Solid-State NMR Experiment with the JEOL probe

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3/8/2022

Instrument: JEOL 300 MHz solid state
Probe: JEOL 3.2 mm MAS
Sample tube: NM-05410ST32 (Zirconia, ZrO_2)
Sample volume: 27-50 mm^3

Achieve working speed in the probe

The sample tube must have been packed according to a standard procedure described in "Preparation of a solid-state NMR sample" where it
1. have been spun at range of speeds on a benchtop including the maximums speed exceeding by 2 kHz the speed you intend to use in the probe,
2. have demonstrated high stability at high speeds (<0.1%, 1-2Hz)

IMPORTANT: If your sample tube has been already measured before, it **must** still go through the benchtop spinner to **demonstrate stability at all speeds including the one exceeding the working speed by 2K** because packing might have been perturbed by handling!

NOTE 1: The probe has a **brightness adjustment rod** that is easy to perturb when attaching a spin-controller cable. Make sure you perform light adjustment as described below.

NOTE 2: The **MAS angle adjustment screw** has a design problem: if you rotate it CCW too far it will disengage from the MAS adjustment rod. If you start feeling your screwdriver rotating without any resistance, it is off the screw of the rod, and your rotations make no more effect on the MAS angle adjustment. To remedy the problem, carefully rotate the screw CW till you feel a slight resistance again as it engages with the thread on a rod. When you feel a slight resistance rotating the screw, it pulls or pushes the rod up or down and regulates MAS angle again. Be cautious about reaching the other limit too. If it becomes hard to rotate, you must stop or you will break the adjustment rod!

NOTE 3: Sometimes, it will be **difficult for the instrument to pass 1000-1200 Hz speed range**. The MASCONT will be increasing Drive pressure a lot and will overspeed for a moment after it finally passes through this region of speed. This overspeed is safe if your target speed is only 3-5kHz but dangerous if you set 10-15 kHz. Therefore, it is important that you "break" through this speed barrier using a 3kHz target and then you increase speed to the higher settings **without stopping!** If you had to stop spinning for any reason, you **must** set 3000 Hz target speed first, wait till it breaks through the barrier, and then increase spinning speed further.

Put sample in the probe and insert the probe in the magnet

1. Pull the probe out and place it on a floor
2. Put sample tube into the probe, flute - facing outside
3. Close the probe cover
4. Reattach the gas supply and spin control to the probe
5. Put probe in the magnet bore.
6. Enter the File Name in the "Log" section as **[Your initials]_[experiment ID]_probe**, interval=2sec, and click "Start" to start recording the spinning log

Adjust light intensity for the speed measurement

IMPORTANT: Never touch the light adjustment knob while MASCONT is spinning in Auto mode!

- Make sure the MASCONT software is in a manual mode (default mode when stopped): click Manual button.
- Adjust Bearing pressure to 100 kPa (use slider, then arrows; 1kPa/click).
  You should see the sample start spinning.
  - If the sample does not spin:
    - Rotate light adjustment knob to have approximately middle position.
    - Set Bearing pressure to zero and take the sample out:
      - Verify that the flute (turbine) is facing outside.
      - Check if the flute and end cap are inserted tightly and there is no gap between them and a sleeve.
      - Wash off the paint on a bottom cap with ethanol and repaint the speed-counting strip.
        NOTE: Let the marker dry up for 5 min before inserting the tube back into the spinner, otherwise you may transfer some marker paint on a bore of a spinner!
    - If you still cannot start spinning, try a standard sample.
      - If it does not spin either: the spinner needs cleaning —**contact NMR Center Director, Evgenii Kovrigin**
- Adjust the Drive pressure to 4 kPa
- Wait 20 sec for the speed to stabilize (speed will be around 580 Hz)
- Rotate ("walk") the light adjustment knob in small increments (a few degrees) to find the detection region:
  - Walk to reach one end of the (to see the speed drop),
  - walk one step back (to see the speed restored),
  - walk to another end counting small steps till you see the speed drop again
  - step back one step
  - take 1/2 of the counted steps back (to set the knob near the middle of the maximum speed region)
  This adjustment will need to be repeated at the high end of the speed range

For a 10 kHz measurement

- NOTE: After verifying that the speed is stabilizing, jump to next speed **without stopping**. The probe has a problem region around 1200 Hz. You need to pass it once and then increase of speed will be well controlled.
  Record fluctuation amount and pressures for this speed in the table:

Time	Speed, Hz	Fluctuation, Hz	Fluctuation, %	Drive, kPa	Bearing, kPa
	Auto 800				
	Auto 3,000				
	Auto 6,000				
	Auto 10,000, switch to Manual, adjust light, switch back to Auto				
	Auto 10,000				

- Proceed with experiments.

For a 17 kHz measurement

- Start with 800 Hz. After speed is stabilized to +-2Hz, jump to next speed without stopping. Record fluctuation amount and pressures for this speed in the table:

Time	Speed, Hz	Fluctuation, Hz	Fluctuation, %	Drive, kPa	Bearing, kPa
	Auto 800				
	Auto 3,000				
	Auto 6,000				
	Auto 10000, switch to Manual, adjust light, switch back to Auto				
	Auto 10,000				
	Auto 14,000				
	Auto 17,000, switch to Manual, adjust light, switch back to Auto				
	Auto 17,000				

- Proceed with NMR experiments

Experiment setup

1. Log into a computer, launch Delta 5.0.3, click Spectrometer Control icon, choose JNM-ECX300, Connect, enter username and password, click **Connect**.
2. In Samples tab, de-verify last sample
3. Create a new sample: click "+", click Sample Name field, enter name, click Shared and Verified (means sample is in the probe)
4. To use existing experiments, click "Update Jobs", select, and "Update"
5. To make a new experiment set, enter a job title and create new job with this title
   - If other jobs were left from previous users - delete them
   - click Add Experiment
   - Select the experiment:
     - for 13C expt: for example, cpmas_tuned_c13_AGK_10kHz.jxp
     - for 31P: select one-pulse or cpmas...
6. click **auto_gain** and **force_tune** (to allow manual tuning; uncheck for a repeated acquisition)
7. Check Favorites tab
   - adjust necessary parameters

Load a standard shim set

8. Click on **Samples** tab
   The **Shims** item appears on the top toolbar of the window.
9. Click **Shims: Load Shims : User Shims**
   - (if not there yet) Navigate to **maint/My Documents/JEOL/Delta 5.0/shims**
   - select **standard-latests.shim**
   - click a green checkmark

Coarse Tuning and Matching

10. Click Submit Job
    - **Do NOT use tuning number off the Delta screen. Use the updated tuning table attached to a side of a magnet.**
    - Insert a correct capacitor stick
      NOTE: The capacitor stick is wobbly - if you accidentally touch it during subsequent tuning/matching, the probe might go out of tune. If you touched the stick: recheck tuning of Low Frequency channel
    - Turn on the probe display (button on the right)
    - Dial Tune and Match positions for the nucleus from the table on the amp.
    - Look at the tune interface to see how far we are from tuned state.
      *It may be enough to only adjust Match and then Tune rods a little and get down to <15 LED elements with amplification button at 10x and the knob at the rightmost clockwise position. This is enough, **you don't need the spectral analyzer protocol; proceed with Fine Tuning with the Tune Interface.***

Tuning and matching with frequency analyzer

11. First, tune low-frequency channel using the spectral analyzer:
    o Attach black extender cord to the wall power
    o Turn on the frequency analyzer
    o Attach yellow cable to Low Frequency connector on the probe
    o Click [TG] next to screen label
    o Set the center of spectrum: **TG:Freq**: enter frequency on keypad, hit **MHz** unit key, and hit **ENTER**
        ▪ 13C: 75.5520 MHz, -65 dB, stick A - *(EK: 10/28/21)*
        ▪ 31P: 121.6533 MHz, no stick *(EK: 2/9/2022)*
        ▪ 7Li: 116.7899 MHz, no stick
        ▪ 6Li: 44.2241 MHz, stick C
    o (Optional) Set a marker at the center frequency (to better see the tuning result)
    o tune and match
        ▪ change spectral width as needed: TG:SPAN, enter and hit ENTER
        ▪ change amplitude of spectrum TG:AMPT:Scale/Div
        ▪ change reference line : TG:AMPT:Reference and turn dial
    o switch cable to the tune interface

Fine Tuning with the Tune Interface

12. Check the computer screen - if the system is still in Tune mode. If it is timed out - stop the experiment and Submit again.
13. Look at the with tune interface. If amplification is at 10x and the knob is at the maximum: count the LED lights. If <10-13, your probe is well tuned, skip this section.
    o move match in direction of reducing signal and then 1-2 lights past it. Remember the direction you were turning!
    o move tune to reduce signal;
    o move match again in the same direction till the minimum and 1-2 lights past it.
    o repeat tuning/matching
    o In the end, with amplification at 10x and the turn knob at the maximum, you should see 10-15 lighted elements on the tune interface
    o on Delta screen: make sure that it did not switch for proton automatically due to a time out! If it did you must stop the experiment and resubmit it.
    o Record number of LEDs you see lit.
    o click **Done**.

Tuning proton (if proton channel is used in the experiment)
    o Dial Tune and Match positions from the probe table
    o Check the tune interface, adjust Match and Tune
    o If you need frequency analyzer, set the center of proton spectrum to 300.630 MHz, -65 dB
    o fine tune with tune interface.
    o Record number of LEDs you see lit.
    o click **Done**

Acquisition

Acquisition starts automatically as soon as you click Done in tuning.

IMPORTANT: You must **stop** the experiment and resubmit it to check tuning on a tune interface one more time, because carbon channel may have detuned during proton tuning adjustment! Look at the tune interface and verify that number of LEDs remained the same as you recorded above.

- As experiment is collected: see Monitor tab. Click Process and (Play) symbol to show frequency-domain data as they accumulate.
- Note: Processing in Delta - only to view the data
- Topspin and MNova are installed on the workstation to have a better look at the data if needed.
- Copy the file with "-1.jdf" extension to a flash drive for analysis in TopSpin or MNova (on your computer)

Finishing your work

- Stop spinning your sample
- Click [Stop] in the "Log" section to stop recording the spinning log. It is viewable in *Desktop\Libraries\Documents\My Documents\MSCONT\Log*
- **Remove any unfinished experiments from your queue**
  - Click on **Queue** tab
  - Click on gray X sign to delete any experiments still appearing in the queue
    NOTE: If you don't clean up your queue, next user may not be able to start their own experiments because your experiments will be blocking the queue!
- Take the probe out and remove your sample
- Close the probe head cover and insert the probe back into the magnet
- **Re-insert a default stick A**
- Close the benchtop spinner cover
- **Turn off** the frequency analyzer
- Put its cables around it (off the floor)
- Disconnect black extender cord (for frequency analyzer) from the wall power socket
- Clean all the tools that you used for packing your sample
- Disconnect Delta software from the spectrometer
- **Stop the Kiosk.**
- **CLOSE GAS SUPPLY ON A WALL**
- Wipe off the sample prep bench if you used it.
- Take all your chemicals and samples back to your lab

Import of data to MNova or TopSpin

Please, follow step-by-step instructions:
 http://nmr-center.nmrsoft.com/JEOL300/JEOL_300.html#topimport

Adjustment of the MAS angle

- Spin up AGK sample at 15 kHz
- Create a job and pick experiment MAS_Adjust_KBr_Br79.
- Click "force-tune" , "auto-gain". See if 'repeat' is checked.
- Tune Low Frequency channel to 79Br, (13C carbon is OK too)
    - insert stick A,
    - Use printout table on the amp for the settings: Tune=3690, Match = 1787
    - Touch tune and match to see 13-14 elements on the amp
    - Click Done on screen
- Adjust Magic Angle adjustment screw while watching the screen. You need to have spinning sidebands extend to 4ms. Make very small adjustments and wait. The screw has a significant slack when changing turning direction.

Other nuclei that are not in the probe spec table

1. Calculate X-frequency using 75.5650 MHz for carbon and ratio of gamma (or frequencies in JEOL table)
2. Tune probe on the frequency analyzer (this gives you coarse approximation)
3. Tune on the tune interface (both matching and tuning will need to be adjusted).