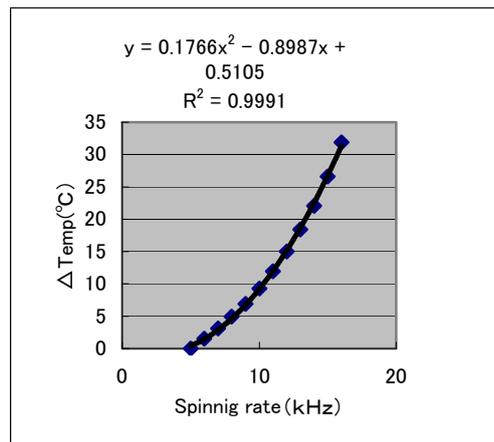
T. Takahashi, H. Kawashima, H. Sugisawa and T. Baba, *Solid State Nuc. Magn. Reson.*, 15 (2), 119 (1999).

✂ For the calibration of the temperature, use a lead nitrate sample.
The amount of shift in lead nitrate is 0.753 ppm/°C.

The following figure shows an example of a temperature calibration curve.

- Sample tube: Silicon nitride
- Gas: Dry air
- Pressure of bearing gas: 0.15 MPa
- Gas temperature: Room temperature (25 °C)

The vertical axis is the rate of a temperature increase based on the temperature when the sample tube is at the minimum speed (in this case 5 kHz).



✂ When you perform a variable temperature measurement, take the temperature increase due to spinning into consideration, and set up the temperature so that the temperature of the sample tube does not exceed the specification for the probe. If the spinning speed approaches top speed, the temperature of the sample will be considerably higher than the temperature shown on the display.

For a sample that deteriorates, melts, ignites, or explodes when the temperature rises, decide the setting temperature by taking into consideration the temperature increase due to spinning.

- **Tuning after variable temperature**

After the sample reaches the measurement temperature, be sure to tune the probe.

- **When variable temperature (VT) ends**

If spinning is stopped or samples are exchanged immediately after VT measurement is terminated, it will cause a problem. Set the temperature to 30 °C, stop the spinning after the probe temperature approaches the room temperature, remove the VT adapter, and then exchange samples.

3.2 ADJUSTMENT OF MAGIC ANGLE

1. Insert the standard sample KBr.
2. Perform spinning.
3. Set LF channel to Bromine79 observation.
Check that the combination of the stick and the tuning dial is appropriate for the bromine 79 observation.
4. Load the pulse sequence **mas_adjust_KBr.jxp** to the **Experiment Tool**.
5. Click the **Submit** button.
The pulses occur and the measurement starts.
6. Adjust the phase by the following procedure.
 - a. Click the **Monitor** tab.
The **Monitor** tab opens.
 - b. After selecting the process list in the **Processing Preferences** panel, click the **Process**  button to change the display.
 When the **Processing Preferences** panel does not appear, click the **Processing** button on the far right side.
 - c. Perform the phase adjustment using **Phasing Tools**.
 When the **Phasing Tools** panel does not appear, click the **Phasing** button on the far right side.
7. Adjust the magic angle.
Following the instruction manual for the probe, adjust the magic angle so that the spinning sideband of KBr becomes the maximum as shown in Figure 3.1.
 The magic-angle adjustment mechanism has some backlash of the gears.
Adjust in one direction when fine-tuning.

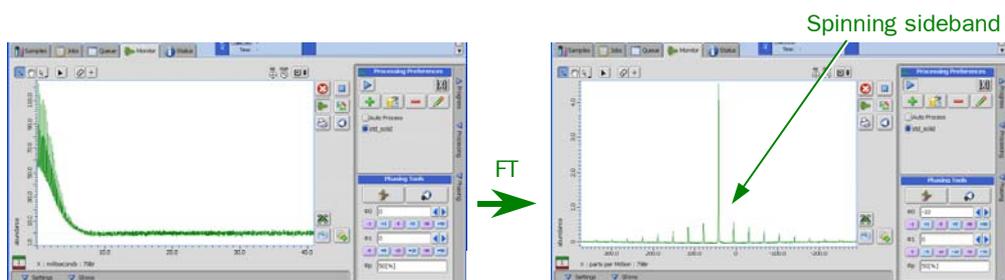


Fig. 3.1 FID (left) and the spectrum (right) after magic angle adjustment

8. After magic-angle adjustment is completed, display the **Queue** tab and terminate the measurement.
- ✍ Adjustment of the magic angle may change the resolution. Be sure to check the resolution according to Sect. 3.5 “Adjustment of the resolution”, and adjust the shim values if necessary.

— CAUTION —

When you first adjust the magic angle, receive instructions from an experienced person.

An incorrect adjustment might damage the probe.

3.3 SETTING OF IRRADIATION FREQUENCY

1. Insert the standard sample “adamantane”.
2. Perform spinning.
3. Load the pulse sequence **single_pulse_solid.jxp** into the **Experiment Tool**.
4. **recvr_gain** is set.
5. Click the **Submit** button.
The pulses occur, and the measurement starts.
- ✍ When the measurement is completed, the **1D Processor** window automatically opens.
6. From the **Pointer bar** in the processed data display area, select **Copy position**, and left-click on the irradiation position to copy the position.

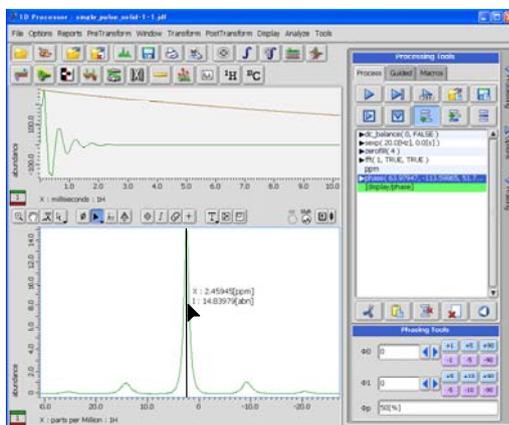


Fig. 3.2 Display when copying the irradiation position

7. Load the pulse sequence you want to use into the **Experiment Tool**; then paste the copied irradiation position to the irradiation frequency (**irr_offset** etc.) by right clicking.

3.4 SETTING PULSE WIDTH

Set the pulse width for the solid-state NMR measurement the same as for the liquid NMR measurement. At first, measure the 360° pulse width, and set the 90° pulse width to 1/4 of the 360° pulse width. The actual procedure for setting the pulse width is as follows.

■ Setting of pulse width of observation channel

1. Insert the standard sample or the sample you want to measure in the probe.
For ^1H and ^{13}C , insert the “adamantane” standard sample.
2. Perform spinning.
3. Set **single_pulse_solid.jxp** for the ^1H measurement and **single_pulse_dec_solid.jxp** for the ^{13}C measurement in the **Experiment Tool**.
4. **recvr_gain** is set.
5. Click the **Submit** button.
The pulses occur, and the measurement starts.
When measurement ends, the **1D Processor** window automatically opens.
6. Select the **Copy position** mode from the pointer bar in the processed data display area, and left-click on the observation position to copy the position.

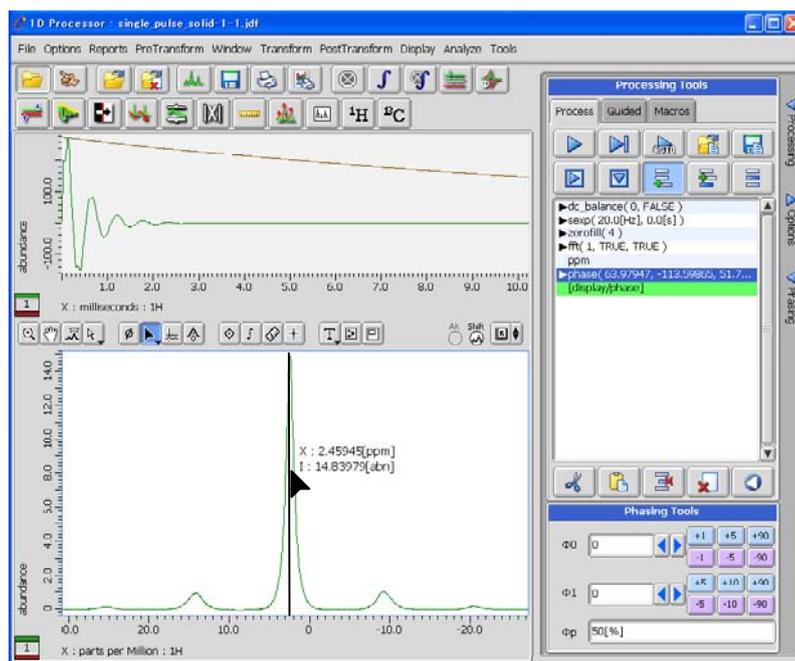


Fig. 3.3 Display when copying the observation position

7. Set **obs_angle_prep** to 90 deg.
8. Set up an array measurement for **obs_width_90**.

9. Click the **Sumit button.**

The pulse occurs, and the measurement starts.

When the measurement is completed, the nD Processor window automatically opens.

10. Perform data processing.

☞ Refer to the user’s manual “Data processing” for instruction on processing the data obtained by the array measurement.

After data processing, the result is displayed by selecting the **Linearize**.

11. Find the 360° pulse width.

In the spectrum after the **Linearize** processing, the pulse width where the signal intensity is nearest to 0 (zero) is the 360° pulse width. Furthermore, for longer pulse widths, the peaks should be positive.

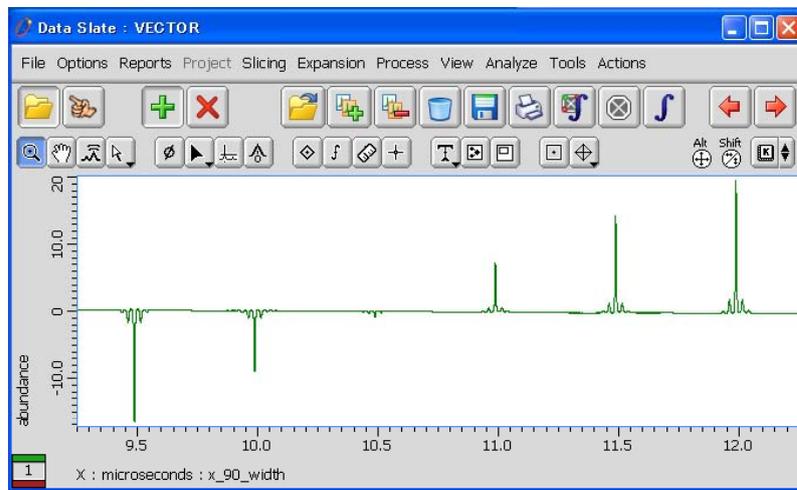


Fig. 3.4 Spectrum after carrying out Linearize processing

12. Obtain the 90° pulse width as one fourth of the 360° pulse width you found.

■ Measuring the pulse width of the irradiation channel

For the same frequency, the spectrometer is adjusted so that the pulse width does not differ in the observation channel and the irradiation channel. Therefore, it is not necessary to measure the pulse width of the irradiation channel.

3.5 ADJUSTMENT OF RESOLUTION

1. Set the adamantane standard sample.
2. Perform spinning.
3. Load the pulse sequence: **setup/reso_adjust_adm.jxp** in the **Experiment Tool**.
4. Confirm that **repeat** was selected.
5. Click the **Submit** button.
The pulses occur, and the measurement starts.
6. Adjust the phase by the following procedure.
 - a. Click the **Monitor** tab.
The **Monitor** tab appears.
 - b. After selecting the process list in the **Processing Preferences** panel, click the **Process**  button to change the display.
 -  If the **Processing Preferences** panel does not appear, click the **Processing** button on the far right side.
 - c. Perform phase adjustment using **Phasing Tools**.
 -  If the **Phasing Tools** panel does not appear, click the **Phasing** button on the far right side.
7. Expand near the peak, and check the half-height width.
 -  When spectrum data points are lacking, select the process list that performed the **Zerofill** process.

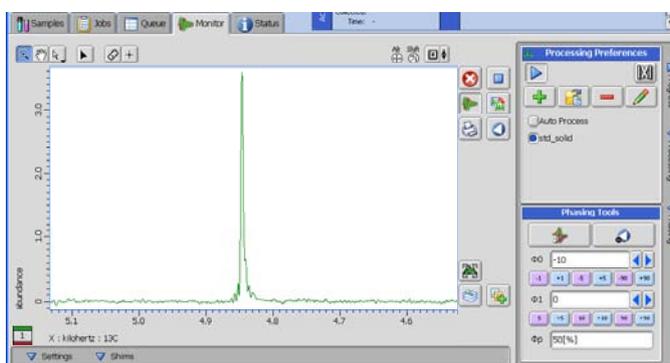


Fig. 3.5 View Tool window for resolution adjustment

8. If the half-height width is larger than the specifications, adjust the shims according to the following procedure.
 - a. Open the **Shims Control** window by clicking the **Shims** button in the **Monitor** tab.
 - b. Adjust **Z1** and **Y** to maximize the peak intensity.
 - c. Adjust **X2** and **YZ** to maximize the peak intensity.
 - d. Adjust **Z3** to maximize the peak intensity.
 - e. Repeat steps **b** to **d** until the half-height width satisfies the specifications.
 -  This is the case where the magic angle is in the Y-direction.
9. When shim adjustment is completed, display the **Queue** tab, and terminate the measurement.

3.6 REFERENCE SETTING

In the solid-state NMR, the reference cannot be corrected by using the lock signal as in the solution NMR. Therefore, the reference is set up using the spectrum of an external-reference sample. There are two methods for setting the reference: setting in the Delta and setting using the Z0 shim.

3.6.1 External Reference Setting

1. Prepare the spectrum with the external-reference substance, and carry out the reference setting.
 ☞ Refer to the user's manual "Data processing" for details for setting the reference.
2. In the **Delta Console** window, select **Tools-Geometry Tools-Copy Ruler Reference**.

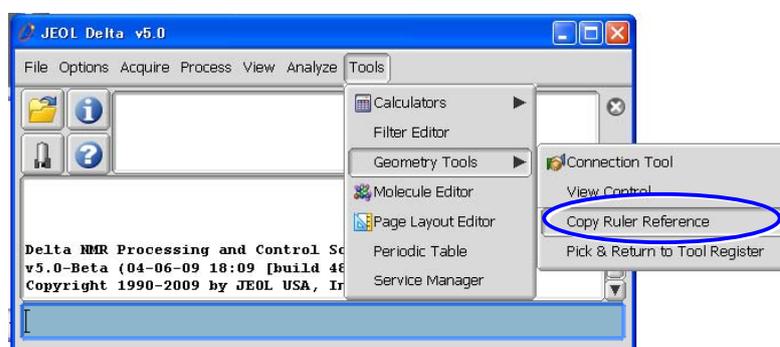


Fig. 3.6 Delta Console window

The **Copy Ruler Reference** window opens.

3. First, click the **Source** button, and select the spectrum with the external reference. Next, click the **Target** button, and select the spectrum on which you want to set the reference.

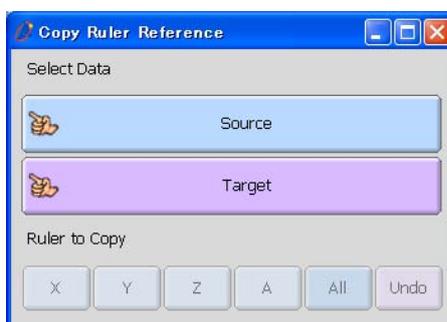


Fig. 3.7 Copy Ruler Reference window

Hidden buttons, such as **X**, appear.

4. Click an axis to set the reference.
 The reference is set up.

-  Before repeating the above procedure, be sure to click the **Undo** button to cancel the settings.
-  For the external reference, use the spectrum that was measured just before or was measured immediately after the measurement of the target spectrum. If a long time period exists between these two measurements, the error of the chemical shift becomes larger due to the drift of the static magnetic field.

3.6.2 Reference Setting by Using Z0 Shim

Measure the spectrum of the external-reference sample, and set up a reference by adjusting Z0. When this method is used, perform the reference setting before measuring the target sample.

We recommend that you correct Z0 periodically by this method. If the value of Z0 and the measurement time are recorded, the average amount of drift can be calculated from the values. Z0 drift can be corrected automatically by setting this amount of drift to the drift canceler that is explained in the following section.

The reference setting is performed by the following procedure.

1. Calculate the amount of drift of Z0 for an observed nucleus.
2. Measure the reference substance, and examine the difference of the chemical shift.
3. Change Z0 by the value that is obtained by multiplying the amount of drift calculated in step 1 by the difference of the chemical shift obtained in step 2.

For example, supposing that the spectrum of ^{13}C shifts 10 ppm when moving Z0 by 1,000 Hz, the amount of change of Z0 to ^{13}C will be set to 100 Hz/ppm. At this time, if there is a difference of 2 ppm from the correct chemical-shift value of the reference substance ^{13}C , chemical shifts can be adjusted by changing Z0 by 200 Hz.

3.7 ADJUSTMENT OF CROSS-POLARIZATION CONDITIONS

Adjustment of CP (Cross-Polarization) conditions is performed to satisfy the Hartmann-Hahn conditions. The Hartmann-Hahn conditions are different between low-speed spinning and high-speed spinning. Therefore, you need to adjust the conditions according to the spinning speed.

 In this section, adjustment of CP conditions is explained for a spin 1/2 nucleus.

3.7.1 Adjustment of Cross-Polarization Condition under Low-speed Spinning

The Hartmann-Hahn condition under low-speed spinning is the following equation.

$$\gamma^I B^I = \gamma^S B^S$$

Under actual work conditions, set the values of **irr_amp_cp** and **obs_amp_cp** so that the 90° pulse width for the observation nucleus equals the 90° pulse width for the irradiation nucleus.

1. Set the standard sample (such as, adamantane).
2. Perform spinning at 5 kHz.
3. Load the pulse sequence **cpmas.jxp** into **Experiment Tool**.
4. Set **scans** to a multiple of 2.
5. Set **obs_shape_cp** to **constant_cp**.
6. Set **irr_amp_cp** value of **Proton**.
7. Set the array measurement for **obs_amp_cp** of **Carbon13**.
8. Click the **Submit** button.

The pulses occur, and the measurement starts.

If the measurement ends, the **nD Processor** window automatically opens.

9. Perform the data processing.

 Refer to the user's manual "Data processing" for processing the data obtained by the array measurement.

After data processing, the result is displayed by selecting **Linearize**.

10. Examine the optimum **obs_amp_cp** value.

In the spectra for which you carried out the **Linearize** processing, the value of **obs_amp_cp** with the strongest signal intensity is the optimum value for cross-polarization conditions.

 Under high-speed spinning, two or more **obs_amp_cp** with strong signal intensities exist. In this case, refer to the adjustment of CP conditions under high-speed spinning ( Section 3.7.2).

3.7.2 Adjustment of CP Condition under High Speed Spinning

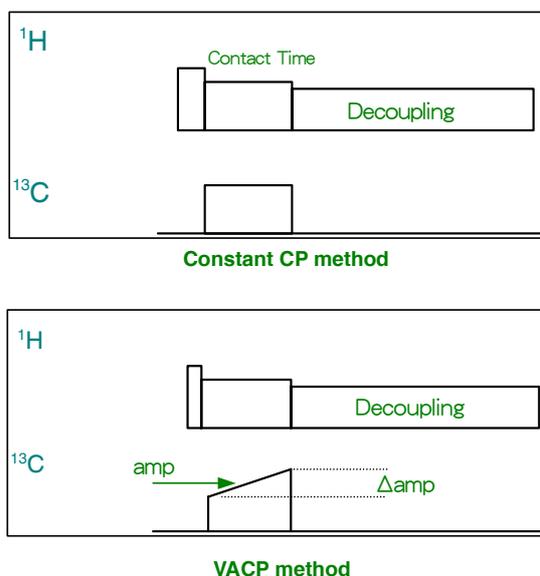
The Hartmann-Hahn conditions, taking into consideration spinning speed ω_r , under high-speed spinning, are as follows:

$$\gamma^I B^I = \gamma^S B^S + n \cdot \omega_r \quad (n = \pm 1, \pm 2)$$

Under actual work conditions, set the value of **irr_amp_cp** and **obs_amp_cp** so that it satisfies the conditions for every spinning speed.

3.7.3 Adjustment of VACP Conditions

CP conditions under high-speed spinning are very sensitive to errors in the condition settings. Therefore, in an actual measurement, the sensitivity decreases abruptly due to causes such as inhomogeneity of the magnetic field. In order to compensate for such imperfection, the modulation is applied to the output power of the observation channel during spin lock, thereby increasing sensitivity.



-  If the VACP method is used, the contact time will become a little longer.
-  The slope to use in the VACP method depends on the spinning speed.

1. Set the adamantane standard sample.
2. Adjust spinning speed.
The slope of the VACP depends on the spinning speed.
3. Set **obs_shape_cp** to **RAMP_cp**.
4. Set up the **irr_amp_cp** value of **Proton**, and the **obs_amp_cp** value of **Carbon13**.
5. Perform an array measurement for **obs_amp_grad** of **Carbon13**.
6. Click the **Submit** button.
The pulses occur, and the measurement starts. When the measurement ends, the **nD Processor** window automatically opens.

7. Perform data processing.

☞ Refer to the user's manual "Data processing" for processing the data obtained by the array measurement.

After data processing, the result is displayed by selecting **Linearize**.

8. Set up the `obs_amp_grad` value of **Carbon13.**

In the spectra for which you carried out **Linearize** processing, the value of **obs_amp_grad** with the strongest signal intensity is the optimum value of cross-polarization conditions.

9. Perform array measurement of **Carbon13 to set `obs_amp_cp`.****3.7.4 Selecting a Method for Cross Polarization**

There are several methods for the cross polarization in the CPMAS measurement. You can change the method by choosing combinations in `irr_shape_cp` and `obs_shape_cp`.

	<code>irr_shape_cp</code>	<code>obs_shape_cp</code>
Constant CP	<code>constant_cp</code>	<code>constant_cp</code>
RAMP CP	<code>constant_cp</code>	<code>RAMP_cp</code>
	<code>RAMP_cp</code>	<code>constant_cp</code>
APHH CP (Adiabatic Passage Hartmann Hahn CP)	<code>constant_cp</code>	<code>APHH_cp</code>
	<code>APHH_cp</code>	<code>constant_cp</code>
ad freq sweep CP (Adiabatic FREQUENCY sweep CP)	<code>ad_freq_cp</code>	<code>constant_cp</code>
FM CP (Frequency Modulation CP)	<code>constant_cp</code>	<code>fm_cp</code>
	<code>fm_cp</code>	<code>constant_cp</code>
	<code>fm_cp</code>	<code>fm_cp</code>
NICP (Nuclear Integrated CP)	<code>nicp</code>	<code>constant_cp</code>
	<code>sadis_cp</code>	
sadis CP (Simultaneous ADIabatic frequency Sweep)	<code>nicp</code>	<code>sadis_cp</code>
	<code>sadis_cp</code>	

3.8 ADJUSTMENT OF DECOUPLING CONDITIONS

For a sample containing ^1H , it is necessary to perform high-power decoupling (☞ Sect. 2.3). Since very strong RF pulses are used for high-power decoupling, it is necessary to decrease the decoupling power in the measurements in which the data acquisition time **x_acq_time** is 100 ms or more.

3.8.1 Setting of CW (Continuous Wave) Decoupling Conditions

In the solid-state NMR, since very strong RF pulses are applied in comparison with the solution NMR, RF power is applied only during data acquisition.

When the data acquisition time is about 100 ms or less, you can use the value of **irr_amp_dec** at 100% (the maximum power which can be used in the equipment). When the data acquisition time is longer, you need to lower the value of **irr_amp_dec** and measure.

3.8.2 Setting of TPPM Decoupling Conditions

In the decoupling of TPPM (Two Pulse Phase Modulation), adjust the pulse width **irr_pwidth** and phase shift value **irr_tppm_shift**.

1. Set the standard sample glycine.
2. Set **irr_noise** to **TPPM**.
3. Perform the array measurement for **irr_width_tppm** and **irr_phs_tppm**.
4. Click the **Submit** button.
 - The pulses occur, and the measurement starts.
 - When the measurement ends, the **nD Processor** window automatically opens.
5. Perform data processing.
 - ☞ Please refer to the user's manual "Data processing" for information on processing the data obtained by the array measurement.
6. Take a slice of C_α carbon in the 3D processed spectrum.
7. Obtain the values of **irr_width_tppm** and **irr_phs_tppm** with the strongest signal intensity in the two-dimensional data of the YZ plane.

3.8.3 Setting of XiX Decoupling Conditions

To perform XiX (X inverse-X) decoupling, adjust the pulse width: **irr_width_xix**.

1. Set the standard sample glycine.
2. Set **irr_noise** to **XiX**.
3. Perform an array measurement for **irr_width_XiX**
 -  The optimum value of **irr_width_XiX** is around 1.85 or 2.85 times the reciprocal of the spinning speed.
4. Click the **Submit** button.
 - The pulses occur, and the measurement starts.
 - When the measurement ends, the **nD Processor** window automatically opens.
5. Perform data processing.
 -  Refer to the user's manual "Data processing" for the instructions for processing the data obtained by the array measurement.
6. Obtain **irr_width_xix** that gives the strongest signal intensity of the C_α carbon.
 -  The best condition of the XiX depends on the spinning speed. When you change the spinning speed in a measurement, adjust the measurement conditions according to the spinning speed.

3.8.4 Setting of SPINAL64 Decoupling Conditions

To perform the **SPINAL64** decoupling, adjust the pulse width of **irr_width_tppm**.

1. Set the standard sample glycine.
2. Set **irr_noise** to **SPINAL64**.
3. Perform an array measurement for **irr_width_tppm**.
4. Click the **Submit** button.
 - The pulses occur, and the measurement starts
 -  When the measurement ends, the **nD Processor** window automatically opens.
5. Perform data processing.
 -  Refer to the user's manual "Data processing" for the instructions for processing the data obtained by the array measurement.
6. Obtain **irr_width_tppm** that gives the strongest signal intensity of the C_α.

3.8.5 Setting of CM Decoupling Conditions

To perform CM (Cosine Modulation) decoupling, adjust the pulse width of **irr_width_cm** and the phase-shift value of **irr_phs_tppm**.

1. Set the standard sample glycine.
2. Set **irr_noise** to **CM**.
3. Perform an array measurement for **irr_width_cm** and **irr_phs_tppm**.
4. Click the **Submit** button.
 - The pulses occur, and the measurement starts.
 - If the measurement ends, the **nD Processor** window automatically opens.
5. Perform data processing.
 - ☞ Refer to the user's manual "Data processing" for instructions for processing the data obtained by the array measurement.
6. Take a slice of the C_α carbon in the 3D processed spectrum.
7. From the 2D data of the YZ plane, obtain the values of **irr_width_cm** and **irr_phs_tppm** that give the strongest signal intensity.

3.8.6 Setting of SWf-TPPM Decoupling Conditions

To perform SWf-TPPM (SWept-Frequency Two Pulse Phase Modulation) decoupling, adjust the pulse width of **irr_width_tppm** and the phase-shift value of **irr_phs_tppm**.

1. Set the standard sample glycine.
2. Set **irr_noise** to **swfTPPM**.
3. Perform an array measurement for **irr_width_tppm** and **irr_phs_tppm**.
4. Click the **Submit** button.
 - The pulses occur, and the measurement starts.
 - If the measurement ends, the **nD Processor** window automatically opens.
5. Perform data processing.
 - ☞ Refer to the user's manual "Data processing" for the instructions for processing the data obtained by the array measurement.
6. Take a slice of the C_α carbon in the 3D processed spectrum.
7. Obtain the values of **irr_width_tppm** and **irr_phs_tppm** that give the strongest signal intensity in the two-dimensional data of the YZ plane.

4

ADJUSTMENT OF MEASUREMENT CONDITIONS AND PROCESSING CONDITIONS

Chapter 4 explains the method of adjusting measurement conditions and processing conditions.

Although data can be obtained by using the initial values of the basic conditions for a measurement, more useful data can be obtained by using the optimum values for each sample.

4.1	SETTING PULSE WIDTH IN SINGLE PULSE MEASUREMENT	4-1
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4.1 SETTING PULSE WIDTH IN SINGLE PULSE MEASUREMENT

Usually, the flip angle **obs_angle_prep** is set to 90 deg for a solid-state NMR measurement. However, for a sample with a very long relaxation time, making the flip angle small shortens the waiting time of **relaxation_delay**.

Moreover, for nuclei with quadrupole interactions, caution is required for setting the **obs_width**. In the case of nuclei with nuclear quadrupole interaction, the 90° pulse width depends on the strength of the interaction. When the nuclear quadrupole interaction is small, the 90° pulse width is almost the same width as that in the solution. However, as the nuclear quadrupole interaction increases, the 90° pulse width shortens. When the nuclear quadrupole interaction is strong enough, the 90° pulse width becomes $1/(I+1/2)$ times the 90° pulse width of the solution (I is the nuclear spins number). Therefore, for this kind of nuclei, set **obs_width** to less than $1/(I+1/2)$ of the 90° pulse width of the solution. Furthermore, when performing a quantitative measurement, it is desirable to set the pulse width to $1/(I+1/2)/2$ times the 90° pulse width of the solution or less.

4.2 SETTING WAITING TIME IN SINGLE PULSE MEASUREMENT

The optimum value of **relaxation_delay** in a single-pulse measurement is determined by T_1 of the observed nucleus. When the measurement is carried out using a 90° pulse, theoretically the accumulation efficiency (= signal intensity/accumulation time) becomes optimum if **relaxation_delay** is about 1.2 times the T_1 of the observed nucleus (as shown in the following figure). When T_1 of the observed nucleus is very long, set a small flip angle **obs_angle_prep** and measure it.

However, when performing a quantitative measurement, setup the **relaxation_delay** to 5 or more times the longest T_1 among the observed peaks.

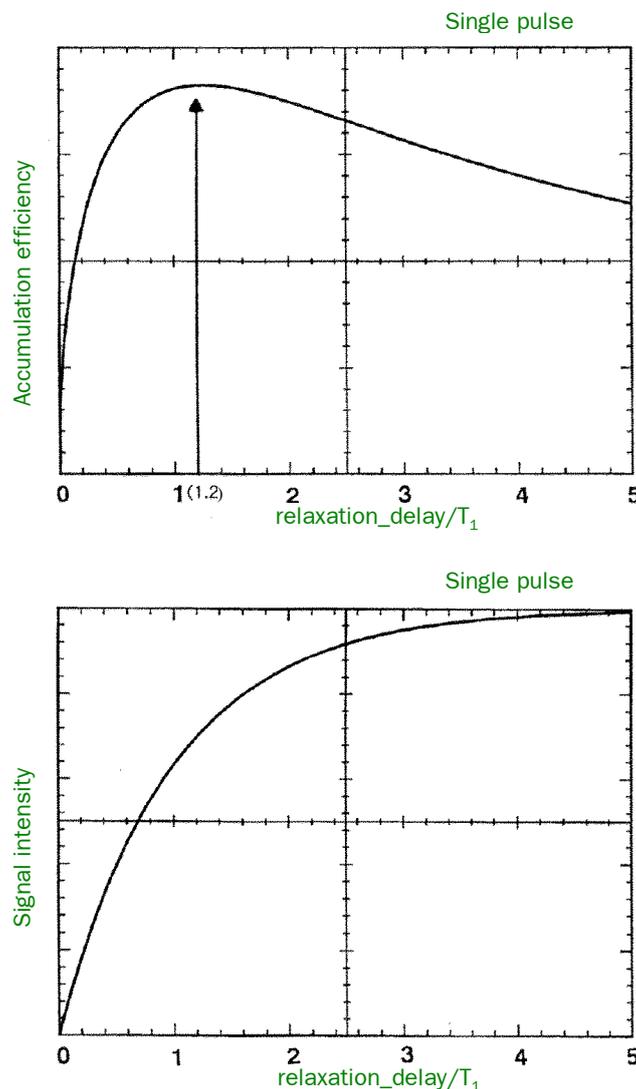


Fig. 4.1 Accumulation efficiency and signal intensity versus the ratio of the waiting time (relaxation_delay**) and the T_1 (relaxation time) of the observed nucleus**

- ✍ The accumulation efficiency becomes its maximum at **relaxation_delay**/ $T_1 = 1.2$. Since the efficiency will decrease quickly if you set a shorter **relaxation_delay**, you will need to set a slightly longer **relaxation_delay**.

4.3 SETTING CONTACT TIME IN CP METHOD

The contact time (**contact_time**) is the time required to transfer the magnetization from ^1H to ^{13}C . The efficiency of the magnetization transfer changes depending on the length of the transfer time. As an example, the relationship between the contact time and the signal intensity of the ^{13}C nucleus of polypropylene is shown in the following figure. The maximum signal intensity occurs during 1 to 2 ms for typical organic compounds. There are also samples that require longer contact time among samples with rapid molecular motion (rubber and plastic crystals such as adamantane, camphor, and hexamethyl benzene) or samples with many quaternary carbons.

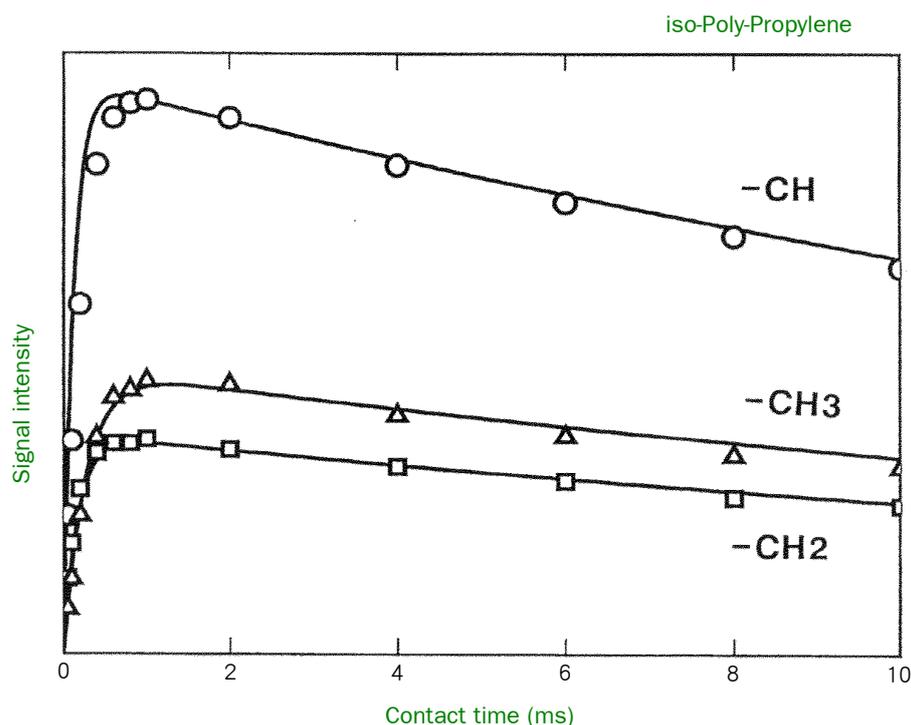


Fig. 4.2 Relationship between contact time and peak intensity

✎ Generally, the peak intensity reaches its maximum in about 1 to 2 ms for ^{13}C that connects directly to ^1H , and about 1 to 5 ms for a quaternary carbon.

4.4 SETTING WAITING TIME IN CP METHOD

For the CPMAS method, the optimum value of **relaxation_delay** is determined by the T_1 of ^1H . Theoretically, the accumulation efficiency (= signal-to-noise ratio/accumulation time) becomes optimum, if **relaxation_delay** is about 1.2 times the T_1 value of ^1H as shown in the following figure. For the sample whose T_1 of ^1H is difficult to measure, change the **relaxation_delay** if necessary to improve the accumulation efficiency using the following values as estimations:

- Approximately 2 to 5 s when the sample includes the methyl group as one of its main components.
- Approximately 5 to 10 s for a polymer that contains almost no methyl groups.
- Approximately 5 to 60 s for a crystal that contains no methyl group.

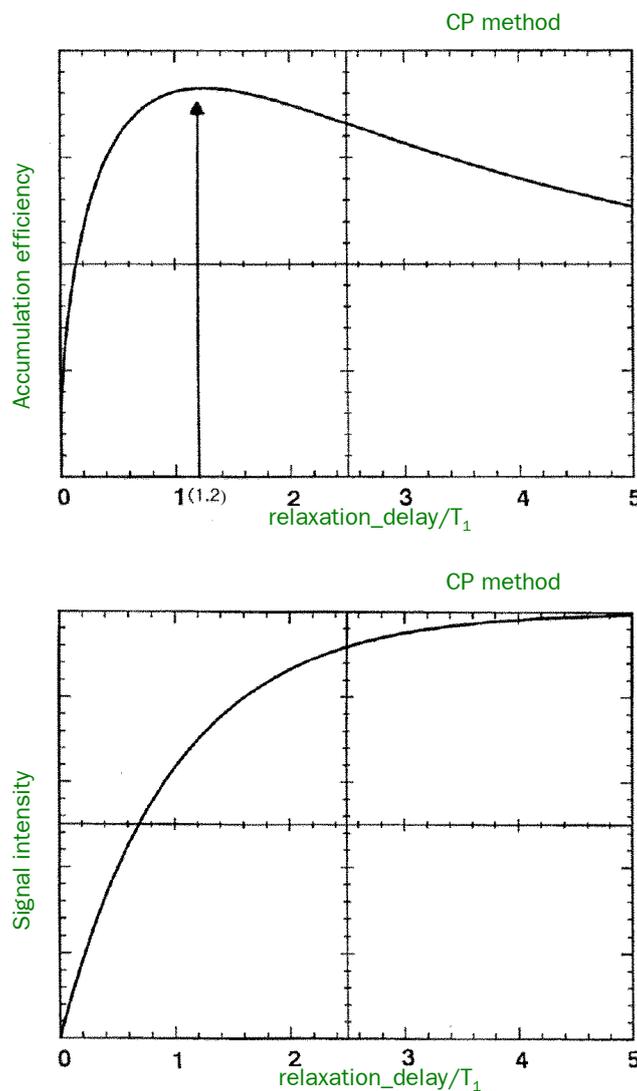


Fig. 4.3 Accumulation efficiency and signal intensity versus the ratio of the waiting time (relaxation_delay) to the T_1 (relaxation time) of ^1H

- ✍ The accumulation efficiency becomes its maximum at **relaxation_delay**/ T_1 = 1.2. Since the efficiency will decrease quickly if you set a shorter **relaxation_delay**, you will need to set a slightly longer **relaxation_delay**.

4.5 SETTING SAMPLING POINT (X_POINTS)

The parameter **x_points** specifies the number of sampling points to acquire FID data. For a solid-state NMR measurement, this parameter is used to adjust the decoupling time. Since decoupling time is the same as acquisition time, it is expressed as **x_acq_time**. High-power RF will be input to the probe during **x_acq_time**.

In order to reduce the load of the probe, it is necessary to shorten **x_acq_time**. However, if **x_acq_time** is too short, the FID signal will not be acquired. Ideally it is best that **x_acq_time** is as short as possible while still acquiring the entire FID signal. A good example and a bad example are shown in the following figure. As estimates, **x_acq_time** is about 20 ms in polymers and about 40 to 100 ms in crystals.

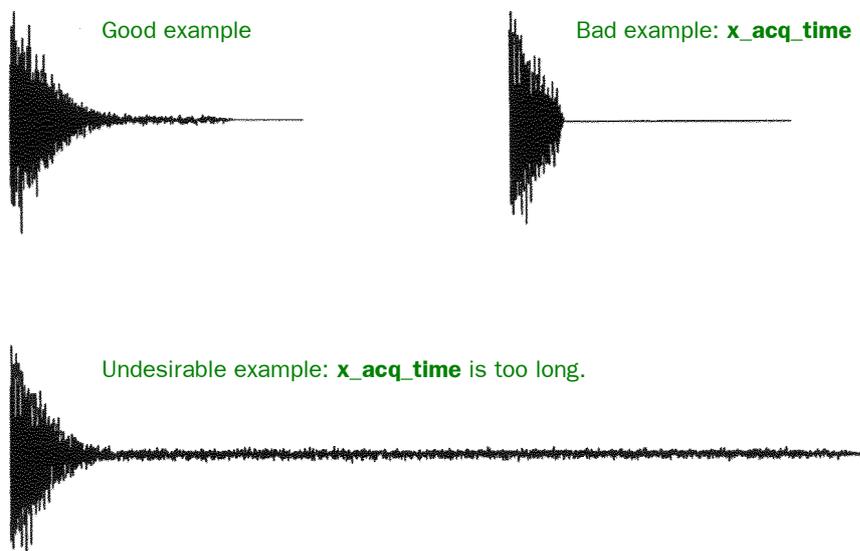


Fig. 4.4 Good and bad examples of acquisition time

4.6 HOW TO USE FORWARD LINEAR PREDICTION

Forward linear prediction is a technique used for complementing the data by predicting the missing data from the acquired data when the entire data of FID is not acquired due to setting the sampling points too small.

1. Recall data.
2. Set the value of Zerofill as follows.
 - a. Select **PreTransform-Zerofill**.
 - b. Set **Times** of **Zerofill** in the process list to two or more.
 -  Forward linear prediction complements the data for only the zero-filled part of the data.
When **Times** was 1, or zero-filling was not processed, It complements the data after zero-filling two times.
3. Set **Flip** as follows.
 - a. Select **PreTransform-FID Prediction-Flip**.
 - b. Set up **Order** of **Flip** in the process list.
4. Click the **Process**  button.
The process starts.

4.7 HOW TO USE BACKWARD LINEAR PREDICTION

Backward linear prediction is a technique used for predicting several points at the beginning of FID and replacing them. You can use it when the FID includes ringing. Moreover, backward linear prediction can predict several points at the beginning of FID that were missing in a measurement and extrapolate them. This method is used in measurements with wide observation ranges such as multinuclear measurements.

■ Substitution of data point

1. Recall the data.
2. Set up **Blip** as follows.
 - a. Select **PreTransform–FID Prediction–Blip**.
 - b. Set up each **Blip** parameter in the process list.
3. Click the **Process**  button.
The process starts.

■ Addition of data point

1. Recall the data.
2. Extrapolate the data as follows.
 - a. Select **PreTransform–Shift**.
 - b. Set up the number of points to add to **Shift** in the process list.
3. Set up **Blip**.
 - a. Select **PreTransform–FID Prediction–Blip**.
 - b. Set up each **Blip** parameter in the process list.
4. Click the **Process**  button.
The process starts.

5

MULTINUCLEAR MEASUREMENT

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5.1 OUTLINE OF MULTINUCLEAR MEASUREMENT

The solid high-resolution NMR measurement method of rare spin systems (^{13}C , ^{15}N , ^{29}Si , ^{31}P , ^{113}Cd , and others) of nuclear spins $1/2$ is widely used for the structural analysis of materials. Especially, the ^{13}C nucleus is an indispensable nucleus to analyze the polymeric material, and various measurement techniques have been developed. On the other hand, in nuclei with nuclear spin greater than one half, it is difficult to obtain the chemical shift because of the quadrupole interaction.

Although some nuclei such as ^1H and ^{19}F have nuclear spins of $1/2$, they are difficult to measure using the solid-state NMR method. The reasons for the difficulty in handling these nuclei in the solid state are high natural abundance (100%) and a large gyromagnetic ratio. A large gyromagnetic ratio means a strong magnetic dipole interaction, and a high natural abundance means that the observation spins have complex interactions with each other. Therefore, it is difficult to measure high-resolution spectra of these nuclei in the solid state. In solution NMR, a large gyromagnetic ratio and a high natural abundance mean a high detection sensitivity. Therefore, such characteristics are desired for the solution NMR measurement, but it is not desired for the solid-state NMR measurement. These nuclei are called “abundant-spin system.”

In this chapter, nuclei for measurement are classified according to how they correspond to the technique of the solid high resolution NMR measurement, and each measuring method is explained (see Table. 5.1).

Table. 5.1 Classification of High-Resolution Techniques

Classification	Typical nucleus	Spin number	Technique of high resolution
Rare spin	^{13}C , ^{29}Si , ^{15}N	$1/2$	MAS, Heteronuclear decoupling
Abundant spin	^1H , ^{19}F	$1/2$	High speed MAS, CRAMPS
$I = 1, \eta \cong 0$	^2H , ^6Li	1	MAS
Half integer spin	^{11}B , ^{23}Na , ^{27}Al	$(2n+1)/2$	DOR, DAS, MQ-MAS

5.2 METHOD OF MEASURING RARE SPIN NUCLEUS OF SPIN 1/2

Since a rare spin system is easy to treat due to its small interaction compared with other nuclei, it is the kind of nucleus most generally measured using the solid-state NMR. Because these nuclei are spin 1/2, there is no nuclear quadrupole interaction. Moreover, since the homonuclear dipole interaction is also weak, MAS (Magic Angle Spinning) can eliminate anisotropic interactions other than the C-H heteronuclear dipole interaction. Heteronuclear Dipolar Decoupling can eliminate the C-H heteronuclear dipole interaction. A high-resolution spectrum is obtained by combining MAS and Heteronuclear Dipolar Decoupling. Moreover, a sample containing the ^1H nucleus is measured by the CPMAS method to improve the sensitivity and accumulation efficiency.

Usually, samples of rare spin systems are measured by using the single pulse method with decoupling or the CPMAS method.

Mainly used sequence

- **single_pulse_solid.jxp**
- **single_pulse_dec_solid.jxp**
- **cpmas.jxp**

5.3 METHOD OF MEASURING $^1\text{H}/^{19}\text{F}$

In order to measure ^1H and ^{19}F , it is necessary to suppress the broadening of the line caused by the strong homonuclear dipolar interaction. Since the homonuclear dipolar interaction of ^1H and ^{19}F is very strong, MAS of about 10 kHz cannot give a high-resolution spectrum. However, in the ^{19}F nucleus, since the range of chemical shift is wide, useful information can be obtained by performing MAS above 15 kHz. Moreover, for a sample with a low density of ^1H , such as inorganic materials, MAS can give a high-resolution spectrum at several kilohertz, and useful information may be obtained. The signal observation of the sample may be difficult due to the background signal originating in the probe when the ^1H or ^{19}F nucleus is observed. In this case, the target signal can be observed by eliminating the background signal using the DEPTH2 method.

Usually, a sample of an abundant-spin system is measured by using the single-pulse or the depth2 method.

Mainly used sequence

- **single_pulse_solid.jxp**

5.4 METHOD OF MEASURING NUCLEUS OF SPIN 1

For a nucleus whose nuclear spin is 1 and asymmetry parameter η is nearly equal to zero, a high-resolution spectrum is obtained by MAS. The asymmetry parameter is the parameter showing the asymmetry of the electric field gradient around the nucleus. For deuterium substituted for ^1H in an organic compound, η can be considered as 0. Moreover, ^6Li is also measured with high resolution by MAS.

Usually, a sample of a rare spin system is measured by using a single pulse.

Mainly used sequence

- **single_pulse_solid.jxp**

5.5 METHOD OF MEASURING NUCLEUS OF HALF-INTEGER SPIN

For the nuclei that have half-integer spin other than $1/2$ spin, such as $3/2$ and $5/2$, the peak due to central transition can be narrowed by MAS, because the central transition is not affected by the first-order quadrupolar interaction. Moreover, since the residual second-order quadrupolar interaction is inversely proportional to the magnetic field strength, broadening of the line is suppressed by the high magnetic field, and the separation capability of the peaks increases. By using the NMR instrument with a high-magnetic field, even for a nucleus like ^{27}Al , the peak separation becomes possible to a certain extent. Although available spin systems are limited, the analysis for the some material can be carried out.

However, the broadening of the line by residual second-order nuclear quadrupolar interaction has prevented separation of the peaks for many samples. Some techniques that remove this residual interaction in a nucleus of a half-integer spin and acquire a high-resolution spectrum have been proposed.

Three typical techniques for obtaining a high-resolution spectrum are the DOR (Double Rotation) method, the DAS (Dynamic Angle Spinning) method, and the MQ (Multiple Quantum)-MAS method. Because the DOR method and the DAS method need a special probe for these techniques, they are not generally used. Since the MQ-MAS method can be performed using a MAS probe that is widely available, this technique is easy to use.

Usually, a sample of a half-integer spin system can be measured using a single pulse under high-speed spinning or the MQMAS method.

Mainly used sequences for measurement

- **single_pulse_solid.jxp**
- **mqmas_3Q_z.jxp**
- **mqmas_5Q_z.jxp**

Mainly used sequences for adjustment

- **mqmas_3Q_z_setup.jxp**
- **mqmas_5Q_z_setup.jxp**

6

MEASUREMENT OF RELAXATION TIME

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6.5	RELAXATION TIME MEASUREMENT OF ¹ H BY INDIRECT OBSERVATION USING CP METHOD	6-6

6.1 OUTLINE OF RELAXATION-TIME MEASUREMENT

The relaxation time of a solid sample has useful information about the molecular motion of the specific site. Also, for optimizing the measurement parameters or performing the quantitative measurement, it is necessary to measure the exact relaxation time of each peak in advance.

The following sections explain the methods of measuring the relaxation time.

☞ Refer to the user's manual "Application" for information about the processing **Curve analysis**.

6.2 RELAXATION TIME MEASUREMENT BY DIRECT MEASUREMENT

For the sample that can be measured by a single pulse to obtain the NMR spectrum, you can perform the relaxation-time measurement by direct observation without using CPMAS. There are two methods of relaxation-time measurement by direct observation.

- Inversion-recovery method
- Saturation-recovery method

The saturation-recovery method is effective for measuring the samples where the T_2 relaxation time is small enough in comparison with the T_1 relaxation time.

■ Relaxation-time measurement by inversion-recovery method

The inversion-recovery method is used generally as the relaxation-time measurement method. Although the measurement procedure is the same as that for a solution, the following pulse sequence is used.

(inversion_recovery.jxp)
(inversion_recovery_dec.jxp)

☞ Refer to the user's manual "Application" for the measurement and processing of the inversion-recovery method.

■ T_1 calculation-method for T_1 data obtained by the saturation-recovery method

The saturation-recovery method saturates the magnetization, and observes the recovery to obtain the relaxation time. For a peak that changes by a single exponential function, the strength of the magnetization $M(\tau)$ is expressed as a function of the delay time (τ) by the following formula in the saturation-recovery method.

$$M(\tau) = M_0 \{1 - \exp(-\tau / T_1)\}$$

1. Load the pulse sequence **saturation_recovery.jxp** into **Experiment Tool**.
When measuring the T_1 of ^{13}C , select **saturation_recovery_dec.jxp**.
2. Set the array parameters for **interval** based on the estimated T_1 value.
Setup the array of values to perform the T_1 measurement (the saturation-recovery method) in decreasing order. The arrow buttons in Figure 6.1 enable you to switch between increasing and decreasing order.

6.3 RELAXATION TIME MEASUREMENT OF ^{13}C BY TORCHIA METHOD

One technique for measuring the relaxation time of a solid sample is the Torchia method. The relaxation time is obtained by measuring the differences between the spectra by the inversion-recovery method using CP and the spectrum by the CPMAS method. Since the CPMAS method is used, the waiting time can be shortened compared with the relaxation-time measurement by direct observation.

For a peak that changes by a single exponential function, the strength of the magnetization $M(\tau)$ is expressed as a function of the relaxation delay time (τ) by the following formula.

$$M(\tau) = M_0 \exp(-\tau/T_1)$$

1. Load the pulse sequence **torchiaT1_cpmas.jxp** into **Experiment Tool**.
2. Set scans to a multiple number of two.
3. Set the array parameters for **interval** based on the estimated T_1 value.
Setup the array variable for performing the Torchia method in decreasing order. The arrow buttons enable you to switch between increasing and decreasing order.
4. Click the **Set Value** button.
The array parameter window closes, and the values you set are entered into **interval** in the **Experiment Tool**.
5. Click the **Submit** button.
The measurement starts.

Although data-processing procedure is the same as that for the inversion-recovery method, use the following approximation formulas.

Weighted Linear Spin Lock:	The weighted linear least squares method The weight is reduced for the measurements having long τ .
Unweighted Linear Spin Lock:	Linear least-squares method without weights
Nonlinear Spin Lock:	Nonlinear least-squares method

 Refer to the user's-manual "Application" for information about the measurement and processing of the inversion-recovery method.

6.4 MEASUREMENT OF $T_{1\rho}$ (T_1 IN THE ROTATING FRAME)

$T_{1\rho}$ (T_1 in the rotating frame) is measured by using CPMAS. For the $T_{1\rho}$ measurement of ^{13}C , after transferring the excited magnetization by the CP method, the $T_{1\rho}$ is measured by spin locking the magnetization. Since the CPMAS method is used, the waiting time can be shortened in comparison with the direct-observation method.

For a peak that changes by a single exponential function, the strength $M(\tau)$ of magnetization is expressed as a function of the relaxation delay time (τ) by the following formula.

$$M(\tau) = M_0 \exp(-\tau / T_{1\rho})$$

1. Load the pulse sequence **cpmas_spin_lock.jxp** to **Experiment Tool**.
When measuring the $T_{1\rho}$ without CP, select **spin_lock.jxp** or **spin_lock_dec.jxp**.
2. Set the Array parameters for **obs_width_lock** based on the estimated $T_{1\rho}$ value.
Setup the array variable for performing the Torchia method in decreasing order. The arrow buttons enable you to switch between increasing and decreasing order.
3. Click the **Set Value** button.
The array parameter window closes, and the values you set are entered into **obs_spin_lock** in the **Experiment Tool**.
4. Click the **Submit** button.
The measurement starts.

Although the data processing procedure is the same as that of the inversion-recovery method, use the following approximation formulas.

Weighted Linear Spin Lock:	The weighted linear least-squares method. The weight is deduced for the measurements having long tau_interval .
Unweighted Linear Spin Lock:	Linear least-squares method without weight.
Nonlinear Spin Lock:	Nonlinear least-squares method.

 Refer to the user's-manual "Application" for the measurement and processing of the inversion-recovery method.

6.5 RELAXATION TIME MEASUREMENT OF ^1H BY INDIRECT OBSERVATION USING CP METHOD

In the solid-state NMR, when measuring the relaxation time of the ^1H nucleus, indirect observation can be performed using the CP method. When the spectrum of ^1H is broad and cannot be observed directly, or when the sample consists of many elements, this indirect observation method is effective. The principle and measurement procedures are the same as that of the measuring method by direct observation.

■ Relaxation time measurement by inversion-recovery method

When the relaxation time of ^1H is measured by using the inversion-recovery method with CPMAS, the following pulse sequence is used.

inversion_recovery_1h_cpmas.jxp

In the usual inversion-recovery method using CPMAS, the inversion-recovery method is performed after the magnetization transfer. However, in the relaxation-time measurement of ^1H , the magnetization transfer is performed after the inversion-recovery method.

■ Measurement of $T_{1\rho}$

The following pulse sequence is used for measuring the $T_{1\rho}$ (T_1 in the rotating frame) of ^1H by the CPMAS method.

cpmas_spin_lock_1h.jxp

Although the spin lock is applied after magnetization transfer in the usual $T_{1\rho}$ measurement, the magnetization transfer is performed after the spin lock in the $T_{1\rho}$ measurement of the ^1H nucleus.



MQMAS METHOD

Nuclei having a half-integer spin have quadrupolar interactions that do not exist in nuclei with a nuclear spin $1/2$. Therefore, MAS by itself usually cannot obtain a high-resolution spectrum, and the MAS data cannot be used for the analysis of a complicated compound. In order to measure a nucleus having a half-integer spin, it is necessary to perform a measurement that removes this quadrupolar interaction.

The DOR (Double Rotation) method, the DAS (Dynamic Angle Spinning) method, and the MQ (Multiple Quantum)-MAS method are known as measuring methods that remove quadrupolar interactions. However, since the DOR method and the DAS method need a special probe, they are not general techniques.

Chapter 7 explains the MQMAS method that is the most generally used method for the measurement of a nucleus with a half-integer spin.

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7.1 OUTLINE OF MQMAS METHOD

The MQMAS method was proposed by Frydman and Harwood in 1995.

Reference: A.Medek, J.S.Harwood, and L.Frydman. JACS, 117, 12779-12787 (1995).

The MQMAS method has the advantage that it can eliminate quadrupolar interaction without using a special probe in contrast to the DOR and DAS methods.

Moreover, since it can be adjusted comparatively easily, it can be generally used as the measuring method.

■ Feature of theMQMAS method

For nuclei having a spin 1/2, information about how many sites exist can only be obtained by the MAS spectrum. For nuclei having a half-integer spin, the site analysis is difficult when you only use the MAS spectrum because of the influence of quadrupolar interactions.

As an example, the ^{87}Rb MAS spectrum of rubidium nitrate (RbNO_3) is shown below.

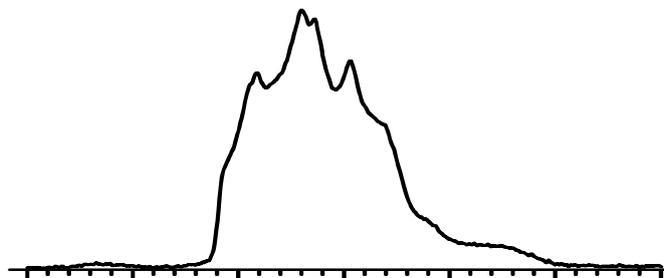


Fig. 7.1 ^{87}Rb -MAS spectrum (300 MHz)

Although three different sites exist in rubidium nitrate, such information cannot be obtained from the MAS spectrum. The following figure shows the spectrum measured by the MQMAS method.

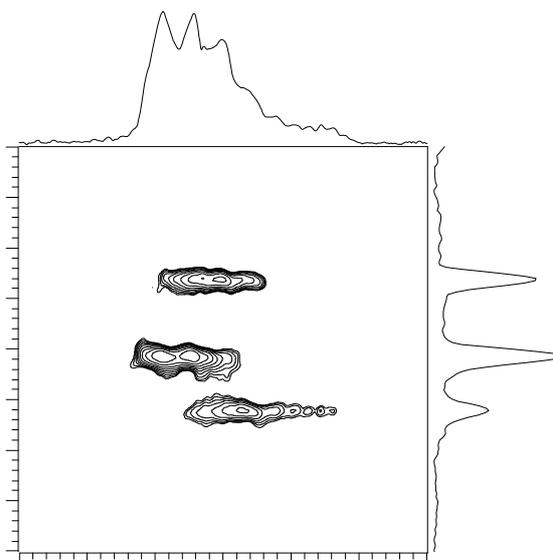


Fig. 7.2 ^{87}Rb MQMAS spectrum (300 MHz)

As seen in the above spectra, for the spectrum that cannot be analyzed using only the MAS spectrum, measuring with MQMAS can obtain information on the three different sites. Moreover, the MQMAS spectrum shows the MAS spectrum along the direct observation axis and the isotropic spectrum along the evolution (indirect observation) axis. Therefore, various kinds of information can be obtained from the peak positions and the line-shape analysis of the slice data in the MQMAS spectrum.

■ Points to notice on the MQMAS method

Although the MQMAS method is a technique with the ability to obtain various kinds of information, some factors exist that influence the quality of the data.

- a) High RF power required
- b) The probe must withstand high voltage
- c) High magnetic field required

High RF power is indispensable in the MQMAS method in order to cause the magnetization transfer with multiple-quantum coherence. If the power weakens, the signal intensity will decrease, and the peak may not be detected. Furthermore, an artifact signal may appear. Moreover, in order to use high RF power, the probe must be able to withstand high voltage.

The greatest problem of MQMAS is the weak signal intensity, and the measurement time is very long. Therefore, it is very effective to increase the signal intensity with a high magnetic field and with high-speed spinning, and shorten the measurement time.

Furthermore, the quadrupolar interaction that causes the lines to broaden decreases with a high magnetic field and high-speed spinning. Therefore, not only does the signal intensity increase, but the resolution also improves markedly as a result of using a high magnetic field and high-speed spinning.

7.2 PRINCIPLE

The MQMAS method is the technique for controlling magnetization transfer by the pulse sequence and the phase cycling. Here, the two typical MQMAS methods are explained.

■ 3QMAS method

The most fundamental pulse sequence in the current MQMAS method and the pathway of magnetization transfer are shown below.

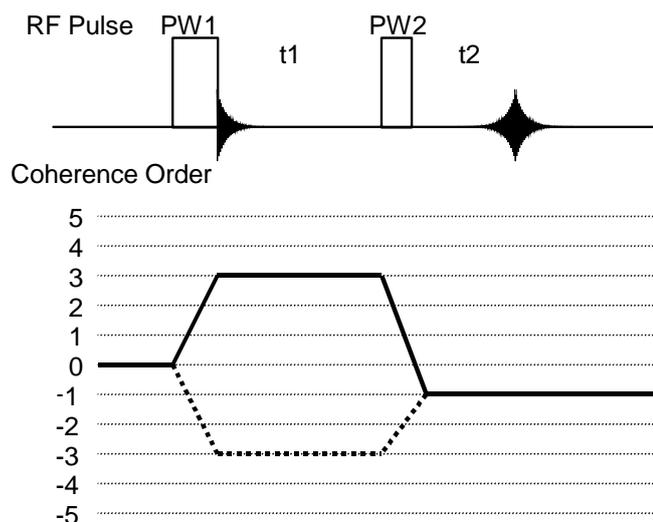


Fig. 7.3 Pulse sequence of 3QMAS method, and magnetization transfer

Since this sequence uses 3-quantum coherence, it is called the 3Q (Triple Quantum) MAS method. The pulse sequence of the 3QMAS method consists of two simple pulses. The spin system is excited to 3 quantum by the first pulse, and evolved during time t_1 by using phase cycling in which only 3-quantum coherence remains. Finally, its coherence is converted to single-quantum coherence by a second pulse in order to detect the coherence. Using such a pulse sequence separates the interaction of anisotropic and isotropic terms.

■ 3QMAS method with Z-filter

The 3QMAS method has taken out two magnetization transfer coherence pathways, $0 \rightarrow 3 \rightarrow -1$ and $0 \rightarrow -3 \rightarrow -1$. However, since these two pathways are asymmetric, the 3QMAS method has a problem in that it easily causes artifacts. In order to solve the problem, a Z filter is added to the sequence. This is the 3QMAS with the Z filter.

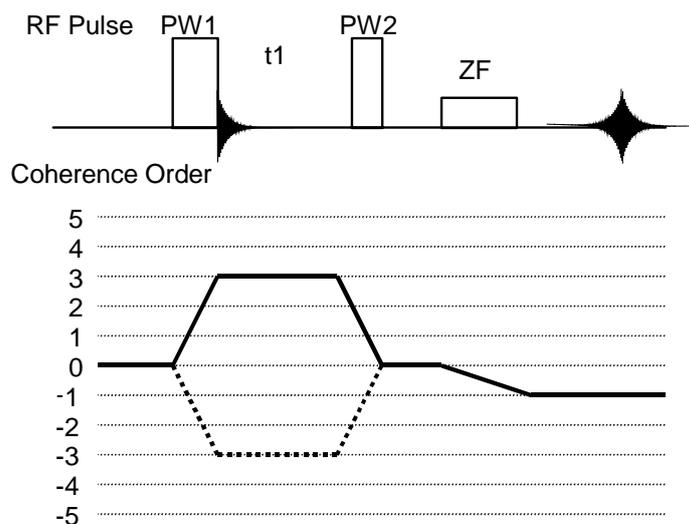


Fig. 7.4 The pulse sequence of the 3QMAS with the Z filter, and magnetization transfer pathway

In the 3QMAS with the Z filter, the spin system is excited to 3 quantum by the first pulse in the same way as with the usual 3QMAS, and evolved during time t_1 by using phase cycling in which only 3-quantum coherence remains. Then, 3-quantum coherence is converted to zero quantum coherence, and signals other than the Z-axis are eliminated after the second pulse. Finally, the signal of the Z-axis is excited to single-quantum coherence by the last pulse in order to detect it.

In the 3QMAS with the Z filter, since the coherence transfer pathways are $0 \rightarrow 3 \rightarrow 0 \rightarrow -1$ and $0 \rightarrow -3 \rightarrow 0 \rightarrow -1$, it has an advantage of making it hard for artifacts to appear. Moreover, since the selective excitation pulse is used for the last single pulse, the side band signal does not appear on the direct-observation axis.

7.3 ADJUSTMENT

Here the 3QMAS with the Z filter measurement is explained as an example because it is most commonly used.

7.3.1 Adjustment of Power

Two power levels are used in the MQMAS measurement with the Z filter. They are the high output power level used to excite the multiple-quantum coherence and the power level for the selective excitation of the Z filter.

In order to perform the MQMAS measurement, adjust each power level first.

■ Adjustment of the high power output

The high power output used in the MQMAS measurement is the maximum power that the probe can endure. Usually, the **obs_amp_pulse** is set to 100% with the attenuator value written in the probe file. Also, the 90° pulse width for the sample is measured for that power.

1. Set the sample.
2. Perform spinning.
3. Load the pulse sequence **single_pulse_solid.jxp** to the **Experiment Tool**.
4. Set **obs_angle_prep** to 90 deg.

The 90° pulse width is not equal to 1/4 of the 360° pulse width because of the influence quadrupolar interaction of the nucleus having the half-integer spin. Therefore, use the value of the strongest signal intensity as the 90° pulse width.
5. Set **obs_amp_pulse** to 100%.
6. Set up an array measurement for **obs_width_90**.
7. Click the **Submit** button.

The pulses occur, and the measurement begins.
When measurement ends, the **nD Processor** window opens automatically.
8. Perform data processing.

 Refer to the user's manual "Data processing" for the procedure for processing the data obtained by the array measurement.
After data processing, the result is displayed by **Linearize**.
9. Seek the **obs_width_90** having the strongest signal intensity in the spectrum after carrying out **Linearize** processing.

This value is the 90° pulse width of the sample.

■ Adjustment of the selective excitation pulse

The pulse for the Z filter uses the power of selective excitation. Select the RF intensity so that the 90° pulse of the target sample may be 12 to 15 μs . Adjustment of the pulse width is performed for the highest signal intensity in the same way as the adjustment of the high-power output pulse.

1. Set the sample.
2. Perform spinning.
3. Load the pulse sequence **single_pulse_solid.jxp** to **Experiment Tool**.
4. Set **obs_angle_prep** to 90 deg.
5. Set **obs_width_90** from 12 to 15 μs .
6. Set up an array measurement for **obs_amp_pulse**.
7. Click the **Submit** button.

The pulses occur, and the measurement starts.

If the measurement ends, the **nD Processor** window opens automatically.

8. Perform the data processing.

☞ Refer to the user's manual "Data processing" for the procedure for processing the data obtained by the array measurement.

After data processing, the result is displayed by **Linearize**.

9. Seek the **obs_amp_pulse** having the strongest signal intensity in the spectrum after carrying out **Linearize** processing.

This value is the power of the Z filter.

✂ If initially you set **obs_amp_pulse** to a higher value, and perform the array measurement, you might take a 270° pulse or 450° pulse incorrectly. To prevent this, set the initial value for the array measurement at a smaller value.

7.3.2 Adjustment of Parameters

To adjust the MQMAS measurement, search for the conditions that give the strongest signal intensity by using the sequence for adjustment. For the 3QMAS with the Z filter measurement, the following adjustment sequence is used.

Mqmas_3Q_z_setup.jxp

1. Set the sample.
2. Perform spinning.
3. Load the pulse sequence **mqmas_3Q_z_setup.jxp** to the **Experiment Tool**.

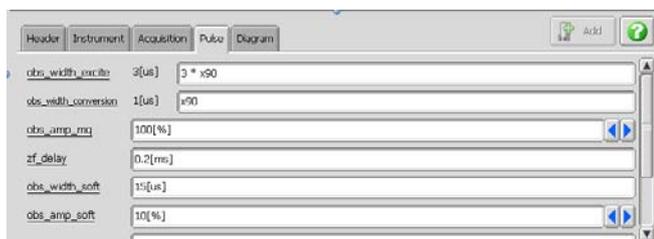


Fig. 7.5 Pulse section of the Experiment Tool

4. Enter suitable values in **scans**.
In the MQMAS measurement, since the sensitivity is poorer than with a single-pulse measurement, you need to increase the number of scans to accumulate. Also for the 3QMAS measurement using 3-quantum coherence, set the number of scans to multiples of 6 times the integral number.
5. Enter suitable values in **obs_width_soft** and **obs_amp_soft**.
The **obs_width_soft** uses the 90° pulse width used by “Adjustment of the selective excitation pulse” in Sect. 7.3.1, and the **obs_amp_soft** uses the **obs_amp_pulse** at that time.
6. Enter a suitable value in **obs_width_pw** and **obs_width_conversion**.
The **obs_width_conversion** is the 90° pulse width which is obtained in Sect. 7.3.1 “Adjustment of high power output”, and the **obs_width_pw** is set to about 3 times **obs_width_conversion**.
7. Set the array measurement for **obs_width_pw**.
8. Click the **Submit** button.
The pulses occur and the measurement starts.
When the measurement ends, the **nD Processor** window opens automatically.
9. Perform data processing.
 Refer to the user’s manual “Data processing” for the procedure for processing the data obtained by the array measurement.
After data processing, the result is displayed by **Linearize**.
10. Obtain **obs_width_pw** with the strongest signal intensity in the spectrum that is processed by **Linearize**.
11. Set **obs_width_pw**.
Enter the value obtained in step 10 to **obs_width_pw**.
12. Perform an array measurement for **obs_width_conversion**.
Carry out steps 7 to 11 for **obs_width_conversion**.
13. Perform the array measurement again for **obs_width_pw**.
Carry out steps 7 to 11 again for the **obs_width_pw**, and look for the optimum pulse width.
14. Repeat steps 7 to 13.
Repeat steps 7 to 13 for the **obs_width_pw** and **obs_width_conversion** until optimum values are obtained for both pulses.
15. Set array measurement for **obs_width_soft**.
Look for the **obs_width_soft** with the largest signal intensity.
 Since the parameters obtained by the adjustment sequence will be copied and used in the MQMAS measurement, do not close the **Experiment Tool** after adjustment.

7.4 MEASUREMENT

Use the pulse sequence prepared for the MQMAS measurement. For the 3QMAS with the Z filter, you can use the sequence **3qmas_z.jxp**. For measurement parameters, copy the parameters that are obtained by the adjustment in Sect. 7.3 and use them to perform the measurement.

1. Load the pulse sequence **mqmas_3Q_z.jxp** to the **Experiment Tool**.
2. Set up parameters.

Copy the parameters from those obtained in Sect. 7.3 as follows.

 - a. While **mqmas_3Q_z_setup.jxp** is opened, select **Experiment—Edit—Copy Attributes** from the menu in the **Spectrometer Control** window.
 - b. While **mqmas_3Q_z.jxp** is opened, select **Experiment—Edit—Paste Attributes** from the menu in the **Spectrometer Control** window.

The parameter of **mqmas_3Q_z_setup.jxp** is copied to **mqmas_3Q_z.jxp**.
3. Set up **y_sweep**.

Perform the scaling processing (☞ Sect. 7.6.2) for the t1 axis of the MQMAS spectrum. Therefore, it is necessary to set a wider **y_sweep** width than the line width of the 1D spectrum. Moreover, if spinning sideband signals appear, set **y_sweep** to an integer multiple of the rotational frequency to reduce the influence of sideband signals and improve the sensitivity.
4. Set up **scans** and **y_points**.

Since the MQMAS measurement has poor sensitivity, it is necessary to increase the number of scans to accumulate. Determine the number of scans for accumulation while adjusting the **total_time** and **y_points** in reference to the signal intensity at the time of adjustment.

Also, for the 3QMAS measurement using 3-quantum coherence, set the number of scans to multiples of 24.
5. Click the **Submit** button.

The pulse occurs and the measurement starts.

When the measurement ends, the **nD Processor** window automatically opens.

7.5 PROCESSING

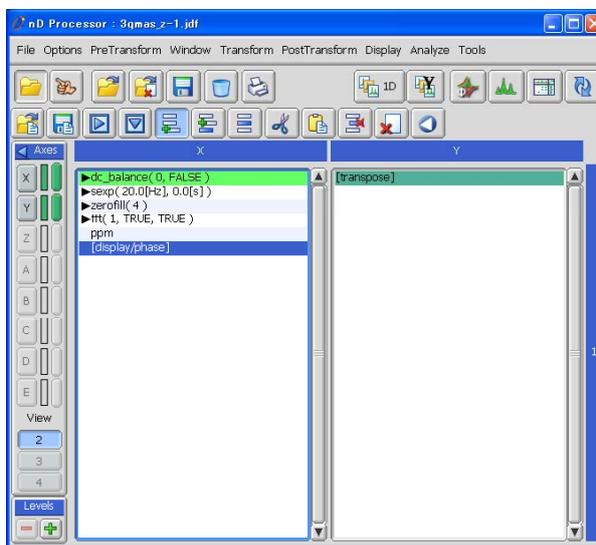
In the MQMAS method, since it is necessary to perform the shearing process for the data (☞ Sect. 7.6.1), you need to divide the data into echo and anti-echo components during the data processing. The flow of MQMAS processing is shown below.

- a) F2 axis Fourier transform
- b) F2 axis phase correction
- c) PN conversion
- d) Shearing process (☞ Sect. 7.6.1)
- e) Window function processing
- f) PN inverse conversion
- g) F1 axis Fourier transform
- h) F1 axis phase correction
- i) Scaling processing (☞ Sect. 7.6.2)

■ Processing procedure

This section explains the data processing after the measurement is completed and the data is transferred from the spectrometer.

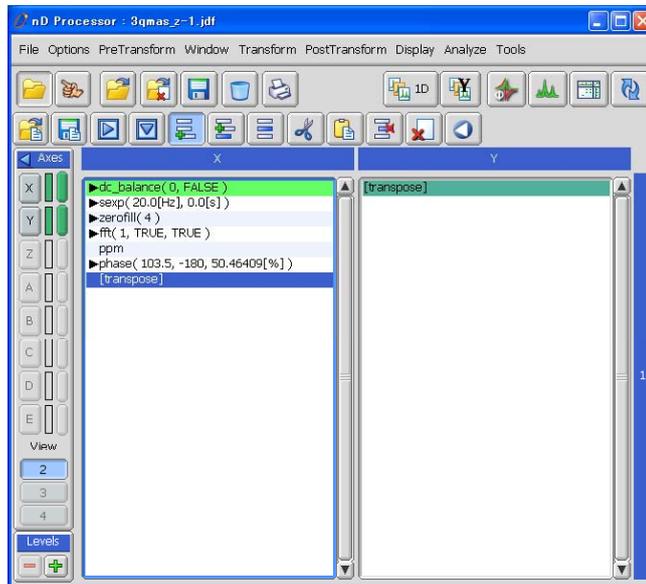
When the measurement is completed, the data is transferred from the spectrometer to the data processing computer, and the **nD Processor** window opens. Usually, **1d_solid.list** is opened in the process list of the data after the MQMAS measurement. Here, the data-processing procedure will be explained based on the assumption that the data processing is performed as it is in its current state.



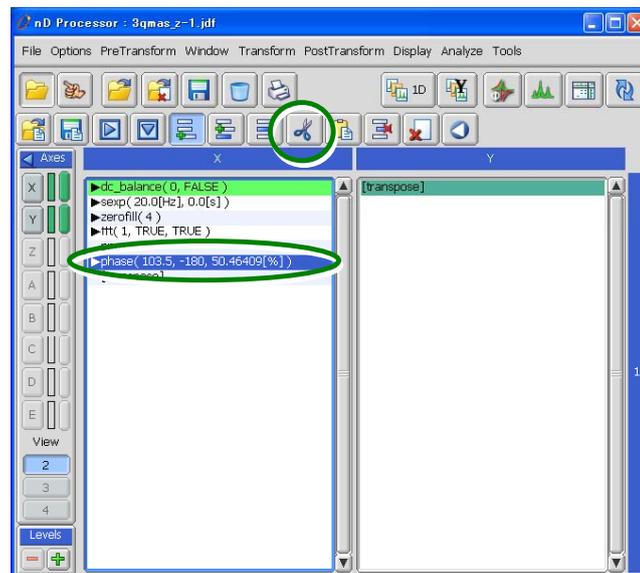
1. Press the 1D button.

Fourier transformation is performed on the F2 axis.

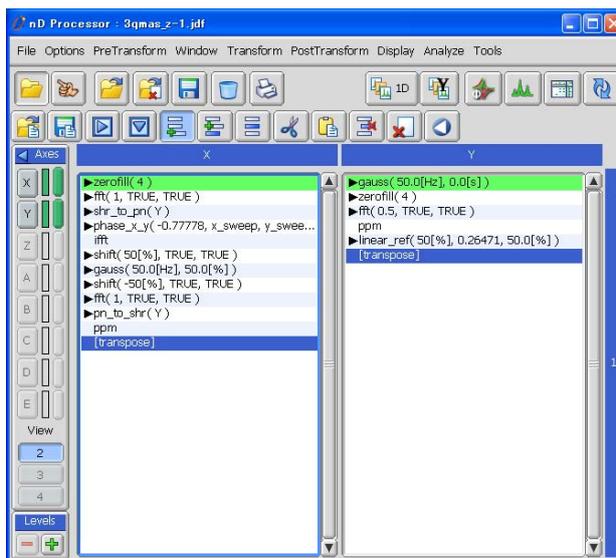
2. Close the window after performing phase correction of the F2 axis.
The phase of the F2 axis is applied to **nD Processor**.



3. Cut the value of the phase of the F2 axis as follows.
Highlight the **phase: -- : -- : --** line, and press the **Cut**  button.



4. Click the **Open Process List**  button to load the process list of MQMAS.
The process list to load is different for every nuclear spin number of the measurement nucleus and measuring quantum number of the measurement method.
- | | |
|---|--------------|
| For nuclear spins 3/2: | 3s3qmas.list |
| For nuclear spins 5/2 and excitation 3 quantum: | 5s3qmas.list |
| For nuclear spins 5/2 and excitation 5 quantum: | 5s5qmas.list |



5. Set the phase of F2 axis.

Highlight **transpose**, and click the **Paste**  button. The phase correction that was cut in step 3 is added.

6. Perform phase correction of the F1 axis.

Click the **2D Phase**  button, and perform phase correction of F1 axis in the open window.

7. Display the two-dimensional spectrum.

Click the **Data Viewer**  button to display the two-dimensional spectrum.

7.6 APPENDIX

This section describes special processing required in the MQMAS method.

7.6.1 Shearing process

Since the MQMAS method measures the echo, the top of the echo signal (the starting point of FID) shifts along with the t_1 evolution time. As an example, a two-dimensional FID signal of the ^{23}Na nucleus in sodium sulfate (Na_2SO_4) is shown below.

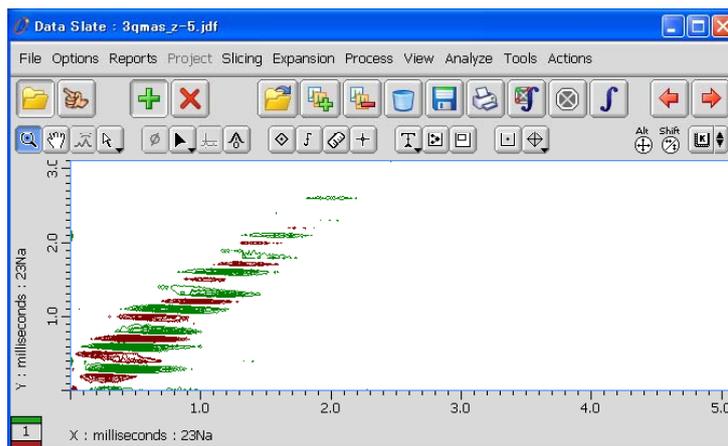


Fig. 7.6 Two-dimensional FID signal of sodium sulfate (Na_2SO_4)

If the Fourier transform is carried out by the usual method for such two-dimensional FID data, it will become a tilted two-dimensional spectrum. Therefore, we must change it into an ordinary spectrum by performing the shearing process.

After the Fourier transform of F2 axis, shearing conversion performs the phase correction that increases the first order phase of the F1 axis linearly. Figure 7.7 shows the relation between FID and the spectrum when the sampling starting position of an echo signal is shifted.

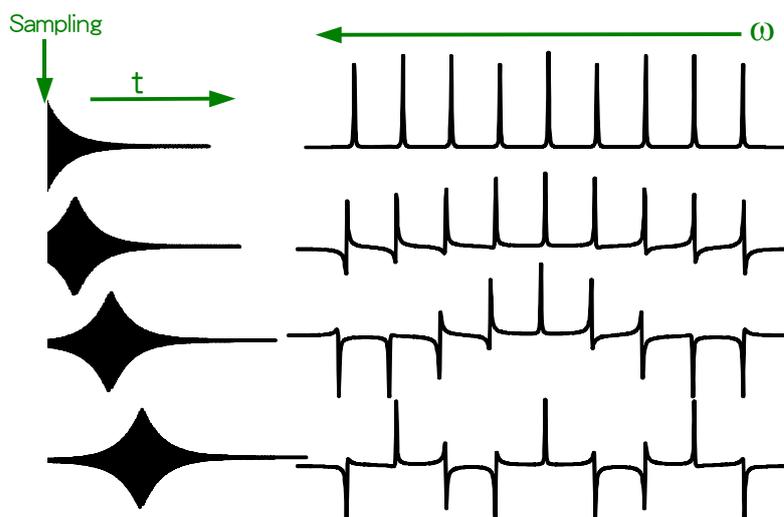


Fig. 7.7 Relation between FID and the spectrum when sampling start position is shifted

Thus, you can see that the shift of the sampling starting position of an echo signal causes the first order phase shift. The shearing process makes this phase shift disappear.

In data processing of MQMAS, after using PN conversion to divide the data into echo and anti-echo components, the shearing process in the opposite direction is performed on each component.

7.6.2 Scaling Processing

The second-order quadrupole coupling shifts the peak position in the MAS spectrum of a nucleus with half-integer spin. In addition to the shift caused by the second-order quadrupole coupling, the multiple-quantum chemical shielding shifts the peak position in the isotropic axis of the MQMAS spectrum. Therefore, it is necessary to correct the scaling of the chemical shift in the MQMAS spectrum.

The scaling coefficient at this time was determined based on the nuclear spin number of the measurement nucleus (I) and the quantum number of measurement (p).

$$\text{Scaling factor} = |R-p|$$

$$R(I, p) = p \{36 I (I+1) - 17 p^2 - 10\} / \{36 I (I+1) - 27\}$$

In the MQMAS method, because the scaling processing is performed at the end of processing, **y_sweep** changes from the value at the measurement. For example, in 5Q-MAS measurement for spin 5/2-nuclei, since **y_sweep** becomes 0.14118 times the set value, it is necessary to set the observation range a little wider when setting it before the measurement.

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