

User Guide: Solid-State NMR

*Varian NMR Spectrometer Systems
With VNMR 6.1C Software
Pub. No. 01-999162-00, Rev. C0402*



VARIAN

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Agilent Technologies

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A0800 – Initial release for VNMR 6.1C software
B0301 – *MERCURYplus* updates—`cppwr` and `dbl v12` parameters in XPOLAR1 experiment.
C0402 – Updated INOVA CP/MAS parameters for XPOLAR1 and Multipulse

Applicability of manual:

Varian NMR spectrometer systems with
Varian solids modules running VNMR 6.1C software

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SAFETY PRECAUTIONS

The following warning and caution notices illustrate the style used in Varian manuals for safety precaution notices and explain when each type is used:

WARNING: *Warnings are used when failure to observe instructions or precautions could result in injury or death to humans or animals, or significant property damage.*

CAUTION: *Cautions are used when failure to observe instructions could result in serious damage to equipment or loss of data.*

Warning Notices

Observe the following precautions during installation, operation, maintenance, and repair of the instrument. Failure to comply with these warnings, or with specific warnings elsewhere in Varian manuals, violates safety standards of design, manufacture, and intended use of the instrument. Varian assumes no liability for customer failure to comply with these precautions.

WARNING: *Persons with implanted or attached medical devices such as pacemakers and prosthetic parts must remain outside the 5-gauss perimeter of the magnet.*

The superconducting magnet system generates strong magnetic fields that can affect operation of some cardiac pacemakers or harm implanted or attached devices such as prosthetic parts and metal blood vessel clips and clamps.

Pacemaker wearers should consult the user manual provided by the pacemaker manufacturer or contact the pacemaker manufacturer to determine the effect on a specific pacemaker. Pacemaker wearers should also always notify their physician and discuss the health risks of being in proximity to magnetic fields. Wearers of metal prosthetics and implants should contact their physician to determine if a danger exists.

Refer to the manuals supplied with the magnet for the size of a typical 5-gauss stray field. This gauss level should be checked after the magnet is installed.

WARNING: *Keep metal objects outside the 10-gauss perimeter of the magnet.*

The strong magnetic field surrounding the magnet attracts objects containing steel, iron, or other ferromagnetic materials, which includes most ordinary tools, electronic equipment, compressed gas cylinders, steel chairs, and steel carts. Unless restrained, such objects can suddenly fly towards the magnet, causing possible personal injury and extensive damage to the probe, dewar, and superconducting solenoid. The greater the mass of the object, the more the magnet attracts the object.

Only nonferromagnetic materials—plastics, aluminum, wood, nonmagnetic stainless steel, etc.—should be used in the area around the magnet. If an object is stuck to the magnet surface and cannot easily be removed by hand, contact Varian service for assistance.

Warning Notices (*continued*)

Refer to the manuals supplied with the magnet for the size of a typical 10-gauss stray field. This gauss level should be checked after the magnet is installed.

WARNING: Only qualified maintenance personnel shall remove equipment covers or make internal adjustments.

Dangerous high voltages that can kill or injure exist inside the instrument. Before working inside a cabinet, turn off the main system power switch located on the back of the console.

WARNING: Do not substitute parts or modify the instrument.

Any unauthorized modification could injure personnel or damage equipment and potentially terminate the warranty agreements and/or service contract. Written authorization approved by a Varian, Inc. product manager is required to implement any changes to the hardware of a Varian NMR spectrometer. Maintain safety features by referring system service to a Varian service office.

WARNING: Do not operate in the presence of flammable gases or fumes.

Operation with flammable gases or fumes present creates the risk of injury or death from toxic fumes, explosion, or fire.

WARNING: Leave area immediately in the event of a magnet quench.

If the magnet dewar should quench (sudden appearance of gasses from the top of the dewar), leave the area immediately. Sudden release of helium or nitrogen gases can rapidly displace oxygen in an enclosed space creating a possibility of asphyxiation. Do not return until the oxygen level returns to normal.

WARNING: Avoid helium or nitrogen contact with any part of the body.

In contact with the body, helium and nitrogen can cause an injury similar to a burn. Never place your head over the helium and nitrogen exit tubes on top of the magnet. If helium or nitrogen contacts the body, seek immediate medical attention, especially if the skin is blistered or the eyes are affected.

WARNING: Do not look down the upper barrel.

Unless the probe is removed from the magnet, never look down the upper barrel. You could be injured by the sample tube as it ejects pneumatically from the probe.

WARNING: Do not exceed the boiling or freezing point of a sample during variable temperature experiments.

A sample tube subjected to a change in temperature can build up excessive pressure, which can break the sample tube glass and cause injury by flying glass and toxic materials. To avoid this hazard, establish the freezing and boiling point of a sample before doing a variable temperature experiment.

Warning Notices (*continued*)

WARNING: Support the magnet and prevent it from tipping over.

The magnet dewar has a high center of gravity and could tip over in an earthquake or after being struck by a large object, injuring personnel and causing sudden, dangerous release of nitrogen and helium gasses from the dewar. Therefore, the magnet must be supported by at least one of two methods: with ropes suspended from the ceiling or with the antivibration legs bolted to the floor. Refer to the *Installation Planning Manual* for details.

WARNING: Do not remove the relief valves on the vent tubes.

The relief valves prevent air from entering the nitrogen and helium vent tubes. Air that enters the magnet contains moisture that can freeze, causing blockage of the vent tubes and possibly extensive damage to the magnet. It could also cause a sudden dangerous release of nitrogen and helium gases from the dewar. Except when transferring nitrogen or helium, be certain that the relief valves are secured on the vent tubes.

WARNING: On magnets with removable quench tubes, keep the tubes in place except during helium servicing.

On Varian 200- and 300-MHz 54-mm magnets only, the dewar includes removable helium vent tubes. If the magnet dewar should quench (sudden appearance of gases from the top of the dewar) and the vent tubes are not in place, the helium gas would be partially vented sideways, possibly injuring the skin and eyes of personnel beside the magnet. During helium servicing, when the tubes must be removed, follow carefully the instructions and safety precautions given in the magnet manual.

Caution Notices

Observe the following precautions during installation, operation, maintenance, and repair of the instrument. Failure to comply with these cautions, or with specific cautions elsewhere in Varian manuals, violates safety standards of design, manufacture, and intended use of the instrument. Varian assumes no liability for customer failure to comply with these precautions.

CAUTION: Keep magnetic media, ATM and credit cards, and watches outside the 5-gauss perimeter of the magnet.

The strong magnetic field surrounding a superconducting magnet can erase magnetic media such as floppy disks and tapes. The field can also damage the strip of magnetic media found on credit cards, automatic teller machine (ATM) cards, and similar plastic cards. Many wrist and pocket watches are also susceptible to damage from intense magnetism.

Refer to the manuals supplied with the magnet for the size of a typical 5-gauss stray field. This gauss level should be checked after the magnet is installed.

Caution Notices (*continued*)

CAUTION: Check helium and nitrogen gas flowmeters daily.

Record the readings to establish the operating level. The readings will vary somewhat because of changes in barometric pressure from weather fronts. If the readings for either gas should change abruptly, contact qualified maintenance personnel. Failure to correct the cause of abnormal readings could result in extensive equipment damage.

CAUTION: Never operate solids high-power amplifiers with liquids probes.

On systems with solids high-power amplifiers, never operate the amplifiers with a liquids probe. The high power available from these amplifiers will destroy liquids probes. Use the appropriate high-power probe with the high-power amplifier.

CAUTION: Take electrostatic discharge (ESD) precautions to avoid damage to sensitive electronic components.

Wear grounded antistatic wristband or equivalent before touching any parts inside the doors and covers of the spectrometer system. Also, take ESD precautions when working near the exposed cable connectors on the back of the console.

Radio-Frequency Emission Regulations

The covers on the instrument form a barrier to radio-frequency (rf) energy. Removing any of the covers or modifying the instrument may lead to increased susceptibility to rf interference within the instrument and may increase the rf energy transmitted by the instrument in violation of regulations covering rf emissions. It is the operator's responsibility to maintain the instrument in a condition that does not violate rf emission requirements.

Introduction

This manual is designed to help you perform solid-state NMR experiments using a Varian solid-state NMR module on a Varian NMR spectrometer system running VNMR version 6.1C software. The manual contains the following chapters:

- **Chapter 1, “Overview of Solid-State NMR,”** provides an short overview of solid-state NMR, including the types of solids modules, probes, and accessories available.
- **Chapter 2, “CP/MAS Solids Operation,”** covers using the CP/MAS solids module and related pulse sequences.
- **Chapter 3, “Wideline Solids Module Operation,”** covers using the wideline solids module.
- **Chapter 4, “CRAMPS/Multipulse Module Operation,”** covers using the CPAMPS/multipulse module and related pulse sequences.
- **Chapter 5, “Solid-State NMR Accessories,”** covers using the rotor synchronization, rotor speed controller accessory, and solids variable temperature accessories.
- **Chapter 6, “Solid-State NMR Experiments,”** is a guide to pulse sequences useful for performing solid-state NMR experiments.

Notational Conventions

The following notational conventions are used throughout all VNMR manuals:

- Typewriter-like characters identify VNMR and UNIX commands, parameters, directories, and file names in the text of the manual. For example:
The shutdown command is in the `/etc` directory.
- The same type of characters show text displayed on the screen, including the text echoed on the screen as you enter commands during a procedure. For example:
`Self test completed successfully.`
- Text shown between angled brackets in a syntax entry is optional. For example, if the syntax is `seqgen s2pul<.c>`, entering the “.c” suffix is optional, and typing `seqgen s2pul.c` or `seqgen s2pul` is functionally the same.
- Lines of text containing command syntax, examples of statements, source code, and similar material are often too long to fit the width of the page. To show that a line of text had to be broken to fit into the manual, the line is cut at a convenient point (such as at a comma near the right edge of the column), a backslash (\) is inserted at the cut, and the line is continued as the next line of text. This notation will be familiar to C programmers. Note that the backslash is not part of the line and, except for C source code, should not be typed when entering the line.
- Because pressing the Return key is required at the end of almost every command or line of text you type on the keyboard, use of the Return key will be mentioned only in cases where it is *not* used. This convention avoids repeating the instruction “press the Return key” throughout most of this manual.
- Text with a change bar (like this paragraph) identifies material new to VNMR 6.1C that was not in the previous version of VNMR. Refer to the document *Release Notes* for a description of new features to the software.

Other Manuals

This manual should be your basic source for information about using the spectrometer hardware and software on a day-to-day basis for solid-state NMR. Other VNMR manuals you should have include:

- *Getting Started*
- *Walkup NMR Using GLIDE*
- *User Guide: Liquids NMR*
- *VNMR Command and Parameter Reference*
- *VNMR User Programming*
- *VNMR and Solaris Software Installation*

All of these manuals are shipped with the VNMR software. These manuals, other Varian hardware and installation manuals, and most Varian accessory manuals are also provided online so that you can view the pages on your workstation and print copies.

Types of Varian NMR Spectrometer Systems

In parts of this manual, the type of spectrometer system (^{UNITY}INOVA, *MERCURY-VX*, *MERCURY*, *GEMINI 2000*, *UNITYplus*, *UNITY*, or *VXR-S*) must be considered in order to use the software properly.

- ^{UNITY}INOVA and *MERCURY-VX* are the current systems sold by Varian.
- *UNITYplus*, *UNITY*, and *VXR-S* are spectrometer lines that preceded the ^{UNITY}INOVA.
- *MERCURY* and *GEMINI 2000* are spectrometer lines that preceded the *MERCURY-VX*.

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We want to provide the equipment, publications, and help that you want and need. To do this, your feedback is most important. If you have ideas for improvements or discover a problem in the software or manuals, we encourage you to contact us. You can reach us at the nearest Varian Applications Laboratory or at the following address:

Palo Alto Applications Laboratory
Varian, Inc., NMR Systems
3120 Hansen Way, MS D-298
Palo Alto, California 94304 USA

Chapter 1. Overview of Solid-State NMR

Sections in this chapter:

- 1.1 “Line Broadening,” this page
- 1.2 “Spin-Lattice Relaxation Time,” page 15
- 1.3 “Solids Modules, Probes, and Accessories,” page 15

Before techniques were developed to obtain high-resolution NMR spectra of compounds in the solid state, the spectra of these samples were generally characterized by broad, featureless envelopes caused by additional nuclear interactions present in solid state. In liquid state, these interactions average to zero due to rapid molecular tumbling.

1.1 Line Broadening

One cause of line broadening is heteronuclear and homonuclear *dipolar coupling*. This coupling arises from the interaction of the nuclear magnetic dipole under observation with those of the surrounding nuclei, and is directly proportional to the magnetogyric ratios of the nuclei and inversely proportional to the distance between them. In strongly coupled organic solids, the heteronuclear dipolar coupling between a ^{13}C nucleus and a bonded proton can be 40 kHz. In order to remove the heteronuclear dipolar coupling, a strong rf field equal to or greater than the interaction energy must be applied at the proton resonance frequency.

A second cause of line broadening in polycrystalline compounds is *chemical shift anisotropy (CSA)*. This is the result of nuclei with different orientations in the applied magnetic field resonating at different Larmor frequencies. The observed spread of the chemical shifts is called the chemical shift anisotropy and can be as large as a few hundred ppm. This interaction can be removed by rapidly rotating the sample about an axis oriented at an angle of 54 degrees 44 minutes (54.73° , the “magic angle” in magic angle spinning, or MAS) to the applied magnetic field. The spinning speed of the sample must be greater than the CSA in order to reduce the resonance to a single, narrow (approximately 1 ppm) line at the isotropic frequency. If the spinning speed is less than the CSA, a pattern of sidebands occurs about the isotropic peak at integral values of the spinning frequency. The CSA scales linearly with B_0 .

A third source of line broadening in solids occurs when observing nuclei that possess an electric quadrupole. The *quadrupolar interaction* can be as large as several MHz. For nonintegral spin quadrupolar nuclei, the central transition is much narrower (about 10 kHz) and therefore can be narrowed to a single, narrow line by magic angle spinning. The residual (second order) linewidth of the central transition is inversely proportional to the applied magnetic field.

1.2 Spin-Lattice Relaxation Time

An additional characteristic of some nuclei in the solid state, for example ^{13}C , is a long spin-lattice relaxation time (T_1). To overcome this problem, the abundant nuclei (usually protons) in the system are used. These are polarized with a spin locking pulse (CP). The polarization is then transferred to the rare spins by applying an rf field at the Larmor frequency of the rare spins that is of such a magnitude as to make the energy levels of the abundant and rare spins the same in the rotating frame (Hartmann-Hahn match condition). Following a transfer of energy from the polarized abundant spins to the rare spins, the rare spin field is turned off and the resulting signal observed under conditions of high-power proton decoupling. The recycle time is then set according to the proton T_1 , which is usually much shorter than the rare spin T_1 .

The polarization transfer can give an increase in sensitivity. The rare spin response is enhanced by a factor of up to the ratio of the magnetogyric ratios of the two spin systems. For the $^{13}\text{C}\{-^1\text{H}\}$ system, this is a factor of 4. However, as the enhancement is distance related, caution should be exercised in using the cross-polarization experiment for quantitative analysis.

1.3 Solids Modules, Probes, and Accessories

Varian supplies a complete line of solid-state NMR modules, probes, and accessories.

Solids modules include CP/MAS, wideline, CRAMPS/multipulse, and complete solids. CP/MAS, wideline, and CRAMPS/Multipulse hardware and operation are covered in Chapters 2, 3, and 4, respectively, of this manual.

The Varian complete solids module is capable of performing all experiments possible with the Varian CP/MAS, wideline, and CRAMPS/multipulse modules. The major components of complete solids module are the following:

<i>UNITYINOVA or UNITYplus System</i>	Wideband ADC with Sum to Memory Solids cabinet High-band & low-band 1-kW amplifier Pneumatics/tachometer box
<i>MERCURYplus and MERCURY-Vx systems</i>	100 Watt High-band and 300 Low-band amplifiers for CP/MAS experiments Pneumatics/tachometer box
<i>UNITY or VXR-S System</i>	Wideband ADC Solids cabinet High-band & low-band 1-kW amplifier Pneumatics/tachometer box Wideband receiver Sync module Two fine attenuators

For operation of the complete solids module, refer to the operations sections in the chapters 2 to 4 for the CP/MAS, wideline, and CRAMPS/multipulse modules.

A wide variety of solids probes and probe accessories are available, including wideline, multipulse, and magic-angle probes.

Optional solids accessories include rotor synchronization, rotor speed controller, and the solids variable temperature accessory. Chapter 5 covers using these accessories.

Chapter 2. CP/MAS Solids Operation

Sections in this chapter:

- 2.1 “CP/MAS Solids Modules,” this page.
- 2.2 “Rotor Characteristics and Composition,” page 20.
- 2.3 “Preparing Samples,” page 21
- 2.4 “Spinning the Sample,” page 22.
- 2.5 “Adjusting Homogeneity,” page 29.
- 2.6 “Adjusting the Magic Angle,” page 32.
- 2.7 “Calibrating the CP/MAS Probe,” page 35.
- 2.8 “Referencing a Solids Spectrum,” page 37
- 2.9 “XPOLAR1—Cross-Polarization,” page 38
- 2.10 “Optimizing Parameters and Special Experiments,” page 41.
- 2.11 “Useful Conversions,” page 44.

2.1 CP/MAS Solids Modules

CP/MAS hardware differs between systems. This section provides an overview of the hardware (excluding probes) for:

- *UNITYINOVA*, *UNITYplus*, and *UNITY* systems with 100/300 Watt CP/MAS accessory
- *UNITYINOVA*, *UNITYplus*, and *UNITY* systems with a full solids bay containing one or more 1 kW amplifiers
- *MERCURYplus* and *MERCURY-Vx* systems with the 100/300 CP/MAS option

CP/MAS Hardware for 100/300 Watt Systems

The CP/MAS option is available for most narrow bore *UNITY* and all *UNITYINOVA*, *UNITYplus*, *MERCURYplus* and *MERCURY-Vx* systems. A class A/B AMT 3900A-15 linear amplifier, with a maximum output of 100 W for up to 250 ms, replaces the standard ¹H/¹⁹F liquids linear amplifier for all systems. *UNITYINOVA*, *UNITYplus*, and *UNITY* systems use the standard lowband amplifier which has an output of 300 W. The *MERCURYplus* and *MERCURY-Vx* system lowband amplifier is replaced by the 300 W lowband amplifier used in the *UNITYINOVA* system.

The *UNITYINOVA*, *UNITYplus*, and *UNITY* system CP/MAS accessory amplifier chassis is distinguished from standard amplifier chassis by the presence of three amplifier bricks as compared to two amplifier bricks in the standard chassis. The *MERCURYplus* and *MERCURY-Vx* system CP/MAS amplifier chassis is housed in an accessories console attached to the standard console.

Full-Solids $^1\text{H}/^{19}\text{F}$ 1 kW Amplifiers

UNITY*INOVA*, UNITY*plus*, and UNITY wide bore systems can be equipped with the full bay solids option that includes a 1 kW $^1\text{H}/^{19}\text{F}$ amplifier. The amplifier is a class AB tube amplifier, tunable to either ^1H or ^{19}F , driven by the standard 50 W high band amplifier, and produces 1 kW at 400 MHz and below. Power output at 500 to 900 MHz is lower and specifications are available for individual amplifiers.

Cavity tuned amplifiers used in older systems are distinguished from the current amplifiers by the external control box used to tune the cavity. These older amplifiers are often referred to as CPI amplifiers in recognition of the manufacturer of the tube.

Current and newer systems incorporate the CMA amplifier manufactured in Fort Collins, Colorado, USA by Varian Inc. These amplifiers offer the option of either class AB or class C operation. CMA amplifiers are tuned manually using calibrated tuning knobs. The amplifier is enabled or disabled using the switches on the front panel of the full solids bay.

- Enable high power amplifier operation
Place the HI BAND amplifier switch in the HI POWER position (an orange LED will illuminate) and enable high power with the silver button (a green LED will illuminate).
- Disable high power amplifier operation
Place the HI BAND amplifier switch in the LO POWER position and press the red button. The 50 W amplifier remains enabled.

CPI and CMA amplifiers operate in both pulsed and continuous (CW) modes. The parameter `ampmode` is used to select the operation mode for CPI amplifiers. When the parameter `ampmode` is not present the amplifier is set in the default CW mode (`ampmode = 'c'` or `'d'`) which is correct for CP/MAS experiments. CMA amplifier modes; CLASS C, CLASS AB (CW), or GATE ACTIVE (pulsed), are selected using the three position switch on the front panel of the amplifier. Set the switch to CLASS AB mode for CP/MAS experiments, GATE ACTIVE mode for ^1H or ^{19}F observe, or CLASS C for special multipulse experiments. The `ampmode` parameter must be either set to the correct value or in the default mode as it determines the operation of the 50 W $^1\text{H}/^{19}\text{F}$ amplifier that drives the CMA amplifier.

Full-Solids Lowband 1 kW Amplifiers

The high power lowband amplifier in the full solids bay is a class A linear amplifier and is either an AMT 3201 (older systems) or AMT 3200 series amplifier. These amplifiers produce 1 kW at full power over a range of 6 to 220 MHz (up to ^{31}P for systems with ^1H at 500 MHz or ^{13}C for systems with ^1H at 900 MHz).

The 3201 amplifier on older systems does not have a power meter on the front panel. Input to the older amplifier is from the standard 300 W lowband amplifier in the console. The high power amplifier is enabled or disabled using the switches on the front panel of the full solids bay.

- Enable high power amplifier operation
Place the LO BAND amplifier switch in the HI POWER position (an orange LED will illuminate) and enable high power with the silver button.
- Disable the high power amplifier and return to the standard amplifier
Place LO BAND amplifier switch in the LO POWER position and press the red button. The 300 W amplifier remains enabled.

The 3200 amplifier on newer systems has a power meter on the front panel. Input drive is provided by the milliwatt transmitter board in the console. The high power amplifier is enabled or disabled using the switches on the front panel of the full solids bay.

- Enable high power amplifier operation
Place the LO BAND amplifier switch in the HI POWER position (an orange LED will illuminate) and enable high power with the silver button.
- Disable the high power amplifier operation
Place LO BAND amplifier switch in the LO POWER position and press the red button. If a 300 W lowband amplifier is present in the console it will now be enabled.

Low-band amplifiers operate in either pulsed or CW mode. The operation mode is controlled by the `ampmode` parameter. When the parameter `ampmode` is not present the amplifier is set in the default (CW) mode (`ampmode = 'c'` or `'d'`) which is correct for CP/MAS experiments.

Fine Attenuators

UNITY INOVA and UNITYplus Systems

The standard UNITY INOVA and UNITYplus system transmitter board provides fine power control over a range of 0 to 60 dB in 4095 steps. Output in voltage or field strength is linear and quadratic in power. The attenuator control in dB is shown in Figure 1. A rough rule is; for a 2 fold change in fine power there is a 6 db change in the coarse power (`tpwr` or `dpwr`). Power is controlled using the parameters: `tpwrf`, `dpwrf`, `dpwrf2`, and `dpwrf3`. Aliases of these parameters ending in `m` rather than `f` are used in some pulse sequences, including XPOLAR1. The parameters `crossp` and `dipolar` in XPOLAR1 are two different values that set `dpwrf` during the cross polarization and decoupling periods respectively.

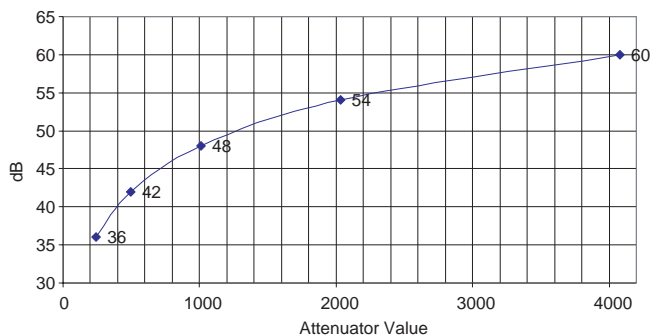


Figure 1. Attenuator Control Graph for INOVA Systems

MERCURYplus and MERCURY-Vx Systems

The transmitter board provides fine power control over a range of 0 up to 40 db in 255 amplitude steps using the parameters `tpwrf` and `dpwrf`. Output in voltage or field strength is linear and quadratic in power. The attenuator control in dB is shown in Figure 2.

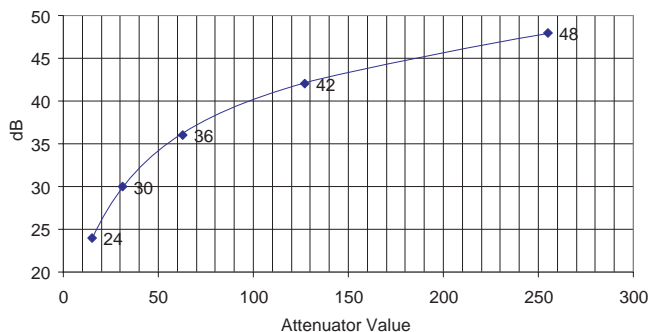


Figure 2. Attenuator Control Graph for Mercury Systems

UNITY Systems

Fine attenuator control is provided over a 6 db range in steps from 0 of 4095 on one or both transmitter boards. It is necessary to use both the fine and course attenuators on UNITY systems to set the power levels for CP/MAS experiments. UNITY systems use the same XPOLAR1 aliases described above. In addition a new coarse power setting, `cppwr` (alias for `dpwr`) used during cross polarization, is created by setting `dblvl2='y'`. The parameter `dpwr` then applies only to the decoupling power. UNITY systems with a fine attenuator only on the highband channel must first set the observe power using the course attenuator and then high band channel using both the course and fine attenuators. CP/MAS is very difficult if the fine attenuators are absent on both channels.

The XPOLAR sequence (described in older versions of this manual) can be used with UNITY systems.

Pneumatics and Tachometer Box and Rotor Speed Control

A pneumatics/tachometer box is used for controlling air flow and spinning speeds of MAS rotors for all systems. A manual box allows adjustment of bearing and drive pressure with knobs and is independent of the console. Alternatively a rotor speed controller is available for UNITY INOVA and all MERCURY systems with the solid option. Rotor speed control is obtained by modulation of the drive flow and is under computer control. The Rotor Speed Controller tachometer box is distinguished from the manual tachometer box by a 9 pin connector on the lower right. The connector is used to connect the optional cable from the tachometer box to the back of the acquisition computer on UNITY INOVA or the to Spinner board in the magnet leg on MERCURY systems. Rotor speed control software is located in the MSR board of INOVA and the Spinner board of MERCURY systems. A UNITY INOVA system equipped with both the Rotor Synchronization and Rotor Speed Control options and appropriate cables for the acquisition computer can trigger pulses on the tachometer signal using the pulse sequence commands `xgate`, `rorotsync`, and `rotorperiod`.

The operation of the Pneumatics and Tachometer Box is described in section 2.4 “Spinning the Sample,” page 22.

An older standalone PC may be present to provide rotor speed control for UNITYplus and UNITY. Instructions for this controller are provided in older manuals.

2.2 Rotor Characteristics and Composition

Varian high-speed rotors (with and without vent holes) are composed of zirconia or of silicon nitride (Si_3N_4) with pMMA, Kel-f, or Torlon end caps. The cap twist-fits into the rotor body and is held with two O-rings. Always check the maximum spin rate specification for Varian rotors and end caps as listed [Table 1](#).

Table 1. Characteristics of Varian Rotors and End Caps

<i>Item</i>	<i>Material</i>	<i>Color</i>	<i>Recommended Temperature Range (C)</i>	<i>Max Spin Rate Ambient (Hz)</i>	<i>Max Spin Rate VT (Hz)</i>	<i>Varian Part No.</i>
Rotor, 7 mm	Zirconia	white or off-white	—	7200	—	00-991036-00
Rotor, 7 mm	Silicon nitride	gray	-125° to +125°	9500	9000	00-990874-00
Rotor, 5 mm	Silicon nitride	gray	-125° to +125°	15000	13000	00-992521-00
Rotor, 5 mm	Silicon nitride (CRAMPS)	gray	-125° to +125°	15000	13000	00-993263-00
Cap, 7 mm	Torlon	green	-125° to +125°	9500	9000	00-991646-01
Cap, 7 mm	Torlon, vented	green	-125° to +125°	5000	—	00-991647-00
Cap, 5 mm	Torlon	green	-125° to +125°	15000	9000	00-992519-00
Cap, 5 mm	Torlon, vented	green	—	5000	—	00-992524-00
Cap, 7 mm	pMMA	colorless-clear	-125° to ambient	9500	9000	00-991038-00
Cap, 5 mm	Kel-F, vented	colorless-opaque	-125° to +80°	5000	5000	01-902171-00
Cap, 7 mm	Kel-F	colorless-opaque	-125° to +80°	7000	7000	00-992558-00
Cap, 5 mm	Kel-F	colorless-opaque	-125° to +80°	7000	7000	00-993228-00
Cap, 5 mm	Kel-F	colorless-opaque	-125° to +80°	7000	7000	00-993262-00

Current Si_3N_4 rotors are of two-piece construction. If the rotor plug breaks loose from the rotor body, reinsert the plug and secure it with cyanoacrylate.

Tachometer sensing on high-speed rotors is on the rotor bottom. Zirconia rotors are marked with a permanent black marking pen or black enamel paint so that 50% of the bottom of surface area is shaded black; silicon nitride (Si_3N_4) rotors are marked with white enamel paint in the same fashion. Centrifugal force and rotor crashes cause the black and white markings to flake off around the edges resulting in inaccurate tachometer readings. Reapply the black or white half circle. Make the diameter marking straight.

Below -100°C, a potential for slipping due to differential contraction with the ceramic rotor exists. Kel-F end caps (colorless-opaque) have a VT upper limit of about +70°C and should not be spun faster than 6500 Hz at any temperature. Use pMMA (colorless-clear) end caps only at room temperature and below. Visually distinguishing between Kel-F and pMMA end caps can be difficult, so you may want to mark them appropriately.

Rotor and end cap compositions are given in [Table 2](#).

Table 2. Background Nuclei of Rotor Material

<i>Material</i>	<i>Background</i>
Kel-F end cap	C (not cross-polarizable from H), F (cross-polarizable)
Vespel, Torlon, pMMA end cap	C (cross-polarizable), H
zirconia rotor*	Zr, O, traces of Mg, Y, Al
Si ₃ N ₄ rotor**	Si, N, some Al

*Not recommended for CP/MAS experiments.

**Use Si₃N₄ rotors only for high power CP/MAS applications.

2.3 Preparing Samples

Solid samples are normally packed into hollow rotors and sealed with fluted caps. The method of filling the rotors depends somewhat on the form and nature of the sample. The most critical factor in spinning reliability is the dynamic balance of the filled rotor. Some specific recommendations on filling the rotors and achieving a reasonable balance for different kinds of samples are given below.

Homogeneous Machinable Solids

Although some hard machinable polymers can be made directly into solid rotors, it is much easier to make a plug for the standard hollow rotor. The signal-to-noise difference is not that significant. The fit must be tight enough to prevent the plug from rattling around or slipping out during spinning. The sample material must be homogeneous and free of voids for the spinning rotor to remain balanced.

One way to remove a sample plug is to drill and tap a center hole about halfway through the plug for a 2-56 screw. This is best done on a lathe to facilitate centering and ensure balance. A small screw is then used to extract the plug.

Machine samples of solid materials to 0.440 ± 0.005 in. (11.176 mm) in length with a diameter of 0.1960 ± 0.0005 in. (4.979 mm) for Varian 7-mm rotors or 0.137 in. (3.48 mm) for Varian 5-mm rotors and placed inside a rotor.

Granular and Powdered Materials

The best method for filling the rotors with granular or powder materials is to pour the material into the rotor and leave just enough room for the cap. Granular and powdered materials work best as uniform particles of 100 mesh or finer. If the material can be ground, do so before attempting to pack the rotor (a mortar and pestle is usually sufficient). Fluffy or flaky materials can be packed with a rod machined to a slightly smaller diameter than the internal diameter (ID) of the rotor. Hand pressure is sufficient. Hard packing with a press or hammer is not necessary and can damage the rotors. The cap works best if it is in contact with the top of the sample material and fits snug and flush with the top of the rotor.

Miscellaneous Materials

Sample material types and forms exist that are not machinable solids, granular, or powdered. Some of these materials can be prepared in rotors so that dynamic balance is

preserved. Chances are good that the sample will spin adequately if the material can be made to fill the rotor homogeneously.

Thick sheet or film materials are best handled by cutting or punching many disks, each having the inside diameter of the rotor, and stacking them in the rotor until full.

Coarse and irregular granular materials as well as pellets, beads, flakes, bits, or pieces often cannot be packed homogeneously enough to provide the balance necessary for high speed spinning. Sometimes such materials can be made to spin smoothly by filling the voids with a fine powder that does not give NMR signals, such as KBr, talc, or sulfur flowers and spinning at a lower speed.

Liquid Samples

CAUTION: Organic solvents can dissolve pMMA end caps.

Use an end cap that has a concentric hole drilled through it (a #73 drill is recommended) for liquid samples. Be sure the end cap will not dissolve (organic solvents can dissolve pMMA end caps). Liquid samples can be spun at 200 to 300 Hz, but the liquid may spin out of the rotor and be lost. This fact must be considered when dealing with toxic or noxious samples.

Semi-Solid Samples

Semi solid samples such as phospholipid suspensions can spin faster than liquid samples. Care must be used in filling the rotor to avoid lubricating the end cap with the sample. If the end cap is lubricated with the sample the cap could pop off during the experiment. A very small dot of cyanoacrylic glue can be used to secure the end cap. Do not use too much glue or you will not be able to remove the end cap later.

2.4 Spinning the Sample

WARNING: A projectile hazard exists if a spinning rotor explodes. To prevent possible eye injury from an exploding rotor, avoid spinning rotors outside the magnet. If it is necessary to spin a rotor outside the magnet, use a certified safety shield and full face shield at all times. Never use rotors that have been dropped onto a hard surface, since microscopic cracks in the rotor material can cause rotor explosions at much lower spinning speeds than indicated in **Table 3** and **Table 4**. Never spin zirconia (white) rotors at spinning speeds above 7.2 kHz. Never spin silicon nitride (gray) rotors at speeds above 9.5 kHz. Never apply air drive pressure above 72.5 psig (5.0 bar).

WARNING: Excessive spinning speeds can cause the rotors to shatter and explode. Never spin zirconia (PSZ) rotors (white or off-white in color) above 7.2 kHz or silicon nitride rotors (gray) above 9.5 kHz. For samples that have densities above 3.0 g/cc, decrease the maximum spin rate by 35%.

CAUTION: When removing caps or digging out packed samples, take care not to gouge the rotor. Even small scratches can imbalance the rotor.

Introduction

The following applies to spinning the sample regardless of the type of pneumatics/tachometer box in use. After reviewing these general instructions, see the following sections for operating instructions that apply to the specific pneumatics/tachometer box that is installed on your system.

- Pneumatics/tachometer box with rotor spin speed control from within VNMR, see [“Using the Rotor Speed Controller,” page 25](#).
- Pneumatics/tachometer box with manual spin control, see [“Using the Manual Pneumatics/Tachometer Box,” page 28](#).

Centrifugal force can cause the black and white markings to flake off around the edges. This can cause inaccurate tachometer readings. The black or white half circle can be reapplied on the rotors with a black marking pen and white enamel paint provided in the startup kit. The diameter marking should be straight.

Spinning Rates and Adjusting Bearing and Drive Pressures

Spin rates and the bearing and drive pressures for the Varian CP/MAS probe at ambient temperature are listed in [Table 3](#) for the 7-mm probe and [Table 4](#) for the 5-mm probe.

Table 3. Typical 7-mm CP/MAS Probe Spin Rates With Bearing and Drive Values

<i>Spinning Speed*</i> (Hz \pm 250 Hz)	<i>Bearing</i>		<i>Drive</i>	
	<i>Pressure</i> psig (bar)	<i>Flowrate</i> (LPM \pm 2 LPM)	<i>Pressure</i> psig (bar)	<i>Flowrate</i> (LPM \pm 2 LPM)
2500	28 (2.0)	12.5	7 (0.5)	15.0
4000	28 (2.0)	12.5	14 (1.0)	20.0
5000	36 (2.5)	12.5	21 (1.5)	25.0
6000	36 (2.5)	12.5	28 (2.0)	27.5
7200	36 (2.5)	12.5	36 (2.5)	30.0
8000	44 (3.0)	10.0	51 (3.5)	35.0
8500	44 (3.0)	10.0	58 (4.0)	37.5
9000	44 (3.0)	9.0	65 (4.5)	40.0

* Rates are approximate values for the Varian 7-mm CP/MAS probe at ambient temperature. The actual spin rate will vary depending on the properties of the sample and sample holder.

Table 4. Typical 5-mm CP/MAS Probe Spin Rates With Bearing and Drive Values

<i>Spinning Speed *</i> (Hz \pm 250 Hz)	<i>Bearing</i>		<i>Drive</i>	
	<i>Pressure</i> psig (bar)	<i>Flowrate</i> (LPM \pm 2 LPM)	<i>Pressure</i> psig (bar)	<i>Flowrate</i> (LPM \pm 2 LPM)
4500	28 (2.0)	12.5	7 (0.5)	15.0
7000	28 (2.0)	12.5	14 (1.0)	20.0
11500	49 (3.5)	12.5	35 (2.5)	25.0
13000	56 (4.0)	9.0	63 (4.5)	40.0

* Rates are approximate values for the Varian 5-mm CP/MAS probe at ambient temperature. The actual spin rate will vary depending on the properties of the sample and sample holder

For 5-mm CP/MAS probes, spinning a sample with a small amount of drive gas before applying the initial 28 psig (2.0 bar) of bearing pressure is sometimes useful. The rotor will begin spinning and will therefore become less likely to flutter (slight motion in and out of the stator) during initial spin up.

To avoid rotor explosions, never spin 7-mm zirconia rotors faster than 7200 Hz and never spin 5-mm zirconia rotors in Varian probes. Also, never spin 7-mm silicon nitride rotors faster than 9500 Hz or 5-mm silicon nitride rotors faster than 15000 Hz.

Overcoming Imbalance

Most of the spinning problems encountered with filled rotors result from imbalance caused by the sample material. A damaged rotor might be at fault, but that can be eliminated by

always checking the spinning quality of the empty rotor before packing it with the sample material. Discard damaged rotors. Worn rotor caps can cause imbalance. Changing caps or rotating them between rotors sometimes cures these problems.

If a packed rotor does not spin properly at first, inspect the sample to see if it has been disturbed. If part of the sample broke loose and was thrown out of the rotor, repacking the sample in the rotor might be the solution. Sometimes loose material balances itself if it is kept in the rotor and spun below its vibration speed for a few minutes. If the sample seems intact on the surface and the rotor is not balanced, it is likely that the sample is not homogeneous or not evenly packed. The only solution is to remove all the sample and repack the rotor. With inhomogeneous materials, this repacking may have to be tried more than once. In the case of a machined plug, the plug could have a void in it or it fits too loosely in the rotor cavity.

Probe Adjustments for Improved Spinning

Increased bearing pressure often stabilizes samples that do not spin well. This adjustment must be made at low speed and then ramped up once the rotor spinning is stable.

Using the Rotor Speed Controller

The rotor speed controller for Varian MAS probes can be operated with spinning speed regulation or with a specific airflow setting to control the spinning speed of a sample in a magic angle spinning (MAS) probe. Alternatively, the air flow can be set to a maximum (65535) and the drive-pressure regulator on the pneumatics/tachometer box can be used for manual control the spinning speed.

If the rotor speed controller has not been calibrated, follow the calibration procedures in the *Pneumatics and Tachometer Box Installation* manual before continuing.

Chemmagnetics CP/MAS probes use a different speed controller and are not compatible with this accessory.

Starting the Spinner Speed Controller

1. Enter **spinner** in the VNMR input window to open the Spinner Control window (see [Figure 3](#)).
2. Click on the **High speed spinner (solids style)** control button.
3. Click on **Turn spinner off**.
4. If **Set spinner airflow instead of speed** is engaged (button pressed in and red), click on the button to disengage and set the spinner in regulation or closed-loop mode.
5. Make sure the drive is set to 0.
6. Set the bearing pressure to 0.
7. Using your fingers, insert an end-cap into the rotor to be spun. Rotate the end cap while pushing it into the rotor. Make sure the end cap is fully seated into the rotor.
8. Carefully place the rotor with the end cap into the stator.

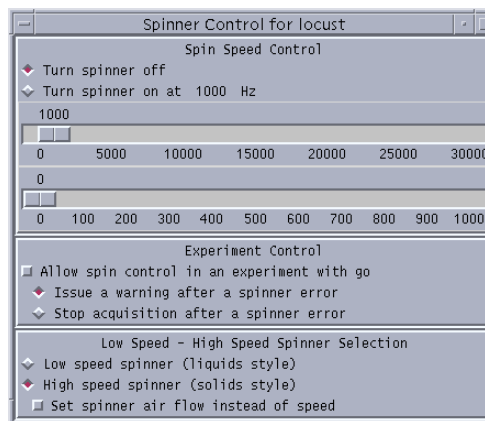


Figure 3. Spinner Speed Control Window

9. Install the probe into the magnet.
10. Set the bearing pressure to a value appropriate for the rotor speed you will be using, see [Table 3](#) and [Table 4](#) for 7 mm and 5 mm rotor bearing pressures.
11. Open the drive valve completely.
The rotor may initially spin when using older controllers but will stop when the electro-pneumatic valve engages.

Regulating Spinning Speed

Direct input of the spinner speed (using the slider bars in the Spinner Control Window, see [Figure 3](#)) uses the closed-loop mode of the spinner speed regulation option. The speed can be increased or decreased by any value and the speed is safely ramped to the new value. Making small changes in speed (1000 to 2000 Hz) is good practice, until you are comfortable with the operation and reliability of a particular rotor and endcap combination. *Never exceed the rated speed for any of the rotor parts or probe.*

1. Set the slider bar to 2500.
The spinner should regulate to ± 2 Hz or better within about 30 seconds to 1 minute.
2. Experiment with a number of set points within the rated speeds of the sample rotor and probe.
3. Set the desired spin speed using the slider bar.

Regulating Spinning Speed within VNMR

This procedure describes how to regulate spinning speed by entering commands in the VNMR input window.

1. Start the rotor speed controller as described in the procedure [“Starting the Spinner Speed Controller”](#) on page 25.
2. Click on the button next to **Allow spin control in an experiment with go**.
This button disables the speed in the Spinner Control window and transfers spin rate control to the *spin* parameter in VNMR.
3. Set up a typical solids experiment:
 - a. Set **spin** to the desired speed.
 - b. Enter **in='ny' go**.

The spinner regulates at the value of *spin*. Include a pre-acquisition delay pad to give the spinner time to stabilize. The parameter *spin* can be included in an array to obtain multiple spin rates in a single experiment. In an array of *spin*, the pre-acquisition delay is applied before each FID.

4. Click next to **Allow spin control in an experiment with go** to return control to the Spinner Control window after the experiment is complete.

Using Air Flow to Set the Spin Speed

This procedure describes how to set the air flow to spin the rotor. This mode of operation is applicable when operating at the extremes of the temperature range of the probe.

1. Enter **spinner** in the VNMR input window to open the Spinner Control window (see [Figure 4](#)).
2. Click on the **High speed spinner (solids style)** control button.
3. Adjust the two **slider bars to zero**.
4. Click the **Set spinner airflow instead of speed**.

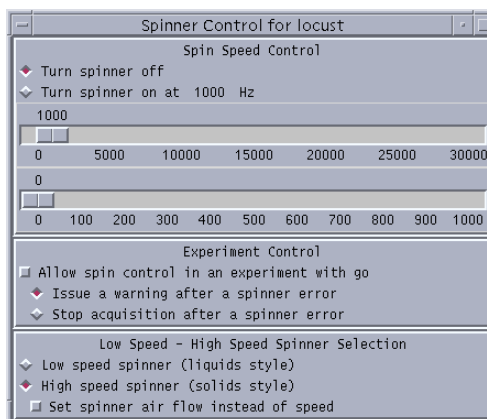


Figure 4. Spinner Speed Control Window

5. Click the **Turn spinner off** button.
6. Adjust the bearing gas pressure to 30 psig for CP/MAS probes.
7. Open the drive pressure regulator fully.

The rotor may initially spin when using older controllers but will stop when the electro-pneumatic valve engages. The spinner is now in an unregulated mode in which the airflow is set directly using the slider bar. The slider bar sets the DAC value that controls the electro-pneumatic value. The DAC has a range of 0 (no air flow) to 65536 (full open). Only the air flow is set there is no spin speed regulation.

8. Set the slider bar at 2500.
9. If the rotor fails to spin or no DAC reading appears on the tachometer, stop the rotor and remove it from the probe, check the paint on the rotor and the tachometer cables. Repeat this procedure beginning at step 1.
10. Adjust the slider bar until the rotor is spinning at the desired speed.

Move the slider bar slowly. If the rotor is spinning, changing the air flow in small steps is good practice.

The fine slider bar (bottom) can be increased by one unit when the mouse pointer is clicked in the bar. The speed displayed in the Acquisition Status window is correct. The speed displayed pneumatics/tachometer box tends to be slower.

Do not let a sample rotor exceed the maximum rating for any of the rotor parts during this process. Speed ratings may vary as a function of temperature and sample density.

Using Drive and Bearing Pressure to Control Spin Speed

1. Follow the setup instructions in [“Using Air Flow to Set the Spin Speed,”](#) page 27.
2. Reduce the drive pressure until the rotor spinning as a result of the bearing air.
3. Set the slider bars to their maximum position (electro-pneumatic valve is now fully open).
4. Adjust the drive pressure to achieve the desired rotor spin speed.

Changing Rotors

This procedure describes how to change rotors with MAS probes.

1. Set either the airflow or the rotor speed to zero and click **Turn spinner off**. *Do not* lower the drive-pressure regulator on the pneumatics/tachometer box.
The sample continues to spin at about 200 Hz with the drive air off. Turn the bearing-pressure regulator on the pneumatics/tachometer box to zero, and the rotor will stop spinning.
2. Lower the probe into its stand. The sample rotor can be removed with a small loop of tape around the index finger.
3. Place the new sample rotor.
4. Raise the probe into the magnet.
Return the bearing pressure to 30 psig (or the desired setting).
5. Set the desired spin speed or air flow.

Using the Manual Pneumatics/Tachometer Box

Table 3 and **Table 4** lists spin rates and the appropriate bearing and drive pressures for the Varian 7-mm and 5 mm CP/MAS probes at ambient temperature. The spin rates shown are approximate values. The actual spin rate varies depending on the properties of the sample and sample holder. Use the following procedure for spinning all samples in high-speed probes:

1. Using your fingers, insert an end-cap into the rotor to be spun. Rotate the end cap while pushing it into the rotor. Make sure the end cap is fully seated into the rotor.
2. Make sure the bearing and drive air pressure are off.
3. Carefully place the rotor with the end cap into the stator and install the probe into the magnet. Turn the air bearing pressure to 28 psig (2.0 bar); the rotor should start spinning slowly at 500–900 Hz.
4. Slowly turn on the air drive pressure to 3.6 psig (0.25 bar) and wait for 15 seconds to allow the rotor to stabilize.
5. Gradually increase the air drive pressure to 7 psig (0.5 bar) and again wait 15 seconds. The spinning speed should gradually increase to about 2500 Hz.
6. Slowly increase the air drive pressure to 14 psig (1.0 bar). The spinning speed should reach about 3700 Hz.
7. If rotor speeds faster than 3700 Hz are required, slowly increase the air bearing pressure to 36 psig (2.5 bar). Then increase the air drive pressure up to 34 psig (2.4 bar); the rotor speed should reach about 7200 Hz. Never apply air drive pressure above 72.5 psig (5.0 bar).

To avoid rotor explosions, never spin zirconia rotors faster than 7200 Hz or spin silicon nitride rotors faster than 9500 Hz. For samples that have densities above 3.0 g/cc, decrease the maximum spin rate by 35%.

It may be necessary to increase the bearing pressure for ill-behaved samples or for very high spinning speeds. Provided that the two flowmeter valves are fully open, they require no adjustment at any time. Never adjust the spin rate with the flowmeter.

Changing Rotors

CAUTION: To prevent damage to the rotor or bearing, always smoothly shut off the rotation gas using the rotation pressure regulator before turning off the bearing gas using the bearing pressure regulator.

1. Decrease the rotor speed smoothly by reducing the drive air pressure.
2. Maintain the bearing air at least 28 psig (1.9 bar).
3. When the rotation air is completely off and the rotor speed has slowed to a few hundred revolution per second, slowly decrease the bearing air pressure to zero.
4. Lower the probe into its stand. The sample rotor can be removed with a small loop of tape around the index finger.
5. Place the new sample rotor.
6. Raise the probe into the magnet.

Rotor Synchronization

If the spectrometer is equipped with a rotor synchronization option (Part No. 00-990385-00), the spinning speed can be read by the acquisition system.

Entering `hsrotor='y'` `su` shows the current spinning speed in the acquisition status window. The parameter `srate` is updated after each experiment to show the spinning speed. Furthermore, if `in='y'`, an acquisition is halted if the spinning speed differs by more than 100 Hz from spinning speed at the start of the acquisition.

For further details on rotor synchronization, refer to the manual *System Operation*.

2.5 Adjusting Homogeneity

For the balance of this manual, *MERCURYcpmas* will refer to *MERCURY-Vx* and *MERCURYplus* systems equipped with the CP/MAS option and *INOVAcpmas* to *UNITYINOVA* and *UNITYplus* systems with a CP/MAS option. *UNITY* systems are described in the previous versions of this manual

Homogeneity should be adjusted as follows on a sample of D₂O, prepared in a standard rotor, and tightly capped using a cap with a concentric drilled hole.

1. Insert and seat the sample in the stator.
2. Install the probe into the magnet.
3. Spin the sample slowly (several hundred Hz or less) with 2.0 bar \pm 0.5 bar bearing pressure. A very low drive (rotation) pressure can be used if necessary. Generally, this slow spinning speed barely registers on the tachometer.

With time, D₂O spins out of the rotor.

4. Enter `rt('vnmr/stdpar/H2') dm='n' su`.
5. Tune the probe to observe ²H by inserting the proper tuning stick and adjusting the probe tuning controls. See the *Getting Started* manual for instructions on how to tune a probe.

- Attach the lock cable from lock preamp to the observe (OBS) connector on the probe.

<i>System</i>	<i>Connector</i>
<i>INOVAcpmas</i>	J5205
<i>MERCURYcpmas</i>	LOCK PREAMP (J5202) or LOCK PROBE (J6002)

- Lock the spectrometer and shim on the lock signal. The principle shims involved in adjusting homogeneity when a magic angle spinning (MAS) probe is used are: Z1, Z2, X, Y, XZ, YZ, XY, and X2Y2.

A typical procedure is:

- adjust Z1, X, Y, and Z2
 - adjust XZ, YZ, XY, and X2Y2
 - readjust Z1 and Z2
 - adjust any other off-axis shims as necessary
- To see how well the field homogeneity has been adjusted, do the following:
 - Turn the lock transmitter off by entering `lockpower=0 lockgain=0 alock='u' su`.
 - Disconnect the lock cable from the probe.
 - Connect the cables so that the observe (OBS) port of the probe is connected to the observe connector on the magnet leg.

<i>System</i>	<i>Connector</i>
<i>INOVAcpmas</i>	J5311
<i>MERCURYcpmas</i>	LO BAND Preamp (J5302) or FROM BB Probe (J6001)

- Acquire a deuterium spectrum using the deuterium parameter set. The deuterium linewidth should be typically between 1 and 5 Hz.
- Finer adjustment and evaluation of the homogeneity is possible using a sample of solid adamantane (not available from Varian). A linewidth between 2 and 10 Hz is typically attainable, see the sample spectrum in [Figure 5](#).

A solids probe is not locked during normal operation and Z0 must be adjusted manually to put the lock on resonance when shimming. When the lock is on resonance the spectrometer will correctly set the transmitter and decoupler frequencies. It will be necessary to periodically reset z0 to compensate for magnet drift whenever you shim. Between shimming sessions it is sufficient to adjust `reffrq`, `tof` and `dof`.

- Continue with section [“Positioning the Probe and Shimming the D₂O FID or Spectrum,”](#) page 30.

Positioning the Probe and Shimming the D₂O FID or Spectrum

- Enter `lockpower=0 lockgain=0 rtp('\vnmr/parlib/xpolar1')`.
- Enter `su`.
- Disconnect** the lock cable from the probe.

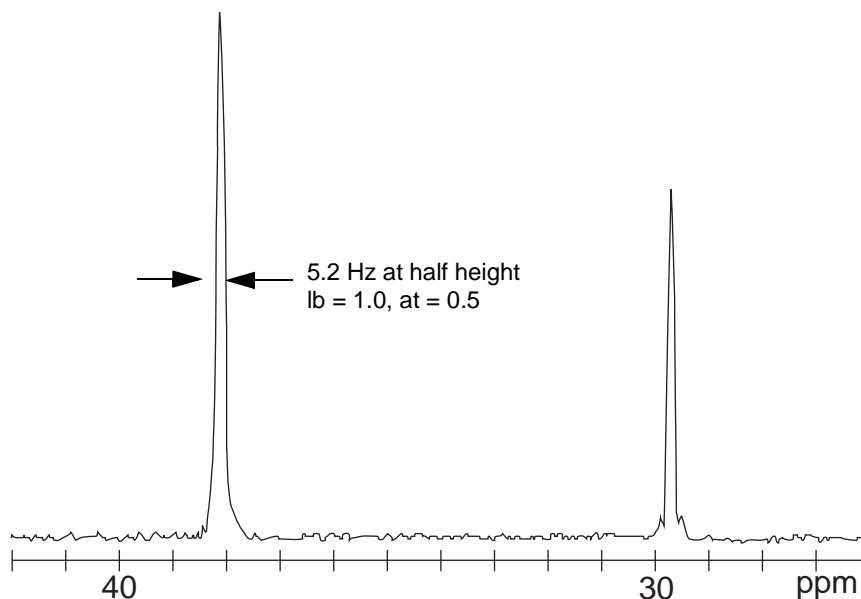


Figure 5. Typical MAS Spectrum of Adamantane

4. **Reconnect** the observe (OBS) port of the probe to the observe channel on the magnet leg.

<i>System</i>	<i>Connector</i>
<i>INOVAcpmas</i>	J5311
<i>MERCURYcpmas</i>	LO BAND Preamp (J5302) or FROM BB Probe (J6001)

5. Enter **xpol='n' dl=1.0 nt=1 gain=4 ga.**
6. Place the cursor near the D₂O resonance and enter **movetof.**
7. Enter **sw=5000 ga.** Obtain another spectrum.
8. Enter **gf acqi.**
In the interactive acquisition mode select FID and within this mode select Spectrum.
9. Find the probe position for which changing the z1 shim will not affect the line position.
 - a. Observe the spectrum, note the initial value of the Z1 shim and the initial position of the probe (distance between the base of the magnet and the top of the probe base or other convenient fixed reference point).
 - b. Make a large positive change in the z1 shim.
The D₂O resonance may move to positive or negative frequency.
 - c. If the D₂O resonance does not move go to step h.
If the D₂O resonance does move make note of the direction and continue with **step d.**
 - d. Loosen the setscrews on the probe flange.
 - e. Change the height of the probe by a few millimeters (either up or down may be necessary).
 - f. Tighten the setscrews and return z1 to the original value.

- g. Make the same large positive change in the z1 shim as in step b. If the D₂O resonance moves again, note the direction and magnitude of the change.
- If the change is smaller, continue moving the probe in the same direction and repeating steps d through g.
- If the change is larger or the same, return the probe and shim to their original position and value. Move the probe in the opposite direction and repeat steps b through g.
- h. When the D₂O resonance no longer changes when z1 is changed, record the height and/or mark the position of the flange on the probe body. Tighten the setscrews on the probe flange.
10. Repeat **step 6** through **step 12** of section “Adjusting Homogeneity,” page 29 for the new probe position. If you interactively fine-adjust the shims and set z0 while observing the FID or spectrum in step 5 it is not necessary to repeat **step 6** through **step 12**.
- A linewidth of 2 to 3 Hz is typical but 6 Hz is acceptable.
11. Continue with 2.6 “Adjusting the Magic Angle,” page 32.

2.6 Adjusting the Magic Angle

Improper adjustment of the magic angle results in incomplete collapse of the chemical shift anisotropy (CSA) pattern. For carbons with significant anisotropy, such as aromatics and carbonyls, this can greatly affect the linewidth of the observed resonance. In general, once adjusted, the magic angle should stay fairly constant. However, this is not guaranteed. The angle should be checked and adjusted as follows:

- When the probe is inserted in the magnet
- Every few days of continuing operation
- If linewidths in any particular sample are suspiciously large

Once typical values for the minimum linewidths are established for any particular instrument, these values can be taken as a reliable indication of proper angle. Adjustment of the angle is neither necessary nor desirable if the first measurement indicates that the minimum linewidth has been achieved.

Coarse Adjustment

A convenient method of setting the sample angle to the approximate magic angle before final optimization with NMR is to use the angle measuring stem (Part No. 00-992825-00) and angle measuring gauge (Part No. 00-992826-00) from the rotor and tool kit. **Figure 6** illustrates how the angle measuring stem and angle gauge are used.

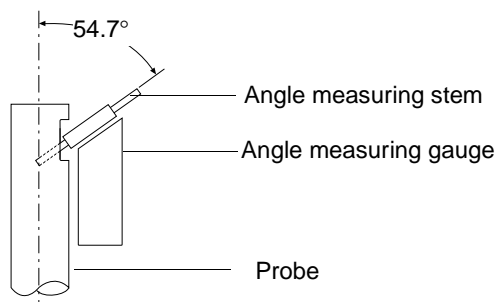


Figure 6. Coarse Adjustment of Sample Angle

Fine Adjustment

The preferred method of adjusting the magic angle uses the ⁷⁹Br spectrum of KBr, which, when spun at the magic angle results in an extensive set of spinning sidebands. As ⁷⁹Br is

very close in frequency to ^{13}C , it is easy to switch between the two nuclei. The magic angle can easily be set or checked as described below.

1. Enter `rt('vnmr/parlib/xpolar1')`.
2. Enter `tn='Br79'` to obtain the parameter set to observe ^{79}Br .
3. Load a rotor with KBr, insert it in the probe, and spin it at 3 kHz.
Grinding the KBr crystals before packing the rotor is helpful.
4. Tune the system for ^{79}Br (remove the capacitor stick if it is present) — retuning is not necessary if the probe is tuned for ^{13}C .
5. Enter `xpol='n' dm='n' d1=0.02 sw=1e5 at=0.02 nt=16 lb=0`.
6. Set the following parameter value according to the spectrometer used:

Parameter	INOVAcpmas	MERCURYcpmas
gain	15	10

7. Enter `su`.
8. Tune the probe.
9. Enter `ga` to obtain a spectrum.
10. Set the cursor on resonance, and enter `nl movetof`.
11. Enter `ga` to obtain a spectrum.
12. Type `df` and phase the fid as in [Figure 7](#) and [Figure 8](#).
13. Enter `gf`.
14. Open the `acqi` window, click the **FID** button, and observe the real-time FID display.
The FID displays a transient that is an exponential decay with a “picket fence” of one or more spikes on it (see [Figure 7](#) and [Figure 8](#)). If the signal is not exactly on resonance, repeat [step 10](#) and [step 12](#).
15. Select IPA and adjust `phfid` to maximize the on resonance FID.
16. Adjust the angle using the fiberglass rod with the adjustment tool.
Maximize the size and number of spikes in the picket fence. The spikes should persist for about 10 ms. The sample angle is now set to the magic angle.
17. Close the `acqi` window and retune the probe to ^{13}C .

An alternative method of adjusting the magic angle uses ^{13}C CP/MAS of the standard sample, hexamethylbenzene (HMB), which has two ^{13}C resonances. Of these, the aromatic carbon line (on the left side of the spectrum) is extremely sensitive to the angular adjustment. [Figure 9](#) shows a typical spectrum, including sidebands, of the aromatic resonance (with `lb=0` and good shims). Adjust the aromatic line for minimum linewidth and maximum intensity.

Once typical values for the minimum linewidths are established for any particular instrument, these values can be taken as a reliable indication of proper angle. Adjustment of the angle is neither necessary nor desirable if the first measurement indicates that the minimum linewidth has been achieved. Typical values are 67 Hz for a 300 MHz system and 90 Hz for a 400 MHz system.

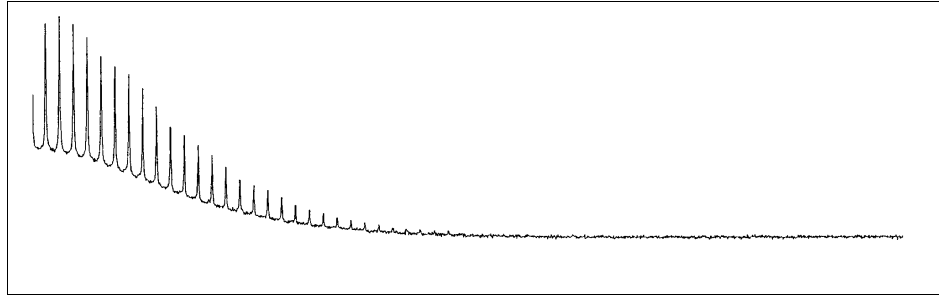


Figure 7. FID Display of KBr on Angle

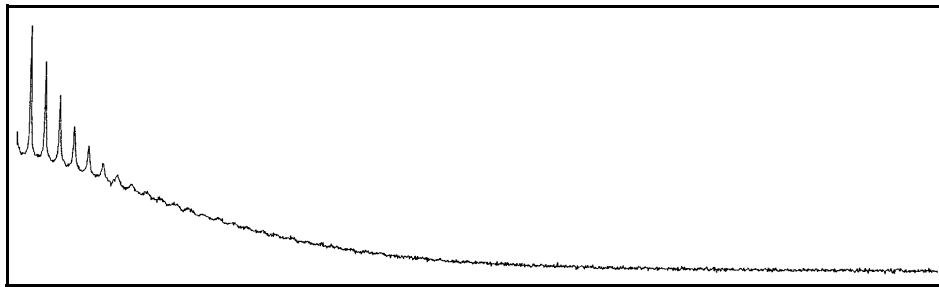


Figure 8. FID Display of KBr 1/2 Turn Off Angle

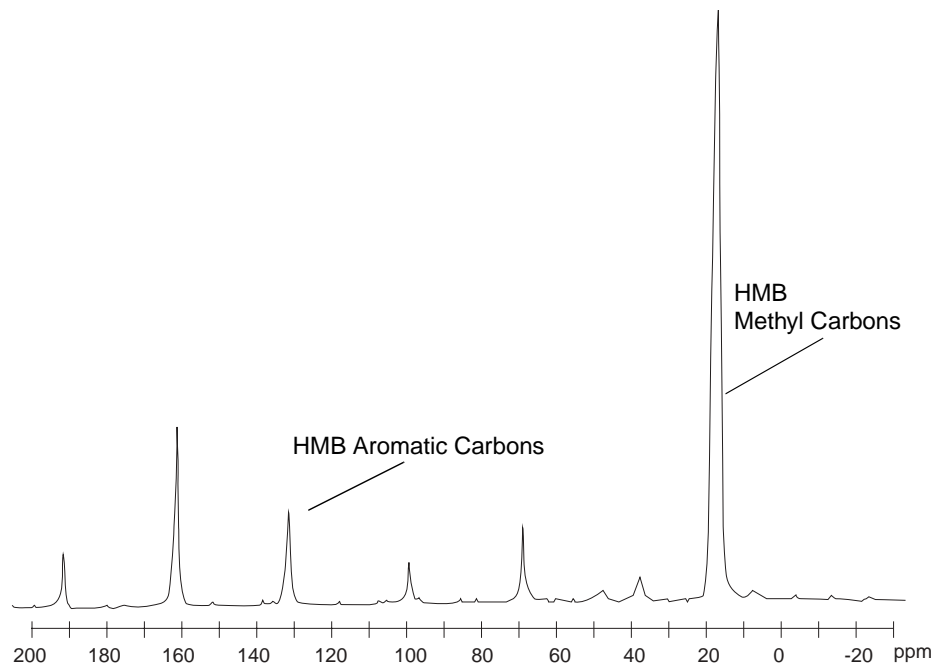


Figure 9. Typical Hexamethylbenzene (HMB) Spectrum

2.7 Calibrating the CP/MAS Probe

Calibrating ^{13}C Nucleus Pulse Width

The following steps cover calibrating the pulse width.

1. Insert a rotor containing liquid-state p-dioxane and spin at 200-300Hz.
Do not spin faster than 200-300 Hz, or the p-dioxane will be forced out of the hole in the rotor cap. The addition of a small amount of CrAcAc (not provided) to the p-dioxane will allow you to use $d1=1.0$ in these tests.
2. Recall the parameters by entering `rt('/vnmr/parlib/xpolar1')`.
3. Enter `tn='C13' reffrq=sfrq d1=10 nt=4 xpol='n' at=0.05 lb=10`.
4. Set the following parameter values according to the spectrometer used:

Parameter	INOVAcpmas	INOVAcpmas (1 kW amplifier)	MERCURYcpmas
gain	40	40	20
tpwr	63	54	63
tpwrm	1600	1600	100
dpwr	63	55	63
dipolar	1600	1600	100

5. Enter `su`.
6. Tune the probe to ^{13}C for p-dioxane.
See *Getting Started* for instructions on how to tune a probe.
7. Enter `ga`.
8. Place the cursor 500 Hz on low field side of the p-dioxane resonance and enter `movetof`.
9. Enter `sw=5000 ga`.
10. Array `pw` from 0 to 5 times the 90° pulse width specification.
11. Increase `tpwrm` as necessary to achieve the 90° pulse width specification or desired 90° pulse width. Do not exceed the 90° pulse width specification.
If you cannot achieve the ^{13}C 90° pulse width specification with `tpwrm` set to full value, you may need to remove any attenuation added to the lowband amplifier and repeat the calibration.
12. Record the values of `tpwr` and `tpwrm` used to obtain the ^{13}C 90° pulse width specification. Save the final data for reference.
Estimate the ^{13}C 90° pulse width using either use the maximum 90° or find the difference between the 360° and 180° and divide by 2. The 180° is not a good measurement of twice the 90° because of r.f. inhomogeneities of the coil.
13. Continue with [“Calibrating Decoupler Power,” this page.](#)

Calibrating Decoupler Power

Using the previously determined pw , calibrate decoupler power (γB_2) as follows.

1. Recall the parameters used in the previous test.
2. Set pw , tpwr , and tpwrm to the values obtained for the ^{13}C 90° pulse width specification in “Calibrating ^{13}C Nucleus Pulse Width,” page 35.
3. Enter $\text{dof}=5\text{e}4,-5\text{e}4$ $\text{d}1=10$ $\text{xp}1='n'$.
4. Enter $\text{at}=0.05$.
5. Set the following parameter values according to the spectrometer used.

Parameter	INOVAcpmas	INOVAcpmas (1 kW amplifier)	MERCURYcpmas
d pwr	63	55	63
dipolar	4095	4095	255

6. Enter ga .
7. When acquisition is finished, measure the reduced coupling on each of the two spectra.
8. Enter $\text{h}2\text{cal}$ to calculate γB_2 .
This is the maximum decoupler power, $\gamma\text{B}_2\text{Max}$. Record this value. If the value of $\gamma\text{B}_2\text{Max}$ fails to meet specifications, remove some of the attenuation from the input to the highband amplifier and repeat the $\gamma\text{B}_2\text{Max}$ calibration.
9. Calculate the $\gamma\text{B}_2\text{CP}$ (^1H cross polarization field):
 - a. $\gamma\text{B}_2\text{CP}=1.0/(4.0*^{13}\text{Cpw}90)$ where $^{13}\text{Cpw}90$ is the value determined in the previous section.
 - b. Adjust dipolr and enter ga .
 - c. Repeat step 6 and 7.
 - d. Adjust the value of dipolr until the value for γB_2 measured in 7 equals the value calculated in step 8a.
 - e. Record the values of dipolr and $\gamma\text{B}_2\text{CP}$. These values will be used in the next section.
10. Continue with “Adjusting the Hartmann-Hahn Match,” this page.

Adjusting the Hartmann-Hahn Match

Hartmann-Hahn matching can be readily accomplished by using a sample of hexamethylbenzene, HMB.

1. Load a rotor with HMB, insert it in the probe, and spin it at about 2500 Hz.
2. Recall the test parameters by entering $\text{rt}(' / \text{vnmr} / \text{parlib} / \text{xpolar}1')$.
3. Enter $\text{xp}1='y'$.
4. Set pw , and tpwr to the values obtained for the ^{13}C pw90 in “Calibrating ^{13}C Nucleus Pulse Width,” page 35.
5. Enter dpwr dipolr and dof values determined in “Calibrating Decoupler Power,” page 36.

Use the second set of values for the ^1H cross polarization field.

6. Enter **crossp=dipolar cntct=2500 at=0.02 d1=1 nt=4 sw=45000**.
7. Set the following parameter values according to the spectrometer used.

Parameter	INOVAcpmas	INOVAcpmas (1 kW amplifier)	MERCURYcpmas
gain	40	40	20
tpwr	60	54	63
tpwrn	array('tpwrn', 40, 95, 100)		array('tpwrn', 52, 0, 5)

8. Enter **lb=50 ga**.
9. When acquisition is finished, enter **dssh** to display the results.
10. Select the spectrum with the lowest value of **tpwrn** that gives the maximum signal and set **tpwrn** to the value of this spectrum.
11. Optimize **pw**.
 - a. Array **pw** from 0 to 2 times its current value.
 - b. Enter **d1=1 ga**.
 - c. When acquisition is finished, enter **dssh** to display the results.
 - d. Select the spectrum with the maximum signal and set **pw** to this value.
 - e. Enter **ga**.
 - f. Save this spectrum for reference.
12. Continue with **“Measuring Signal to Noise,”** page 37.

Measuring Signal to Noise

1. Use the parameters and the value of **tpwrn** from **“Adjusting the Hartmann-Hahn Match,”** page 36.
2. Enter **d1=5 nt=4**.
3. Enter **ga**.
4. Set **delta=10000** and place cursor at the right edge of the spectrum and enter **dnsmax** to measure the signal to noise.
5. Compare the signal to noise to the specifications.
If necessary, increase the gain and repeat **step 2** through **step 4**. Do not overload the ADC.
6. Repeat **step 2** and **step 4** three times and record the signal to noise for each test.
7. Record the average signal to noise for the system.

2.8 Referencing a Solids Spectrum

A solids probe is not locked during operation. If exact chemical shifts are required, a spectrum of a test sample with know chemical shift must be obtained. The HMB signal-to-noise sample can be used for this purpose.

1. Obtain a spectrum of HMB using the parameters that gave the best spectrum in **2.7 “Calibrating the CP/MAS Probe,”** page 35.
2. Enter **cr=100p movetof**.

The transmitter is placed in the center of the spectrum.

- Enter **ga**.
- Put the cursor on the tall methyl line and type **n1 r1(17.43p) ga**.

The reference (`reffrq`) is set only after you use the `r1` command to reference. If you change `tn` without using `r1` the chemical shift scale and reference will be that of the previous nucleus. The new reference (`reffrq`) is saved with the data only after you type `ga`. If you do not acquire a new spectrum you will reference only the display (`rfl` and `rfp`) in the current experiment.

Table 5. Reference Materials and ^{13}C Chemical Shifts

<i>Substance</i>	<i>Chemical shift (ppm)</i>
adamantane	29.2, 38.3
delrin	88.5
glycine	43.6, 176.4
hexamethylbenzene	17.3, 132.1
poly(methyl methacrylate)	19, 45, 51, 176
talc (^{29}Si)	-90

- Save the HMB data set and use it as the starting point for all solids spectra until you re-reference.

The frequency of re-referencing depends upon the drift rate of your magnet. A drift rate of 10 Hz per hour is 2.5 Hz per hour for ^{13}C . A typical ^{13}C linewidth of a solid is between 30 Hz and 300 Hz.

For most purposes, this procedure should be followed only at the time the probe is installed. The ^{13}C chemical shifts of a few reference materials are given in [Table 5](#).

2.9 XPOLAR1—Cross-Polarization

XPOLAR1 is applicable to *MERCURYplus*, *MERCURY-VX*, *UNITYINOVA*, *UNITYplus*, and newer UNITY systems. The parameters that control the attenuators and linear modulators are shown in the diagram of XPOLAR1, see [Figure 10](#).

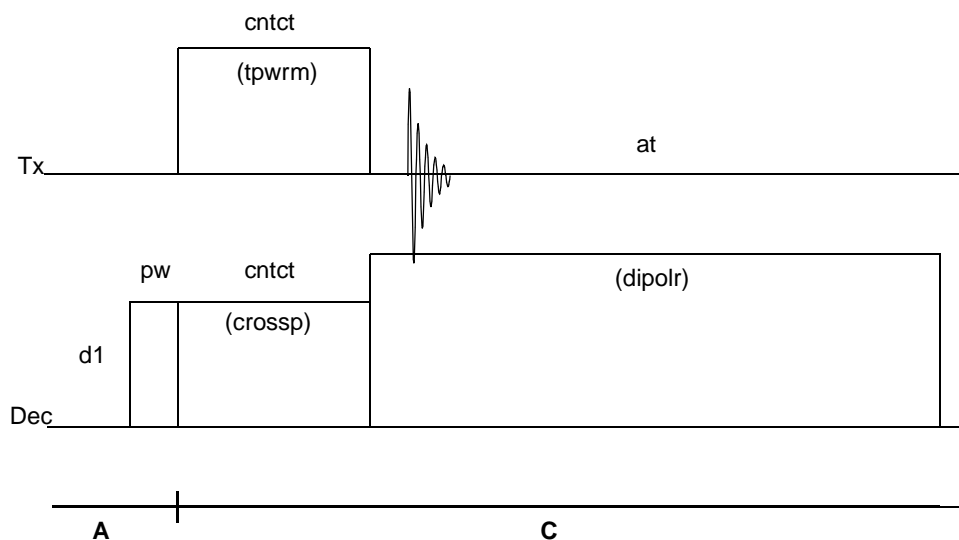


Figure 10. XPOLAR1 Pulse Sequence

Cross-polarization amplitudes should be controlled using the fine attenuator. The fine attenuator has a range of 60 dB for Inova and 48 dB for *MERCURY* systems down from the course attenuator. The coarse attenuator is set to a value corresponding to the maximum specification of the probe. Cross-polarization on the UNITY requires the use of both the coarse and fine attenuators (6 db range).

Applicability

XPOLAR1 can be found in `/vnmr/psglib`. The *MERCURYplus* and *MERCURY-VX* version of XPOLAR1 is not interchangeable with XPOLAR1 for ^{UNITY}INOVA and UNITYplus systems. UNITY systems can use both XPOLAR1 and XPOLAR by setting `dblvl2='y'`.

Macro

When this macro is run on a ^{UNITY}INOVA, UNITYplus, and UNITY, the macro `xpolar1` converts parameters for XPOLAR and most other double- and triple-resonance solids pulse sequences for the XPOLAR1 pulse sequence. Power parameters are left unchanged. Parameters irrelevant to XPOLAR1 are removed. On *MERCURY-VX* or *MERCURYplus* the macro XPOLAR1 will convert parameters contained in experiments run on ^{UNITY}INOVA, UNITYplus, and UNITY when these data sets are loaded on the system and the macro is run.

For users familiar with ^{UNITY}INOVA, UNITYplus, and UNITY solids, note the following:

- If the UNITY power parameters are defined (in an XPOLAR parameter set), they are converted to the corresponding ^{UNITY}INOVA and UNITYplus parameters: (`level1=cppwr level2=dpwr level1f=crossp level2f=dipolr p2=cntct tpwrf=tpwrm`) and `dblvl2` is set to 'n'. If `dblvl2='y'`, both `cppwr` and `dpwr` are used. If `dblvl2='n'`, `cppwr` is not used and `dpwr=cppwr`.
- `xpolar1` does not convert an arbitrary parameter set for solids. First retrieve a solids parameter set (e.g., `xpolar.par` in the VNMR directory `parlib`) and then convert it with the `xpolar1` macro.

Parameters

- `xpol` is set to 'n' for direct polarization or `xpol` is set to 'y' for cross-polarization.
- `pw` is the observe pulse for direct polarization, or the proton 90° pulse for cross-polarization. `pw` is in microseconds.
- `pwX` is the observe 90° pulse, used for TOSS and dipolar dephasing, `pwX` is in microseconds.
- `cntct` is the cross-polarization contact time, in microseconds.
- `tpwr` is the observe power setting .

Spectrometer	Minimum, dB	Maximum, dB
<i>INOVAcpmas</i>	-16	63
<i>MERCURYcpmas</i>	0	63

- `tpwrm` is the observe linear modulator setting .

Spectrometer	Minimum	Maximum
<i>INOVAcpmas</i>	0	4095
<i>MERCURYcpmas</i>	0	255

The parameter `tpwrm` is linearly proportional to the applied transmitter voltage—doubling `tpwrm` halves the value of the pulse width.

- `dpwr` is the decoupler power setting for decoupling throughout the acquisition period .

Spectrometer	Minimum, dB	Maximum, dB
<i>INOVAcpmas</i>	-16	63
<i>MERCURYcpmas</i>	0	63

- `cppwr` (UNITY only) is the decoupler power setting for cross polarization when `dblv12='y'`.
- `dipolr` is the decoupler linear modulator setting during acquisition (0 minimum voltage to 4095 for INOVA or 255 for *MERCURY series* maximum voltage). The value of `dipolr` is linearly proportional to the applied decoupler voltage—doubling `dipolr` doubles the decoupler field strength (in kHz).
- `dblv12` (UNITY only) is set to 'y' to obtain the parameter `cppwr`.
- `crossp` is the decoupler linear modulator setting during cross-polarization and the initial 90° pulse (0 minimum voltage to 4095 for INOVA or 255 for *MERCURY series* maximum voltage). The range is similar to `dipolr`. Doubling `crossp` doubles the cross-polarization field strength (in kHz) and halves the initial proton 90° pulse.
- `p180` greater than 0.0 implements an additional prepulse, followed by a delay `d2`. For direct polarization (`xpol='n'`), `p180` is an observe pulse. For cross-polarization (`xpol='y'`), `p180` is a proton pulse. `p180` is in microseconds.
- `pcrho` greater than 0.0 implements an additional observe pulse following the contact time. Use `pcrho` for observe $T_{1\rho}$ measurements. The units for `pcrho` are microseconds.
- `dm` should be set to 'nny'. The decoupler has a maximum duty cycle of 20%.
- `pdp` set to 'y' implements interrupted decoupling for a period `pdpd2` to cause suppression of protonated carbons.
- `pdpd2` is set greater then 0.0 (see `pdp`), `pdpd2` is in microseconds
- `d2` is set greater than 0.0 (see `p180`), `d2` is in seconds.
- `srate` is the sample spinning speed, in Hz.
- `hsrotor` set to 'y' allows automatic update of the value of `srate` if automatic spinning speed control is used.
- `toss` set to 'y' implements timed spin echoes to suppress spinning side bands. Timing is determined from the value of `srate`.

Note that for `toss='y'` or `pdp='y'`, `srate` must be set correctly because delays are calculated from $1.0/srate$.

2.10 Optimizing Parameters and Special Experiments

This section provides information on parameters used for specific optimizations, such as contact time and repetition rate. Also included in this section are special experiments for the high-performance CP/MAS module. With each of these experiments is a sample spectrum and an illustration of the XPOLAR1 pulse sequence used.

Contact Time Array

For samples in which cross-polarization is used, the contact time, that is, the time during which cross-polarization occurs, must be optimized with the parameter `cntct`. This is necessary because two processes are occurring simultaneously:

- Build-up of magnetization due to cross-polarization
- Loss of magnetization due to rotating-frame relaxation

A time exists for which an optimum in the magnetization occurs.

The optimum `cntct` can lie anywhere from 100 to 5000 μs . Generally the optimum value is similar for a class of compounds, but for new types of samples an optimization of `cntct` is highly desirable. **Figure 11** shows a typical optimization. Note that a simultaneous optimum for all carbons in a spectrum does not necessarily occur. A value of 1000

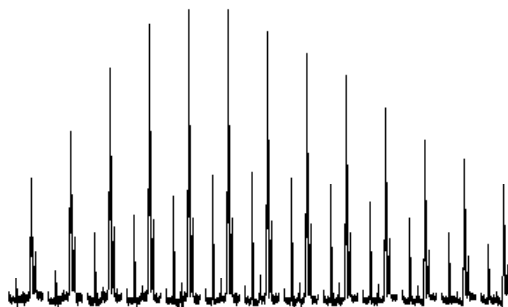


Figure 11. Array of Contact Times

μs is adequate for protonated carbons and crystalline solids. A value of 3000 μs is needed for non-protonated carbons and solids with internal motion.

Optimizing the Repetition Rate

Acquisition times in CP/MAS spectra are determined by the desired spectral resolution. Typically, set `sw=50kHz`. With `at=0.05`, this gives at least 2048 data points and a digital resolution of 4 Hz, a reasonable value.

The repetition rate is determined by the parameter `d1`, the delay between experiments. CP/MAS spectra are acquired with 90° observe pulses. In this case, the optimum repetition rate is $1.25 \cdot T_1$. For cross-polarization spectra, this T_1 is the value of the protons; for `xpol='n'`, it is the T_1 of the carbon or other nucleus. T_1 values can vary widely, as in liquids. At 300 MHz, a `d1` of 5 seconds is usually acceptable for polymers; at 400 MHz, 10 seconds can be better.

Suppressing Spinning Sidebands

NMR spectra of solids at high magnetic fields often have significant spinning sidebands. While these sidebands contain information about the chemical shift anisotropy, they can complicate the interpretation of complex spectra. The sidebands can be eliminated using the TOSS (TOtal Sideband Suppression) technique. The TOSS pulse sequence is selected by setting `toss='y'` in the XPOLAR1 sequence (see **Figure 10**). Note that the parameter `srate` should be set to the spinning speed in Hz.

TOSS is less effective at high spinning speeds. Note that if suppression is not complete, check that `srate` is correct. TOSS uses 180° pulses based on `pwx`. It may be necessary to adjust `pwx` to optimize the TOSS experiment.

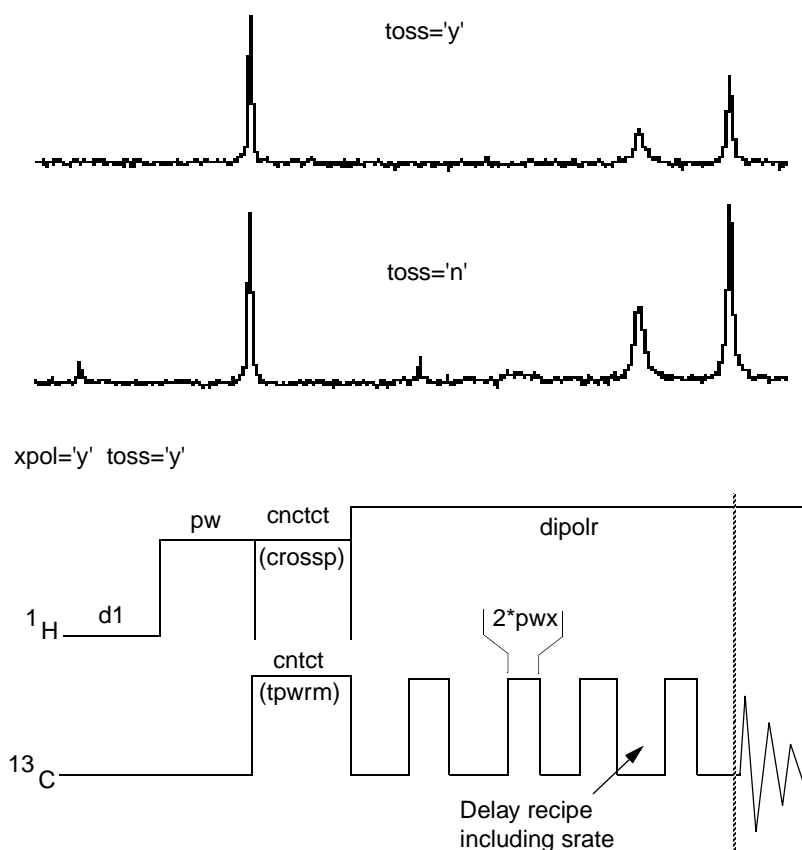


Figure 12. TOSS Experiment on Alanine (Spectrum and Sequence)

Suppressing Protonated Carbon (Interrupted Decoupling)

Off-resonance decoupling and related experiments in which J-coupling is involved are not routinely possible in solids because dipolar coupling as well as J-coupling is present. One experiment exists, however, that is used in solids to discriminate between carbon types, and that is the protonated carbon suppression experiment of Opella and Fry. In this experiment, the decoupler is turned off for 40 to 100 μs before acquisition to dephase the protonated carbons.

The technique is effective primarily for non-mobile carbons; mobile carbons, like methyl groups, are typically not suppressed as well. **Figure 13** shows a typical protonated carbon suppression experiment on alanine, obtained by setting `pdp` (protonated dephasing) equal to 'y', setting `srate` to the spinning speed, and entering appropriate values for `pdpd2` (in μs), the dephasing time.

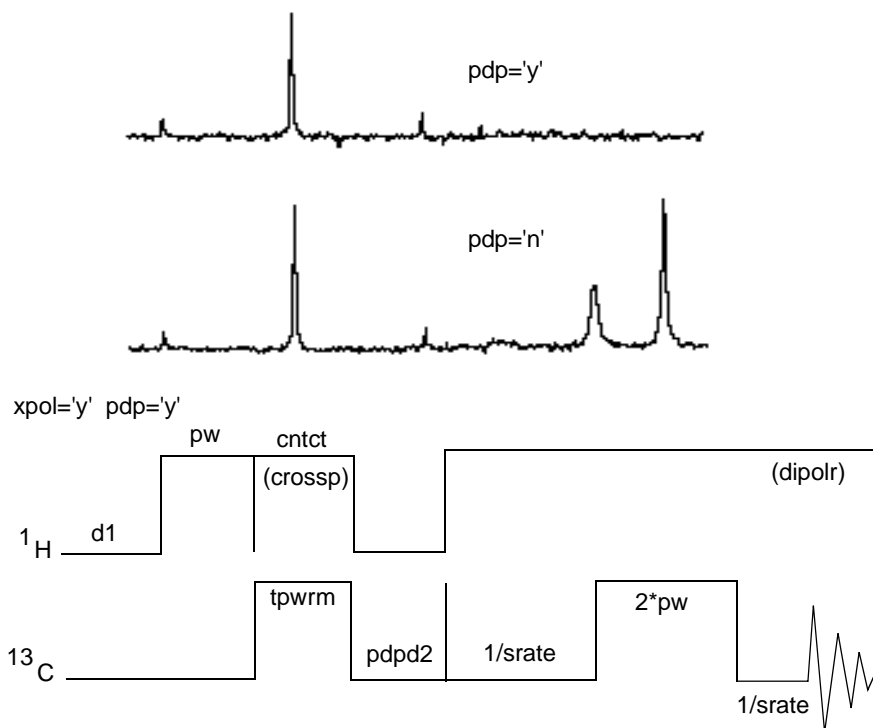


Figure 13. Protonated Carbon Suppression of Alanine (Spectrum and Sequence)

^{13}C $T_{1\rho}$ Experiments

Measurements of the spin-lattice relaxation time in the rotating frame ($T_{1\rho}$) are possible using the standard XPOLAR1 pulse sequence. Anytime that `pcrho` is set to a non-zero value, a $T_{1\rho}$ decay is introduced; thus, by setting `pcrho` to an array, $T_{1\rho}$ is measured. Typical values for `pcrho` would range from 50 to 5000 μs .

To analyze a $T_{1\rho}$ experiment for the decay time constant, enter
`analyze('expfit', 'pcrho', 't2', 'list')`

In experiments other than $T_{1\rho}$ experiments, `pcrho` should be set to 0. **Figure 14** shows the spin-lattice relaxation measurement pulse sequence.

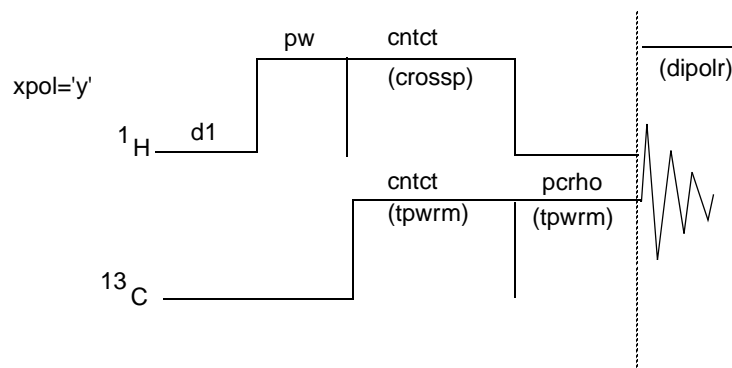


Figure 14. Rotating-Frame Spin-Lattice Relaxation Measurements Sequence

^1H T_1 Through ^{13}C Cross-Polarization

^1H T_1 can be measured using the XPOLAR1 pulse sequence by setting it up to perform a standard inversion-recovery experiment on the protons followed by cross-polarization of the remain ^1H magnetization to the carbons. Figure 15 illustrates the pulse sequence.

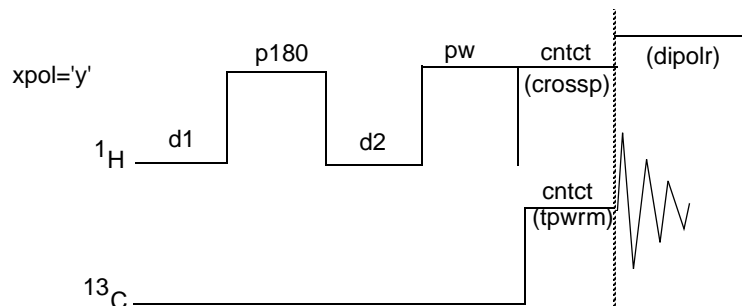


Figure 15. Pulse Sequence for Measuring ^1H T_1

2.11 Useful Conversions

Convert from 90° pulse width to γH :

$$\gamma H_2 (\text{kHz}) = \frac{250}{90^\circ \text{pulsewidth}} (\mu\text{s})$$

Convert from field strength in gauss to field strength in gauss:

$$^1\text{H}: \gamma H (\text{kHz}) \approx 4.3 * \gamma H (\text{gauss})$$

$$^{13}\text{C}: \gamma H (\text{kHz}) \approx \gamma H (\text{gauss})$$

Convert from rf fields to power levels:

$$P (\text{watts}) \propto (\gamma H)^2$$

Chapter 3. Wideline Solids Module Operation

Sections in this chapter:

- 3.1 “Wideline Solids Module,” this page.
- 3.2 “Wideline Experiments,” page 50.
- 3.3 “SSECHO Pulse Sequence,” page 51.
- 3.4 “Data Acquisition,” page 51.
- 3.5 “Standard Wideline Samples,” page 53.
- 3.6 “Data Processing,” page 55.

Unnarrowed spectra of solid samples can often reveal a great amount of information. In wideline NMR, no attempt is made to narrow the resonances (as done by CP/MAS), and patterns up to 0.5 MHz or wider can occur.

As lineshape is of the utmost importance, the spectrometer must be able to measure very broad lines without any distortion. It is for this reason that the transmitter power is high. γH_1 must be large enough to uniformly excite the entire spectrum. (The effects of a finite 90° pulse width may be investigated with simulations using the solids analysis software accessory.) With linewidths in excess of 100 kHz, an increase in ADC speed is necessary. In fact, the typical spectral widths used often greatly exceed the linewidths because many spectra are obtained under over-digitized conditions.

3.1 Wideline Solids Module

The wideline module for the Varian spectrometer modifies and extends the basic capability of the system in a number of areas. The main components of the wideline module are the wideband ADC, high-power amplifier, and the solids cabinet.

Wideline ADC Board

A wideline analog-to-digital conversion (ADC) board is added to the system in addition to the standard ADC board. Based on the spectral width (the parameter *sw*), the software determines which ADC board is to be used—values of *sw* greater than 100 kHz will automatically use the faster ADC.

Two versions of the wideline ADC board exist:

- The newer version of the Wideline ADC board (Part No. 00-993350-00) was shipped with UNITY*plus* systems. It has its own on-board memory, which consists of 2 x 64 Kword buffers (maximum *np* is 131072), together with its own sum-to-memory (STM) circuitry. Data is summed at this speed without additional overhead. This board also contains a Bessel filter, either 256 kHz (6-pole Bessel) or 1 MHz (4-pole Bessel). This filter is switched in when *sw* is less than 256,000 Hz; otherwise, the 1 MHz filter on the receiver is used.

- The older Wideline ADC board was shipped with UNITY and VXR-S systems. It acquires data in a fundamentally different manner. Data is temporarily stored in its on-board, 2 x 8 Kword buffer (maximum np is 16384). After each FID is collected, data is transferred to the normal acquisition memory and the fast memory is cleared. This process requires an overhead of about 32 μ s for each complex point.

Both ADC boards are single VERSAbus boards containing sample-and-hold modules, ADC chips, memory, and control logic, and each board is capable of digitizing 12 bits in 500 ns. The ADC conversion time is adjustable in 25 ns steps, so there are only a limited number of actual values that the spectral width can take. The entered value of *sw* is automatically adjusted to the nearest valid spectral width.

The standard Observe Receiver board for UNITY^{INOVA} and UNITY^{plus} systems has the correct bandwidth amplifier and is not replaced. For UNITY and VXR-S systems, the Wideline Receiver and Filter board is a replacement of the standard 100 kHz receiver and contains filters appropriate for both small and large spectral widths. Improved filters give better baseline and phase characteristics; however, they may show a 10% reduction in signal-to-noise as determined by the standard ¹³C test.

For spectral widths above 100 kHz, 6-pole true Bessel filters are used. The outputs from these filters are routed to the wideband ADCs. The permissible values of the parameter *fb*, which are identical to the 3 dB points of these filters, are listed in [Table 6](#).

For 100 kHz and below, the signal is routed through a pair of 8-pole quasi-elliptical filters to standard ADCs. The characteristics of these filters provide superior performance for both phase and amplitude flatness across the full spectral width.

The Wideline NMR Module for the UNITY^{INOVA} system is a board that includes two 5-MHz 12-bit ADCs and 2 MB of onboard memory.

Table 6. Bessel Filter Outputs

<i>sw</i> (kHz)	<i>fb</i> (kHz)
100 – 225	256
> 225	1000
300 – 540	300
540 – 1260	700
1260 – 1800	1000
> 1800	2400

High-Power Amplifier

The wideline high-power (1 kW) amplifier is intended mainly for use in solid-state NMR studies. The amplifier is housed in a third cabinet, as shown in [Figure 16](#), and configured to permit maximum flexibility. Manual controls permit selection of either the solids amplifier or the standard liquids amplifier for the observe function.

CAUTION: Never use probes designed for liquids studies with amplifiers intended for solid-state studies. The high power from these amplifiers will destroy liquids probes.

Because the wideline package is for low-band (12 to 200 MHz) nuclei, no ¹H or ¹⁹F high-power amplifier is provided unless the CP/MAS module or CRAMPS/Multipulse module is also installed. The 1-kW power amplifier is one of the following models:

- The AR Model 1000LPM10 covering the range of 9 MHz to 200 MHz with 60 dB of gain and a maximum output power exceeding 60 dBm over this range.
- The AMT Model M3201 covering a range of 6 MHz to 220 MHz with 10 dB of gain and a maximum power output exceeding 60 dBm over this range.

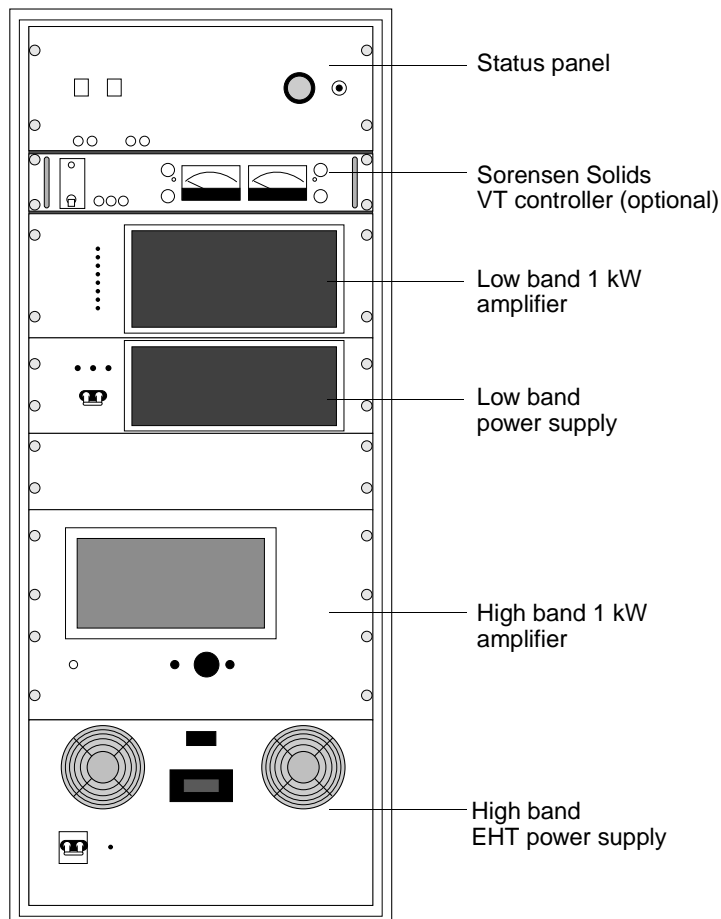


Figure 16. Solids Cabinet Layout, Open Front View

Both amplifiers are linear, with gating provided for noise blanking. Operational details for the high-power amplifiers are included in the manuals provided by the manufacturers of the amplifiers. These should be read before operating the amplifier.

AR Linear Amplifier

The AR linear amplifier is gated off whenever the receiver is gated on. A time of at least 30 μs is required for the bias to come on fully and thus for the amplifier to provide full output power. Allowance for this delay must be made in any pulse sequence programming, using `rof1`. The amplifier can be driven in either of two modes:

- Continuous wave (CW)—the maximum power output is limited to 200 W but the duty cycle can be 100%
- Pulsed—the maximum power output is 1 kW but the maximum pulse width is 8 ms with a maximum duty cycle of 10%.

The amplifier is fully protected against thermal overload, excessive duty cycle, and excessive pulse width. Status lights on the front panel and switches for this unit are visible by opening the front door of the third cabinet.

Although you should study the AR manual before using the amplifier, an abbreviated set of operating instructions are given here (words in all capital letters refer to controls on the front panel).

The gating input to the amplifier is of positive logic, with a 5 V on and 0 V off signal. The amplifier is class A with noise blanking in the CW mode. In the pulsed mode, the amplifier operates class AB and the gating input acts as a gating signal. When gated off, the output is greatly attenuated.

- To operate in the continuous mode, turn on the POWER button, wait for the STANDBY button to light, then press the OPERATE button. In the continuous mode, the gating signal input should be disconnected at the AR front panel.
- To operate in the pulsed mode, press the OPERATE button to set the amplifier in the standby mode. Press the PULSED button, then the OPERATE button once again. The amplifier is now in the pulsed mode, with pulse gating, not noise blanking. The maximum rated power output in the pulsed mode is 1 kW (60 dBm). This should not require adjustment of the amplifier gain.
- To return to the continuous mode, switch back to the standby mode by pressing the OPERATE button, followed by powering off the amplifier.

The AR amplifier has been calibrated at 100 MHz so that when its front panel gain control is set to the marked position and the manual attenuators are set to 0, the power output is equal in dBm to the value of t_{pwr} , in other words, $t_{pwr}=60$ delivers 1 kW (60 dBm) and $t_{pwr}=50$ delivers 100 W (50 dBm). This calibration may not be precise at other frequencies, but provides a first approximation.

AMT Linear Amplifier

The AMT linear amplifier is gated off whenever the receiver is gated on. A time of at least 8 μ s is required for the bias to come on fully and thus for the amplifier to provide full output power. Allowance for this time delay must be made in any pulse sequence programming, using `rof1`.

The maximum pulse width is 20 ms at full output and with a maximum duty cycle of 10%. The AMT amplifier is fully protected against thermal overload and it indicates excessive duty cycle and excessive pulse width. Status lights on the front panel and the power switch are visible inside the front door of the third cabinet as well as on the status panel. The gating input to the amplifier is of positive logic, with a 5 V on and 0 V off signal.

CAUTION: Never operate a high-power amplifier unless terminated by an appropriate 50-ohm load.

Decoupler Amplifier

The three possibilities for the decoupler amplifier in wideline systems are as follows:

- Standard decoupling operation.
- 100 W CP/MAS decoupler—operation of this is the same as for CP/MAS.
- 1 kW decoupler amplifier.

Status Panel

The high power amplifiers are controlled by a status panel.

The HI POWER ENABLE subpanel contains two switches:

- The OFF button grounds the inputs of both high power amplifiers and routes the transmitters through the standard ^{UNITY}INOVA, UNITY*plus*, and UNITY electronics appropriate for liquids operation (note that both amplifiers are left powered up by this switch).
- If HI POWER ENABLE is OFF, the position of the HI POWER/LO POWER switch is immaterial—the high-power amplifiers cannot receive any rf drive. The ON switch activates the cabinet, enabling the HI POWER/LO POWER toggle switches.

Observe Transmitter

For both the solids and standard liquids channels, the computer-controlled attenuators are in-line. The power level is controlled by the parameter t_{pwr} in 1 dB increments from -16 to 63 dB standard (0 to 63 dB is standard on UNITY and VXR-S systems). Maximum power output is obtained with $t_{pwr}=63$. To get low power from the high-power amplifier, t_{pwr} should be decreased by approximately 6.

Note that the output of the Observe Transmitter board can be routed to a low-power (300 W) amplifier (LOW POWER position on the third cabinet, see [Figure 16](#)) or to a high-power (1 kW) amplifier (HI POWER position).

3.2 Wideline Experiments

Wideline NMR experiments can be divided into three main areas, based on spin quantum number (I). The experiments possible are certainly not restricted to just one of these categories, but are normally used in one group rather than in all. [Table 7](#) lists commands and parameters related to wideline experiments.

Table 7. Wideline Experiment Commands and Parameters

Commands	
<code>ssecho</code>	Set up solid-state echo pulse sequence
<code>tmove</code>	Left-shift FID to time-domain cursor
<code>tshift</code>	Adjust tau2 to current cursor position
Parameters	
<code>dotflag { 'y', 'n' }</code>	Display FID as connected dots
<code>lsfid { number, 'n' }</code>	Number of complex points to left-shift np
<code>scalesw { number > 0.0, 'n' }</code>	Scale spectral width in directly detected dimension

Dipolar Nuclei ($I = 1/2$)

The most common dipolar nucleus is ^1H . Many of the dipolar nuclei are not usefully observed under wideline conditions without ^1H decoupling. Although the standard wideline probe does not allow double-resonance experiments, a CP/MAS probe can be used for many such experiments.

In ^1H wideline experiments, lineshape or chemical shift is usually of minor importance. The most interesting parameters are relaxation rates such as T_1 , T_2 , and $T_{1\rho}$. In many measurements the relevant part is the first few microseconds of the FID. The FID may not even be transformed.

Normally the breadth of a line comes from two sources, dipolar coupling and chemical shift anisotropy. There are a number of techniques, referred to as line narrowing, or multipulse techniques, to remove dipolar coupling contributions to lineshape.

Quadrupolar Nuclei ($I = 1$ or $3/2$)

For all quadrupolar nuclei, the main cause of linewidth is the quadrupolar coupling of the nuclei being observed. The observed magnitude of the quadrupolar coupling is dependent on orientation in the magnetic field and is responsible for the apparent difference between single crystal and powder spectra.

The most commonly observed quadrupolar nucleus in wideline is ^2H (deuterium), along with ^{23}Na and a few other nuclei. Lineshape is of prime consideration in most experiments involving these nuclei, with relaxation measurements also of interest.

To ensure an accurate representation of the lineshape, most spectra are measured via an echo sequence, first described by Mansfield (*Phys. Rev.*, **137**, A961, (1965)), commonly known as the “solid echo” sequence. To simplify phasing of the transformed FID, the echo is Fourier transformed from the top onwards in time. The “extra” data points are ignored using `lsfid`. To accurately define the echo top, these echoes are usually over-digitized.

Quadrupolar Nuclei ($I > 3/2$)

Quadrupolar nuclei are also observed via echo sequences; however, as different types of lineshape information may be sought, a number of different echo sequences may be used, depending on the quantum transitions of interest (I. D. Weisman and L. H. Bennett, *Phys. Rev.*, **181**, 1344, (1969)).

3.3 SSECHO Pulse Sequence

One basic pulse sequence, SSECHO, is provided to support quadrupolar wideline experiments. This pulse sequence can perform conventional “solid echo” experiments, with or without composite pulses. It also supports inversion-recovery solid echo experiments, as well as echo experiments with unequal pulse widths. The details of this pulse sequence are discussed in Chapter 6, which also provides a model for users for whom other variations of the experiment may be of interest. Since this pulse sequence, like all others, undergoes periodic revision and improvement, you are encouraged to print the version current in your software with the `ptext` command: `ptext ('/vnmr/psglib/ssecho.c')`. The SSECHO pulse sequence is not appropriate for proton relaxation studies.

3.4 Data Acquisition

For data acquisition, consider sample preparation, shimming, and pulse-width calibration.

Sample Preparation

The main requirement is that the sample be no longer than 25 mm nor greater than 5 mm in diameter. Samples must fit into the coil of the probe and be electrically insulated from the coil. The most convenient sample carrier is a 15 mm length of 5 mm outside diameter NMR tube, which can be sealed with Parafilm or some other background-free material. For best results, the sample should be kept small in comparison with the length of the coil and

should be placed symmetrically in the coil when in the probe. Remember that the NMR tube has a ^{29}Si , $(^{13}\text{Na})^{27}\text{Al}$ and ^{11}B background signal.

WARNING: Dangerous high voltage exists inside the probe that can cause burns or serious injuries. Follow the instructions below to avoid the hazard.

When changing samples, take the following precautions:

- Set the HI POWER ENABLE switch to OFF.
- Disconnect the transmitter cable from the probe.
- Be especially careful of damaging the coil supports when inserting or removing a sample from the coil as well as when changing coils. These supports are fragile and can be easily damaged.

Shimming

Because of the width of the resonances encountered in wideline work, shimming is rarely necessary (or possible!) on each sample. The following approach is typical:

1. When the probe is first installed, insert a sealed sample of D_2O in the probe for shimming purposes.
2. Tune the probe to ^2H , as described in the probe installation manual, and then connect the (otherwise unused) lock cable to the observe channel of the probe.
3. Use the interactive acquisition window to lock the spectrometer in the usual way, and then adjust the important shims. Usually it is only important to adjust X, Y, Z1 Coarse, and Z2 Coarse.
4. When finished shimming, turn the lock off and adjust Z0 so that the lock signal is on-resonance. This ensures that the field will be in the same position as used for liquids work, so that the usable frequencies will be the same.
5. Set `lpower=0`. This ensures that at the time of the next `su` command, the lock transmitter is deactivated, removing a source of potential frequency interference.

Pulse-Width Calibration

Although it is possible to perform pulse width calibrations on the sample of interest using solid-state echo experiments, calibrations done in this manner can be misleading. For example, there is not usually a null at the 180° pulse for quadrupolar nuclei. As a general rule, all pulse width calibrations should be made with solutions. A sample of D_2O can be used for ^2H work, while a 1 M solution of a salt in water can be used for other nuclei such as ^{23}Na .

The acquisition controller board of the $^{\text{UNITY}}\text{INOVA}$ has a timing resolution of 12.5 ns, which limits your ability to specify a pulse width to increments of 0.0125 μs . Similarly, the $^{\text{UNITY}}\text{plus}$ and $^{\text{UNITY}}$ have a timing resolution of 25 ns, thus limiting pulse width specification to increments to 0.025 μs . Adjustment of the power with the parameter `tpwr` will alter the 90° pulse width parameter `pw90`. In addition, the parameter `tpwrm` can be used with $^{\text{UNITY}}\text{INOVA}$ and $^{\text{UNITY}}\text{plus}$ systems.

3.5 Standard Wideline Samples

Two standard wideline samples are provided with the system, malonic acid-d₄ for ²H and sodium nitrate for ²³Na wideline NMR. These samples are provided as an aid to becoming familiar with the operation of the wideline module and do not have any associated specifications.

Obtaining a Wideline Spectrum of Deuterium

The deuterium powder pattern spectrum of malonic acid-d₄ can be obtained in the following manner (this is not the only way to operate the wideline module, but does provide a convenient starting point):

1. Determine the 90° pulse using a solution, in this case, 2% D₂O (for most other quadrupolar nuclei, a 1 M solution of a salt in water should be used). Put the relevant tuning rod into the probe. Connect the correct coil in the correct pair of connectors on top of the probe body. Refer to the probe installation manual for details on setting up the wideline probe.
2. Place a sealed sample of 2% D₂O in the probe and put the probe into the magnet. Connect body air, VT gas and the “Normal” connector on the magnet leg to the probe. No filters are necessary. Make sure that the 30–60 MHz 1/4-wavelength cable is on the magnet leg.
3. Enter `setup('H2','d2o') dm='n' su`. Tune the probe as described in the probe installation manual.
4. Now, instead of the observe channel, connect the lock channel to the probe. Lock the spectrometer in the usual way.
The spectrometer can now be shimmed using `acqi`, but there is no point trying to obtain a resolution that is markedly better than the lines to be observed, so that only the gradients X, Y, Z1 Coarse, and Z2 Coarse need be optimized.
5. Make sure that the lock and spinner are deactivated by selecting LOCK OFF, SPIN OFF, SPIN=0 and setting `lockpower=0`.
6. Replace the lock connection with the observe channel. Check the tuning and then make sure that the probe is connected to the “Normal” position on the preamplifier.
7. If not already done, reset the solids cabinet, and make sure the broadband 1 kW amplifier is on and that no interlocks are activated. Set the switch panel so that the LOWBAND is on HI POWER.
8. Set `sw=1E5 pw=2 np=1E4 d1=4 nt=1`. Set `tpwr` to the standard value for the system. If no value has been determined previously, set `tpwr=55`.
9. Set `gain='n'` and acquire a spectrum. Phase correct the result and ensure that the spectrometer is working correctly. If necessary, use `movetof` to place the D₂O signal exactly on resonance.
10. Check these adjustments by reacquiring a spectrum.
11. Array `pw` to determine the 180° or 360° pulse width. Set `gain='y'` (because arrayed experiments cannot use Autogain) and acquire the data. Determine the 90° pulse width to 25 ns resolution.
12. Set `pw` and `pw90` to the 90° pulse width value.

This completes the calibration procedure.

13. Replace the D₂O sample with the malonic acid-d₄ sample and tune the probe.
14. Enter **ssecho** to convert the **s2pu1** parameter set to one suitable for the SSECHO pulse sequence. Set **tau1=20 tau2=15 nt=16**.
15. Set **gain='n'** and enter **go** to acquire data.
16. Enter **df** to display the FID. Use the phase button and the mouse to maximize the real (cyan) channel. Set **lsfid=0**. Put a single cursor on the echo maximum and enter **tmove**. Transform the FID.
17. Phase correct the spectrum using **rp** only (set **lp=0**). Select two cursors and set each on top of a horn of the powder pattern. Enter **split** to move the right cursor to half way between the two horns. Entering **movetof** then sets the observe transmitter to this position.
18. Reacquire data, this time with **d1=10**.
19. Enter **df** to display the FID. Maximize the real channel as in [step 16](#) and put a single cursor at the echo maximum, putting it between data points if necessary.
This FID can either be transformed or data reacquired starting from the cursor position. If the FID is to be transformed, then enter **tmove wft**. Phase correct the spectrum as before. If new data is to be acquired starting at the cursor position, enter **tshift** followed by **go** or **ga**.

Other spectra can now be acquired using these parameters.

Obtaining a Wideline Spectrum of ²³Na

Sodium does not normally have a parameter set in **stdpar**, so it is necessary to call up some standard set and modify it. The easiest way to do this is shown in [step 1](#) below.

1. Enter **setup('H2','d2o') tn='Na23' dm='n' su**.
2. Set up the probe with the correct coil and tuning rod (if any) and put in a sealed sample of NaCl (1 M in H₂O). Tune the probe as described in the probe installation manual.
3. Follow [step 5](#) through [step 12](#) in “[Obtaining a Wideline Spectrum of Deuterium](#),” [page 53](#).
4. Remove the sealed sample of NaCl (1 M in H₂O) and replace it with the sample to solid sodium nitrate.
5. Tune the probe and enter **ssecho** to convert to the QUAECHO sequence and acquire 16 transients using a **d1** of 1 second.
6. Process the spectrum the same as for deuterium, except that the center of the powder pattern is the center of the highest line.

Hints for Performing Wideline Experiments

If a powder pattern shows more than 3-4% asymmetry in the height of the horns, check that the sample is centered in the coil. If this is the case, check the tuning of the probe. If neither results in a significant improvement, shift the transmitter position 1000 Hz towards one horn. Finally, recalibrate the 90° pulse with a solution sample, then retune the probe to the same reflected power level.

- T_1 can be very long in solids. It may be necessary to set **d1** to values of the order of 100 seconds in some cases.

- Remember that for solid samples of quadrupolar nuclei, the 90° pulse usually cannot be determined from a pw array.

3.6 Data Processing

Most data processing needs of wideline spectra are the same as that for other spectra. There are, however, several specialized applications, for which software is provided. Since most wideline spectra are collected in a spin-echo mode, it can be extremely important to start acquisition, or at least Fourier transformation, on top of the echo. The FID display program provides a point-by-point (if `dotflag='Y'`), two-color display of the real and imaginary channels of the FID in order to provide the best possible examination of the details of the FID. One or two time cursors can also be displayed and are not constrained to fall on top of individual data points but may be used to interpolate as well (for example, to estimate the time of the echo). A left shift of the FID may be used to shift the FID until the echo occurs at the first point of the FID.

Normally, the echo top is well enough defined so that left shifting removes all distortion. However, this is not always the case, especially with very short T_2 echoes. A means of fractionally left shifting has been provided as follows:

```
lsfid='n' phfid='n'
ft
ft('inverse',n,expn)
jexpn
scalesw=1.0/n
df
wft
```

In this example, n in the `ft` command is a interpolation factor (power of 2); `expn` is an experiment number for the interpolated FID; `df` interpolates the FID by a factor of n and the echo top may be picked more accurately; `scalesw=1.0/n` will correct `sw`.

It is also common to collect wideline spectra with the transmitter placed in the exact center of the resonance. Software is provided to allow “phasing the FID” to place as much as possible of the FID in the real channel. This operation means that the frequency-independent phase shift of the spectrum is as close to zero as possible, which is beneficial since frequency-domain phasing of wideline spectra can be difficult at best. In addition, spectral symmetry can be forced by software that sets the imaginary channel of the FID to zero.

Chapter 4. CRAMPS/Multipulse Module Operation

Sections in this chapter:

- 4.1 “Introduction to Multipulse Experiments,” this page
- 4.2 “CRAMPS/Multipulse Module Hardware,” page 57
- 4.3 “Multipulse Experiments and User Library,” page 60
- 4.4 “Multipulse Tune-Up Procedure (FLIPFLOP),” page 60
- 4.5 “ ^1H CRAMPS Experiment (BR24 or MREV8),” page 64
- 4.6 “How to Obtain Good CRAMPS Spectra,” page 65
- 4.7 “Quadrature ^1H CRAMPS,” page 66
- 4.8 “Fast MAS Assisted with a Multiple-Pulse Cycle (WaHuHaHS),” page 67
- 4.9 “FLIPFLOP - Pulse Width and Phase Transient Calibration,” page 68
- 4.10 “BR24 and CYLBR24 - Multiple Pulse Line Narrowing (24-pulse cycle),” page 69
- 4.11 “MREV8 and CYLMREV - Multiple Pulse Line Narrowing (8-pulse cycle),” page 70
- 4.12 “WaHuHa and WaHuHaHS - MP-Assisted High-Speed Spinning (4-pulse cycle),” page 71

4.1 Introduction to Multipulse Experiments

Multipulse describes a class of experiments that require the interleaving pulses with the acquisition of the data points of the FID. Combined Rotation and Multipulse, CRAMPS, is the most common ^1H high-resolution experiment. CRAMPS is used to obtain high-resolution MAS ^1H spectra of organic materials. The CRAMPS pulse sequence uses the BR24 multiple-pulse cycle. A BR24 multiple-pulse cycle applies 24 ^1H 90° pulses in the dwell time between the acquisition of complex data points. Multiple-pulse cycles such as BR24 removes strong ^1H - ^1H dipolar interactions that broaden the spectra of organic materials. Slow-spinning MAS averages the ^1H chemical shift tensor to yield typical line widths of 0.25 ppm to 3 ppm.

Hardware for the ^1H CRAMPS experiment is provided by the ^1H CRAMPS/Multipulse Module or by a Full Solids setup and is described in this chapter along with setup procedures.

Multiple-pulse cycles are often employed without interleaved data acquisition in many solids sequences for the purpose of decoupling and recoupling, or during the evolution period in two-dimensional experiments. This chapter describes the procedures used to adjust the pulsewidth and phase transient for CRAMPS and other multiple-pulse cycle experiments. The tune-up sequences described in section 4.4 “Multipulse Tune-Up Procedure (FLIPFLOP),” page 60.

4.2 CRAMPS/Multipulse Module Hardware

Multipulse capability is available with all UNITYINOVA and UNITY*plus* spectrometers. UNITY and VXR-S spectrometers require an additional Sync Module to improve pulse-timing stability. The main CRAMPS/multipulse module hardware is the motor control box, 1-kW amplifier, sync module (UNITY and VXR-S systems only), and the CRAMPS probe.

The ^1H CRAMPS experiment requires the following:

- $^1\text{H}/^{19}\text{F}$ 1-kW amplifier (see 2.1 “CP/MAS Solids Modules,” page 16)
 - Fast ADC (2 MHz or 5 MHz)
 - Solids high-power preamplifier
 - Suitable MAS probe with pneumatics hardware
- See 2.2 “Rotor Characteristics and Composition,” page 20 to 2.4 “Spinning the Sample,” page 22 for information about MAS spinning.

$^1\text{H}/^{19}\text{F}$ 1-kW Amplifier

$^1\text{H}/^{19}\text{F}$ 1-kW amplifiers suitable for CRAMPS are described in section 2.1 “CP/MAS Solids Modules,” page 16. The CRAMPS experiment generally requires more than 100 Watts of power. A very small-diameter rotor will facilitate running the experiments with a 100 Watt CP/MAS amplifier in some cases.

Amplifier Tuning

The CPI amplifier is tuned to either ^1H or ^{19}F . At 600 MHz only ^1H tuning is possible. INPUT TUNING uses the 20-turn pot at the front of the amplifier chassis. The output tuning uses the external Motor Control Box. A 3-position selector switch is used to choose TUNE, LOAD and STANDBY (AUX). The COARSE and FINE toggles are momentary contact and can be pushed in two directions (designated IN and OUT) to adjust either the TUNE or LOAD depending upon the selection set on the 3-position selector switch.

A CMA amplifier is tuned to either ^1H or ^{19}F . INPUT TUNE and INPUT MATCH are 20 turn pots at the bottom-front of the amplifier chassis. OUTPUT TUNE and OUTPUT MATCH are digital knobs at the center-front of the chassis.

Tune the Amplifier

1. Connect the amplifier output (the cable to the connection XMTR J5313 on the preamplifier) through at least a 30 db attenuator to an oscilloscope or a power meter. The attenuator must handle 50 Watts or more.
2. Do one of the following depending upon the type of amplifier:
 - CMA amplifier only
 - Select the mode as either GATE ACTIVE or CLASS C as required (see “Amplifier and Receiver Blanking,” page 58).
 - CMA or CPI amplifier
 - a. Set a single repeating pulse of $p_w = 300 \mu\text{s}$ with a $d_1 = 30 \mu\text{s}$ for either ^1H or ^{19}F . Tune the input tuning pot(s) for maximum power or voltage.
 - b. Iteratively adjust the output tuning (tune and "load" or "match") for maximum power or voltage.

- c. After tuning at lower power, fine tune at the maximum power that will be used in order to obtain the maximum linearity of the CPI or the CMA.
- d. Record the values for future reference.

Overdrive Mode

The CPI amplifier contains an OVERDRIVE RESET button on the front panel. An overdrive state is indicated by the lighted red word on the relay panel at the top of the solids bay. Press to reset when the word is lighted. The CMA amplifier contains a TRIP RST button and an overdrive state is indicated by a red light on the front of the chassis. In overdrive mode the amplifier is shut down. An overdrive fault is caused by excessive power or an arc in the probe, and sometimes by pulsing into a mismatched cable. The overdrive usually must be reset when the acquisition computer is restarted.

Amplifier and Receiver Blanking

The BR24 pulse sequence for CRAMPS, makes use of amplifier blanking to remove amplifier noise during the acquisition of data points between the pulses. Set the parameter `ampmode = p` or `d` for pulsed mode. The parameter `ampmode` is also set correctly if the parameter is not present. The newer CMA amplifiers should be run with the toggle in the GATE ACTIVE (pulsed) position. Older CPI amplifiers are automatically set to pulsed mode using the value of the `ampmode` parameter.

In pulsed mode the CPI and CMA amplifiers are turned on at the beginning of the period `rofl=1` before the pulse. They are ready for full RF output after `rofl=1.5` to `2.0` μs . The minimum value of `rofl=1.5` μs is used for CRAMPS. The amplifiers are turned off after a period `rofl=0.2` to `0.5` μs after the pulse. For ^1H CRAMPS the noise and RF “ring down” over a period of about 2.0-3.0 μs before detection of a data point is possible. During this period the T/R switch (if present - see Solids Preamplifiers below) immediately gates to receive mode and then after a delay a trigger is sent to turn the receiver on. When using the fast ADC the receiver then turns on within about 1.0 μs

The delay between triggering the T/R switch and the receiver is set by a hardware adjustment on the magnet leg. The default value is about 2.0 microseconds for a highband nucleus and about 8.0 microseconds for a lowband nucleus. The purpose is to protect the receiver (outside of pulse-sequence control) from pulse ring down that will “certainly” be present. If one collects a data point before the receiver turns on by setting `tau` too short in BR24 or FLIPFOP, the result will be a null signal. In this case lengthen `tau`. The hardware delay is accessible to users and can be made shorter if desired to allow smaller values of `tau`.

Optionally, a CMA amplifier may be set in CLASS C (nonlinear) mode. In this case the RF pulse of the 50-Watt driver amplifier turns the CMA on and off. Blanking instructions of the pulse sequence are ignored. Set `ampmode='c'` to operate the 50 watt driver in continuous mode. CLASS C mode provides a slightly shorter unblanking time (`rofl`) but RF output in CLASS C mode is not linear. It will be necessary to retune and recalibrate the parameters `tpwr` and `tpwrfor` `tpwrm` when using CLASS C mode.

FAST ADC (2 MHz or 5 MHz)

The CRAMPS experiment requires an optional fast ADC, which may be either 2 MHz or 5 MHz. This device sits in the acquisition card cage and is connected to the receiver ports WB CH A and WB CH B (J246 and J247) with a pair of BNC cables. These ports provide the real and imaginary FID signals and bypass the analog filters. The unfiltered FID signal from

the receiver and the fast ADC have a sufficiently short turn-on time for detection between the pulses of BR24. Note that the value of *sw* in BR24 is set to 2 MHz to select the fast ADC but the true dwell time is longer since the pulse sequence is responsible for turning on and off the receiver and digitizer.

Note that the dwell time of the 500 kHz ADC of UNITYINOVA is sufficiently fast for BR24 but the turn-on time is not. Optionally, one can bypass the fast ADC with a custom cable (not provided) that connects the unfiltered receiver outputs to the 500 kHz ADC. A special BR24 pulse sequence can be written that compensates for the slower turn-on time of the 500 kHz ADC. This configuration can be set up by users, but it is not supported.

Solids Preamplifiers

For 300 MHz and 400 MHz systems an optional special high-power, 0-400 MHz preamplifier module is available. This preamplifier has a passive T/R switch (in contrast to the active T/R switch of the standard preamplifier module) and additional heat sinking on the diodes to withstand a greater RF duty cycle. This preamplifier may also be used for low band solids observe. This preamplifier can be used in-line during ¹H decoupling and is labeled High Power - 990888. Set *rof2* = 0.2 μ s.

Newer systems and all systems 500 MHz and above use a ¹H/¹⁹F high-power preamplifier module is supplied with an active T/R switch. The preamplifier module has a built-in 1/4 cable and a high-pass filter (needed for CP/MAS) and can be used in-line during decoupling. The appearance of this preamplifier is indistinguishable from standard ¹H/¹⁹F module. Check the part numbers and instrument documentation if there is any doubt about an existing preamp. Set *rof2*=0.5 μ s.

Other preamplifiers are not suitable for CRAMPS and cannot be in line during CP/MAS decoupling. Ring down of these preamps may be too long or the diodes may not withstand the RF duty cycle.

MAS Probes for CRAMPS

Any CP/MAS probe with a ¹H-decoupler channel can be used for ¹H CRAMPS. The quality of the result depends upon the minimum pulse width that can be obtained and the inherent resolution of the sample. Highly crystalline materials have linewidths of less than 0.5 ppm. To achieve these line widths one should use a 1.5 μ s 90° pulse or less. Amorphous polymers may have minimum line widths of 3 ppm. A 90° pulse of 3.0 to 4.0 microseconds may provide all the narrowing that is needed to obtain a result. Consult the probe specification to determine the available 90° pulse.

Varian provides a 5 mm narrow-body single-tuned CRAMPS probe for 300 MHz and 400 MHz magnets, which can be tuned from ¹⁹F to ¹H. This probe uses a body and a 5 mm rotor similar to the Auto-MAS CP/MAS probes. The zirconia stator of the Auto-MAS probe uniquely provides very low ¹H background. For widebore magnets a 5 mm Chemagnetics CRAMPS probe is available. In addition, any Auto-MAS CP/MAS probe or widebody Chemagnetics CP/MAS probe with a rotor size of 5 mm or less can be used for CRAMPS.

Sync Module (UNITY, VXR-S only)

The Sync Module, located on the wideline receiver, provides a buffered 500 kHz signal derived from the master oscillator. Its output is connected to the EXT TIMEBASE input on the output board. A pulse sequence can delay until the next clock edge by using the pulse sequence element *xgate*(1.0). Clocking the beginning of the pulse sequence on 500 kHz output improves timing stability of the pulses for UNITY and VXR-S spectrometers.

4.3 Multipulse Experiments and User Library

The macros for some of the multipulse NMR sequences are located in `macLib`. The macros for other multipulse NMR sequences are located in the user library `userLib`.

User Library—Terms and Conditions

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4.4 Multipulse Tune-Up Procedure (FLIPFLOP)

The pulse sequence `flipflop.c` is used to perform both the XX (FLIPFLIP) or X-X (FLIPFLOP) tune-up experiments.

To tune up for CRAMPS or other multiple-pulse sequences accurate measurement of the proton 90° pulse and minimization of the effects of RF inhomogeneity is required. The procedure that follows uses a narrow-line liquid sample with repeating X pulses and interleaved acquisition.

Prepare the Sample

1. Fill a small glass bulb with a single-line protonated solvent such as benzene, dioxane or water.

An organic solvent is recommended since its effect on probe tuning is similar to that of an organic solid. Add a bit of the relaxation agent CrAcAc (not provided) to the organic solvent to shorten T_1 .

2. Center the bulb in the coil.

Alternatively, a small solid sample of RTV (silicon rubber caulk from the hardware store) will provide a ^1H linewidth sufficient for tuning. Spin the RTV at about 2 kHz during these measurements.

Configure the Spectrometer

1. Connect the preamplifier and cable that are used for ^1H detection to the ^1H port of the probe to be used.
If this is a tune-up for ^1H decoupling instead of CRAMPS, the preamplifier must remain in line during the decoupling experiment.
2. The presence or absence of the preamplifier in the circuit will make a significant difference in pulse widths. A *Solids preamplifier* that is suitable for CRAMPS can also remain in line during decoupling. **Do not** use the standard T/R switch in a decoupling circuit unless you know it has been specified for solids.

Adjust the Homogeneity and Determine an Approximate 90° Pulse

1. Collect a single pulse ^1H spectrum of the sample.
2. Shim for a minimum line width (<50 Hz).
3. Roughly measure the 90° pulse and place the signal on resonance.
It is convenient but not mandatory to use Z0 to place the signal on resonance with $\text{tof}=0.0$. Be sure the receiver gain is low so as to avoid overload ($\text{gain}<20$) and d1 is set to insure full recovery of the signal.

Calibrate the Exact 90° Pulse Width (FLIPFLIP or XX)

This procedure is accomplished by retuning the probe or amplifier while observing a repeating cycle of alternating X and -X pulses. The procedures for tune-up are as follows:

1. Enter the macro **flipflop**.
2. Set the following permeates according to the system in use:

Parameter	<i>UNITY</i> <i>UNITYplus</i>	<i>INOVA</i> or <i>UNITY</i> or <i>VXR-S</i>	Comments
d1	1.0 sec	1.0 sec	Longer for samples with no relaxation agent
rof1	1.5 μsec	1.5 μsec	
rof2	0.2 μsec	0.2 μsec	
pw	<1.5 μsec	<1.5 μsec	1.5 usec is optimal for CRAMPS
tau	7.0 μsec	7.0 μsec	add pulse width in excess of 1.5 μsec the value base value, e.g. is $\text{pw}=2.5$ then $\text{tau}=8.0$ usec
phase1	0	0	
phase2	0	0	
phfid	0	0	
nt	1	1	
trig	'n'	'y'	Rotor sync. module is required to set $\text{trig}='y'$

3. Acquire a FID and enter **df** to display both the real and imaginary points.
Obtain the imaginary trace with the imaginary menu button. Adjust the phase to minimize the imaginary channel. If this is not possible, check to be sure the FID is on resonance.

- Optionally
 - a. Type `phaser=phfid, phfid='n'`
 - b. Reacquire the spectrum.

This will adjust the pulse phase to place the signal in one of the two ADC channels. Otherwise, it usually sufficient to observe a phased display. The real channel should appear similar to [Figure 17](#). or [Figure 18](#).

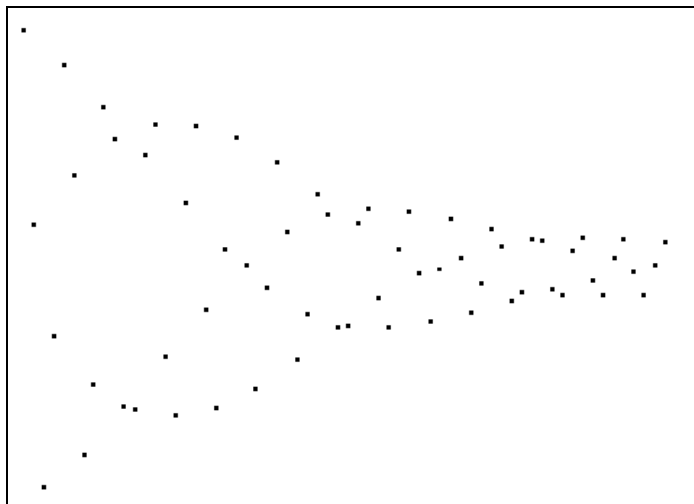


Figure 17. Real Channel FID Pattern

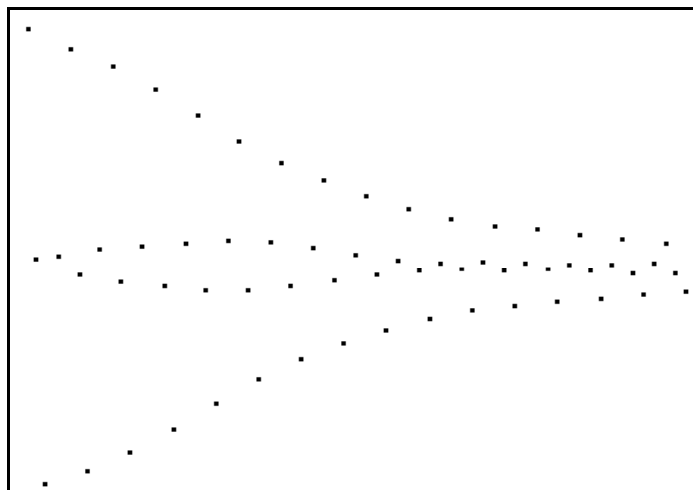


Figure 18. FLIPFLIP FID at Exact 90° Pulse

4. Type `gf` and then `acqi`.
5. Press the **FID** button and then press again to select the FID display.
6. Press **IPA** and adjust the `tpwrf` slider to achieve a display similar to [Figure 18](#).

The ideal signal pattern (1.0,0.0,-1.0,0.0)N results from a 90° pulse. The bulge among the first few zero-points and the decay are due to RF inhomogeneity. A distribution of `pw90` values interferes to cause the pattern of [Figure 18](#).

The RF homogeneity can be enhanced by reducing the sample size and by using care to center the sample in the coil. Data similar to [Figure 18](#) is suitable for most CRAMPS experiments. Probes with a strong ^1H background (typically the Vespel, modules of Chemagnetics CP/MAS probes) will show an initial offset of all the points, that decays to zero. Probe background is subtracted by the BR24 experiment and can usually be ignored.

Remove phase transient (FLIPFLOP or X-X)

1. Type `phase2=2`.
This changes the experiment to FLIPFLOP or X-X.
2. Type `gf` and then `acqi`.
The result should be a parallel set of points similar to [Figure 19](#) or [Figure 20](#). The transmitter must be on resonance to correctly run X-X.
3. Adjust the system tuning (see “[System Tuning](#),” [page 63](#)) to remove the curvature of [Figure 19](#), and obtain a result similar to [Figure 20](#).

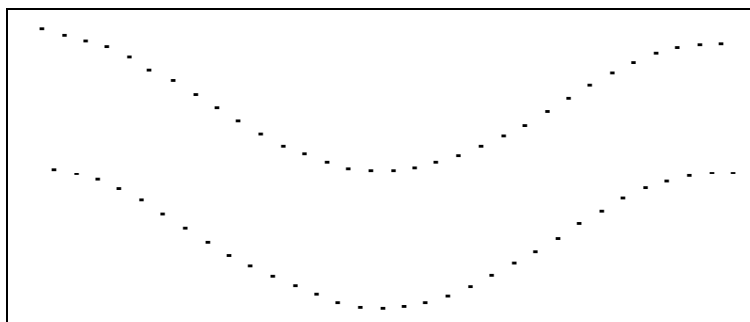


Figure 19. FLIPFLOP “Tram Tracks”

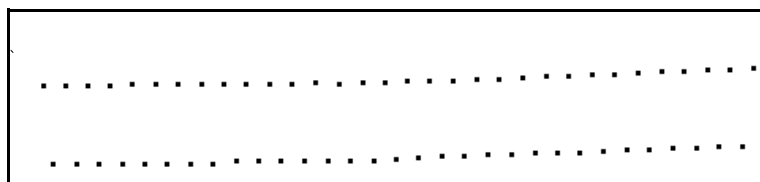


Figure 20. FLIPFLOP Desired FID

System Tuning

The ideal signal pattern is (1,0,0)N. Curvature similar to [Figure 19](#) results from phase transient or phase “glitch”. Phase transient is a small shift, $f(t)$ in phase during the rise and fall times of the pulse. Asymmetric phase transient ($\phi(\tau)$ during the rise time is not equal to $-\phi(\tau)$ during the fall time) causes a net phase shift with each pulse of X-X. This shift causes a frequency offset of the entire pattern. The same effect will occur in the CRAMPS experiment.

Phase transient can be removed or balanced by adjusting tuning of the duplex circuit containing probe, amplifier, quarter-wave cable and preamplifier. A small adjustment of the probe tuning capacitor is often quite effective. In this case record the value of the reflected

output on the tune-interface or note the frequency of the minimum reflected output with qtune. Return to this value when tuning the sample. Phase transient can also be removed more-or-less permanently by carefully choosing the precise length of the cable between the preamplifier and the probe, or if accessible, the 1/4 cable on the preamp. In this case, continue to use the same cables for future experiments. Theoretically, tuning of the CMA or CPI amplifier can also affect phase transient. In practice amplifier tuning does not usually remove phase transient.

4.5 ¹H CRAMPS Experiment (BR24 or MREV8)

BR24 is the standard experiment used to obtain ¹H CRAMPS data. MREV8 provides slightly less narrowing efficiency but can accommodate a larger chemical range.

1. Use the tune-up sample, with a calibrated parameter set for FLIPFLOP
2. Type **br24** or **mrev8**.
3. Set **pw** to the calibrated pulse width
4. Set **tpwr** and **tpwrf** to the calibrated power levels.
5. Type **tau = 3.5 μs** plus any excess pw greater than 1.5 μs.
6. Verify the following:
rof1 = 1.5 μs and **rof2 = 0.2 μs**.
7. Set the following parameters:
p1=pw (BR24 only).
d1 is correct (**d1=1.0** with a relaxation agent)
Set **trig='n'** (**trig='y'** for UNITY and VXR-S with a Sync Module)
8. Array **tof** in 1 kHz steps form -1e4 to +1e4.
9. Type **ga**.

The resulting display should show a single resonance that moves with **tof**. Measure the frequency shift of the resonance with each change in offset. This value divided by 1000 is the experimental multiple-pulse scale factor, *S*. *S* will probably be offset dependent. Choose **tof** with the greatest narrowing (a value of **tof=-2000** to **-5000** is often obtained). This will be the optimum **tof** for future experiments. Note the shift of the spectrum when **tof** is on resonance. This shift should be zero. If the offset is large (>500 Hz), it will be necessary to repeat **step 3** and **step 4**, on [page 62](#).

Optional:

- a. Fine adjust the phase transient using BR24 or MREV8 to obtain a zero offset.
 - b. Run a set of repeating scans in **acqi** mode and tune phase transient to place the signal with **tof=0** at zero frequency.

Probe heating may cause a time dependent line shift that results from a change in phase transient due to a change in probe tuning. If this is a problem increase the VT air (Chemagnetics probes) and the body air and use steady-state scans if necessary to begin the run at equilibrium.
10. Record the tuning values for Qtune or the tune interface for future use in tuning the probe with the sample.
 11. Insert a sample of solid adipic acid or glycine and retune to the previous values.

12. Set the spin rate at < 2 kHz.
13. Set **d1=5** for glycine and **d1=60** for adipic acid.
14. Type **nt=2 ga**
The result for adipic acid should be similar to **Figure 21**.
15. Scale the spectrum.
 - a. Place two cursors on the two upfield lines of adipic acid or glycine.
 - b. Type **scalesw=sfrq/delta**.
16. Reference the spectrum.
 - a. Place a cursor on the upfield of the two lines
 - b. Type **r1(sfrq*2.0/scalesw)** to reference this line at 2.0 ppm.
 - c. The chemical shift scale and reference are now correct and an additional line should be present at 13 to 14 ppm.
17. Run the experimental sample with the same data set and tuning.

4.6 How to Obtain Good CRAMPS Spectra

MREV8 and BR24 pulse sequences must be used with slow spinning so that the length of a rotor cycle, τ_r , greater than one multiple-pulse cycle, τ_{auc} . Interference between these two cycles will negate the narrowing effects. Typical spinning speeds for ^1H CRAMPS are less than 2 kHz, and at these speeds the multiple-pulse cycle does all the narrowing of ^1H - ^1H dipolar interactions.

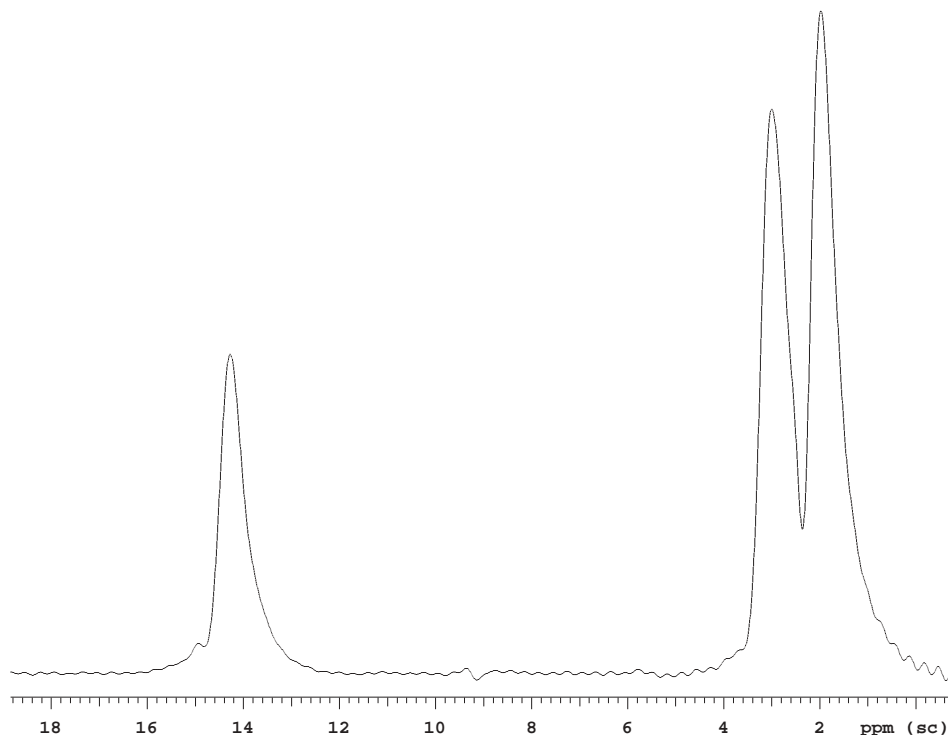


Figure 21. Adipic Acid Spectrum

The transmitter is typically set upfield ($\tau_{of} = -2000$ to -5000 Hz) from the spectrum of interest and line narrowing is usually best at these frequencies. MREV8 and BR24 spectra also always have a quadrature image and a zero-frequency signal (the "pedestal") and it is necessary to set the transmitter off resonance to avoid overlap with these signals. The section below ("[Quadrature 1H CRAMPS](#)," [page 66](#)) describes how to avoid images and a pedestal. A pedestal can also be caused by ^1H background in the probe. Background experiences a flip angle much less than 90° and does not precess. The result is a zero-frequency signal.

Multipulse sequences deliver substantial RF to the probe. Probe heating is a possibility, especially if the sample is lossy, and heating can cause a probe tuning change and a degradation of the CRAMPS spectrum. Use VT air when available and consider using steady-state scans to establish a steady-state tuning condition in the probe. If you are collecting many scans, tune with a duty cycle about the same as that of the spectrum (similar $d1$, τ_{au} and ss).

The power for obtaining minimum ^1H 90° pulse width for a particular CP/MAS probe (unless otherwise mentioned) is usually a value that can be sustained for about 50 ms with a 100% duty cycle (i.e. ^1H decoupling). The duty cycle of a CRAMPS sequence is about 30% to 50%. At this power level it is safe to run a CRAMPS experiment with the same total-time and longer acquisition times or slightly shorter pulses can be considered. There is no specific rule here except that one should consult the manufacturer before exceeding specifications in the case a probe is under warranty. Use as short a 90° pulse that you feel is safe for a given probe.

The quality of a CRAMPS spectrum is improved by shortening the interpulse spacing, τ_{au} . The lower limit for τ_{au} is determined by the time required to collect the data point during one of the $2 \cdot \tau_{au}$ periods of the pulse sequence. The recommended $\tau_{au} = 3.5 \mu\text{s}$ provides a $5.5 \mu\text{s}$ window to collect a data point when $pw = 1.5 \mu\text{s}$. Smaller values will result in a null signal (see "[Amplifier and Receiver Blanking](#)," [page 58](#)). One can shorten τ_{au} can be shortening by changing the hardware adjustment that delays receiver turn on. The result will be a signal that includes some probe ring down, which will appear as a larger pedestal. The CRAMPS sequences also subtract ring down with a phase cycle of 2 scans so one can afford a certain amount of ring down in ones CRAMPS data points, as long as it does not saturate the ADC.

4.7 Quadrature 1H CRAMPS

The pulse sequences CYLBR24 and CYLMREV provide quadrature detection and suppress the pedestal and the image. For MREV8 and BR24 an off-resonance signal created by a 90° pulse does not precess in the XY plane. Instead the combination of precession and pulses rotates the magnetization about an axis tilted relative to Z. The real and imaginary components projected on the XY plane are not equal and the result in the spectrum is a quadrature image. In addition, if magnetization is not completely tilted to the plane of multipulse precession by the preparation pulse, the remaining component of the magnetization will not precess and cause a pedestal.

The two quadrature multipulse experiments have 4-scan phase cycles. For each of the four scans the phase and flip angle of the preparation pulse are set to rotate the magnetization to each of the four 90° positions in the plane of precession. [Table 8](#) and [Table 9](#) show these phases and flip angles. In these sequences the flip angle and small-angle phase are varied

scan to scan. When set properly, a four scan phase cycle should remove both the image and the pedestal and it should be possible to set the transmitter in the center of the spectrum.

Table 8. Multiacquisition Quadrature Corrections for MREV8

<i>Acquisition</i>	<i>M(0)</i>	<i>Preparation Pulse (degrees)</i>
1	(0,1,0)	90 ₀
2	1/√2(1,0,-1)	135 ₂₇₀
3	(0,-1,0)	90 ₁₈₀
4	1/√2(-1,0,1)	45 ₉₀

Table 9. Multiacquisition Quadrature Corrections for BR24

<i>Acquisition</i>	<i>M(0)</i>	<i>Preparation Pulse (degrees)</i>
1	1/√2(1,1,0)	90 ₃₁₅
2	1/√6(1,-1,-2)	145 ₂₂₀
3	1/√2(-1,-1,0)	90 ₁₃₅
4	1/√6(-1,1,2)	35 ₄₅

There are no drawbacks to using the quadrature sequences instead of BR24 and MREV.

4.8 Fast MAS Assisted with a Multiple-Pulse Cycle (WaHuHaHS)

High MAS spin rates (>15 kHz) also average ¹H-¹H dipolar interactions and are an alternative to ¹H CRAMPS. Used with direct polarization alone, spinning speeds approaching 30 kHz provide line narrowing that can compare with ¹H CRAMPS. An advantage of fast spinning is greater sensitivity. Fast-spinning spectra can be acquired with analog filters f_b set just greater than the spectral width for a large sensitivity improvement. It is in fact useful to set sw equal to the spin rate to eliminate any sidebands. In contrast multipulse methods must use open analog filters to avoid pulse ring-down, and folded noise from the full receiver bandwidth (2-5 MHz) lowers the signal to noise.

One multipulse sequence, WaHuHaHS, can be used with fast MAS spinning. WaHuHaHS is a semi-windowless version of the original multipulse sequence, WaHuHa. Both sequences have a four-pulse cycle. In WaHuHaHS two of the interpulse delays are set to zero and the total cycle time, τ_{auc} , is short enough to be used with high speed spinning. The result is often an improvement over high-speed spinning alone or slow spinning ¹H CRAMPS.

WaHuHaHS requires the same multiple-pulse set-up procedure described above for MREV8 and BR24.

4.9 FLIPFLOP - Pulse Width and Phase Transient Calibration

The flipflop.c pulse sequence (Figure 22) is the standard sequence for multiple-pulse tune up. It is applicable for UNITY*plus* and UNITY INOVA as well as UNITY and VXR-S with a Sync Module. It is used for measurement of the pulse width and removal of phase transient.

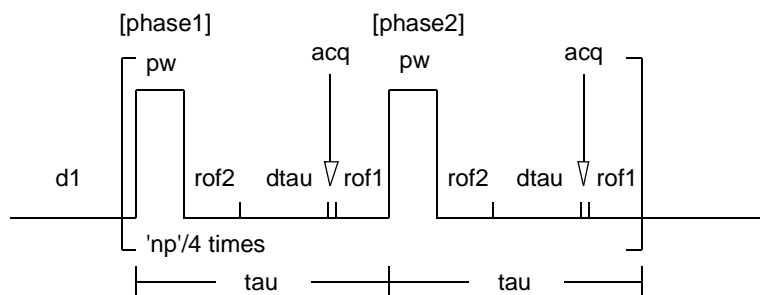


Figure 22. Pulse Sequence for flipflop.c

Macro

The macro `flipflop` calls the sequence and a parameter set.

Parameters

`pw` is the 90° pulse length, in microseconds.

`phase1` is the phase of the first 90-degree pulse, and is set to 0 (x).

`phase2` is the phase of the second 90 degree pulse. It is set to 0 (x) for FLIPFLIP and 2 (-x) for FLIPFLOP.

`trig='y'` for UNITY and VXR-S with a Sync Module. Otherwise `trig='n'`.

`np` is the number points and `np=128` or `256`.

`tau` is interpulse delay, in microseconds, including `pw`. The minimum `tau` is about 7.0 μ s when `pw=1.5 μ s`. See `rof1` and `rof2`.

`rof1` is the amplifier unblinking time before each pulse. The receiver is also immediately blanked and a T/R switch if present is placed in transmit mode. Set `rof1=1.5 μ s`.

`rof2` is the receiver unblinking time after each pulse. A T/R switch is placed in receive mode immediately. For ^1H the receiver comes on after about 2.0 μ s. For lowband nuclei the receiver is set to come on after 8.0 ms. these two times are controlled by hardware adjustment in the magnet leg. Set `rof2=0.2 μ s` for a High-Power preamp. Set `rof2=0.5 μ s` for a Solids $^1\text{H}/^{19}\text{F}$ preamp.

4.10 BR24 and CYLBR24 - Multiple Pulse Line Narrowing (24-pulse cycle)

Br24 (Figure 23) is the usual sequence used for ^1H CRAMPS. CYLBR24 is a modification that allows quadrature detection with the transmitter in the center of the spectrum. The sequences are applicable for UNITY*plus* and UNITY INOVA as well as UNITY and VXR-S with a Sync Module.

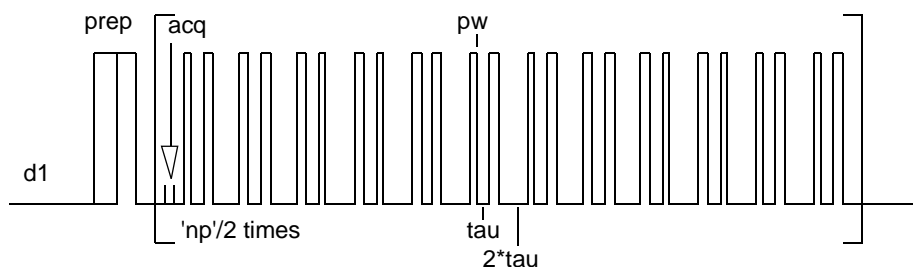


Figure 23. BR24 Pulse Sequence

Macros

The macro `br24` converts a S2PUL or FLIPFLOP data set for BR24. `cylbr24` converts a data set for quadrature BR24. All relevant parameters are preserved if the initial data set is FLIPFLOP, BR24, CYLBR24, MREV8 or CYLMREV.

Parameters

`pw` is the 90° degree pulse-length, in microseconds.

`p1` is the preparation pulse, in microseconds, whose phase is controlled by the parameter `phase1`. To minimize the “pedestal” `p1` should be set to the 90° flip angle and `phase1=135`.

`tau` is the interpulse delay, in microseconds, including `pw`. The BR24 cycle is $36 \cdot \tau$ long and is repeated `np/2` times to build up a FID.

`trig='y'` for UNITY and VXR-S with a Sync Module. Otherwise `trig='n'`.

`tauc` is the cycle time, in microseconds and is the actual dwell time for the FID. `tauc` is not changed and is for information only.

`mp_at` is the sum of all cycles, in microseconds, and is the true acquisition time. `mp_at` is not changed and is for information only.

`sw=2e6` turns on the fast ADC without analog filters. `sw` does not determine the dwell time (see `tauc`).

`scalesw` is a scale factor that converts `sw=2e6` to the correctly scaled spectral width. $\text{scalesw} = (1.0 / \text{tauc} \cdot \text{sw}) \cdot S$ where `S` is the multiple-pulse scale factor for Br24 (0.385 for ideal pulses).

`rof1` and `rof2` (see 4.9 “FLIPFLOP - Pulse Width and Phase Transient Calibration,” page 68)

4.11 MREV8 and CYLMREV - Multiple Pulse Line Narrowing (8-pulse cycle)

MREV8 (Figure 24) is a sequence used for ^1H CRAMPS. CYLMREV is a modification that allows quadrature detection with the transmitter in the center of the spectrum. The sequences are applicable for UNITY*plus* and UNITY INOVA as well as UNITY and VXR-S with a Sync Module.

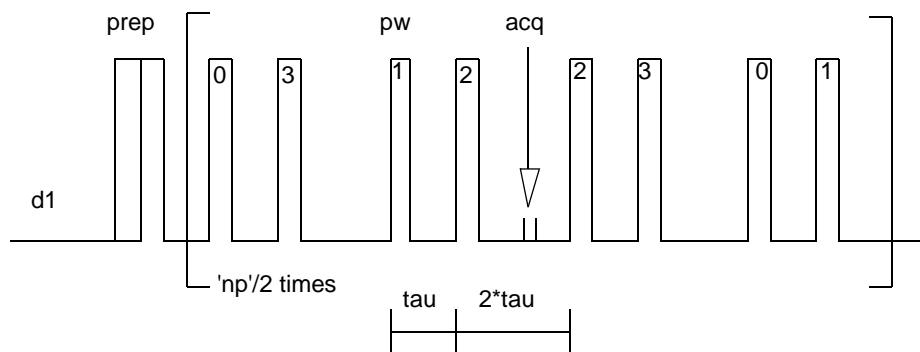


Figure 24. MREV8 Pulse Sequence

Macros

The macro `mrev8` converts a S2PUL or FLIPFLOP data set for BR24. `cylmrev` converts a data set for quadrature MREV8. All relevant parameters are preserved if the initial data set is FLIPFLOP, BR24, CYLBR24, MREV8 or CYLMREV.

Parameters

`pw` is the 90° degree pulse-length, in microseconds.

`tau` is the interpulse delay, in microseconds, including `pw`. The MREV8 cycle is $12 \cdot \tau$ long and is repeated $n_p / 2$ times to build up a FID.

`trig` = 'y' for UNITY and VXR-S with a Sync Module. Otherwise `trig` = 'n'.

`tauc` is the cycle time, in microseconds and is the actual dwell time for the FID. `tauc` is not changed and is for information only.

`mp_at` is the sum of all cycles, in microseconds, and is the true acquisition time. `mp_at` is not changed and is for information only.

`sw=2e6` turns on the fast ADC without analog filters. `sw` does not determine the dwell time (see `tauc`).

`scalesw` is a scale factor that converts `sw=2e6` to the correctly scaled spectral width. $\text{scalesw} = (1.0 / \text{tauc} \cdot \text{sw}) \cdot S$ where S is the multiple-pulse scale factor for MREV8 (0.471 for ideal pulses).

`rof1` and `rof2` (see 4.9 “FLIPFLOP - Pulse Width and Phase Transient Calibration,” page 68)

4.12 WaHuHa and WaHuHaHS - MP-Assisted High-Speed Spinning (4-pulse cycle)

WaHuHa (Figure 25) is the original 4-pulse multipulse sequence. WaHuHaHS is a semi-windowless version of WaHuHa and is often used in conjunction with high speed spinning. The sequences are applicable for UNITY*plus* and UNITY^{INOVA}.

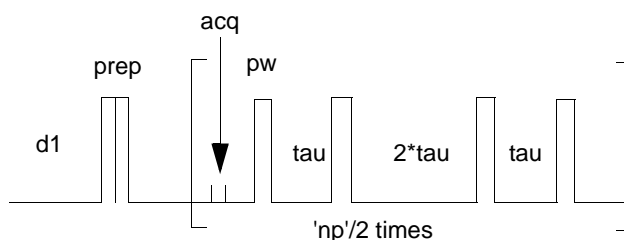


Figure 25. WaHuHa Pulse Sequence

Macros

The macros wahuha and wahuhaHS convert a S2PUL or FLIPFLOP data set for BR24. cylmrev converts a data set for quadrature MREV8. All relevant parameters are preserved if the initial data set is FLIPFLOP, BR24, CYLBR24, MREV8 or CYLMREV.

Parameters

pw is the 90° degree pulse-length, in microseconds.

tau is the interpulse delay, in microseconds, including pw. The WaHuHa cycle is 6 * tau long and the WaHuHaHS is 4 * tau + 2 * pw. They are repeated np/2 times to build up a FID.

tauc is the cycle time, in microseconds and is the actual dwell time for the FID. tauc is not changed and is for information only.

mp_at is the sum of all cycles, in microseconds, and is the true acquisition time. mp_at is not changed and is for information only.

sw=2e6 turns on the fast ADC without analog filters. sw does not determine the dwell time (see tauc).

scalesw is a scale factor that converts sw=2e6 to the correctly scaled spectral width. scalesw=(1.0/tauc*sw)*S where S is the multiple-pulse scale factor for WaHuHa (0.707 for ideal pulses).

rof1 and rof2 (see 4.9 “FLIPFLOP - Pulse Width and Phase Transient Calibration,” page 68)

Chapter 5. Solid-State NMR Accessories

Sections in this chapter:

- 5.2 “Rotor Synchronization Operation,” this page.
- 5.3 “Rotor Speed Controller Accessory Operation,” page 76.
- 5.4 “Variable Temperature Operation with Solids,” page 78

5.1 Pneumatics/Tachometer Box

The variable temperature (VT) Pneumatics/Tachometer Box is used with Varian VT CP/MAS probes. The Pneumatics/Tachometer Box handles all air/gas supply distribution to the probe. The supply line is permanently connected to the wall supply, which must be clean, dry air. The wall supply should be at a pressure not exceeding 120 psig (8 bar) and be filtered to 0.6 micron.

CAUTION: Failure to maintain a clean and dry air supply shortens probe life.

This section contains general information about the RT and VT Pneumatics/Tachometer Boxes and installation instructions.

Figure 26 shows a Pneumatics/Tachometer Box for VT (variable temperature) CP/MAS probes. This box is mounted on a leg of the magnet in a convenient position. The four hoses coming out of the left side of the pneumatics box are connected to the probe ROTATION/DRIVE, BEARING, BODY GAS, and the EJECT port of the magnet. These connectors are of a high-pressure, quick-disconnect type.

5.2 Rotor Synchronization Operation

In a number of experiments it is desirable to trigger an event at a precise point in the rotation period of a rotor. Usually this is less relevant from transient to transient than it is within a single transient. Even within a single transient, the required delay before the trigger point may be some seconds or minutes. This delay is long enough for the rotor to change speed enough so that “dead reckoning” is not sufficiently accurate. The rotor synchronization accessory offers the spectroscopist the ability to synchronize events with the absolute position of a CP/MAS rotor, as well as to read the rotor speed at any time.

Hardware Description

The rotor synchronization hardware detects the optical transition from dark to light of the detection mark on a rotor and provides a pulse as a trigger to a circuit on the Acquisition Controller or Pulse Sequence Controller board. The dark-to-light edge can be used in three ways:

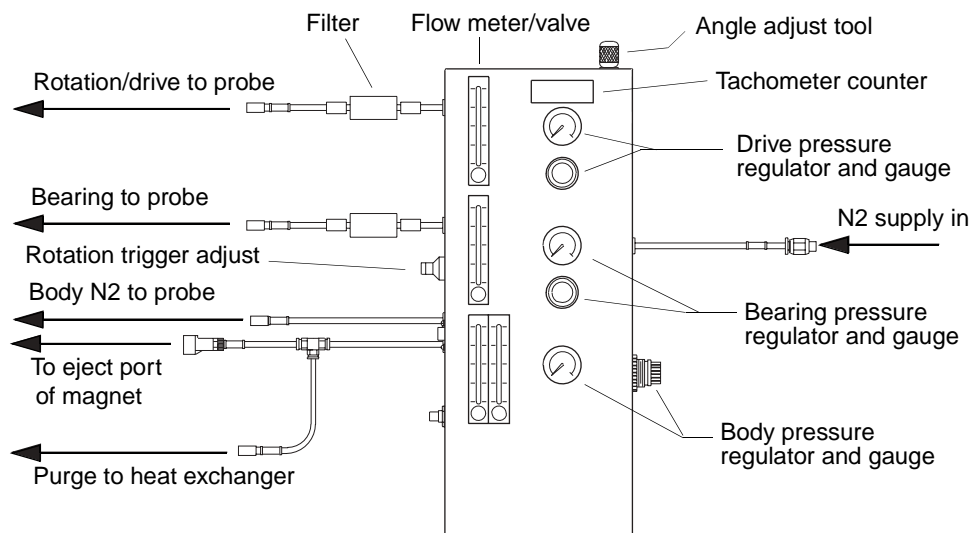


Figure 26. Pneumatics/Tachometer Box for CP/MAS Probes

- The time between successive edges can be measured (note that the edges are always in the same sense, so that this interval is one rotor period). This has a precision of 50 ns. This is shown as “mode 1” in [Figure 27](#).
- An event can be triggered on the n th edge (in all cases here n is an integer). In this mode, the rotor is providing an external timing event to the Acquisition Controller or Pulse Sequence Controller board. This provides a means of delaying until the next dark-to-light rotor edge. This is “mode 2” in [Figure 27](#).
- The Acquisition Controller board or Pulse Sequence Controller board can be instructed to delay precisely n rotor periods. This is done by interrupting an internal counter that is normally reset at each rotor edge, delaying n edges and then counting the counter down to zero. At this point the delay is finished. Thus, in principle, the error in the delay will be only that percentage that the first and the last periods differ. This is shown as “mode 3” in [Figure 27](#).

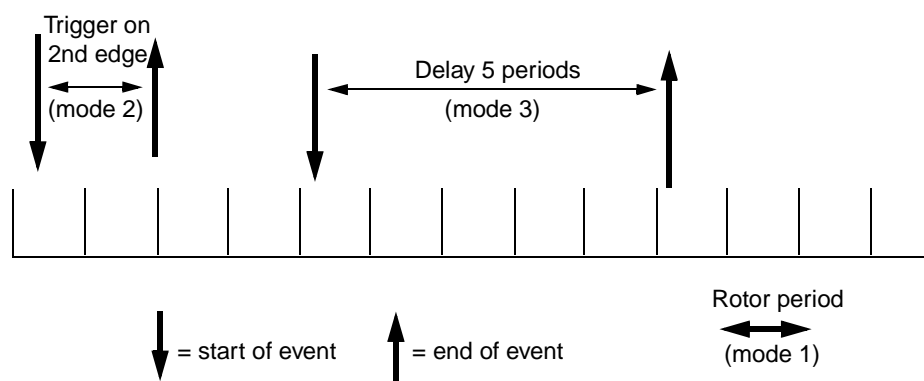


Figure 27. Different Modes of the Rotor Synchronization Accessory

A potential source of error exists in determining the point of the light transition on which to trigger the digital circuitry. This is a factor determined by two variables: the light detection circuitry and the markings on the rotor.

For light detection, the tachometer box provides the light source and the detector. The rotor has a blackened sector on its base (Figure 28) so that as it rotates, differing amounts of light are reflected. The light is transferred through light pipe to the stator base. The reflected light is sampled by another light pipe and brought back to the tachometer box where it is photodetected. The resulting current is amplified and used to toggle a Schmitt trigger that is the input to the external time base of the Acquisition Controller or Pulse Sequence Controller board.

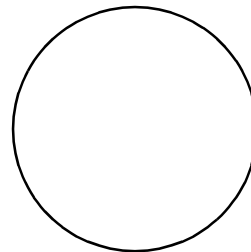


Figure 28. Base of a Varian High-Speed Spinning Rotor

In principle, detection in the Doty probe is the same. Figure 29 shows a Doty double-bearing rotor with a blackened sector on the inside of the lower drive cap. The light pipes, however, are not as precise and the detection is more indirect, thus giving a lower signal-to-noise ratio.

The photodetection is performed in the base of the probe and then transferred to an external amplifier with adjustable gain control. The amplifier output is then sent to the tachometer box where it is further conditioned before being used to drive the Acquisition Controller board or Pulse Sequence Controller board.



Figure 29. Doty Double Bearing Rotor

Specifications

The specifications for the rotor synchronization accessory depend on both the probe and the electronics. The values given below reflect those that can be obtained in optimum circumstances and, as such, do not imply a guarantee of performance. If performance is severely degraded from these values, the first remedy is to check the sector markings on the rotor, because any lack of definition here will have profound effects on stability of the result.

Varian High-Speed Spinning Probe

Jitter in one TTL rotor period (measured with an oscilloscope from falling edge to falling edge) is ≤ 500 ns for spinning speeds to 8 kHz. This corresponds to an angular uncertainty of $\leq 0.5^\circ$ at a spinning speed of 3600 Hz. An edge is detected normally as the negative-going transition of the reflected light going from at least a value of -39 dBm to no more than -45 dBm, measured at the end of the fiber optics.

CAUTION: Never spin PSZ (zirconia) rotors (white or off white in color) above 7.5 kHz or silicon nitride rotors (gray) above 9 kHz. High spinning speeds will cause the rotors to shatter.

Doty Scientific Probe

Jitter in a TTL rotor period is ≤ 2 μ s for spinning speeds to 5 kHz. This corresponds to an angular uncertainty of $\leq 2^\circ$ at a spinning speed of 3600 Hz. This is expected over the temperature range of -50 $^\circ$ C to $+100$ $^\circ$ C, provided that the tachometer amplifier gain is correctly adjusted to give a signal of no less than 1 Vpp into the tachometer box.

Using Rotor Synchronization

Table 10 lists parameters used with the rotor synchronization accessory.

Table 10. Rotor Synchronization Controls

Parameters	
<code>hsrotor</code> {'y', 'n'}	Display rotor speed for solids operation
<code>in</code> {'y', 'n'}	Interlock
<code>srate</code> {0–107, in Hz}	Spinning rate for magic angle spinning

The rotor synchronization accessory can be used in a number of ways, from simple monitoring of spinning speed to sophisticated synchronized experiments. In all cases, the accuracy of the readout is dependent on the marking of the sectors on the rotor. Figure 28 shows the marking on the base of Varian high-speed spinning rotors and Figure 29 shows the marking inside the lower rotor cap for Doty rotors.

Rotor Markings

For Varian high-speed spinning rotors, the base of zirconia rotors may be blackened using a black permanent marker. Make sure that the dividing line across the diameter is clear and that the black sector is solid black. The base of silicon nitride rotors may be whitened similarly using typewriter correction fluid. Avoid using a water-based correction fluid because it is more likely to spin off the rotor. White paint can also be used.

For Doty rotors, use the supplied black and white paints. Ensure that the dividing line between black and white is sharp. Periodically check that the black and white markings are still sharp. Over time, the high spinning speeds may cause the paint to “fly off.” Repaint the rotors when needed.

Sample Spinning

The sample is packed in the rotor in the normal way. The rotor is spun in accordance with the instructions in “Spinning the Sample,” page 22, and the spinning speed may be read on the tachometer box LCD display. Note that for Varian probes, the optical fibers should be plugged into the tachometer box, and for Doty probes the probe should be connected to the Doty tachometer amplifier, the switch on the amplifier set away from the OPTICAL OFF position, and the OPTICAL OUT BNC connected with a coax cable to the EXTERNAL INPUT of the tachometer box.

Spinning Speed

The parameter `hsrotor` is an experiment-based parameter, not a globally accessible parameter. If you join another experiment to do rotor synchronization, `hsrotor` may also need to be created in that experiment. The spinning speed of the rotor may be displayed in the ACQUISITION STATUS window if the parameter `hsrotor` is set to 'y'. If the speed does not show, enter `hsrotor?`

If `hsrotor` is undefined, enter `create('hsrotor', 'string')`, and then enter `hsrotor='y' su` to activate the spinning speed display. Once the setup is complete, the correct rotor speed should appear in the Acquisition Status window. This checks that the rotor sync accessory is working.

CP/MAS operates in the normal manner with rotor synchronization installed. Manual entry of `srate` (spinning speed in Hz) is accepted; however, `srate` is updated at the end of each acquisition to reflect the actual spinning speed at the end of the acquisition. At the start

of each acquisition, the initial spinning speed is noted. If, during acquisition, the speed alters by more than 100 Hz and the interlock parameter `in` is set to 'Y', acquisition is halted.

The flexibility of rotor synchronization is mainly through the construction of pulse sequences using rotor sync elements (refer to the *VNMR User Programming Manual* for information on creating pulse sequences).

5.3 Rotor Speed Controller Accessory Operation

The Varian rotor speed controller accessory provides computer control of the spin rate of a CP/MAS sample. By using the controller in a closed loop mode, the sample spinning rate can be held constant to a few hertz or better over a long acquisition time (days or weeks). During variable temperature operation, the rotor controller can keep the spin rate from changing while varying the operating temperature. The setting of a desired rate is much easier because fine control is provided for and slow drift is automatically compensated.

Rotor Speed Controller Hardware

The rotor speed controller accessory consists of the following hardware:

- Modified Varian VT pneumatics/tachometer box
- PC-compatible computer with 16-bit timer-counter and DAC cards
- Cabling to connect PC, pneumatics/tachometer box, and Sun workstation

The use of a PC computer provides an inexpensive, powerful, and dedicated processor for rotor speed controlling tasks. The PC houses 16-bit DAC and counters for measuring the rotor speed and supplying a 0 to 5 V signal to the pneumatics transducer inside the pneumatics/tachometer box. Operator control of the PC and software takes place through a RS-232 link to the Sun host computer.

Rotor Speed Controller Software

The rotor controller is run with the `rcontrol` software, which has a menu driven interface. The main menu provides choices that initiate the following:

- Open loop
- Closed loop
- Configuration routines
- Exit from the `rcontrol` software

Open Loop Mode

In open loop (O) mode, the program requests a DAC value (0 to 65385) and then continually displays the rotor speed on the screen. Open loop mode is useful when spinning a sample up for the first time—perhaps, to check packing balance—or to calibrate the electro-pneumatic regulator span and zero settings.

The DAC value can be changed while continuously displaying the rotor speed by pressing the following keys and simultaneous key combinations on the PC keyboard:

<i>Actions</i>	<i>Keys</i>
Decrease DAC value by 1 unit	f
Decrease DAC value by 100 units	l
Decrease DAC value by 1000 units	Shift-l
Increase DAC value by 1 unit	Shift-f
Increase DAC value by 100 units	h
Increase DAC value by 1000 units	Shift-h
Exit to main menu	q

Closed Loop Mode

In closed loop (C) mode, the desired rotor speed is entered. The control algorithm then takes over to control the rotor speed. While controlling is active, the DAC value, latest increment to the DAC, and the difference of the rotor speed and the set point are displayed each time through the control loop.

To stop the speed control process, press the q key. After the process is stopped, you can enter a new rotor speed, save the data log file, or exit to the main menu.

To save the data log file (DAC and rotor speed values), choose the L option from the main menu. You can specify the number of data points to log (4000 points maximum) and a control loop divisor N. For example, if N is set to 10, a DAC and rotor speed pair is logged every 10th time through the control loop. Log data is written to disk only after termination of the closed loop control session and confirmation by the user.

Configuration Routines

The configuration (F) choice at the main menu displays the current gain settings used in the closed loop control process and allows you to change them. Besides the gain values, the configuration routines allow you to set the following:

- Loop delay, set in milliseconds
- Increment clamp value for the loop increment

The loop delay specifies a time delay between outputting to the DAC and reading the rotor speed. Note that too short a time may lead to wild oscillations in the closed loop mode when the gain settings are large.

The increment clamp value sets the maximum change to the DAC word and is a useful type of “adaptive gain” that can allow gain settings that produce good control so long as the change in set point is not too large.

Typical ranges for the gain settings are shown in [Table 11](#). G3 and G4 set to 0 produce good control when the ranges shown in the table are used for the other gains.

Table 11. Rotor Controller Gain Setting and Typical Ranges

<i>Gain Setting</i>	<i>Typical Ranges</i>
G1	4 to 5
G2	1 to 2

<i>Gain Setting</i>	<i>Typical Ranges</i>
G3	0
G4	0
G5	0.5 to 1, with a loop delay of 500 to 700 ms and an increment clamp of 5000

The configuration parameters can be saved to a file on the PC (e.g., `gain.set`). Upon initial startup, the parameters in this file are loaded in order to set the configuration. Be sure to make copies of the configuration parameters file (`gain.set`), or write down the current settings if you wish to experiment with changing the rotor control configuration.

Additional Operation Note

The PC computer has been set up such that a monitor and keyboard is not required in order to pass the POST (Power On Self Diagnostics) test, which occurs before the operating system is loaded from disk. These options are set into the CMOS BIOS setup at the factory. If the CMOS fails for some reason, the BIOS setup will have to be reconfigured.

The most likely cause for CMOS failure is drainage on the battery that powers the CMOS when the computer is off. This battery is continuously recharged while the computer is on, so even if the rotor speed controller is not in use, it is wise to keep the computer powered up.

If the computer does need to be turned off, do not leave it off for extended periods of time (weeks or months). If the CMOS does lose its memory settings, a video card, PC monitor, and keyboard will have to be attached so that the CMOS set up program (not part of DOS) can be run.

5.4 Variable Temperature Operation with Solids

This section provides general instructions on the solids variable temperature (VT) accessory. The accessory installation manual for the system provides more detailed instructions on solids VT.

Varian Solids VT System

The Varian solids variable temperature accessory (Part No. 00-958994-00) can be added to a Varian VT CP/MAS probe for VT operation. When this accessory is added, connection of the gas supplies to the probe is altered in the following ways.

- Body nitrogen is needed whenever the probe is in operation. The connection of the VT gas supply is described in the VT installation manual.
- The VT controller is connected to a booster power supply and the booster power supply is connected to the probe. This is accomplished with the solids VT cable as described in the VT installation manual.
- The liquids upper barrel is pushed down so it touches the top of the probe. This, together with the Varian bore vent assembly, serves as the exhaust stack.
- VT operation requires the use of Torlon end caps.

Doty Solids VT System

The Varian solids VT accessory can also be added to the Doty CP/MAS probe for VT operation. When this accessory is added, connection of the gas supplies to the probe is altered in the following ways:

- Body cooling gas is also needed whenever the probe is not at ambient temperature. Connect the VT gas supply to the probes is made as described in the Doty manual.
- The VT controller is connected to the boost supply and the boost supply is connected to the probe.
- The liquids upper barrel is pushed down so it touches the top of the probe. The upper barrel then acts as an exhaust stack.

VT operation requires Vespel end caps. Vespel is less susceptible to thermal deformation at high temperatures and has a lower coefficient of expansion, so is less likely to slip out at low temperatures.

Changes in temperature should always be kept small because rapid changes can cause rotor crashing.

Chapter 6. Solid-State NMR Experiments

Sections in this chapter:

- 6.1 “XPOLAR—Cross-Polarization, UNITY,” page 81
- 6.2 “XPOLAR1—Cross-Polarization,” page 85
- 6.3 “XPWXCAL—Observe-Pulse Calibration with Cross-Polarization,” page 87
- 6.4 “XNOESYSYNC—Rotor Sync Solids Sequence for Exchange,” page 89
- 6.5 “MASEXCH1—Phase-Sensitive Rotor Sync Sequence for Exchange,” page 90
- 6.6 “HETCORCP1—Solid-State HETCOR,” page 92
- 6.7 “WISE1—Two-Dimensional Proton Wideline Separation,” page 93
- 6.8 “XPOLWFG1—Cross-Polarization with Programmed Decoupling,” page 93
- 6.9 “XPOLXMOD1—Waveform Modulated Cross-Polarization,” page 95
- 6.10 “VACP—Variable Amplitude Cross-Polarization,” page 97
- 6.11 “XPOLEDIT1—Solids Spectral Editing,” page 98
- 6.12 “3QMAS1—Triple-Quantum 2D for Quadrupole Nuclei,” page 99
- 6.13 “PASS1—2D Sideband Separation for CP/MAS,” page 101
- 6.14 “CPCS—Cross-Polarization with Proton Chemical Shift Selection,” page 102
- 6.15 “CPCOSYPS—Cross-Polarization Phase-Sensitive COSY,” page 103
- 6.16 “CPNOESYPS—Cross-Polarization Phase-Sensitive NOESY,” page 104
- 6.17 “R2SELPULS1—Rotation Resonance with Selective Inversion,” page 106
- 6.18 “DIPSHFT1—Separated Local Field Spectroscopy,” page 108
- 6.19 “SEDRA2—Simple Excitation of Dephasing Rotational-Echo Amplitudes,” page 109
- 6.20 “REDOR1—Rotational Echo Double Resonance,” page 111
- 6.21 “DOUBLECP1—Double Cross-Polarization,” page 113
- 6.22 “T1CP1— T_1 Measurement with Cross-Polarization,” page 115
- 6.23 “HAHNCP1—Spin 1/2 Echo Sequence with CP,” page 116
- 6.24 “SSECHO1—Solid-State Echo Sequence for Wideline Solids,” page 117
- 6.25 “WLEXCH1—Wideline Solids Exchange,” page 119
- 6.26 “HS90—90-Degree° Phase Shift Accuracy,” page 121
- 6.27 “MREVCS—Multiple Pulse Chemical-Shift Selective Spin Diffusion,” page 122
- 6.28 “MQ_SOLIDS—Multiple-Quantum Solids,” page 123
- 6.29 “SPINDIFF—Spin Diffusion in Solids,” page 124
- 6.30 “FASTACQ—Multinuclear Fast Acquisition,” page 124
- 6.31 “NUTATE—Solids 2D Nutation,” page 125

This chapter describes CP/MAS, triple-resonance, wideline, and multipulse pulse sequences for solid-state NMR. To aid in identification, the names of pulse sequences are given in all capital letters. In general, most of these experiments are intended for *UNITY**INOVA* and *UNITYplus* systems. Running these sequences on *UNITY*, and *VXR-S* systems may require some modifications. None of these sequences are available on *MERCURY* and *GEMINI 2000* systems.

The macros for some of the solid-state NMR sequences are located in `mac.lib`. The macros for other solid-state NMR sequences are located in the user library `user.lib`.

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6.1 XPOLAR—Cross-Polarization, UNITY

XPOLAR is the basic sequence for CP/MAS, MAS and solid-state relaxation measurements for *UNITY* systems (for *UNITY**INOVA* and *UNITYplus* systems, see [page 85](#)). XPOLAR can be run either as a standard single pulse experiment, including the inversion recovery experiment, with the parameter `xpol` set to 'n', or more typically as a cross-polarization experiment, with the parameter `xpol` set to 'y'. The use of the XPOLAR sequence allows the removal of strong dipolar coupling by using a strong decoupling field applied during the acquisition of the data.

A characteristic of some nuclei in the solid state, for example ^{13}C , is a long spin-lattice relaxation time (T_1). To overcome this problem, the abundant nuclei (usually protons) in the systems are polarized with a spin locking pulse and the polarization is then transferred to the rare spins by applying an rf field at the Larmor frequency of the rare spins that is of such magnitude as to make the energy levels of the abundant and rare spins the same in the rotating frame, the Hartmann-Hahn match condition. Following a transfer of energy from the polarized spins to the rare spins, the rare-spin field is turned off and resulting signal observed under conditions of high-power proton decoupling. The recycle time is then set according to the proton T_1 , usually much shorter than the rare-spin T_1 .

For samples that use cross-polarization, the “contact” time (the time during which cross-polarization occurs) should be optimized with the parameter `p2`. This is necessary because

two processes happen simultaneously, the magnetization buildup from cross-polarization and the magnetization loss from rotating-frame relaxation. A time exists for which an optimum in the magnetization occurs. The rising and falling exponential intensities can be analyzed with the `contact_time` macro, which calculates both T_{CH} and ${}^1H T_{1\rho}$.

Applicability

XPOLAR is available on all systems.

Suppressing Spinning Sidebands

NMR spectra at high magnetic fields often have significant spinning sidebands. While these spinning sidebands contain information about the chemical shift anisotropy, they can complicate the interpretation of complex spectra. The sidebands can be eliminated using the TOSS (TOtal Sideband Suppression) technique. The TOSS pulse sequence is selected by setting `toss='y'`. Note that the parameter `srate` should be set to the spinning speed in Hz. TOSS uses 180° pulses based on the parameter `pw`. It may be necessary to adjust `pw` to optimize the TOSS experiment. Figure 30 shows the pulse sequence diagram for cross-polarization with TOSS.

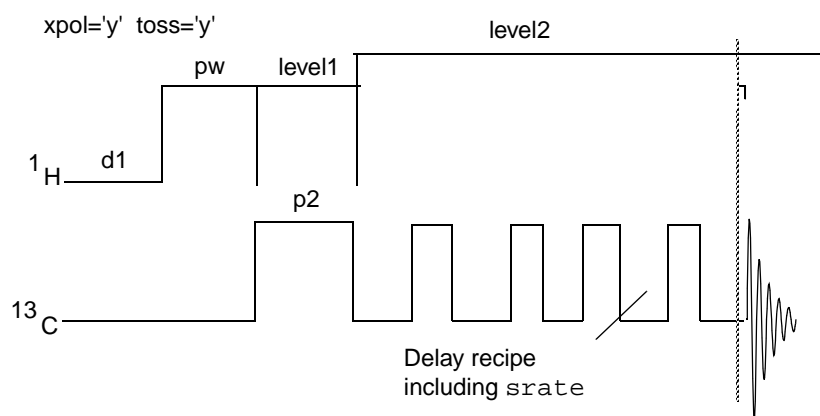


Figure 30. TOSS Pulse Sequence

Suppression of Protonated Carbons (Interrupted Decoupling)

Off-resonance decoupling and related experiments, such as DEPT, in which J-coupling is involved are not usually possible in solids because through-space dipolar coupling as well as J-coupling is present. An experiment exists, however, that can be used to discriminate between protonated and nonprotonated carbons—this is the protonated carbon suppression experiment of Opella and Fry. In this experiment, the decoupler is turned off before acquisition to dephase the protonated carbons.

The technique is effective for non-mobile carbons. Mobile carbons, like methyl groups, are typically not suppressed as well. The experiment is run by setting `pdp='y'`, setting `srate` to the spinning speed and entering appropriate values for the dephasing time `d2` (in seconds). Figure 31 shows the pulse sequence diagram for cross-polarization with interrupted decoupling.

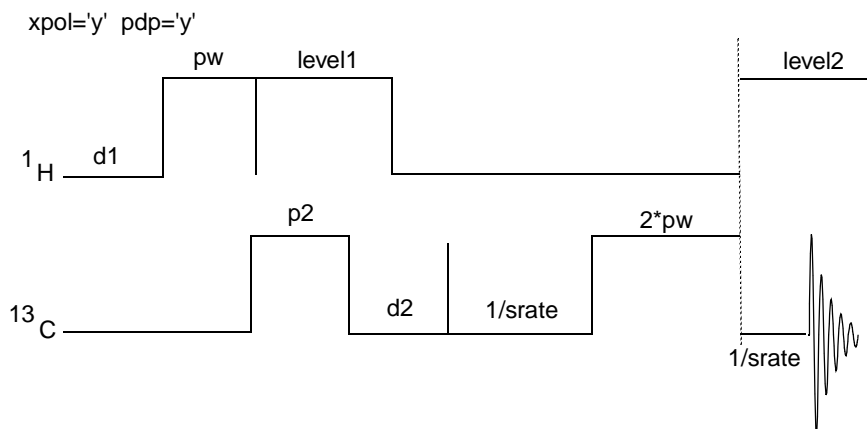


Figure 31. Protonated Carbon Suppression Sequence

Measurement of ^{13}C $T_{1\rho}$

Measurements of the spin-lattice relaxation time in the rotating frame ($T_{1\rho}$) are possible using the standard XPOLAR pulse sequence. The parameter $p3$ is the spinlock time after cross-polarization. Typical values for $p3$ range from 50 to 5000 microseconds. [Figure 32](#) is a diagram of the sequence.

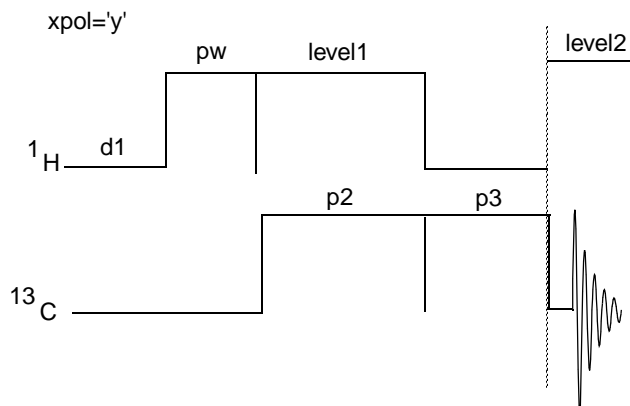


Figure 32. Rotating-Frame Spin-Lattice Relaxation Measurements Sequence

To analyze a $T_{1\rho}$ experiment of the decay time constant, enter:
`analyze('expfit','p3','t2','list').`

The `analyze` command has four arguments. The first argument is `expfit`. The `analyze` program provides an interface to the curve fitting program `expfit`, supplying it with the input data in the form of a text file `analyze.inp` in the current experiment. `analyze.inp` is generated by a line listing of the peaks of interest in a spectrum and by the `fp` command, which measures the peak height of each peak in an array of spectra. The second argument of `analyze` is the name of the arrayed parameter, which in the case of ^{13}C $T_{1\rho}$ experiments using the `xpolar` sequence is the parameter `p3` (for `xpolar1`, use `pchro`). The third argument is the type of analysis to be performed, for example use `t2` for the exponentially decreasing data points of a $T_{1\rho}$ experiment. The fourth argument, `list`, results in the construction of the file `analyze.list`, where the summary of the data analysis and calculations are stored in the current experiment. A hard copy can be

obtained just as with any other text file. The graphical display of the data can be viewed on screen by using the command `exp1` or plotted with the command `pexp1`.

Measurement of the ^1H T_1 through Cross-Polarization

Proton T_1 can be measured using the XPOLAR pulse sequence by performing a standard inversion-recovery experiment on the protons followed by cross-polarization of the remaining ^1H magnetization to the carbons. Figure 33 is a diagram of the pulse sequence. The `xpolar` macro sets up parameters for the XPOLAR pulse sequence.

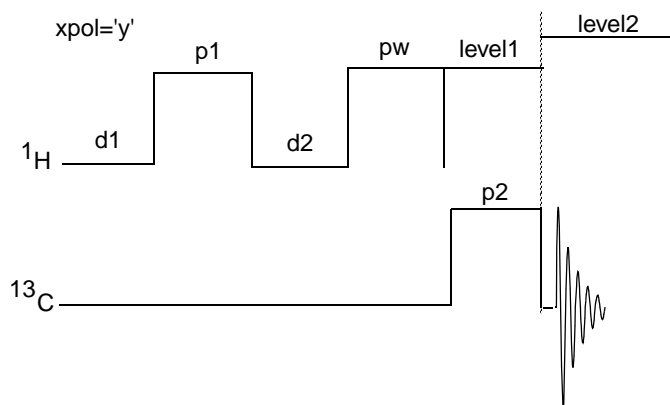


Figure 33. Pulse Sequence for Measuring ^1H T_1

Parameters

`xpol` is set to 'n' for direct polarization or set to 'y' for cross-polarization.

`pw` is the observe pulse for direct polarization or the proton 90° pulse for cross-polarization. `pw` is in microseconds.

`p1` is the initial observe pulse (direct polarization), usually set to a 180° inversion pulse, or the initial proton pulse, usually set to a 180° pulse (cross polarization). `p1` is in microseconds.

`p2` is the cross-polarization contact time, in microseconds.

`p3` is a pulse, in microseconds, for an X-nucleus only spin-lock following `p2`.

`dm` should be set to 'nny'. The decoupler has a maximum duty cycle of 20%.

`d2` is delay between `p1` and `pw` (for inversion-recovery) if `pdp` = 'n'. If `pdp` = 'y', `d2` is a delay for interrupted decoupling for protonated carbon suppression. `d2` is in seconds.

`srate` is the sample spinning rate, in Hz.

`toss` set to 'y' invokes timed spin-echoes to suppress spinning side bands.

`level1` controls decoupler power during cross-polarization.

`level1f` controls fine decoupler power during cross-polarization.

`level2` controls decoupler power during acquisition.

`level2f` controls fine decoupler power during acquisition time.

`level1` and `level2` control decoupler power and should be used for Hartmann-Hahn matching. The decoupler is set with the `config` display and can be either class C, with a

maximum level of 255, or linear, with a maximum of 63. 0 is the minimum power on UNITY systems and -16 is the minimum on ^{UNITY}INOVA and UNITYplus systems. level1f and level2f are only active for linear attenuators and they give an additional 6 dB range for UNITY systems and 60 dB range for ^{UNITY}INOVA and UNITYplus systems, divided into 4095 steps. level1 and level2 override dpwr.

References

Cross-Polarization Technique

Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.

Stejskal, E. O.; Schaefer, J.; Waugh, J. S. *J. Magn. Reson.* **1977**, *28*, 105.

Spinning Sidebands

Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.

Dixon, W. T. *J. Magn. Reson.* **1981**, *44*, 220.

Dixon, W. T. *J. Magn. Reson.* **1982**, *49*, 341.

Dixon, W. T. *J. Magn. Reson.* **1985**, *64*, 332.

Protonated Carbon Suppression

Opella, S. J.; Fry, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5856.

Relaxation Times

Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384.

6.2 XPOLAR1—Cross-Polarization

XPOLAR1 is applicable to *MERCURYplus*, *MERCURY-VX*, ^{UNITY}INOVA, UNITYplus, and newer UNITY systems. The parameters that control the attenuators and linear modulators are shown in the diagram of XPOLAR1, see [Figure 34](#).

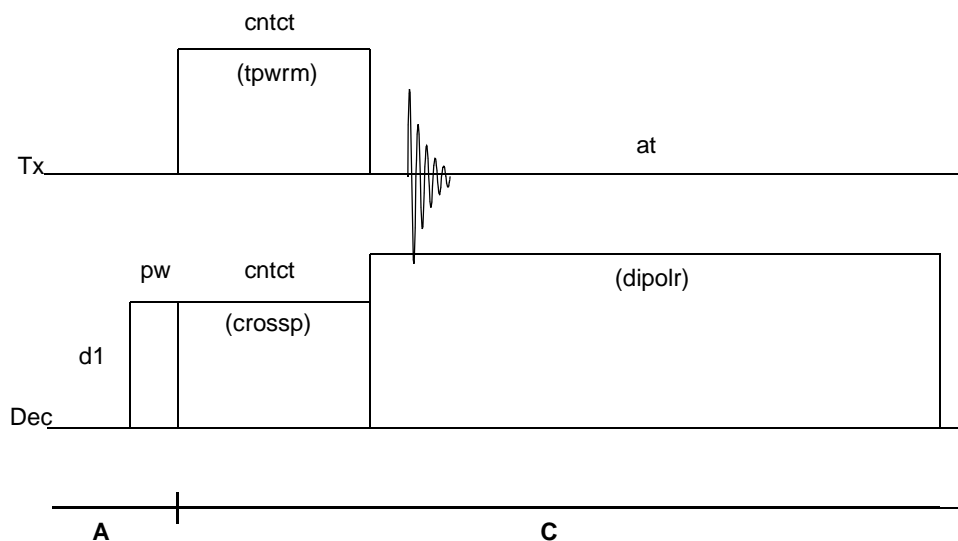


Figure 34. XPOLAR1 Pulse Sequence

Cross-polarization amplitudes should be controlled using the fine attenuator. The fine attenuator has a range of 60 dB for Inova and 48 dB for *MERCURY* systems down from the course attenuator. The coarse attenuator is set to a value corresponding to the maximum specification of the probe. Cross-polarization on the UNITY requires the use of both the coarse and fine attenuators (6 db range).

Applicability

XPOLAR1 can be found in `/vnmr/psglib`. The *MERCURYplus* and *MERCURY-VX* version of XPOLAR1 is *not interchangeable* with XPOLAR1 for ^{UNITY}INOVA and UNITY*plus* systems. UNITY systems can use both XPOLAR1 and XPOLAR by setting `dblvl2='y'`.

Macro

When this macro is run on a ^{UNITY}INOVA, UNITY*plus*, and UNITY, the macro `xpolar1` converts parameters for XPOLAR and most other double- and triple-resonance solids pulse sequences for the XPOLAR1 pulse sequence. Power parameters are left unchanged. Parameters irrelevant to XPOLAR1 are removed. On *MERCURY-VX* or *MERCURYplus* the macro XPOLAR1 will convert parameters contained in experiments run on ^{UNITY}INOVA, UNITY*plus*, and UNITY when these data sets are loaded on the system and the macro is run.

For users familiar with ^{UNITY}INOVA, UNITY*plus*, and UNITY solids, note the following:

- If the UNITY power parameters are defined (in an XPOLAR parameter set), they are converted to the corresponding ^{UNITY}INOVA and UNITY*plus* parameters: (`level1=cppwr level2=dpwr level1f=crossp level2f=dipolr p2=cntct tpwrf=tpwrm`) and `dblvl2` is set to 'n'. If `dblvl2='y'`, both `cppwr` and `dpwr` are used. If `dblvl2='n'`, `cppwr` is not used and `dpwr=cppwr`.
- `xpolar1` does not convert an arbitrary parameter set for solids. First retrieve a solids parameter set (e.g., `xpolar.par` in the VNMR directory `parlib`) and then convert it with the `xpolar1` macro.

Parameters

- `xpol` is set to 'n' for direct polarization or `xpol` is set to 'y' for cross-polarization.
- `pw` is the observe pulse for direct polarization, or the proton 90° pulse for cross-polarization. `pw` is in microseconds.
- `pwX` is the observe 90° pulse, used for TOSS and dipolar dephasing, `pwX` is in microseconds.
- `cntct` is the cross-polarization contact time, in microseconds.
- `tpwr` is the observe power setting .

Spectrometer	Minimum, dB	Maximum, dB
<i>INOVAcpmas</i>	-16	63
<i>MERCURYcpmas</i>	0	63

- `tpwrm` is the observe linear modulator setting .

Spectrometer	Minimum	Maximum
<i>INOVAcpmas</i>	0	4095
<i>MERCURYcpmas</i>	0	255

The parameter `tpwrm` is linearly proportional to the applied transmitter voltage—doubling `tpwrm` halves the value of the pulse width.

- `dpwr` is the decoupler power setting for decoupling throughout the acquisition period .

Spectrometer	Minimum, dB	Maximum, dB
<i>INOVAcpmas</i>	-16	63
<i>MERCURYcpmas</i>	0	63

- `cppwr` (UNITY only) is the decoupler power setting for cross polarization when `dblvl2='y'`.
- `dipolr` is the decoupler linear modulator setting during acquisition (0 minimum voltage to 4095 for INOVA or 255 for *MERCURY series* maximum voltage). The value of `dipolr` is linearly proportional to the applied decoupler voltage—doubling `dipolr` doubles the decoupler field strength (in kHz).
- `dblvl2` (UNITY only) is set to 'y' to obtain the parameter `cppwr`.
- `crossp` is the decoupler linear modulator setting during cross-polarization and the initial 90° pulse (0 minimum voltage to 4095 for INOVA or 255 for *MERCURY series* maximum voltage). The range is similar to `dipolr`. Doubling `crossp` doubles the cross-polarization field strength (in kHz) and halves the initial proton 90° pulse.
- `p180` greater than 0.0 implements an additional prepulse, followed by a delay `d2`. For direct polarization (`xpol='n'`), `p180` is an observe pulse. For cross-polarization (`xpol='y'`), `p180` is a proton pulse. `p180` is in microseconds.
- `pcrho` greater than 0.0 implements an additional observe pulse following the contact time. Use `pcrho` for observe $T_{1\rho}$ measurements. The units for `pcrho` are microseconds.
- `dm` should be set to 'nny'. The decoupler has a maximum duty cycle of 20%.
- `pdp` set to 'y' implements interrupted decoupling for a period `pdpd2` to cause suppression of protonated carbons.
- `pdpd2` is set greater than 0.0 (see `pdp`), `pdpd2` is in microseconds
- `d2` is set greater than 0.0 (see `p180`), `d2` is in seconds.
- `srate` is the sample spinning speed, in Hz.
- `hsrotor` set to 'y' allows automatic update of the value of `srate` if automatic spinning speed control is used.
- `toss` set to 'y' implements timed spin echoes to suppress spinning side bands. Timing is determined from the value of `srate`.
Note that for `toss='y'` or `pdp='y'`, `srate` must be set correctly because delays are calculated from $1.0/srate$.

6.3 XPWXCAL—Observe-Pulse Calibration with Cross-Polarization

The pulse sequence XPWXCAL, derived from XPOLAR1, is used to calibrate the observe 90° pulse if observe pulses are to be used explicitly in pulse sequences. Because cross-

polarization is used for preparation, XPWXCAL can be run in less time than XPOLAR1 with `xpol='n'`. Figure 35 is a diagram of the sequence.

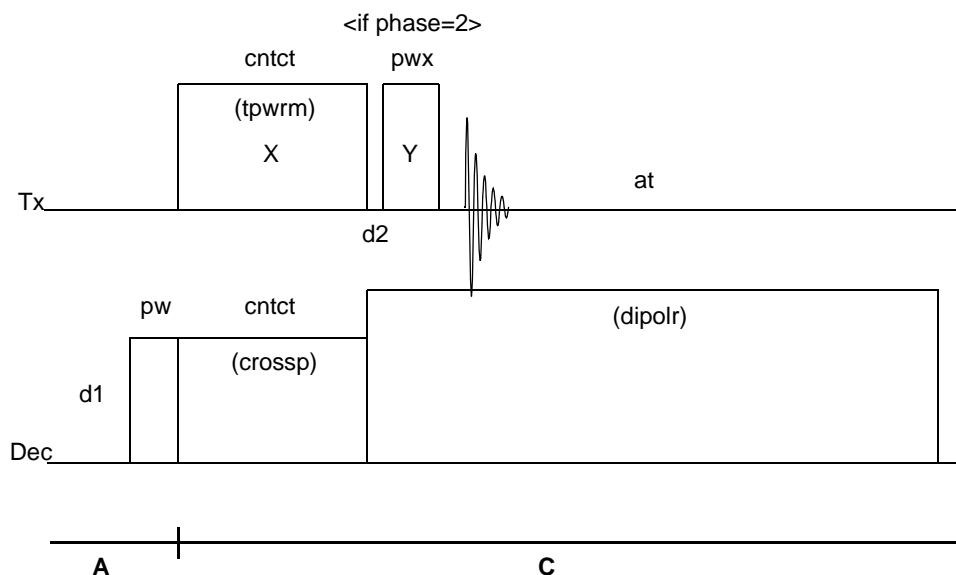


Figure 35. XPWXCAL Pulse Sequence

Applicability

XPWXCAL is available only on ^{UNITY}INOVA and UNITYplus. It is found in `userlib`.

Macro

The macro `xpwxcal` converts a parameter set, obtained with XPOLAR or XPOLAR1, for the XPWXCAL experiment. Power levels and the proton 90° pulse width are retained. By default, `pwx=pw` and `phase=2`.

Parameters

`xpwxcal` uses the ^{UNITY}INOVA and UNITYplus parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See page 85 for a description of these parameters.

`pwx` is the observe 90° pulse length. `pwx` follows the contact time and, when set to 90° , rotates the observe magnetization to the minus z axis and nulls the NMR signal. Array `pwx` between the 0° and 360° pulse. The first null is the observe 90° pulse. The signal is negative for 180° , null for 270° , and positive for 360° .

When the Hartmann-Hahn condition is matched for a non-spinning sample, the proton 90° pulse `pw` equals `pwx`. In the presence of spinning, a match that causes maximum spectral intensity will be offset in power above or below the true Hartmann-Hahn condition. If observe pulses are used explicitly in a sequence (TOSS, REDOR1, HETCORCP1, etc.) `pwx` must be measured separately, and it is usually present as a separate parameter. For HETCORCP1, `pwx` must be set to `pw` (by adjusting `tpwrm`), and `pw` is used for both observe and proton pulses.

phase=2 sets the phase of pwx 90° to the contact pulse and is necessary for measurement of pwx . Setting phase=1 sets the two phases the same, and all array members of a pwx array have the same intensity.

6.4 XNOESYSYNC—Rotor Sync Solids Sequence for Exchange

The XNOESYSYNC sequence is the CP/MAS equivalent of a NOESY, but with the first 90° pulse replaced with cross-polarization. Unlike normal NOESY, the mixing time can be rotor synchronized. In the solid state, exchange can occur via the spinning sidebands unless the mixing time is synchronized to the rotor period. When this is done, cross peaks appear when self or chemical exchange occurs. Figure 36 is a diagram of the sequence.

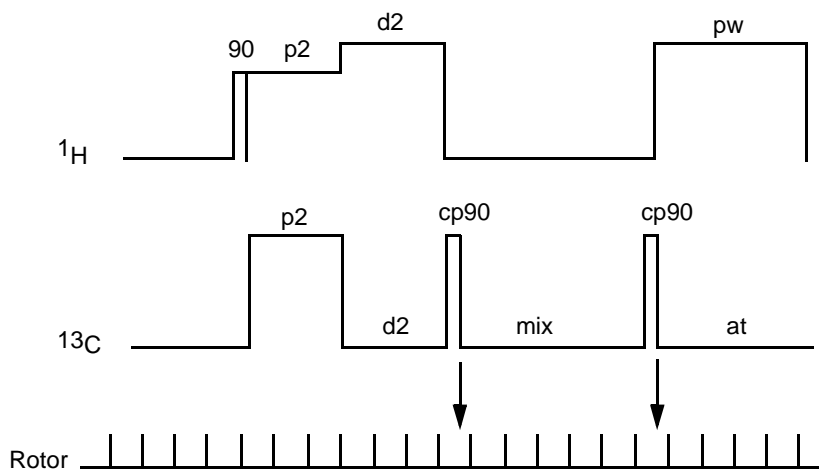


Figure 36. XNOESYSYNC Pulse Sequence

Macro

The `xnoesyssync` macro sets up parameters for the XNOESYSYNC pulse sequence.

Parameters

`pw` is the ^1H 90° pulse, in microseconds, for cross-polarization.

`p2` is the contact time, in microseconds.

`d2` is the evolution time, in seconds.

`dm` is set to 'nny' for no proton decoupling during the mixing time, or `dm` is set to 'nyy' for proton decoupling during the mixing time.

`level11` controls decoupler power during cross-polarization.

`level11f` controls fine decoupler power during cross-polarization.

`level12` controls decoupler power during acquisition.

`level12f` controls fine decoupler power during acquisition time.

`phase` is 0 for P type, `phase` is 1 for N type, or `phase` is 1,2 for phase sensitive. The Veeman experiment requires `phase=0`.

`cp90` is the ^{13}C 90° pulse, in microseconds.

`mix` is the mixing time, in seconds.

`sync` is set to 'y' to run rotor with sync; `sync` is set to 'n' to run unsynchronized (normal NOESY).

Technique

The minimum phase cycle is 16 transients and the full cycle is 64 transients.

The synced experiment requires SSBs to be present, so the spin rate should be slow enough.

Because the mix time is recalculated on the basis of the number of integral rotor periods that is nearest to the desired mix time, `mix` will not be exactly correct. The correct value is calculated and printed at `go` time.

Normally, the sync experiment is run as a P-type experiment. Process the data with sinebell weighting, `wft2d('ptype')` and `foldt`.

References

Szeverenyi, N. M.; Sullivan, M. J.; Maciel, G. E. *J. Magn. Res.* **1982**, *47*, 462.

DeJong, A. F.; Ketgens, A. P. M.; Veeman, W. S. *Chem. Phys. Lett.* **1984**, *109*, 337.

6.5 MASEXCH1—Phase-Sensitive Rotor Sync Sequence for Exchange

MASEXCH1 is a rotor-synchronized CP/MAS exchange sequence similar to XNOESYSYNC, except that this sequence can yield a phase-sensitive spectrum rather than an absolute-value plot. This experiment should be run under slow spinning conditions since spinning sidebands intensities carry the information. A normal MAS spectrum, including sidebands, is obtained along the diagonal. Cross-peaks appear when solid-state chemical exchange or molecular reorientation is present. [Figure 37](#) is a diagram of the sequence.

Applicability

MASEXCH1 is available on ^{UNITY}INOVA and UNITYplus and present in `userlib`. It requires a rotor-synchronization accessory. Rotor-speed control is also recommended. On request, a related sequence C13EXCH is available for older systems.

Macro

The macro `masexch1` converts a parameter set obtained with XPOLAR or XPOLAR1 for the MASEXCH1 experiment. Power levels and pulse widths are retained. The default is `phase=1, 2, 3, 4` and the data are transformed with `wft2d(1, 0, 0, 1, 1, 0, 0, -1, 0, -1, 1, 0, 0, 1, 1, 0)`.

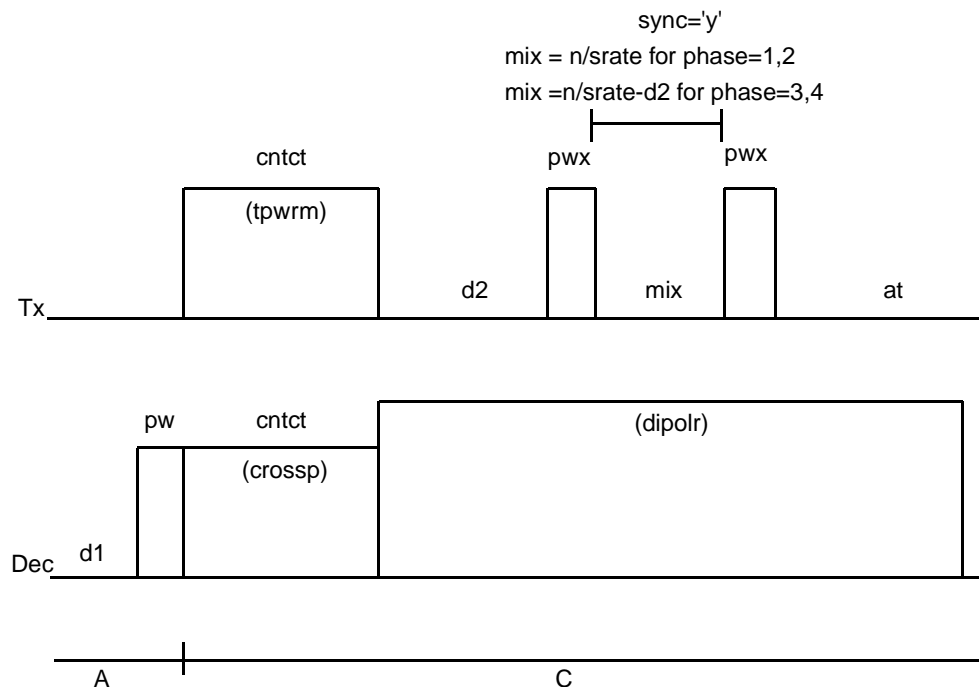


Figure 37. MASEXCH1 Pulse Sequence

Parameters

MASEXCH1 makes use of the *UNITY INOVA* and *UNITYplus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw` and `cntct`. See [page 85](#) for a description of these parameters.

`pwx` is the observe 90° pulse in microseconds.

`phase` is 1, 2 for P type, the Veeman experiment, for transformation with `wft2d(1, 0, 0, 1, 0, -1, 1, 0)` and 1, 2, 3, 4 for the phase sensitive spectrum according to the reference for transformation with `wft2d(1, 0, 0, 1, 1, 0, 0, -1, 0, -1, 1, 0, 0, 1, 1, 0)`. The phase-sensitive spectrum is the sum of a Veeman experiment, `phase=1, 2` and a time-reversed experiment, `phase=3, 4`.

`mix` is the mixing time, in seconds. For `phase=1, 2, 3, 4` the minimum mixing time is equal to $(n_i - 1 / sw1)$. For `phase=1, 2` the minimum mixing time is 0.0.

`sync='y'` to run with rotor synchronization. `sync='n'` to run unsynchronized (normal) NOESY.

`nt` is a minimum of 16.

Reference

Luz, Z.; Spiess, H. W.; Titman, J. J. *Israel J. of Chem.* **1992**, 32, 145.

6.6 HETCORCP1—Solid-State HETCOR

HETCORCP1 is a ^1H – ^{13}C heteronuclear chemical shift correlation (HETCOR) experiment for solid-state materials. Analogous to solution-state HETCOR experiments, this sequence provides correlation between ^1H and ^{13}C chemical shifts. The HETCORCP1 experiment differs from the solution-state HETCOR in that correlation depends on dipolar interactions rather than J coupling.

Applicability

HETCORCP1 is available on ^{UNITY}INOVA, UNITY*plus*, and UNITY systems. It is found in psglib.

Macro

The macro `hetcorcp1` converts a parameter set, obtained with XPOLAR or XPOLAR1, for the solids HETCOR experiment HETCORCP1. Power levels and the proton 90° pulse width are retained. Default parameters set up for a phase-sensitive hypercomplex data set acquisition. The correct `sw1` is calculated and `srate` is set to the preferred value. Set the actual spin rate equal to `srate`. A single decoupler offset `dof` is used throughout.

Parameters

`hetcorcp1` uses the ^{UNITY}INOVA and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See [page 85](#) for a description of these parameters.

`setup` is set to 'n' to obtain a 2D spectrum (normal operation). Set `setup`= 'y' to obtain a single t_1 FID, `blew` is the number of BLEW-12 cycles. You may use `setup` set to 'y' to obtain a one-dimensional spectrum using a “proton chemical shift selection pulse” or to observe the pulse sequence with `dps` for `ni` greater than 1.

`pw` is both the ^1H 90° pulse and the ^{13}C 90° pulse—the pulses must be equal. Adjust `tpwrm` (using `xpwxcal`) to make the pulse lengths equal.

`wim` is the number of WIM-24 cycles used for cross-polarization. For best results, set the length of the WIM-24 cross-polarization to occupy one-half a rotor period, for example, `wim`=1, `pw`=4.0, and `srate`=5208 yields 96 microseconds of CP and a rotor cycle of 192 microseconds.

`srate` is the actual rotor speed (see `wim` above). It is preferable, but not necessary, to use rotor speed control.

`bmult` is the number of BLEW-12 cycles per f_1 dwell time. Set parameter `sw1` to the value $1.0 / (\text{bmult} * 12 * \text{pw} * 1e-6)$. Default values are `bmult`=2 for `phase`=1, 2 (hypercomplex), alternatively `bmult`=1 for `phase`=3 (TPPI).

`phase`=1, 2 for the hypercomplex method (use `wft2da` for the 2D FT); `phase`=3 for TPPI (use `wft2d(1, 0, 0, 0)` for the 2D FT).

`dipof2` is set to 'y' to use a second decoupler offset during acquisition. `dof` determines the f_1 offset, which may be set above or below the ^1H chemical shift region if a pedestal is present in f_1 . In this case, set `dipoff` for the center of the ^1H shift region for best decoupling. `dipof2` is set to 'n' to use `dof` during the evolution period and decoupling.

Reference

Bielecki, A.; Burum, D. P.; Rice, D. M.; Karasz, F. E. *Macromolecules* **1991**, *24*, 4820.

6.7 WISE1—Two-Dimensional Proton Wideline Separation

WISE1 correlates the CP/MAS spectrum of the observe nucleus with the proton wideline spectrum due to ^1H - ^1H and X - ^1H interactions. An optional mixing period provides an exchange experiment that mixes wideline patterns due to proton spin diffusion. The method was first presented by Zumbulyadis for the study of amorphous silicon semiconductors. The method was extended to polymers, and Schmidt-Rohr et al added a mixing period was.

WISE1 is useful for the characterization of polymers with complex morphology that includes hard and soft domains. Domains are distinguished by the wideline spectrum, broad if rigid and narrow if motionally averaged. Corresponding observe chemical shifts indicate the segmental composition of the regions. With a spin diffusion mixing period WISE1 additionally determines proximity of the domains in space. WISE1 also provides the means to obtain the proton wideline spectrum a UNITY*plus* system with only a standard digitizer. For WISE1, `sw1` can be set in excess of 100 kHz.

The macro `wise1` converts a parameter set, obtained with XPOLAR or XPOLAR1, for the WISE experiment. Power levels and proton 90° pulse width are retained. Default parameters set up for WISE with no mix period and a 200-kHz spectral width.

Applicability

WISE1 is available for UNITY*plus* and UNITY*INOVA* systems and can be found in SolidsLib version 2.1.

Parameters

WISE1 uses the UNITY*plus* parameters, `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw` and `cntct` (see [page 85](#) for a description of these parameters).

`mixflag='y'` adds two 90° pulses that bracket a mixing period for proton spin diffusion.
`mixflag='n'` provides a proton pulse, evolution period, and cross polarization.

References

Zumbulyadis, N. *Physical Review B* **1986**, *33*, 6495.

Schmidt-Rohr, K.; Clauss, J.; Spiess, H. W. *Macromolecules* **1992**, *25*, 3273–3277

6.8 XPOLWFG1—Cross-Polarization with Programmed Decoupling

XPOLWFG1 is a version of XPOLAR1 that provides for programmed decoupling during acquisition using an optional waveform generator. Decoupler patterns are found in `.DEC` files in the directory `shape1ib`. In principle any decoupler pattern can be used, though it should be noted that most “liquids” patterns, `waltz`, `xy32`, etc., are not necessarily useful for solids. Several useful patterns are described below and are included in the `shape1ib` directory of SolidsLib, version 2.1.

XPOLWFG1 gates the waveform generator on and off with a fastline (no AP bus delay) at the beginning and end of the acquisition period if `dm= 'nny'` and `dmm= 'ccp'`. If `dm= 'c'` the usual continuous wave decoupling is applied and as usual if `dm= 'n'` no decoupling is applied.

XPOLWFG1 does not include `p180`, `toss`, `pdp` and `pcrho` at present.

Applicability

XPOLWFG1 is available for UNITY*plus* and UNITY INOVA systems and can be found in SolidsLib version 2.1.

Macro

The macro `xpolwfg1` converts a parameter set, obtained with XPOLAR or XPOLAR1, for programmed decoupling. Power levels and proton 90° pulse width are retained. Default parameters include `dseq= 'tppm2'` and `dres=90`. The value of `dmf`, the decoupler modulation frequency, is estimated with the relation $dmf = (dipolr/crossp) * (1/4 * pw)$. This value should be fine-tuned for optimum decoupling.

Parameters

`xpolwfg1` uses the UNITY*plus* parameters, `tpwr`, `tpwrn`, `dpwr`, `cppwr`, `crossp`, `dblvl2`, `pw` and `cntct` (see [page 85](#) for a description of these parameters).

`dm` is set to `'nny'` to obtain decoupling.

`dmm` is set to `'ccp'` to obtain programmed decoupling during acquisition and set to `'c'` for continuous decoupling. For `dmm= 'c'` the `wfg` parameters are hidden.

`dmf` is the decoupler modulation frequency and is set equal to one over four times the decoupler 90° pulse. `dmf` must be calibrated and depends upon the value of `dipolr`. The macro makes an estimate as described above. Calibrate `dipolr` with a sample of dioxane and the macro `h2cal` or to fine tune, obtain spectra versus `dmf` and choose that with the greatest narrowing.

`dres` is the waveform resolution, and it depends on the decoupler waveform.

Waveforms

Three waveforms are included in the `shapelib` of Solidslib 2.1. For each waveform name.DEC, set `dseq= 'name'`. Set `dmf` and `dres` according to the text in each `shapefile`.

`tppm2.DEC` provides phase-modulated decoupling as presented by Bennett et al. For crystalline materials—for example, glycine and linear polyethylene—PM decoupling narrows the residual linewidth up to about 30% over CW decoupling. The pattern consists of approximate π pulses with alternating phases of about $\pm 10^\circ$ to 30° . Vary `dmf` and the phase angle in the .DEC file for best decoupling at a particular field strength and spinning speed.

`blew 48.DEC` provides decoupling with BLEW-48 according to Burum et. al. BLEW-48 decouples protons from themselves but leaves a scaled $^{13}\text{C}-^1\text{H}$ dipolar interaction.

`fs1g2.DEC` provides phase continuous frequency switched Lee-Goldberg decoupling. This pattern decouples protons from themselves, but leaves a residual ^{13}C - ^1H dipolar interaction.

Reference

Bennett, A. E; Rienstra, C. M.; Auger, M.; Lakshmi, K. V.; Griffin, R. G. *Poster 368*. 36th Experimental Nuclear Magnetic Resonance Conference, 1995.

6.9 XPOLXMOD1—Waveform Modulated Cross-Polarization

XPOLXMOD1 provides modulation of the X-channel of the Hartmann-Hahn match with a selected waveform file. A second sequence, XPOLHMOD1, modulates the proton channel. In general, modulated CP improves signal-to-noise and quantitation of CP/MAS spectra at high spinning speeds. These two sequences provide access to a variety of the phase-frequency and amplitude-modulated CP methods in the literature.

Two macros `xmodcos` and `xmodramp` create specific amplitude modulated cosine and ramped waveform (`.DEC`) files. This sequence requires a waveform generator on the appropriate channel (X or H). Without a waveform generator, or for general purposes, use VACP instead. [Figure 38](#) is a diagram of the sequence.

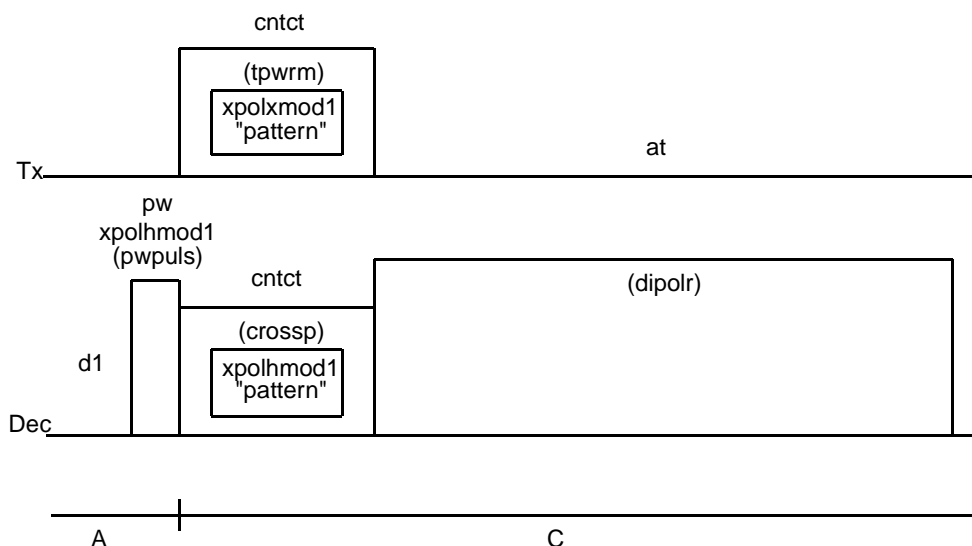


Figure 38. XPOLXMOD1 Pulse Sequence

Applicability

XPOLXMOD1 and XPOLHMOD1 are available on UNITY*plus* and UNITY *INOVA* and present in `userlib`. One waveform generator is required, and it can be placed on channel 1 or channel 2 as needed.

Macros

The macros `xpolxmod1` and `xpolhmod1` convert a parameter set obtained with XPOLAR or XPOLAR1 for these experiments. Power levels and pulse widths are retained.

For VNMR 5.1 and later `crossp` scales the proton waveform and `tpwrm` scales the X waveform. The macros `xmodramp` and `xmodcos` create their respective `.DEC` files. They also serve as a prototype for the creation of custom waveforms.

Parameters

`XPOLXMOD1` and `XPOLHMOD1` make use of the `UNITYplus` and `UNITY INOVA` parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw` and `cntct`. See [page 85](#) for a description of these parameters. All other functions (i.e. `toss`, etc) of `XPOLAR1` are also present.

`pattern` is a string with the name of the `.DEC` file used for modulation.

`pwpu1s` is the amplitude of the linear modulator during only the initial proton pulse of `XPOLHMOD1`.

`crossp` is the amplitude of the proton linear modulator during cross polarization and this value scales the waveform for `XPOLHMOD1`.

`tpwrm` is the amplitude of the X linear modulator during cross polarization and this value scales the waveform for `XPOLXMOD1`.

Waveforms

Two macros are provided to calculate commonly used waveforms, a cosine function and a ramp. For general waveforms to be used for cross polarization, a duration of 1.0 in the first column must be 0.2 microseconds. `dmf` and `dres` are not used to control the cross polarization waveform. You can also set programmed decoupling during acquisition by the usual procedure using `dmf` and `dres`.

`xmodcos(frac,per,amp)` creates a waveform with the following function:

$$\text{amp} * (1.0 - \text{frac}/2.0 + (\text{frac}/2.0) * \cos(t/\text{per}))$$

where t is time. The resulting `.DEC` file has the form `xmodcos_frac_per_amp.DEC` where `frac` is $\times 10000$ and `per` is in microseconds. The defaults are `per=1/srate` (the value needed for reference 1) and `amp=1023`.

`xmodramp(frac,per,amp)` creates a waveform with the following function:

$$\text{amp} * (1.0 - \text{frac}/2.0 + (\text{frac}/2.0) * (1.0 - 4.0 * t/\text{per}))$$

for $0.0 < t < \text{per}/2.0$

and

$$\text{amp} * (1.0 - \text{frac}/2.0 + (\text{frac}/2.0) * (-1.0 + 4.0 * t/\text{per}))$$

for $\text{per}/2.0 < t < \text{per}$

The resulting `.DEC` file has the form `xmodramp_frac_per_amp.DEC` where `frac` is $\times 10000$ and `per` is in microseconds. The defaults are `per=1/srate` and `amp=1023`.

`amp` is the amplitude of the waveform, `amp=1023`. VNMR 5.1 and later software provide scaling of `amp` with the value of `crossp` or `tpwrm`. For earlier versions, set `amp` to its fixed value during the pulse sequence (< 1023), where `amp=1023` is a full amplitude of the linear modulator.

`frac` is the fraction of modulated intensity, a value between 0 and 1.0.

`per` is the period of cosine modulation for 0 to 2π radians. For a ramp, the slope is negative $(1 - 4t/\text{per})$ for $t=0$ to $\text{per}/2$ and positive $(1 + 4t/\text{per})$ for $t=\text{per}/2$ to per . Set `per` relative to `cntct` to obtain a specific shape or ramp during the contact time.

References

Hediger, S.; Meier, B. H.; Ernst, R. R. *Chem. Phys. Lett.* **1993**, *213*, 627.

6.10 VACP—Variable Amplitude Cross-Polarization

As typical field strengths and rotor speeds used for CP/MAS increase, a problem that develops is the rotor speed dependence of cross-polarization. Usually signal-to-noise drops and the zero-speed Hartmann-Hahn match splits into a set of sidebands.

A straight-forward solution is to vary the pulse amplitude during the contact time of the cross-polarization. A set of alternating amplitudes with an increasing difference during the contact time is quite effective in removing the spinning speed dependence of cross-polarization. In the VACP sequence, during the contact time, ^1H power is varied among 11 levels with the appropriate amplitudes. The difference between the maximum and minimum values of γB_2 (in Hz) should be at least twice the maximum rotor speed to be used. **Figure 39** is a diagram of the VACP sequence.

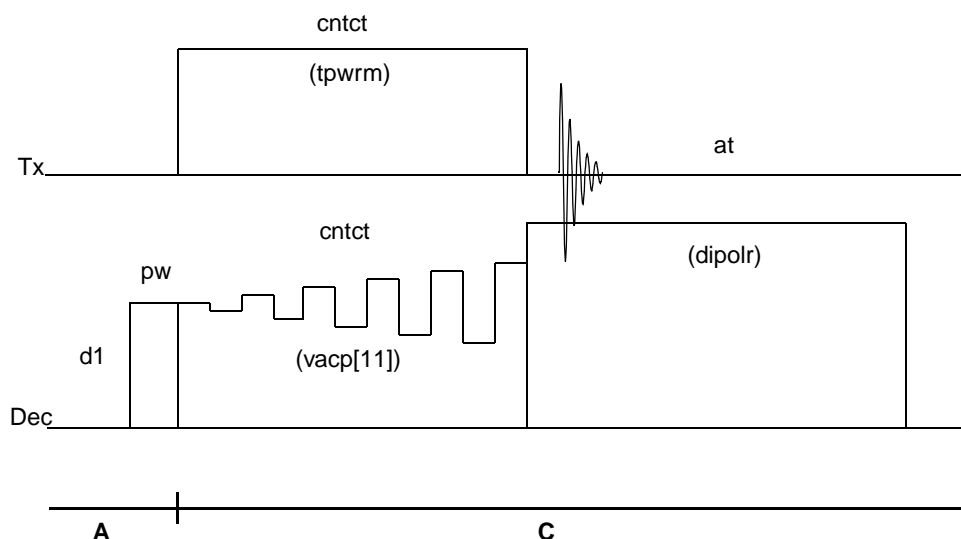


Figure 39. VACP Pulse Sequence

Applicability

VACP is available on ^{UNITY}INOVA, UNITYplus, and UNITY. It is found in `userlib`.

Macro

The `vacp` macro sets up parameters for the VACP pulse sequence and can take two or three arguments. `vacp` sets default levels for the arrayed parameter `vacp`. Units are the same as `crossp`. `vacp[0]=crossp`, `vacp[n]-vacp[n-1]=500`, and `n=11`. Syntax is as follows: `vacp(<vacp[n]-vacp[n-1],vacp[0]>,n>>`. The `vacplist` macro lists VACP levels and resets `array=' '` (two single quotes).

Parameters

VACP uses the ^{UNITY}INOVA and UNITYplus parameters *tpwr*, *tpwrm*, *dpwr*, *cppwr*, *dipolr*, *dblvl2*, *pw*, and *cntct*. See [page 85](#) for a description of these parameters.

vacp is an array of linear modulator settings to be used during cross-polarization. After *vacp* is set, set *array=' '*. The command *da* is inoperative when *array=' '*. Use the *vacplist* macro instead to display the *vacp* array.

Reference

Peersen, O.; Wu, X.; Kustanovich, I.; Smith, S. O. *J. Magn. Reson.* **1993**, *104* (Series A), 334.

6.11 XPOLEDIT1—Solids Spectral Editing

XPOLEDIT1 provides for spectral editing of CH₃, CH₂, CH and C carbons by use of differences in their cross polarization properties. The sequence provides a 180° phase shift during the contact time (depolarization) followed by a return to the original phase (repolarization). Individual carbon types can be nulled with appropriate delays *p3* and *p4* and spectral editing can be achieved by addition and subtraction of subspectra obtained with the different delays. [Figure 40](#) is a diagram of the XPOLEDIT1 sequence.

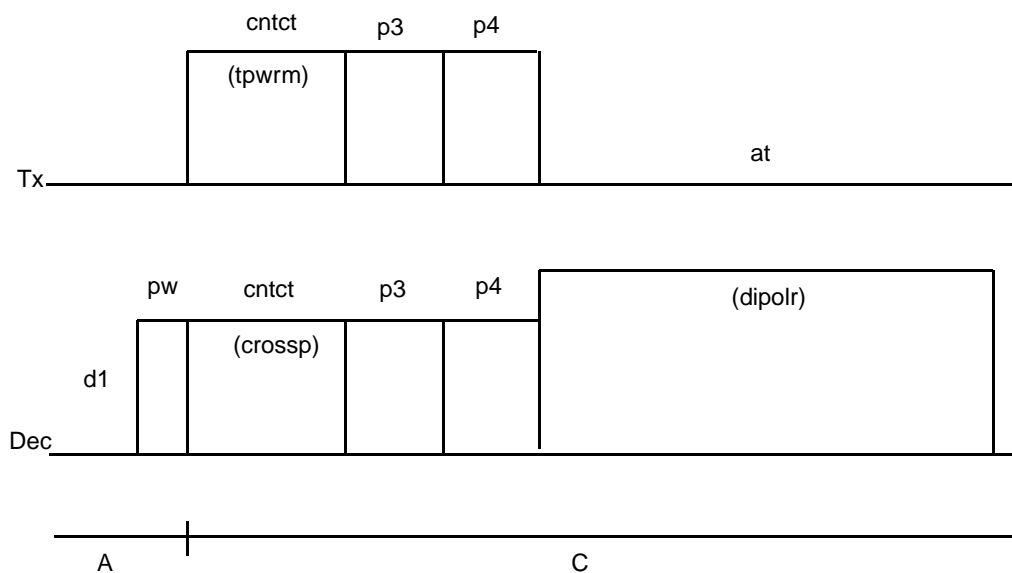


Figure 40. XPOLEDIT1 Pulse Sequence

Applicability

XPOLEDIT1 is available on ^{UNITY}INOVA and UNITYplus and present in *userlib*.

Macro

The macro *xpoledit1* converts a parameter set obtained with XPOLAR or XPOLAR1 for XPOLEDIT1. Power levels and pulse widths are retained.

Parameters

XPOLEDIT1 makes use of the ^{UNITY}INOVA and UNITYplus parameters `tpwr`, `tpwrn`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw` and `cntct`. See page 85 for a description of these parameters.

`p3` is the depolarization time, in microseconds. The phase of the proton channel is reversed.

`p4` is the repolarization time, in microseconds.

References

Sangil, R.; Bildsoe, H.; Jacobsen, H. J. *J. Magn. Reson.* **1994**, *107* (Series A), 67.

6.12 3QMAS1—Triple-Quantum 2D for Quadrupole Nuclei

3QMAS1 is a two-pulse, two-dimensional experiment for the detection of isotropic spectra of quadrupole nuclei ($I=n/2$, $n/2 > 1/2$) in the solid state (an optional third selective refocusing pulse may also be present). Isotropic spectra of quadrupole nuclei are produced in the *f1* dimension. The resonance frequencies are determined by both the chemical shift and the quadrupole interaction and are field dependent.

The lineshape in the *f2* dimension is similar to that obtained with MAS alone. Because resonances are resolved in *f1* the lineshapes are easily simulated individually with a general simulation program such as STARS. The shift in *f1* and the lineshape in *f2* are related and provide redundant information about quadrupole and chemical shift tensor components.

Figure 41 is a diagram of the 3QMAS1 sequence.

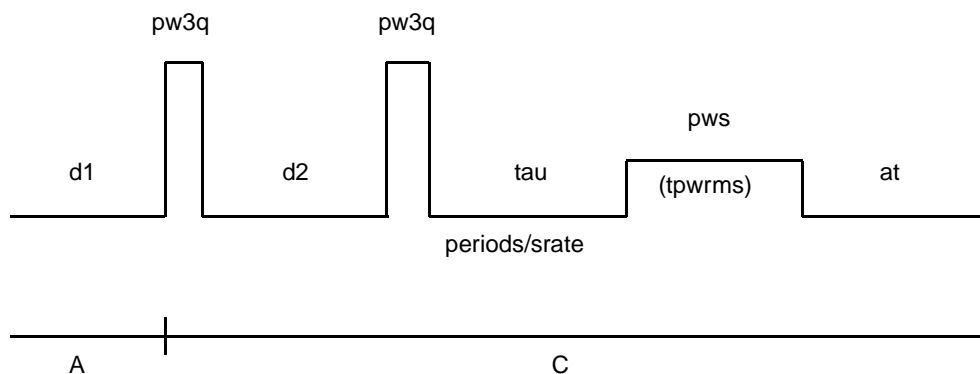


Figure 41. 3QMAS1 Pulse Sequence

The pulse sequence and phase cycle are based on work done by D. Massiot *et al* and were first provided by J. Stebbins of Stanford University. We thank the authors for the opportunity to view their work before publication.

Applicability

3QMAS1 is available for all UNITY systems and can be found in the `userlib`. The default parameters of the setup macro are applicable for only ^{UNITY}INOVA and UNITYplus. The processing parameter `daslp` is present in VNMR 5.2 and later.

The 3QMAS1 experiment requires only MAS hardware and in many circumstances this method can replace the need to do the more complicated experiments, double rotation

(DOR) and dynamic angle spinning (DAS). 3QMAS1 is a robust experiment that is well worth trying before contemplating the use of DOR or DAS.

Macro

The macro `s3qmas1` converts a parameter set for the triple-quantum MAS experiment 3QMAS1. `pw3q` is set to 180° pulse length (the minimum practical pulse length needed to excite triple quantum coherence) with the assumption that `pw` is the 90° pulse length. If `tpwrm` is not present (as in many older parameter sets), `s3qmas1` creates it and sets it to the value of `tpwrf`. If `tpwrf` is not present, `tpwrm` is set to 4095. The default is `pws=0.0` for no refocusing pulse and `sw1=sw`. The macro `s3qmas1` creates the processing parameter `daslp` used for shearing (applicable for VNMR 5.2 or greater).

Parameters

3QMAS1 makes use of the ^{UNITY}INOVA and UNITYplus parameters `tpwr`, `tpwrm`, `dpwr`, `dpwrm` and `pw`. See [page 117](#) for a description of these parameters.

`pw` is the observe 90° pulse, in microseconds, for a solution-state sample of the quadrupole nucleus. The macro `s3qmas1` uses `pw` to calculate the default 180° pulse. `pw` is not used in the pulse-sequence.

`pw3q` is the length of pulses 1 and 2 of 3QMAS1. It is used to generate triple quantum coherence (pulse 1) and then return it to single quantum coherence (pulse 2) for detection. The default is `pw3q=2*pw`. Set `pw3q` to a larger value (e.g., `pw3q=8*pw`) for greater triple-quantum signal-to-noise in some cases.

`tpwr` is the observe coarse-attenuator setting for pulses 1 and 2.

`tpwrm` is the observe linear-modulator setting for pulses 1 and 2.

`tpwrs` is the observe coarse-attenuator setting for the selective refocusing pulse (pulse 3). The default is `tpwrs=tpwr`.

`tpwrms` is the observe linear-modulator setting for the selective refocusing pulse (pulse 3). The default is `tpwrms=tpwrm/5`, but this pulse must be calibrated.

`pws` is the length of the optional selective refocusing pulse (pulse 3). The default is `pws=0.0` and the refocusing pulse is absent. For refocusing, set `pws=10*pw` for the default value of `tpwrms=tpwrm/5`.

`srate` must be set to the actual rotor speed. This value is used with periods to calculate the delay, `tau`, before the refocusing pulse.

`periods` is the number of rotor periods before the selective refocusing pulse. This delay is present only if `pws>0.0` and by default it is absent.

`daslp` is a processing parameter required to shear the triple-quantum 2D dataset and rotate the narrow axis of each correlation to the f1 dimension. Set `daslp<0.0` for $I=3/2$ and `daslp>0.0` for $I=5/2$. `daslp` is available for VNMR version 5.2 and later (refer to the *VNMR Command and Parameter Reference*).

`phase=1, 2` are the sine and cosine components of hypercomplex Fourier transform, `wft2da`.

References

Frydman, L.; Harwood, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 5367.

Medek, A.; Harwood, J. S.; Frydman, L. *J. Am. Chem. Soc.* **1995**, *117*, 12779–12787.
 Baltsberger, J. H.; Xu, Z.; Stebbins, J. F.; Wang, S. H.; Pines, A. *J. Am. Chem. Soc.* **1996**.

Massiot, D.; Touzo, B.; Trumeau, D.; Coutures, J. P.; Virlet, J.; Florian, P.; Grandinetti, P.J. *Poster: 37th ENC and Solid State NMR 1996*, *6*, 73-84.

6.13 PASS1—2D Sideband Separation for CP/MAS

The PASS1 experiment produces a 2D plot with an isotropic spectrum in f_1 and a MAS sideband pattern in f_2 . There is negligible loss of signal intensity. Chemical shift tensor components can be determined from the sideband intensities in f_2 . **Figure 42** is a diagram of the PASS1 sequence.

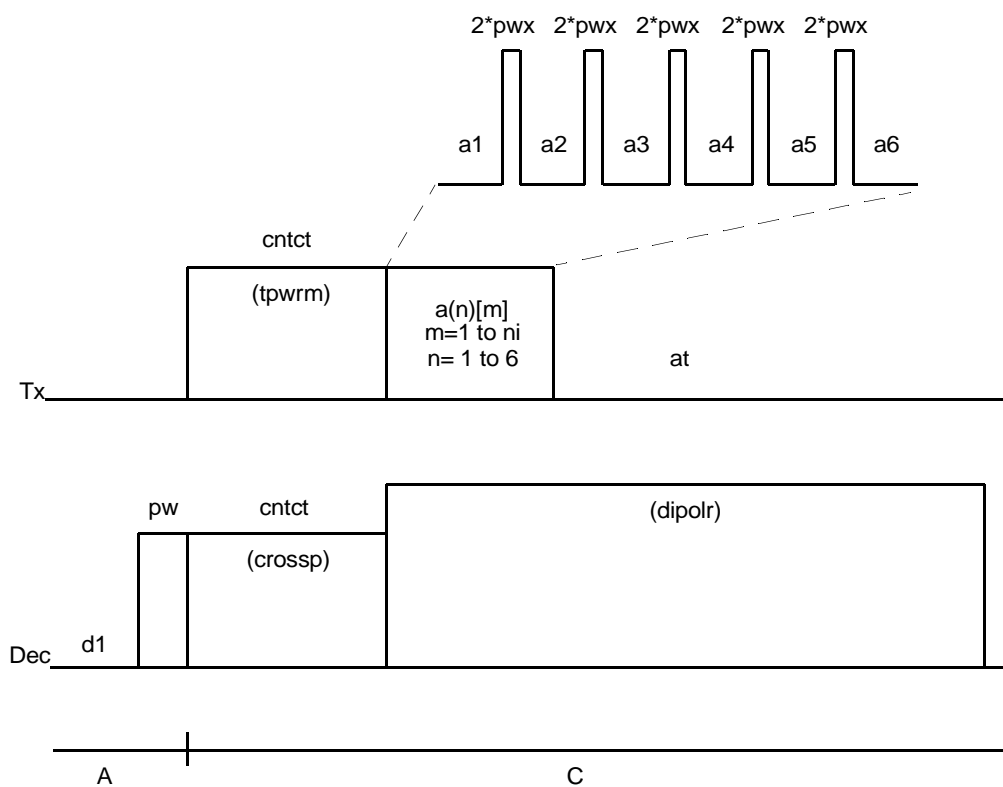


Figure 42. PASS1 Pulse Sequence

Applicability

PASS1 is available on ^{UNITY}INOVA and UNITYplus and present in userlib.

Macro

The macro `pass1` converts a parameter set obtained with XPOLAR or XPOLAR1 for the 2D PASS experiment. Power levels and pulse widths are retained.

Parameters

PASS1 makes use of the ^{UNITY}INOVA and UNITYplus parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw` and `cntct`. See page 85 for a description of these parameters.

`pw` is the observe 90° pulse, in microseconds.

`pass` is set to 'y' for 2D PASS. Set `pass` = 'n' for normal cross polarization.

`sw1` is not used and may be set arbitrarily (`sw1`=16 is recommended).

`nt` must be a multiple of 243.

`a(n) [(m)]` is a set of arrays containing the PASS delay values in units of `1/srate`. These are converted to absolute delays using the value of `srate`. For the current experiment `n`=6 and `m`=16 to obtain a manifold of 16 sidebands. Other values can be calculated numerically using reference 1. The user might place an import function in the pulse sequence to enter these values automatically from a text file.

Reference

Antzukin, O. N.; Shekar, S. C.; Levitt, M. H. *J. Magn. Reson.* **1995**, *115A*, 7.

6.14 CPCS—Cross-Polarization with Proton Chemical Shift Selection

Figure 43 is a diagram of the CPCS experiment developed by Spiess and coworkers to study component mixing on a molecular scale. This novel experiment involves a multiple-pulse selection of ¹H magnetization based on chemical shift differences during a mixing time, ¹H spin diffusion during a mixing time, and high-resolution ¹³C CP/MAS detection.

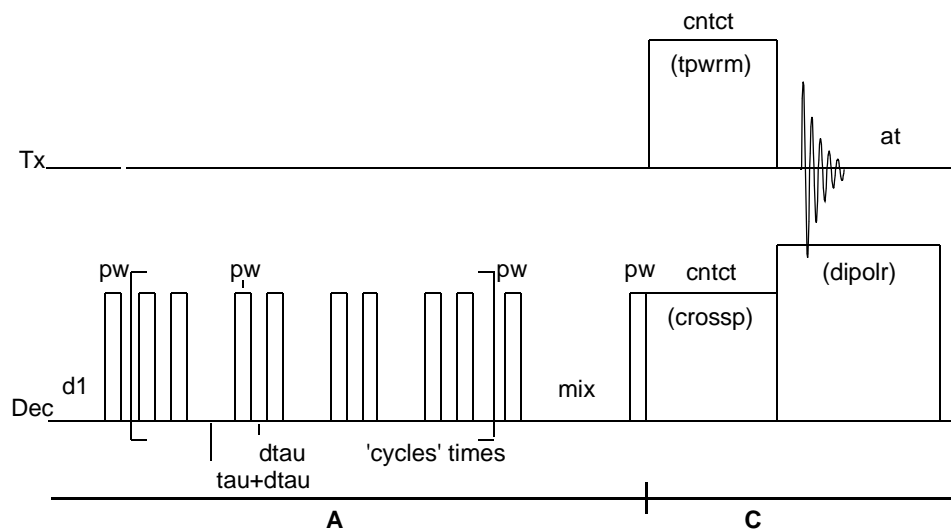


Figure 43. CPCS Pulse Sequence

Macro

The `cpcs` macro sets up parameters for the CPCS pulse sequence.

Parameters

`pw` is the ^1H 90° pulse for cross-polarization, in microseconds.

`p2` is the contact time, in microseconds.

`d2` is the evolution time, in seconds.

`dm` is set to 'nny' for no proton decoupling during the mixing time; `dm` is set to 'nyy' for proton decoupling during the mixing time.

`level1` controls decoupler power during cross-polarization.

`level1f` controls fine decoupler power during cross-polarization.

`level2` controls decoupler power during acquisition.

`level2f` controls fine decoupler power during acquisition time.

`tau` is the time, in microseconds, between the start of pulses in the multiple pulse sequence. In the case of MREV8, the cycle length is 12τ long.

`mix` is the mixing time for spin diffusion, in seconds.

`cycles` is the number of times through the multiple pulse sequence.

Reference

Spieß, H. W.; Schmidt-Rohr, K.; Clauss, J.; Blumich, B. *Magn. Reson. Chem.* **1990**, *28*, S3.

6.15 CPCOSYPS—Cross-Polarization Phase-Sensitive COSY

The CPCOSYPS sequence is similar to the high-resolution COSY experiment. CPCOSYPS can be run as a direct polarization experiment or the first 90° pulse can be replaced with a cross-polarization pulse element. [Figure 44](#) is a diagram of the sequence.

As with COSY, correlations are present between resonances that share a J-coupling. CPCOSYPS is of greatest use when J-coupling is large, for example, ^3P in organometallic compounds. When J-coupling is small, use CPNOESYPS, which depends on the through-space dipolar interaction.

Applicability

CPCOSYPS, found in `userlib`, is available only on `UNITYINOVA` and `UNITYplus`.

Macro

The macro `cpcosyps` converts a parameter set, obtained with XPOLAR or XPOLAR1, for the solids homonuclear correlation experiment CPCOSYPS. Power levels and the ^1H 90° pulse width are retained. Default parameters set up for a phase-sensitive hypercomplex acquisition with `sw1=sw` and `xpol='y'`.

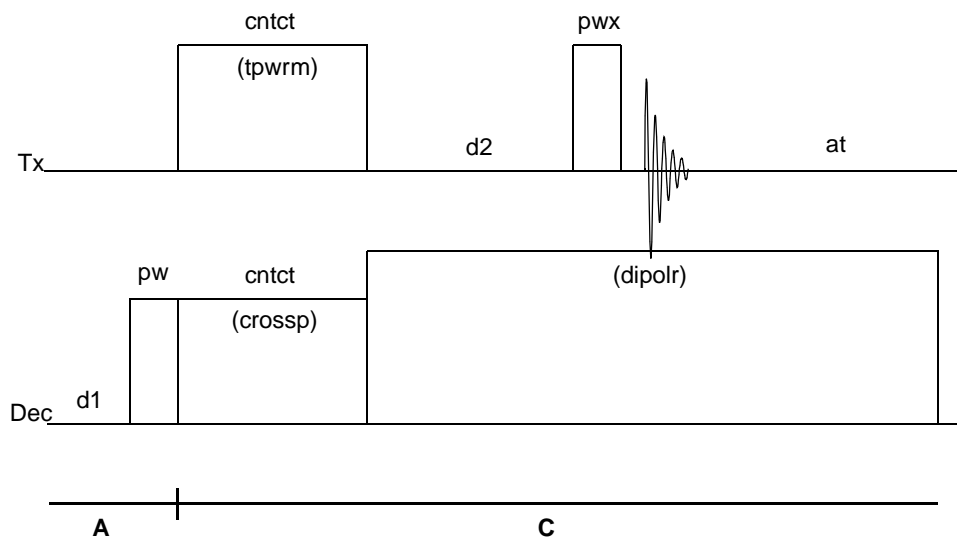


Figure 44. CPCOSYPS Pulse Sequence

Parameters

`cpcosyps` uses ^{UNITY}*INOVA* and *UNITYplus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See [page 85](#) for a description of these parameters.

`xpol` is set to 'n' for preparation by direct polarization; `xpol` is set to 'y' for preparation by cross-polarization.

`pw` is the observe 90° pulse (`xpol` = 'n') or the proton 90° pulse (`xpol` = 'y'). `pw` is in microseconds.

`pwx` is the mixing pulse, in microseconds. If `xpol` = 'n', `pwx` = `pw`; if `xpol` = 'y', it is set to the observe 90° pulse.

`srate` is the measured MAS spinning speed. CPCOSYPS does not require rotor speed control. However, with rotor speed control, set `sw1` equal to `srate` to remove spinning sidebands in both dimensions.

`phase` = 1, 2 for the hypercomplex method (use `wft2da` for the 2D FT); `phase` = 3 for TPPI (use `wft2d(1, 0, 0, 0)` for the 2D FT).

Reference

Wu, G.; Wasylishen, R. E. *Organometallics* **1992**, *11*, 3242.

6.16 CPNOESYPS—Cross-Polarization Phase-Sensitive NOESY

The CPNOESYPS sequence is a 3-pulse 2D exchange correlation sequence similar to the high-resolution NOESY experiment. CPNOESYPS can be run as a direct polarization experiment or the first 90° pulse can be substituted with a cross-polarization pulse element. [Figure 45](#) is a diagram of this sequence.

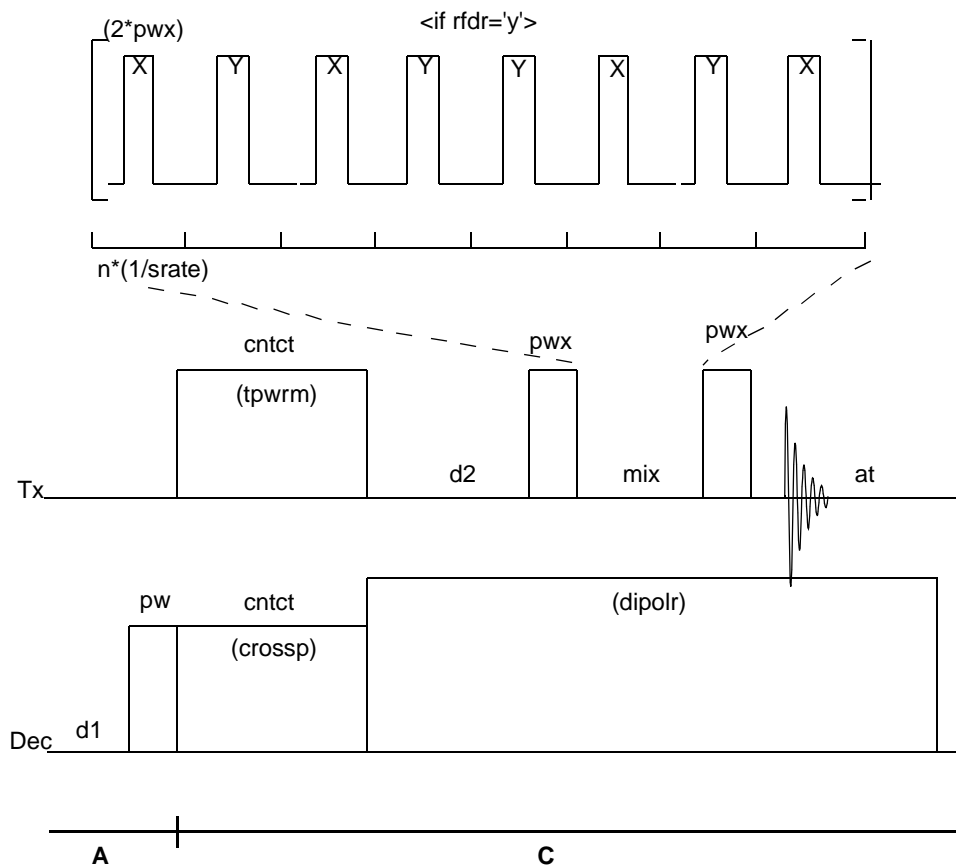


Figure 45. CPNOESYPS Pulse Sequence

For CPNOESY, cross peaks occur between resonances that share mutual through-space dipolar coupling or interact through weak spin diffusion. Coupling can be enhanced with the insertion of rotor synchronized π pulses during the mixing period. Cross peaks are also observed between resonances with chemical exchange and CPNOESYPS can be used to observe exchange between static powder spectra. Use XNOESYSYNC to characterize molecular motion in the presence of MAS.

Applicability

CPNOESYPS, found in `userlib`, is available only on `UNITYINOVA` and `UNITYplu`

Macro

The macro `cpnoesy`s converts a parameter set, obtained with `XPOLAR` or `XPOLAR1`, for the solids 2D exchange correlation experiment CPNOESYPS. Power levels and the proton 90° pulse width are retained. Default parameters set up for a phase-sensitive hypercomplex acquisition with `rfd`r set to 'y'. Also, `sw1` is set equal to `sw` and `xpol`='y'.

Parameters

cpnoesy_{ps} uses ^{UNITY}INOVA and UNITY_{plus} parameters *tpwr*, *tpwrm*, *dpwr*, *cppwr*, *dipolr*, *crossp*, *dblvl2*, *pw*, and *cntct*. See [page 85](#) for a description of these parameters.

xpol is set to 'n' for preparation by direct polarization; *xpol* is set to 'y' for preparation by cross-polarization.

pw is the observe 90° pulse (*xpol* = 'n'), or the proton 90° pulse (*xpol* = 'y'). *pw* is in microseconds.

pw_x is the length of pulses two and three and is to *pw* (if *xpol* = 'n'). *pw_x* is in microseconds.

mix is the mixing period in milliseconds (see also *rfdr* below). Use caution because *dm* = 'y' during the mix period may lead to an unacceptable duty cycle.

sync set to 'y' is used with *rfdr* = 'y' to provide dipolar recoupling during the *mix* period. *sync* set to 'n' provides the usual NOESY mixing period.

rfdr set to 'y' (set *sync* = 'y') sets the mixing period to a multiple of 8 rotor periods, close to the value of *mix*. The rotor period is obtained from the value of *srate*. π pulses are applied at the middle of each rotor period, with the phase cycle 'xy8' to cause dipolar recoupling. *rfdr* set to 'n' sets the mixing period equal to the value of *mix* and pulses are not applied.

srate is the actual spinning speed. CPNOESY_{PS} with *rfdr* = 'y' requires rotor speed control.

Reference

Bennett, A. E.; Ok, J. H.; Griffin, R. G.; Vega, S. *J. Chem. Phys.* **1992**, *96*, 8624.

6.17 R2SELPULS1—Rotation Resonance with Selective Inversion

The R2SELPULS1 pulse sequence is used for the rotational resonance experiment with a selection inversion pulse of Griffin and coworkers. [Figure 46](#) is a diagram of the sequence.

Rotational resonance (r^2) is obtained between nuclei coupled by the through-space dipolar interaction when the chemical shift difference between the resonances is an integral multiple of the rotor speed. At the r^2 condition, each resonance is split into a characteristic doublet pattern that can be simulated to obtain the coupling constant and internuclear distance. If one of the resonances is selectively inverted, the two will equilibrate to a common signal intensity. The recovery curve can also be simulated to obtain the coupling constant. Rotational resonance is often used for the determination of the structure of biomolecular materials such as membrane proteins. CPNOESY with *rfdr* = 'y' provides similar information.

Applicability

R2SELPULS1, found in *userlib*, is available only on ^{UNITY}INOVA and UNITY_{plus}.

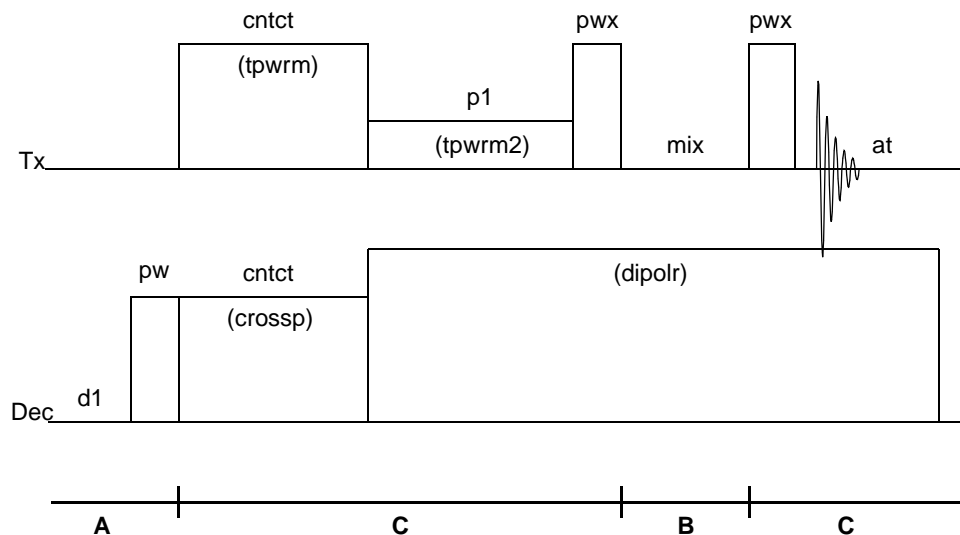


Figure 46. R2SELPULS1 Pulse Sequence

Macro

The macro `r2selpuls1` converts a parameter set, obtained with `XPOLAR` or `XPOLAR1`, for rotational resonance with selective inversion, `R2SELPULS1`. Power levels and the proton 90° pulse width are retained. The length of the inversion pulse is estimated to be $50 * \text{pwx}$ and the power is set accordingly. Fine calibration of the inversion pulse is required.

Parameters

`r2selpuls1` uses `UNITYINOVA` and `UNITYplus` parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See [page 85](#) for a description of these parameters. The selective inversion pulse must be calibrated.

`pwx` is the observe 90° pulse, in microseconds.

`p1` is the observe selective-inversion pulse, in microseconds. The default is $50 * \text{pwx}$. For closely spaced resonances, `p1` may need to be longer to achieve greater selectivity. It should be noted that for strong coupling, significant mixing occurs during the inversion pulse and so a shorter (less selective) inversion pulse may be preferred.

`tpwrms` is the observe linear modulator setting for the selective pulse. The default is `tpwrm/50`. To obtain `tpwrms` for a given inversion pulse length `p1`, set `tof2` (see `tof2` below), set `mix` to 0.0, and array the value of `tpwrm` about the default value. Choose the value corresponding to the maximum negative signal for the resonance of interest.

`tof2` is the transmitter offset of the resonance to be selectively inverted. To obtain `tof2`, use `xpolar1` to acquire a spectrum in a second experiment, place the cursor on the resonance of interest, and enter `movetof`. Set `tof2` in `r2selpuls1` equal to the this `tof`.

`mix` is the mixing period in milliseconds. Use caution, because setting `dm= 'y'` during the mix period may lead to an unacceptable duty cycle.

srate is the actual spinning speed. Rotational resonance requires spinning speed control. Set the spinning rate equal to the frequency difference between the two resonances of interest (first sideband) or to an integral n th division (n th sideband).

References

- Raleigh, D. P.; Levitt, M. H.; Griffin, R. G. *Chem. Phys. Lett.* **1988**, *146*, 71.
 Raleigh, D. P.; Cruzet, F.; Das Gupta, J. K.; Levitt, M. H.; Griffin, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 4502.

6.18 DIPSHFT1—Separated Local Field Spectroscopy

The DIPSHFT1 pulse sequence is the separated local field spectroscopy (SLF) experiment of Munowitz and Griffin, using windowless MREV8 as described by Zilm. Figure 47 is a diagram of the sequence.

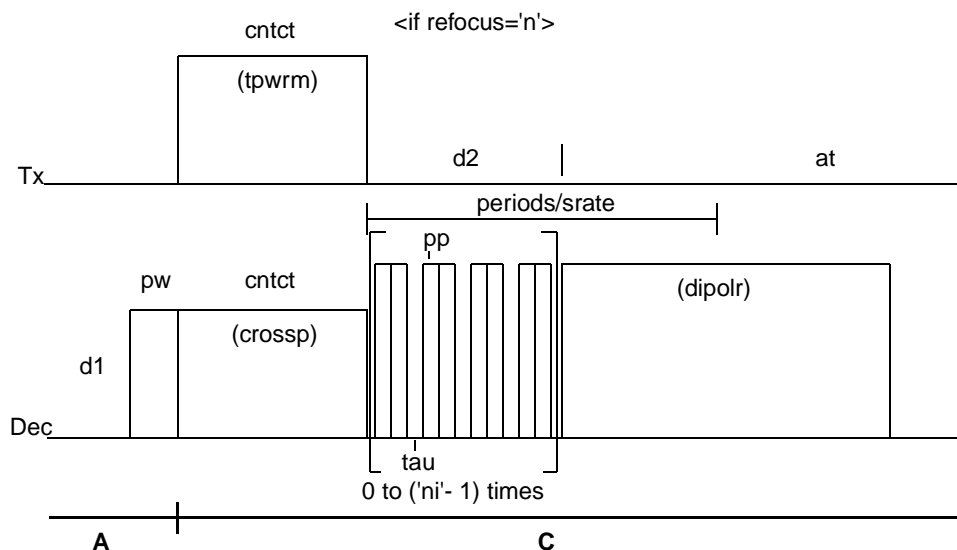


Figure 47. DIPSHFT1 Pulse Sequence

Applicability

DIPSHIFT, found in `userlib`, is available for ^{UNITY}INOVA and UNITYplus systems.

Macro

The macro `dipshft1` converts a parameter set, obtained with XPOLAR or XPOLAR1, for DIPSHFT1. Power levels and the proton 90° pulse width are retained. The value of `pp` is estimated from `pw`, `dipolr`, and `crossp`. Further calibration of `pp` may be necessary. Parameters `refocus` and `setup` are both set to 'n'.

Parameters

`dipshft1` uses ^{UNITY}*INOVA* and *UNITYplus* parameters `tpwr`, `tpwrn`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See [page 85](#) for a description of these parameters.

`pp` is the proton 90° pulse, in microseconds, used for MREV8 proton decoupling during the evolution period; `dipolr` sets the pulse power level. Typically, `dipolr` is set at the maximum decoupling field strength of the probe, and `pp` is set as short as possible. `pp` can be estimated with the equation $pp = pw * (crossp / dipolr)$ if `dblvl2 = 'n'`.

`setup` is set to 'n' to obtain a 2D spectrum (normal operation); `setup` is set to 'y' to obtain a single t_1 FID, `mrev8` is the number of MREV8 cycles. `setup` is usually only used to observe the pulse sequence with `dps` for `ni` greater than 1.

`tau` is the delay, in microseconds, associated with the MREV8 pulses. Usually $tau = pp$. A single `mrev8` cycle time is $(8 * pp + 4 * tau)$. The f_1 dwell time is equal to one `mrev8` cycle. Set the value of `sw1` to $1.0 / (8 * pp + 4 * tau)$. Note that the maximum `sw1` is limited by the `mrev8` cycle time. A small value of `pp` is preferred.

`periods` is an even integral number of rotor periods allocated to the evolution period. The maximum evolution period ($FID\# = ni$) must be less than this number of rotor periods. If not, an error message results noting the two times. To correct the problem, increase `sw1` (if possible) or `periods`, or decrease `ni` or `srate` along with actual spinning rate.

`srate` is the actual spinning speed. DIPSHIFT1 benefits from rotor speed control, but control is not required.

`refocus` set to 'y' reveals the parameter `sense`. If `sense` is set to 'r' ("reverse"), a single observe refocusing pulse is applied at `periods/2` and the evolution period precedes this pulse. If `sense` is set to 'f' ("forward"), a simultaneous refocusing pulse is applied and evolution occurs symmetrically about the refocusing pulses, with two `mrev8` cycles per f_1 dwell. Phase shifts are less severe, but the maximum `sw1` is smaller.

`refocus` set to 'n' provides the simplest DIPSHIFT1 pulse sequence, allowing the largest value of `sw1`. Refocusing pulses are not used; phase correction must be performed in f_1 . The parameter `sense` is hidden when `refocus` is set to 'n'.

`sense` is set to 'r' or 'f'. See `refocus` above.

Reference

Munowitz, M. G.; Griffin, R. G.; Bodenhausen, G.; Huang, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 2529.

6.19 SEDRA2—Simple Excitation of Dephasing Rotational-Echo Amplitudes

In the last few years, there has been much interest in the measurement of the homonuclear ^{13}C dipolar interaction for measurement of internuclear distance in solids. Unfortunately, the magic angle spinning required to obtain a high-resolution spectrum also averages the dipolar interaction to zero. Therefore, special methods are needed to obtain the ^{13}C connectivity information.

SEDRA, Simple Excitation of Dephasing of Rotational-Echo Amplitudes, is one of the new experiments created for this purpose. [Figure 48](#) is a diagram of SEDRA.

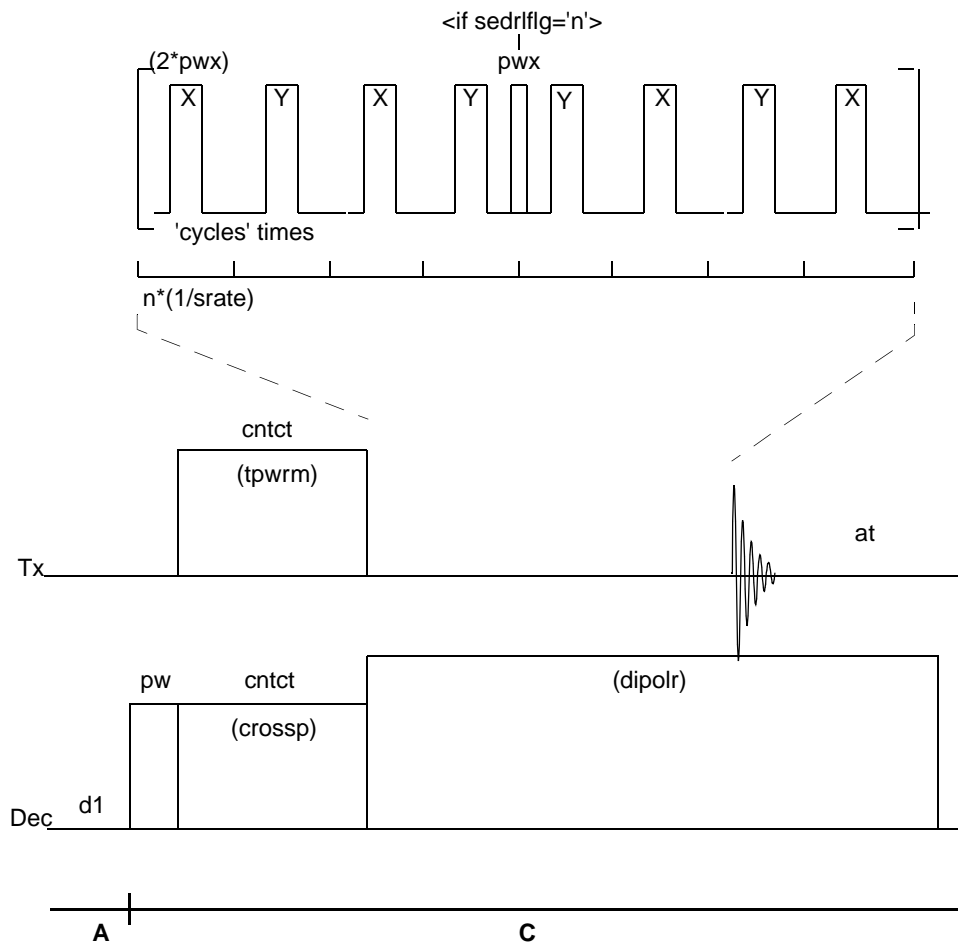


Figure 48. SEDRA2 Pulse Sequence

SEDRA is applied after cross-polarization and consists of a train of π pulses synchronized with the middle of each rotor period. Acquisition follows at the next rotor period and proton decoupling is maintained throughout. SEDRA pulses reintroduce the dipolar interaction and cause a diminution of the intensity. Typically, plots of spectral intensity versus the number of rotor cycles are generated and the internuclear distance can be determined by simulation of the resulting curve. A $\pi/2$ pulse placed every 8 cycles cancels the effect of SEDRA and provides a control experiment.

Applicability

SEDRA2, found in `userlib`, is available only on `UNITYINOVA` and `UNITYplus`.

Macro

The macro `sedra2` converts a parameter set, obtained with `XPOLAR` or `XPOLAR1`, for the transverse SEDRA experiment of Guillion and Vega. Power levels and the proton 90° pulse width are retained. The value of `pwx` must be calibrated (use `XPWXCAL`).

Parameters

sedra2 uses UNITY*INOVA* and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See [page 85](#) for a description of these parameters.

`pw` is the observe 90° pulse, in μs . It determines the length of π pulses of SEDRA.

`cycles` is the number of 8-pulse SEDRA cycles before acquisition. Each SEDRA cycle has a length of 8 rotor periods and a π pulse is applied at the middle of each rotor period. Usually `cycles` is an integer from 0 to the maximum number of cycles. Typical values are 0 to 8.

`sedraflag` set to 'n' causes a 90° pulse to be applied at the middle of each 8 pulse SEDRA cycle. This pulse partially refocuses the effects of SEDRA and provides a control. If `sedraflag` is set to 'y', a 90° pulse is not applied, allowing full SEDRA evolution. Usually, `sedraflag` is set to 'n', 'y'. For a simultaneous array of `cycles` and `sedraflag`, set array to '`cycles, sedraflag`', and not the reverse.

`phaseflag` is set to 'n' for normal operation. If `phaseflag` is set to 'y' and `sedraflag` is set to 'n', 90° pulses are applied with 180° phase alternation for successive SEDRA cycles. Better refocusing of the control pulse sequence should lead to a larger SEDRA effect. (Caution: setting `phaseflag` to 'y' is not fully tested.)

Reference

Guillion, T.; Vega, J. *Chem. Phys. Lett.* **1993**, *194*, 423.

6.20 REDOR1—Rotational Echo Double Resonance

NMR measurement of internuclear distance, by using multidimensional methods, has been of great importance for the determination of biomolecular structures in solution. It is desirable to obtain similar data from the solid-state for study of membrane protein structures that have been largely inaccessible with solution state methods. REDOR, Rotational Echo Double Resonance, is a useful approach to this goal. [Figure 49](#) is a diagram of the pulse sequence.

The REDOR experiment provides internuclear distance data between a pair of heteronuclei (often ^{13}C and ^{15}N) by means of their mutual dipolar interaction. REDOR is a high-resolution solids experiment and is therefore performed with magic angle spinning, MAS, and usually proton cross-polarization, CP. The heteronuclear dipolar interaction is partially averaged by MAS. Multiple ^{13}C and ^{15}N pulses, synchronized with the MAS rotor speed, reintroduce dipolar information into the spectrum as a variation of spectral intensity with time. Because REDOR is often performed with cross-polarization and proton decoupling, it is a triple-resonance experiment requiring a three channel spectrometer and a triple-resonance probe.

After initial cross-polarization, a variable number of π pulses are applied to the ^{13}C channel, each synchronized with the end of successive rotor periods, with acquisition beginning at the following rotor period. At the middle of each rotor period, π pulses are applied to the ^{15}N channel. These ^{15}N pulses cause signal loss, due to the dipolar interaction. A spectrum without ^{15}N pulses serves as a control experiment. The typical plot is (So-S)/S, where S is the spectral intensity the and ^{15}N pulses and So is the intensity without. The carbon-nitrogen bond distance is determined by simulation of the curve.

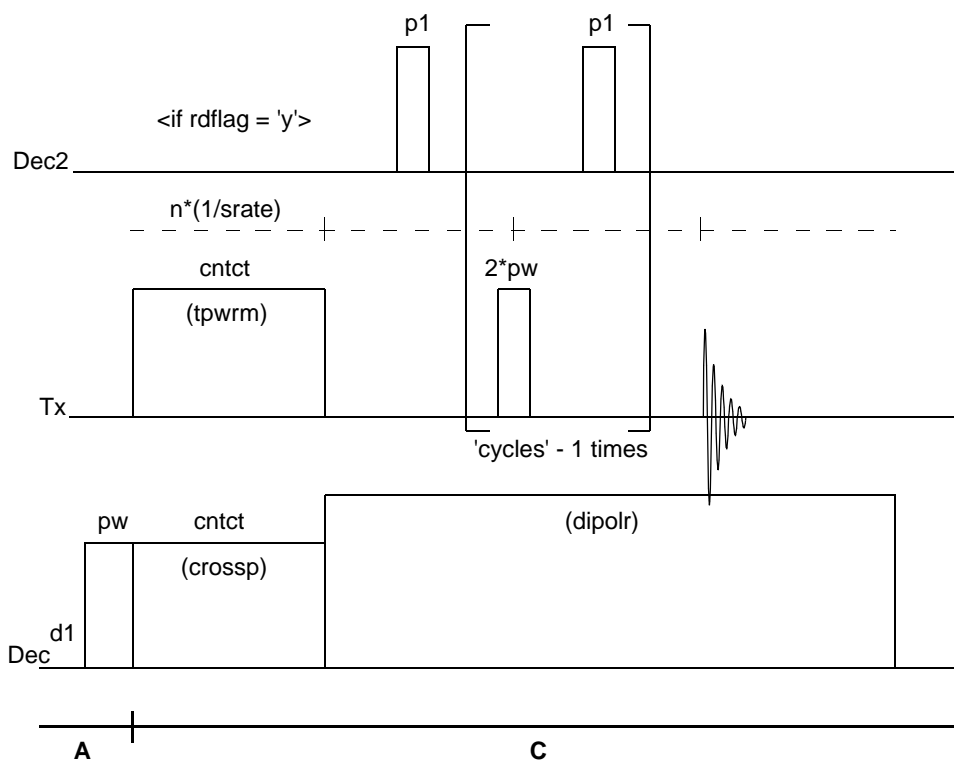


Figure 49. REDOR1 Pulse Sequence

Applicability

REDOR1 is available only on ^{UNITY}INOVA and UNITYplus systems.

Macro

The macro `redor1` converts a parameter set, obtained with XPOLAR or XPOLAR1, for the REDOR experiment with $x\gamma 8 \pi$ pulses on the observe channel. Observe and decoupler power levels and the proton 90° pulse width are retained. Third channel power levels and pulse width must be calibrated (see `p1` below). Default parameters yield an array of spectra for 2 to 32 rotor cycles. Alternate spectra are obtained without and with third channel π pulses. For best results, adjust `tof` and `dof2` (see `dof2` below) so that the peak of interest is on-resonance.

Parameters

`redor1` uses ^{UNITY}INOVA and UNITYplus parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See [page 85](#) for a description of these parameters.

`rdflag` is set to 'y' to apply π pulses to both the observe and third channel and thus obtain REDOR modulation of the peak intensity. `rdflag` is set to 'n' to apply π pulses only to the observe channel and thus obtain observe peak intensity without REDOR modulation. Typically, the array `rdflag='n', 'y'` is used.

`cycles` is the number of rotor cycles before detection. An array is most often set with `cycles=2, 4, ...` to the number of maximum cycles, typically 64. Be sure the parameter array is in the order '`cycles, rdflag`', and not the reverse.

`px` is the observe 90° pulse length, in microseconds (obtained with `xpwxcal` after you have adjusted the Hartmann-Hahn match).

`dpwr2` is the third-channel coarse attenuator setting (–16 dB to 63 dB).

`dpwr2` is the third-channel linear modulator setting (0 to 4095)

`dn2` is the third-channel nucleus.

`dfrq2` is the third-channel frequency, in MHz.

`dof2` is the third-channel decoupler offset, in Hz. `dof2` should be determined by direct observation of the spectrum of the third-channel nucleus.

`p1` is the third-channel 180° pulse, in microseconds. The power levels `dpwr2` and `dpwr2` determine the required pulse length. `p1` is set with the REDOR1 experiment. Set `cycles` to a small value (such as 4) and `rdflag='y'`. For given third-channel power levels, array `p1` from 0 to about 30 microseconds. Set `p1` equal to the value corresponding to first intensity minimum.

`srate` is the actual spin speed. REDOR1 requires rotor speed control. Synchronization of the π pulses with the rotor period is obtained by automatic calculation of delays from the value of `srate`.

`dec2flag` is set to 'n' for normal operation. `dec2flag` interchanges the pulses for the observe and third channels and is used only for oscilloscope (or `dps`) observation of pulses on a two-channel instrument.

References

Guillion, T.; Schaefer, J. *Adv. in Magn. Reson.* **1989**, *13*, 57.

Guillion, T.; Schaefer, J.J. *Magn. Reson.* **1989**, *81*, 196.

Garbow, J. R.; McWherter, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 238.

6.21 DOUBLECP1—Double Cross-Polarization

Double Cross is the original triple-resonance experiment in the solid state. Typically, the nucleus observed is ^{15}N . The results are obtained by plotting the difference between the ^1H - ^{15}N cross-polarization and the ^1H to ^{15}N to ^{13}C cross-polarization spectra for different ^{15}N - ^{13}C contact times. [Figure 50](#) is a diagram of the pulse sequence.

Applicability

DOUBLECP1 is available only on `UNITYINOVA` and `UNITYplus`. It is found in `userlib`.

Macro

The macro `doublecp1` converts a parameter set, obtained by `XPOLAR` or `XPOLAR1`, for the double cross-polarization experiment. Observe and decoupler power levels and the proton 90° pulse width are retained. Third-channel power levels and the dilute-spin Hartmann-Hahn match must be calibrated (see `crossp2` below).

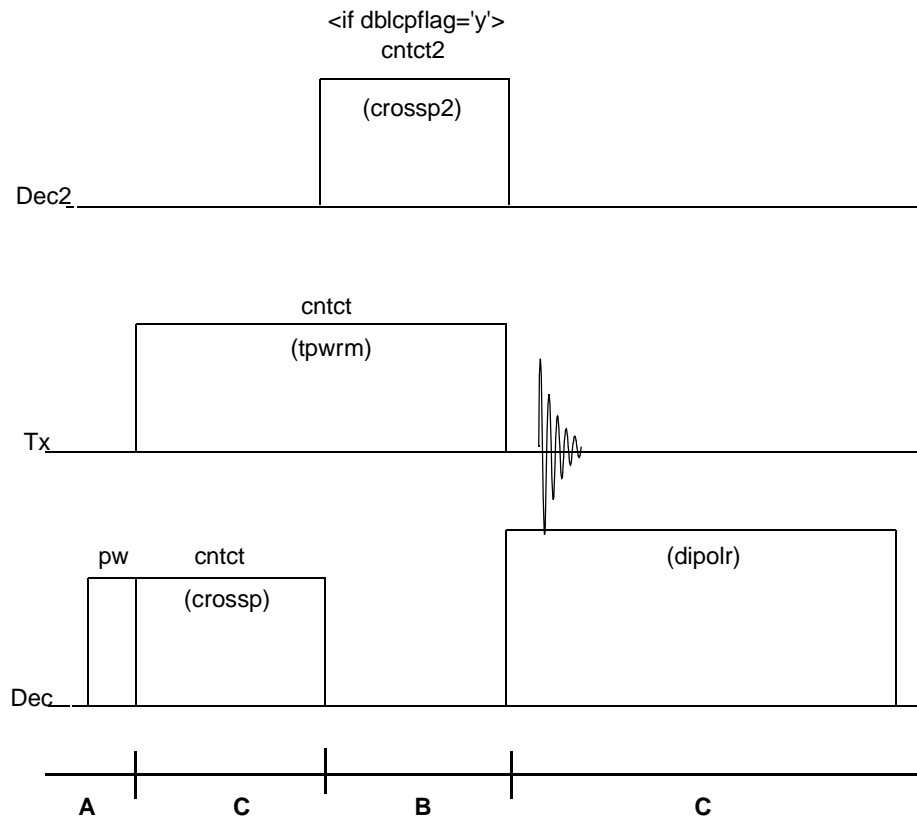


Figure 50. DOUBLECP1 Pulse Sequence

Parameters

doublecp1 uses the ^{UNITY}INOVA and UNITYplus parameters tpwr, tpwrm, dpwr, cppwr, dipolr, crossp, dblv12, pw, and cntct. See [page 85](#) for a description of these parameters.

dbcpflag is set to 'y' to do double cross-polarization. A Hartmann-Hahn match between the observe nucleus and third-channel nucleus follows a standard cross-polarization. The second cross-polarization drains polarization from the observe nucleus and lowers the signal intensity. If dbcpflag is set to 'n', this second cross-polarization is omitted. A positive difference signal is obtained by subtracting spectra with dbcpflag='n' minus dbcpflag='y', or by dbcpflag='y' and third-channel irradiation off minus on-resonance.

dn2 is the third-channel nucleus.

dof2 is the third-channel decoupler offset, in Hz. dof2 is best obtained by direct observation of the spectrum of the third-channel nucleus.

dpwr2 is the third-channel coarse attenuator setting (–16 dB to 63 dB).

crossp2 is the third-channel linear modulator setting (0 to 4095). The parameters crossp and crossp2 determine the Hartmann-Hahn match for the dilute-spin cross-polarization. The dilute-spin Hartman-Hahn match is determined with DOUBLECP1.

Array the value of `crossp2`. The Hartmann-Hahn match corresponds to the minimum signal intensity.

`cntct2` is the contact time for the dilute-spin cross polarization, in microseconds.

References

Schaefer, J.; Stejskal, E. O.; Garbow, J. R.; McKay, R. A. *J. Magn. Reson.* **1984**, *59*, 150.

Stejskal, E. O.; Schaefer, J.; McKay, R. A. *J. Magn. Reson.* **1984**, *57*, 471.

6.22 T1CP1— T_1 Measurement with Cross-Polarization

The pulse sequence T1CP1 is used to measure the T_1 of X-nuclei (e.g., ^{13}C) by cross-polarization (CP), as published by Torchia. [Figure 51](#) is a diagram of the sequence.

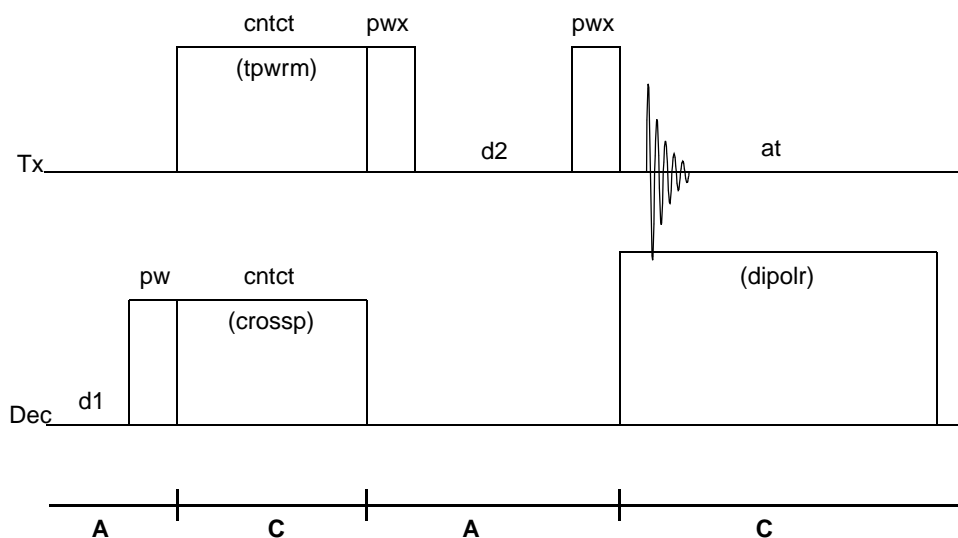


Figure 51. T1CP1 Pulse Sequence

Macro

The macro `t1cp` converts a parameter set obtained by `XPOLAR` or `XPOLAR1`, for the measurement of T_1 . Observe and decoupler power levels and the 90° pulse width are retained. By default $pwx=pw$. Fine calibration of pwx is recommended.

Parameters

T1CP1 uses the `UNITYINOVA` and `UNITYplus` parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dplvl2`, `pw`, and `cntct`. See [page 85](#) for a description of these parameters.

pwx is the observe 90° pulse, in microseconds.

d_2 is the delay of the T_1 inversion recovery, in seconds.

Reference

Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613.

6.23 HAHNCP1—Spin 1/2 Echo Sequence with CP

The HAHNCP1 pulse sequence provides a $90 - \tau - 180 - \tau$ Hahn spin echo. If $xpol = 'y'$, the initial 90° pulse is replaced by cross-polarization. If $xpol = 'n'$, the spin echo sequence is done.

Use HAHNCP1 to obtain static lineshape for spin-1/2 powder spectra to avoid pulse ring down and first order ('lp') phase correction of the lineshape. Values of τ_{au1} and τ_{au2} as short as 10 microseconds can be used. Set τ_{au2} less than τ_{au1} to observe the spin echo and process data with $lsfid$ less than 0 to begin acquisition at the top of the spin echo. The phase cycle is that of Rance and Byrd. [Figure 52](#) shows a diagram of the HAHNCP1 sequence.

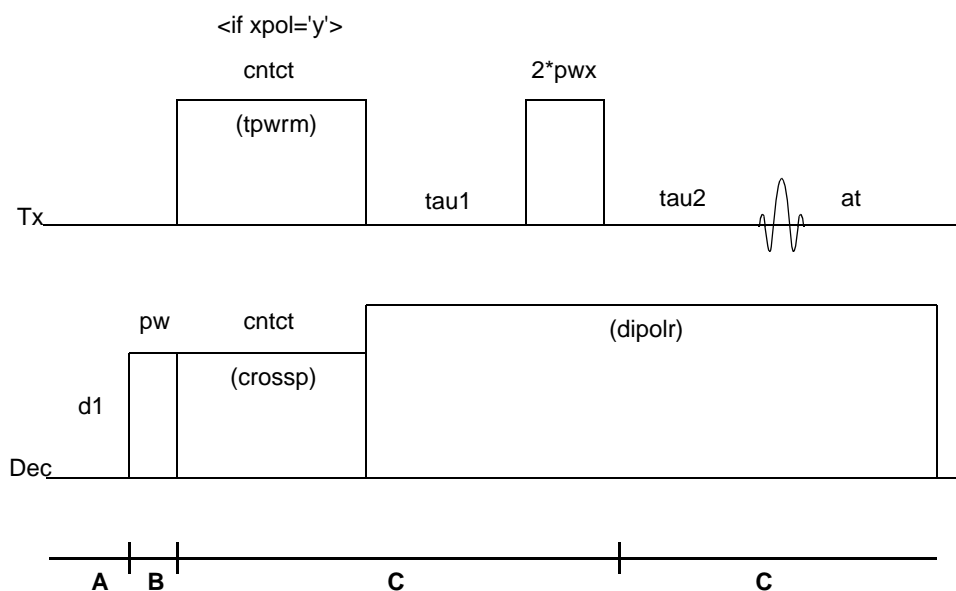


Figure 52. HAHNCP1 Pulse Sequence

Applicability

HAHNCP1 is available only on ^{UNITY}INOVA and UNITYplus. It is found in `userlib`.

Macro

The macro `hahncp1` converts a parameter set obtained by XPOLAR or XPOLAR1, for the spin echo experiment. Observe and decoupler power levels and the 90° pulse width are retained, as well as the value of $xpol$. By default, $pwx = pw$. Fine calibration of pwx is recommended, $\tau_{au1} = \tau_{au2} = 10$ (in microseconds).

Parameters

HAHNCP1 uses ^{UNITY}INOVA and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See [page 85](#) for a description of these parameters.

`xpol` is set to 'n' for direct polarization, or set to 'y' for cross polarization.

`pw` is the observe 90° pulse, in microseconds. The 180° pulse is $2.0 * pw$.

`tau1` is the delay, in microseconds, between the 90° pulse (contact pulse if `xpol='y'`) and the 180° pulse.

`tau2` is the delay, in microseconds, between the 180° pulse and the acquisition. The additional delay for filter response (`alpha+fn/beta`) is also present.

Reference

Hahn, E. L. *Phys. Rev.* **1950**, *80*, 580.

Carr, H. Y.; Purcell, E. M. *Phys. Rev.* **1954**, *94*, 630.

Rance, M.; Byrd, R. A. *J. Magn. Reson.* **1983**, *52*, 221.

6.24 SSECHO1—Solid-State Echo Sequence for Wideline Solids

Non-narrowed spectra of solids samples can often reveal a considerable information. In wideline NMR, no attempt is made to narrow the resonances, and patterns of 100 kHz or wider can occur.

For wideline NMR, the line shape is of the utmost importance and the spectrometer must be able to measure very broad lines without distortion. For this reason, the transmitter power must be high and the value of γB_1 must be large enough to uniformly excite the entire spectrum. (The effects of a finite 90° pulse can be investigated with simulations using the solids analysis software accessory.) With linewidths in excess of 100 kHz, an increase in ADC (analog-to-digital converter) speed, 2 MHz or 5 MHz, is necessary. Often, the typical spectral widths used far exceed the linewidths. Oversampling and digital filtering are used to reduce the data size.

For quadrupolar nuclei, the main cause of linewidth is the quadrupolar coupling of the nuclei being observed. The observed magnitude of the quadrupolar coupling is dependent on orientation in the magnetic field and is responsible for the apparent difference between single crystal and powder spectra.

The most commonly observed quadrupolar nucleus for wideline work is ²H, along with ²³Na and a few other nuclei. Line shape is of prime consideration in most experiments involving these nuclei. Relaxation measurements are also of interest. To measure an accurate representation of the line shape, most spectra are measured with an echo sequence, first described by Mansfield, commonly known as the “solid echo” or “quadrupolar echo” sequence. To simplify phasing of the transformed FID, the echo is Fourier transformed from the top of the echo onwards in time, and these echoes are usually oversampled. For quadrupolar nuclei ($I > 3/2$), because different types of line shape information may be sought, a number of different echo sequences may be used, depending on the quantum transitions in interest. [Figure 53](#) is a diagram of the SSECHO1 pulse sequence.

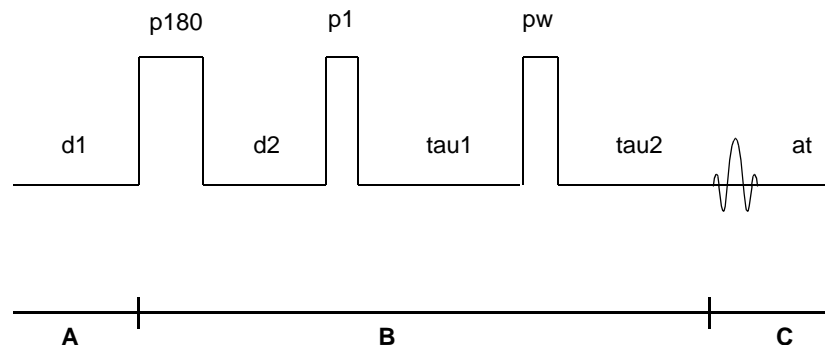


Figure 53. SSECHO1 Pulse Sequence

Applicability

SSECHO1 is available only on ^{UNITY}INOVA and UNITYplus. It is found in `userlib`.

Macro

The macro `ssecho1` converts a parameter set for the quadrupole echo pulse sequence SSECHO1. Power parameters and `pw` are retained. If `tpwrm` is not present (as in many older parameter sets), `ssecho1` creates it and sets it to the value of `tpwrf`. If `tpwrf` is not present, `tpwrm` is set to 4095. The default parameters provide for a quadrupole echo with a pulse delay of 20 microseconds.

^{UNITY}INOVA and UNITYplus Power Parameters

`ssecho1` makes use of the generic power parameters `tpwr`, `tpwrm`, `dpwr`, `dpwrm`, and `pw` for ^{UNITY}INOVA and UNITYplus systems. These parameters have a consistent definition in most ^{UNITY}INOVA and UNITYplus single-resonance (i.e., wideline and CRAMPS) pulse sequences. They are also consistent with the parameters of `xpolar1` (with `xpol = 'n'`) with the exception that the parameter `dipolr` replaces `dpwrm` in `xpolar1` as the decoupler linear modulator voltage level.

`tpwr` is the observe power setting (–16 dB minimum to 63 dB maximum power).

`tpwrm` is the observe linear modulator voltage setting (0 minimum to 4095 maximum voltage). The value of `tpwrm` is linearly proportional to the applied signal voltage. Doubling `tpwrm` halves the value of the pulse width.

`dpwr` is the decoupler power setting (–16 dB minimum to 63 dB maximum power).

`dpwrm` is the decoupler linear modulator voltage setting during acquisition (0 minimum to 4095 maximum voltage). `dpwrm` is linearly proportional to the applied decoupler voltage. Doubling `dpwrm` doubles the decoupler field strength (in kHz).

`pw` is the observe 90° pulse, in microseconds.

Other Parameters

`echo` set to 'y' implements either a quadrupole echo or a composite echo (see `compul` below). `echo` set to 'n' implements a single pulse (the first pulse of the quadrupole echo)

with width p_w . The delay before acquisition is $\tau_{a1} + \tau_{a2} + p_w$. A difference spectrum 'n' - 'y' selects a quadrupole echo spectrum in the presence of a large central resonance.

compul set to 'y' implements a composite pulse echo, $135(x) - 90(-x) - 45(x)$, instead of a quadrupole echo, if echo = 'y'.

p1 is the width of the first pulse of the quadrupole echo, in microseconds, set to 90° or if set to zero, $p1 = p_w$. When p1 is 0, it is hidden.

p_w is the width of the second pulse of the quadrupole echo in microseconds, set to 90° if spin $I=1$, or set less than 90° if spin I is greater than or equal to $3/2$ (I is the nuclear spin quantum number).

p180 is an optional inversion pulse, in microseconds, for T_1 studies. If p180 is 0, this parameter is hidden (see d2 below).

d2 is the delay, in seconds, between the inversion pulse and the quadrupole echo; if p180 is 0, d2 is not used and is hidden.

τ_{a1} is the delay, in microseconds, between pulses p1 and p_w of the quadrupole echo pulse sequence.

τ_{a2} is the exact (see NOTE below) delay, in microseconds, between the second pulse and acquisition. Set τ_{a2} less than τ_{a1} to begin acquisition before the top of the echo. Use lsfid greater than 1 to begin the Fourier transform at the echo peak (see below).

NOTE: The delay to compensate for filter group delay (controlled by parameters α , β , and β_b) is not present in ssecho1. Adjust τ_{a2} or use lsfid to set the beginning point of the Fourier transform.

References

Mansfield, P. *Phys. Rev.* **1965**, *137*, A961.

Weisman, I. D.; Bennett, L. H. *Phys. Rev.* **1969**, *181*, 1344.

6.25 WLEXCH1—Wideline Solids Exchange

Two-dimensional NMR offers a unique method of characterizing molecular order and molecular dynamics in solid materials such as polymers. This technique can be used to study “ultra-slow” (on the NMR time scale) dynamic processes occurring on a time scale of 1 millisecond to 100 seconds. In an axially symmetric ^2H powder pattern (Pake doublet), the exchange signal patterns supply immediate information about the type and rate of the dynamic process.

Two-dimensional ^2H exchange spectroscopy can be used to determine the angle at which a selectively deuterated group rotates during a defined mixing period t_{mix} . Isolated cross-peaks are observed in 2D-exchange spectra of liquids and crystals. The exchange signals in the 2D-exchange spectra of solid powders are actually very broad spectra. The molecular reorientation of the deuterated group in the molecule occurs at a particular angle relative to the molecular axis. At a given mixing time, one ellipse for each of these reorientation angles can be measured.

Applicability

WLEXCH1 is available only on ^{UNITY}INOVA and UNITYplus. It is found in userlib.

Macro

The macro `wlexch1` converts a solids parameter set obtained with `SSECHO1` to the WLEXCH1 spin $I=1$ solids exchange experiment. Power levels and `pw` are retained. If `tpwrm` is not present (as in many older parameter sets), `wlexch1` creates it and sets it to the value of `tpwrf`. If `tpwrf` is not present, `tpwrm` is set to 4095.

It is recommended that you set the 90° pulse `pw` with `tpwrm` (use `s2pull1`) and obtain a quadrupole echo spectrum (use `ssecho1`) before running `wlexch1`. The default parameters provide a mixing period of zero and quadrupole echo pulse delay of 60 microseconds. **Figure 54** is a diagram of the WLEXCH1 pulse sequence.

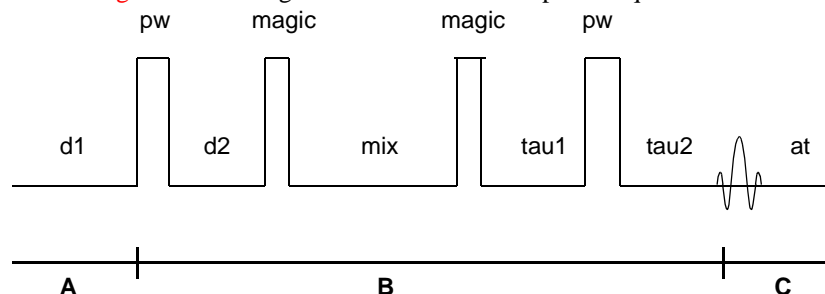


Figure 54. WLEXCH1 Pulse Sequence

Parameters

`wlexch1` makes use of the `UNITYINOVA` and `UNITYplus` parameters `tpwr`, `tpwrm`, `dpwr`, `dpwrm`, and `pw`. See [page 117](#) for a description of these parameters. `wlexch1` is based on the quadrupole echo pulse sequence `ssecho`, and `tau1` and `tau2` have similar definitions.

`pw` is the observe 90° pulse, in microseconds, pulses 1 and 4 of WLEXCH1.

`magic` is a 54.7° pulse, in microseconds, pulses 2 and 3 of WLEXCH1.

`mix` is the mixing period, in seconds, for development of the elliptical ridges due to molecular motion.

`phase` is set to 1,2 for hypercomplex phase sensitive detection. Use the command `wft2d(1,0,0,0,0,0,0,N)` for transformation (usually $0.5 < N < 2.0$). Spin lattice relaxation during the mixing period affects the intensities of the sine and cosine arrays unequally. Use of `N` other than 1, corrects for unequal relaxation times. Set `N` to zero the antidiagonal of the 2D spectrum.

`tau1` is the delay, in microseconds, between pulses `p1` and `pw` of the quadrupole echo pulse sequence.

`tau2` is the exact (see NOTE below) delay, in microseconds, between the second pulse and acquisition, set the value of `tau2` to less than `tau1` to begin acquisition before the echo, use `lsfid` greater than 1 to begin the Fourier transform at the echo peak (see below).

NOTE: The delay to compensate for filter group delay (controlled by parameters `alfa`, `beta`, and `fb`) is not present in WLEXCH1. Adjust `tau2` or use `lsfid` to set the beginning point of the Fourier transform.

References

Schmidt, C.; Blumich, B.; Spiess, H. W. *J. Magn. Reson.* **1988**, *79*, 269.

Blumich, B.; Spiess, H. W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1655.

6.26 HS90—90-Degree° Phase Shift Accuracy

At the completion of use of the multiple pulse tune-up sequences FLIPFLIP and FLIPFLOP, the spectrometer is tuned for multiple-pulse experiments. An optional sequence is the HS90 sequence $((90(x)-90(y)-90(y)-90(x))_2-acq)_n$, which tests the exactness of the 90° phase shift. This sequence, first described by Haubenreisser and Schnabel, is a very accurate measure of phase shift errors. The sequence is 8 pulses per acquisition point. **Figure 55** is a diagram of HS90.

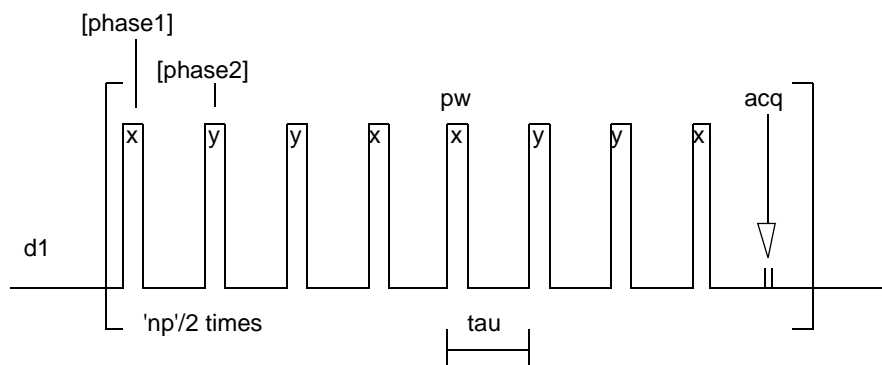


Figure 55. HS90 Pulse Sequence

A benefit of this sequence is that it is insensitive to B_1 homogeneity. Any phase error between x and y is shown as an oscillation in the number of points per cycle is related to the phase error. The phase error can be determined by counting the number of points in one cycle of a sine wave. Divide 360 by this number. The result is the phase error in degrees. If the result is less than 0.1 degrees, there is no error; if the result is greater than 0.1 degrees, there may be a fault in the transmitter board.

The macro `hs90` recalls the sequence and a modified parameter set.

Parameters

`pw` is the pulse length in microseconds, usually set to a 90° pulse.

`phase1` is the phase of the first 90° pulse and is set to 0 (x).

`phase2` is the phase of the second 90° pulse and is set to 1 (y).

`trig` is set to 'y' or 'n' depending on the system. On *UNITYINOVA* and *UNITYplus*, the pulse sequence is not tied to any internal triggering mechanism and `trig` should always be set to 'n'. On *UNITY* and *VXR*, data acquisition is triggered to an internal 500 kHz clock, so `trig` must be set to 'y', and the signal of the 500 kHz clock plugged into the external trigger input located on the Pulse Sequence Controller board.

`np` is usually set to 128 points.

`tau` is 20 microseconds.

Reference

Haubenreisser, U.; Schnabel, B. *J. Magn. Reson.* **1979**, *35*, 175.

6.27 MREVCS—Multiple Pulse Chemical-Shift Selective Spin Diffusion

Figure 56 shows the diagram of a novel experiment, called MREVCS, developed by Spiess and coworkers, that involves a multiple-pulse selection of ^1H magnetization based on chemical shift differences during the mixing time, ^1H spin diffusion during a mixing time, and high-resolution ^{13}C CP/MAS detection to study the mixing of components on a molecular scale. This version is for ^1H detection.

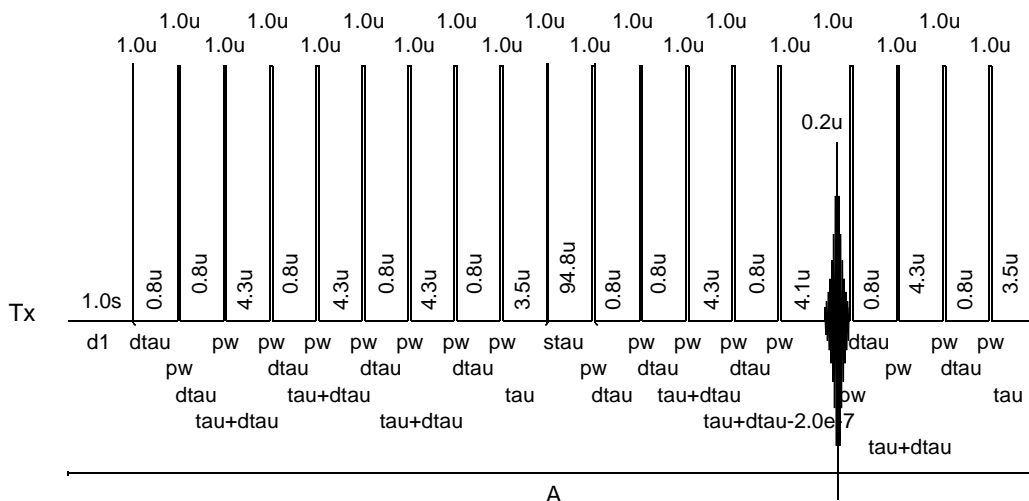


Figure 56. MREVCS Pulse Sequence

Macro

The macro `mrevcs` retrieves a parameter set suitable for the MREVCS experiment.

Parameters

The parameters are analogous to those in all multiple-pulse experiments:

`pw` is the 90° pulse, in microseconds.

`tau` is the time delay, in microseconds, between pulses. In the case of MREV8, the cycle time is $12 * \text{tau}$.

`mix` is the mixing time, in microseconds, for ^1H spin diffusion.

`cycles` is the number of times through the multiple pulse cycle.

`cycles` and `tof`, in combination, determine the chemical shift.

Reference

Spiess, H.; Schmidt-Rohr, K.; Clauss, J.; Blumich, B. *Magn. Reson. Chem.* **1990**, *28*, S3.

6.28 MQ_SOLIDS—Multiple-Quantum Solids

A ^1H multiple-quantum spectrum can be obtained in the solid state in the manner of Pines and Baum. The pulse sequence, called MQ_SOLIDS, generates even order multiple-quantum transitions and detection uses the magic echo sequence. Figure 57 is a diagram of the sequence.

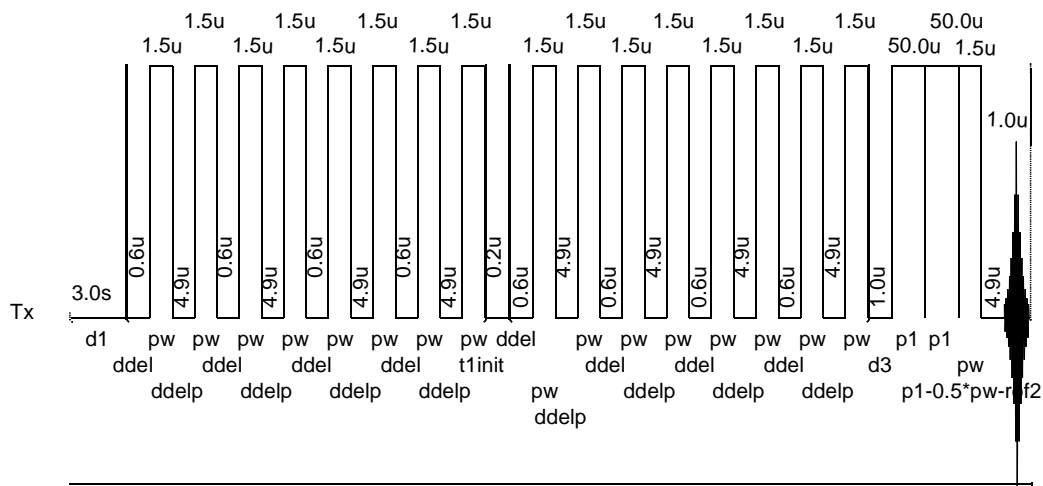


Figure 57. MQ_SOLIDS Pulse Sequence

Macro

Macro `mq_solids` generates the parameters for the multiple-quantum experiment.

Parameters

`d1` is the short interpulse delay, in microseconds.

`delp` is the long interpulse delay, in microseconds.

`mloop` is the number of times (typically, 7) through the first multiple pulse cycle.

`shift` is the TPPI phase increment. The units of this parameter have not been fully checked. Use the `display` command to confirm units.

`t1inc` is the t_1 increment in the convention of a 2D experiment. The units of this parameter have not been fully checked. Use the `display` command to confirm units.

`t1init` is the initial delay increment. The units of this parameter have not been fully checked. Use the `display` command to confirm units.

Reference

Baum, J.; Munowitz, M.; Garroway, A. N.; Pines, A. *J. Chem. Phys.* **1985**, *83*, 2015.

6.29 SPINDIFF—Spin Diffusion in Solids

SPINDIFF is a pulse sequence for 2D exchange spectroscopy in which spin diffusion is occurring in solid dense homonuclear dipolar coupled spin systems. Figure 58 is a diagram of the sequence.

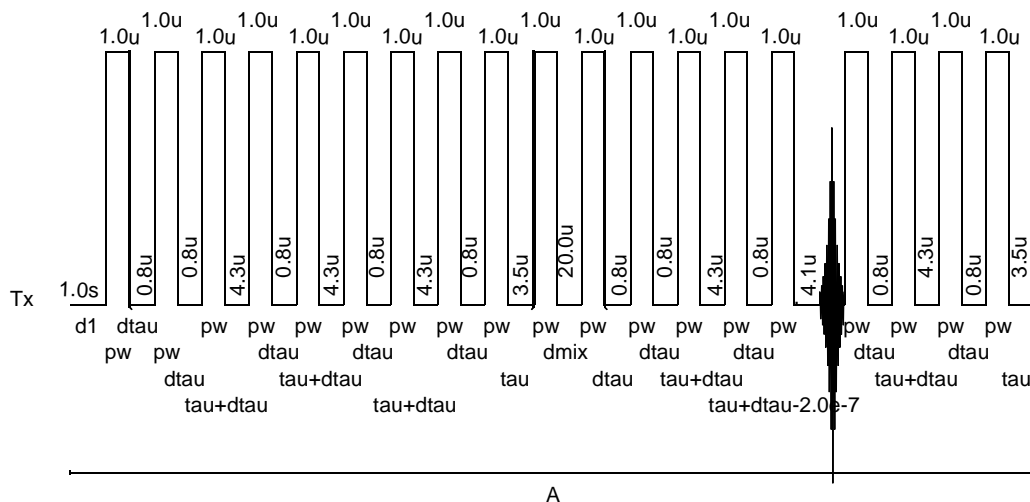


Figure 58. SPINDIFF Pulse Sequence

Macro

The macro `spindiff` retrieves a parameter set suitable for the SPINDIFF experiment.

Parameters

The parameters used are analogous to those used in other multiple-pulse experiments:

`pw` is the 90° pulse length, in microseconds.

`tau` is time delay between the pulses, in microseconds.

`mix` is the mixing time, in microseconds, for spin diffusion.

`ni` is the number of increments, as defined in standard 2D NMR usage. `ni s` is typically set to either 64 or 128.

Reference

Zheng, L.; Fishbein, K. W.; Griffin, R. G.; Herzfeld, J. *J. Am. Chem. Soc.* **1993**, *115*, 6254.

6.30 FASTACQ—Multinuclear Fast Acquisition

Fast acquisition of data has interesting applications, particularly in high-temperature, fast kinetic studies. Of particular interest is the ability to perform fast acquisitions in the following manner: to do in double resonance (X,Y) the fastest possible acquisition of sequential spectra of two nuclei—for example, *pulse – acquire (27Al) – pulse acquire (2H) – pulse – acquire (27Al)*—storing FIDs in separate buffers.

The particular example used here is the simultaneous observation of ^{27}Al and ^2H . For this experiment, a triple-resonance probe was used with the coil doubly tuned to ^{27}Al (referred to as the high frequency) and ^2H (referred to as the low frequency). Both NMR frequencies were picked off the high-frequency port. It was possible to observe the ^2H signal due to the imperfect isolation between the two channels.

By coding a pulse sequence using the offset pulse sequence statement in conjunction with large values of τ_{of} (in MHz), two FIDs, one at ^{27}Al and the other at ^2H , were collected in 37 milliseconds, of which 20 milliseconds is the acquisition time of the two FIDs. By adding a loop statement and setting the value if n_f (number of FIDs) is greater than one, a series of alternating multinuclear FIDs can be collected. Figure 59 is a diagram of the fast acquisition pulse sequence, called FASTACQ.

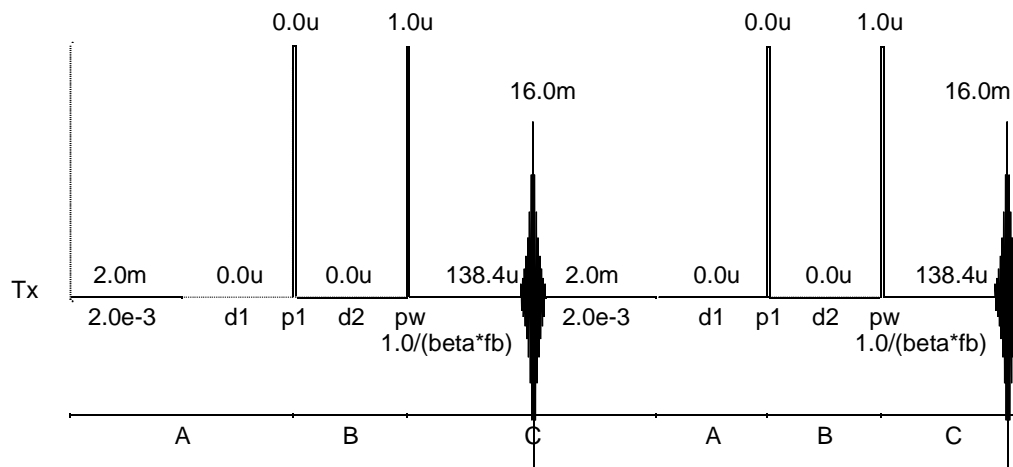


Figure 59. FASTACQ Pulse Sequence

Macro

The macro `fastacq` recalls the FASTACQ sequence and a modified parameter set.

Parameters

`nf` is the number of FIDs to be collected.

`τof` is the offset, in Hz, to be used for the low-frequency nucleus.

`freqout` is the difference, in MHz, between the high frequency nucleus, defined by `τn`, and the low frequency nucleus.

Processing and Display

Data is processed by the command `wft('nf')`. This allows the data to be transformed in the form of an arrayed experiment. All the data can be displayed with the `dssh` command. Portions of the data can be displayed with the standard arguments of the command `dssh`.

6.31 NUTATE—Solids 2D Nutation

NUTATE is a two-dimensional solids nutation experiment patterned after that of Lippmaa and coworkers. The experiment illustrates the effect of pulse width on the spectra obtained.

The 2D spectrum places chemical shift along F_2 and γB_1 along F_1 . **Figure 60** is a diagram of the sequence.

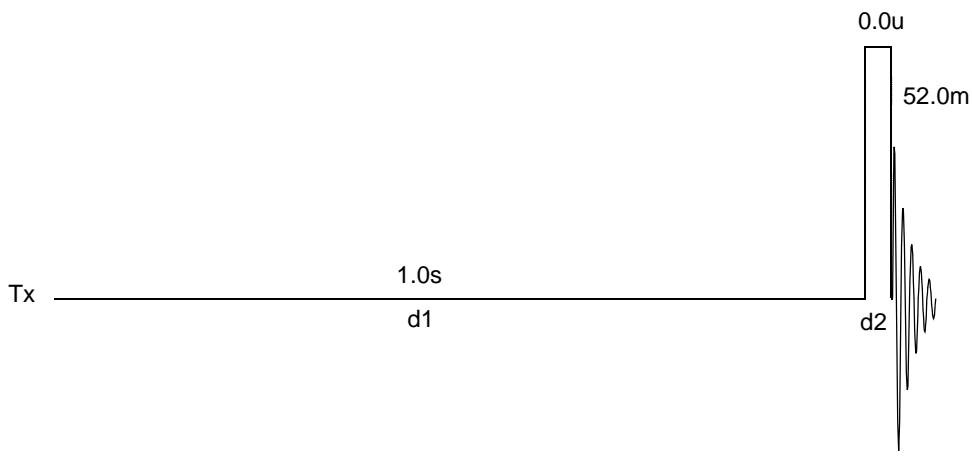


Figure 60. NUTATE Pulse Sequence

Macro

The macro `nutate` converts an S2PUL sequence parameter set into a 2D nutation experiment.

Parameters

`tpwr` should be set so that a 90° pulse length should be about 50 kHz (or whatever other value is desired).

`sw1` controls the length of the tip angle, using as the increment value $1/sw1$, in an analogous way to all standard 2D experiments.

Processing

The data is processed by the command `wft2d(0,0,0,1)`.

Reference

Samoson, A.; Lippmaa, E. *J. Magn. Reson.* **1988**, *79*, 255.

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