

Temperature Calibration under Ultrafast MAS Conditions

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For conventional fast magic-angle spinning (MAS) frequencies (≤ 15 kHz), there is a known heating of the sample due to the friction between the rotor and the bearing gas. At the recently achievable ultrafast MAS frequencies of up to 35 kHz, a more dramatic heating effect is expected. Using the ^{119}Sn NMR signal of the chemical shift thermometer $\text{Sm}_2\text{Sn}_2\text{O}_7$, this frictional heating effect is quantified, and a calibration of the sample temperature under ultrafast MAS conditions is described. An empirical expression is given which allows the determination of the sample temperature as a function of the bearing gas temperature and the spinning frequency. © 1999 Academic Press

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INTRODUCTION

In magic-angle spinning (MAS) experiments, the sample temperature is usually controlled by adjusting the temperature of a gas flow applied to the rotor. In Bruker systems, for example, the temperature of the bearing gas is varied, whereas in Chemagnetics systems, a separate gas stream, additional to the drive and bearing gas, of variable temperature is applied. For all cases, however, it is well known that the actual sample temperature is significantly influenced by the sample rotation; with increasing spinning frequencies, the rotor and the sample heat up due to the friction between the rotor and the bearing gas (*1*). Since temperature control is crucial for many experiments, in particular for variable-temperature (VT) MAS experiments, the actual sample temperature needs to be measured internally. Such a calibration can be achieved by the physical mixing of the sample with a chemical shift thermometer. Although the mixing technique is the most straightforward and precise approach for temperature determination, it is, however, inappropriate in many cases, for example when the sample is reactive or valuable. Therefore, a general quantification of the frictional heating effect is desirable and of particular importance for many applications of ultrafast MAS techniques.

For rotor frequencies of up to 15 kHz, a systematic and

quantitative investigation of the influence of MAS on the sample temperature has been performed using the ^{119}Sn resonance of $\text{Sm}_2\text{Sn}_2\text{O}_7$ as a chemical shift thermometer (*1*). For a MAS probe utilizing rotors of 4-mm outer diameter (od), an equation for the true sample temperature at a given bearing gas temperature and spinning frequency was obtained. It should be noted that for MAS probes utilizing rotors of 7 mm od and allowing moderate spinning rates of up to 6 kHz, no significant heating effect was observed (*1*).

An important recent advance in the field of solid-state NMR has been the development of probes utilizing rotors of 2.5-mm od, which allow MAS to be performed at rotation frequencies of up to 35 kHz (*2*). This ultrafast MAS technique affords significant resolution enhancements for strongly dipolar coupled systems. For rigid ^1H systems, this has been demonstrated for both a model compound (*3*) and hydrogen-bonded structures of current chemical interest (*4, 5*). In the latter case, the interpretation of the ^1H spectra is only possible at these ultrafast MAS frequencies. Moreover, in ^{19}F NMR, ultrafast MAS achieves both dipolar decoupling and averaging of the chemical shift anisotropy, thus yielding high-resolution spectra, as has been shown for inorganic fluorides (*6*) and fluoropolymers (*7, 8*). Additionally, such high MAS frequencies have been used to simplify ^{23}Na and ^{27}Al multiple-quantum (MQ) MAS spectra by the effective removal of heteronuclear dipolar couplings, such that the origin of the observed MQ MAS spinning-sideband patterns (*9, 10*) in first-order quadrupolar systems is more easily elucidated (*11*).

In this Communication, we extend the preceding work (*1*) to ultrafast MAS conditions, where the MAS-induced heating effect is expected to be much more pronounced. For a spinning frequency of 35 kHz, Bruker's manual for the 2.5-mm MAS probes mentions a heating effect of approximately 55 K, based on ^{207}Pb NMR spectra of $\text{Pb}(\text{NO}_3)_2$.

EXPERIMENTAL

All experiments were performed on a Bruker ASX 500 spectrometer at a ^{119}Sn Larmor frequency of 186.5 MHz using a commercial Bruker MAS probe utilizing rotors of 2.5-mm od

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(2). The inner diameter of these rotors is 1.3 mm, corresponding to a sample volume of approximately 12 μl . The spinning frequency, ν_r , was varied in steps of 5 kHz between 5 and 30 kHz and in steps of 2.5 kHz between 30 and 35 kHz. An electronic Bruker MAS unit was used for spinning control and stabilization within ± 10 Hz.

The bearing gas (air) was cooled or heated, and controlled by the Bruker VT unit and the probe thermocouple, while the drive gas was used at ambient temperature. The thermocouple is located in the bearing gas stream, at the position directly before the gas enters the boron nitride stator. The bearing gas temperature, T_b , was varied in steps of 10 K between 240 and 350 K. After each change of temperature, the sample was allowed to equilibrate for 5 min before recording the NMR spectrum. Under these conditions, neither any broadening nor asymmetry of the ^{119}Sn resonance line of $\text{Sm}_2\text{Sn}_2\text{O}_7$, which would be indicative of localized inhomogeneous heating effects, was observed. For spinning frequencies $\nu_r < 30$ kHz, the bearing gas pressure was set to 3 bar, whereas for $\nu_r \geq 30$ kHz, as a consequence of the requirement to use drive pressures above 2 bar, a bearing gas pressure of 4 bar was necessary. For each spectrum, 128 transients were averaged using a recycle time of 500 ms, which is much longer than the spin–lattice relaxation time $T_1 \sim 0.1$ ms (12).

The isotropic chemical shift, δ_{iso} , of the ^{119}Sn resonance of $\text{Sm}_2\text{Sn}_7\text{O}_7$ was determined relative to the ^{119}Sn resonance of SnO_2 , the latter at $\delta_{\text{iso}} = -604.3$ ppm serving as a secondary reference to the primary standard $\text{Sn}(\text{CH}_3)_4$ at $\delta_{\text{iso}} \equiv 0$ ppm. For $\nu_r \geq 5$ kHz, the linewidths of the ^{119}Sn resonances of $\text{Sm}_2\text{Sn}_2\text{O}_7$ and SnO_2 were 4 and 2 ppm, respectively. The chemical shift values could be obtained from the spectra with an accuracy of ± 0.2 ppm.

RESULTS AND DISCUSSION

The sample temperature was calculated from the isotropic chemical shift of the ^{119}Sn resonance of $\text{Sm}_2\text{Sn}_2\text{O}_7$. The temperature dependence of the frequency of this ^{119}Sn resonance line has been investigated in detail by van Moorsel *et al.* (13), who showed that the origin of the phenomenon is the hyperfine interaction between the paramagnetic electron spin and the ^{119}Sn nucleus. Considering only the ground and first excited states of Sm^{3+} and using the Van Vleck equation, they derived an analytical expression describing the dependence of δ_{iso} on the sample temperature. Thus, using their equation, the true sample temperature T_s can be calculated from the observed chemical shift. Figure 1 shows a plot of the determined sample temperature, T_s , as a function of the spinning frequency, ν_r , (Fig. 1a) and the bearing gas temperature, T_b , (Fig. 1b).

From Fig. 1, the expected increase in sample temperature with increasing spinning frequency is clearly evident. For rotors of 2.5-mm od, the maximum obtainable MAS frequency equals 35 kHz. At this frequency, the friction between the rotor

and the bearing gas heats the sample by 30–40 K. This is about twice as much as has been observed for conventional rotors with 4-mm od at a MAS frequency of 15 kHz (1). Thus, the frictional heating effect is indeed much more pronounced under ultrafast MAS conditions. In the previous study (1), a small cooling effect was observed for bearing gas temperatures above 300 K, when increasing the MAS frequency from 2 to 5 kHz. However, this could not be directly observed in this investigation, since the ultrafast MAS equipment does not allow sufficiently stable rotor spinning below 5 kHz. Nevertheless, for all bearing gas temperatures at low MAS frequencies ($\nu_r < 15$ kHz), the initial sample temperatures T_s are observed to be slightly lower than the bearing gas temperatures.

For lower bearing gas temperatures T_b , an increased MAS heating effect is observed, since the viscosity of the gas, and hence the friction with the rotor, is higher at lower T_b . At $\nu_r = 35$ kHz, for example, the difference $T_s - T_b$ equals 39 and 33 K at $T_b = 240$ and 350 K, respectively. This complicates ultrafast MAS experiments at low temperatures in two ways; first, the bearing gas must be cooled down more to compensate for this more pronounced heating effect, and, second, the colder the bearing gas, the higher the drive gas pressure that must be applied in order to keep the spinning frequency constant. For standard Bruker equipment, the critical limit of drive and bearing gas pressures is reached at $T_b \approx 200$ K, such that for routine applications of ultrafast MAS, the minimum achievable sample temperature is about 240 K. It is interesting to note that to provide room temperature conditions at $\nu_r = 35$ kHz, the bearing gas must be cooled down to about 260 K.

From inspection of Figs. 1a and 1b, it is clear that an empirical expression describing the dependence of T_s on ν_r and T_b needs, at least, to include terms $\propto \nu_r$ and $\propto \nu_r^2$ and a term linear in T_b . Grimmer *et al.* (1) have shown that, under MAS conditions, the sample temperature T_s can be empirically described as a function of the bearing gas temperature T_b and the spinning frequency ν_r using an expression of the form

$$T_s = a_0 + a_1 \cdot T_b + a_2 \cdot \nu_r + a_3 \cdot (T_b \cdot \nu_r) + a_4 \cdot \nu_r^2. \quad [1]$$

In a two-dimensional least-squared procedure, a fit of our experimental sample temperature matrix $T_s(T_b, \nu_r)$ to Eq. [1] resulted in the coefficients

$$a_0 = (-12.1 \pm 1.5) \text{ K}$$

$$a_1 = (1.019 \pm 0.005)$$

$$a_2 = (0.62 \pm 0.07) \text{ K} \cdot \text{kHz}^{-1}$$

$$a_3 = (-2.3 \pm 0.2) \cdot 10^{-3} \text{ kHz}^{-1}$$

$$a_4 = (3.64 \pm 0.09) \cdot 10^{-2} \text{ K} \cdot \text{kHz}^{-2}. \quad [2a-e]$$

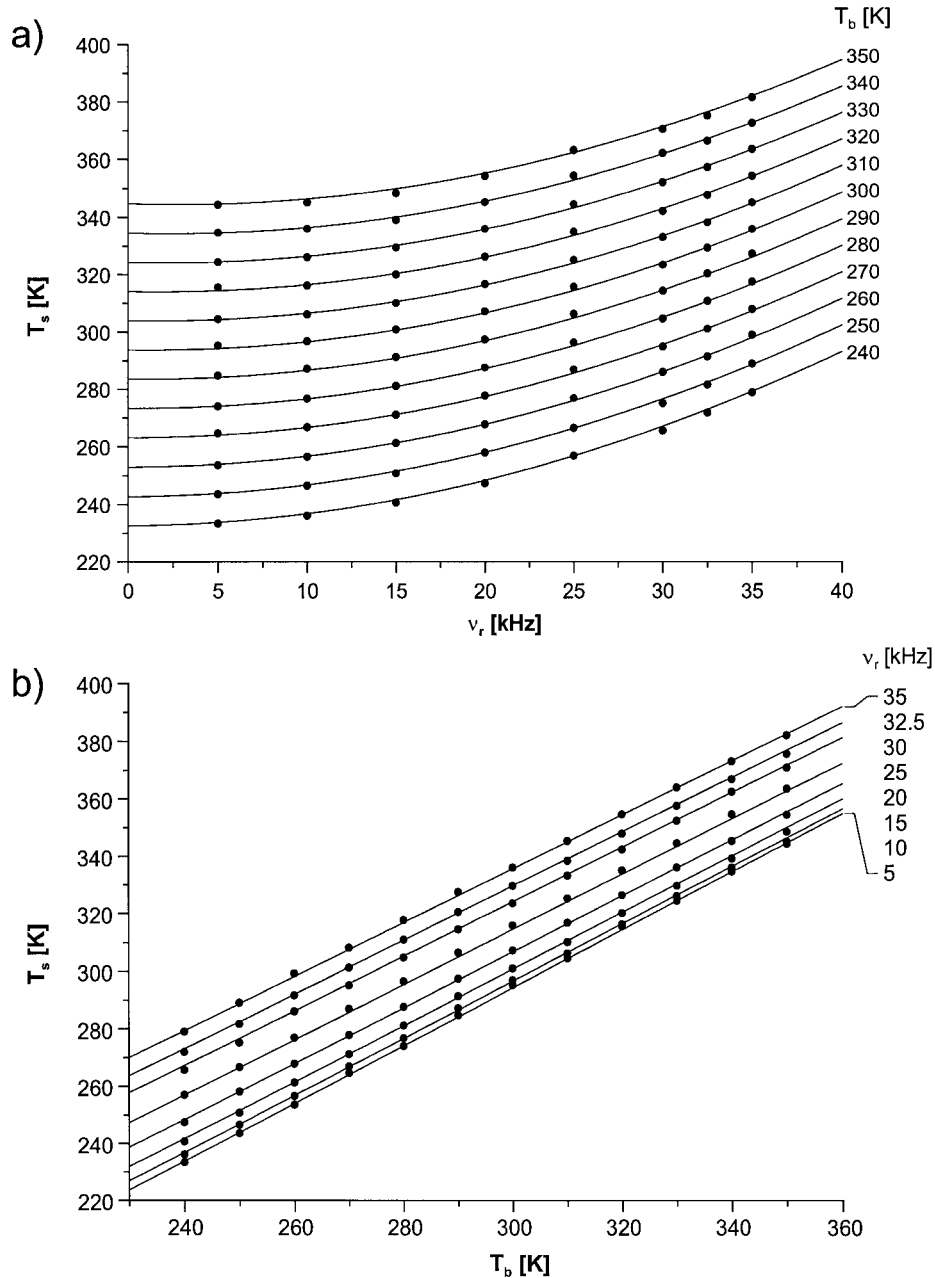


FIG. 1. Sample temperature T_s , as determined from the ^{119}Sn isotropic chemical shift of $\text{Sm}_2\text{Sn}_2\text{O}_7$, for (a) different MAS frequencies, ν_r , and (b) different bearing gas temperatures, T_b .

The negative sign of a_0 indicates quantitatively a cooling effect. For the static case, $\nu_r \equiv 0$ kHz, Eq. [1] reduces to

$$T_s = -12.1 \text{ K} + 1.019 T_b \approx T_b - 12 \text{ K}, \quad [3]$$

giving a difference ($T_b - T_s$) on the order of magnitude of 10 K. In our case, the static condition, $\nu_r \equiv 0$ kHz, implies the applica-

tion of bearing gas (in our experiments at a pressure of 3 bar), but no drive gas, such that the sample is cooled due to the Joule–Thomson effect (1, 14). Normally, static spectra at room temperature will be recorded applying neither bearing nor drive gas, resulting in ambient temperature conditions, but if bearing gas is used for cooling or heating, the sample temperature should be carefully measured or calculated from Eqs. [1] and [2a–e].

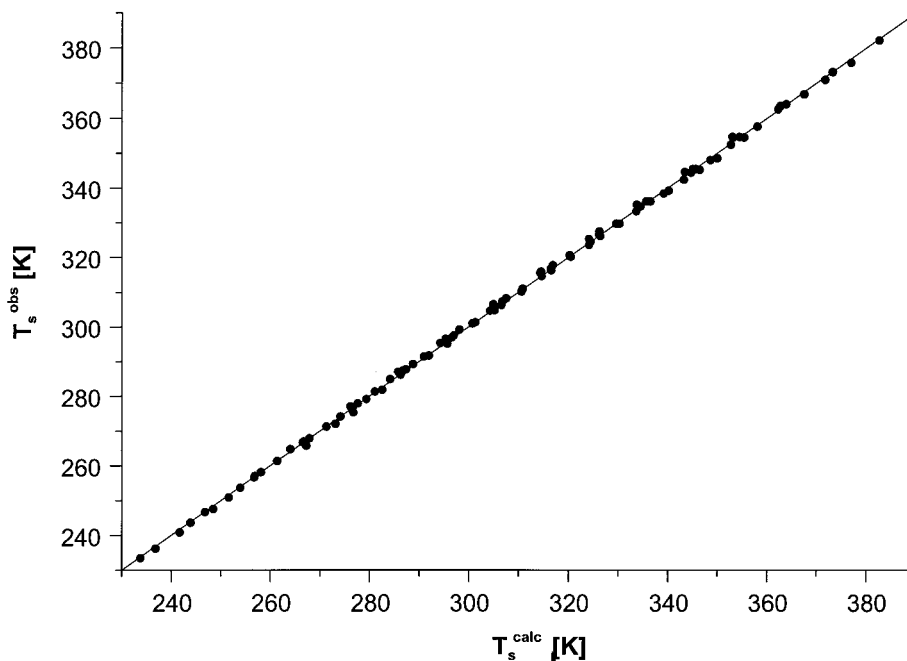


FIG. 2. Calculated versus observed sample temperature T_s . The experimental data shown in Fig. 1 are related to results calculated using Eqs. [1] and [2a–e].

In Fig. 2, the observed sample temperature T_s^{obs} (as derived from the ^{119}Sn chemical shift) is plotted versus the temperature T_s^{calc} , calculated from the bearing gas temperature T_b and the spinning frequency ν_r using Eqs. [1] and [2a–e]. The data fit to a straight line with a slope of 1.000 ± 0.002 , an offset of 0.0 ± 0.6 K and a reliability factor of 0.9998. This demonstrates that the empirical expression reflects the dependence of T_s on T_b and ν_r to a high degree of accuracy for the whole range of parameters, i.e., $240 \text{ K} \leq T_b \leq 350 \text{ K}$ and $\nu_r \leq 35 \text{ kHz}$.

It is expected that the sample temperature T_s is predominantly determined by the bearing gas temperature T_b . From the coefficients in Eqs. [2a–e], it is clear that approximately 80% of the resulting temperature is given by the term $a_1 \cdot T_b$, while the other terms contribute in the order of up to 20% and correct for the influence of sample spinning as well as the thermal properties of the probe.

Although the inclusion of terms $\propto \nu_r$ and $\propto \nu_r^2$ in Eq. [1] represents a completely empirical approach, the ν_r^2 dependence of the heating effect and its physical origin can be rationalized in terms of the Newtonian friction which is present in the case of fast motion and turbulent flow. It causes a frictional energy proportional to the square of the velocity of the rotor. Approaching the speed of sound, also higher order contributions of terms $\propto \nu_r^n$ with $n > 2$ are expected. In practice, however, the ν_r dependence of the sample temperature can be empirically described to a sufficient accuracy neglecting such terms.

In conclusion, for ultrafast MAS experiments using rotors of 2.5-mm od, the sample temperature is increased by 30–40 K

when spinning at 35 kHz. This frictional heating effect is exacerbated at low bearing gas temperatures. By use of an empirical expression—Eq. [1] with the coefficients given in Eqs. [2a–e]—the sample temperature can be straightforwardly predicted as a function of the bearing gas temperature and the spinning frequency to an accuracy of about ± 2 K, which is sufficient for most applications. For the precise determination of the five coefficients a_i , about 20 experiments at various T_b and ν_r should be sufficient, such that the full calibration of a probe needs less than 2 h. In order to determine the temperature more precisely, both the sample and a chemical shift thermometer must be measured in the same experiment, either by mixing the two compounds or by packing the two components separately in the rotor using a divider.

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