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A General Protocol for Temperature Calibration of MAS NMR Probes at Arbitrary Spinning Speeds

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Abstract

A protocol using ^{207}Pb NMR of solid lead nitrate was developed to determine the temperature of magic-angle spinning (MAS) NMR probes over a range of nominal set temperatures and spinning speeds. Using BioMAS and fastMAS probes with typical sample spinning rates of 8 and 35 kHz, respectively, empirical equations were devised to predict the respective sample temperatures. These procedures provide a straightforward recipe for temperature calibration of any MAS probe.

Keywords

temperature calibration; ^{207}Pb NMR; Magic-angle spinning

Temperature control is essential to many physical studies of thermosensitive samples such as biomolecules and engineered materials. In both solution- and solid-state NMR, the disparities between the set temperature and the true sample temperature inside the probe are well known. Thus, careful calibration is required to obtain the desired value or range of sample temperatures for a particular investigation. The ^{207}Pb NMR resonance of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) has become the accepted thermometer for calibration of sample temperature in magic-angle spinning (MAS) probes [1; 2; 3]. If the MAS rate is varied, however, the heating effects due to friction between the bearings, the variable temperature (VT) gas, and the spinning rotor complicate the relationship between frictional heating and heat diffusion. Thus to achieve comprehensive temperature calibration, an empirical approach may be preferred to an analytical formalism for description of the sample temperature as a function of both set temperature and MAS rate.

To test this idea, we used a Varian VNMRS system equipped with a BioMAS probe (3.2 mm, 3.0 – 13.3 kHz) and a FastMAS probe (1.6 mm, 15 – 35 kHz), each operating in a 14.1 T magnet. Both probes supply VT gas and bearing gas separately to achieve temperature regulation. The VT gas flow rate was set to 40 liters per minute using an FTS low-temperature source running at -70°C , whereas the bearing and drive gas were both operated at ambient temperature. For the BioMAS probe, the drive gas pressure was set between 3 and 13 psi, whereas the bearing gas was varied between 11 and 20 psi. For the FastMAS probe, the drive gas was varied between 3 and 40 psi, the bearing gas between 5 and 15 psi.

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The set temperature range was between -30.0 and 45.0 °C, controlled to within ± 0.2 °C. The true temperature at each spinning condition was calculated based on the linear relationship between the chemical shift of lead nitrate and the sample temperature: $\delta(T) = -3714.6 \text{ ppm} + (0.760 \text{ ppm/K}) * T$, where T is the temperature in degrees Kelvin [2]. The chemical shifts of ^{207}Pb were referenced to 0 ppm based on a calculation from frequency ratios of ^{207}Pb and ^{13}C , as recommended by IUPAC guidelines [4]. The ^{13}C spectrum was referenced directly to the methylene carbon of adamantane at 38.48 ppm [5]. Using this method, the chemical shifts of lead nitrate were determined more conveniently and accurately than by analyzing the powder lineshape of a static sample to derive the isotropic chemical shift under ambient sample conditions [6].

To illustrate the procedure, we focus mainly on trials with the BioMAS probe. As expected, excellent linear correlations ($R^2 \geq 0.9998$) were observed between sample temperature (T_s) and set temperature (T_o) at each MAS rate (ω_r) for both the BioMA and FastMAS probes (Fig. 1) and as reported previously [1; 2; 7]. Each of these relationships may be expressed as

$$T_s(T_o, \omega_r) = a(\omega_r) * T_o + b(\omega_r) \quad (1)$$

To find the sample temperature at any given set temperature (T_o) and MAS rate (ω_r), it is necessary to incorporate the dependence of the MAS rate into Eq. 1. This is possible by expressing $a(\omega_r)$ and $b(\omega_r)$ as functions of MAS rate (ω_r). Considering the slopes $a(\omega_r)$ first, the values are found to be nearly identical at different spin rates (0.9692 – 0.9736 shown in Fig. 1 for the BioMAS probe; 0.9786 – 0.9822 for the FastMAS probe (not shown), also reported previously for a 2.5-mm Bruker probe [7]). By using degrees Celsius as the unit of temperature, the effect of the tiny differences among slopes is minimized. Thus Eq. 1 may be simplified by using an average value of $a(\omega_r)$. Turning to the intercepts $b(\omega_r)$, Fig. 2 shows an exponential dependence on the MAS rate:

$$b(\omega_r) = b_0 + A * \exp(\omega_r / r) \quad (2)$$

where A and r are constants.

Neither step of this procedure involves more than three adjustable parameters, so the coefficients $a(\omega_r)$ and $b(\omega_r)$ should be better determined than with the 5-parameter fit described in Ref. [7]. Thus the temperature is specified completely for the BioMAS probe using the following coefficients:

$$T_s(b) = 0.97 * T_o + 1.34^\circ\text{C} * \exp(\omega_r / 7.53 \text{ kHz}) - 0.77^\circ\text{C} \quad (3)$$

Using an analogous procedure, the equation for the FastMAS probe is found to be

$$T_s(f) = 0.98 * T_o + 3.79^\circ\text{C} * \exp(\omega_r / 19.6 \text{ kHz}) - 3.49^\circ\text{C} \quad (4)$$

In practice, these results show, for instance, that a set temperature of -10 °C for a delicate sample spinning at 10 kHz corresponds to -5.4 °C in the BioMAS probe and -7.0 °C in the fastMAS probe, respectively.

Eqs. (3) and (4) add to the researcher's physical insight by revealing the independent contributions of the set temperature (T_o) and MAS rate (ω_r) to the sample temperature (T_s). In the absence of MAS ($\omega_r = 0$), Eq (3) becomes $T_s(b) = 0.97 * T_o + 0.57^\circ\text{C}$, resembling a

typical equation used for temperature calibration of liquid-state NMR probes that are not equipped for MAS. Conversely, the heating effect arising from MAS is reflected only in the intercept $b(\omega_r)$. Although the frictional heating should be proportional to the square of the MAS rate (ω_r), the heat generated is not absorbed completely by the rotor, but instead diffuses to some extent with the VT and bearing gases. As a consequence, $b(\omega_r)$ need not be proportional to the square of the MAS rate (ω_r); in our trials an exponential growth provided the best empirical fit.

Because the separate bearing and VT gas streams are directed at the drive tip and the central sample-containing part of the rotor, respectively, we expected that the main source of the frictional heating would involve the rotor and the VT gas. This hypothesis was confirmed for the BioMAS probe: using an 8.0-kHz spin rate and temperature setting of 22 °C, we measured an essentially negligible 0.1 °C change in temperature when the bearing gas pressure was varied between 13.4 and 19.1 psi. This negative result suggests that even in challenging spinning situations that require raising the bearing gas pressure by as much as 2–3 psi (e.g., thin-walled rotors, heterogeneous materials), its impact on frictional heating may be neglected. However, the flow rate and pressure of the VT gas should be kept constant. For probes that use the bearing gas to regulate temperature, the operating pressure should be maintained at a constant value.

Finally, the reliability of the sample temperatures (T_s) predicted from Eqs. (3) and (4) was assessed by comparing the measured sample temperatures for both BioMAS and FastMAS probes. Fig. 3 shows an excellent correlation between the predicted and measured values, with slopes close to 1 (0.9985, 1.0023) and intercepts near 0 (0.0114, 0.0131). The maximum deviations in our data sets were 0.56 °C for the BioMAS probe and 0.79 °C for the FastMAS probe, respectively, acceptable for most practical applications and superior to deviations of ± 2 K reported about a decade ago [7]. In addition to consistency, the excellent accuracy of our protocol is illustrated by the finding that under ambient conditions (room temperature of 20 °C, no spinning), the predicted temperatures are 19.97 and 19.90 °C for BioMAS and Fast MAS probes, respectively.

In summary, these results demonstrate the feasibility of calibrating NMR sample temperatures for any MAS probe at spinning rates up to 35 kHz using $\text{Pb}(\text{NO}_3)_2$, using a method that is straightforward, reliable, and physically insightful. The true sample temperature can be predicted accurately with an empirical equation based on set temperature and MAS rate, allowing us to adjust the sample temperature as desired for spectroscopic experiments and (bio)chemical materials of interest.

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Fig. 1.

Sample temperature (T_s) vs. set temperature (T_o) at different MAS rates (ω_r) for a BioMAS probe. Similar results are obtained for a FastMAS probe (data not shown). Error limits were estimated from the linewidth of the lead nitrate signal in the ^{207}Pb NMR spectrum.

Fig. 2.
Dependence of the intercept $b(\omega_r)$ on MAS rate ω_r for the BioMAS probe.

Fig. 3. Predicted sample temperature vs. measured sample temperature for BioMAS (a) and FastMAS (b) probes. Error limits were estimated from the linewidth of the lead nitrate signal in the ^{207}Pb NMR spectrum.