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Communication

Determination of sample temperature in unstable static fields by combining solid-state ^{79}Br and ^{13}C NMR

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ABSTRACT

Monitoring the isotropic chemical shifts to calibrate the sample temperature presupposes a perfect stability of the static magnetic field. It can be difficult to satisfy this requirement in solid-state NMR measurements. This paper describes a simple way to recover the accurate temperature dependence of the ^{79}Br resonance after subtracting changes of resonance frequency due to variations of the static field, monitored by the ^{13}C resonance.

1. Introduction

Accurate temperature control during NMR experiments is a prerequisite for dynamic and structural investigations [1–3]. This requirement is particularly challenging in high-resolution solid-state spectroscopy with magic angle spinning (MAS) when employing high gas flow rates for driving and bearing, with a separate flow to control of the temperature. High-power radio-frequency (rf) irradiation and friction can lead to significant heating of the sample that cannot be monitored accurately by variable-temperature control units.

Several approaches for determining the sample temperatures in solid-state NMR experiments have been reported. NMR thermometers can exploit the temperature dependence of the isotropic chemical shifts of specific compounds containing ^{13}C [1–3], ^{15}N [4], ^{31}P [5,6], ^{119}Sn [7–9], ^{207}Pb [10–12] and ^{1}H [13,14]. Very recently, spin–lattice relaxation rates of ^{79}Br in KBr powder have been exploited, in addition to chemical shifts, for the determination of the sample temperature under magic-angle spinning conditions over a wide temperature range from 20 to 320 K [15].

Monitoring isotropic chemical shifts to calibrate the sample temperature presupposes a perfect stability of the static magnetic field. It can be difficult to satisfy this requirement in solid-state NMR measurements. Solid-state NMR probes typically do not incorporate any field-frequency lock. Apart from the inherent slow drifts of the static field, a significant instability of B_0, on time-scales between a few tens of minutes and hours, is indeed commonly observed after inserting a solid-state NMR probe into a magnet and setting the relevant shim currents, or indeed after changing the target temperature.

In this communication we describe a simple approach to compensate for the effects of unstable static fields that can mask the temperature dependence of ^{79}Br isotropic chemical shifts. Since KBr has only one isotropic ^{79}Br resonance line flanked by a family of spinning sidebands, a single spectrum cannot provide a conclusive proof that the observed shift is purely induced by temperature. To overcome this problem, we used ^{13}C resonance signals from adamantane mixed with KBr to monitor any change of the external magnetic field B_0. Adamantane molecules freely rotate in a cubic phase between 208 and 543 K and the two ^{13}C chemical shifts appear to be insensitive to temperature, at least over the range probed in this work. Both KBr and adamantane in natural abundance provide strong signals and the difference between the ^{79}Br and ^{13}C resonance frequencies is only about 0.4%. Thus one can record both resonances in two consecutive single-pulse experiments within a few seconds without the need to retune the NMR probe.

2. Results and discussion

The experiments were conducted at two static fields using a Bruker 800 MHz wide-bore spectrometer equipped with a

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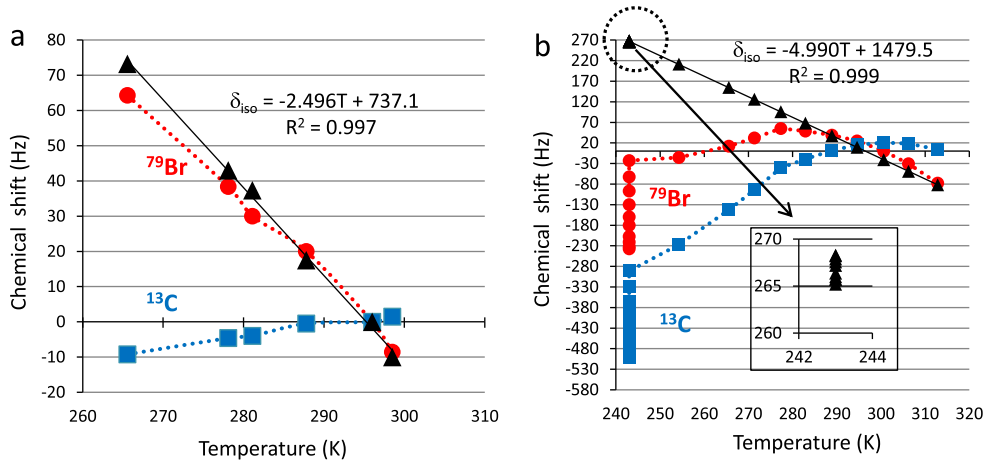

Fig. 1. Dependence of the observed isotropic chemical shifts of ^{79}Br (red circles) and ^{13}C (blue squares) of a mixture of KBr and adamantane powders versus temperature recorded in two magnetic fields, and of the corrected isotropic chemical shifts of ^{79}Br (black triangles) adjusted for field changes determined from the ^{13}C shifts: (a) B_0 = 9.4 T using a 4.0 mm probe with a spinning frequency ν_{rot} = 7 kHz and (b) B_0 = 18.8 T using a 3.2 mm probe and ν_{rot} = 2 kHz. The flow of the variable temperature gas was 2000 l/h in both cases. At 18.8 T, ten spectra of both ^{13}C and ^{79}Br were recorded on a time scale lasting from 30 min up to 10 h after the lowest temperature of 243 K became stable. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2 mm E-free MAS probe and a Bruker 400 MHz wide-bore spectrometer equipped with 1.3, 2.5 and 4.0 mm MAS probes. The ^{79}Br and ^{13}C spectra were acquired using four scans each with a recovery interval of 1.0 and 4.0 s, respectively. No decoupling was applied for recording ^{79}Br spectra of KBr while low-power PISSARRO decoupling [16–18] was used during the acquisition of ^{13}C spectra of adamantane.

Fig. 1 shows the temperature dependence of the observed ^{79}Br and ^{13}C chemical shifts recorded at two static fields B_0 = 9.4 T (99.8818 MHz for ^{79}Br, 100.2455 MHz for ^{13}C) and B_0 = 18.8 T (200.4446 MHz for ^{79}Br, 201.1682 MHz for ^{13}C) using 4.0 and 3.2 mm probes, respectively, and setting both ^{79}Br and ^{13}C chemical shifts arbitrarily to zero at 296 K, referring to [15].

In each case, for decreasing temperatures, the single-pulse experiments were started only when the temperature reading of the temperature controller had been stable for at least 20 min. A roughly linear down-field shift of the ^{79}Br signal is observed initially in both magnets when decreasing the temperature. The ^{13}C lines of adamantane reveal small but significant up-field shifts at B_0 = 9.4, and down-field shifts at 18.8 T. Quite unexpectedly however, a striking reversal of the trends of both ^{79}Br and ^{13}C chemical shifts was observed at 18.8 T below 290 K. This, at first glance puzzling, apparent reversal of the direction of the ^{79}Br chemical shift is in fact due to the change of the static field. This must be due to a progressive cooling of the shim coils, which appears to lag behind the cooling of the probe. To separate the temperature dependence of ^{79}Br chemical shifts from their field dependence, it suffices to subtract the latter's contribution monitored through the ^{13}C resonance. As shown in Fig. 1 this permits one to recover an unequivocal linear temperature dependence of the ^{79}Br chemical

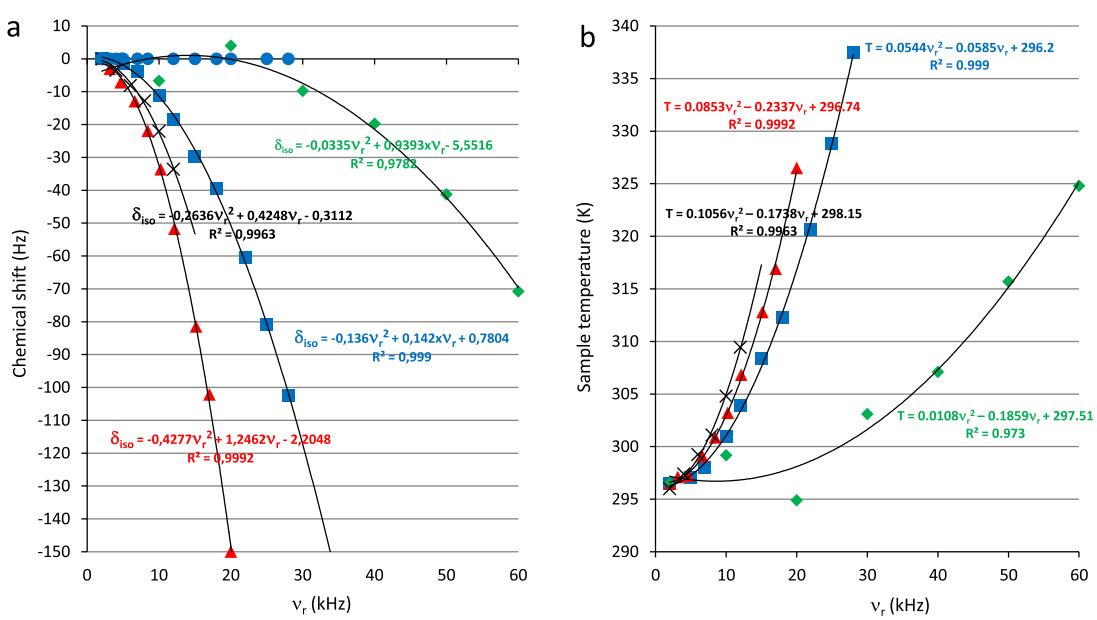

Fig. 2. (a) Plot of the ^{79}Br chemical shifts versus spinning frequency recorded for KBr using rotors with diameters of 4 mm (black crosses), 3.2 mm (red triangles), 2.5 mm (blue squares) and 1.3 mm (green lozenges). The ^{13}C chemical shifts of adamantane recorded with a 2.5 mm diameter rotor at different spinning frequencies are also shown (blue circles). (b) Frictional heating of the sample for each type of rotor, using the same symbols and colors as in (a). The linear fits shown in Fig. 1 were used to convert ^{79}Br shifts to temperatures. The flow of the gas was 800 l/h for the 2.5 mm rotor and 2000 l/h for all other rotors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

shift [14]. A least-squares analysis of the data yields the same slope −0.025 ± 0.002 ppm/K at both B_0 = 9.4 and 18.8 T, with correlation coefficients close to 1. It is worth pointing out that in the temperature range probed in this work, the observed drift of B_0 does not lead to any loss of spectral resolution, which would of course hamper monitoring of the chemical shifts. Otherwise, shimming would be necessary before recording both ^{79}Br and ^{13}C spectra at each temperature. If a ^{15}N chemical-shift thermometer were preferred, as described in Ref. [4], this would require a blend with another ^{15}N labeled compound with a chemical shift that does not depend on the temperature.

Fig. 2a shows plots of the ^{79}Br chemical shift versus spinning frequency recorded for KBr in rotors with 1.3, 2.5, 3.2 and 4.0 mm diameter without any temperature regulation.

In all cases the acquisition was not begun until the ^{79}Br chemical shift had become stable. The constant ^{13}C chemical shift of adamantane recorded with a 2.5 mm rotor is also included. The upfield shifts of the ^{79}Br resonances may be attributed to increasing frictional heating of the sample with increasing spinning frequencies and can be fitted by using polynomial functions included in the figure. The corresponding frictional heating of the sample shown in Fig. 2b for each type of rotor was calculated by using linear fits in Fig. 1 to convert shifts to temperatures. In the absence of an active temperature control, we observed a *ca.* 20% increase in the line-width of the ^{79}Br signal at the highest spinning frequencies employed in this work with different types of rotors. This is a strong indication of inherent temperature gradients ranging from 3 to 5 °C within fully packed rotors. Increasing the flow of the gas to control the temperature can attenuate these gradients. The precise calibration of temperature gradients within the sample, mandatory for accurate determination of temperature-induced phase transitions and for the study of the activation of specific motional processes, would require the restriction of the sample to thin, disc-shaped regions, positioned at the center of the rotor and at its bottom and top ends.

3. Conclusion

We have shown that a simple blend of KBr and adamantane powders can be used as a reliable chemical-shift thermometer to measure the sample temperature accurately in real time, even in unstable static fields. We presented a simple way to determine the accurate temperature dependence of the ^{79}Br resonance after subtracting changes of resonance frequency due to changes of the static field, monitored by the ^{13}C resonance of adamantane.

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References

[1] G.C. Campbell, R.C. Crosby, J.F. Haw, ^{13}C chemical shifts which obey the Curie law in CP/MAS NMR spectra. The first CP/MAS chemical-shift thermometer, J. Magn. Reson. 69 (1986) 191–195.
[2] J.F. Haw, R.A. Crook, R.C. Crosby, Solid–solid phase transitions for temperature calibration in magic-angle spinning, J. Magn. Reson. 66 (1986) 551–554.
[3] A.N. Klymachyov, N.S. Dalal, Squaric acid as an internal standard for temperature measurements in ^{13}C MAS NMR, Solid State Nucl. Magn. Reson. 7 (1996) 127–134.
[4] B. Wehrle, F. Aguilar-Parrilla, H.-H. Limbach, A novel ^{15}N chemical shift NMR thermometer for magic-angle spinning experiments, J. Magn. Reson. 87 (1990) 584–591.
[5] H. Pan, B.C. Gerstein, NMR of ^{31}P in $(VO)_2P_2O_7$ as an internal temperature standard in high-temperature NMR, J. Magn. Reson. 92 (1991) 618–619.
[6] C.S. Zuo, K.R. Metz, Y. Sun, A.D. Sherry, NMR temperature measurements using a paramagnetic lanthanide complex, J. Magn. Reson. 133 (1998) 53–60.
[7] C.P. Grey, A.K. Cheetham, C.M. Dobson, Temperature-dependent solid-state ^{119}Sn MAS NMR of $Nd_2Sn_2O_7$, $Sm_2Sn_2O_7$, and $Y_{1.8}Sm_{0.2}Sn_2O_7$. Three sensitive chemical shift thermometers, J. Magn. Reson. 101 (1993) 299–306.
[8] B. Langer, I. Schnell, H.W. Spiess, A.-R. Grimmer, Temperature calibration under ultrafast MAS conditions, J. Magn. Reson. 138 (1999) 182–186.
[9] T.F. Kemp, G. Balakrishnan, K.J. Pike, M.E. Smith, R. Dupree, Thermometers for low temperature Magic Angle Spinning NMR, J. Magn. Reson. 204 (2010) 169–172.
[10] A. Bielecki, D.P. Burum, Temperature dependence of ^{207}Pb MAS spectra of solid lead nitrate. An accurate, sensitive thermometer for variable temperature MAS, J. Magn. Reson. A 116 (1995) 215–220.
[11] T. Takahashi, H. Kawashima, H. Sugisawa, T. Baba, ^{207}Pb chemical shift thermometer at high temperature for magic-angle spinning experiments, Solid State Nucl. Magn. Reson. 15 (1999) 119–123.
[12] P.K. Isbester, A. Zalusky, D.H. Lewis, M.C. Douskey, M.J. Pomije, K.R. Mann, E.J. Munson, NMR probe for heterogeneous catalysis with isolated reagent flow and magic-angle spinning, Catal. Today 49 (1999) 363–375.
[13] A.E. Aliev, K.D.M. Harris, Simple technique for temperature calibration of a MAS probe for solid state NMR spectroscopy, Magn. Reson. Chem. 32 (1994) 366–369.
[14] S.V. Dvinskikh, V. Castro, D. Sandstrom, Heating caused by radio-frequency irradiation and sample rotation in ^{13}C magic-angle spinning NMR studies of lipid membranes, Magn. Reson. Chem. 42 (2004) 875–881.
[15] K.R. Thurber, R. Tycko, Measurement of sample temperatures under magic-angle spinning from the chemical shift and spin-lattice relaxation rate of ^{79}Br in KBr powder, J. Magn. Reson. 196 (2009) 84–87.
[16] M. Weingarth, P. Tekely, G. Bodenhausen, Efficient heteronuclear decoupling by quenching rotary resonance in solid-state NMR, Chem. Phys. Lett. 466 (2008) 247–251.
[17] M. Weingarth, G. Bodenhausen, P. Tekely, Low-power decoupling at high spinning frequencies in high static fields, J. Magn. Reson. 199 (2009) 238–241.
[18] M. Weingarth, G. Bodenhausen, P. Tekely, Probing the quenching of rotary resonance by PISSARRO decoupling, Chem. Phys. Lett. 502 (2011) 259–265.