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Solid State Nuclear Magnetic Resonance 7 (1997) 333–336

SOLID STATE
Nuclear Magnetic
Resonance

Short Communication

Determining temperature in a magic-angle spinning probe using the temperature dependence of the isotropic chemical shift of lead nitrate

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Accepted 11 November 1996

Abstract

The calibration of temperature in a magic-angle spinning probe with lead nitrate is discussed. The effects of rotation frequency on temperature are demonstrated. © 1997 Elsevier Science B.V.

Keywords: Temperature; Calibration; Lead nitrate; Magic-angle spinning

1. Introduction

To obtain magic-angle spinning (MAS) spectra at other than ambient temperature requires one to calibrate the temperature in the MAS chamber, a process that may be difficult. The typical probehead contains a thermocouple that reports the temperature at a point several millimetres away from the sample, introducing some uncertainty. The temperature difference between this site and the MAS chamber depends on various parameters of the probe, including the pressure drop, the temperature gradient along the air path and the rotation frequency, as well as the mass of the sample. We examine these effects, specifically rotation frequency, on the measured temperature in a standard MAS probe. Calibration is possible because of recent measurements of the temperature-dependent chemical shift of ^{207}Pb in solid lead nitrate using magic-angle spinning [1]. Substantial gradients exist that may result in the temperature in the probe chamber being quite different from that at the thermocouple.

2. Experimental

Experiments were carried out using a 7 mm MAS probe on a Bruker MSL-300 NMR spectrometer with a B-VT1000 temperature controller to heat the bearing air. To focus on the effects of rotation frequency, we kept the bearing pressure at the pressure regulator constant at 1.5 bar in these experiments. Rotation frequency was varied by changing the drive gas pressure over a small range. Since the flow of heated gas is determined principally by the bearing-air flow,

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PII S0926-2040(96)01291-X

this was the measure we took to attempt to maintain a constant bearing-air flow. The heater is downstream of the pressure regulator, and this procedure does not quite maintain the head pressure across the orifices in the stator assembly when the temperature is changed. This effect is easily observed by the fact that an increase of the heater setting at constant drive pressure (at the pressure regulator) causes the spinner to speed up, even though the pressure regulator indicates that the pressure at its site is constant.

3. Results and discussion

It has been reported that magic-angle spinning spectra of ^{207}Pb in lead nitrate show a shift and line-shape change with rotation frequency [2], as well as a deliberate change of temperature. The earliest reports assumed this was a temperature effect, which has been shown quite convincingly by a careful study of line shapes [3]. More recently, the temperature coefficient of the chemical shift of ^{207}Pb in solid lead nitrate has been reported [1], and this can be used as a reporter of the temperature in the MAS chamber.

Our measurement of the temperature coefficient of the lead resonance in lead nitrate in our Bruker MAS probe at 2000 Hz is consistent with that of Bielecki and Burum [1]. We find the data at 2000 Hz fit extremely well to a linear relation of the type

$$\delta(T) = a_0 + b_0 T \qquad (1)$$

where a_0 and b_0 are parameters and T is the temperature in the MAS chamber. We determine a temperature coefficient, b_0, of $0.76(\pm 0.01)\,\mathrm{ppm\,K^{-1}}$, compared to the reported value of $0.753\,\mathrm{ppm\,K^{-1}}$ [2].

Bielecki and Burum do not report the absolute shift at any temperature. In our measurements we refer all data to an isotropic shift for lead nitrate of -3490.4 ppm at 295 K, as determined in a static sample at near-ambient conditions [4]. Such a sample should have minimal effects of gradients or other factors that may affect the shift in an MAS experiment. This choice sets an absolute scale of temperature as a function of isotropic chemical shift, making $a_0 = -3714.6(\pm 0.2)$ ppm.

A plot of shift versus *apparent* temperature (T_{app}, the temperature at the thermocouple) is also highly linear and obeys an equation similar to the actual shift-vs-temperature relation:

$$\delta_{app}(T_{app}, \omega_r) = a(\omega_r) + b(\omega_r) T_{app} \qquad (2)$$

where the coefficients are functions of the rotation frequency. The apparent temperature coefficient, b, in our MAS probe is $0.826\,\mathrm{ppm\,K^{-1}}$ at a rotation speed of 2000 Hz, clearly very different from the actual coefficient, and the offset is $a = -3734.15$ ppm. Similar data are given for the static sample [4] and for rotation frequencies of 1000 Hz and 3000 Hz (Table 1). It is clear that a and b depend strongly on rotation frequency, showing that the temperatures in the MAS chamber and at the thermocouple are quite different and are strongly rotation-frequency dependent. For example, near room conditions, the temperature in the MAS chamber varies by over 3 degrees simply by changing the rotation frequency from 1000 Hz to 3000 Hz!

Another means of depicting the temperature effects is shown in Fig. 1, where temperature in the MAS chamber is plotted against apparent temperature at the thermocouple for the three rotation frequencies. The dotted line in this figure indicates the relationship one would expect if these two temperatures were identical at all conditions. Clearly, there are effects that generally make the temperature in the MAS chamber higher than at the thermocouple. These depend on the heater setting and the rotation frequency.

The principal sources of these temperature differ-

Table 1
Parameters a and b of the apparent temperature dependence of the lead nitrate isotropic chemical shift as a function of rotation rate [a]

Spinning rate (Hz)	a (ppm)	$a_0 - a$ (ppm)	b ($\mathrm{ppm\,K^{-1}}$)	b/b_0
static [b]	−3775.1 (0.9)	60.5	0.965 (0.003)	1.270
1000	−3747.0 (1.6)	32.4	0.872 (0.005)	1.147
2000	−3734.15 (1.1)	19.55	0.826 (0.004)	1.087
3000	−3725.43 (1.9)	10.83	0.796 (0.006)	1.047

[a] Numbers in parentheses indicate the standard deviation of each parameter.
[b] Done in a different probe with a different reference position.

ences are gradients in the probe caused by heat losses and heat generation. We have focused on the effects of rotation frequency, but similar effects will be seen in the variation with pressure drop (flow rate). It is clear from data such as those at an apparent temperature of 295 K that an increase in rotation frequency increases the temperature in the probe. However, this is moderated as the mean temperature is increased, so that, at higher temperatures, the dependence on rotation frequency becomes less significant, but never negligible.

Aside from heat lost through the walls of the tube during transfer from the heater to the MAS chamber, there are two mechanisms that could affect the temperature in the MAS chamber. The first is Joule–Thomson cooling of the air as it passes from the region of high pressure through the orifices. A rough estimate indicates a cooling of the gas by about 0.5 K for the conditions under which we operate — a source of error, but not sufficient (and also of the wrong sign) to account for the change of temperature. In addition, there may also be heat loss through the walls of the transfer line that would tend to lower the temperature. This latter mechanism will become more important as the temperature of the heated gas is increased from room temperature.

The second effect is frictional heating of the air in the air bearing [5]. This factor causes an increase of the air temperature. This should increase with increased spinning rate — in line with the observed effects. We speculate that frictional heating in the bearing at higher spinning rates offsets cooling by loss in transfer and by Joule–Thomson cooling, resulting in a net heating of the sample. Frictional heating should increase approximately as the square of the rotation frequency. In addition, because the viscosity of the gas increases as it is heated, the frictional heating should become more important as the gas is heated. This is borne out by the trends in the data on Fig. 1.

The practical implication of these measurements is that there is not only a simple temperature shift on changing rotation frequency; the apparent temperature coefficient is a strong function of rotation frequency. Lead nitrate thermometry can easily be used to measure the temperature within the MAS chamber accurately and quickly. As currently configured, MAS probes must be calibrated at each rotation

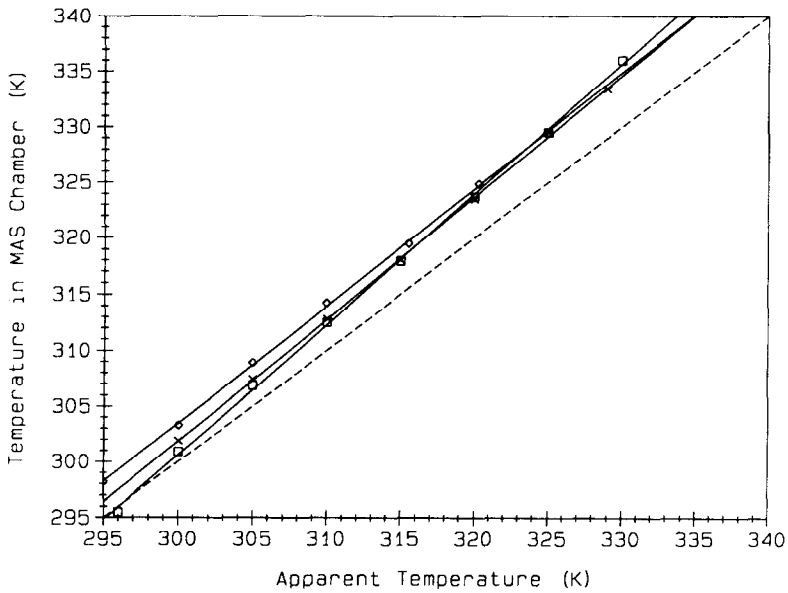

Fig. 1. Sample temperature vs apparent temperature in a magic-angle spinning probe for various spinning rates. □: $\nu_r = 1000$ Hz; ×: $\nu_r = 2000$ Hz; ◇: $\nu_r = 3000$ Hz.

frequency to ensure proper temperature measurement.

References

[1] A. Bielecki and D.P. Burum, J. Magn. Reson., 116 (1995) 215.
[2] A. Sebald, NMR: Basic Principles and Progress, 31 (1994) 111–144.
[3] L.C.M. van Gorkom, J.M. Hook, M.B. Logan, J.V. Hanna and R.E. Wasylishen, Magn. Reson. Chem., 33 (1995) 791–795.
[4] G. Neue, C. Dybowski, M.L. Smith, M. Hepp and D.L. Perry, Solid State NMR, 6 (1996) 241.
[5] T. Bjorholm and H.J. Jakobsen, J. Magn. Reson., 84 (1989) 204–211.