Variable Temperature (VT) Using the Doty 4mm DI-4 Probe

updated: 5 Jan 2019 (cgf)

Brief Summary

Documentation at the Doty website is good:

General description:
   http://dotynmr.com/products/accessories-supplies/rotors-caps-and-other-accessories/
More details for our 4mm DI-4 probe:
   http://dotynmr.com/download/ACCS-4-mm.pdf
Sample packing instructions for rotors and sealing cells:
   http://dotynmr.com/download/4-mm-DI-Packing-Sealing-Cell-Instructions-2.pdf

All VT work requires that the user be *very* familiar with the details of setup and dangers of such use. It is relatively easy to damage the equipment, much more so than with liquids NMR (and VT is quite dangerous to the equipment there). Therefore, all users must be trained prior attempting any type of VT. The user must also interact with staff as to any questions that arise, as well as report any unusual behavior.

Note that, as always in ssNMR, the spinning speed is limited by the rotor type (thick wall or thin wall), and the cap type (kel-f, torlon, glass-filled torlon, etc). For VT, the material and rotor thickness also limit the temperatures that can be reached.

Doty DI-4 Rotor and Cap Materials: MAS, VT, and Other Limitations[1]

rotor type	cap type	mas	VT	limitations
thick wall	GFT	≤ 18 kHz	to probe limits	not for ^{1}H, not for some ^{29}Si and ^{13}C
thick wall	torlon[2]	≤ 18 kHz	-30 to +80°C	exceptional chem resistance; dependence on humidity is limiting; not for ^{1}H and some ^{13}C
thick wall	vespel[3]	≤ ? kHz	to probe limit	for some extended VT; not for ^{1}H and some ^{13}C
thick wall	Kel-F	≤ 9 kHz	-20 to +70°C	background free but for ^{19}F ^{13}C ^{35}Cl; best for ^{13}C; easy to damage during assembly; when not in structural element like a cap, can got to +150°C
thin wall	GFT	≤ 12 kHz	to probe limits	not for ^{1}H, not for some ^{29}Si and ^{13}C
thin wall	torlon[2]	≤ 12 kHz	-30 to +80°C	exceptional chem resistance; dependence on humidity is limiting; not for ^{1}H and some ^{13}C
thin wall	vespel[3]	≤ ? kHz	to probe limits	for some extended VT; not for ^{1}H and some ^{13}C
thin wall	Kel-F	≤ 9 kHz	-20 to +70°C	background free but for ^{19}F ^{13}C ^{35}Cl; best for ^{13}C; easy to damage during assembly; when not in structural element like a cap, can got to +150°C
thin wall	any cap + sealing cell	≤ 9 kHz	-20 to +70°C do not boil solvent!	typically use Kel-F cell (Ultem for ^{19}F studies are available)

[2] Torlon caps are not recommended, as humidity adversely affects the size and therefore the fit of the caps (i.e., they work either in high humidity or low humidity, but not both).

[3] Vespel caps are available as a special purchase, but it appears that GFT is preferred in all(?) cases.

A. *Setup for VT experiments with ssNMR:*

1. See staff for the initial setup of the instrument, which involves:
   ✘ changing pneumatics at the back of the BCU chiller
   ✘ teeing the bearing gas and bearing sense gas together for the input for the BCU chiller
   ✘ putting in the VT adapter connector for the BCU chiller output to go into the Doty probe
   ✘ unchecking the limit temp checkbox in the VT Configuration panel (requires admin passwd)

2. The user needs to change the following in topspin,
   – turn off the VT correction in the VT panel
   – select SelfTune with Doty probe selection, then Restore to Channel 2

3. Calibrate the temperatures you need for the experiments:
   → the temperature calibration is dependent on many factors (e.g., see KR Thurber and R Tycko, J Magn Reson 196(1) (2009) 84-87:
     → for example calibration data, see: /home/00_shared_docs/NMR-TempCal.xls
     → the example calibration data was obtained using chemical shifts from $K^{79}Br$ (I did not do T_1 measurements [yet]), where the equation from Thurber is: -0.0250±0.0004 ppm/K
     → the reference chemical shift was taken using (assumed ambient temp would be correct with no heating and no decoupling): mas=3kHz, decoupler off (PLW2=PLW12=0Watts), d1=5s, parameter-set=4mm_KBr_VT-calibration.gUW
   – spinning speed (current calibration: 8kHz)
   – ^1H decoupler strength (calib: 104 kHz, which is pw90=2.4μs at 200Watts)
   – acquisition time (calib: aq=30ms)
   – repetition rate (calib: d1=15s)