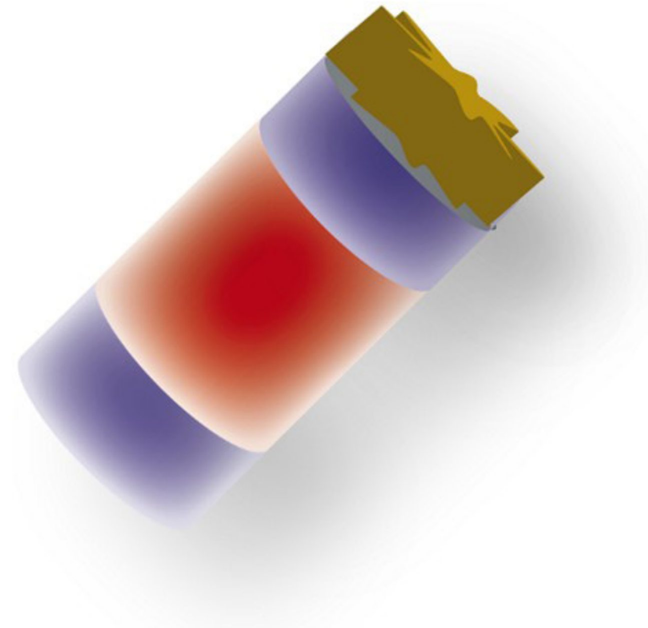
Quantification of frictional heating at ultra-fast magic-angle spinning

Kristof Grohe



Content

Overview

On the following pages it is shown that the frictional heating from 0 to 111 kHz spinning speed of venturi and non-venturi 0.7 mm probe-heads is in the range of 25 K.

In order to clarify the amount of frictional heating at different spinning speeds, a KBr[1] sample as well as a solution of 1M $[Co(CN)_6]^{3-}$ complex[2] in water were used as NMR thermometers, measuring the temperature dependent chemical shift. In case of KBr, the sample temperature at 10 kHz spinning speed was taken as a reference. It was approximated that at this speed, the sample temperature resembles the probe-temperature as displayed in TopSpin.

The weaknesses of that approximation emerge by using the 1M ^{59}Co solution. Here, the temperature can also be measured while the sample is static. It turned out, that the temperature of the supplied gas for bearing and drive has an influence on the sample temperature (**Figure 6 and 7**, first 3 points). The probe heads which were used were a 0.7 mm standard-bore S6 DVT on an 800 MHz Ascend spectrometer and a 0.7 mm wide-bore W2 DVT probe on a 500 MHz Ascend Aeon Spectrometer. The stator of the standard-bore probe-head has a counter bearing (no venturi) and an open shielding (window) while the wide-bore probe-head is a venturi system with a closed shielding and sample insert/eject.

Using KBr as NMR-thermometer with and without temperature control

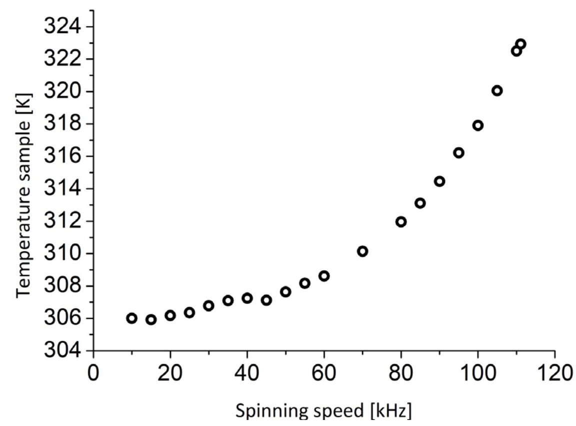
The chemical shift of KBr is linearly proportional with the real sample temperature. A rise of the temperature of 1 K changes the chemical shift by -0.025 ppm. For a spinning speed of 10 kHz, it was approximated that the frictional heating is zero. A first series was recorded without VT gas stream.

Table 1

Spinning speed [kHz]	T probe [K]	delta shift [ppm]	T sample [K]
10	306.0	0	306.0
15	305.1	0.002	305.9
20	306.1	-0.0046	306.2
25	305.7	-0.0088	306.4
30	305.5	-0.0195	306.8
35	305.4	-0.0273	307.1
40	305.3	-0.031	307.2
45	305.1	-0.0281	307.1
50	304.9	-0.041	307.6
55	304.8	-0.0542	308.2
60	304.7	-0.0654	308.6
70	304.6	-0.1035	310.1
80	304.5	-0.1489	312.0
85	304.4	-0.1777	313.1
90	304.3	-0.2114	314.5
95	304.2	-0.2554	316.2
100	304.2	-0.2976	317.9
105	304.1	-0.3513	320.1
110	304	-0.4126	322.5
111.111	304	-0.4233	322.9

Spinning speed related sample heating of a 0.7 mm S6 standard-bore probe in an 800 MHz Ascend Spectrometer, measured by chemical shift change of ^{79}Br.

Figure 1



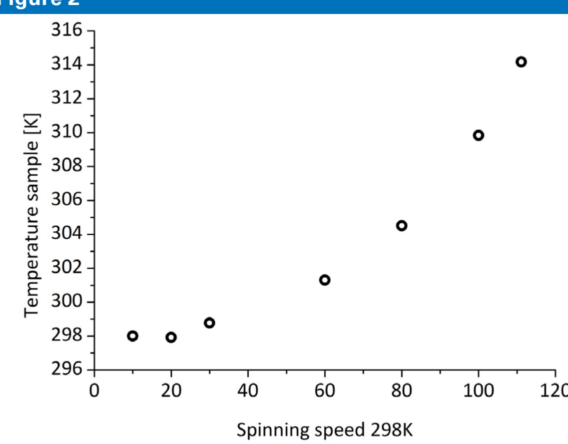
Spinning speed related sample heating of a 0.7 mm S6 standard-bore probe in an 800 MHz Ascend Spectrometer, measured by chemical shift change of ^{79}Br, according to table 1.

Table 2

Spinning speed [kHz]	T sample [K]
10	298.0
20	297.9
30	298.8
60	301.3
80	304.5
100	309.8
111.111	314.2

Spinning speed related sample heating of a 0.7 mm S6 standard-bore probe in an 800 MHz Ascend Spectrometer, measured by chemical shift changes of ^{79}Br. The VT gas stream was set to 400 l/h at 298 K.

Figure 2



Spinning speed related sample heating of a 0.7 mm S6 standard-bore probe in an 800 MHz Ascend Spectrometer, measured by chemical shift changes of ^{79}KBr. The VT gas stream was set to 400 l/h at 298 K.

Similarly, the sample temperature was measured with active temperature control at 298K, 400 L/h VT gas.
The data shown suggest a rise of temperature of around 17 to 20 K when the spinning speed is raised from minimum (8-10 kHz) to maximum (111.111 kHz) spinning speed for the used probe head.

As the next step, the efficiency of VT-cooling is determined. Therefore, the sample was spun at 110 kHz while changing the VT-temperature from 268 K to 298 K.

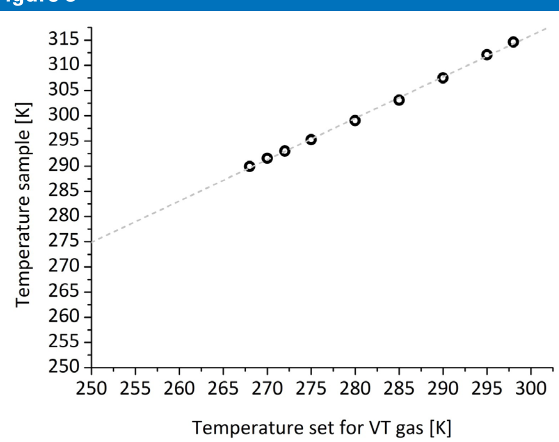
Hereby, the temperature of the sample changed approximately 0.82 K at a VT-gas temperature change of 1 K.

Table 3

temp VP at 110 kHz	delta chem shift	T sample [K]
298	-0.4152	314.6
295	-0.3527	312.1
290	-0.2378	307.5
285	-0.1274	303.1
280	-0.0261	299.0
275	0.0682	295.3
272	0.1253	293.0
270	0.1614	291.5
268	0.201	290.0

VT-gas temperature related sample heating of a 0.7 mm S6 standard-bore probe in an 800 MHz Ascend Spectrometer, measured by chemical shift changes of ^{79}KBr as a function of VT temperature. The VT gas stream was set to 900 l/h at 110 kHz spinning speed.

Figure 3



VT-gas temperature related sample heating of a 0.7 mm S6 standard-bore probe in an 800 MHz Ascend Spectrometer, measured by chemical shift changes of ^{79}KBr as a function of VT temperature. The VT gas stream was set to 900 l/h at 110 kHz spinning speed.

Using 1M $[Co(CN)_6]^{3-}$ as an NMR Thermometer

The chemical shift of ^{59}Co, as a 1 molar solution of $K_3[Co(CN)_6]$ in water, has a strong dependence of the sample temperature. One Kelvin temperature change results in a shift change of -1.4 ppm. Thus, this sample is well suited for measuring the sample temperature at magic angle spinning conditions. The small, fast tumbling, complex in an aqueous solution enables reference measurements at static conditions.

Measurements with the 0.7 mm S6 standard-bore probe in an 800 MHz Ascend spectrometer using $[Co(CN)_6]^{3-}$.

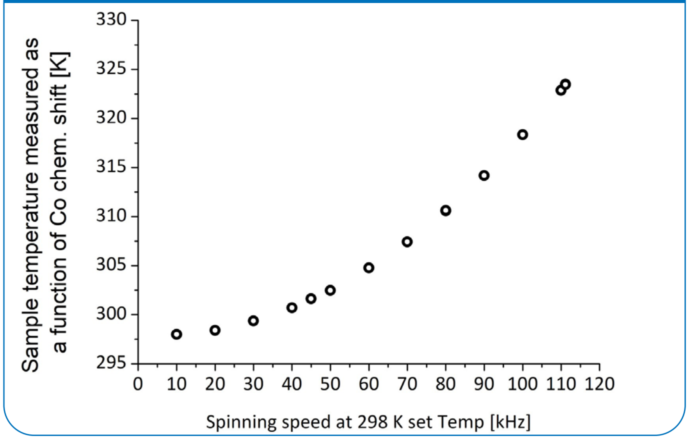
Similarly, like seen in table 1, the sample temperature was measured as a function of different spinning speeds. The VT-gas temperature was set to 298 K at a gas-stream of 900 l/h.

Table 4

Spinning speed	$\Delta\sigma$ Co [ppm]	T sample [K]
10	0	298.0
20	-0.5929	298.4
30	-1.93	299.4
40	-3.792	300.7
45	-5.09	301.6
50	-6.2627	302.5
60	-9.4826	304.8
70	-13.2104	307.4
70	-13.1977	307.4
80	-17.6256	310.6
80	-17.6787	310.6
90	-22.6677	314.2
100	-28.5	318.4
110	-34.8242	322.9
111.111	-35.7214	323.5
111.111	-35.6633	323.5

Spinning speed related sample heating of a 0.7 mm S6 standard-bore probe in an 800 MHz Ascend Spectrometer, measured by chemical shift changes of ^{59}Co. The VT gas stream was set to 900 l/h at 298 K.

Figure 4



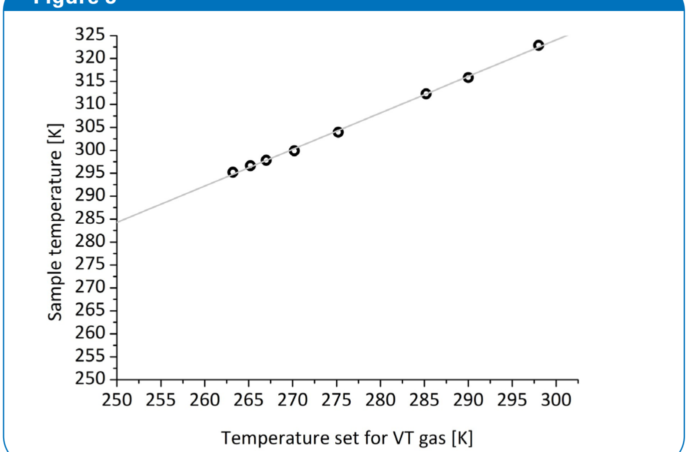
Spinning speed related sample heating of a 0.7 mm S6 standard-bore probe in an 800 MHz Ascend Spectrometer, measured by chemical shift changes of ^{59}Co. The VT gas stream was set to 900 l/h at 298 K.

Table 5

T set	Δσ Co [ppm]	T sample [K]
298	0	322.9
290	9.8945	315.8
285.2	14.8052	312.3
275.2	26.532	303.9
270.2	32.1756	299.9
267	35.1073	297.8
265.2	36.7198	296.6
263.2	38.772	295.2

VT-gas temperature related sample heating of a 0.7 mm S6 standard-bore probe in an 800 MHz Ascend Spectrometer, measured by chemical shift changes of ^{79}KBr as a function of VT temperature. The VT gas stream was set to 900 l/h at 110 kHz spinning speed.

Figure 5



Sample temperature measured by chemical shift changes of Co as a function of VT temperature. The VT gas stream was set to 900 l/h at 110 kHz spinning speed. At a VT temperature change of 1 K, the sample temperature changes by 0.8 K.

Measurements at 0.7 mm S4 wide-bore probe in a 500 MHz Ascend Aeon spectrometer.

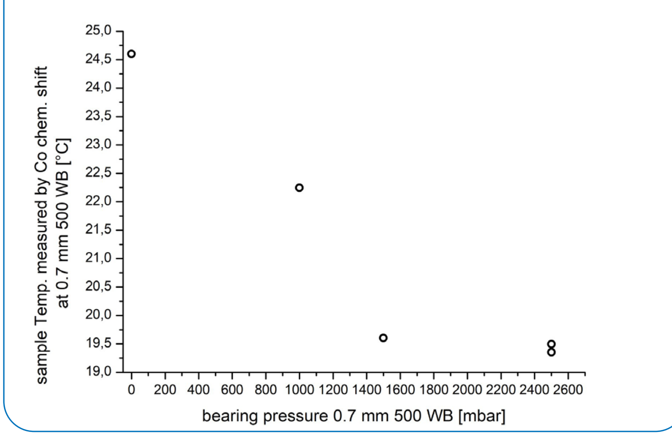
To get a complete picture, the frictional heating of the cobalt complex-sample was measured additionally using a wide-bore probe W2 in a 500 MHz Ascend Aeon spectrometer. In addition to the spinning speed related temperature change, the influence of the supply-gas temperature is shown.

Table 6

bearing pressure [mbar]	T sample [°C]
0	24.6
1000	22.2
1500	19.6
2500	19.5
2500	19.4

Temperature change as a function of bearing pressure 500 MHz wide-bore W2. No VT-gas, no frame cooling.

Figure 6



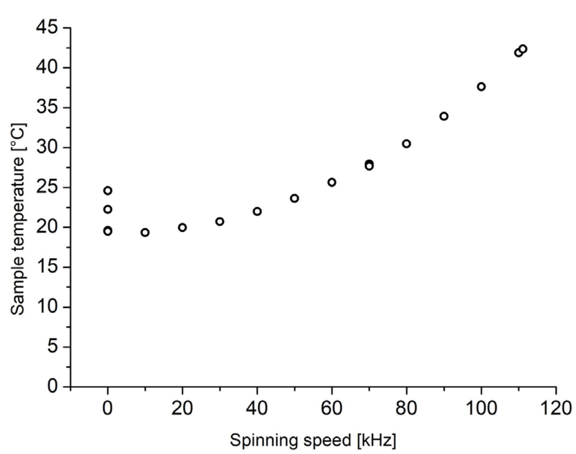
Temperature change as a function of bearing pressure 500 MHz wide-bore. No VT-gas, no frame cooling.

Table 7

Spinning Speed [kHz]	T sample [°C]
0	24.6
0	22.2
0	19.6
0	19.5
10	19.3
20	20.0
30	20.7
40	22.0
50	23.6
60	25.6
70	27.9
70	27.7
80	30.5
90	33.9
100	37.6
110	41.9
111,111	42.3

Sample temperature as a function of spinning speed. VT cooling and frame-cooling where off. The initially measured temperatures at 0 kHz spinning are measured at different bearing-pressure, according to table 6.

Figure 7



Sample temperature as a function of spinning speed. VT cooling and frame cooling where off. The initially measured temperatures at 0 kHz spinning are measured at different bearing pressure, according to table 6.

Conclusion

The heating due to friction while spinning the sample from 0 to 111.111 kHz is in the range of 18 to 25 K. The efficiency of VT cooling leads to a decrease of sample temperature in the range of 0.8 K per K VT temperature reduction. Starting from 25°C, a probe-temperature value (as displayed in TopSpin) in the range of -10°C is sufficient to achieve a sample temperature around 20 to 25°C at 111.111 kHz spinning speed.

The relation of the sample temperature and the temperature measured at the thermoelement (probe-temperature) should be calibrated for each probe-head individually. This can be done using a sample which contains water (-0.01 ppm shift per K), or by using the KBr standard sample. Unnecessarily deep cooling has a negative influence on spinning behavior, as it enlarges the air-density and lowers the speed of sound. Magic angle adjustment can be biased as the mechanics inside the probe-head could be deformed due to drastic temperature changes.

Adjustment of the magic angle should be done at the desired final sample-temperature.

References

[1] Kent R. Thurber, Robert Tycko, Measurement of sample temperatures under magic-angle spinning from the chemical shift and spin-lattice relaxation rate of 79Br in KBr powder, J. Magn. Reason., 196, 1, 2009, 84-87.
[2] Jean-Max Tyburn, Variable Temperature Unit User manual, Bruker, 1998, 98-99.

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info@bruker.com
www.bruker.com