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A spinning thermometer to monitor microwave heating and glass transitions in dynamic nuclear polarization

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As previously demonstrated by Thurber and Tycko, the peak position of ^{79}Br in potassium bromide (KBr) allows one to determine the temperature of a spinning sample. We propose to adapt the original design by using a compact KBr tablet placed at the bottom of the magic angle spinning rotor, separated from the sample under investigation by a thin disk made of polytetrafluoroethylene (or 'Teflon'®). This design allows spinning the sample up to at least 16 kHz. The KBr tablet can remain in the rotor when changing the sample under investigation. Calibration in the range of $98 < T < 320$ K has been carried out in a static rotor by inserting a platinum thermometer. The accuracy is better than ± 0.9 K, even in the presence of microwave irradiation. Irradiation with 5 W microwaves at 263 GHz leads to a small temperature increase of 3.6 ± 1.4 K in either static or spinning samples. The dynamic nuclear polarization enhancement decreases with increasing temperature, in particular when a frozen glassy sample undergoes a glass transition. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: dynamic nuclear polarization; magic angle spinning (MAS); MAS thermometry; potassium bromide (KBr); glass transition

Introduction

When combining magic angle spinning (MAS) with dynamic nuclear polarization (DNP), it is difficult to determine the real sample temperature because distinct gas flows are used for bearing, spinning and cooling, whereas Joule–Thomson effects and dielectric heating due to high-power *rf* pulses and microwave irradiation, both of which are required for DNP–NMR, may contribute to unpredictable temperature gradients across the sample. The temperature can have dramatic effects on the internal dynamics of samples, relaxation rates and signal enhancement by DNP.[1] In particular, electron spin relaxation rates can be highly temperature dependent in the vicinity of $T = 100$ K so that relatively small temperature changes may have significant effects on DNP enhancements.[2] In the late 1960s, Van Geet[3] showed that proton chemical shifts of liquid alcohols can provide accurate estimates of the sample temperature. In the solid state, the use of NMR peak positions as a measure of temperature is more challenging because the lines tend to be broad, particularly in static samples. Thurber and Tycko[4] have shown that the central transition of ^{79}Br (spin $I = 5/2$) in solid potassium bromide (KBr) provides a reasonably sharp NMR line with a position that is very sensitive to the temperature, both in static and spinning samples. They suggested that ^{79}Br shifts might be useful in the presence of microwave irradiation required for DNP. Rosay *et al.*[2] used the design of Thurber and Tycko[4] to observe heating effects caused by microwave irradiation but were limited to low spinning frequencies (1.2 kHz), presumably because of the imperfect cylindrical symmetry of the rotors, which contained a plug of KBr powder in an axial arrangement. We propose a new design (Fig. 1) that allows spinning frequencies up to at least 16 kHz. The sample under investigation can be easily changed while leaving the KBr tablet in place.

Although the chemical shift of ^{207}Pb in $Pb(NO_3)_2$ [5] is known to have a sharper central transition and features a greater range of chemical shifts as a function of temperature, microwave irradiation of such an explosive compound appears fraught with danger. Recently, Dupree and coworkers[6] have shown that the central transition of ^{119}Sn in $Sm_2Sn_2O_7$ provides a more accurate temperature determination in spinning samples around 100 K, but concerns that intense microwave irradiation might interact with this highly dielectric[7] and paramagnetic[8] material lead us to prefer KBr. This material also is useful to adjust the magic angle (because deviations from the ideal angle lead to line broadening) and to measure the spinning frequency (which determines the spacing between the spinning sidebands).[9] Note that optical measurements of the spinning frequency are challenging for transparent sapphire rotors that are often used for DNP.

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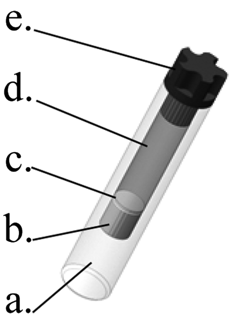

Figure 1. (a) Sapphire rotor with 3.2 mm outer diameter, (b) 10 mg KBr tablet, (c) polytetrafluoroethylene isolating disk of 0.25 mm thickness, (d) sample in a solvent that forms a glass near 100 K (e.g. 1 M $_{13}$C acetate in 60% glycerol-d8 or methanol-d4, 30% D_2O, 10% H_2O with 12 mM (TOTAPOL) and (e) drive cap.

Calibration of the Thermometer Integrated into the Rotor

The temperature in a rotor inserted into a low-temperature–DNP–MAS probe (Bruker Biospin) was measured with a PT100 thermometer sealed in a ceramic container (PRTD–TDI, 1.2 mm outer diameter) that was inserted into an empty sapphire rotor. The flow of the variable temperature (VT) unit was kept constant at 2000 l/h, like for spinning experiments, whereas the bearing temperature (BT) flow of the bearing gas and the driving temperature (DT) flow of the driving gas were switched off. After stabilizing for 1 h, the temperature T_{PT} was measured five times with the PT100 thermometer at 10-min intervals. No fluctuations were observed. The PT100 thermometer was calibrated at $T_{PT} = 77.4$ K with liquid nitrogen and at $T_{PT} = 273.2$ K with melting ice, both at atmospheric pressure. The PT100 thermometer output T_{PT} was compared with the 'nominal' temperature T_{VT} indicated by the VT unit. The PT100 sensor was then replaced by a KBr tablet. Figure 1 shows how a tablet of 10 mg compressed dry KBr powder and an isolating polytetrafluoroethylene (PTFE) disk of 0.25 mm thickness are placed in the MAS rotor.

The position of the central transition of ^{79}Br (spin $I = 5/2$) was measured in a non-spinning sample as a function of the nominal temperature T_{VT} of the variable temperature (VT) controller by reproducing the exact conditions of the calibration. The fitted full width at half height of the central transition of ^{79}Br in a non-spinning sample at $T_{VT} = 140.0$ K (Fig. 2a) was found to be $\Delta\nu = 916.8 \pm 0.6$ Hz in a static field $B_0 = 9.4$ T where the ^{79}Br Larmor frequency is 100.24 MHz (400 MHz for protons). The position of the central transition of ^{79}Br is not affected by the spinning frequency so that the calibration can be carried out at arbitrary spinning frequencies. The ^{79}Br peak position and width were determined using Origin, taking the center of gravity of the magnitude of the Fourier transforms of the free induction decays, thus avoiding fitting and phasing errors. Possible drifts of the static field were monitored by measuring the ^{13}C-NMR spectrum of adamantane at 298 K spinning at 4 kHz, as proposed by Morcombe and Zilm.[10] The stability of the static field was checked, and the temperature calibration was corrected by measuring the NMR spectrum of the same sodium acetate sample as used for DNP, which features a ^{13}C peak that shows a negligible temperature dependence. Figure 2b shows the calibration of the ^{79}Br peak position as a function of the PT100 sensor temperature T_{PT}.

Our design makes it possible to empty the rotor without removing the KBr tablet and allows one to preserve *ca* 70% of the inner rotor volume for the sample under investigation. The peak position of KBr can be measured while running arbitrary NMR experiments, in particular, DNP–MAS experiments, without changing the sample. Note that the dimensionless dielectric constant of KBr ($\varepsilon = 4.6$)[11] is much smaller than that of sapphire ($\varepsilon = 10$),[12] whereas the masses of the tablet and the empty sapphire rotor are 10 and 325 mg, respectively, so that dielectric heating of the KBr tablet should not significantly contribute to the heating of the sample. The heating effect of the microwave irradiation has been verified to be independent of the MAS frequency by measuring the chemical shifts at $\nu_{rot} = 0$, 8 and 16 kHz with the same nominal temperature T_{VT}. No significant variations have been observed.

Results and Discussion

Effects of microwave irradiation

The ^{79}Br peak position allows one to quantify the heating effects of the microwave irradiation at various temperatures in both solid and liquid samples, in static or spinning rotors (Fig. 3). A sapphire rotor containing a 10 mg tablet of compressed KBr and a PTFE disk was filled with the following: (i) dry polycrystalline 1-^{13}C sodium acetate, or (ii) a 1 M solution of 1-^{13}C sodium acetate and 12 mM TOTAPOL 1-(TEMPO-4-oxy)-3-(TEMPO-4-amino)propan-2-ol in a glass-forming solvent mixture of 60% glycerol-d8, 30% D_2O and 10% H_2O.

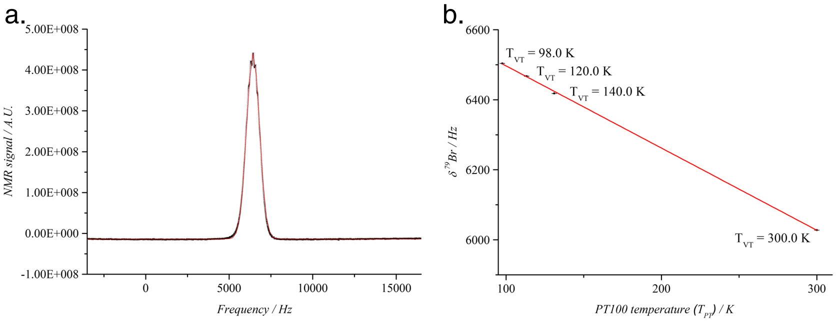

Figure 2. (a) ^{79}Br central transition (experimental = black points; Lorentzian fit = red line) obtained at the nominal temperature $T_{VT} = 140.0$ K in a non-spinning sample with 128 scans in 38 s. The fitted line width at half the height of the central transition is $\Delta\nu = 916.8 \pm 0.6$ Hz, the ^{79}Br Larmor frequency being 100.24 MHz (400 MHz for protons) at 9.4 T. (b) Experimental peak positions of the central transition of ^{79}Br in a 10 mg KBr tablet in a non-spinning sapphire NMR rotor with linear fit for $98.0 < T_{VT} < 300.0$ K. The temperature in the rotor has been previously measured for the same nominal temperatures T_{VT} using a 1.2-mm outer diameter PRTD (TDI) PT100 thermometer that was calibrated with liquid nitrogen at $T_{PT} = 77.4$ K and melting ice at $T_{PT} = 273.2$ K. Each measurement was repeated five times and averaged. The error bars on the ordinates are too small to be visible on this scale.

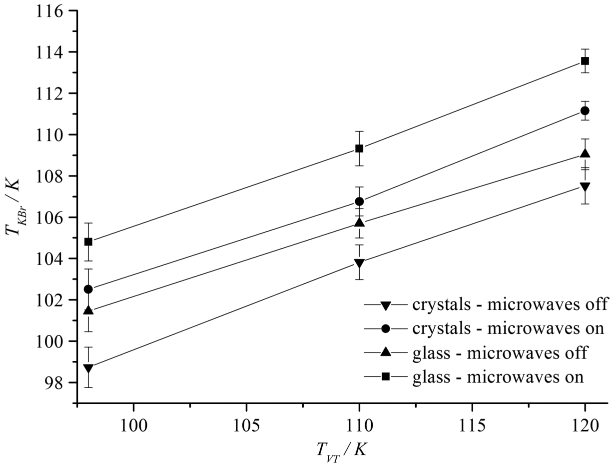

Figure 3. Temperature in a sample of solid polycrystalline 1-^{13}C sodium acetate [downward-pointing triangles (▼) and dots (•)] and a frozen glassy solution of the same acetate suitable for DNP (1 M 1-^{13}C sodium acetate with 12 mM TOTAPOL, 60% glycerol-d8, 30% D_2O, 10% H_2O) [triangles (▲) and squares (■)] as a function of the nominal temperature T_{VT} without [triangles (▲) and (▼)] and with [dots (•) and squares (■)] microwave irradiation (*ca* 5 W at 263 GHz). An increase in the true temperature T_{KBr} of 3.6 ± 1.4 K caused by the microwave irradiation was observed over a nominal range of $98.0 < T_{VT} < 120.0$ K for both polycrystalline and frozen glassy samples. The fitted full line width at half the height of the central transition at $T_{VT} = 140.0$ K and 8 kHz spinning frequency is $\Delta\nu = 99.53 \pm 0.26$ Hz, the ^{79}Br Larmor frequency at 9.4 T being 100.24 MHz (400 MHz for protons).

We observed an increase in the true temperature T_{KBr} of 3.6 ± 1.4 K caused by 5 W microwave irradiation at 263 GHz over a range $98.0 < T_{VT} < 120.0$ K for both polycrystalline and frozen glassy samples. This increase is rather modest and does not significantly modify the physical state of the sample. In samples with larger dielectric constants, in particular in ionic or metallic conductors, sample heating may be significantly higher and could be exacerbated by spinning in the magnetic field.[13]

Effects of glass transitions on DNP enhancements

Even small increases in temperature, such as illustrated in Fig. 3, may have dramatic effects on the enhancement factors that can be achieved by DNP. The choice of appropriate solvent mixtures is critical in DNP experiments. Two solutions that are suitable for DNP were prepared with 1 M 1-^{13}C sodium acetate and 12 mM TOTAPOL, the first with 60% glycerol-d8, 30% D_2O and 10% H_2O and the second with 60% methanol-d4, 30% D_2O and 10% H_2O. A sapphire rotor containing a 10-mg KBr tablet and a 0.25-mm-thick PTFE disk was filled with either solution. The enhancement factor $\varepsilon_{DNP}(^1H)$ or $\varepsilon_{DNP}(^{13}C)$ and the ^{79}Br peak positions were measured for several nominal temperatures T_{VT}. The 'true' sample temperatures T_{KBr} were calculated using Fig. 2b. The relative DNP enhancements $\varepsilon_{DNP}/\varepsilon_{DNP}^{max}$ (normalized with respect to the maximum enhancement ε_{DNP}^{max} that could be achieved for each sample at the lowest temperature, which was in the vicinity of $\varepsilon_{DNP}^{max} \simeq 20$) were plotted in Figs. 4a and b as a function of the true sample temperature T_{KBr}.

One can observe a sudden decrease of ε_{DNP} around 110 K in a frozen 60/40 (v/v) methanol/water mixture, probably because of the glass transition, which occurs at[15,16] $T_g = 112$ K for such a mixture. No sharp variation is observed in a frozen 60/40 (v/v) glycerol/water solution, which has a glass transition temperature[14] $T_g = 162$ K (Fig. 4b). The change in molecular motions that occurs at the glass transition may affect the electron and nuclear relaxation rates and therefore lower the DNP enhancements.[17,18]

Conclusions

We have demonstrated that it is possible to measure the 'true' temperature T_{KBr} in a sample that is spinning up to at least 16 kHz using a small KBr tablet inserted into the rotor. The heating caused by 5 W microwave irradiation was found to be limited to a few degrees. We have highlighted the deleterious effects of glass transitions in frozen solutions on the DNP enhancement. This allows one to select solvent mixtures that are most appropriate for DNP and to understand the temperature dependence of DNP enhancements.

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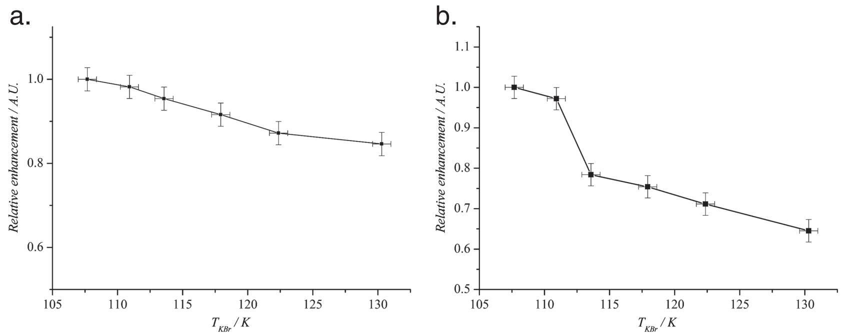

Figure 4. Relative DNP enhancements $\varepsilon_{DNP}/\varepsilon_{DNP}^{max}$ in frozen glassy solutions of 1 M 1-^{13}C-acetate with 12 mM TOTAPOL dissolved (a) in 60% glycerol-d8, 30% D_2O and 10% H_2O, and (b) in 60% methanol-d4, 30% D_2O and 10% H_2O, as a function of the true sample temperature T_{KBr} determined using the calibration of Fig. 2b. The enhancements were measured for ^{13}C signals after cross-polarization from ^{1}H to ^{13}C. The sudden drop of the DNP enhancement around 110 K observed in (b) can be ascribed to the glass transition of the 60/40% methanol/water mixture. In the glycerol/water mixture of (a), the glass transition occurs near $T_g = 162$ K.[14]

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