User Guide: Solid-State NMR

Varian NMR Spectrometer Systems
With VNMR 6.1C Software

Pub. No. 01-999162-00, Rev. A0800

VARIAN

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Varian NMR spectrometer systems with
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Technical contributors: Dave Rice, Laima Baltusis, Frits Vosman, Dan Iverson, Evan Williams
Technical writers: Michael Carlisle
Technical editor: Dan Steele

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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.
- Chapter 3, "Wideline Solids Module Operation," covers using the wideline solids module.
- Chapter 4, "CRAMPS/Multipulse Module Operation," covers using the CPAMPS/ multipulse module.
- 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 more than 40 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*, UNITY*plus*, 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.
- UNITY*plus*, UNITY, and VXR-S are spectrometer lines that preceded the UNITY*INOVA*.
- *MERCURY* and *GEMINI 2000* are spectrometer lines that preceded the *MERCURY-VX*.

Help Us to Meet Your Needs!

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:

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}C-{^{1}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:

UNITY*INOVA or UNITYplus System*	Wideband ADC with Sum to Memory Solids cabinet High-band & low-band 1-kW amplifier Pneumatics/tachometer box
UNITY or VXR-S System	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

CP/MAS hardware differs between systems.

CP/MAS Hardware for UNITY*INOVA* and UNITY*plus* systems

On UNITY*INOVA* and UNITY*plus* systems, CP/MAS hardware consists of a class A/B AMT 3900A-15 linear amplifier that replaces the standard liquids linear amplifier. The CP/MAS linear amplifier produces output power of up to 100 W in the high band (^{1}H/^{19}F) for up to 250 ms. The low band remains the same as for the original standard liquids amplifier.

The fine power control over a range of 0 to 60 dB in 4095 steps is provided by the Transmitter board, which is standard on UNITY*INOVA* and UNITY*plus* systems. The parameters controlling this are `dpwrm`, `dpwrm2`, and `dpwrm3`. The attenuator control is linear, meaning the control is finer in the higher region than in the lower region of the attenuator, as shown in Figure 1. In addition, a pneumatics/tachometer box is used for controlling air flow and spinning speeds.

CP/MAS Hardware for UNITY and VXR-S Systems

The CP/MAS solids module is the only one of the solids hardware configurations that does not require the solids cabinet. Apart from the special probe, the hardware for the standard-performance CP/MAS solids module consists of a 100 W, narrow-band decoupler pulse

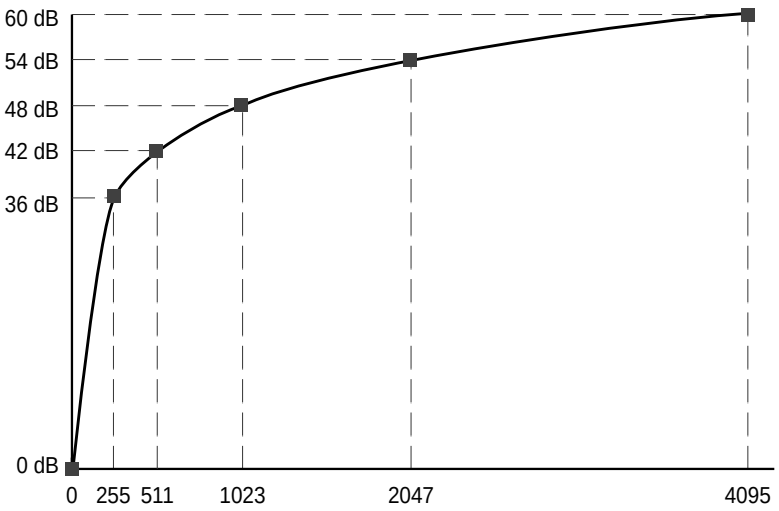


Figure 1. Linear Attenuator Control Graph

amplifier, a fine attenuator, a power control box (on 200 MHz and 300 MHz systems), and a pneumatics/tachometer box. The amplifier is class AB, capable of delivering 100 W for up to 250 ms.

Power Control Box (200-MHz and 300-MHz Systems Only)

A free-standing power control box with an ON/OFF switch activates the 100 W decoupler and observe amplifiers (class C only). This box should be located in a convenient location near the operator. The computer controls the power levels for decoupling.

Fine Attenuator (UNITY only)

In a basic UNITY system, the power levels for observe and decouple transmitters are set by computer-controlled attenuators with a 63-dB range in 1-dB steps. This is not fine enough control for solids experiments, so the decoupler channel is supplemented with a fine attenuator with a 6-dB range in 4096 steps. The fine attenuator is controlled by the parameter `dpwrf`, which ranges from 0 (least power) to 4095 (most power). VXR-S uses the parameter `dhp`, which ranges from 0 to 255 (maximum power).

Decoupler Amplifier

The decoupler amplifier is housed in the lower right side of the console. This amplifier increases the output of the standard decoupler to about 100 W to provide sufficient power for dipolar decoupling. The output goes to the probe, through a high-pass filter at the DEC connector on the probe.

The amplifier on the 200 MHz and 300 MHz systems can be left in the decoupler line, since when the amplifier is turned off, its input and output are connected. A safety circuit shuts off the amplifier and sounds a buzzer if the output of the amplifier is not connected to 50 ohms. If this happens, the ON/OFF switch on the amplifier must be turned to off, the fault rectified, and then the switch turned back to on.

The amplifier on the 400 MHz system has a separate power switch instead of the control box, and when the amplifier is turned off, the input and output are not connected. Included on this amplifier is dynamic overload protection.

The decouple amplifier is driven by the normal liquids decoupler output, which can be as high as 50 W at maximum output. This is more than sufficient to drive the decoupler amplifier, and if used at full power, can damage the decoupler. Although the parameter `level2` has been set to 63 in this manual, do not use values higher than those that deliver 25 W (200- and 300-MHz systems) or 10 W (400-MHz system) to the input of the decoupler amplifier.

2.2 Preparing the Sample and Rotor

Solid samples are normally packed into hollow rotors. These rotors are sealed with fluted caps that are driven for spinning. 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.

Rotor Composition

Doty rotors are either of zirconia, silicon nitride, or sapphire, with Kel-F or Vespel end caps. See the manual from the rotor manufacturer for details.

Varian high-speed rotors are composed of zirconia or of silicon nitride (Si_3N_4) with pMMA or Torlon (type 4203) end caps. Refer to the probe installation manual for a list of rotors and end caps and their associated part numbers, color, temperature range, and maximum spin rates.

During VT operation, Torlon end caps can exceed the +100°C specification of the 7-mm probe. 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. pMMA end caps (colorless-clear) must only be used at room temperature and below. These are currently supplied with Varian RT CP/MAS probes. Visually distinguishing between Kel-F and pMMA end caps can be difficult, so you may want to mark them appropriately. The background nuclei for these materials are listed in Table 1.

Table 1. Background Nuclei of Rotor Material

Material	*Background*
Kel-F end cap	C (not cross-polarizable), F
Vespel, Torlon, pMMA end cap	C (cross-polarizable), H
sapphire rotor	Al, O
zirconia rotor	Zr, O, traces of Mg, Y, Al
Si_3N_4 rotor	Si, N, some Al

CAUTION: **Spinning a rotor for more than a few minutes in a vibrating state can cause permanent damage to the bearing surface of both the rotor and stator. Once this happens the rotor will probably not spin adequately again, even if perfectly balanced.**

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.

For Varian 7-mm rotors, the solid sample should be machined as a plug to fit into the rotor. Ideal dimensions should be 0.440 ± 0.005 in. (11.176 mm) long, by 0.1960 ± 0.0005 in. (4.979 mm) in diameter (0.137 in. (3.48 mm) for Varian 5-mm rotors).

Granular and Powdered Materials

For granular or powder materials, the best method for filling the rotors is by pouring the material into the rotor, leaving just enough room for the cap. Granular and powdered materials work best as uniform fine particles (100 mesh or finer). If the material can be ground, it is better to 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 should be 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 snugly and flush with the top of the rotor.

Miscellaneous Materials

Many different sample types and forms exist that are neither machinable solids nor granular or powdered materials. Some of these materials can be prepared in rotors so that dynamic balance is preserved, while others cannot. Basically, if the material can be made to fill the rotor homogeneously, chances are good that it will spin adequately.

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.

CAUTION: **Organic solvents can dissolve pMMA end caps.**

Liquid Samples

For liquid samples, use an end cap that has a concentric hole drilled through it (a #73 drill is recommended). Be sure the end cap will not dissolve (organic solvents can dissolve pMMA end caps). Liquid samples can be spun at several hundred 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.

2.3 Spinning the Sample

On Varian high-speed rotors, tachometer sensing is on the rotor bottom. Zirconia rotors are marked with a permanent black marking pen or black enamel so that 50% of the bottom of surface area is shaded black; silicon nitride (Si_3N_4) rotors are marked with white enamel in the same fashion.

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 correction fluid. The diameter marking should be straight.

Doty high-speed rotors have optical markings inside the bottom cap; other Doty probes use electrostatic sensing (triboelectric). See the Doty manual for instructions on reapplying the optical marking.

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 2. 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).**

Table 2. Typical Spin Rates with Associated Bearing and Drive Values

Spinning Speed (Hz ±250 Hz)	*Bearing*		*Drive*	
	Pressure psig (bar)	*Flow rate (LPM ±2 LPM)*	*Pressure psig (bar)*	*Flow rate (LPM ±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
6500	36 (2.5)	12.5	35 (2.4)	29.5
7200	36 (2.5)	12.5	36 (2.5)	30.0
7500	39 (2.7)	12.5	44 (3.0)	32.5
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)	09.0	65 (4.5)	40.0

To Spin Samples in Doty Probes

Either one or two air supplies can be used for sample spinning in the Doty probe. Because the control box supplied for CP/MAS has two controllers, split streams are recommended. The techniques for doing this are covered in the Doty probe manual.

To Spin Samples in High-Speed Probes

Table 2 lists spin rates and the appropriate bearing and drive pressures for the Varian 7-mm VT CP/MAS probe 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 either 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.

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.**

To remove a sample, take care to decrease the rotor speed smoothly. At all times that rotation air is flowing, bearing air should read at least 28 psig (1.9 bar). Only when the rotation air is completely off should the bearing be carefully decreased to zero.

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.

If a packed rotor does not spin properly at first, inspect it to see if the sample has been disturbed. Part of the sample may have broken loose and been thrown out of the rotor, in which case, repacking might be the solution. Sometimes loose material balances itself if kept in the rotor and spun below its vibration speed for a few minutes. If the sample seems intact on the surface, then it is more than likely not homogeneous or did not pack evenly.

In the case of a machined plug, the material can have a void or it can fit too loosely in the rotor cavity. 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.

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

At times, worn rotor caps cause imbalance. Changing caps or rotating them between rotors sometimes cures these problems.

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.

2.4 Adjusting Homogeneity

Homogeneity should be adjusted as follows on a sample of D_2O, prepared in a standard rotor, and tightly capped using a cap with a concentric drilled hole.

1. Insert and seat the sample and install the probe into the magnet; spin slowly (several hundred Hz or less) with 2.0 bar ±0.5 bar bearing pressure and a very low drive (rotation) pressure. Generally, this slow spinning speed barely registers on the tachometer. Note that, with time, D_20 spins out of the rotor.
2. Tune the probe to observe ^2H by inserting the proper tuning stick and adjusting the probe tuning controls.
3. Attach the lock cable to the observe (OBS) connector on the probe.
4. Lock the spectrometer, and shim on the lock signal. A typical procedure is to first adjust Z1, X, Y, and Z2, then to adjust XZ, YZ, XY, and X2Y2. Readjust Z1 and Z2. Finally adjust any other off-axis shims as necessary.
5. To see how well the field homogeneity has been adjusted, do the following:
    a. Turn the lock transmitter off by entering `lockpower=0 lockgain=0 su.` Disconnect the lock cable from the probe.
    b. Connect the cables so that the observe (OBS) port of the probe is connected to the observe connector on the magnet leg.
    c. Acquire a deuterium spectrum using the deuterium parameter set contained in the library of standard parameter sets. 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, as shown in the sample spectrum in Figure 2.

2.5 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

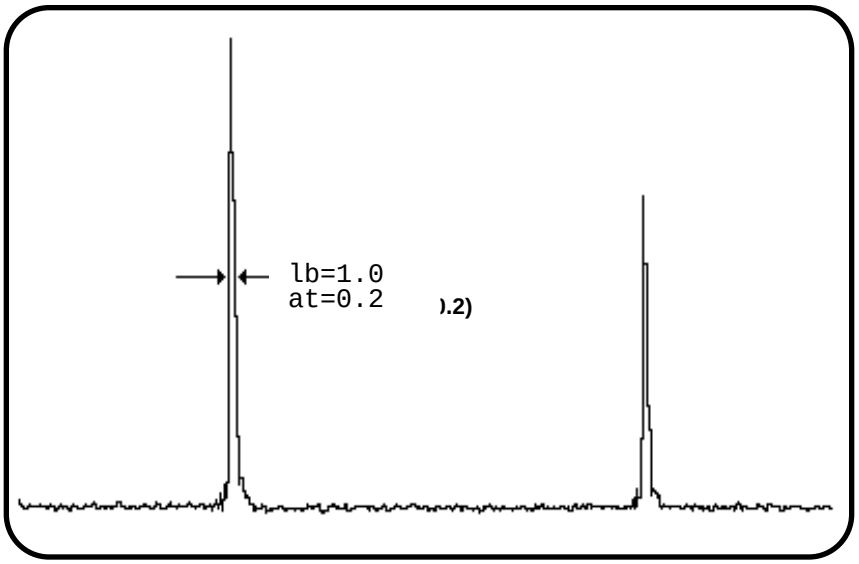


Figure 2. Typical MAS Spectrum of Adamantane

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 day or second day 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 3 illustrates how the angle measuring stem and angle gauge are used.

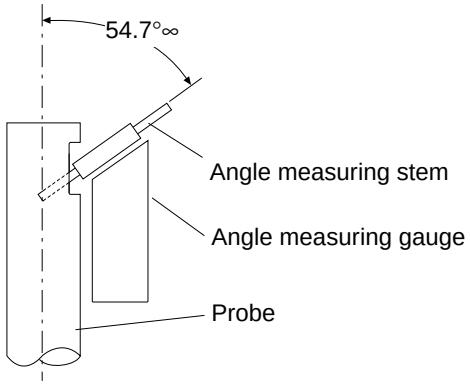


Figure 3. Tools for Coarse Adjustment of Sample Angle

Fine Adjustment

The preferred method of adjusting the magic angle uses the ^{79}Br spectrum of KBr, which has a large chemical shift anisotropy (CSA). When spun at the magic angle, this results in an extensive set of spinning sidebands. As ^{79}Br is very close in frequency to ^{13}C, it is easy to switch between the two nuclei. The magic angle can easily be precisely set (or checked) as described below.

1. Enter **`tn='Br79'`** to obtain the parameter set to observe ^{79}Br.

   If the following message appears

   ```
   Requested nucleus, 'Br79' is not an entry in the nucleus table nuctabXX
   ```

   where `XX` is `2d`, `3d`, or `4d`, then add this nucleus with the following VNMR commands. Note that the first VNMR command invokes the `vi` text editor (familiarity with this UNIX text editor is assumed).

   ```
   vi('/vnmr/nuctables/nuctabXX')
   ```

   Remember to use `nuctab2d`, `nuctab3d`, `nuctab4d`, or `nuctab5d` in place of `nuctabXX`. Add one of the following lines above the `Br81` line:

   - For 200-MHz systems, add:

     ```
     Br79   50.180 1.480e6   low yes 0.0
     ```

   - For 300-MHz systems, add:

     ```
     Br79   75.180 1.480e6   low yes 0.0
     ```

   - For 400-MHz systems, add:

     ```
     Br79 100.208 1.4842e6 low yes 0.0
     ```

   Exit `vi` and then enter `tn='Br79'` again. No error should be generated.

2. Load a rotor with KBr, insert in the probe, spin at 3 kHz, and tune the system for ^{79}Br. Grinding the KBr crystals before packing the rotor is helpful.

3. Set **`seqfil='s2pul' sw=1e5 at=0.02 nt=1`**. Enter **`ga`** to obtain a single transient spectrum. Set the cursor on resonance, and enter `movetof`.

4. Set **`phfid=0`** and enter **`gf`**. Now 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 4 and Figure 5). If the signal is not exactly on

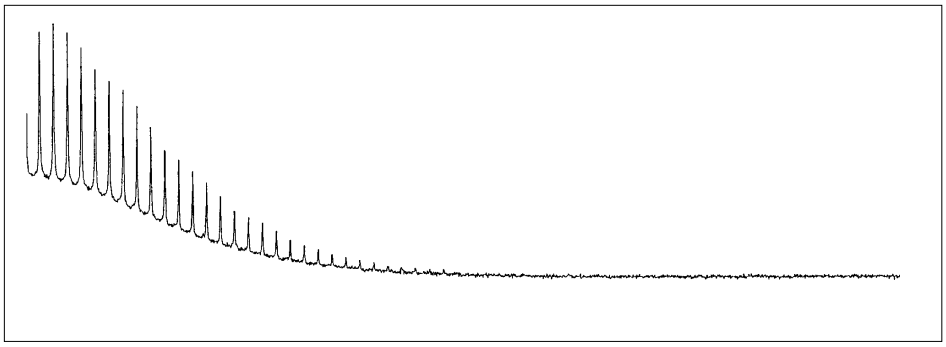


Figure 4. FID Display of KBr on Angle

   resonance, adjust Z0 until it is, then select IPA and adjust `phfid` to maximize the on resonance FID.

5. Adjust the angle using the appropriate method below:

   - *Varian RT CP/MAS probes* – Turn the screw between the two copper coax lines in the probe baseplate.
   - *Varian VT CP/MAS probe* – Turn the fiberglass rod with the adjustment tool.
   - *Doty CP/MAS probe* – Turn the smaller gold rod.

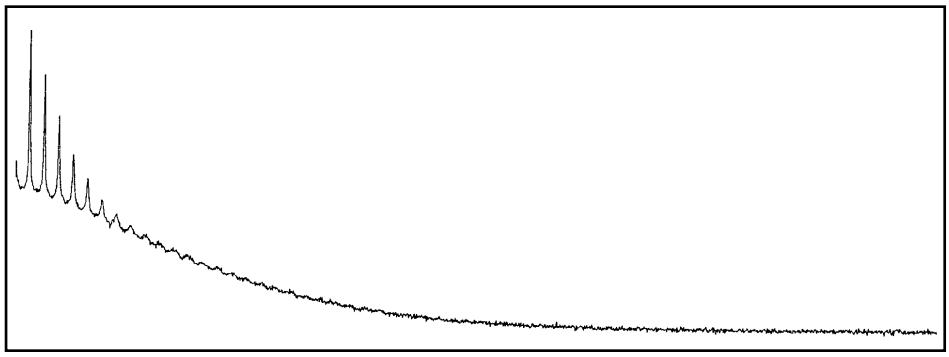


Figure 5. FID Display of KBr 1/2 Turn Off Angle

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.

6. Close the `acqi` window and retune the probe to the appropriate nucleus.

The same sample and general procedure can be used to monitor spinning stability, both in angle and in speed. An angular instability shows in two ways: the shape and size of the exponential varies from transient to transient, and the picket fence is unstable in length and amplitude if the rotor is vibrating.

Instability in the spinning speed can be measured by inspecting the summed FID. If acquisition is continued for a time, the speed variation can be determined from the broadening of pickets well down the fence in time. Run a four-transient FID and enter `df`. With the FID now displayed, use cursors and related commands to edit the display. Measure the resolution of a picket at the start and at the end of the FID display. Similar values indicate good spinning stability.

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 6 shows a typical spectrum, including sidebands, of the aromatic resonance. Adjust the aromatic line for minimum linewidth and maximum intensity.

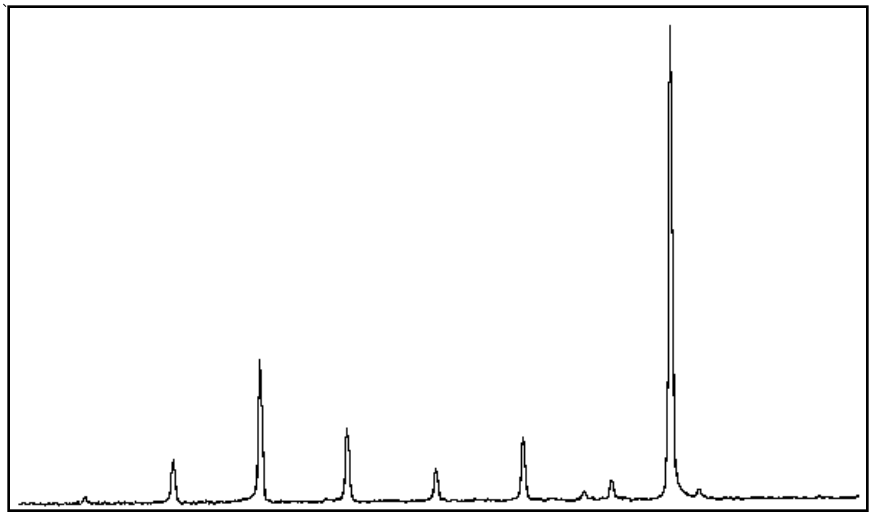


Figure 6. Typical Hexamethylbenzene (HMB) Spectrum

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.

2.6 XPOLAR Pulse Sequence

The Varian-supplied XPOLAR (cross-polarization) pulse sequence is used to obtain CP/MAS NMR spectra of solids. This sequence is used for most experiments. For more information on the XPOLAR pulse sequence, see page 59 (UNITY systems) or page 63 (UNITY*INOVA* and UNITY*plus*)

2.7 Calibrating Pulse Width

The steps below provide instructions for calibrating the pulse width, as well as for connecting the amplifiers and setting the parameters.

CAUTION: **To avoid severe damage to the probe, make sure that the values for the parameters level1 and level2 do not exceed the values given for maximum power for the probe.**

1. Insert a rotor containing p-dioxane and spin it at about 200 Hz.
2. Record a spectrum using gated decoupling (`dm='nny'`) and calibrate the 90° flip time.
3. Recall the parameters from `parlib/xpolar` and set **`d1=5 nt=1 xpol='n' tpwr=45 tpwrf=4095`**. Vary **`pw`**.

   If needed, you can create `tpwrf` with the following commands:

   `create('tpwrf','integer') setlimit('tpwrf',4095,0,1).`

Depending on the probe, 90° pulse widths can range anywhere from 4.0 to 9.0 µs. The observe transmitters can deliver up to 300 W for up to 20 ms (except on VXR-S). Develop a matrix of `tpwr` and `tpwrf` values as they relate to `pw90` and save the matrix for later reference.

CAUTION: **Do not use more than 5% duty cycle for a pulse longer than 0.2 second for the decoupler. For the standard XPOLAR pulse sequence, an error message displays when the duty cycle reaches 20%. Refer to individual probe data sheet for maximum pulse duration.**

2.8 Calibrating Decoupler Power

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

1. Recall test parameters by entering **`rt('/vnmr/tests/hmb')`**.
2. Set **`dof=5e4,-5e4 d1=10`**.
3. Set **`level2`** and **`level2f`** such that the power output is about 80 watts.
4. Enter **`ga`**.

5. When acquisition is finished, measure the reduced coupling on each of the two spectra.

CAUTION: **To avoid damaging the probe, do not exceed the probe decoupler power limit.**

6. Enter **h2cal** to calculate γB_2. If necessary, alter `level2` to obtain a satisfactory value of γB_2.

2.9 Adjusting the Hartmann-Hahn Match

Hartmann-Hahn matching can be readily accomplished by using a sample of hexamethylbenzene (HMB) or adamantane. These substances are not easily cross-polarized. However, they have a high degree of symmetry and so, once cross-polarized, gives rise to very intense signals.

1. Load a rotor with HMB or adamantane, insert it, and spin it slowly (about 2500 Hz for HMB or 1800 Hz for adamantane). Adjust the spinning speed so that none of the sidebands of the aromatic carbons overlap the methyl resonance.
2. Recall the test parameters by entering **rt('/vnmr/tests/hmb')**. Set **xpol='y'**. Set **pw** to a 90° ^{13}C pulse. Set **p2=2500 at=0.05 d1=4 nt=4.**
3. Set **level2** and **level2f** as determined in the previous section and array **level1** to pass across the Hartmann-Hahn condition, with the value of `level1` not to exceed `level2`. Enter a fixed value of **gain**, because Autogain cannot be used in an arrayed experiment.
4. Enter **ga**. When acquisition is finished, enter **dssh** to display the results. Select the spectrum with the maximum signal and set **level1** to the value +1 for this spectrum (in the next step, we reduce `level1f`).
5. Array **level1f** with the full range, 0 to 4000 in steps of 500.
6. Enter **ga**, and when acquisition is finished, enter **dssh**. Select the value of **level1f** that gives the maximum signal.

   For an even closer match, array `level1f` in smaller steps around this value.

   For systems equipped with an observe fine attenuator, `tpwrf` can also be used.

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 XPOLAR 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 `p2`. 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

Thus a time exists for which an optimum in the magnetization occurs.

The optimum `p2` 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 `p2` is highly desirable. Figure 7 shows a typical optimization. Note that a simultaneous optimum for all carbons in a spectrum does not necessarily occur. Generally a value of 1000 µs is adequate for normal, crystalline solids and 3000 µs for soft solids.

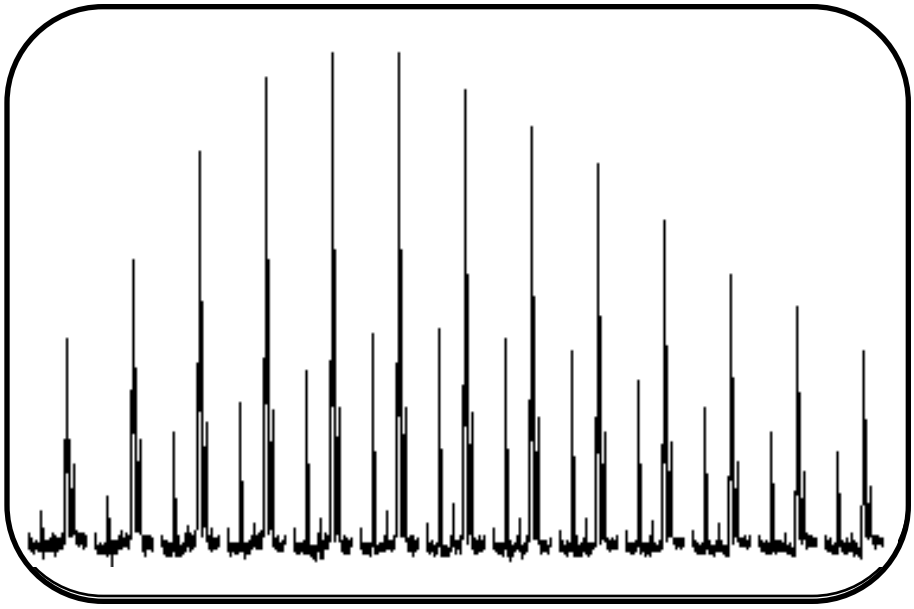


Figure 7. Array of Contact Times

Optimizing the Repetition Rate

Acquisition times in CP/MAS spectra are determined by the desired spectral resolution. Typically, set `sw=300p` (or `sw=300*sfrq`). With `at=0.064`, this gives at least 2048 data points and a digital resolution of 4 Hz, a reasonable value.

The repetition rate is consequently determined by the parameter `d1`, the delay between pulses. CP/MAS spectra are acquired with 90° observe pulses. In this case, the optimum repetition rate is 1.25*T_1. For cross-polarization spectra, this T_1 is the T_1 of the protons; for gated-decoupling spectra, it is the T_1 of the carbon or other nucleus. These 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 is 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 XPOLAR sequence (see Figure 8). Note that the parameter `srate` should be set to the spinning speed in Hz.

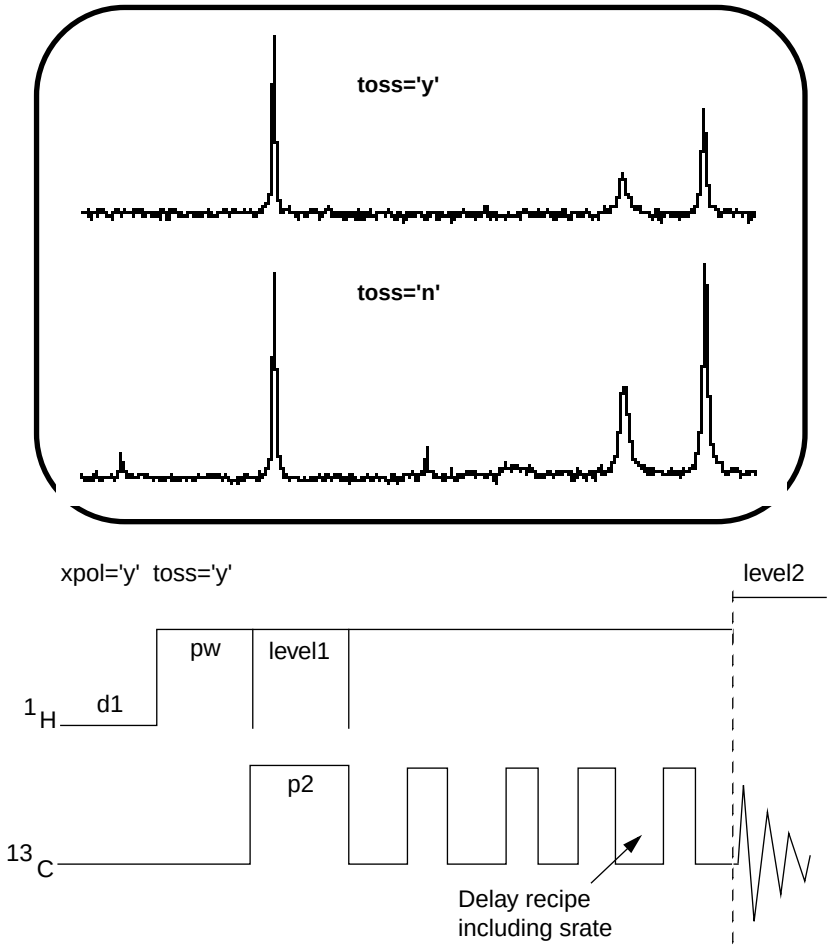


Figure 8. TOSS Experiment on Alanine (Spectrum and Sequence)

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

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 9 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 `d2` (in seconds), the dephasing time.

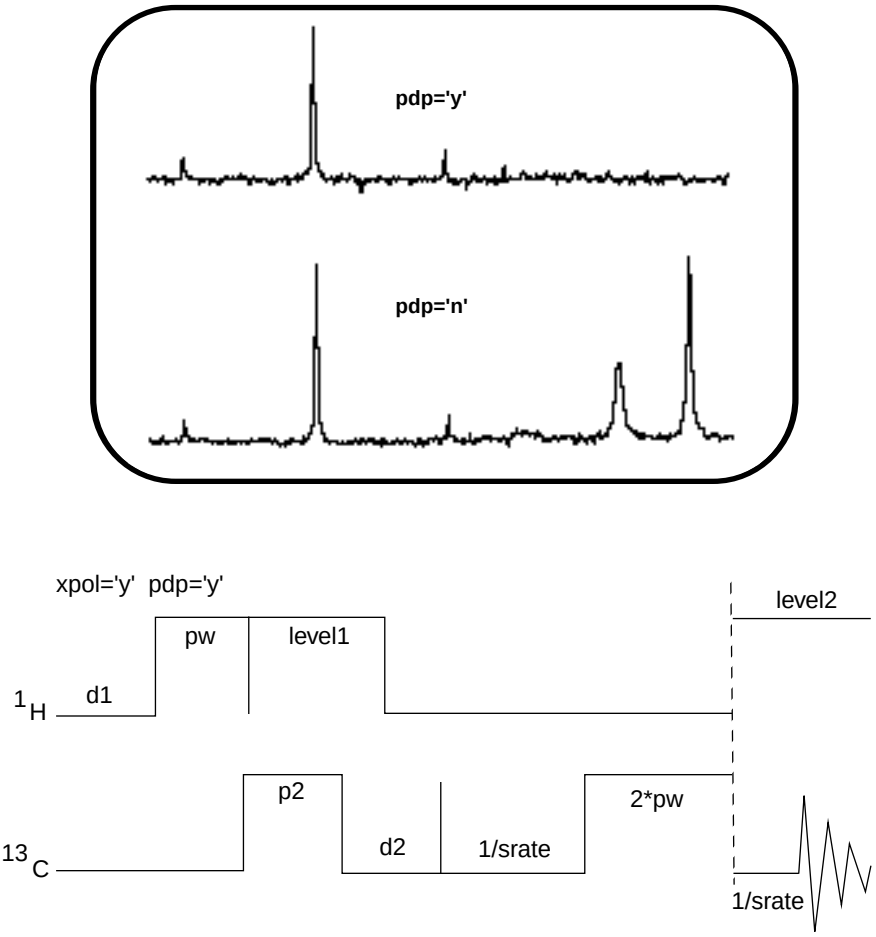


Figure 9. Protonated Carbon Suppression of Alanine (Spectrum and Sequence)

^{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 XPOLAR pulse sequence. Anytime that `p3` is set to a non-zero value, a $T_{1\rho}$ decay is introduced; thus, by setting `p3` to an array, $T_{1\rho}$ is measured. Typical values for `p3` would range from 50 to 5000 µs.

To analyze a $T_{1\rho}$ experiment for the decay time constant, enter

```
analyze('expfit','p3','t2','list')
```

or use the menu buttons for T_2 analysis. In experiments other than $T_{1\rho}$ experiments, `p3` should be set to 0. Figure 10 shows the spin-lattice relaxation measurement pulse sequence.

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

^{1}H T_1 can be measured using the XPOLAR pulse sequence by setting it up to perform a standard inversion-recovery experiment on the protons followed by cross-polarization of the remain ^{1}H magnetization to the carbons. Figure 11 illustrates the pulse sequence.

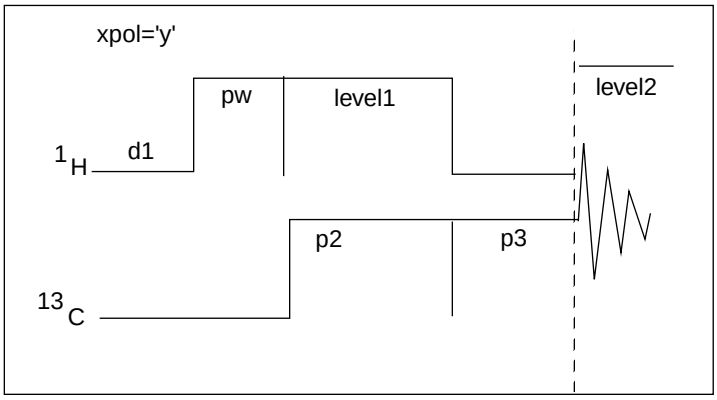


Figure 10. Rotating-Frame Spin-Lattice Relaxation Measurements Sequence

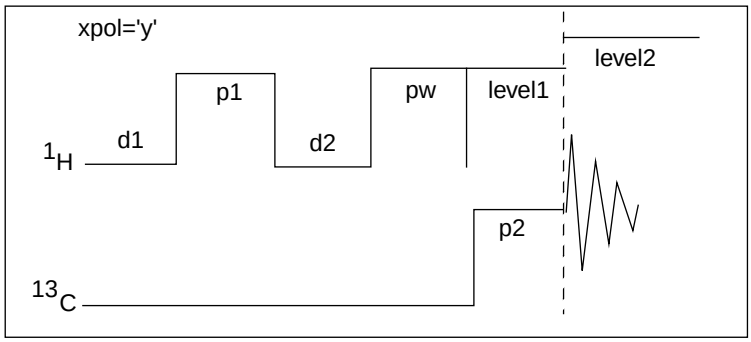


Figure 11. Pulse Sequence for Measuring ^{1}H T_1

2.11 Spectral Referencing

A variety of methods are found in the literature for spectral referencing. Some involve a small sealed capsule of TMS centered in the sample. Others use a small piece of polyethylene as a secondary reference. For most purposes, primary and secondary referencing are not necessary, and external secondary spectral referencing can be used as follows:

1. Insert a standard sample (e.g., HMB).
2. Obtain a spectrum and set spectral referencing. (For HMB, set the cursor on the aromatic line and enter `rl(132.1p)).`
3. Adjust the display window as desired (for ^{13}C, enter `wp=200p sp=0).`
4. Remove the standard sample and insert the sample of interest. Obtain a spectrum.

Both field drift and field shifts affect this type of referencing. Field drift is typically small and can be ignored. Field shifts due to magnetic susceptibility effects are finite but small. Chemical shifts measured as described above are in all cases reasonable, but for a series of similar compounds, the relative chemical shifts are even better.

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 3.

The `setref` command adjusts referencing so that the solvent frequency is correct, even when no reference substance is present in the sample.

`setref` uses absolute resonance frequencies as defined in a file `/vnmr/nuctables/nuctabref`; currently, about 25 of the most common nuclei are covered in this file. `setref` can easily be expanded to cover any other nucleus as well; a recipe on how to expand `setref` is given in the header of the file `/vnmr/nuctables/nuctabref`.

Table 3. Reference Materials and ^{13}C Chemical Shifts

Substance	*Chemical shift (ppm)*
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

2.12 Further Reading on Solid-State NMR

General Sources on Line Narrowing in Solids

Gray, G. A.; Hill, H. D. W. *Industrial Res. and Dev.* **1980** (March).

Miknis, F. P.; Bartuska, V. J.; Maciel, G. E. *Am. Lab.* **1979** (November).

Griffin, R.G. *Anal. Chem*. **1977**, *49*, 951A.

Fyfe, C. A. *Solid State NMR for Chemists*. CFC Press: Guelph, 1983.

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.

Relaxation Times

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

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.

Frye, J.; Maciel, G. E. Magical Angle Adjustment with KBr. *J Magn. Res.* **1980**.

2.13 Useful Conversions

Convert from 90° pulse width to γH:

$$\gamma H_2(kHz) = \frac{250}{90°\,pulse\,width}(\mu s)$$

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

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

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

Convert from rf fields to power levels:

$P\ (watts) \propto (\gamma H)^2$

Chapter 3. Wideline Solids Module Operation

Sections in this chapter:

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. $\gamma H1$ 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 µs 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 ^{13}C 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 4.

Table 4. Bessel Filter Outputs

`sw` *(kHz)*	`fb` *(kHz)*
100 – 225	256
> 225	1000
300 – 540	300
540 – 1260	700
1260 – 1800	1000
> 1800	2400

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.

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 12, 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 ^{1}H or ^{19}F 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.

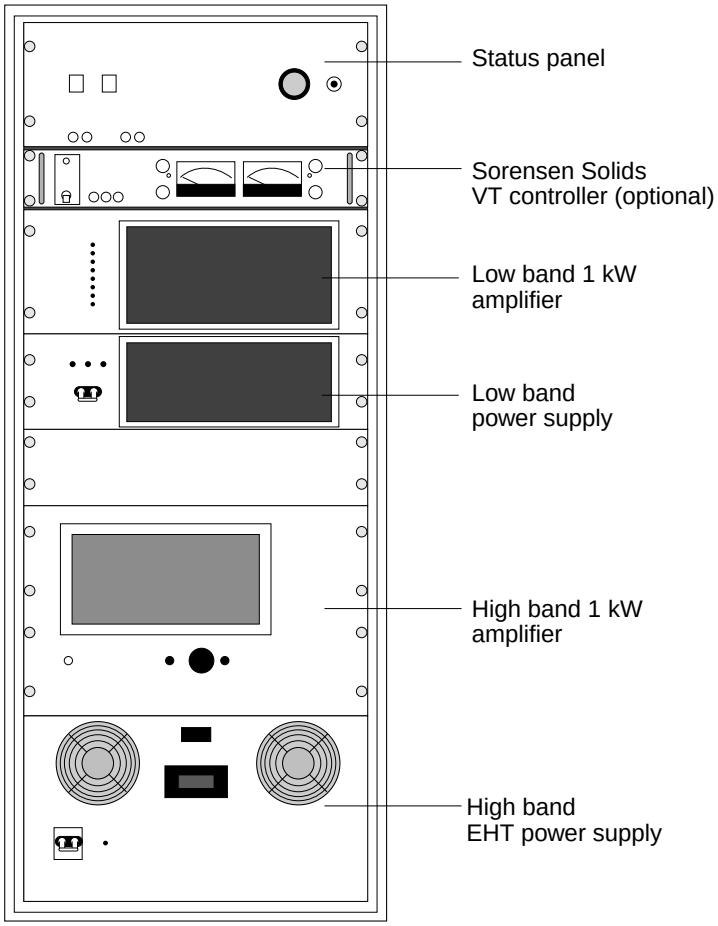


Figure 12. Solids Cabinet Layout, Open Front View

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 `tpwr`, in other words, `tpwr=60` delivers 1 kW (60 dBm) and `tpwr=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 µs 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 `tpwr` 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 `tpwr=63`. To get low power from the high-power amplifier, `tpwr` 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 12) 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 5 lists commands and parameters related to wideline experiments.

Table 5. Wideline Experiment Commands and Parameters

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

Dipolar Nuclei (I = 1/2)

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

In ^{1}H 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 ^{2}H (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, (^{l3}Na)^{27}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 ^{2}H, 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 ^{2}H 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 UNITY*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 UNITY*plus* and 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 UNITY*INOVA* and UNITY*plus* systems.

3.5 Standard Wideline Samples

Two standard wideline samples are provided with the system, malonic acid-d_4 for ^2H and sodium nitrate for ^{23}Na 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-d_4 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% D_2O (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% D_2O 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 D_2O 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 D_2O sample with the malonic acid–d_4 sample and tune the probe.
14. Enter **ssecho** to convert the s2pul 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 isplay 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 ^{23}Na

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 H_2O). 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 41.
4. Remove the sealed sample of NaCl (1 M in H_2O) and replace it with the sample to solid sodium nitrate.
5. Tune the probe and enter ssecho to convert to the QUADECHO 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); `exp`*n* 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:

The CRAMPS/multipulse module is available for 300-MHz and 400-MHz spectrometer systems. It provides wideline capability for ^{1}H and ^{19}F, including the ability to perform multipulse experiments such as MREV8 and BR24. The standard liquids high-band amplifier is boosted to an upper limit of 1 kW by a tuned, linear amplifier. The main components are a wideband ADC, high-band high-power amplifier, fine attenuator, and pneumatics/tachometer control box.

For UNITY and VXR-S systems, the sync module is used to synchronize acquisition to the master clock. Also, the liquids observe receiver is replaced by a wideband observe receiver, described in “Wideline Solids Module,” page 34.

4.1 CRAMPS/Multipulse Module Hardware

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.

Motor Control Box

The motor control box is used to adjust the output load and tuning of the 1 kW proton amplifier (see below). It consists of a selector switch with 3 positions—TUNE, LOAD and STANDBY (or AUX)—and two 3-position toggle switches, COARSE and FINE. The toggles are momentary contact and can be pushed sideways in two directions (which are designated IN and OUT).

The box moves the end plates of the cavity in or out to affect the tuning process. In each of the active positions, the plate position is displayed on a meter on the box.

1-kW Amplifier

The decoupler amplifier uses an EIMAC cavity tube. Thus the amplifier has both low-voltage power supplies and a high-voltage supply. The high-voltage power supply (EHT) is 2.3 kV and is produced by the unit in the bottom of the solids cabinet. Low-voltage supplies are produced by a unit in the bottom of the cabinet behind the EHT.

The amplifier is tuned by three controls to the frequency at which it is to be used. It is able to produce up to 1 kW output for periods up to 250 ms, or lower levels for longer periods.

The amplifier runs in a linear mode and can be considered to be a gain stage added to the liquids high-band amplifier. The 1 kW stage operates in either blanked or unblanked modes in exactly the same manner as its low-power driver. It should never be driven by more than 50 W (47 dBm).

Three controls are used to tune the amplifier: INPUT TUNING, on the front of the amplifier, and OUTPUT TUNE and LOAD, on the remote motor control box.

When used for CRAMPS/Multipulse in the observe transmit chain, the amplifier is run blanked, rather than unblanked as in CP/MAS. As a result, sufficient unblanking time (`rof1`) must be allowed for the amplifier to turn on. The whole transmit amplifier chain requires a `rof1` of 1.5 (µs) for this. The reblanking time is very short, so that `rof2` can be set to zero. These timings ignore any probe ring-down issues.

If the system is equipped with 6-dB fine attenuators, `tpwrf` and `tpwr` must be set and used, whether high power is selected or not.

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)` at an appropriate point. This is commonly used in multipulse sequences to improve stability when running high-resolution experiments for a long time. The *VNMR User Programming Manual* describes its use in more detail.

CRAMPS Probe

The standard CRAMPS probe has a VT range from –120° to +160° C and can typically tune from the ^{19}F frequency to that of ^{1}H. It is optimized for ^{1}H and is essentially background free for that nucleus. In order to achieve low ^{1}H background, many components are made of a fluorocarbon, so that a high ^{19}F background exists. This may not necessarily preclude ^{19}F line narrowing experiments, but care must be taken.

WARNING: **Dangerous high rf voltage in the system can cause serious injury or death. To avoid electrical shock completely turn off rf and disconnect all rf cables before removing the probe.**

WARNING: **Spinner rotors have very high kinetic energy and can disintegrate at any time. To prevent possible cuts or blindness, wear a certified full-faced safety shield and cover all exposed skin while observing a rotating sample**

The CRAMPS probe has a 5-mm rotor and is designed to spin to 8 kHz. The probe does not have high sensitivity because sensitivity is not normally an issue in multipulse experiments, where proton is an abundant spin. Where rare spin conditions apply, the damping box can be removed, in which case the ring-down time will be longer.

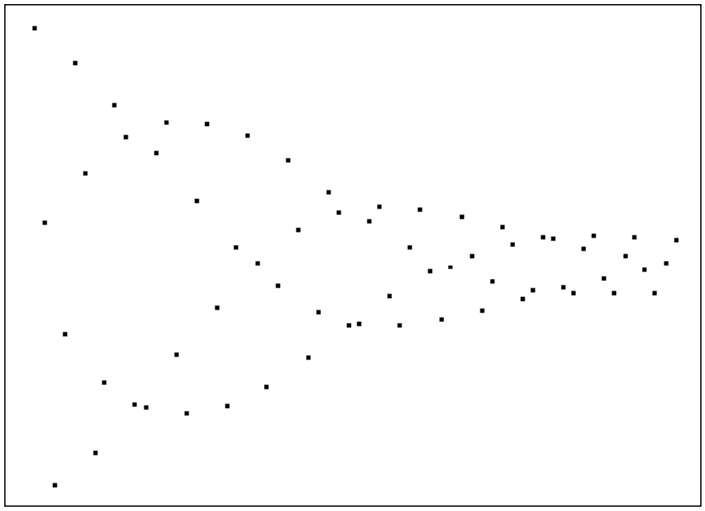
4.2 Running the FLIPFLIP Pulse Sequence

The FLIPFLIP pulse sequence is set up by running the `flipflop` macro and setting the parameter `phase2` to 0, as follows:

1. Enter `flipflop` and set **`d1=4 pw=1.5 fb=1e6 sw=2e6 np=128 tau=7 rof1=1.5 rof2=0`**.
2. Set **`phase1=0 phase2=0 phaser=0 phfid=0`** or **`'n' trig='n' gain=0 nt=1 dp='y'`**.

   Note that `trig='n'` is needed for UNITY*INOVA* and UNITY*plus* systems because the 500-kHz synching signal is not available; otherwise, set `trig='y'`.
3. Acquire a FID and enter **`df`** to display both real and imaginary components. Adjust the phase to minimize the imaginary signal. If this is not possible, check that the signal is on resonance.
4. Enter **`phaser=phfid phfid='n'`** and reacquire.

   The imaginary channel should be minimal. The real channel should show a FID pattern similar to Figure 13.



```
 ACQUISITION        SAMPLE             PROCESSING          FLAGS
sfrq  399.952     date   Apr 1 93     lb     not used     il           n
tn          H1    file        exp     sb     not used     in           n
np         128       DECOUPLING       gf     not used     dp           y
sw       2e+06     dn            H1    awc    not used     trig         y
fb       1e+06     dof            0    lsfid          0        SPECIAL
bs          16     dm             n    phfid  not used     srate     1542
ss           0     dpwr          30    fn          4096     temp      27.0
tpwr        54
tpwrf     3500                         werr                 tauc    10.000
pw       1.500                    0    wexp          df     mp_at 0.000640
tau      3.500                         wbs
d1       4.000                         wnt                  phase1       0
tof    -2986.3                            FLAGS             phase2       0
nt           1                         ai cdc ph            phaser       0
ct           1
```

Figure 13. Real Channel FID Pattern

5. Count the number of points in one cycle of the FID and the reestimate **pw** for a 90° pulse from the relationship `pw=pw * 4/`*n*, where *n* is the number of points in one cycle.
6. Repeat the acquisition, adjusting **pw** and then **tpwr** to get approximately a 1.5 µs 90° pulse.
7. Enter **gf**, then connect the `acqi` window. Select FID and then IPA. Adjust **tpwrf** until a pattern similar to Figure 14 is obtained. This occurs at the exact 90° pulse.

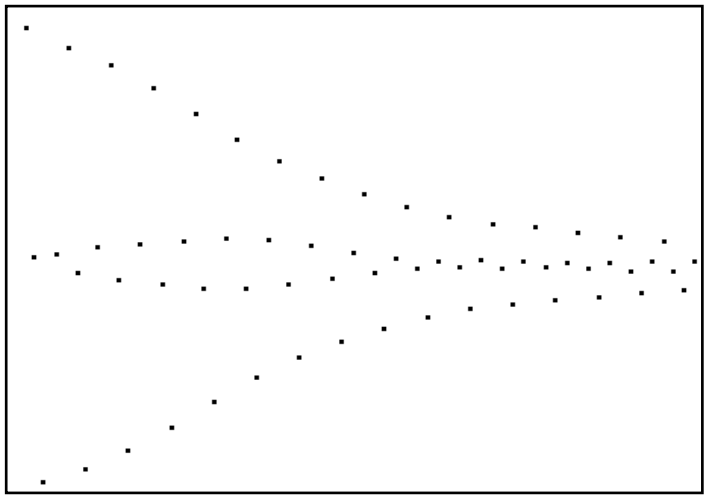


Figure 14. FLIPFLIP FID at Exact 90° Pulse

For further information on the FLIPFLIP pulse sequence, refer to page 100.

4.3 Running the FLIPFLOP Pulse Sequence

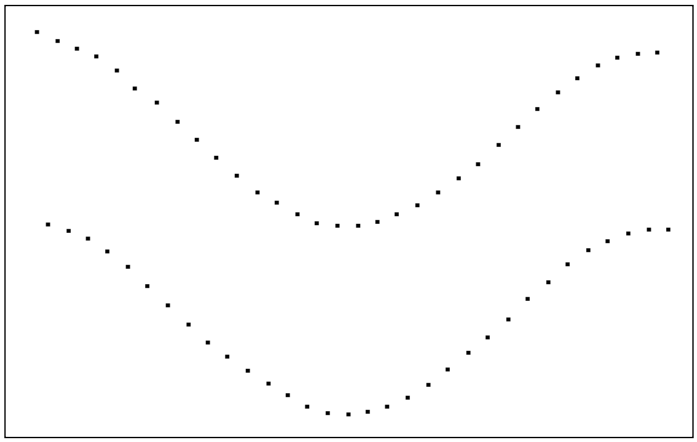
To run the FLIPFLOP pulse sequence rather that the FLIPFLIP pulse sequence, set `phase2=2`. This train of pulses alternately flips the spins into the XY plane—giving an NMR signal—and back to the Z axis—giving no NMR signal.

This sequence is used for other adjustments in most CRAMPS/Multipulse spectrometers, but because of the phase shifting circuit used in the UNITY*INOVA* and UNITY*plus* systems, this sequence is only used to remove “phase glitch” caused by asymmetric phase transients at the beginning and end of each pulse. The resulting FID of the FLIPFLOP pulse sequence appears as a set of “tram tracks” as shown in Figure 15.

The adjustment to remove phase glitch is done either at the probe or at the 1 kW high band amplifier. After setting `phase2=2`, enter `gf` and then interactively observe the FID, using the `acqi` window.

If the FID shows a sine wave in the tram tracks, carefully adjust the probe tune or match to remove it. If this cannot be done, carefully adjust the 1 kW amplifier tune or load. The desired result is shown in Figure 16.

Finally, set `phase2=0` and repeat the `pw90` determination as outlined above, using the FLIPFLIP process. No re-examination of gating is required, but the 90° pulse should be set as precisely as possible.



```
 ACQUISITION          SAMPLE              PROCESSING            FLAGS
sfrq  399.952     date   Apr 1 93     lb     not used     il            n
tn          H1    file         exp     sb     not used     in            n
np         128       DECOUPLING       gf     not used     dp            y
sw       2e+06     dn            H1    awc    not used     trig          y
fb       1e+06     dof            0    lsfid          0       SPECIAL
bs          16     dm             n    phfid  not used     srate      1542
ss           0     dpwr          30    fn          4096     temp       27.0
tpwr        54
tpwrf     2794                         werr                 tauc     10.000
pw       1.400                         wexp          df     mp_at  0.000640
tau     10.000                         wbs
d1       4.000                         wnt                  phase1         0
tof    -2986.3                            FLAGS             phase2         0
nt           1                         ai cdc ph            phaser     65.7
ct           0
```

Figure 15. FLIPFLOP “Tram Tracks”

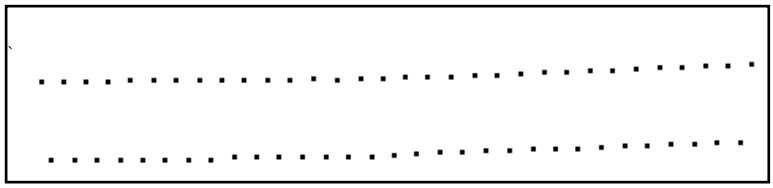


Figure 16. FLIPFLOP Desired FID

For further information on the FLIPFLOP pulse sequence, refer to page 101.

4.4 Using MREV8 to Demonstrate Multipulse Operation

The MREV8 pulse sequence demonstrates the operation of the multipulse system.

1. Enter **`mrev8`** to set up the parameters for the MREV8 pulse sequence.
2. Make sure that **`tau=3.5`**, **`rof1=1.5`**, and **`rof2=0`**.
3. Enter **`go`**. A FID should be obtained.

If the FID is off resonance, enter `gf` or enter `acqi` and adjust probe tune/match to place the FID on resonance.

4. Array **`tof`** from `-1e4` to `1e4`, in 1000-Hz steps.
5. Set **`d1=20`** and enter **`ga`**.

   The resultant displayed spectra should show a single resonance that moves with `tof`. Note that changing `tof` by 1000 Hz does not move the peak by 1000 Hz!
6. Write down the value of `tof` that gives the sharpest line. This is a guide for later use of the multipulse sequences.

For further information about the MREV8 pulse sequence, refer to page 103.

Chapter 5. Solid-State NMR Accessories

Sections in this chapter:

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 17 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:

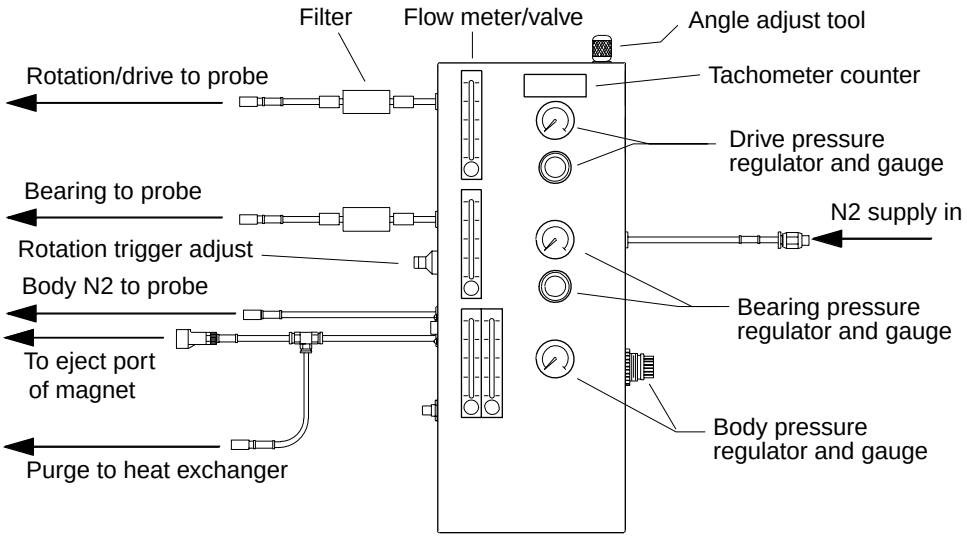


Figure 17. Pneumatics/Tachometer Box for CP/MAS Probes

- 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 18.
- 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 18.
- 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 18.

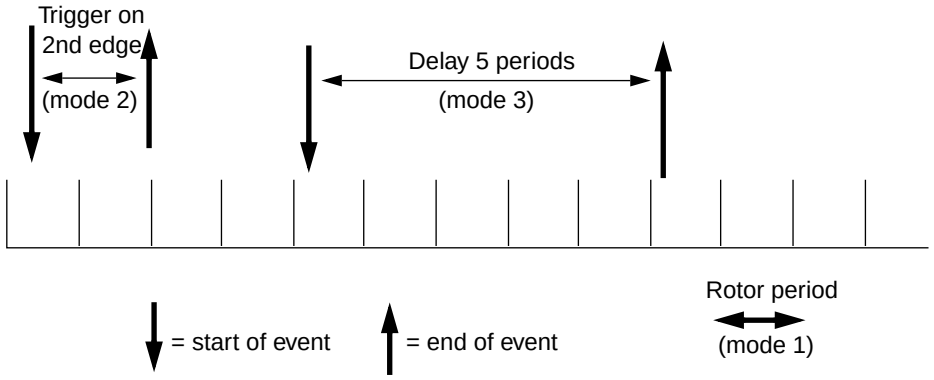


Figure 18. Different Modes of the Rotor Synchronization Accessory

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 19) 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.

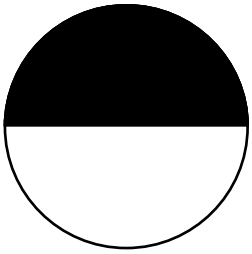


Figure 19. Base of a Varian High-Speed Spinning Rotor

In principle, detection in the Doty probe is the same. Figure 20 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 20. 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 ≤ 0.5° 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 µs for spinning speeds to 5 kHz. This corresponds to an angular uncertainty of ≤ 2° at a spinning speed of 3600 Hz. This is expected over the temperature range of –50 °C to +100 °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 6 lists parameters used with the rotor synchronization accessory.

Table 6. Rotor Synchronization Controls

Parameters	
`hsrotor` {'y', 'n'}	Display rotor speed for solids operation
`in` {'y', 'n'}	Interlock
`srate` {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 19 shows the marking on the base of Varian high-speed spinning rotors and Figure 20 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 20, 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:

Actions	*Keys*
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 7. G3 and G4 set to 0 produce good control when the ranges shown in the table are used for the other gains.

Table 7. Rotor Controller Gain Setting and Typical Ranges

Gain Setting	*Typical Ranges*
G1	4 to 5
G2	1 to 2

Gain Setting	*Typical Ranges*
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:

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 UNITY*plus* 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 `maclib`. The macros for other solid-state NMR sequences are located in the user library `userlib`.

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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 UNITY*plus* systems, see page 63). 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 21 shows the pulse sequence diagram for cross-polarization with TOSS.

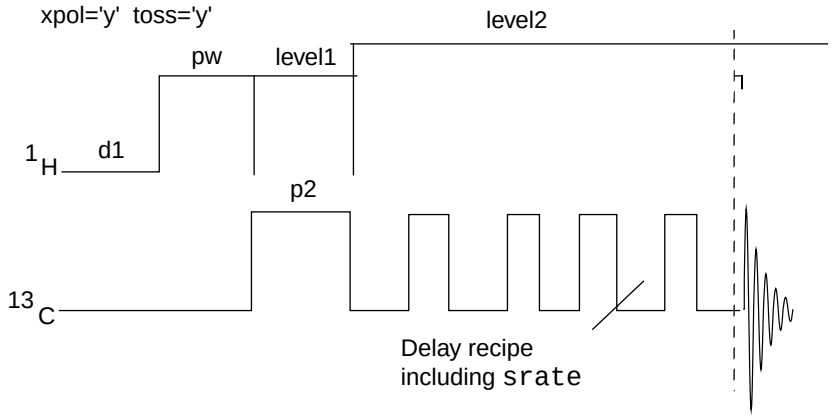

Figure 21. TOSS Pulse Sequence

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 22 shows the pulse sequence diagram for cross-polarization with interrupted decoupling.

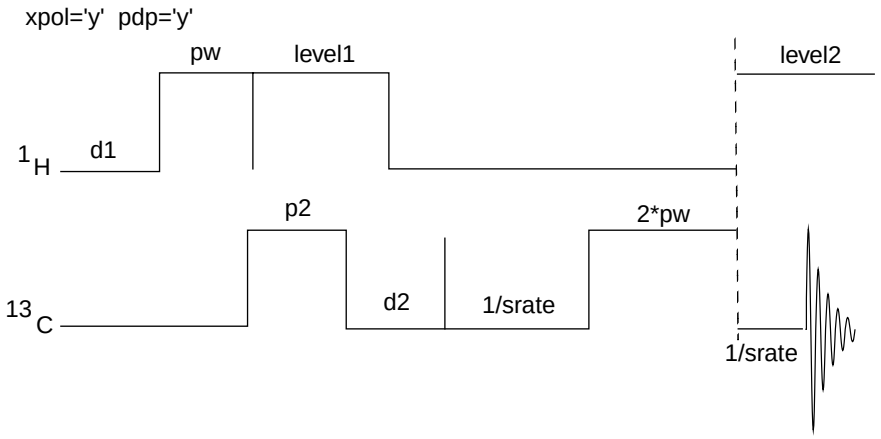

Figure 22. Protonated Carbon Suppression Sequence

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 23 is a diagram of the sequence.

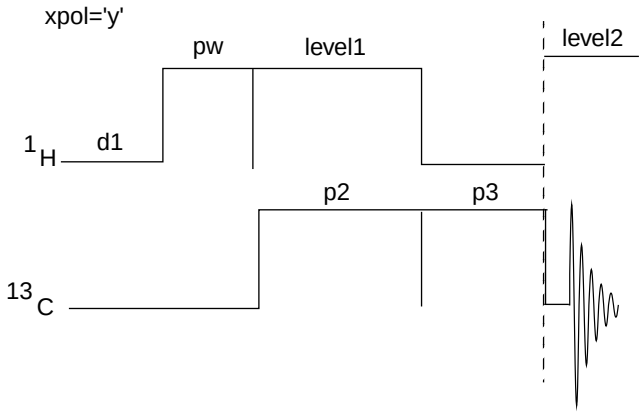

Figure 23. Rotating-Frame Spin-Lattice Relaxation Measurements Sequence

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 24 is a diagram of the pulse sequence. The `xpolar` macro sets up parameters for the XPOLAR pulse sequence.

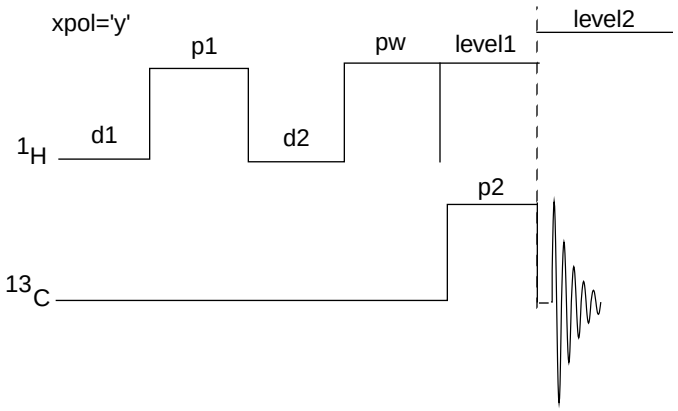

Figure 24. Pulse Sequence for Measuring ^1H T_1

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 UNITY*plus* 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 UNITY*plus* systems, divided into 4095 steps. `level1` and `level2` override `dpwr`.

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6.2 XPOLAR1—Cross-Polarization, UNITY*INOVA* & UNITY*plus*

XPOLAR1 is a version of XPOLAR that has been modified for UNITY*INOVA* and UNITY*plus* systems. It contains the same functionality as XPOLAR (described on page 59) with the exception that the parameters that control the attenuators and linear modulators have been renamed. Figure 25 is a diagram of XPOLAR1.

For UNITY*INOVA* and UNITY*plus*, it is recommended that you control the power levels associated with cross-polarization entirely with the linear modulator, which has a range of 60 dB, and set the coarse attenuator to a value corresponding to the maximum specification of the probe. The parameter `level1` has been disabled (it can be re-enabled as `cppwr` with `dblvl2='y'`). Other parameters have been given more descriptive names, as described below.

Applicability

XPOLAR1 is available only on UNITY*INOVA* and UNITY*plus* systems and can be found in `psglib`.

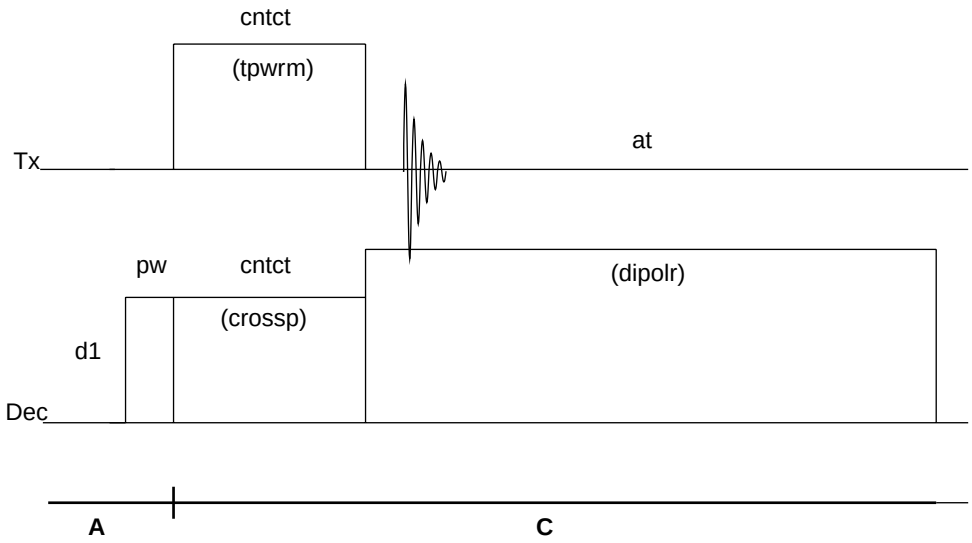

Figure 25. XPOLAR1 Pulse Sequence

Macro

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. 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=dipol p2=cntct tpwrf=tpwrm`) and `dblvl2` is set to `'y'`.

Note that `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

The following parameters have consistent definition throughout all UNITY*INOVA* and UNITY*plus* solids pulse sequences. Most sequences, other than XPOLAR and XPOLAR1, assume `xpol='y'` (for cross-polarization) and `xpol` is not settable.

- `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.
- `cntct` is the cross-polarization contact time, in microseconds.
- `tpwr` is the observe power setting (–16 dB minimum to 63 dB maximum power).
- `tpwrm` is the observe linear modulator setting (0 minimum voltage to 4095 maximum voltage). 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 during the acquisition period (–16 dB minimum to 63 dB maximum power). See also `cppwr` and `dblvl2` below.
- `dipolr` is the decoupler linear modulator setting during acquisition (0 minimum voltage to 4095 maximum voltage). The value of `dipolr` is linearly proportional to

the applied decoupler voltage—doubling `dipolr` doubles the decoupler field strength (in kHz).

- `cppwr` is the decoupler power setting during cross-polarization and during the initial proton 90° pulse (–16 dB minimum power to 63 dB maximum power). The parameter `cppwr` is active only if `dblvl2='y'`. If `dblvl2='n'`, only `dpwr` is used.
- `dblvl2` set to `'y'` activates `cppwr` during cross-polarization and the initial proton 90°° pulse. For UNITY*INOVA* and UNITY*plus*, setting `dblvl2` to `'n'` is recommended.
- `crossp` is the decoupler linear modulator setting during cross-polarization and the initial 90° pulse (0 minimum voltage to 4095 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.
- For UNITY*INOVA* and UNITY*plus*, the recommended settings are `dblvl2` to `'n'`, `dpwr` to the maximum power rating of the probe, the cross-polarization field strength controlled by `crossp`, and the decoupling field strength controlled by `dipolr`. If `dblvl2` is set to `'n'`, the parameters `dblvl2` and `cppwr` are hidden and can be ignored. (Beware: UNITY*INOVA* and UNITY*plus* sequences as written have not been fully tested with a UNITY system. Consult the applications laboratory for support.)

Additional parameters for `xpolar1` on UNITY*INOVA* and UNITY*plus* systems:

- `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 `d2` to cause suppression of protonated carbons.
- `d2` is set greater than 0.0 (see `p180` and `pdp`). `d2` is in seconds.
- `srate` is the sample spinning speed, in Hz.
- `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 because delays of `1.0/srate` are used.

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 26 is a diagram of the sequence.

Applicability

XPWXCAL is available only on UNITY*INOVA* and UNITY*plus*. It is found in `userlib`.

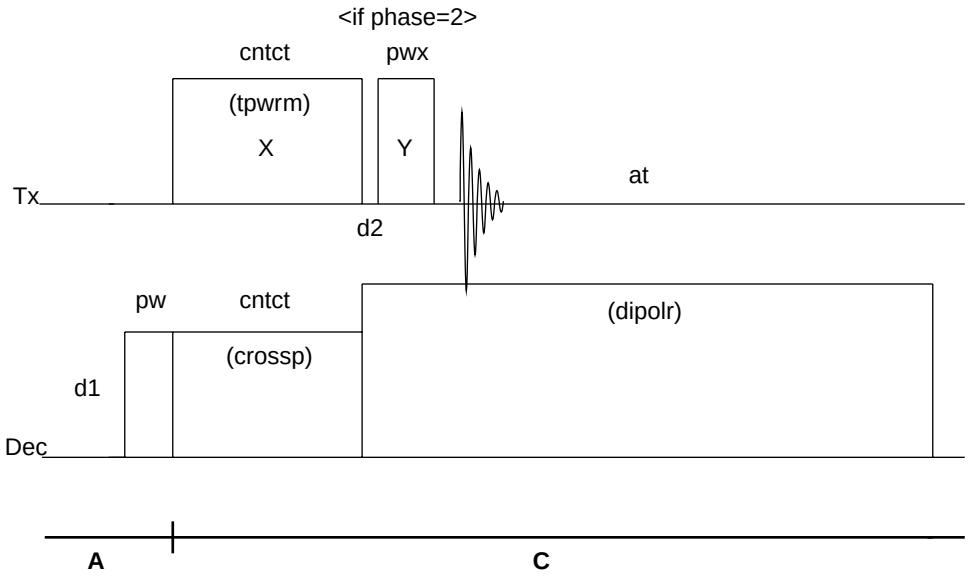

Figure 26. XPWXCAL Pulse Sequence

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 UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See page 63 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 27 is a diagram of the sequence.

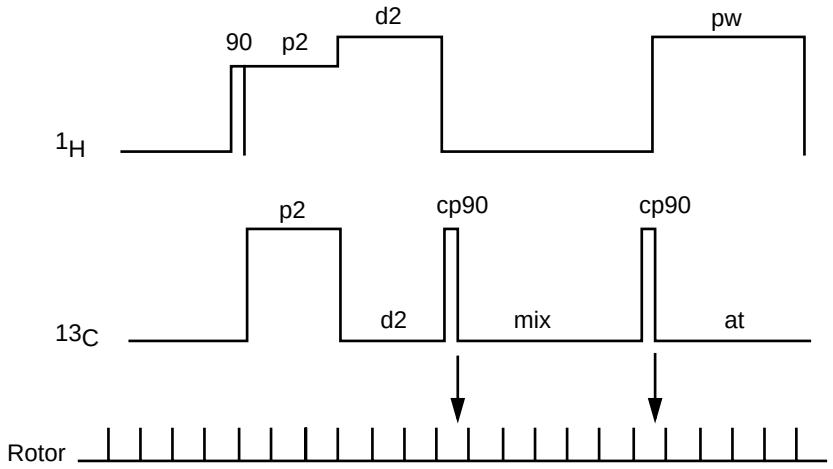

Figure 27. XNOESYSYNC Pulse Sequence

Macro

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

Parameters

`pw` is the ^{1}H 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.

`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.

`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 synched 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 28 is a diagram of the sequence.

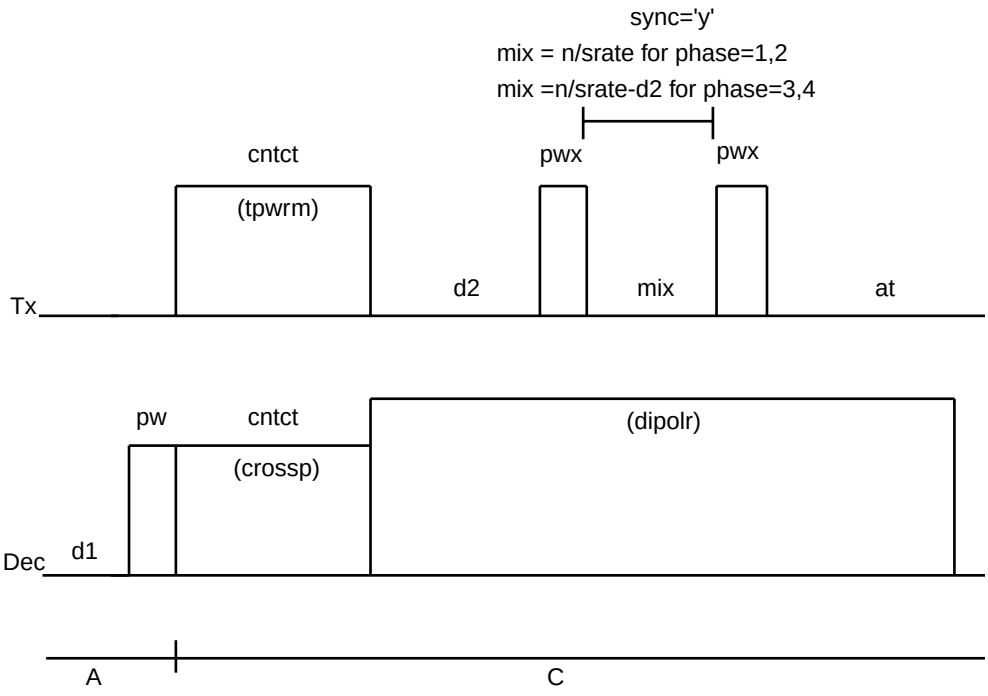

Figure 28. MASEXCH1 Pulse Sequence

Applicability

MASEXCH1 is available on UNITY*INOVA* and UNITY*plus* 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)`.

Parameters

MASEXCH1makes use of the UNITY*INOVA* and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw` and `cntct`. See page 63 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 (`ni-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 ^{1}H –^{13}C heteronuclear chemical shift correlation (HETCOR) experiment for solid-state materials. Analogous to solution-state HETCOR experiments, this sequence provides correlation between ^{1}H 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 63 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 ^{1}H 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/(bmult*12*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 ^{1}H chemical shift region if a pedestal is present in f_1. In this case, set `dipoff` for the center of the ^{1}H 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 ^{1}H–^{1}H and X–^{1}H 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`, `dblv12`, `pw` and `cntct` (see page 63 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 `shapelib`. 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 `shapelib` 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`, `tpwrm`, `dpwr`, `cppwr`, `crossp`, `db1v12`, `pw` and `cntct` (see page 63 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 ±10° to 30 degrees°. 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}C–^{1}H dipolar interaction.

`fslg2.DEC` provides phase continuous frequency switched Lee-Goldberg decoupling. This pattern decouples protons from themselves, but leaves a residual ^{13}C–^{1}H 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 29 is a diagram of the sequence.

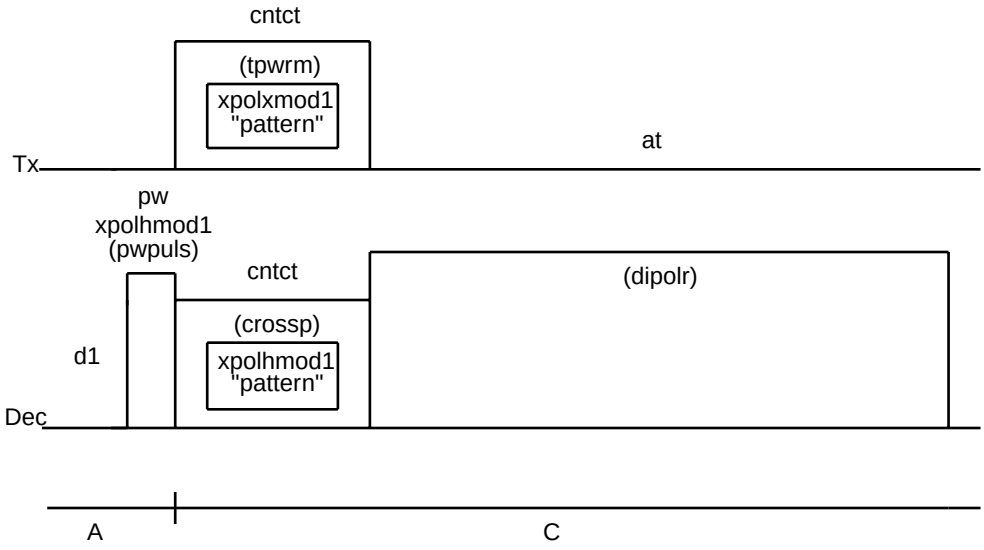

Figure 29. XPOLXMOD1 Pulse Sequence

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 XPOLHMOD1make use of the UNITY*plus* and UNITY *INOVA* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw` and `cntct`. See page 63 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.

`pwpuls` 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:

```
amp*(1.0 - frac/2.0 + (frac/2.0)*cos(t/per))
```

where `t` is time. The resulting `.DEC` file has the form `xmodcos_frac_per_amp.DEC` where `frac` is x10000 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:

```
amp*(1.0 - frac/2.0 + (frac/2.0)*(1.0 - 4.0*t/per))
for  0.0 < t < per/2.0
```

and

```
amp*(1.0 - frac/2.0 + (frac/2.0)*(-1.0 + 4.0*t/per))
```
for per/2.0 < t < per

The resulting `.DEC` file has the form `xmodramp_frac_per_amp.DEC` where `frac` is x10000 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/per`) for `t=0` to `per/2` and positive (`1+4t/per`) for `t=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, ^{1}H 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 30 is a diagram of the VACP sequence.

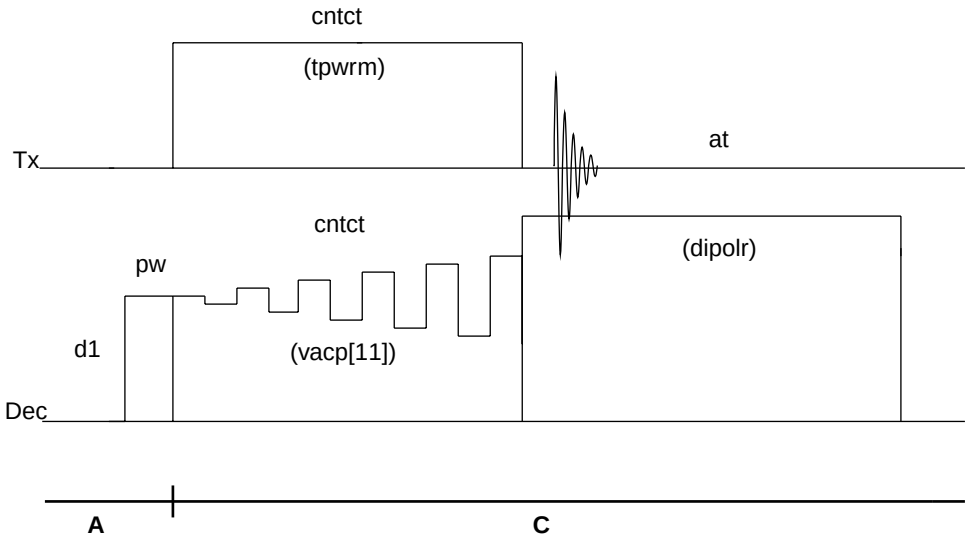

Figure 30. VACP Pulse Sequence

Applicability

VACP is available on UNITY*INOVA*, UNITY*plus*, 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 UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `dblvl2`, `pw`, and `cntct`. See page 63 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 CH_3, CH_2, 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 31 is a diagram of the XPOLEDIT1 sequence.

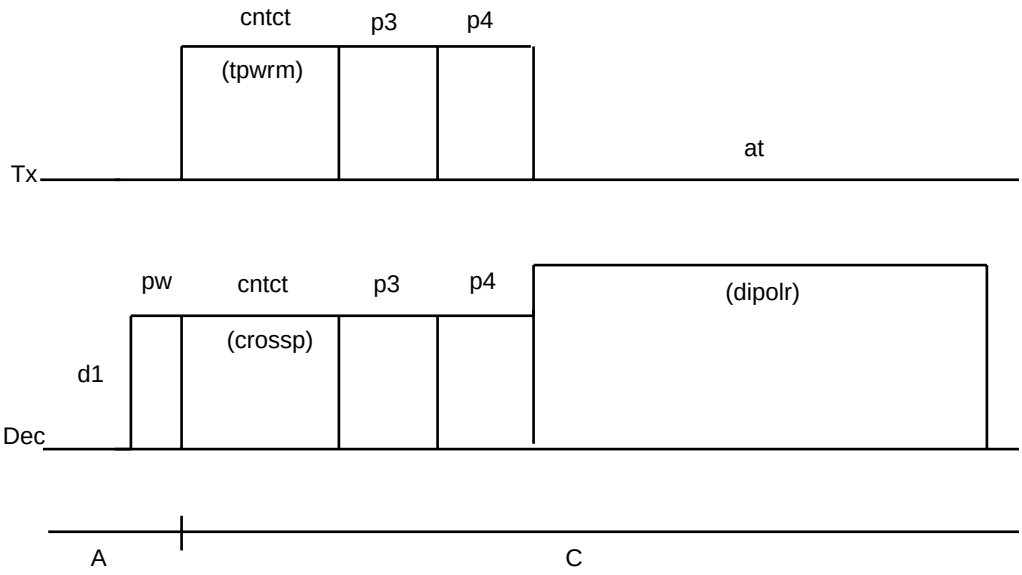

Figure 31. XPOLDIT1 Pulse Sequence

Applicability

XPOLEDIT1 is available on UNITY*INOVA* and UNITY*plus* 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 UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw` and `cntct`. See page 63 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 32 is a diagram of the 3QMAS1 sequence.

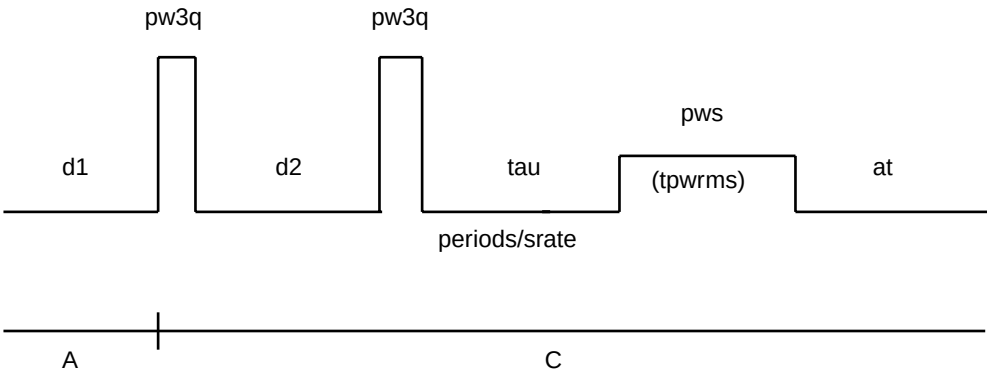

Figure 32. 3QMAS1 Pulse Sequence

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 UNITY*plus*. 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), `3qmas1` 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 s`3qmas1` creates the processing parameter `daslp` used for shearing (applicable for VNMR 5.2 or greater).

Parameters

3QMAS1 makes use of the UNITY*INOVA* and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `dpwrm` and `pw`. See page 95 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 f1 and a MAS sideband pattern in f2. There is negligible loss of signal intensity. Chemical shift tensor components can be determined from the sideband intensities in f2. Figure 33 is a diagram of the PASS1 sequence.

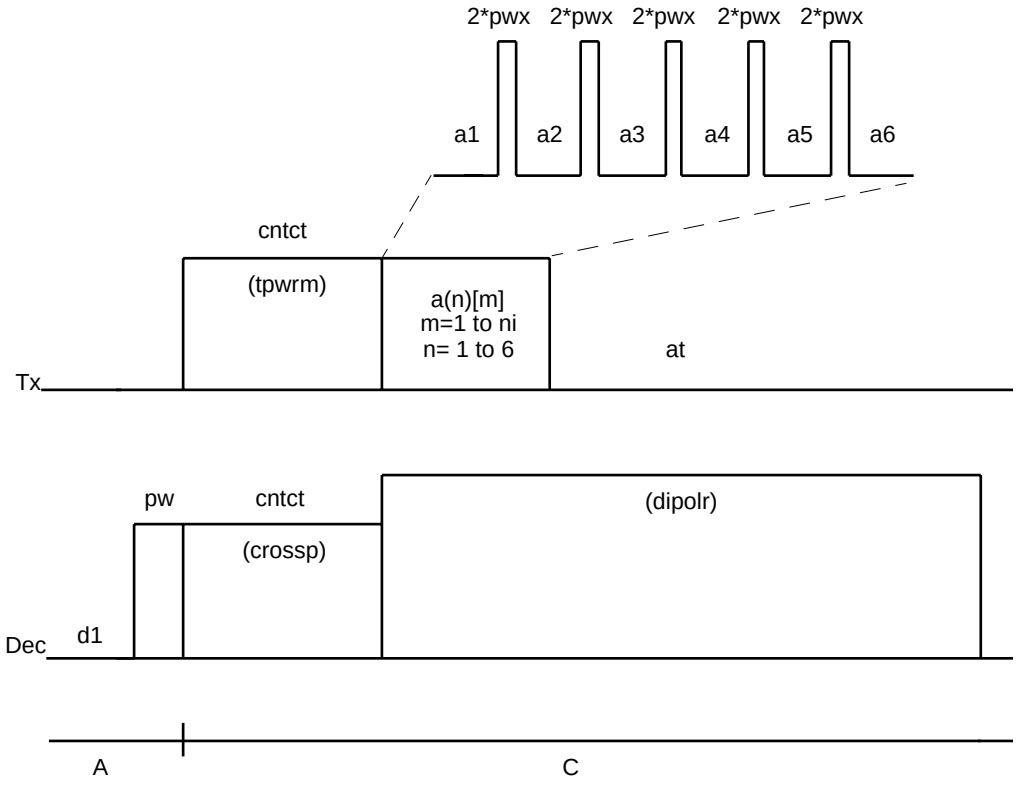

Figure 33. PASS1 Pulse Sequence

Applicability

PASS1 is available on UNITY*INOVA* and UNITY*plus* 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 UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`,`dblvl2`, `pw` and `cntct`. See page 63 for a description of these parameters.

`pwx` 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 34 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 ^{1}H magnetization based on chemical shift differences during a mixing time, ^{1}H spin diffusion during a mixing time, and high-resolution ^{13}C CP/MAS detection.

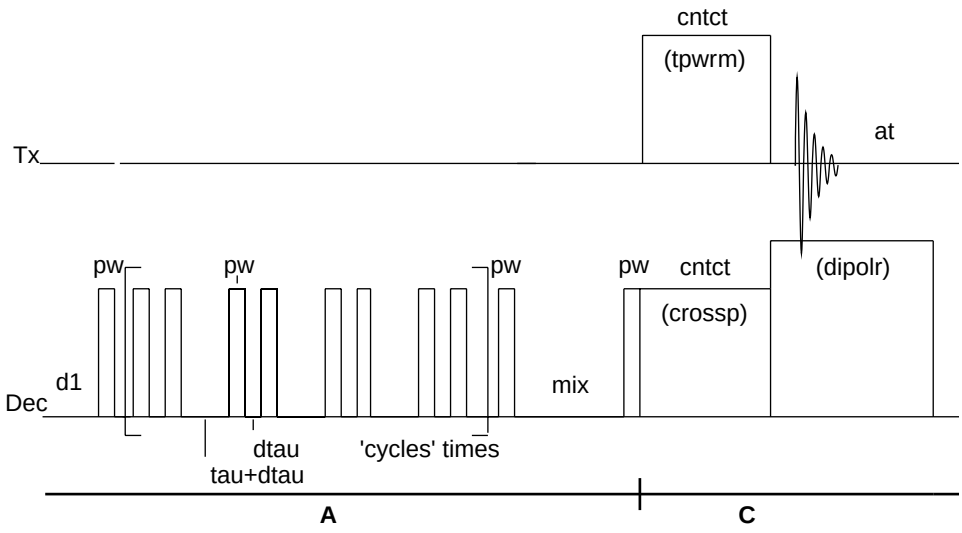

Figure 34. CPCS Pulse Sequence

Macro

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

Parameters

`pw` is the ^{1}H 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 12 `tau` 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 35 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, ^{31}P in organometallic compounds. When J-coupling is small, use CPNOESYPS, which depends on the through-space dipolar interaction.

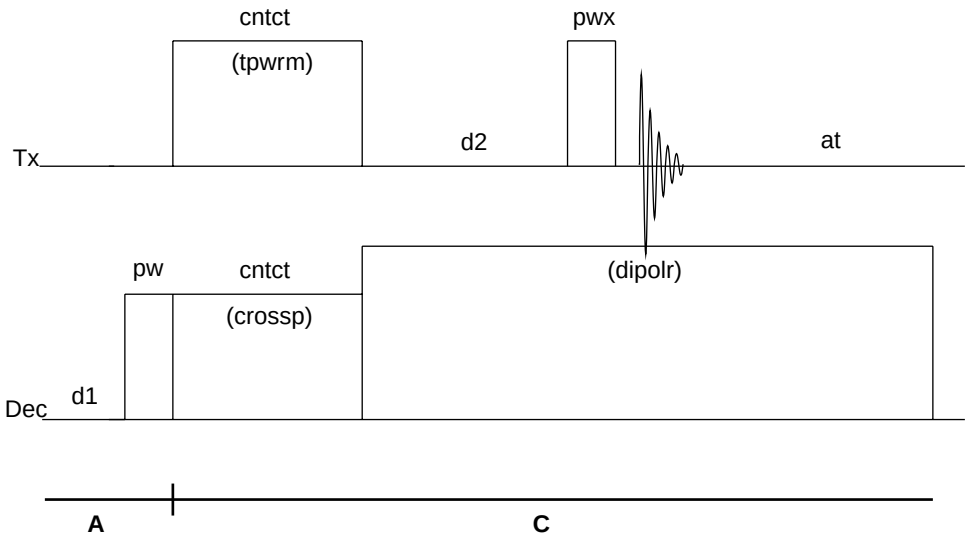

Figure 35. CPCOSYPS Pulse Sequence

Applicability

CPCOSYPS, found in `userlib`, is available only on UNITY*INOVA* and UNITY*plus*.

Macro

The macro `cpcosyps` converts a parameter set, obtained with XPOLAR or XPOLAR1, for the solids homonuclear correlation experiment CPCOSYPS. Power levels and the ^{1}H

90°° pulse width are retained. Default parameters set up for a phase-sensitive hypercomplex acquisition with `sw1=sw` and `xpol='y'`.

Parameters

`cpcosyps` uses UNITY*INOVA* and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See page 63 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 36 is a diagram of this 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 UNITY*INOVA* and UNITY*plu*

Macro

The macro `cpnoesyps` 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

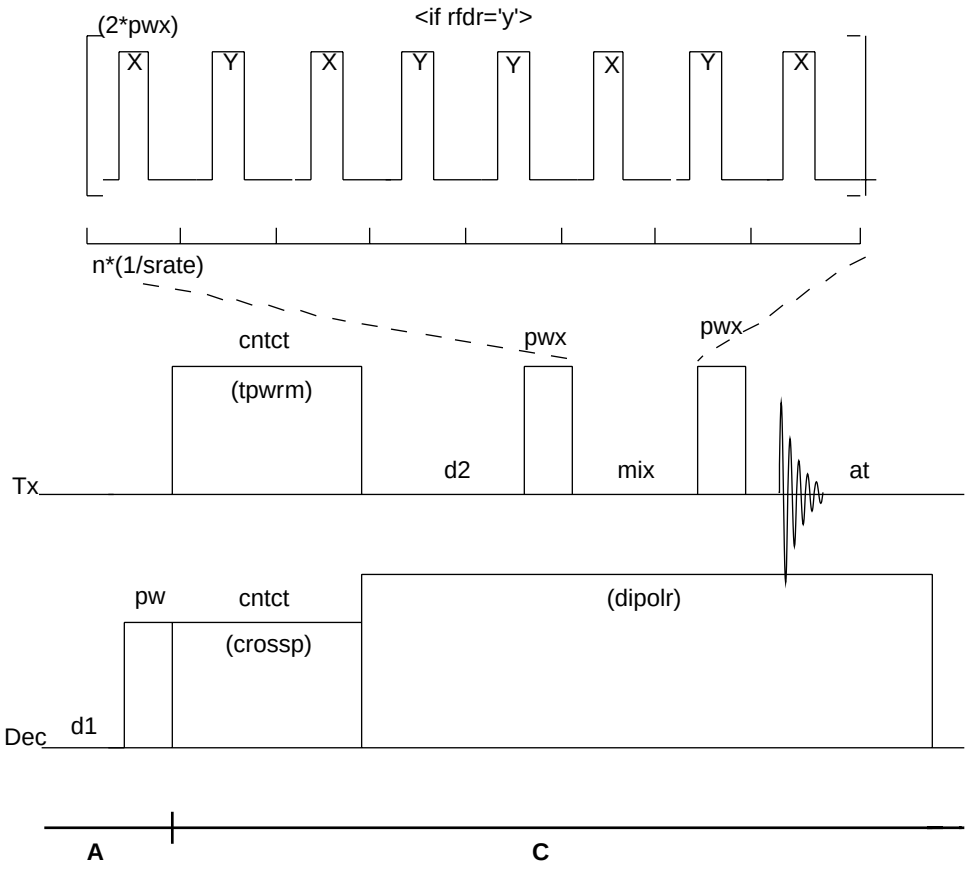

Figure 36. CPNOESYPS Pulse Sequence

hypercomplex acquisition with `rfdr` set to `'y'`. Also, `sw1` is set equal to `sw` and `xpol='y'`.

Parameters

`cpnoesyps` uses UNITY*INOVA* and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See page 63 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 length of pulses two and three and is to `pw` (if `xpol='n'`). `pwx` 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. CPNOESYPS 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 37 is a diagram of the sequence.

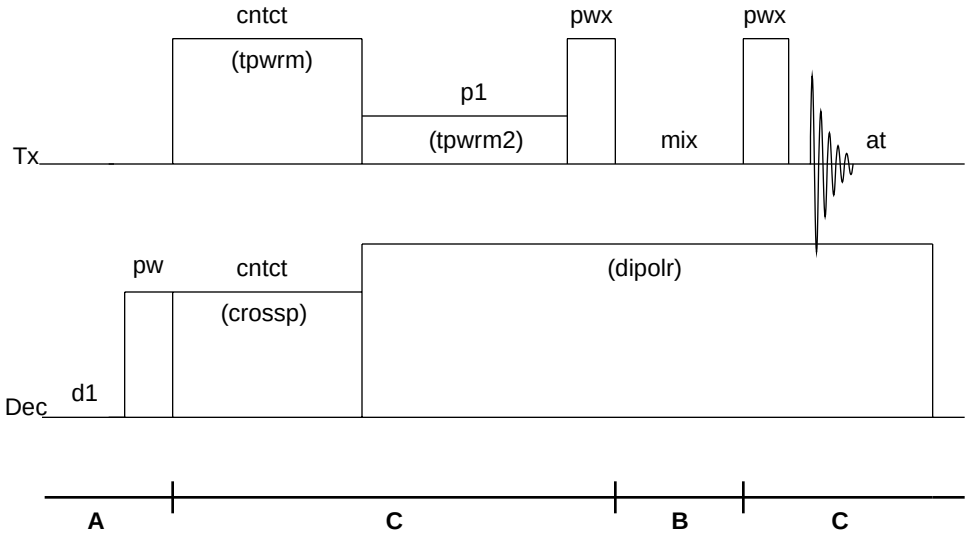

Figure 37. R2SELPULS1 Pulse Sequence

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*.

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*`pwx` and the power is set accordingly. Fine calibration of the inversion pulse is required.

Parameters

`r2selpuls1` uses UNITY*INOVA* and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See page 63 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*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.; Cruezet, 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 38 is a diagram of the sequence.

Applicability

DIPSHIFT, found in `userlib`, is available for UNITY*INOVA* and UNITY*plus* systems.

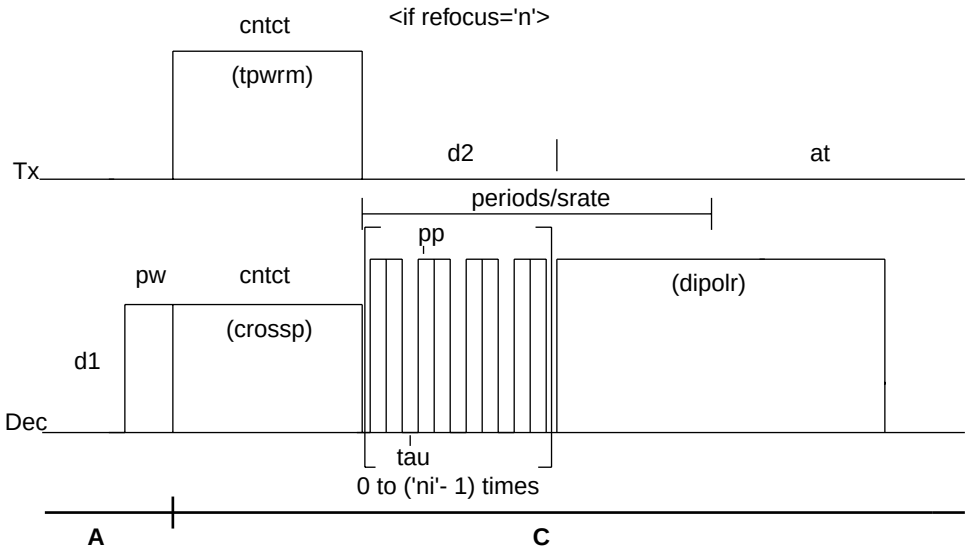

Figure 38. DIPSHFT1 Pulse Sequence

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 UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See page 63 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 he 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 the 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 39 is a diagram of SEDRA.

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 UNITY*INOVA* and UNITY*plus*.

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).

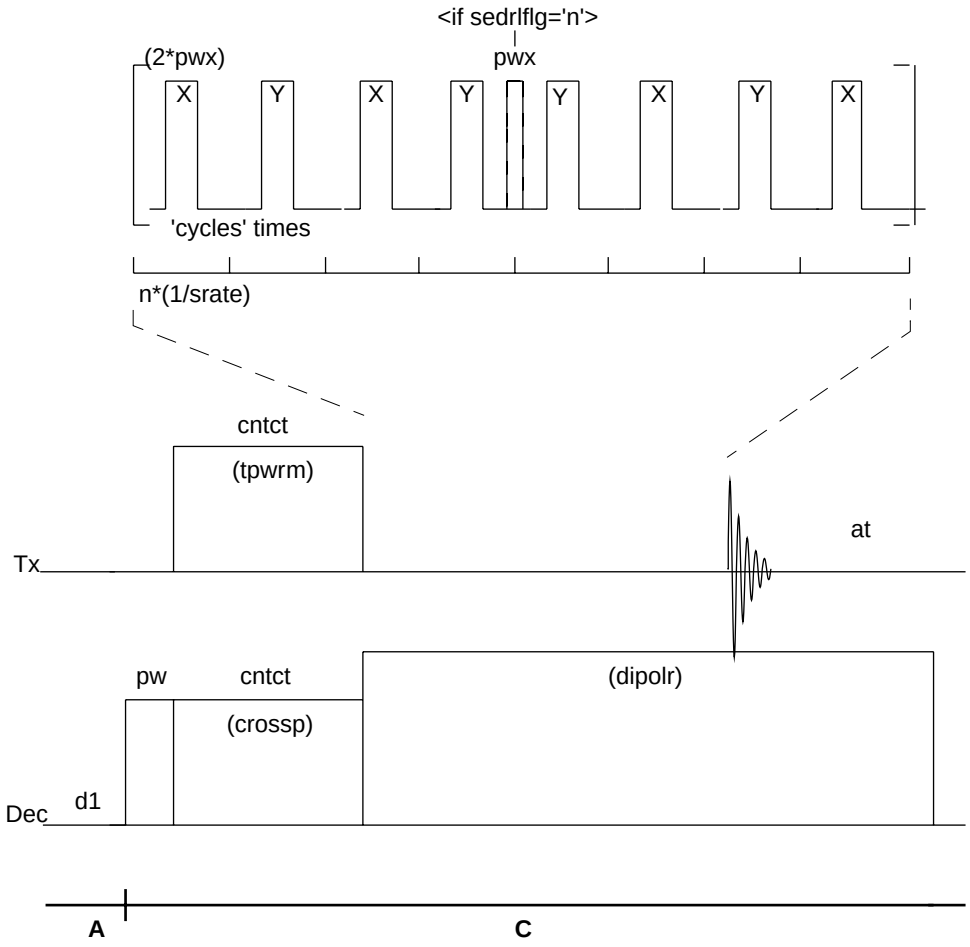

Figure 39. SEDRA2 Pulse Sequence

Parameters

`sedra2` uses UNITY*INOVA* and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See page 63 for a description of these parameters.

`pwx` 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 40 is a diagram of the pulse sequence.

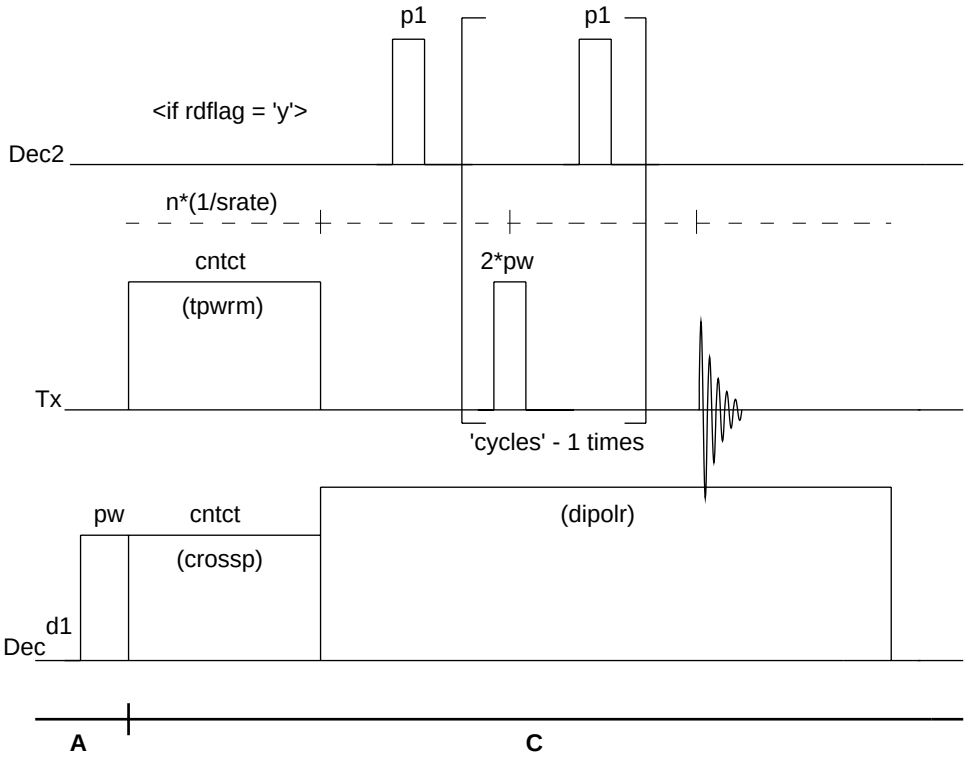

Figure 40. REDOR1 Pulse Sequence

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.

Applicability

REDOR1 is available only on UNITY*INOVA* and UNITY*plus* systems.

Macro

The macro `redor1` converts a parameter set, obtained with XPOLAR or XPOLAR1, for the REDOR experiment with `xy8` π 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 UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See page 63 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.

`pwx` 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).

`dpwrm2` 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 `dpwrm2` 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 ^{1}H-^{15}N cross-polarization and the ^{1}H to ^{15}N to ^{13}C cross-polarization spectra for different ^{15}N-^{13}C contact times. Figure 41 is a diagram of the pulse sequence.

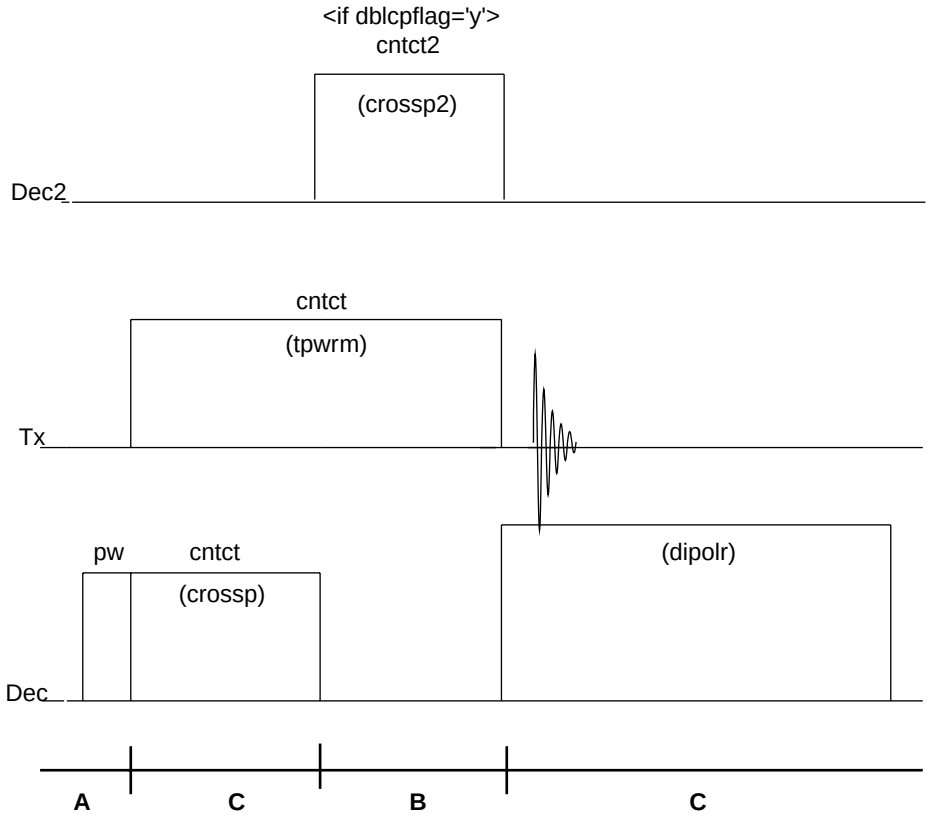

Figure 41. DOUBLECP1 Pulse Sequence

Applicability

DOUBLECP1 is available only on UNITY*INOVA* and UNITY*plus*. 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).

Parameters

`doublecp1` uses the UNITY*INOVA* and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See page 63 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 `dbcplfag='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 42 is a diagram of the sequence.

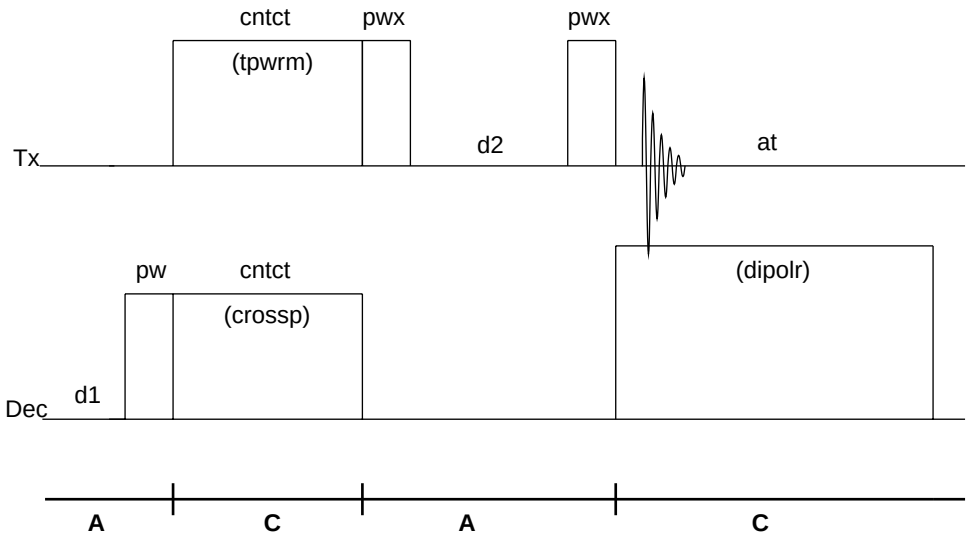

Figure 42. T1CP1 Pulse Sequence

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 UNITY*INOVA* and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dplvl2`, `pw`, and `cntct`. See page 63 for a description of these parameters.

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

`d2` 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 `tau1` and `tau2` as short as 10 microseconds can be used. Set `tau2` less than `tau1` 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 43 shows a diagram of the HAHNCP1 sequence.

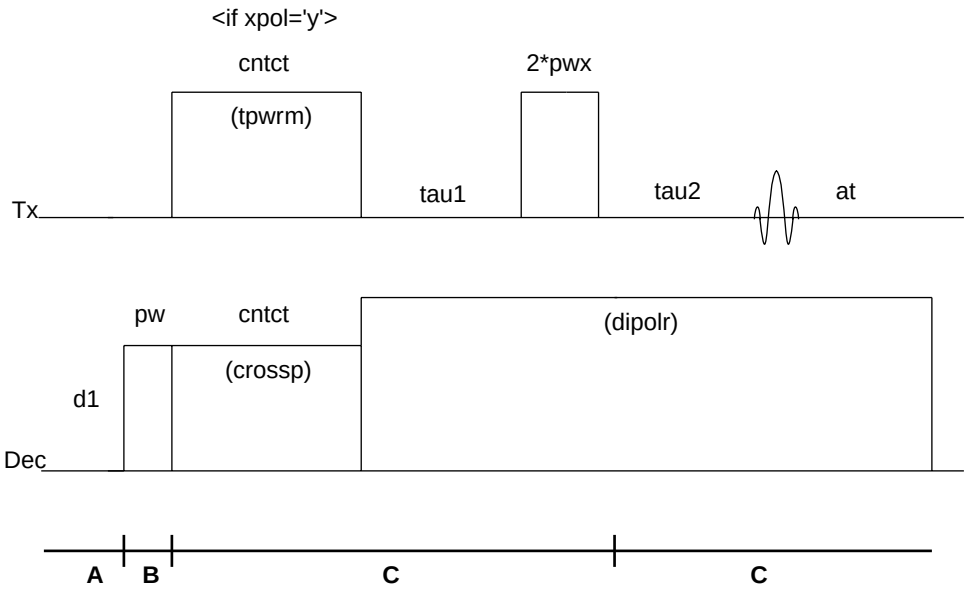

Figure 43. HAHNCP1 Pulse Sequence

Applicability

HAHNCP1 is available only on UNITY*INOVA* and UNITY*plus*. 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, `tau1=tau2=10` (in microseconds).

Parameters

HAHNCP1 uses UNITY*INOVA* and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `cppwr`, `dipolr`, `crossp`, `dblvl2`, `pw`, and `cntct`. See page 63 for a description of these parameters.

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

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

`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 ^{2}H, along with ^{23}Na 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 44 is a diagram of the SSECHO1 pulse sequence.

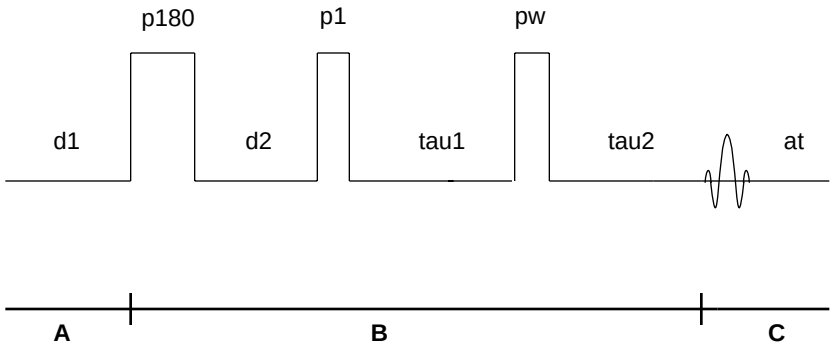

Figure 44. SSECHO1 Pulse Sequence

Applicability

SSECHO1 is available only on UNITY*INOVA* and UNITY*plus*. 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 UNITY*plus* Power Parameters

`ssecho1` makes use of the generic power parameters `tpwr`, `tpwrm`, `dpwr`, `dpwrm`, and `pw`. for UNITY*INOVA* and UNITY*plus* systems. These parameters have a consistent definition in most UNITY*INOVA* and UNITY*plus* 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 `pw`. The delay before acquisition is `tau1+tau2+pw`. 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=pw`. When `p1` is 0, it is hidden.

`pw` 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.

`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 `tau2` less than `tau1` 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 `alfa`, `beta`, and `fb`) is not present in `ssecho1`. Adjust `tau2` 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 ^{2}H powder pattern (Pake doublet), the exchange signal patterns supply immediate information about the type and rate of the dynamic process.

Two-dimensional ^{2}H 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 UNITY*plus*. 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 `s2pul1`) 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 45 is a diagram of the WLEXCH1 pulse sequence.

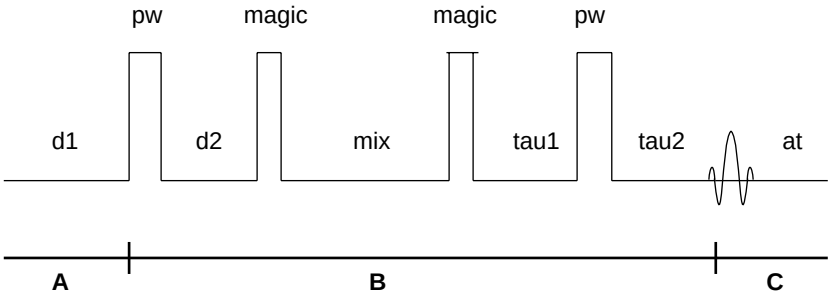

Figure 45. WLEXCH1 Pulse Sequence

Parameters

`wlexch1` makes use of the UNITY*INOVA* and UNITY*plus* parameters `tpwr`, `tpwrm`, `dpwr`, `dpwrm`, and `pw`. See page 95 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 CRAMPS—Combined Rotation and Multiple-Pulse Spectroscopy

Multiple-pulse sequences differ from other NMR experiments in how and when the evolution of the spin system is detected. Ordinarily a short B_1 pulse is used to move the magnetization from the Z direction to the X-Y plane, where it is detected as the spin system evolves in response to various interactions, J-coupling, dipolar, etc. The multiple-pulse FT NMR experiment uses a series of very short 90° pulses and delays that surround windows during which the evolution of the spin system is observed. The spin system responds not only to same interactions that occur in the standard NMR experiment but also to the influence of the B_1 pulses and the delays between the observation windows.

Multiple-pulse experiments such as the WAHUHA or WHH-4 sequence, developed by Waugh, Huber, and Haeberlen; MREV8, developed independently by Mansfield and by Rhim, Elleman, and Vaughan; and BR24, developed by Burum and Rhim, are examples of experiments used to observe the state or condition of the spin systems at intervals called windows. Adding the MAS experiment to a multiple-pulse experiment further reduces the linewidth. Linewidth is reduced with MAS in homonuclear systems in the same way as it is in heteronuclear systems—by averaging the chemical shift anisotropy to zero.

Chemical-Shift Hamiltonian

For any given multiple pulse train, the average chemical-shift Hamiltonian, defined over a complete cycle, can be written in the form

$H_{cs} = s\partial\omega(\boldsymbol{n} \bullet \boldsymbol{I})$

where $\partial\omega$ is the chemical shift offset, *s* is the scaling factor, ***n*** is a unit vector in the rotating frame, and ***I*** is the angular momentum vector. For the three sequences MREV8, BR24, and CORY24, ***n*** does not lie along the z axis and the resulting free precession generated by H_{cs} does not produce real and imaginary components of equal magnitude. Moreover, the signal also contains large amounts of static magnetization, often referred to as “pedestals” if the initial magnetization vector M(0) is not orthogonal to ***n***.

Because of these peculiar features of multipulse NMR, single phase data is often taken, with the receiver phase oriented in such a fashion as to minimize their effects. For MREV8, proper preparation pulses to eliminate pedestals were used from the outset, since their implementation required only traditional quadrature phases. Similar initializing pulses from BR24 have not been emphasized, because of the necessity of 45°phase increments.

Since MREV8 has an average Hamiltonian along (1,0,1), the magnetization trajectory after a 90_x preparation pulse (in degrees) is an ellipse whose principal axes coincide with the rotating-frame axis. Depending on the given window chosen for sampling, the major axis will be aligned along either the x or y axis of the rotating frame. The minor axis is $1/\sqrt{2}$ of the major axis and this produces quadrature images as complex data points are sampled and processed with a complex FFT.

Quadrature Correction

Quadrature correction can be produced by implementing a four-step cycle, where for each step the preparation pulse is chosen such that M(0) successively lies on the semimajor and semiminor axes of the ellipse. That is, the preparation pulse should advance the phase by 90° but also keep M(0) orthogonal to the unit vector ***n***. The initial magnetization vectors, preparation pulses for MREV8, are listed in Table 8.

Table 8. Multiacquisition Quadrature Corrections for MREV8

Acquisition	*M(0)*	*Preparation Pulse (degrees)*
1	(0,1,0)	90_0
2	$1/\sqrt{2}(1.0,–1)$	135_{270}
3	(0,–1,0)	90_{180}
4	$1/\sqrt{2}(–1,0,1)$	45_{90}

For BR24, the average chemical-shift Hamiltonian lies along (1,-1,1) and again the magnetization traces a elliptical path. However, the principal axes are inclined 45° to the rotating frame and the minor axis is $1/\sqrt{3}$ of the major axis. The best choice for preparation pulses therefore requires 45° phase shifts to the transmitter. Even without small-angle phase shifts, a 45° *y* pulse can be used to reduce pedestals and spin-locked magnetization, which is considerably more intense than for MREV8. A four-step method for BR24, akin to that for MREV8, can be implemented by using the preparation pulses listed in Table 9.

For the pulse sequence CORY24, the preparation pulses for a four-step quadrature-correction method are listed in Table 10.

Table 9. Multiacquisition Quadrature Corrections for BR24

Acquisition	*M(0)*	*Preparation Pulse (degrees)*
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}

Table 10. Multiacquisition Quadrature Corrections for CORY24

Acquisition	*M(0)*	*Preparation Pulse (degrees)*
1	1/√2(1,1,0)	90_{315}
2	(0,0,1)	0_{0}
3	1/ √2(–1,–1,0)	90_{45}
4	(0,0,1)	180_{0}

The preparation-pulse flip angles are set in the pulse sequences by scaling the flip time with 25-nanosecond resolution, based typically on a 1.5-microsecond 90° pulse, set during the tune-up procedure. Unlike conventional multiple-pulse experiments, where after the calibration with tune-up sequence the experiments are run off-resonance to minimize interference from the pedestal and maximize resolution, data for the phase cycled experiments need to be acquired with the transmitter positioned roughly in the middle of the spectrum.

The data obtained from a multiple-pulse experiment is processed the same as data obtained from any 1D experiment, with one key exception—the inherent scaling factor in multiple-pulse experiments. The contraction of the chemical shift scale is accommodated in the NMR software by the macro `scalesw` and the parameter of the same name.

References

Waugh, J. S.; Huber, L. M.; Heaberlen, U. *Phys. Rev. Lett.* **1968**, *20*, 180.

Mansfield, P. *J. Phys. C: Solids State Phy.* **1971**, *4*, 1444.

Rhim, W. K.; Elleman, D. D.; Vaughan, R. W. *J. Chem. Phys.* **1973**, *59*, 3740.

Burum, D. P.; Rhim, W. K. *J. Chem. Phys.* **1979**, *71*, 944.

Barbara, T. M.; Baltusis, L. *J. Magn Reson*. **1994,** *106*, 182.

6.27 FLIPFLIP—90-Degree Pulse Calibration

Two calibration experiments, FLIPFLIP and FLIPFLOP, test the system and make the necessary adjustments to achieve the required performance. The experiments use the response of a test sample, usually doped benzene in a microsphere, to the determine the state of the instrument. FLIPFLIP is described below and FLIPFLOP is covered in the next section. On a Varian spectrometer, the experiment a FLIPFLIP and FLIPFLOP are run from

the one sequence FLIPFLOP. The pulse sequence is *(90°(phase1)–acq—90°(phase2)–acq*). The type of experiment being done is determined by the value of the parameter `phase1` and `phase2`.

FLIPFLIP is used to determine the exact 90° pulse. This experiment requires transmitter to be on-resonance for proper results. The FLIPFLIP pulses move the magnetization in 90°° increments. Each pulse in the pulse train is separated by a delay `tau`, during which the receiver is turned on and the evolution of magnetization is detected. The value of `phase1=phase2=0`.

Macro

The macro `flipflop` 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.

`phase2` is the phase of the second 90° pulse and is set to 0.

`trig` is set to `'y'` or `'n'` depending on the system. On UNITY*INOVA* and UNITY*plus*, the pulse sequence in 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

Burum, D. P.; Linder, M.; Ernst, R. R. *J. Magn. Reson.* **1981,** *43*, 463.

6.28 FLIPFLOP—Phase Transient Removal

The FLIPFLOP sequence $(90(x) - acq - 90(-x) - acq)_n$ is used to remove “phase glitch” or phase transient in the probe and pulse amplifier. FLIPFLOP is the second sequence (after FLIPFLIP) normally used in setup. To run a FLIPFLOP sequence rather than a FLIPFLIP sequence, the only parameter that needs to be changed is the parameter `phase2`, which is now set to the value 2.

Phase glitch is manifest as an in-phase oscillation in the data. A flip-flop sequence alternately moves the magnetization from the Z axis onto the X-Y plane using a train of pulses. In the absence of any phase errors, such as phase glitch, the pattern generated by the FLIPFLOP experiment resembles a set of tram tracks. Figure 46 is a diagram of FLIPFLOP.

Unlike the FLIPFLIP sequence, which constantly rotates the magnetization in a single direction, the FLIPFLOP train of pulses alternately flips the spins into the XY plane, giving an NMR signal, then back to the Z axis, giving no NMR signal. Following the adjustment of the phase transients, it is necessary to repeat the FLIPFLIP sequence to readjust the power for the desired 90° pulse length, which may have altered as a result of tuning out the phase transients.

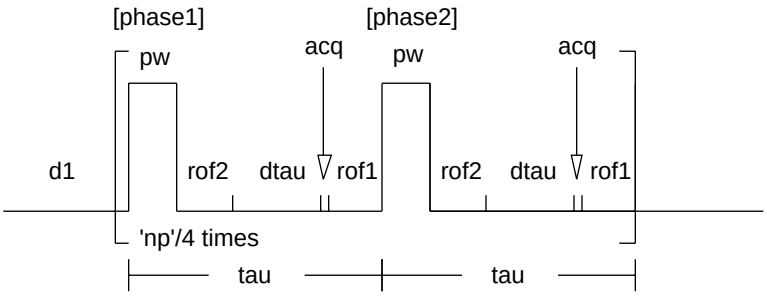

Figure 46. FLIPFLOP Pulse Sequence

Macro

The macro `flipflop` 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 2 (–`x`).

`trig` is set to `'y'` or `'n'` depending on the system. On UNITY*INOVA* and UNITY*plus*, the pulse sequence in 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.

6.29 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 $((90(x)\text{-}90(y)\text{-}90(y)\text{-}90(x))_2\text{-}acq)_n$, 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 47 is a diagram of HS90.

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.

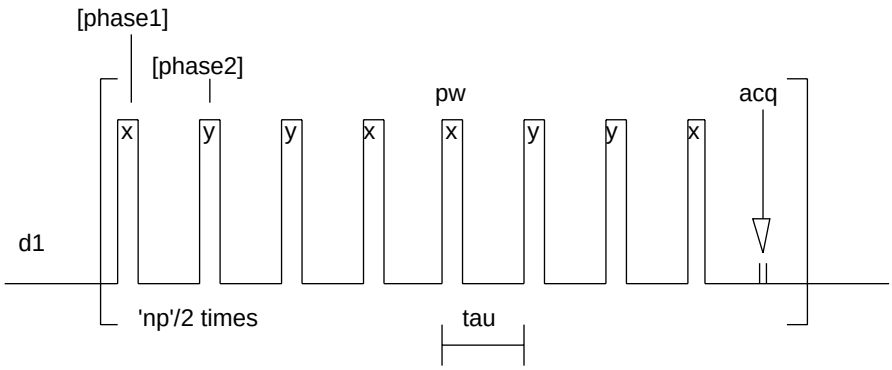

Figure 47. HS90 Pulse Sequence

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 UNITY*INOVA* and UNITY*plus*, the pulse sequence in 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.

6.30 MREV8, Cycled MREV8—Multiple-Pulse Line Narrowing

MREV8 is one of several multiple-pulse sequences that remove strong homonuclear dipolar interactions, allowing for pure chemical shift spectra to be obtained for ^{1}H and ^{19}F nuclei in the solid state. Figure 48 is a diagram of the MREV8 sequence.

Macros

The macro `mrev8` converts a FLIPFLOP, BR24, or S2PUL parameter set into the MREV8 line narrowing pulse sequence.

The macro `cylmrev` converts the MREV8 parameter set to that suitable to run Cycled MREV8. No parameter changes are necessary. The preparation pulse is based on the value of `pw` as listed in Table 8.

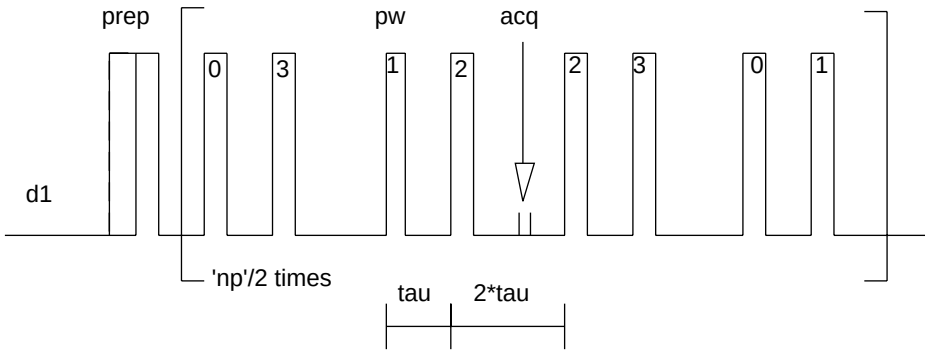

Figure 48. MREV8 Pulse Sequence

Parameters

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

`tau` is the interpulse delay, in microseconds, that includes `pw`. The MREV8 cycle is `12*tau` long and is repeated `np/2` times to build up the FID.

`np` is the number of points acquired.

`trig` is set to `'y'` or `'n'` depending on the system. On UNITY*INOVA* and UNITY*plus*, the pulse sequence in 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.

`tauc` is the cycle time, recalculated each time `tau` is changed. For MREV8, the cycle is `12*tau` long. Altering `tauc` does not have any effect on the experiment.

`mp_at` is the true acquisition time, based on `np` and `tau`. `mp_at` is recalculated each time `np` or `tau` is changed. altering `mp_at` does not have any effect on the experiment.

References

Rhim,W. K.; Elleman, D. D.; Vaughan, R. W. *J. Chem. Phys.* **1973**, *59*, 3740.

Barbara, T. M.; Baltusis, L. *J. Magn Reson*. **1994,** *106*, 182.

6.31 BR24, Cycled BR24—Multiple-Pulse Line Narrowing

BR24 is one of several multiple-pulse sequences that removes the strong homonuclear dipolar interactions, allowing for pure chemical shift spectra to be obtained for ^{1}H and ^{19}F nuclei in the solid state. Figure 49 is a diagram of the BR24 sequence.

Macros

The macro `br24` converts a FLIPFLOP, MREV8, or S2PUL parameter set into the BR24 line narrowing pulse sequence.

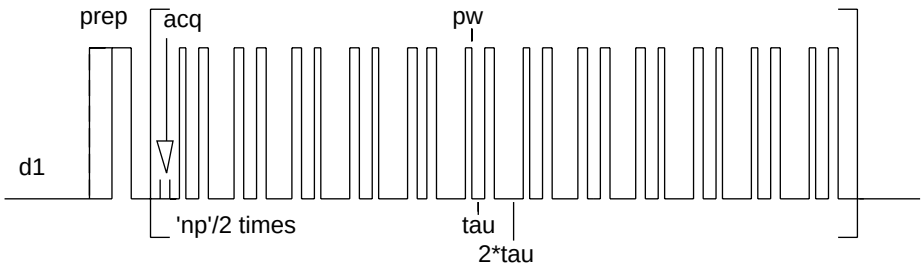

Figure 49. BR24 Pulse Sequence

The macro `cylbr24` converts the BR24 parameter set to that suitable to run Cycled BR24. No parameter changes are necessary, the preparation pulse are based on the value of `pw`, as described in Table 9.

Parameters

`pw` is the 90° 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° pulse length and phase should be set to 135 degrees by using the parameter `phase1`.

`tau` is the interpulse delay, in microseconds, that includes `pw`. The BR24 cycle is `36*tau` long and is repeated `np/2` times to build up the FID.

`np` is the number of points acquired.

`trig` is set to `'y'` or `'n'` depending on the system. On$^{\text{UNITY}}$*INOVA* and UNITY*plus*, the pulse sequence in 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.

`tauc` is the cycle time, recalculated each time `tau` is changed. Altering `tauc` does not have any effect on the experiment.

`mp_at` is the true acquisition time, based on `np` and `tau`. `mp_at` is recalculated each time `np` or `tau` is changed. Altering `mp_at` has no effect on the experiment.

References

D. P. Burum and W. K. Rhim, *J Chem. Phys.* **71**, 944, (1979).

T. M. Barbara and L. Baltusis, *J. Magn Reson.* **106**, 182 (1994).

6.32 CORY24, Cycled CORY24—Multiple-Pulse Line Narrowing

CORY24 is one of several multiple-pulse sequences that removes the strong homonuclear dipolar interactions, allowing for pure chemical shift spectra to be obtained for ^{1}H and ^{19}F nuclei in the solid state. Figure 51 is a diagram of the CORY24 sequence, and Figure 50 is a diagram of Cycled CORY24.

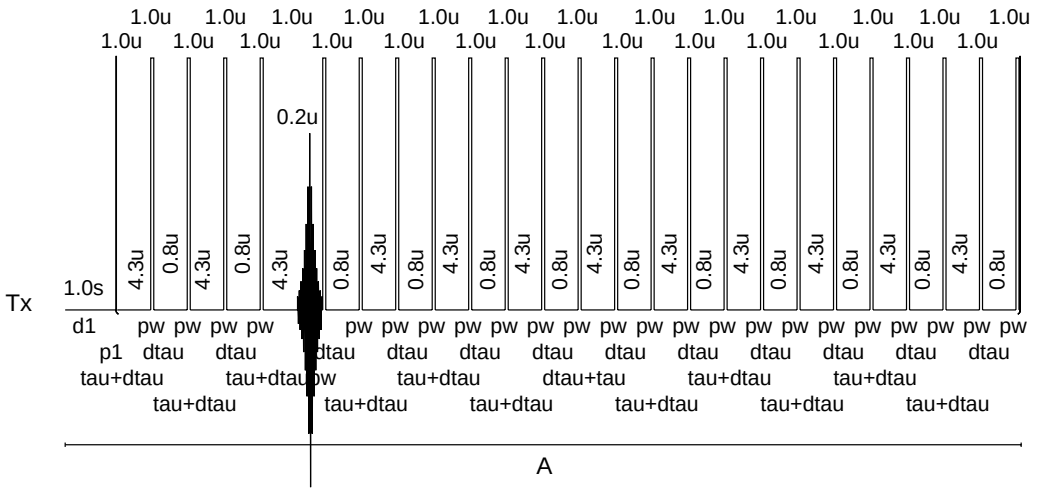

Figure 50. Cycled CORY24 Pulse Sequence

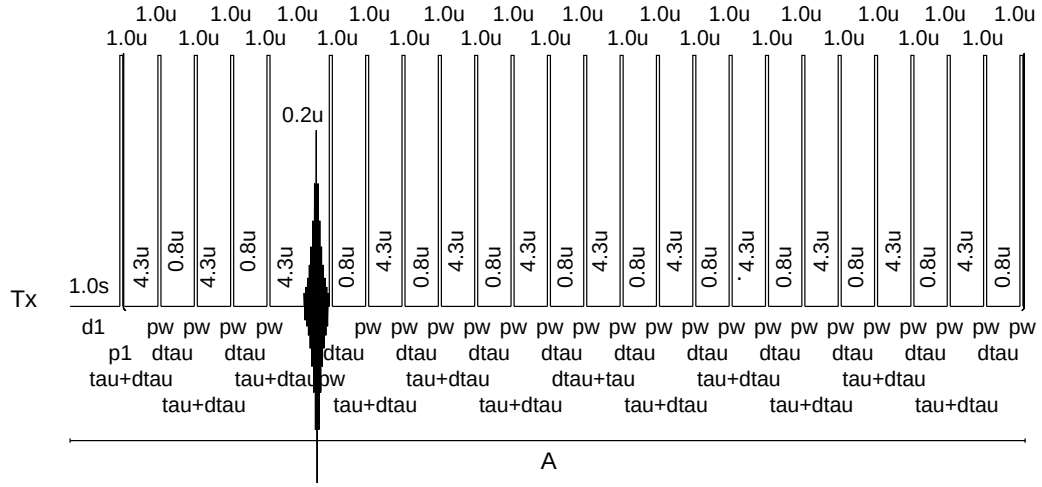

Figure 51. CORY24 Pulse Sequence

Macros

The macro `cory24` converts a FLIPFLOP, MREV8, or S2PUL parameter set into the CORY24 line narrowing pulse sequence.

The macro `cylcory24` converts the CORY24 parameter set to that suitable to run Cycled CORY24. No parameter changes are necessary, the preparation pulse are based on the value of `pw`, as described in Table 10.

Parameters

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

`p1` is the preparation pulse, in microseconds, with phase controlled by `phase1`. To minimize the "pedestal," set `p1` to the 90° pulse length and set the phase to 135 degrees by using the parameter `phase1`.

`tau` is the interpulse delay, in microseconds, that includes `pw`. The CORY24 cycle is `36*tau` long and is repeated `np/2` times to build up the FID.

`np` is the number of points acquired.

`trig` is set to `'y'` or `'n'` depending on the system. On UNITY*INOVA* and UNITY*plus*, the pulse sequence in 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.

`tauc` is the cycle time, recalculated each time `tau` is changed. Altering `tauc` does not have any effect on the experiment.

`mp_at` is the true acquisition time, based on `np` and `tau`. `mp_at` is recalculated each time `np` or `tau` is changed. Altering `mp_at` does not have any effect on the experiment.

References

Cory, D. G. *J. Magn. Reson.* **1991**, *94*, 526.

Barbara, T. M.; Baltusis, L. *J. Magn Reson*. **1994,** *106*, 182.

6.33 MREVCS—Multiple Pulse Chemical-Shift Selective Spin Diffusion

Figure 52 shows the diagram of a novel experiment, called MREVCS, developed by Spiess and coworkers, that involves a multiple-pulse selection of ^{1}H magnetization based on chemical shift differences during the mixing time, ^{1}H 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 ^{1}H detection.

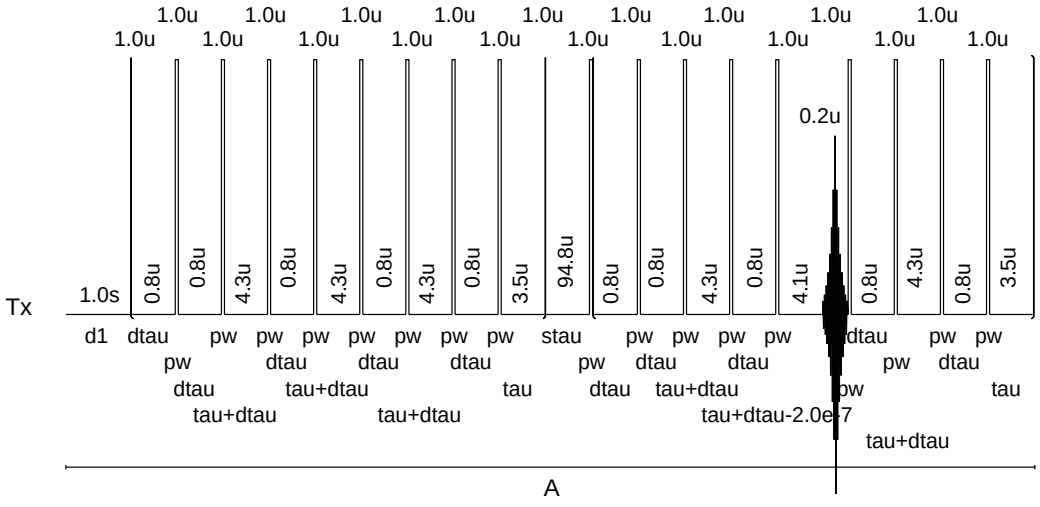

Figure 52. MREVCS Pulse Sequence

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*tau`.

`mix` is the mixing time, in microseconds, for ^{1}H 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.

6.34 MQ_SOLIDS—Multiple-Quantum Solids

A ^{1}H 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 53 is a diagram of the sequence.

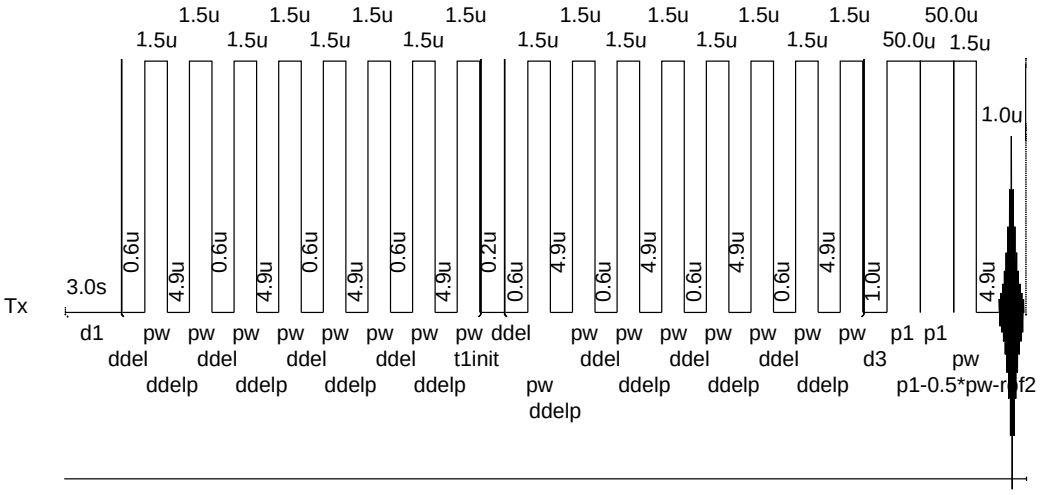

Figure 53. MQ_SOLIDS Pulse Sequence

Macro

Macro `mq_solids` generates the parameters for the multiple-quantum experiment.

Parameters

`del` 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.

6.35 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 54 is a diagram of the sequence.

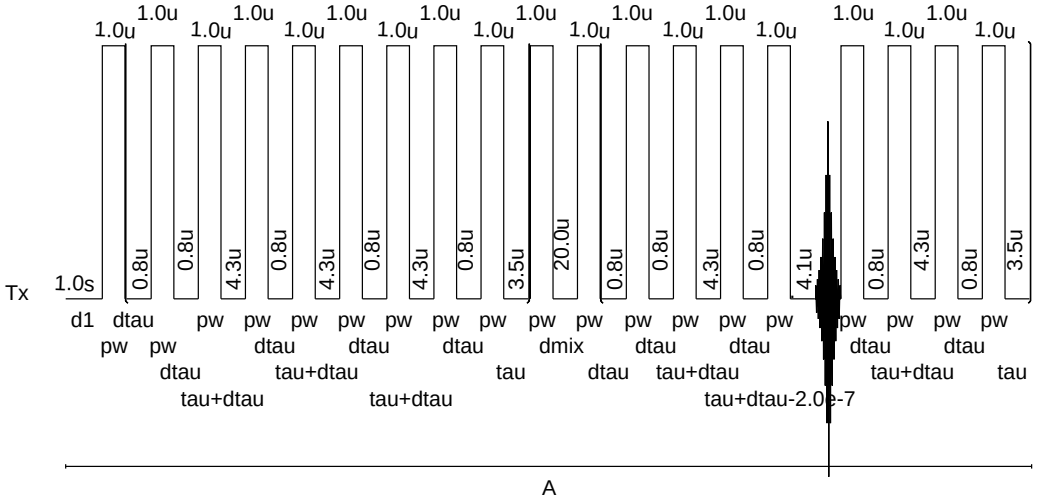

Figure 54. SPINDIFF Pulse Sequence

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.

6.36 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 ^{2}H. For this experiment, a triple-resonance probe was used with the coil doubly tuned to ^{27}Al (referred to as the high frequency) and ^{2}H (referred to as the low frequency). Both NMR frequencies were picked off the high-frequency port. It was possible to observe the ^{2}H 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 `tof` (in MHz), two FIDs, one at ^{27}Al and the other at ^{2}H, 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 `nf` (number of FIDs) is greater than one, a series of alternating multinuclear FIDs can be collected. Figure 55 is a diagram of the fast acquisition pulse sequence, called FASTACQ.

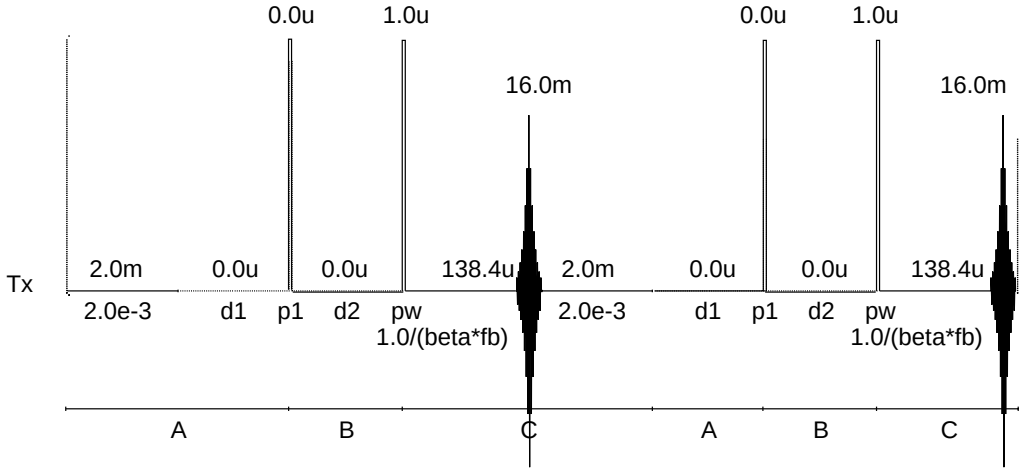

Figure 55. FASTACQ Pulse Sequence

Macro

The macro `fastacq` recalls the FASTACQ sequence and a modified parameter set.

Parameters

`nf` is the number of FIDs to be collected.

`tof` 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 `tn`, 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`.

6.37 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 56 is a diagram of the sequence.

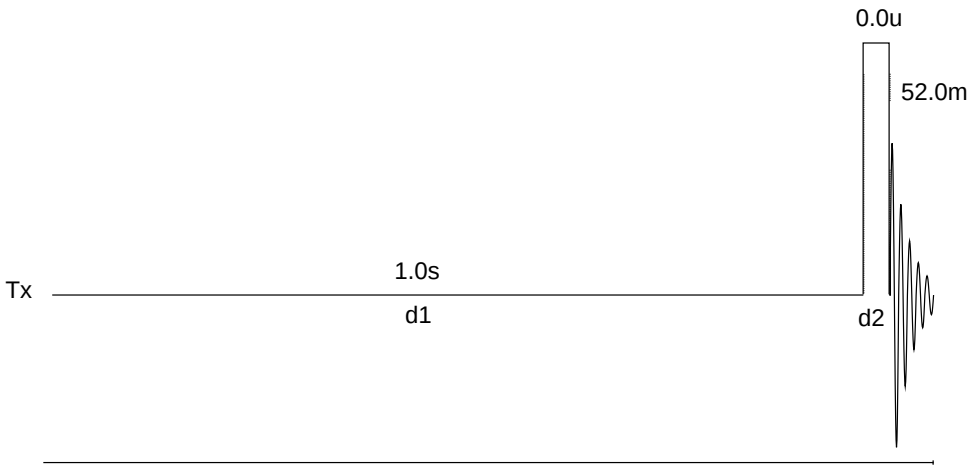

Figure 56. NUTATE Pulse Sequence

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.

Numerics

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