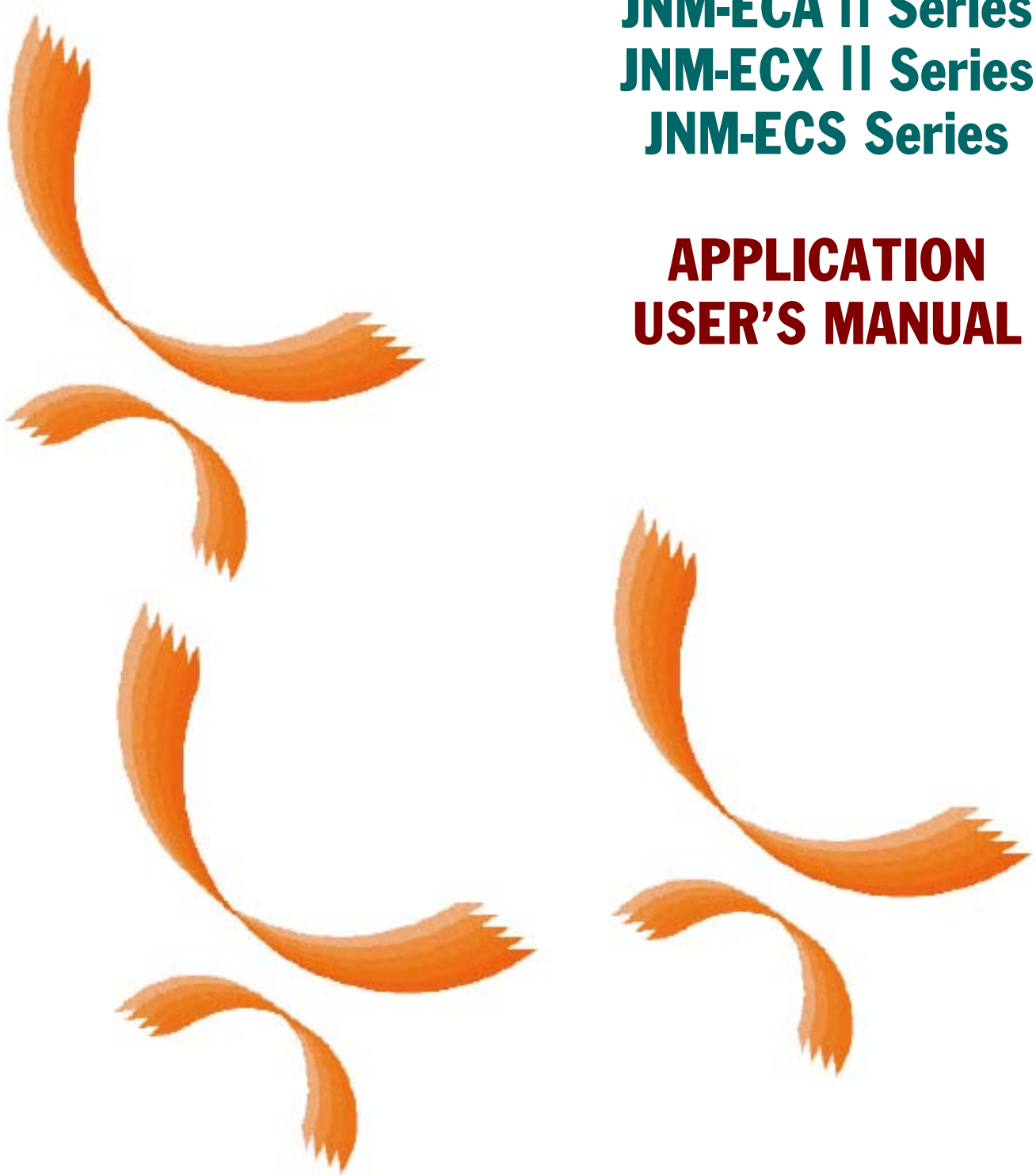
INSTRUCTIONS

JNM-ECA II Series
JNM-ECX II Series
JNM-ECS Series

APPLICATION USER'S MANUAL



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JEOL RESONANCE

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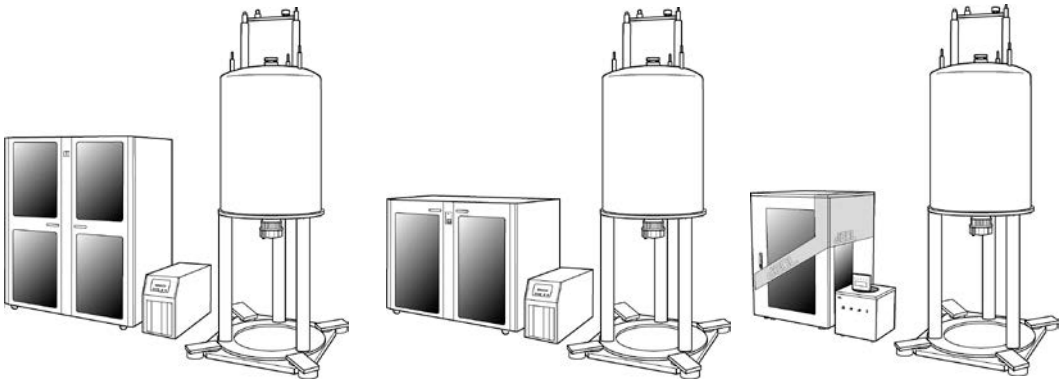
JNM-ECX II Series
JNM-ECS Series

APPLICATION USER'S MANUAL



JNM-ECAII Series　　JNM-ECXII Series　　JNM-ECS Series

This manual explains how to perform more-advanced measurement using the JNM-ECA Ⅱ, JNM-ECX Ⅱ or JNM-ECS Series FT NMR system.

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.

JEOL RESONANCE

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Note: For servicing and inquiries, please contact your service office.

CONTENTS

4 MEASUREMENT OF SR-MAS

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.

- The AC power cord provided with this system is supplied for the particular device so that never use it for any other equipment.

- 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.

PRECAUTIONS FOR USE

The following precautions are important which, if not followed, may result in damage to the instrument itself.

- **Be sure to rotate a sample in SR-MAS experiment.**
  If you measure without flowing the air for sample spinning, the probe may be damaged. However, when you carry out the resolution adjustment using single_pulse.jxp, damage to the probe does not occur even if the measurement is carried out without air flowing.
- **The first time you adjust the magic angle, you need to receive instruction from an experienced person.**
  The SR-MAS probe may be damaged if improper adjustment is performed.

1

RELAXATION TIME MEASUREMENT AND DATA PROCESSING

1.1 RELAXATION TIME MEASUREMENT

There are three kinds of relaxation times, T_1, $T_{1\rho}$, and T_2.
Section 1.1 explains the method for T_1 measurement, which is frequently performed.

1.1.1 Evaluation of Relaxation Time (T1)

To obtain T_1 with high accuracy, array measurement is performed using the variable for recovery times. To set the variable for recovery times to the appropriate value, you need to evaluate the approximate T_1 of the sample in advance.
This section describes the method for a simple T_1 evaluation by means of inversion recovery.

■ Simple T1 evaluation method using the T1 measurement mode by means of inversion recovery

If a peak changes as a single exponential function, the observed magnetization $M(\tau)$ is expressed as a function of the relaxation delay time(τ) by using the inversion recovery method:

$$M(\tau)=M_0\{1-2\exp(-\tau/T_1)\}$$

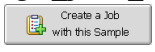
From this equation, T_1 can be evaluated from the delay time when the observed magnetization becomes zero. This delay time is called the null point, and is represented by τ_{null}.
Thus, T_1 is given by

$$T_1=\tau_{null}/\ln 2=1.44\times\tau_{null}$$

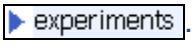
To obtain an accurate value of T_1, first obtain the null point, and then perform the array measurement.

1.1.2 Measurement of Relaxation Time (T1)

■ To obtain the null point

1. Register the sample in the **Samples** tab and perform the necessary preparation before the measurement (☞User's manual, "LIQUID MEASUREMENT").
2. Tune the probe.
3. Verify the 90° pulse width.
   To enhance accuracy of T1 measurement, verify the 90° pulse width of the sample used for measuring relaxation time. To do this, perform array measurement in the single_pulse.jxp or single_pulse_dec.jxp measurement mode.
4. Click the **Create a Job with this Sample** 

button in the Spectrometer Control window.
5. Click the **Add Experiment** 

button in the **Jobs** tab.
The Open Experiment window opens.
6. Click  and double click 

. After the directory list appears, double click **relaxation** in the list.

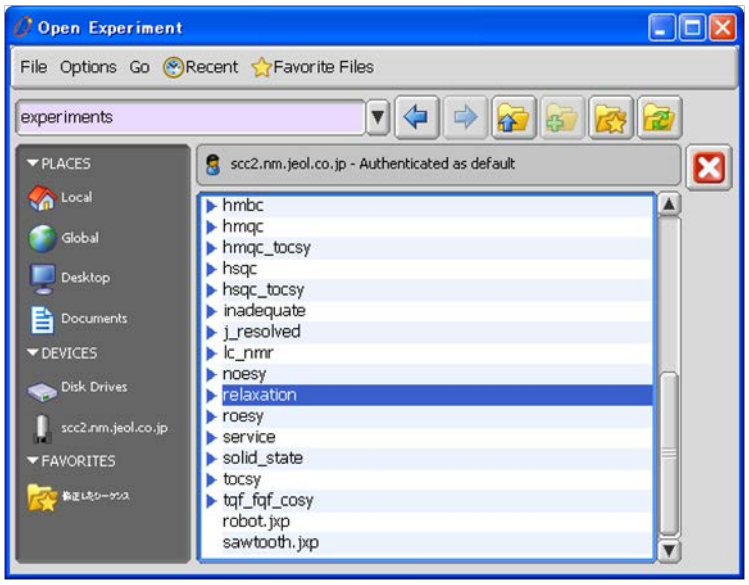
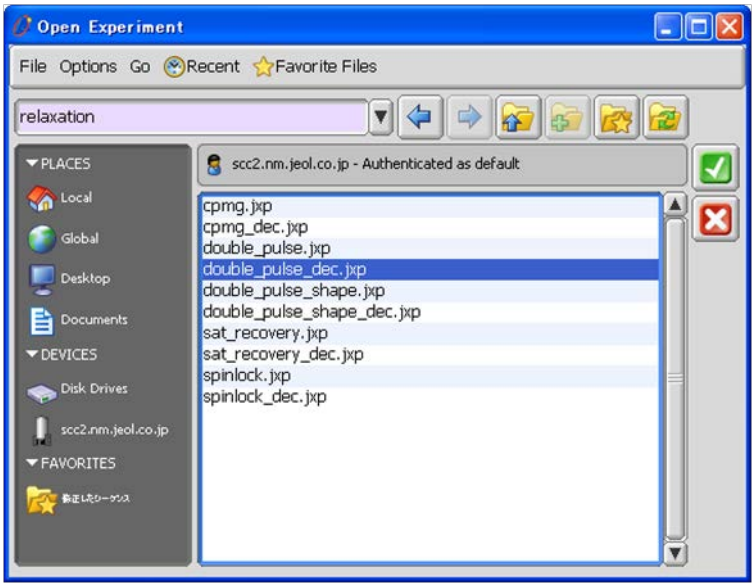


Fig. 1.1 Open Experiment window

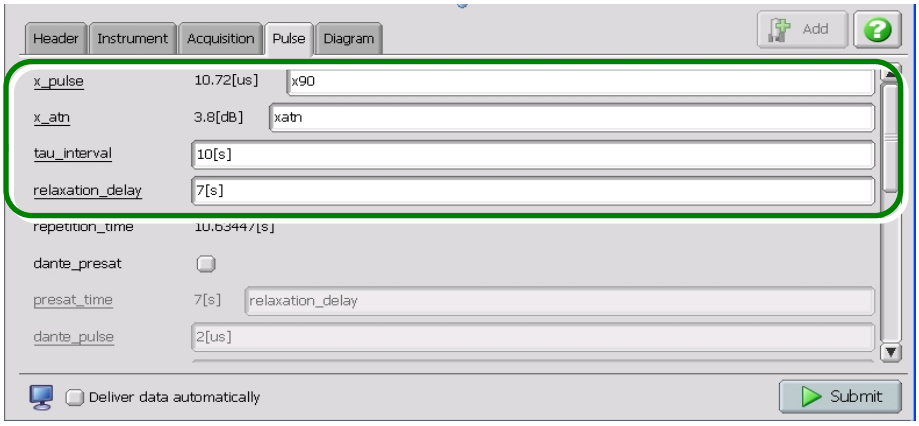
7. To perform T_1 measurement for ^{1}H, select **double_pulse.jxp** from the file name list box.
To perform T_1 measurement for ^{13}C, select **double_pulse_dec.jxp**.



The Experiment Tool window used to set the parameters will open.

8. Enter the following values.

x_ pulse	Enter the 90° pulse width obtained in Step 3.
tau_interval	Enter a value that is at most 1/10 of the expected T_1 as an initial value.
relaxation_delay	Enter a value that is at least 5 times the expected T_1.



9. Click the **Submit** button.
The measurement is carried out.

10. Perform data processing in the 1D processor window, and adjust the phase to turn the peak downward.

11. Increase **tau_interval** in the Experiment Tool window, and perform the measurement again.
Perform the phase correction on the obtained spectrum using the same phase correction values as those obtained in Step 8.
While you repeat this operation, the peak reverses and then turns upward. During the process, the **tau_interval** at the time when the peak disappears is obtained. This is the null point. You can obtain an approximate value of T_1 by multiplying the null point by 1.4.

■ Setting the parameters

1. After obtaining the null point, enter the approximate value of T_1 multiplied by 10 into relaxation_delay.
The peaks in the spectrum have different T_1 values. However, enter 10 times the maximum T_1 value of the peaks used for the T_1 measurement.

2. Based on the obtained approximate value of T_1, set array parameters (array variable) to **tau_interval**.
To enter the array parameter for T_1 measurement by the inversion recovery method, be sure to array the values in descending order starting with the greatest value. Use arrow buttons shown in Fig. 1.2 to switch between ascending and descending order.
Set the initial value of the array parameter (maximum value) to 10 times the approximate value of T_1, corresponding to infinite tau in the inversion recovery.

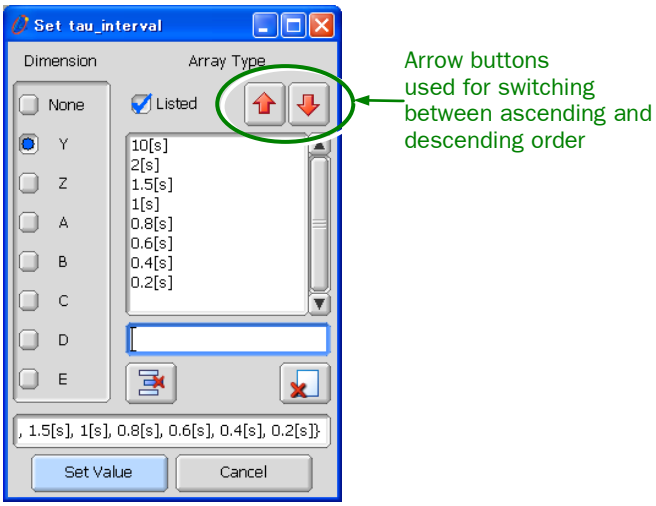


Fig. 1.2 Array parameter window

3. Click the **Set Value** button.
   The array parameter window closes, and the set values are entered into **tau_interval** in the Experiment Tool window.

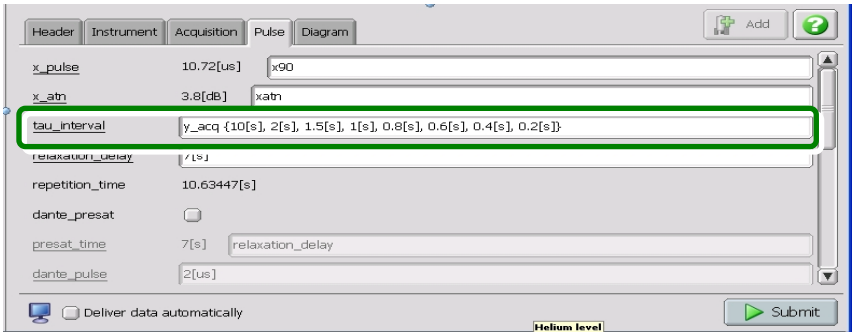


Fig. 1.3 Experiment Tool window

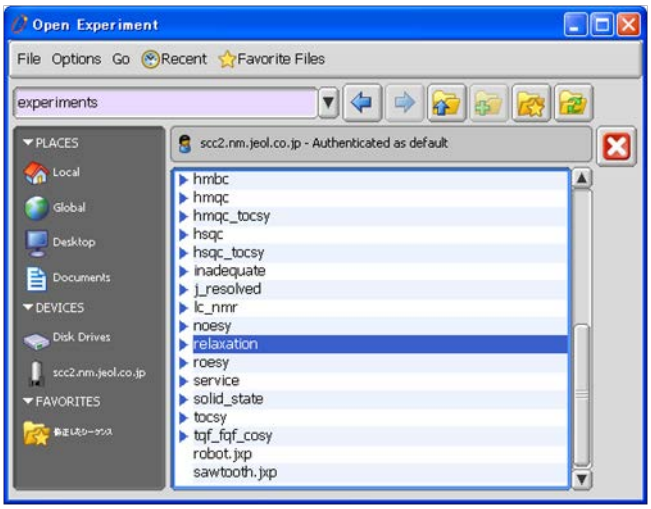
1.1.3 Measurement of Relaxation Time (T2)

To obtain T_2 with high accuracy, the approximate T_1 of the sample must be determined first. For measuring T_1, refer to section 1.1.1, “Evaluation of Relaxation Time (T1)” and section 1.1.2, “Measurement of Relaxation Time (T1)”.

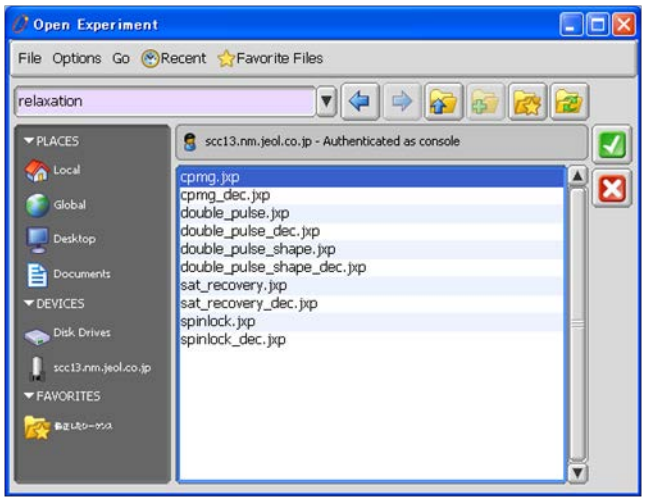
■ T2 Evaluation using the CPMG(Carr-Purcell-Meiboom-Gill) method

1. Register the sample in the **Samples** tab and perform the preparation before measurement (☞User’s manual, “LIQUID MEASUREMENT”).
2. Tune the probe.
3. Verify the 90° pulse width.
   ✍ To enhance accuracy of T2 measurement, verify the 90° pulse width of the sample used to measure relaxation time. To do this, perform array measurement in the single_pulse.jxp or single_pulse_dec.jxp measurement mode.
4. Click the **Create a Job with this Sample** button in the Spectrometer Control window.
5. Click the **Add Experiment** button in the **Jobs** tab.
   The Open Experiment window opens.

6. Click and double click experiments. After the directory list appears, double click **relaxation** in the list.



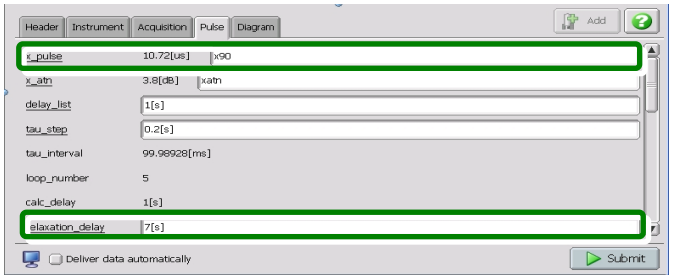
7. To perform T_2 measurement for ^{1}H, select **cpmg.jxp** from the file name list box. To perform T_2 measurement for ^{13}C, select **cpmg_dec.jxp**.



The Experiment Tool window used for setting the parameters will open.

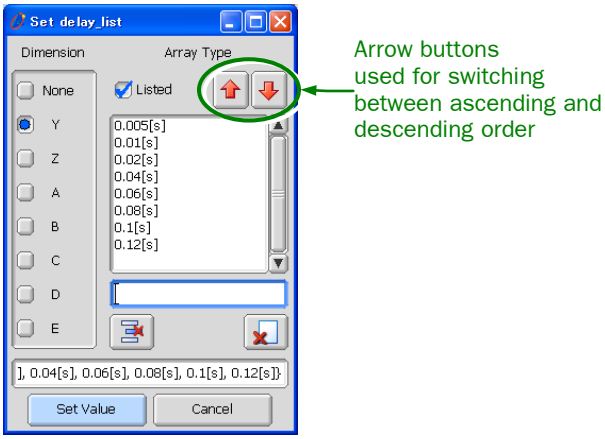
8. Enter the following values.

x_ pulse	Enter the 90° pulse width obtained in Step 3.
relaxation_delay	Enter a value that is at least 10 times the expected T_1.



9. Based on the obtained approximate value of T_2, set array parameters (array variable) to **delay_list**.

To enter the array parameter for T_2 measurement by the CPMG method, be sure to array the values in ascending order starting with the smallest value. Use arrow buttons shown below to switch between ascending and descending order.



10. Click the **Set Value** button.

The array parameter window closes, and the set values are entered into **delay_list** in the Experiment Tool window.

1.1.4 Measurement of Relaxation Time (T1ρ)

To obtain $T_{1\rho}$ with high accuracy, the approximate T_1 of the sample must be determined first. For measuring T_1, refer to section 1.1.1, “Evaluation of Relaxation Time (T1)” and section 1.1.2, “Measurement of Relaxation Time (T1)”.

■ T1ρ Evaluation using the spin-lock method

1. Register the sample in the **Samples** tab and perform the necessary preparation before the measurement (☞User’s manual, “LIQUID MEASUREMENT”).

2. Tune the probe.

3. Verify the 90° pulse width.

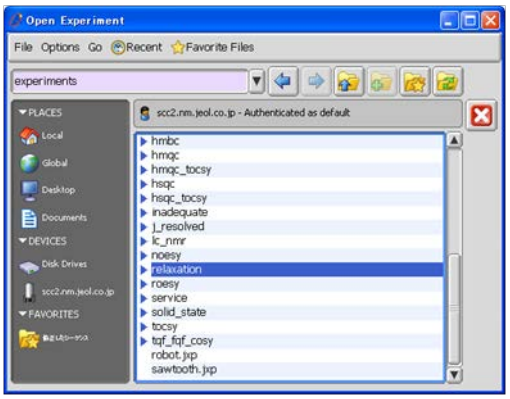
To enhance accuracy of T1ρ measurement, verify the 90° pulse width of the sample used to measure relaxation time. To do this, perform array measurement in the single_pulse.jxp or single_pulse_dec.jxp measurement mode.

4. Click the **Create a Job with this Sample** button in the Spectrometer Control window.

5. Click the **Add Experiment** button in the **Jobs** tab.

The Open Experiment window opens.

6. Click  and double click experiments. After the directory list appears, double click **relaxation** in the list.

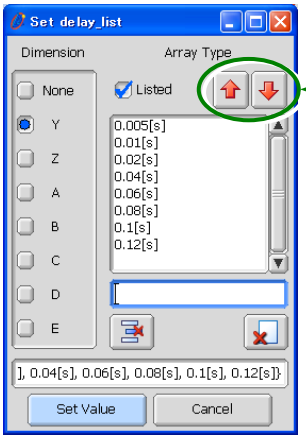


7. To perform $T_{1\rho}$ measurement for ^{1}H, select **spinlock.jxp** from the file name list box. To perform $T_{1\rho}$ measurement for ^{13}C, select **spinlock_dec.jxp**.
The Experiment Tool window used to set the parameters opens.

8. Enter the following values.

x_ pulse	Enter the 90° pulse width obtained in Step 3
relaxation_delay	Enter a value that is at least 10 times the expected T_1

9. Based on the obtained approximate value of $T_{1\rho}$, set array parameters (array variable) to **x_spinlock_time**.
To enter the array parameter for $T_{1\rho}$ measurement by the spin-lock method, be sure to array the values in ascending order starting with the smallest value. Use arrow buttons shown below to switch between ascending and descending order.



Arrow buttons used for switching between ascending and descending order

10. Click the **Set Value** button.
The array parameter window closes, and the set values are entered into **x_spinlock_time** in the Experiment Tool window.

Exceeding the required power and time for spin-locking might damage the probe. Make sure that you enter the appropriate values for x_spinlock_atn and x_spinlock_time.

1.2 RELAXATION TIME DATA PROCESSING

Data processing following measurement is performed in the nD processor window, and then T_1 calculation is performed in the Curve Analysis window. This section explains the procedure for data processing.

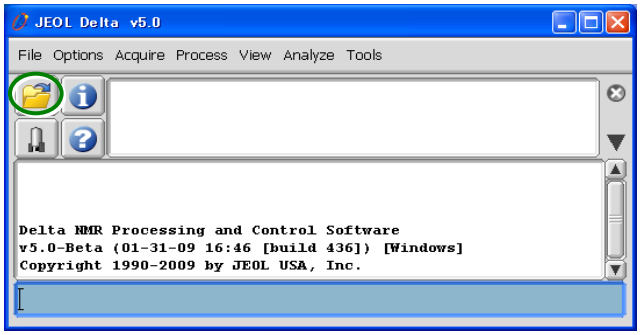
1.2.1 Loading Relaxation Time Measurement Data

First, load the measurement data in the nD Processor window in the same way that is used for 2D measurement data processing.

If measurement data was transferred from the spectrometer immediately after relaxation time measurement finished, and the nD Processor window is already open, you can omit the procedure in Section 1.2.1.

Use the following steps to load the relaxation time measurement data (FID) in the nD Processor window.

1. Click the **Open file** button in the Delta console window.



The File Browser window is displayed.

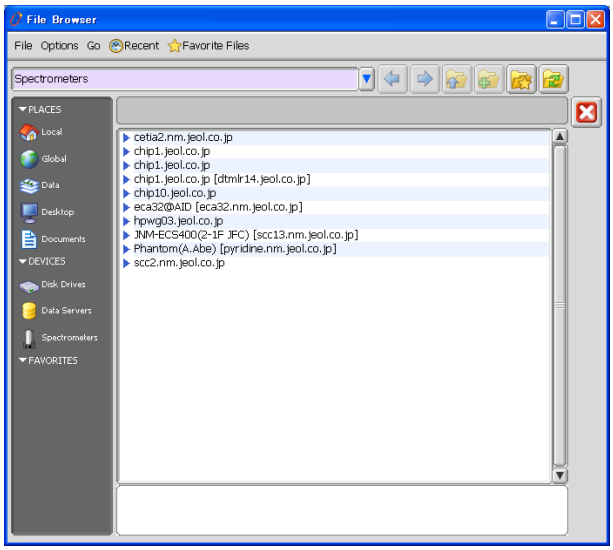


Fig. 1.4 File Browser window

2. Click the Data Servers button and select the spectrometer that has the data that you want to load from the list box.

Be careful because the relaxation time measurement data obtained in the array measurement is represented as having 2D format.

3. Select the data to load and click the button.
The nD Processor window opens.

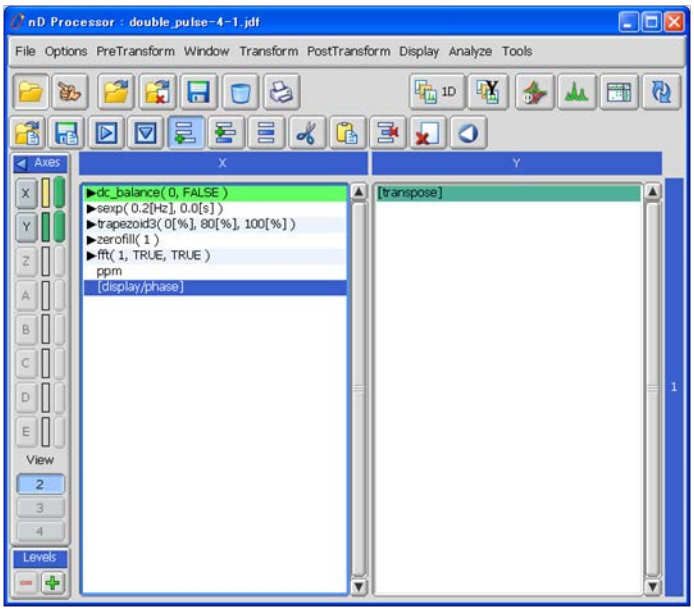
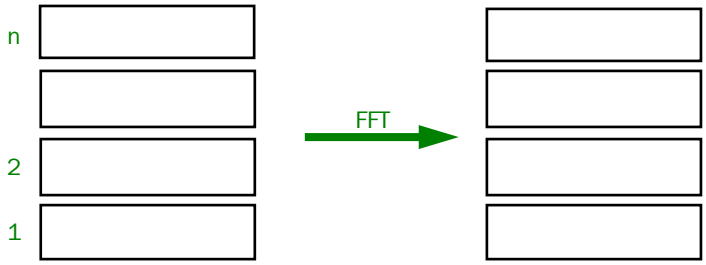


Fig. 1.5 nD Processor window

1.2.2 Processing Relaxation Time Measurement Data

Processing of the relaxation time measurement data is performed by using the following three steps.

- Step 1
  For processing the relaxation time measurement data, all sets of measurement data from the first to the nth are Fourier-transformed together under the same condition.



- Step 2
  The processed data sets are transferred to the Curve analysis window. Then, the peak for relaxation time calculation is selected from any numbered data set by peak picking.
- Step 3
  The relaxation times are obtained by approximate calculation.

The following explains the procedures in the same order as the preceding steps.

1.2.2a Fourier-transforming (Step 1)

- **If an appropriate window function and phase correction values are already known and are saved in the processing list**

1. Load the desired processing list in the nD Processor window.

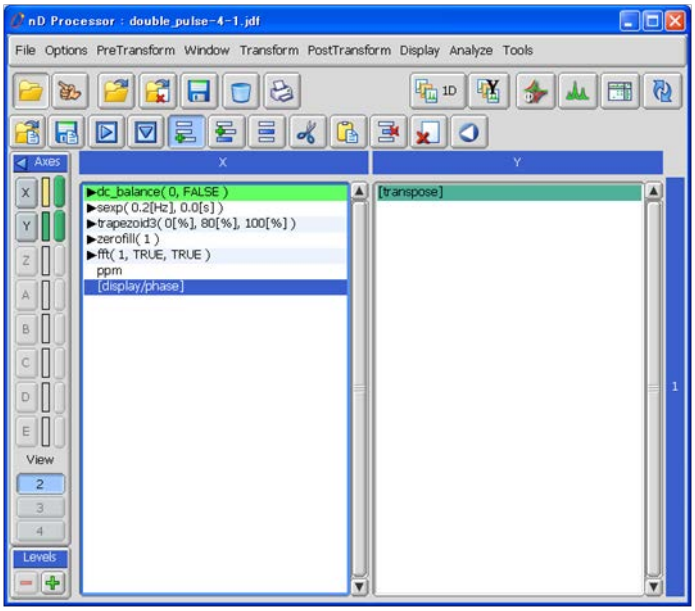


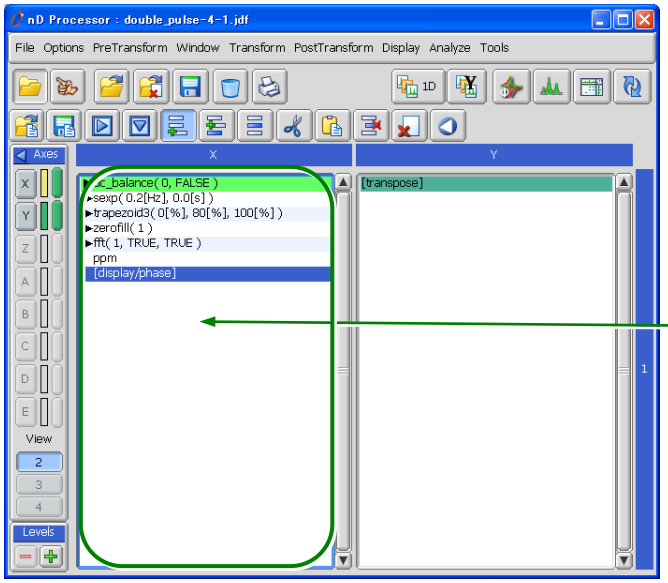
Fig. 1.6 nD Processor window

2. Click either the **Process File And Put In Data Slate** button or the **Process File And Put In Data Viewer** button.
Normally, click the button.
Clicking the button performs the data processing specified in the processing list for the first to the nth measurement data sets, and displays the processed data sets in the Data Slate window.
Clicking the button performs the data processing specified in the processing list for the first to the nth measurement data sets, and displays the processed data sets in the Data Viewer window.

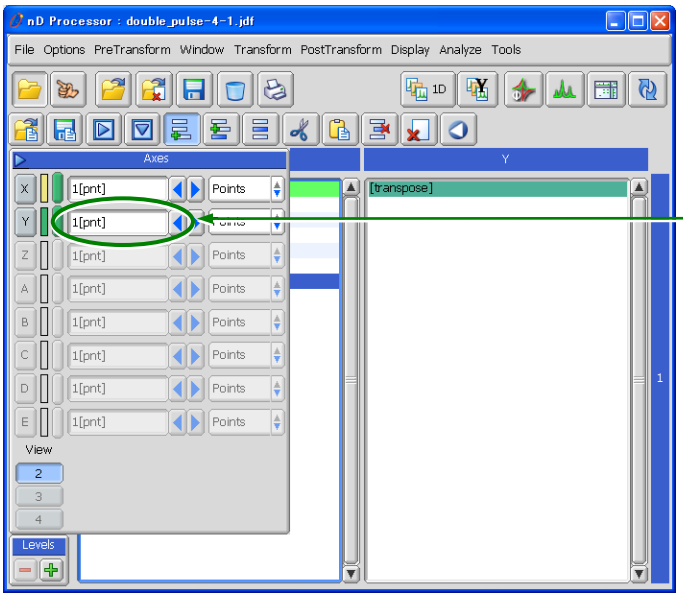
● If an appropriate window function and phase correction values are not known:

Display a set of relaxation time measurement data as 1D slice data in the 1D Processor window, and obtain an appropriate window function and phase correction values.

1. Click the process list area of X axis of the nD processor window.



2. Click the **Axes** Axes button to display the slice position setting screen, and specify the data that you want to slice as the number of points from the number of sets (1 - n) in the relaxation time measured data.
Normally, slice the first set of measurement data as it is easy to correct its phase.



3. Click the **1D** Slice  button.
The slice data at the specified position is displayed in the 1D Processor window.

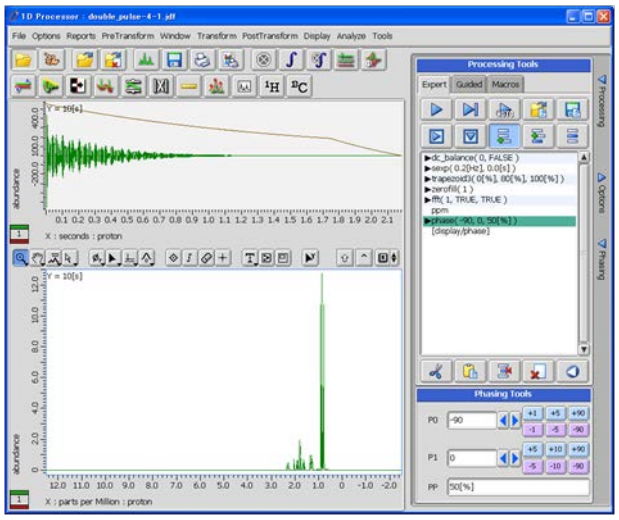


Fig. 1.7 1D Processor window

4. Change the window function and its parameter values, and enter an appropriate window function condition.
This operation is the same one that is used to change the ordinary 1D data window function.

5. Carry out phase correction, and obtain the appropriate phase correction values.
This operation is the same one that is used for correcting the phase of the ordinary 1D data.

Be sure to perform manual phase correction without using automatic phase correction.

- If you cannot correct the phase of the J-coupled peak with J-modulation during T_2 measurement, refer to Reference in Step 7.

6. Close the**1D Processor** window.
The window function condition and the phase correction values obtained in Steps 4 and 5 are automatically inserted in the processing list in the nD Processor window.

7. Click the Process File And Put In Data Slate  button or Process File And Put In Data Viewer  button
Normally, click the  button.
Clicking the  button performs the data processing specified in the processing list for the first to the nth measurement data sets, and displays the processed data sets in the Data Slate window.
Clicking the  button performs the data processing specified in the processing list for the first to the nth measurement data sets, and displays the processed data sets in the Data Viewer window.

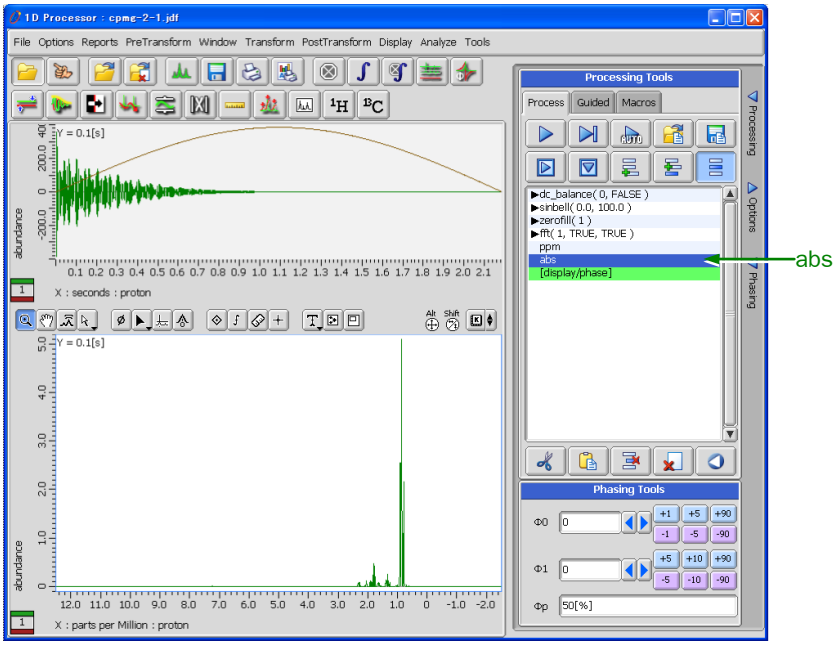
● Reference: If you cannot correct the phase of T_2 (transverse relaxation time) measurement data:

Perform Step 4 using the sinbell window function. Moreover, perform power processing according to the following procedure without the phase correction in Step 5.

a. Click the Append button in the1D Processor window.

b. Select **PostTransform–Abs** from the menu bar.

The power processing step abs is entered in the processing list.



c. Proceed to Step 6.

1.2.2b Selecting a peak (Step 2)

To perform this operation, you need to load the relaxation time measurement data after Fourier transformation in the Curve Analysis window.

■ Opening the Curve Analysis window

◆ Select Analyze–Curve Analysis from the menu bar in the Delta Console window.

The Curve Analysis window opens.

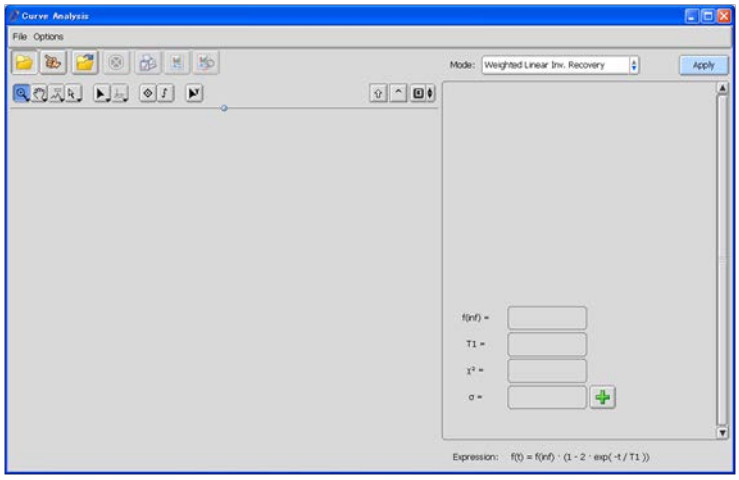


Fig. 1.8 Curve Analysis window

■ Loading the relaxation time measurement data after Fourier transformation in the Curve Analysis window

● If relaxation time measurement data after Fourier transformation is saved on a hard disk

1. Click the **Get Data From File** button in the Curve Analysis window.
2. Click the **Open Data File** button.
   The Open File window opens.

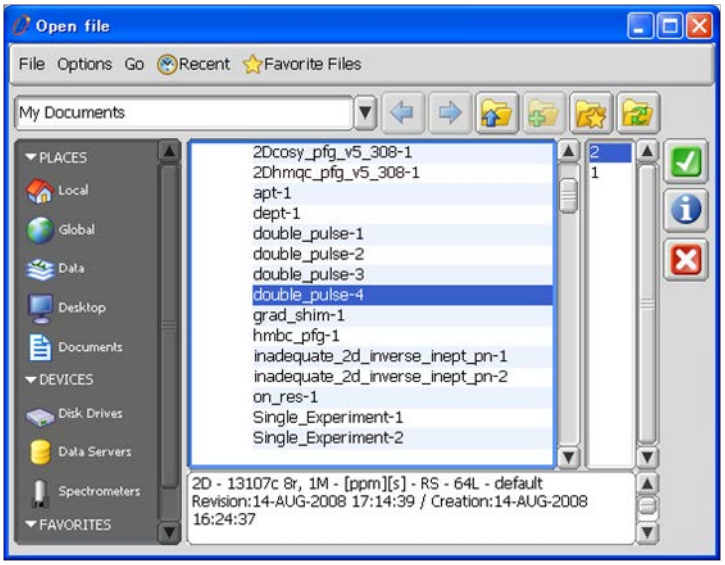
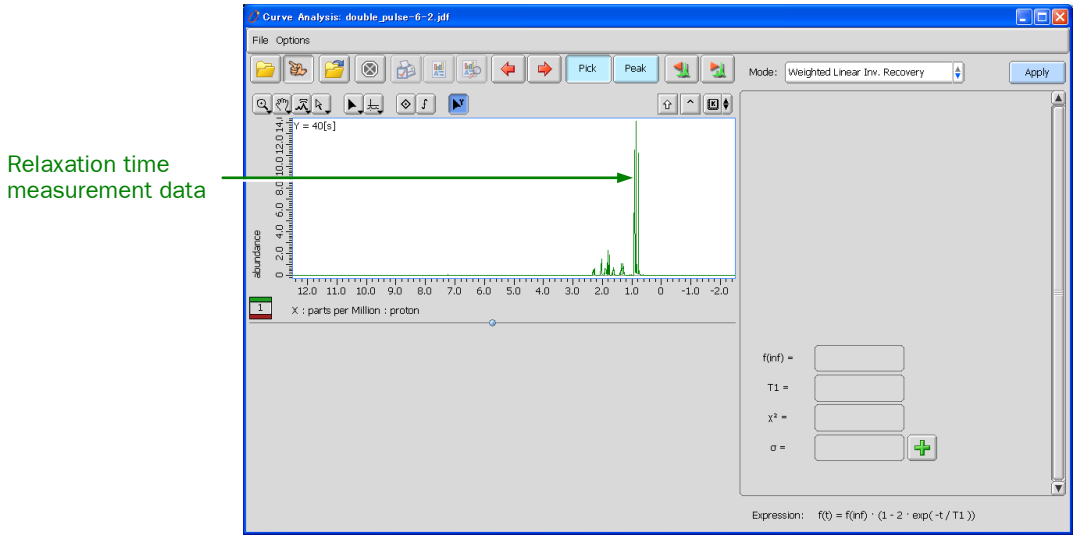


Fig. 1.9 Open File window

3. From the list box in the Open File window, select the file in which the relaxation time measurement data after Fourier transformation is saved, and then click the button.
   This loads the selected relaxation time measurement data into the Curve Analysis window.



● If relaxation time measurement data after Fourier transformation is being displayed

1. Click the **Open Data By Fingering a Geometry** button in the Data Slate window.
2. Click the **Open Data File** button.
   The mouse pointer changes to the shape of a finger.
3. Move the mouse pointer to the area in which the relaxation time measurement data after Fourier transformation is displayed, and click it.
   The selected relaxation time measurement data is loaded in the Curve Analysis window.

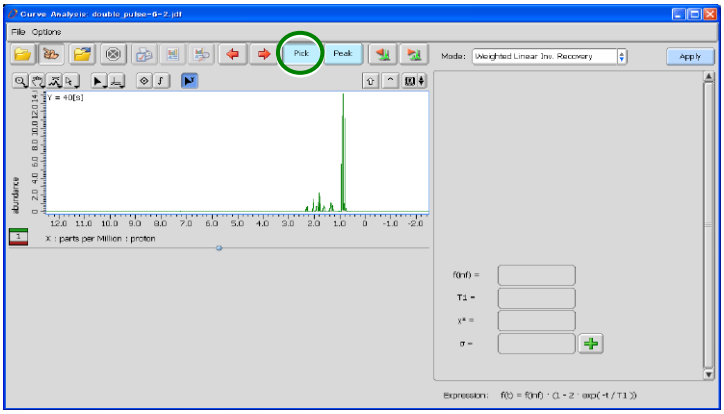
■ To select a peak

Either the **Pick** mode or the **Peak** mode is used to select a peak.
If there are a lot of peaks for T_1 measurement, and you want to print all those T_1 values, the **Peak** mode is useful. You need to list the peaks to be used in the **Peak** mode in the peak-picking list.
The **Pick** mode can be used to obtain T_1 at any position of a spectrum. The top of the peak is not required for T_1 calculation in the **Pick** mode, making it different from the **Peak** mode.

● To select a peak in the Pick mode

This section explains how to select a peak and how to create the table that lists the peak intensity in the **Pick** mode.

1. Click the **Pick** button in the Curve Analysis window.
   The cursor tool bar in the spectral display area changes to the **Pick** mode.

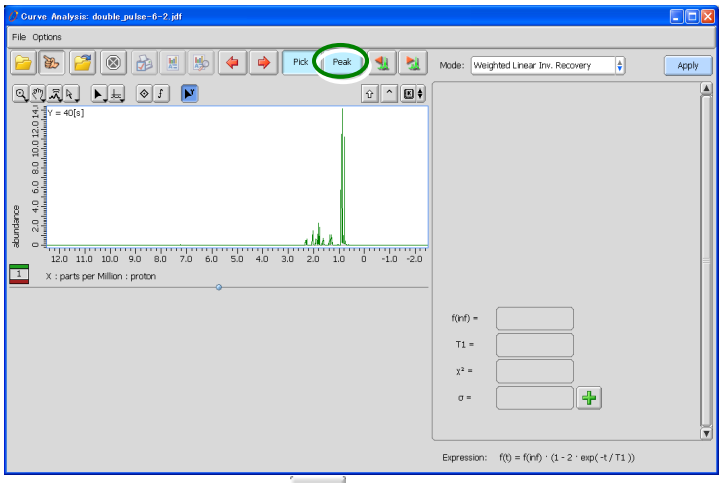


2. Select the **Pick position and perform action** button from the cursor tool.
3. Move the mouse pointer onto the X-ruler in the spectrum display area, and press and hold the left mouse button.
   The cursor is displayed.
4. With the mouse button pressed, move the cursor to the top of the peak whose relaxation time you want to obtain, and release it.
   The pick position marker is displayed at the position at which you released the mouse button.

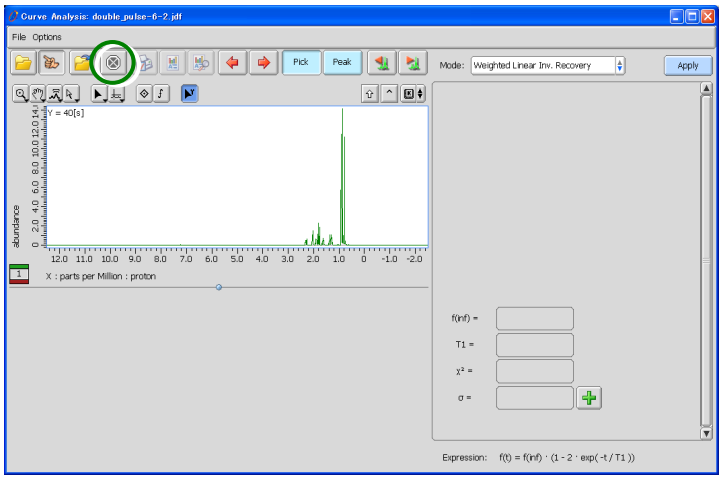
● To select a peak in the Peak mode

This section explains how to select a peak in the **Peak** mode.

1. Click the **Peak** button in the Curve Analysis window.

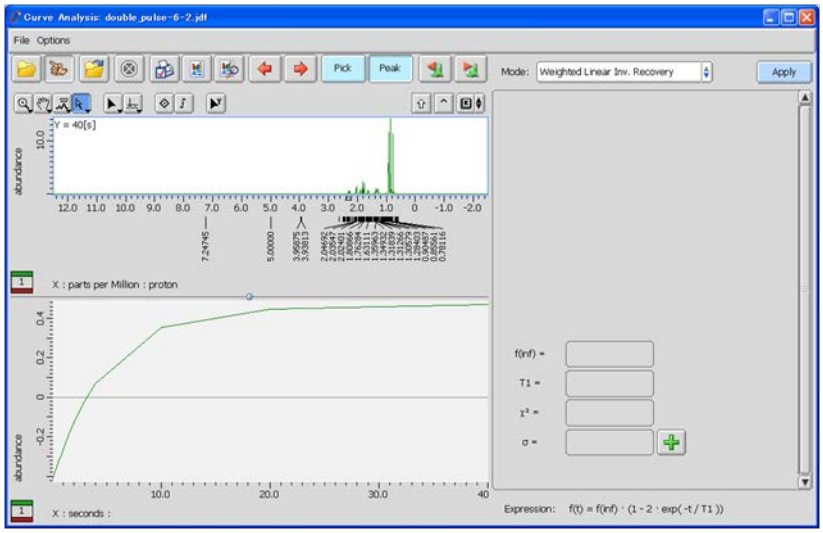


2. Click the **Peak Pick Data**  button.
   Peak picking is carried out.
   If needed, before running **Peak Pick**, change the threshold and noise levels so that small signals or peaks having fine splitting, whose T_1 values are not needed, are not picked up.



3. Click the **Select**  button in the cursor tool on the **Peak** mode.
4. Move the mouse pointer onto the X-ruler of the spectrum display range, press and hold down the left mouse button.
   The cursor appears.

5. Move the cursor to the position that crosses to the top of the peak to obtain the relaxation time, and release the mouse button.
A peak position mark appears at the position at which the mouse button was released.



When printing out the T_1 values of two or more signals at the same time, drag the cursor around the peak area. All peaks that have been listed by peak picking in the area are selected, and numerical markers become blue.

■ How to obtain the integrated value of the peak

You can analyze the data using the integrated value.

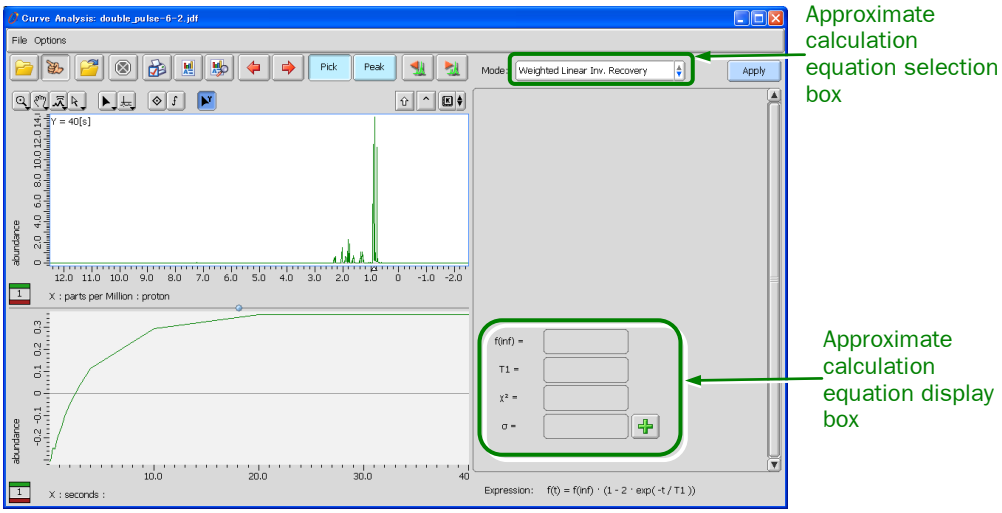
1. Perform peak picking of signals to be integrated in the **Peak** mode as a normal peak picking.
2. Select either **Track** or **Track Drift** from **Options** in the menu bar.
3. Select **Integral** from **Options** in the menu bar.
4. Selecting the peak-picked peaks using **Select peaks** in the peak tools displays a graph in the lower area of the screen (the integration is performed automatically).

1.2.2c Obtaining relaxation times by approximate calculation (Step 3)

This section explains how to obtain relaxation times by approximate calculation.

■ To select an approximate calculation equation

◆ Select the desired approximate calculation equation in the approximate calculation equation selection box.
The selected approximate calculation equation is displayed in the approximate calculation equation display box.



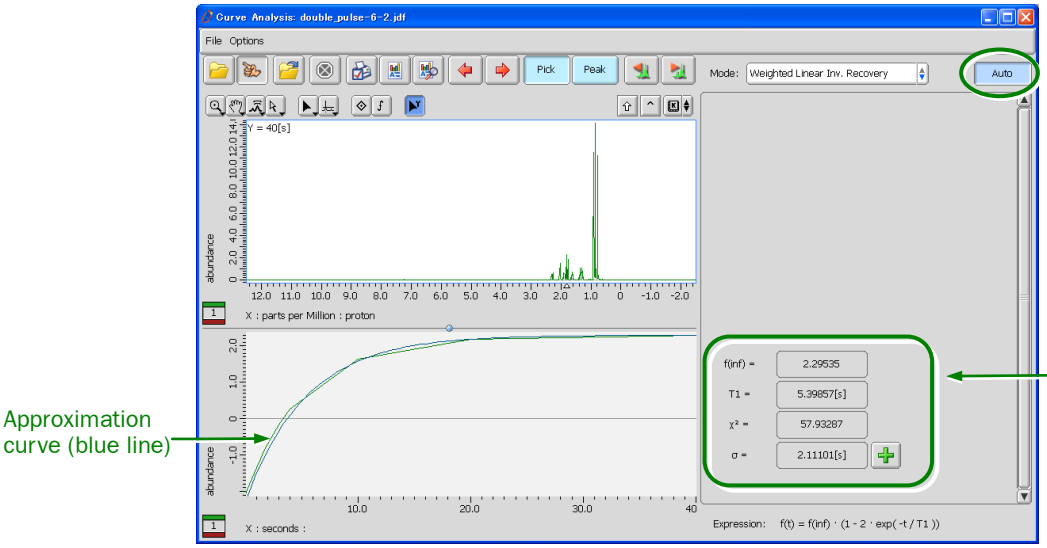
Approximate calculation equation	Description
Weighted Linear	Weighted linear least squares method; Lower weight values are applied to measurement points having higher tau_interval values.
Unweighted Linear	Unweighted linear least squares method
Nonlinear	Nonlinear least squares method

Hereafter, **Inv. Recovery**, **Sat. Recovery**, and **Spin Lock** mean Inversion Recovery method, Saturation Recovery method, and Spin Lock method, respectively.

■ To execute an approximate calculation and obtain relaxation times

◆ Click the **Apply** button.

The approximate calculation is executed, and the calculated result of the relaxation time and the blue approximation curve are displayed.



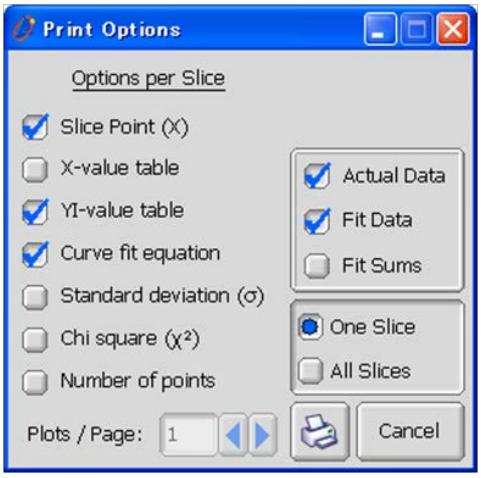
When we enter the selection state by pressing the **Apply** button, the display changes to **Auto**. When changing the peak to obtain a relaxation time or when changing selection of an approximate calculation formula, an approximate calculation is performed automatically.

You can increase functions for calculation by clicking the button at the bottom right in the Curve Analysis window. In this case, you need to enter the approximate value before performing curve fitting.

1.2.3 Plotting Calculation Results

1. Click the **Plot Data File** button in the Curve Analysis window.

The Plot Options dialog box opens.



2. Select the items you want to plot.

To print the results of relaxation time measurements of more than one peak that were selected in the **Peak** mode together, click the **All Slices** button.

3. Click the Plot data with current state button.

The items that were selected in Step 2 are plotted.

2 MEASUREMENT OF DIFFUSION COEFFICIENT AND DATA PROCESSING

2.1 EVALUATION METHOD OF DIFFUSION COEFFICIENT

Generally, diffusion is a process by which the concentration of solution or temperature of a sample approaches uniformity. However, here "diffusion" means self-diffusion, in which a molecule changes its position in solution or in solid state. Therefore, the diffusion coefficient is the measure of the movement speed of a molecule.

■ Evaluation method of diffusion coefficient by NMR

Although the translational motion of a molecule is a 3-dimensional motion, the translational motion that is actually observed by NMR is only the motion parallel to the z-axis because a magnetic field gradient is applied along the z-axis.
If the translational molecular motion is a random walk, the probability that the molecule moves a distance Δz from its initial position during time t is expressed by the following Gaussian function.

$$P(\Delta z, t) = (4\pi Dt)^{1/2} \exp(-\Delta z^2 / 4Dt)$$

where D is the diffusion coefficient of the molecule. In this function, Δz is distributed over a wider range with increasing t.
In PFG NMR, the transverse magnetization produced by a 90° pulse is in the state where the phase is coherent in the beginning. If PFG is then applied, since the spin feels a magnetic field strength corresponding to its z coordinate, the phase of the magnetization changes with the magnetic field strength. If the strength of the magnetic field gradient is G, the duration of the field gradient pulse is δ, and the gyromagnetic ratio is γ, then the final amplitude of phase modulation is $\Phi = \gamma G \Delta z \delta$ for a square-wave field gradient in the direction of z axis. The distribution function of the phase modulation is as follows.

$$P(\Phi, t) = (4\pi Dt)^{-1/2} (\gamma G \delta)^{-1/2} \exp(-\Phi^2 / 4(\gamma G \delta)^2 Dt)$$

Therefore, when a certain coherence disappears due to dephasing by the first PFG, and the coherence is reestablished due to rephasing by the second PFG, the signal intensity is described as follows if the time between the two FG pulses is Δ:

$$I(G, \Delta) = I(0, \Delta) \exp(-D(\gamma G \delta)^2 \Delta)$$

Furthermore, when the influence of the diffusion during the FG pulses cannot be disregarded, it is corrected as follows.

$$I(G, \Delta) = I(0, \Delta) \exp(-D(\gamma G \delta)^2 (\Delta - \delta / 3))$$

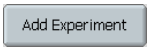
Therefore, the diffusion coefficient D can be evaluated from the formula by changing either the strength of the magnetic field gradient G, the duration of the field gradient pulse δ, or the time between the two magnetic-field-gradient pulses Δ.

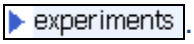
2.2 HOW TO MEASURE PFG STRENGTH

In order to obtain the diffusion coefficient, it is necessary to measure the strength of the magnetic-field gradient (G). Therefore, the maximum G strength of the system being used should be measured before carrying out an actual measurement.

■ Simple way to measure PFG strength

1. Prepare a water sample with the liquid height adjusted to about 5 mm.
   ✍ Prepare a sample tube such as a micro-cell in which the height of liquid is clearly known.
2. Register the sample in the **Samples** tab and perform the preparation before measurement (☞ User's manual, "LIQUID MEASUREMENT").
3. Select the registered sample and click the **Create a Job with this Sample** 

button.
   The **Job** tab opens.
4. Select the job and the sample, and click the **Add Experiment** 

button.
   The Open Experiment window opens.
5. Click the  button and double click 

. The directory list appears, so double click **diffusion** in the list.

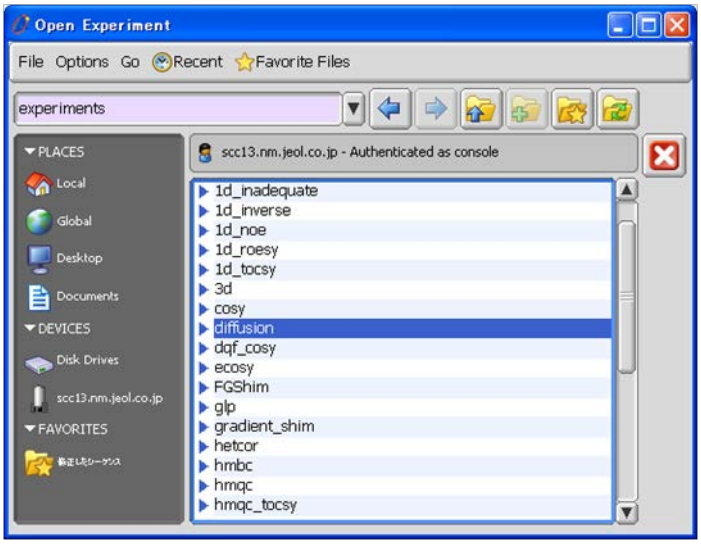


Fig. 2.1 Open Experiment window

6. Select the **fg_power_check.jxp** sequence from the File name list box.
   The Experiment Tool window for setting parameters opens.
7. Set the parameter **grad_amp**.
   ✍ Since a long magnetic-field-gradient pulse will be used in the **fg_power_check.jxp** sequence, do not use a large intensity for the magnetic-field gradient. Set the value of **grad_amp** from 1 to 5%.
8. Click the **Submit** button.
   A measurement is performed.

9. Process the data in the 1D processor window and display the absolute value of the spectrum.

In order to display the absolute value, perform **abs** processing.

10. Measure the frequency at both ends of the obtained rectangular spectrum in Hz.

11. **Select Tools–Calculators–Gradient Strength** from the menu bar of the Delta Console window.

The Gradient Strength dialog box opens.

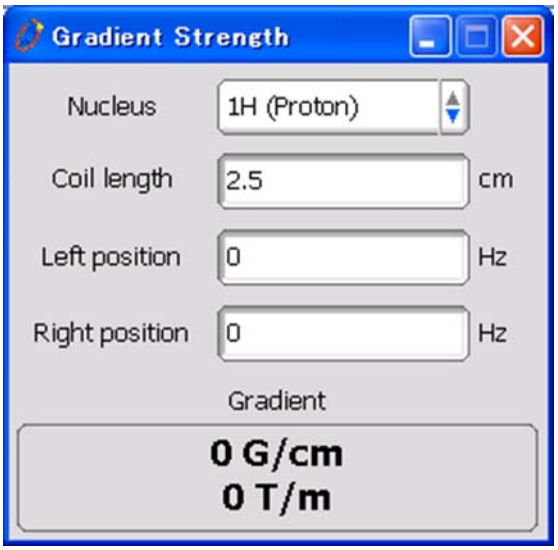


Fig. 2.2 Gradient Strength dialog box

12. Input values into each item of the Gradient Strength dialog box.

Select **1H** (Proton) in **Nucleus,** and input the liquid height of the sample used into **Coil length** column. Moreover, input the frequencies obtained in step 8 into the **Left position** and **Right position** columns.

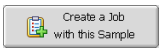
The obtained magnetic-field-gradient strength is displayed in the Gradient Strength dialog box.

The displayed magnetic-field-gradient strength corresponds to the value of **grad_amp** (% of the maximum output) set in Section 7.

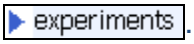
2.3 MEASUREMENT OF DIFFUSION COEFFICIENT (D)

As discussed above, the measurement of the diffusion coefficient can be carried out by changing either the field-gradient strength G, the duration of gradient pulse δ, or the time between two FG pulses Δ.
However, in the measurement in which a time parameter such as the duration of the field gradient pulse δ or time between FG pulses Δ changes, you have to take into account the influences on time, such as relaxation. Therefore, the measurement by changing magnetic-field-gradient strength G is presently in general use. The procedure for measurement of the diffusion coefficient by changing the magnetic-field-gradient strength G (within the range from 100 to 300 mT/m) is explained below.

■ To obtain measurement conditions

1. Register the sample in the **Samples** tab and perform the necessary preparation before measurement (☞User's manual, "LIQUID MEASUREMENT").
2. Stop the sample spinning, and tune the probe.
3. Check the 90° pulse width.
   In order to improve the accuracy of the diffusion coefficient measurement, we recommend that you check the 90° pulse width of the sample you are measuring. For checking the 90° pulse, perform an array measurement using the measurement mode **single_pulse.jxp** or **single_pulse_dec.jxp**.
4. Select the registerd sample and click the **Create a Job with this Sample** 

button.
   The **Job** tab opens.
5. Select the job and the sample, and click the **Add Experiment** 

button.
   The Open Experiment window opens.
6. Click the  button and double click 

. The directory list appears, so double click **diffusion** in the list.

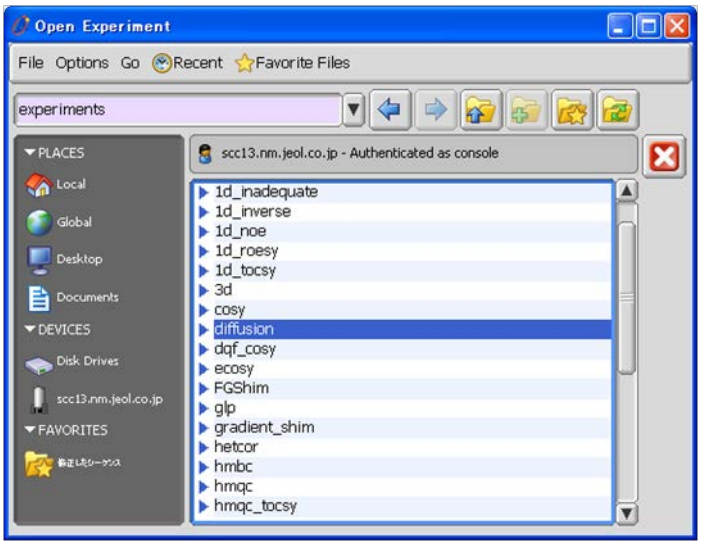


Fig. 2.3 Open Experiment window

7. Select a desired sequence from the File name list box.

The Experiment Tool window for setting parameters opens.

8. Input the following value if needed.

The values of **x_pulse** and **gradient_max** shown below are loaded automatically from the default values in the probe file. If the verified values differ from the values in the probe file, input the verified values into the probe file.

x_pulse	90° pulse width which you obtained in step 3.
gradient_max	The maximum magnetic field strength (T/m) in the system currently used.

In advance measure, the maximum magnetic field strength to be input into **gradient_max**, for every system combination of the probe and the maximum output of the FG power supply, by referring to section 2.2, "HOW TO MEASURE PFG STRENGTH."

9. Input values for the parameters for measuring the diffusion coefficient.

The following three parameters are necessary for measuring the diffusion coefficient.

diffusion_time	Interval of two FG pulses (diffusion time Δ).
delta	Duration of magnetic-field-gradient pulse.
g	Magnetic-field strength (G).

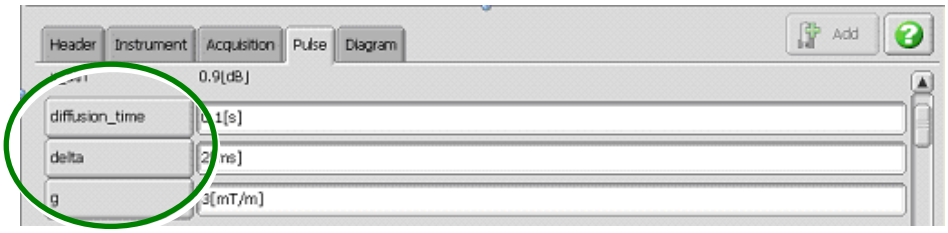


Fig. 2.4 Experiment Tool window

10. Input a number about 10 times the value of T_1 into **relaxation_delay**.

11. Perform an array measurement with the minimum value and the maximum value of the variable magnetic-field strength (**g** parameter) that are used in the actual measurement.

For example, to change magnetic field gradient from 100 mT/m to 300 mT/m, carry out an array measurement at 100 mT/m and 300 T/m.

The instrument cannot output a magnetic field strength greater than **gradient_max**.

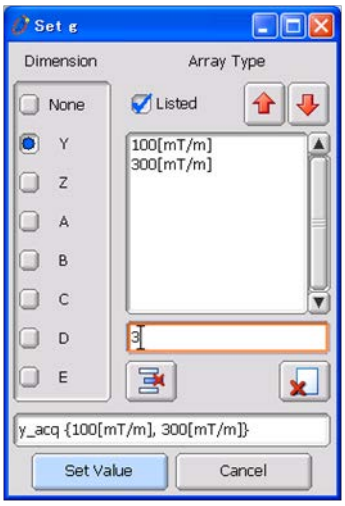
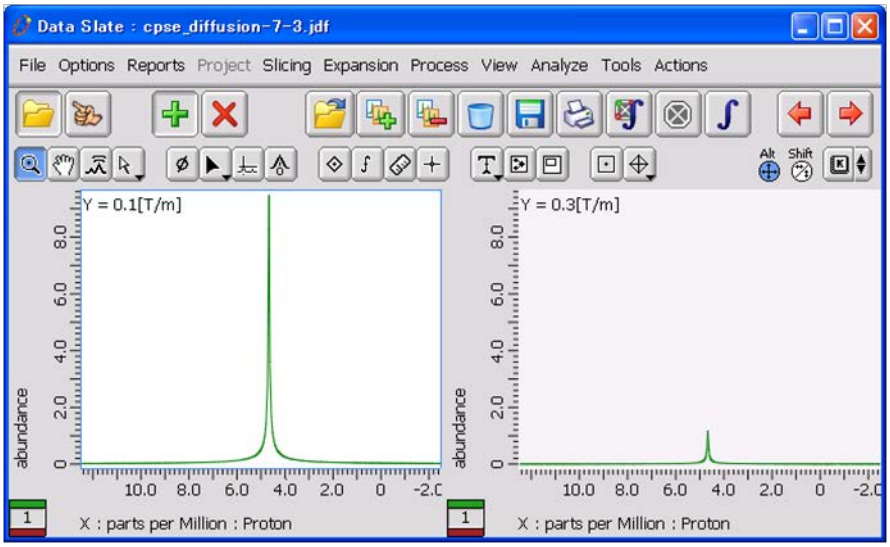


Fig. 2.5 Array parameter dialog box

12. Process the data in the nD processor window, and check the decay of the signal.

Repeat steps 8 and 9, changing the values of **diffusion_time** and **delta** so that the decay ratio of the signal is within the range of 10:1 to 20:1 for the maximum and minimum of field gradient strength.



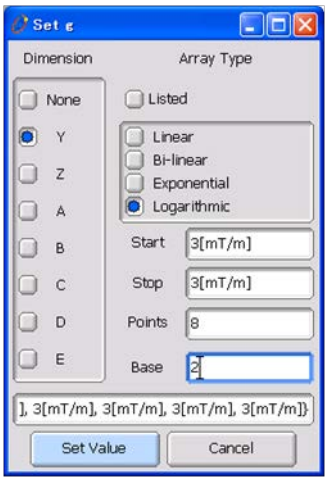
■ Measurement of diffusion time

1. Set up the conditions with various parameters obtained in the procedure "■To obtain measurement conditions".

Set up scans so that you obtain a sufficient S/N ratio even for the decayed signal.

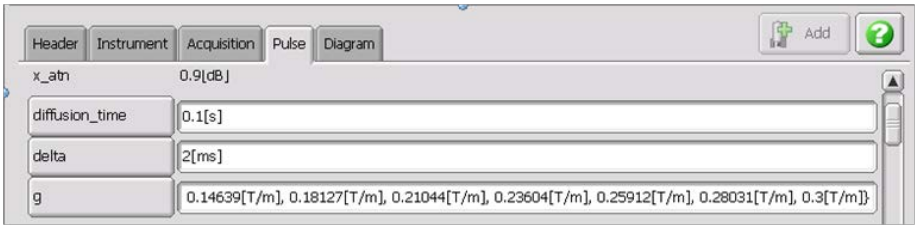
2. Set **g** to suitable array variables in the range of the minimum and maximum value of the variable magnetic-field gradient used in the condition setting.

In measurement of a diffusion coefficient, good measurement can be performed by changing the array variables so that the squares of the magnetic field gradients are at equal interval. For this reason, the array variables can be easily set by selecting **Logarithmic** as an **Array Type** and by setting the **Base** value to 2.



3. Click the **Set Value** button.

This closes the array parameter window, and inputs the set values into the Experiment Tool window.



4. Click the **Submit** button.

Measurement starts.

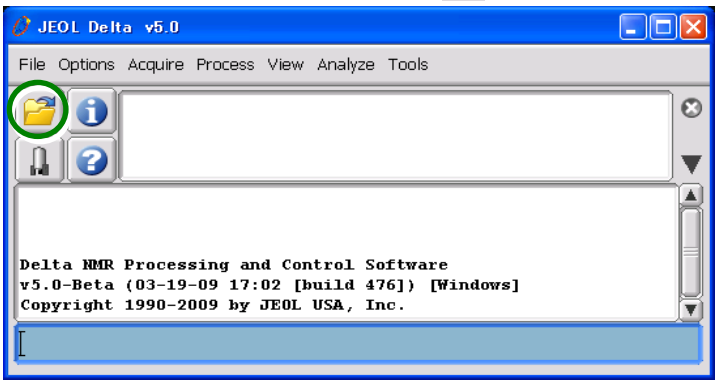
2.4 PROCESSING DIFFUSION MEASUREMENT DATA

After measurement, process the data in nD Processor window, and use the Curve Analysis window for calculation of the diffusion coefficient. The procedure is explained below. First, recall the measurement data into the nD Processor window as in two-dimensional measurement data processing. The operation of section 2.4.1 is not necessary when the measurement data is transmitted from the spectrometer immediately after the end of the diffusion-coefficient measurement, and when the nD Processor window is already displayed.

2.4.1 Loading Diffusion Coefficient Measurement Data

In order to load the diffusion coefficient measurement data (FID) into the nD Processor window, perform the following procedure.

1. Click the **Open file and choose tool** button in the Delta Console window.



The File Browser window appears.

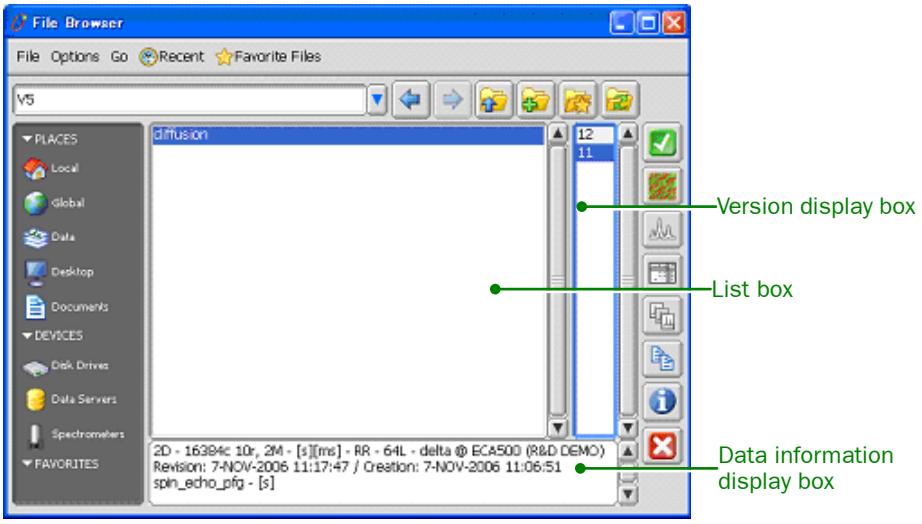
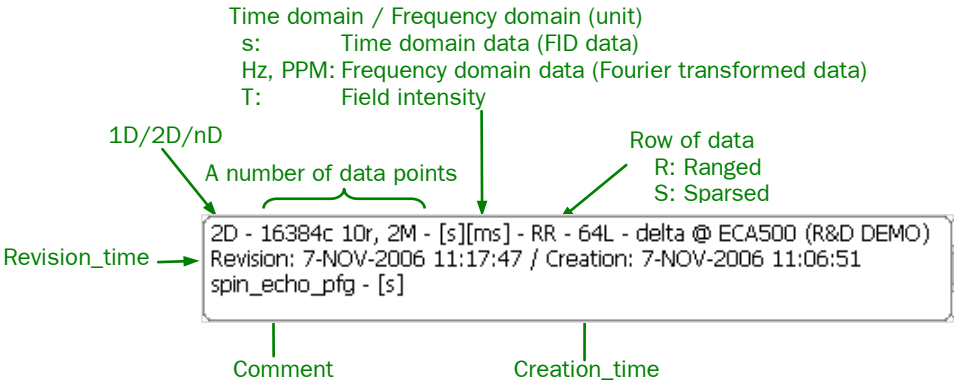


Fig. 2.6 File Browser window

2. Click the data file in the filename list box.

In the data information display box, the data information of the newest version is displayed as shown below. Note that the format of the data obtained by the array measurement is displayed as 2D.



3. After checking the data domain in the data information display box, select the version of the stored FID from the version display box.

If the newest version of the data displayed in step 2 is the time domain data (FID data), selection of a version is unnecessary.

4. Click the  button (or the  button).

The nD Processor window opens.

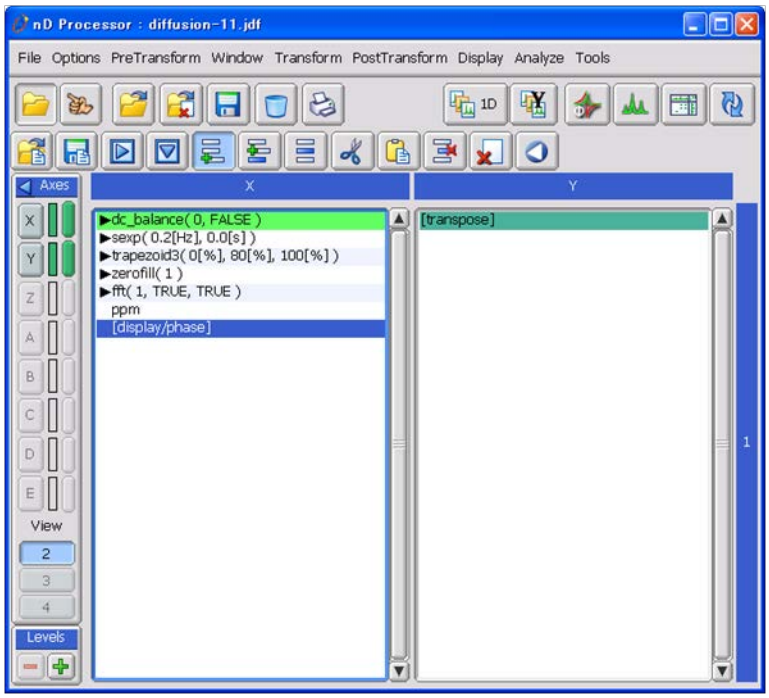
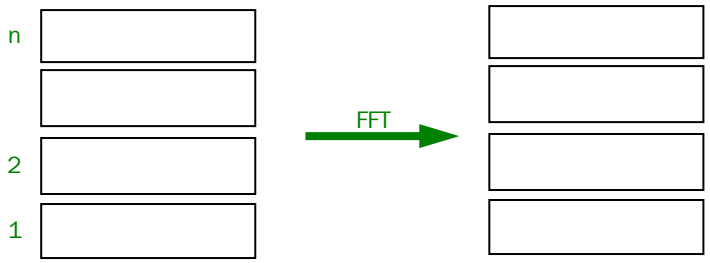


Fig. 2.7 nD Processor window

2.4.2 Procedure for Processing Diffusion Coefficient Measurement Data

The processing of the diffusion coefficient measurement data consists of the following three steps.

- Step 1
  For processing the diffusion measurement data, all sets of measurement data from the first to the nth are Fourier-transformed together under the same condition.



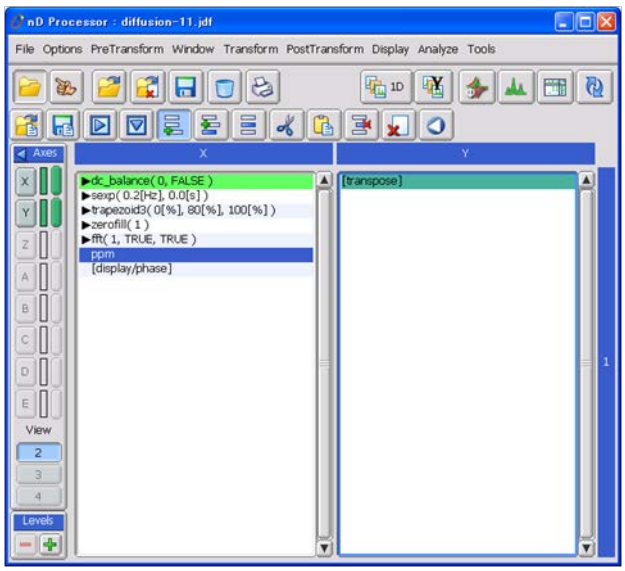
- Step 2
  Transmit the processed data to the Curve Analysis window. Then, select the peaks to calculate the diffusion coefficient by picking the peaks.
- Step 3
  Obtain the diffusion coefficient using the approximate calculation.

The following explains the procedures in the same order as the preceding steps.

2.4.2a Fourier transformation (Step 1)

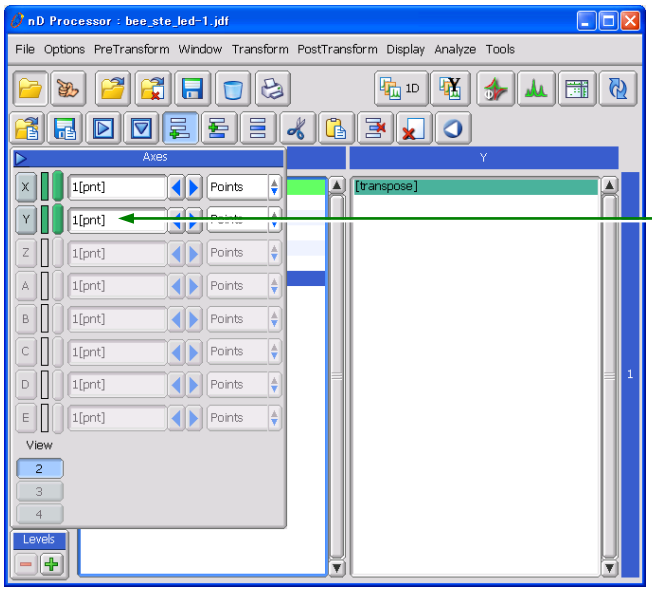
From the diffusion coefficient measurement data, display a 1-dimensional slice in the 1D Processor window, and determine a suitable window function and phase correction value.

1. Click the **X** button in the nD Processor window.
   The X-axis column is highlighted within a blue frame.



2. Click the Axes button to display the slice position setting window, and specify the data that you slice by setting the number the number of points from the number of sets (1-n) in the diffusion coefficient measurement data.

Usually, slice the first measurement data, whose phase correction is easy to carry out.



3. Click the **1D** Slice 1D button.

The slice data at the specified position is displayed in the 1D Processor window.

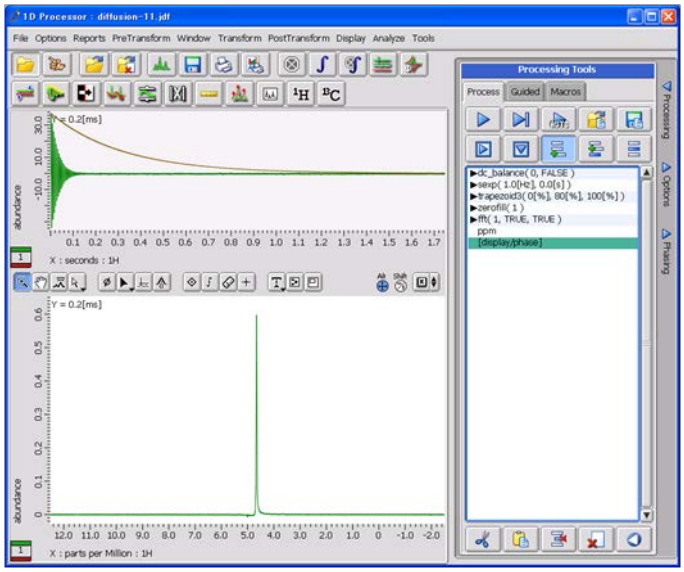


Fig. 2.8 1D Processor window

4. Set up suitable window function conditions, by changing the window function and parameter value.

The operation for changing the window function is the same as that for the usual 1D data.

When calculating the diffusion coefficient, only the height information of the peak is required. Therefore, in order to reduce the contribution of noise, it is sometimes more effective to use a steeper window function than usual.

5. Correct the phase manually to obtain the suitable phase-correction value.

The operation of phase correction is the same as that for the usual 1D data.

Be sure to correct the phase manually without using the automatic phase correction.

You may not be able to correct the phase of a peak having J coupling because of J modulation. If that happens, refer to the following procedure "Reference: When the phase of measurement data can not be corrected".

6. Close the 1D Processor window.

The window function conditions and phase-correction values that were obtained in steps 4 and 5 are automatically entered in the process list of the nD Processor window.

7. Click one of the following icons.

Usually select the Process File And Put In Data Slate button or the Process File And Put In Data Viewer button.

If you click the button, the data processing specified by the process list is applied to the 1 to n-th measurement data sets and, the Data Slate window appears.

If you click the button, the data processing specified the process list is applied to the 1 to n-th measurement data sets, and the Data Viewer window appears.

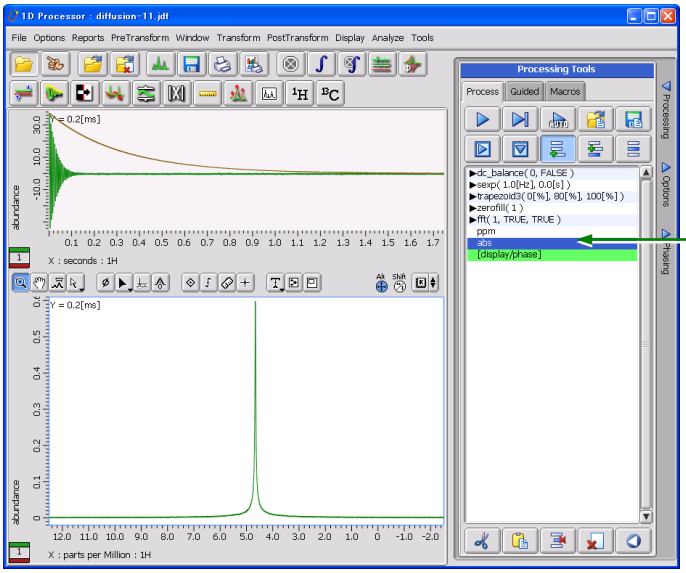
● Reference: When the phase of measurement data cannot be corrected

Perform power processing according to the following procedure instead of the phase correction in Step 5.

a. Click the Append New Item to End of List button in the 1D Processor window.

b. Select **Post Transform–Abs** in the menu bar.

The **abs** function for power processing is entered into the process list.



c. Proceed to Step 6.

2.4.2b Extraction of peaks, and creation of peak-intensity table (Step 2)

To perform this operation, you need to load the diffusion coefficient measurement data after Fourier transformation in the Curve Analysis window, and change the Mode to Diffusion Analysis.

■ Open the Curve Analysis window and change the Mode

1. Select **Analyze–Curve Analysis** from the menu bar in the Delta Console window.

The Curve Analysis window opens.

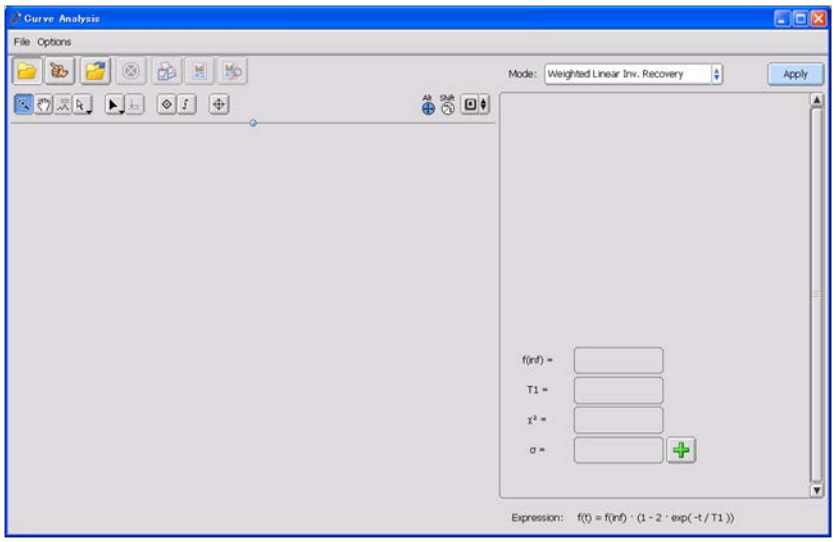
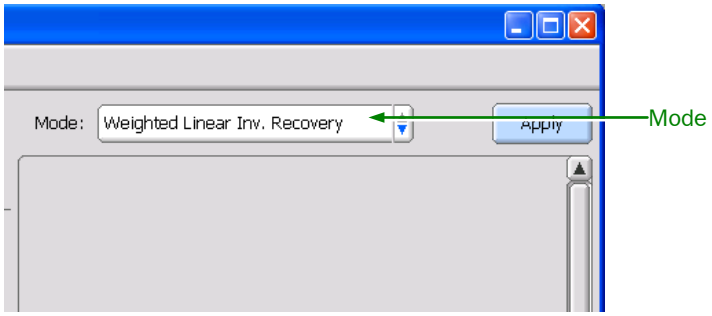


Fig. 2.9 Curve Analysis window

2. Change the Mode to Diffusion Analysis.

The window changes to the **Diffusion Analysis** mode.



■ Loading the Fourier transformed data in the Curve Analysis window

● When Fourier transformed diffusion coefficient measurement data is saved on the hard disk

1. Click the **Get Data From File** button in the Curve Analysis window.
2. Click the **Open Data File** button.

The Open File window opens.

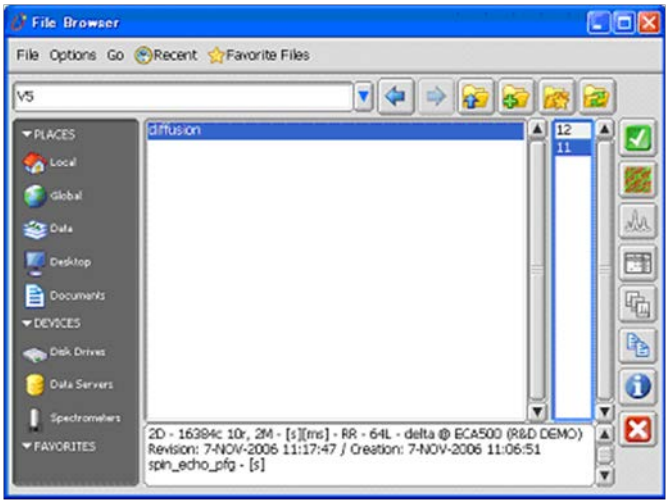
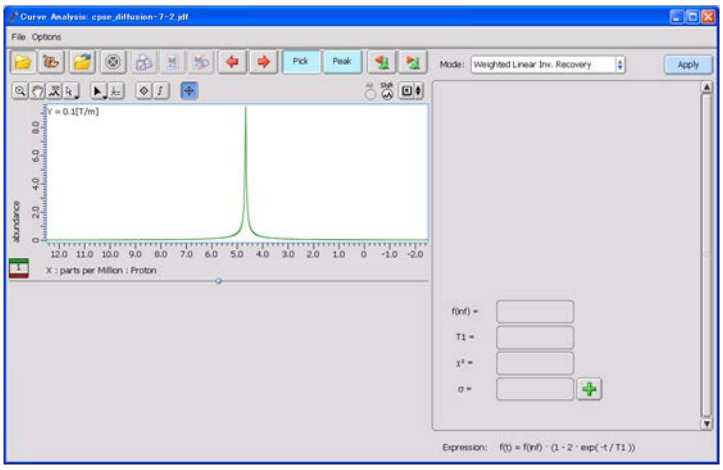


Fig. 2.10 Open File window

3. Select the file containing the Fourier transformed diffusion coefficient measurement data from the list box in the Open File window, and click the button.

The selected diffusion coefficient measurement data appear in the Curve Analysis window.



● When Fourier-transformed diffusion coefficient measurement data are displayed

1. Click the **Open Data By Fingering a Geometry** button in the Data Slate window.
2. Click the **Open Data File** button.
   The mouse pointer changes to the shape of a finger.
3. Move the mouse pointer to the area where the Fourier-transformed diffusion coefficient measurement data are displayed, and click it.
   The selected diffusion coefficient measurement data are loaded into the Curve Analysis window.

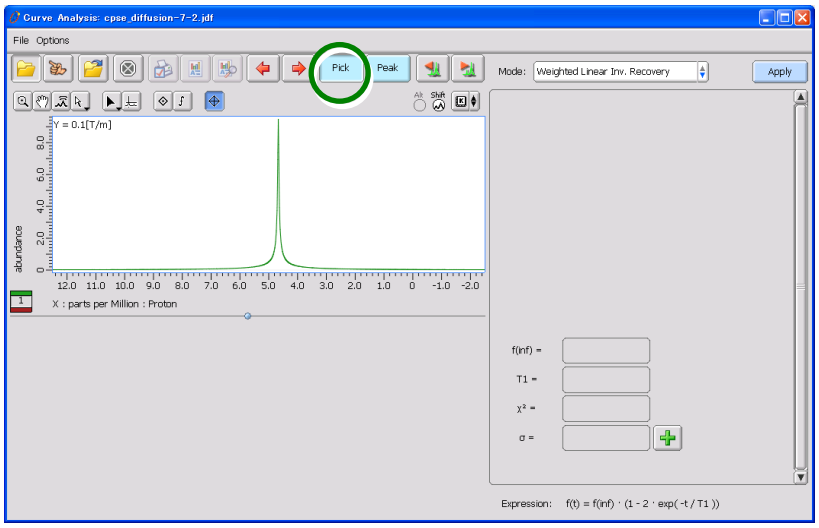
■ For extracting peaks

There are two methods for extracting peaks, **Pick** mode and **Peak** mode.
If you calculate the diffusion coefficients for a large number of peaks, and when printing the diffusion coefficients at the same time, the **Peak** mode is convenient. The peaks to be used in the **Peak** mode should be listed by peak-picking previously.
The **Pick** mode can be used to obtain the diffusion coefficient at any position of a spectrum. The top of the peak is not required for calculating the diffusion coefficient in the **Pick** mode, unlike the **Peak** mode.

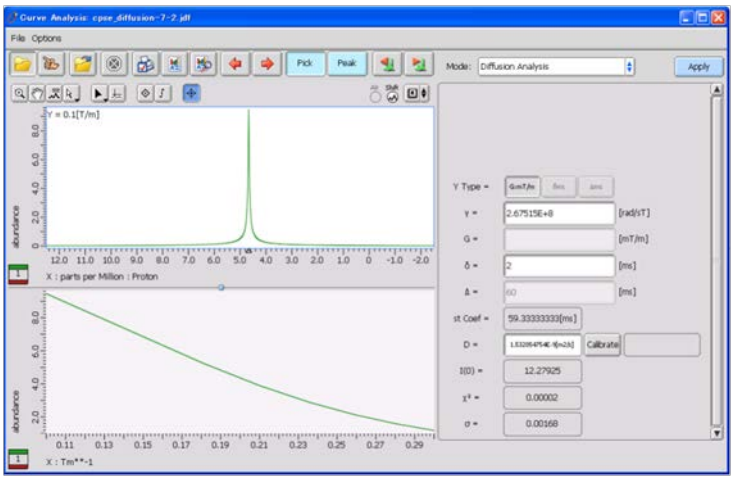
● Method of extracting Peaks in Pick mode

This section explains how to extract peaks in the **Pick** mode and how to create the peak-intensity table.

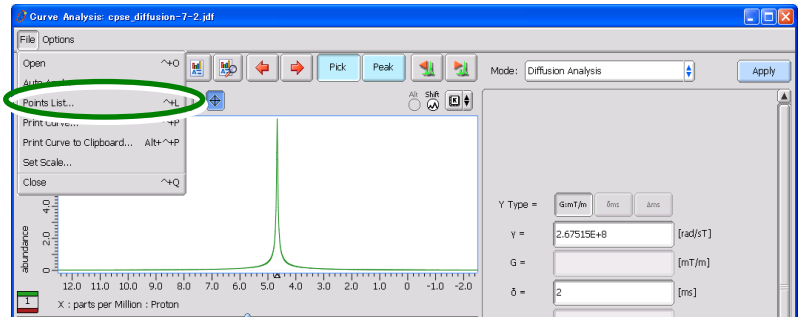
1. Click the **Pick** button in the Curve Analysis window.
   The cursor tool in the spectrum display area changes to in the **Pick** mode.



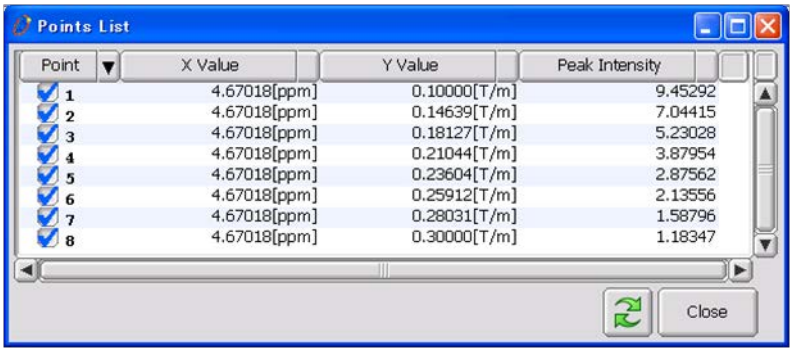
2. Move the mouse pointer onto the X-ruler in the spectrum display area, and press and hold down the left mouse button.
   A cursor appears.
3. While holding down the left mouse button, move the cursor to the top of the peak for which you want to calculate the diffusion coefficient; then release the mouse button.
   A pick position marker appears at the position where you released the mouse button.



4. To display the peak-intensity table, select **File–Point List** in the pull down menu of the **Curve Analysis Tool.**



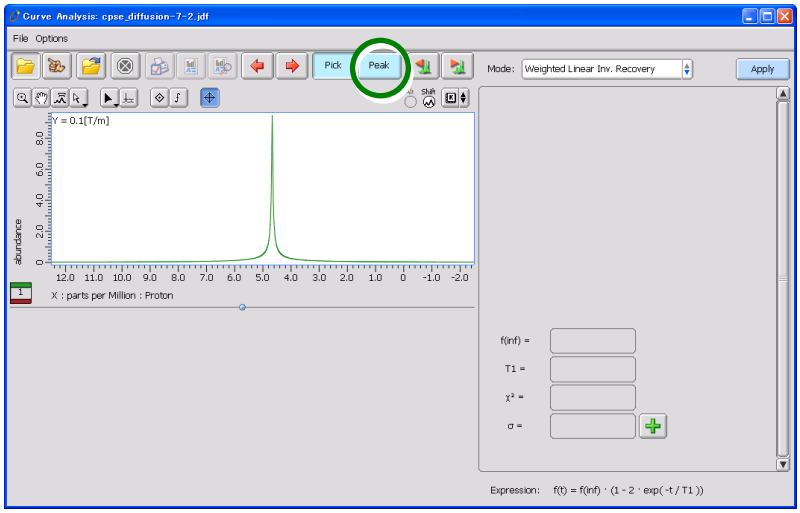
The **Points List** appears.



● Method of extracting Peaks in Peak mode

This section explains how to extract peaks and how to create a peak-intensity table in the **Peak** mode.

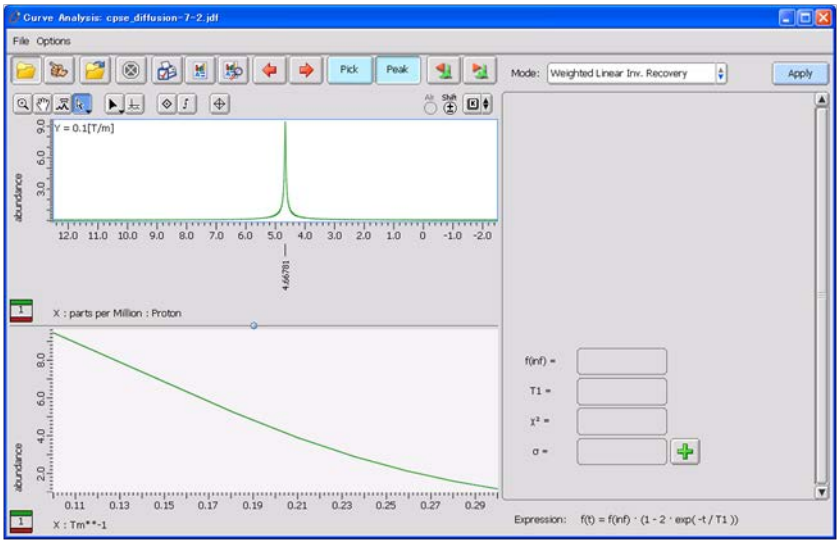
1. Click the **Peak** button in the Curve Analysis window.



2. Click the **Peak Pick Data** button.

Peak picking is performed.

If necessary, before performing peak picking, adjust the threshold level and the noise level in order not to pick up small signals or peaks having fine splittings, for which you do not need to obtain the diffusion coefficients.



3. Select the **Select** button from the cursor tool.

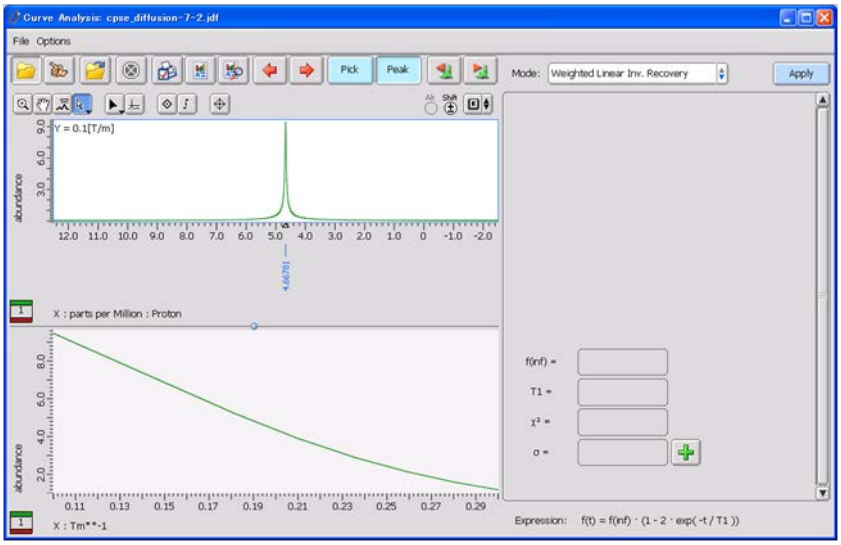
4. Move the mouse pointer onto the X-ruler in the spectrum display area, and press and hold down the left button of the mouse.

A cursor appears.

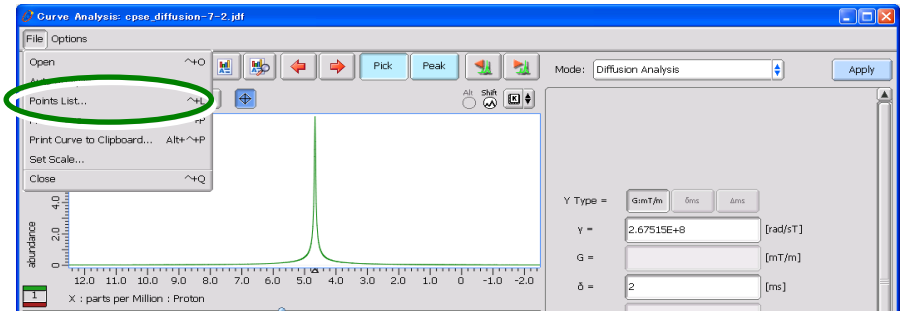
5. While holding down the left mouse button, move the cursor to the top of the peak to obtain the diffusion coefficient; then release the mouse button.

The selected peak color changes to blue.

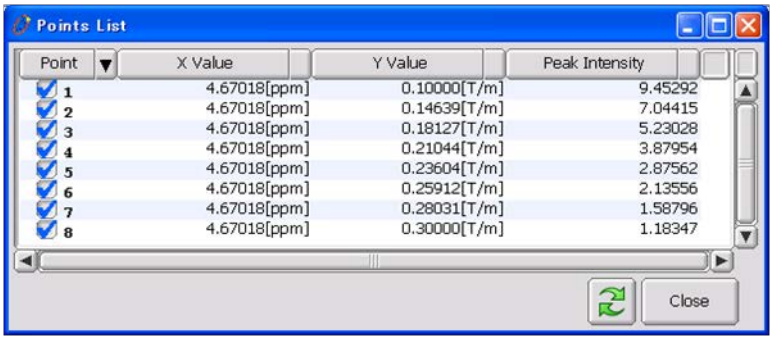
When printing the diffusion coefficient values of two or more peaks at the same time, drag the mouse cursor around the area of the peaks. All the peaks listed in the peak-intensity table in the dragged area are selected, and their numerical markers change to blue.



6. To display the peak-intensity table, select **File–Point List** in the pull down menu of the **Curve Analysis Tool.**



The **Point list** appears.



2.4.2c Method for obtaining the diffusion coefficient by approximate calculation (Step 3)

This section explains how to perform an approximate calculation for the diffusion coefficient.

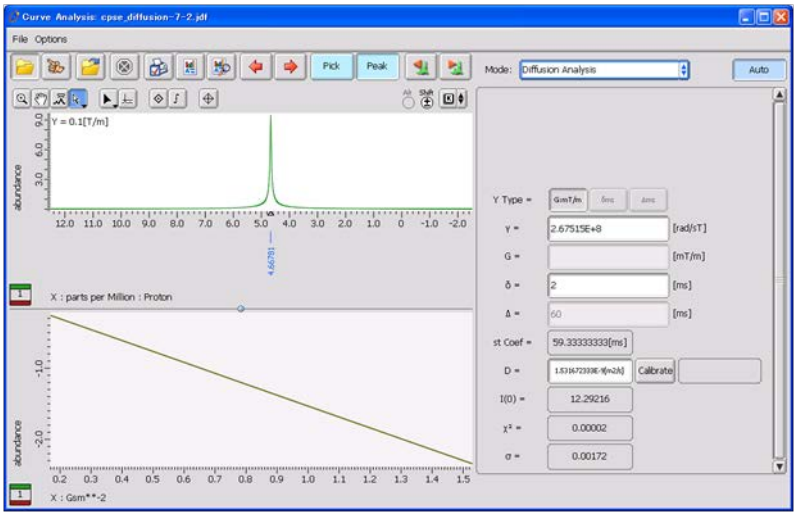
■ Input parameters used for measurement

- Select the variable type used for the array measurement from the Y Type buttons.
- Input the gyromagnetic ratio of the nucleus and the unarrayed variables into the parameter input boxes.
  When the following parameters are used in the sequence, these values are entered as default.

x_domain	Gyromagnetic ratio of an observed nucleus (γ)
g	Amplitude of magnetic-field-gradient pulse (G)
delta	Duration of magnetic-field-gradient pulse (δ)
diffusion_time	Diffusion time (Δ)

■ To obtain diffusion coefficient by approximate calculation

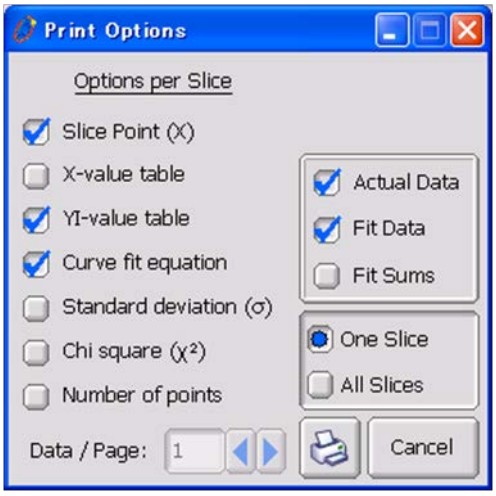
- Click the **Apply** button.
  An approximate calculation is performed, and the result of the calculation of a diffusion coefficient and the approximation curve in yellow are shown.



By clicking the **Apply** button, it changes to **Auto**. When changing the peak to obtain the diffusion coefficient, or when changing the parameter value, an approximate calculation is performed automatically.

2.4.3 Plotting Calculation Results

1. Click the **Plot Data File** button in the Curve Analysis window.
The Plot Options dialog box opens.



2. Select the items that you plot.
When two or more peaks are selected in the **Peak** mode and you want to print the diffusion coefficient values of those peaks at the same time, select **All Slices**.
3. Click the Plot data with current options button.
The items selected in step 2 are plotted.

DOSY MEASUREMENT AND DATA PROCESSING

3.1 GENERAL OF DOSY

The DOSY (Diffusion-Ordered NMR SpectroscopY) method evolves the diffusion coefficient of a sample on one axis in the two-dimensional spectrum by inverse Laplace transformation or curve fitting.

■ Principle of DOSY

As described in Chapter 2 “Measurement of Diffusion Coefficient and Data Processing“, when the phase coherence of spins is lost due to the first FG pulse and is restored by the second FG pulse, the signal intensity is written as follows if the interval of two FG pulses is Δ.

$$I(G,\Delta) = I(0,\Delta)\exp(-D(\gamma G\delta)^2(\Delta - \delta/3))$$

Therefore, when two or more NMR signals overlap in the same chemical shift, since the echo intensity becomes a linear combination of the signals, the echo is given as follows.

$$I(G,\Delta) = \sum_{j=I}^{N} I_j(0,\Delta)\exp(-D_j(\gamma G\delta)^2(\Delta - \delta/3)) \quad \cdots\cdots (3.1)$$

Moreover, for the sample that has a continuous molecular weight distribution like a polymer, the echo intensity is given as follows.

$$I(G,\Delta) = \int_0^{\infty} G(D)\exp(-D(\gamma G\delta)^2(\Delta - \delta/3))dD \quad \cdots\cdots (3.2)$$

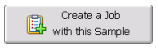
where G (D) is the distribution function of D.

For these signals, the diffusion coefficient is obtained using its peak intensity. Curve fitting is used for a signal like equation (3.1) and inverse Laplace transformation is used for a signal like equation (3.2).

3.2 DOSY MEASUREMENT

A DOSY measurement is basically the same as the diffusion coefficient measurement discussed in the previous chapter. The only difference between DOSY and the diffusion coefficient measurement is that the target of measurement is the multicomponent system (or the system having a molecular weight distribution).

■ To obtain measurement conditions

1. Measure the maximum magnetic-field-gradient intensity of PFG (FG pulse) used for the measurement.
   ☞ For measuring FG pulse strength, refer to Section 2.2, “How to measure PFG strength”.
2. Stop the sample spinning, and tune the probe.
3. Check the 90° pulse width.
   ✍ In order to improve the accuracy of a diffusion coefficient measurement, we recommend you to check the 90° pulse width of the sample to measure. In order to check the 90° pulse, perform an array measurement using the measurement mode of **single_pulse.jxp** or **single_pulse_dec.jxp**.
4. Select the registered sample and click the **Create a Job with this Sample** 

button in the Spectrometer Control window.
   The **Jobs** tab opens.
5. Select the job and the sample, and click the **Add Experiment** 

button.
   The Open Experiment window opens.
6. Click the  button and double click ▶ experiments. The directory list appears, so double click **diffusion** in the list.

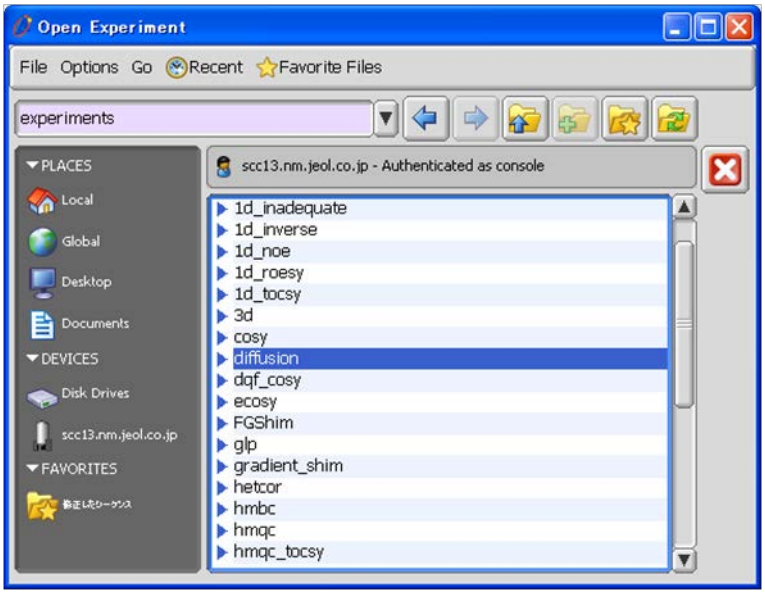


Fig. 3.1 Open Experiment window

7. Select a sequence to use from the File name list box.
   The Experiment Tool window for setting parameters opens.

8. Input the following values if needed.

For the values of **x_pulse** and **gradient_max** shown below, the default values in the probe file are automatically loaded. When the values that you found differ from the values in the probe file, input the values that you found into the probe file.

x_pulse 90° pulse width which you obtained in step 3.

gradient_max The maximum applicable magnetic field strength in the system currently used in [T/m].

For the maximum magnetic field strength to input into **gradient_max**, measure the value for every different combination of the probe and the maximum output of the FG power supply, referring to section 2.2, "How to measure PFG strength".

9. Input parameter values for measuring the diffusion coefficient.

The following three parameters are necessary for measuring the diffusion coefficient.

diffusion_time Time interval of two FG pulses (diffusion time Δ)

delta Duration of magnetic-field-gradient pulse

g Magnetic-field-gradient strength (G)

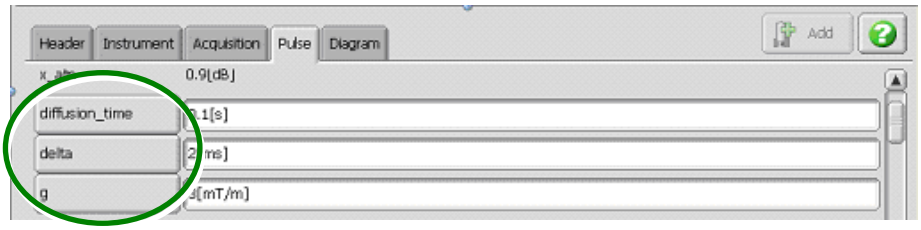


Fig. 3.2 Experiment Tool window

10. Input about 10 times the value of T1 into **relaxation_delay**.

11. Perform an array measurement at the minimum and maximum values of the variable magnetic-field-gradient strength (g parameter) that are used in the actual measurement.

For example, when changing the magnetic field from 100 mT/m to 300 mT/m, perform an array measurement at 100 mT/m and 300 mT/m.

A magnetic field strength greater than **gradient_max** cannot be output.

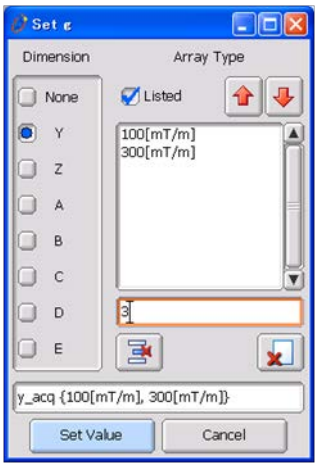


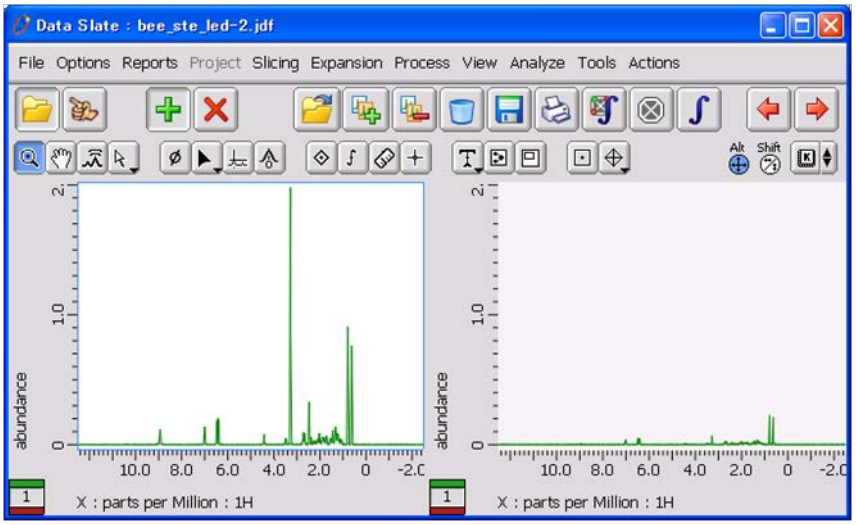
Fig. 3.3 Array parameter dialog box

12. Process the data in the nD processor window, and check the decay of the signal.

Be careful of the following points when two or more kinds of molecules are included.

- When the maximum magnetic field gradient of the system is applied, adjust measurement conditions so that the signal can be observed even for the molecule with the largest diffusion coefficient (so that the signals do not completely decay).
- Also for the molecule with the smallest diffusion coefficient, select the measurement conditions so that the signal intensity decays at least 1/2.

When the measurement sample includes molecules whose diffusion coefficients different largely, suitable decaying data may not be obtained for each kind of molecule. In this case, we recommend that you divide the measurements into a molecule group having a large diffusion coefficient and a molecule group having a small diffusion coefficient, and measure two times under conditions suitable for each group separately.



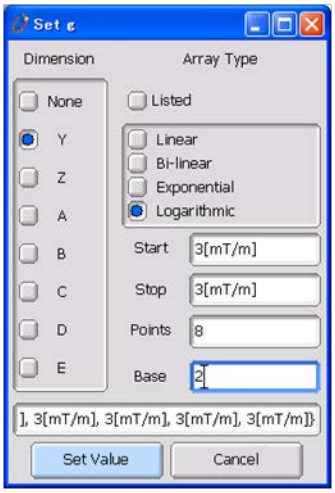
■ DOSY measurement

1. Stop sample spinning, and tune the probe.
2. Check the 90° pulse width.

   In order to improve the accuracy of diffusion coefficient measurement, we recommend that you check the 90° pulse width for the sample to measure. In order to check the 90° pulse, perform an array measurement using the measurement mode of **single_pulse.jxp** or **single_pulse_dec.jxp**.
3. Input various parameters obtained by the above procedure "■To obtain measurement conditions".

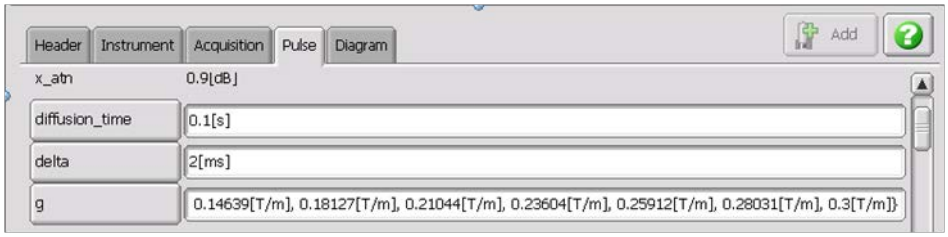
   Set **scans** so that you obtain a sufficient S/N ratio for every molecule group.
4. Set g to a suitable array variable in the range of the minimum and maximum values of the variable magnetic-field-gradient which were used in the condition setting.

   In the measurement of a diffusion coefficient, good measurement can be performed by changing an array variable so that the squares of the magnetic field gradients are at equal intervals. For this reason, the array variable can be easily set by selecting **Logarithmic** as an **Array Type** and setting the **Base** value to **2**.



5. Click the **Set Value** button.

   The array parameter dialog box closes, and the set values are entered into the Experiment Tool window.



6. Click the **Submit** button.

   The measurement starts.

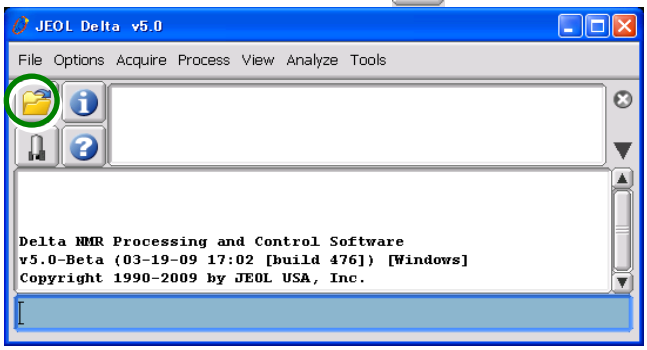
3.3 PROCESSING DOSY DATA

After measurement, process the data in the nD Processor window.
First, measurement data are loaded into the nD Processor window as in two-dimensional measurement data processing. When the measurement data are transmitted from the spectrometer immediately after the end of DOSY measurement and the nD Processor window is already open, the operation of section 3.3.1 is not necessary.

3.3.1 Loading DOSY Measurement Data

In order to load the data (FID) of DOSY measurement into the nD Processor window, perform the following procedure.

1. Click the **Open file** and choose tool  button in the Delta Console window.



The File Browser window appears.

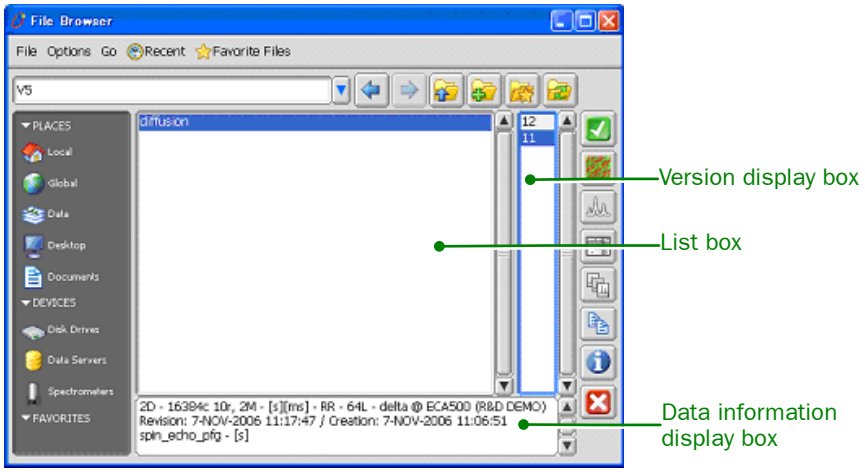
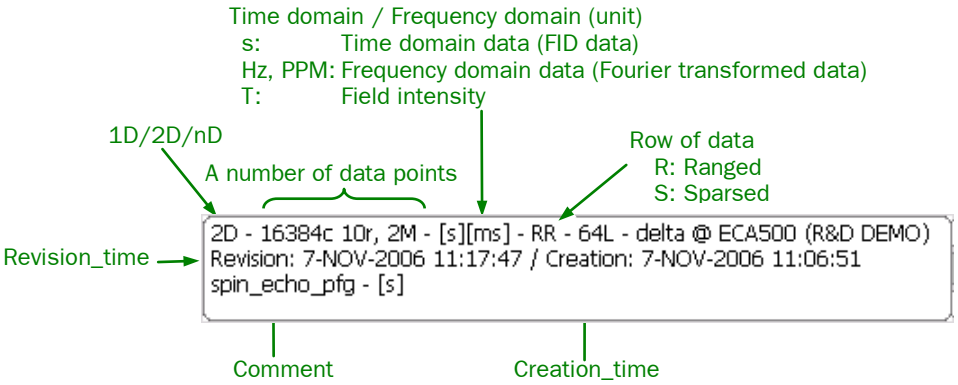


Fig. 3.4 File Browser window

2. Click the data file to load from the list box.

The data information on the newest version is displayed in the data information display box as shown below. Note that the format of the data obtained by the array measurement is displayed as 2D data.



3. Check the data domain in the data information display box, and select the version of stored FID from the version display box.

If the newest version of the data displayed in step 2 is the time domain data (FID data), selection of the version is unnecessary.

4. Click the button (or the button).

nD Processor window opens.

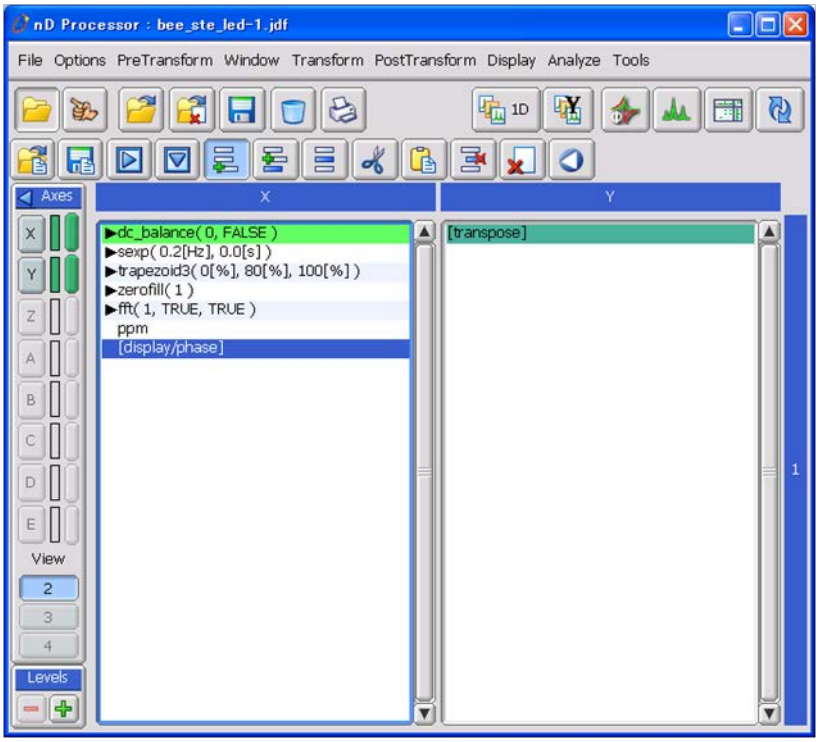
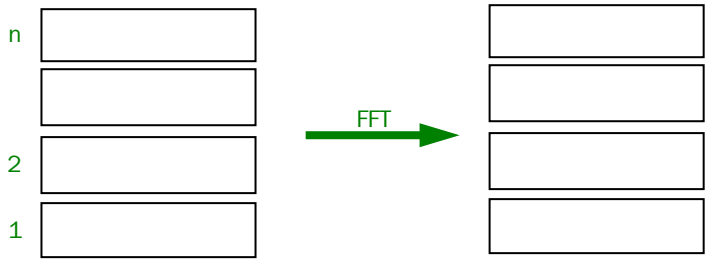


Fig. 3.5 nD Processor window

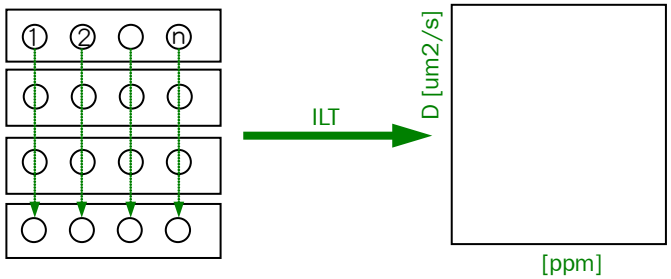
3.3.2 Procedure for Processing DOSY Measurement Data

The processing of the DOSY measurement data consists of the following two steps.

- Step 1
  For processing the X-axis of DOSY measurement data, all sets of measurement data from the first to the nth are Fourier-transformed together under the same condition.



- Step 2
  For processing the Y-axis of DOSY measurement data, Inverse Laplace Transformation is carried out on every data point that is Fourier-transformed along the X-axis as shown in the following schematic diagram.

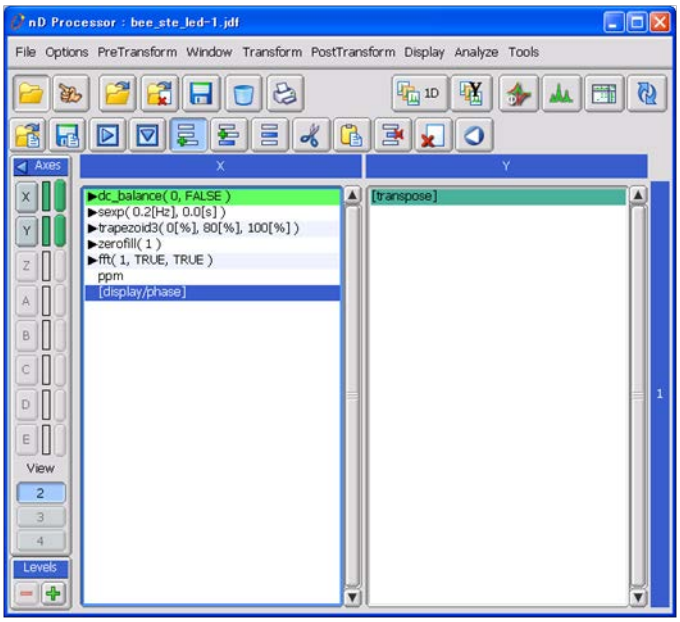


The following explains the procedures in the same order as the preceding steps.

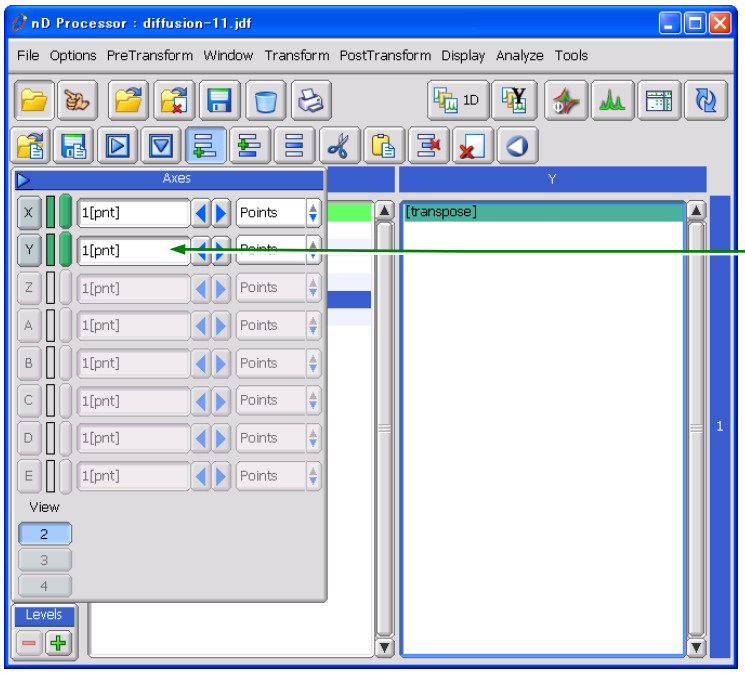
3.3.2a Processing the x-axis of the DOSY measurement data (Step 1)

Display one data of the DOSY measurement data in the 1D Processor window as 1D slice data, and search a suitable window function and phase correction values.

1. Click the **X** button in the nD Processor window.
   The X-axis area is enclosed with a blue frame.



2. Click the Axes button to display the slice position setting screen, and specify the data that you want to slice as the number of points from the number of sets (1-n) in the DOSY measurement data.
   Usually, slice the first measurement data as it is easy to correct its phase.



3. Click the **1D** Slice button.

The slice data at the specified position is displayed in the 1D Processor window.

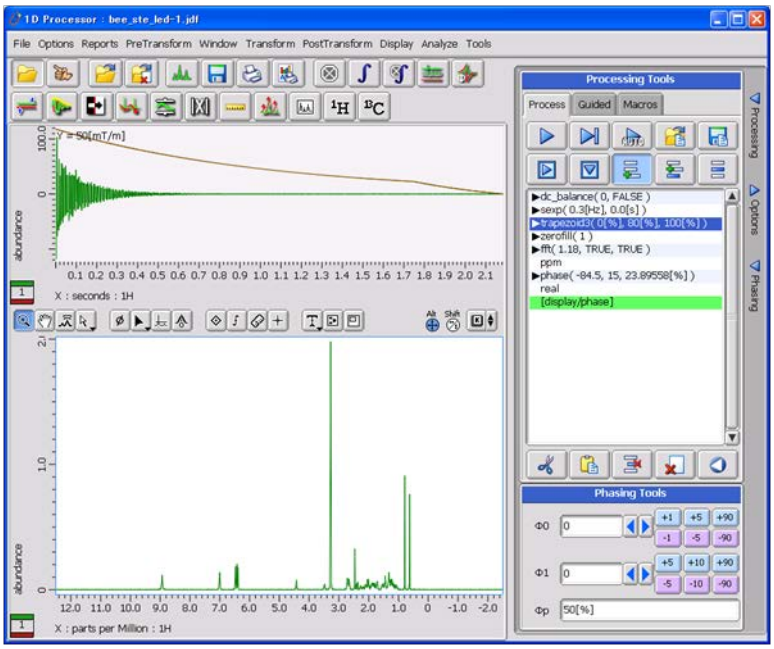


Fig. 3.6 1D Processor window

4. By changing the window function and parameter values, set up suitable window function conditions.

The operation of changing the window function is the same as that for the usual 1D data.

The height information of the peak is required for inverse Laplace transformation of DOSY. Therefore, in order to reduce the contribution of noise, it is more effective to use steeper window function conditions than for the usual data processing.

5. Correct a phase manually, and obtain suitable phase correction values.

The phase correction is the same as that for the usual 1D data.

- Be sure to perform phase correction manually without using the automatic phase correction.
- You may not be able to correct the phase of a peak having J coupling due to J modulation. If that happens, refer to “Reference. When the phase of measurement data cannot be corrected” in section 2.4.2a.

6. Close the 1D Processor window.

The window function conditions and phase correction value, which were obtained in steps 4 and 5, are automatically entered in the process list in the nD Processor window.

7. Select Post Transform–Math–Real from the menu bar.

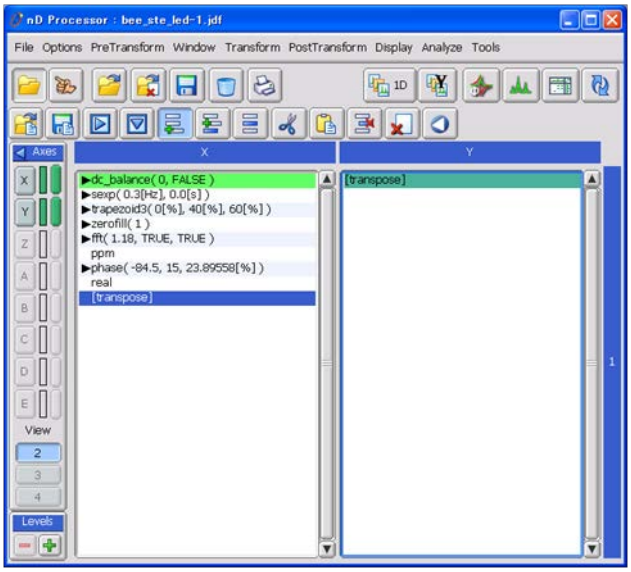
Real processing is set in the process list of the window.

- For the inverse Laplace transformation processing of DOSY, only real data are needed.

3.3.2b Processing the y-axis of DOSY measurement data (Step 2)

Carry out inverse Laplace transformation of the Y-axis for the data that were Fourier transformed in the direction of the X-axis in step 1.

1. Click the Y button in the nD Processor window.



2. Select **Transform–DOSY** from the menu bar, and select the algorithm used for processing.

There are the following algorithms.

DOSY CONTIN This performs inverse Laplace transformation for samples that have continuous diffusion coefficients such as polymers that have the distribution of molecular weight.

DOSY SPLMOD This performs curve fitting for samples that have discrete diffusion coefficients such as low molecular weight mixed samples.

L-Marquardt This performs curve fitting for systems that have few overlapped peaks.

MCR This performs linear analysis method using multiple classification analysis, resulting in 3D data.

MCR-CONTIN This performs the process with the combination of MCR and CONTIN.

MCR-LM This performs the process with the combination of MCR and L-Marquardt.

MCR-SPLMOD This performs the process with the combination of MCR and SPLMOD.

3. Set up the various parameters.

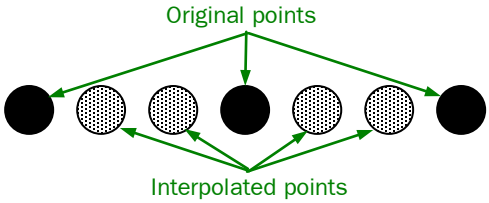
Here are the parameters.

Start This is the minimum value of the range in which to search for peaks to obtain the diffusion coefficient.

Stop This is the maximum value of the range in which to search for the peak to obtain the diffusion coefficient.

Interp This determines the number of points to interpolate in the diffusion coefficient axis (Y-axis).

✍ Example:When the number of data points is three, and Interp is 2, the number of points becomes 7 after processing.



✍ In the CONTIN method, values of Interp that are 15 or less are suitable.

Threshold Threshold level of the peak to used for processing.

✍ When Threshold is 0, the default value in the Delta software is used.

Species Set the total number of components expected.

Peaks Set this to the maximum number of the diffusion coefficient expected for each chemical shift.

✍ In the L-Marquardt method, set Peaks to 1.

Ratio In the SPLMOD method, set this to the minimum ratio of the different diffusion coefficients having equal chemical shift.

✍ This parameter applies only to the SPLMOD method.

Error Set this to the acceptable error in the SPLMOD method as a decimal.

Example: When Error is 0.2, the permissible error is 20%.

✍ This parameter applies only to the SPLMOD method.

Gamma Set this to the gyromagnetic ratio of the nucleus used for processing.

✍ When X_FREQ has been set, this is set to the gyromagnetic ratio of the observation nucleus automatically.

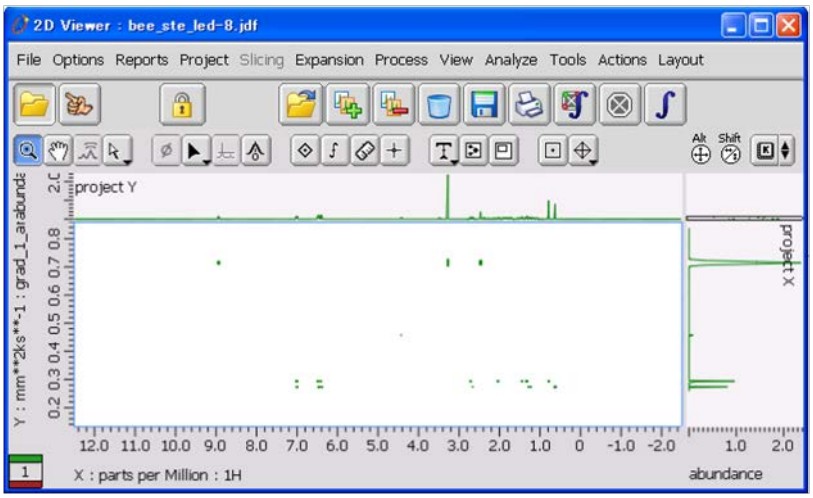
Maxima When this has been selected, curve fitting is performed by only using the top of peak.

Scale This scales the width of a peak.

✍ This parameter is not applied to the CONTIN method.

Positions This is used when the diffusion coefficient is known previously.

4. Click the Process File And Put In Data Viewer button.
Data processing is performed, and DOSY data is displayed.

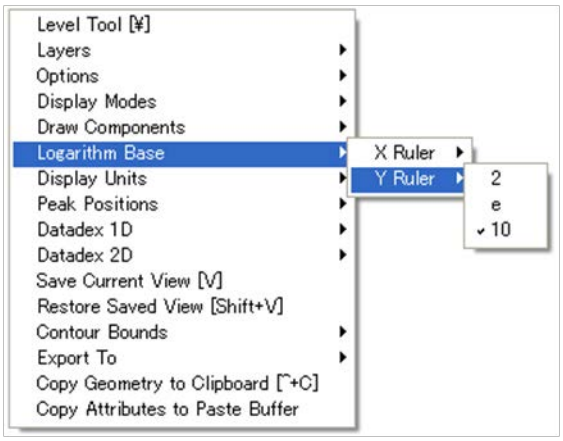


5. Repeat steps 3 and 4 to obtain the search condition for the diffusion coefficient in the suitable range.

● Logarithmic display of diffusion coefficient axis

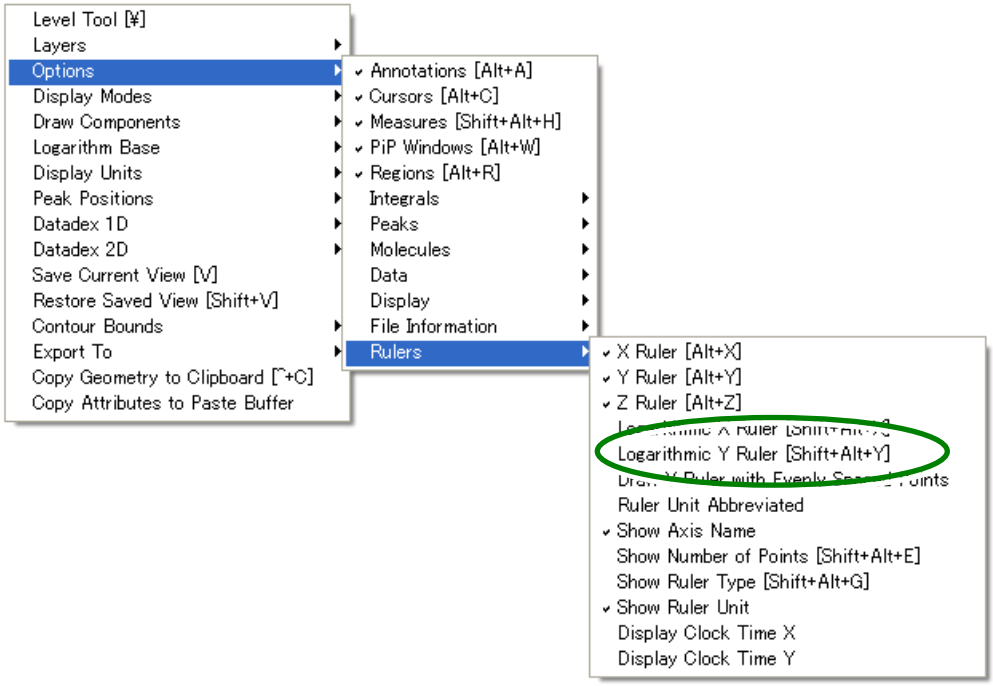
In the diffusion coefficient axis, a logarithmic display may sometimes be more legible. This section explains the procedure for the logarithmic display.

1. Select the DOSY data display area.
2. Right click in the data display area.
A pop-up menu appears.
3. Select the bases of the logarithm from **Logarithm Base–Y Ruler** from the pop-up menu.
The base can be selected from **2** and **10** for common logarithms, and **e** for natural logarithm.



4. Right click in the data display area again.
A pop-up menu appears.

5. Select **Options–Ruler–Logarithmic Y Ruler** from the pop-up menu.



The Y-axis changes to the logarithmic display.

4 MEASUREMENT OF SR-MAS

4.1 GENERAL OF SR-MAS MEASUREMENT

SR-MAS (Swollen Resin Magic Angle Spinning) is a measurement method for gel samples, swollen resin of solid phase synthesis, and heterogeneous systems such as tissue. In order to perform this measurement, it is necessary to use the special SR-MAS probe that can carry out MAS measurement and the special-purpose sample tube for liquid samples that does not leak even if it rotates at several kilohertz.

☞ Refer to the manual of the SR-MAS for the preparation and the operation of the SR-MAS probe.

The pulse sequence used for an SR-MAS measurement is the same sequence as the pulse sequence used for general solution NMR measurement. Therefore, the basic measuring method and data-processing method are the same as those of solution NMR.

✍ However, the pulse sequence using field gradient (FG) cannot be used.

Here, the method of adjustment of the magic angle, the resolution, the temperature controlling, and the relationship between spinning speed and resolution, that are specific to the SR-MAS NMR measurement and different from the general solution NMR measurement in the spectrometer, are explained.

■ SR-MAS measurement

SR-MAS is the acronym of Swollen Resin Magic Angle Spinning. It means that the resin swollen by the solvent is directly measured under the condition of several-kilohertz MAS spinning. The resolution of the spectrum of semisolids (soft solid) and high-viscosity liquids will be improved by reducing the residual weak dipole-dipole interaction of the sample by MAS. Moreover, higher resolution can be achieved by averaging inhomogeneity of the local magnetic field around the rotating axis.

—CAUTION—

Be sure to rotate a sample in SR-MAS experiment.

If you measure without flowing the air for sample spinning, the probe may be damaged.

However, when you carry out the resolution adjustment using single_pulse.jxp, damage to the probe does not occur even if the measurement is carried out without air flowing.

4.2 HOW TO ADJUST MAGIC ANGLE

—CAUTION—

The first time you adjust the magic angle, you need to receive instruction from an experienced person.

The SR-MAS probe may be damaged if improper adjustment is performed.

1. Insert the reference sample "KBr".
2. Start the spinning.
3. Change LF (Lower frequency) channel to **Bromine79** observation.

   Check the combination of the stick and the tuning dial for **Bromine79** observation.
4. Load the pulse sequence experiments/1d/single_pulse.jxp in the Experiment Tool window, and perform the following settings.
   - Set observed nucleus to **Bromine79**.
   - Set **x_sweep** to 1000 ppm.
   - Add the repeat flag to the header, and turn on spinning.
   - Set **scans** to **1**.
5. Click the **Submit** button.

   The measurement starts in the repeat mode.
6. Adjust a phase by the following procedure.

   a. Double-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 is not displayed, click **Processing** button at the right edge.

   c. Adjust the phase by using Phasing Tools.

   When the Phasing Tools panel is not displayed, click the **Phasing** button at the right edge.
7. Adjust the magic angle.

   Turn the adjustment stick to maximize the spinning side band of KBr according to the instruction manual of the probe (Fig. 4.1).

   The gear of the magic-angle adjustment mechanism has some backlash. Therefore, adjust it by turning the dial for fine-tuning only in one direction.

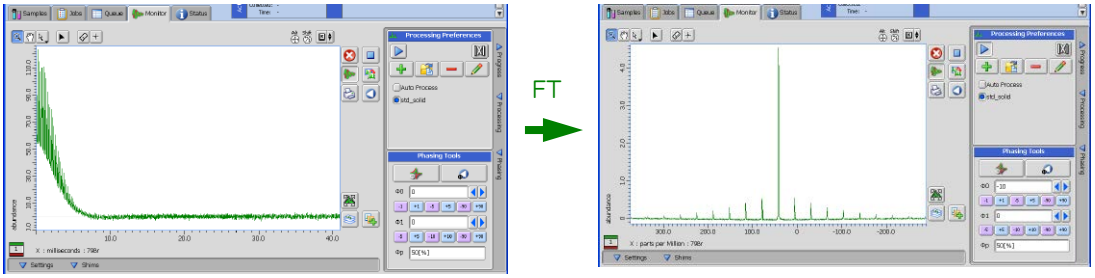


Fig. 4.1 Free Induction Decay (left) and spectrum (right) after magic-angle adjustment

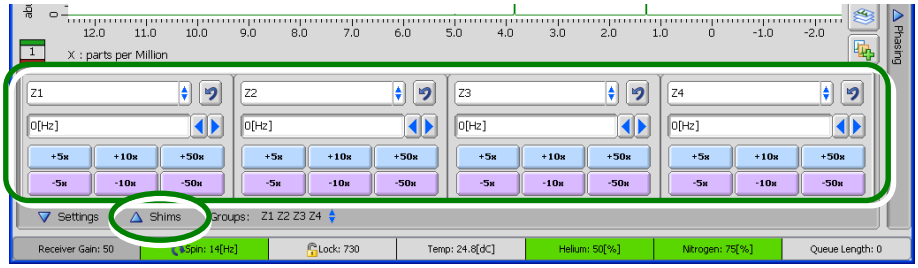
8. After completing magic-angle adjustment, click the button tab to complete the measurement.

   Adjustment of the magic angle may change the resolution. Be sure to check the resolution according to section 4.3 "ADJUSTMENT OF RESOLUTION," and adjust the shim values if needed.

4.3 ADJUSTMENT OF RESOLUTION

You can adjust the resolution while monitoring the current spectrum by using the Monitor tab. While actually monitoring the line shape and the width of the peak, and so on, you can adjust the resolution.

1. Insert the chloroform (CHCl3) sample.
   It is not necessary to perform spinning.
2. Load the pulse sequence (experiments/1d/single_pulse.jxp) on Experiment Tool and perform the following settings.
   - Add the repeat flag to the header and turn on it.
   - Set **scans** to **1**.
3. Click the **Submit** button.
   The measurement starts in the repeat mode.
4. Click the Monitor tab to open the **Monitor** tab.
5. Click the **Shims** button on the **Monitor** tab.
   The **Shims control** panel appears.



6. If the resolution is not good, adjust the resolution as follows.
   a. Adjust Z1 and Y to maximize the peak intensity.
   b. Adjust X2 and YZ to maximize the peak intensity.
   c. Adjust Z3 to maximize peak intensity.
   d. Repeat steps a to c.

   The above shims are used when the magic angle is along the Y-axis direction.
7. Click the button after shim adjustment is complete.
   The measurement stops.

4.4 TEMPERATURE CONTROL

For the SR-MAS probe, the temperature can be controlled in the range from room temperature to +50 °C. The temperature control can be carried out in the same way as for the usual solution NMR measurement. However, in any case, perform temperature control while flowing the air for sample spinning.

—CAUTION—

Be sure to rotate a sample in SR-MAS experiment.

If you measure without flowing the air for sample spinning, the probe may be damaged.

However, when you carry out the resolution adjustment using single_pulse.jxp, you can perform the measurement without air flowing.

4.5 SPINNING SPEED AND RESOLUTION

In some sample systems, the resolution changes when the spinning speed changes. For such a sample system, adjust the spinning speed to optimize the resolution.

INDEX