JOURNAL OF MAGNETIC RESONANCE **87**, 592–597 (1990)

Temperature Gradients and Sample Heating in Variable Temperature High Speed MAS NMR Spectroscopy

FRANCISCO AGUILAR-PARRILLA,* BERND WEHRLE,* HERMANN BRÄUNLING,† AND HANS-HEINRICH LIMBACH*

**Institut für Physikalische Chemie der Universität, Albertstrasse 21, D-7800 Freiburg i. Br., West Germany; and †Wacker-Chemie, Johannes Hess Strasse 24, D-8263 Burghausen, West Germany*

Received July 18, 1989; revised September 22, 1989

High speed magic angle spinning NMR spectroscopy offers the possibility of improving the process of coherent averaging of various parts of the nuclear spin Hamiltonian in the solid state (*1–6*). This considerably reduces the intensities of rotational sidebands. This is a great advantage especially in cross-polarization MAS experiments at high magnetic fields, where rotational sidebands mostly stem from an incompletely averaged chemical-shift anisotropy (CSA). Whereas in usual CPMAS experiments rotational sidebands can be suppressed using TOSS pulse sequences (*7*) incomplete CSA averaging leads to very complicated lineshape changes in the presence of chemical exchange (*8, 9*). Therefore, high speed MAS NMR spectroscopy should enable variable temperature (VT) experiments which are easier to interpret. VT CPMAS experiments have proved to be useful in the study of solid-state dynamics (*10, 11*).

However, so far most work in high speed MAS spectroscopy has focused on achieving high rotation frequencies without considering VT experiments. We show here that such VT experiments at high spinning speeds are feasible. Using a commercial 5 mm high speed MAS probe, we have achieved temperatures down to 80 K. However, we also show that the problem of temperature control in MAS experiments (*12–16*) constitutes an even more serious problem when using high spinning speeds. For example, using a recently developed ^{15}N chemical-shift thermometer (*16*), we observe an increase of the sample temperature of more than 30 K when increasing the spinning speed from 2 to 13 kHz. This increase cannot be monitored by measuring either the inlet or the outlet gas temperature. In addition, we have also studied whether both the driving and the bearing gas supplies need to have the same temperature in order to avoid temperature gradients over the sample; not only is it easier to cool only the bearing gas supply in low temperature experiments, but higher spinning speeds can also be obtained if room temperature gas can be used in order to drive the rotor. Indeed we find that in our setup the temperature gradient over the sample is only of the order of 2 K when room temperature driving gas and low temperature bearing gas are employed.

0022-2364/90 $3.00

Copyright © 1990 by Academic Press, Inc.
All rights of reproduction in any form reserved.

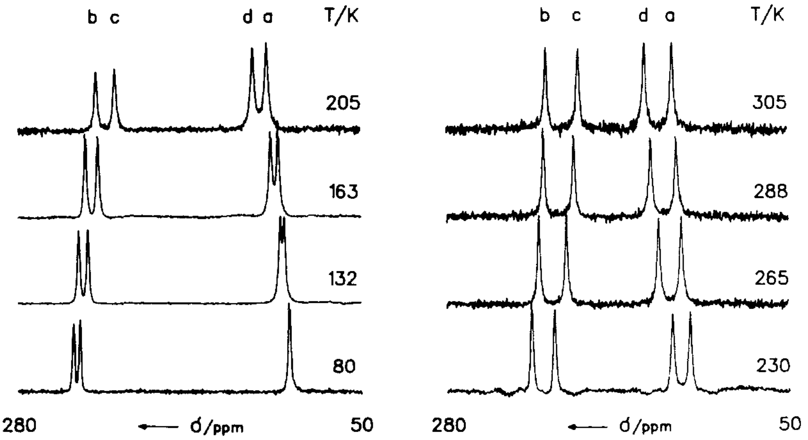

FIG. 1. The 30.41 MHz ^{15}N CPMAS NMR spectra of 95% enriched TTAA as a function of temperature T. Only the inlet bearing gas temperature T_{bi} was lowered whereas the driving gas temperature T_d was always 294 K. Rotation frequency ν_r = 8.8 kHz in all spectra. No line broadening or zero filling was employed. Fifty scans each spectrum on average, 7 ms CP time, 5 s repetition time, 5 μs 90° pulses. See also Table 1.

We have measured the VT ^{15}N CPMAS NMR spectra of TTAA[1]—which constitutes a convenient ^{15}N chemical-shift thermometer (*16*)—in a magnetic field of 7.1 T. The experiments were performed on a Bruker MSL 300 NMR spectrometer equipped with a 5 mm high speed CPMAS probe based on the design of Doty and Ellis (*17*), purchased from Doty Scientific, Columbia, South Carolina. A Bruker B VT 1000 temperature unit was used to control the temperature of the bearing gas stream. The latter was cooled with liquid nitrogen. The heat exchanger used for this purpose has been described previously (*18*). Pure nitrogen was used throughout this study as driving and bearing gas. The inlet bearing gas temperatures T_{bi} could not be measured exactly with this setup; T_{bi} was, therefore, estimated from the reading of the temperature unit.

In order to estimate the sample temperature gradients arising from cooling only the bearing but not the driving gas in low temperature experiments, we have measured the variable temperature ^{15}N CPMAS spectra of TTAA shown in Fig. 1. The temperature dependence of the TTAA line shifts has been described previously (*16*). The rotation frequency was detected optically and adjusted to 8.8 kHz in all spectra. These spinning speeds were achieved using driving gas with a temperature of T_d = 294 K. The individual spectra were recorded half an hour after changing temperature to ensure thermal equilibration of the system. In addition, 20 dummy scans were employed before the spectra were taken. Since only 50 scans were collected on average the total measuring time was about two minutes. No exponential multiplication was employed in the spectra of Fig. 1.

We observed the expected line shifts which have been described previously (*16*). The sample temperatures were calculated from the separation δ_{dc} of the inner line

---

[1] TTAA, 1,8-dihydro-5,7,12,14-tetramethyldibenzo(*b*,*i*)-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene-$^{15}N_4$ (tetramethyldibenzotetraaza(14)annulene).

TABLE 1

Line Separation δ_{dc}, Linewidths W_0 of Signal c in the Spectra of Fig. 1, and Temperature-Induced Line-Shift Changes $\frac{1}{2}(d\delta_c/dT)$ (*16*)

δ_{dc} [ppm]	T [K]	W_0 [Hz]	$\frac{1}{2}(d\delta_{dc}/dT)$ [Hz/K]
44.5	305	80	6.0
51.4	288	73	6.5
61.5	265	73	7.1
79	230	80	8
92.5	205	80	8.3
116	163	70	7.5
129	132	68	5.5
140	80	60	0.9

pair according to Ref. (*16*). All values are assembled in Table 1 together with the linewidth W_0, obtained from line c and the absolute temperature shifts $\frac{1}{2}(d\delta_{dc}/dT)$ of lines c and d calculated according to Ref. (*16*). At 80 K we find quite small linewidths of $W_0 \approx 60$ Hz (2 ppm). This indicates that the value of 4.4 ppm reported previously (*16*) was due mainly to the magnetic field inhomogeneity of the electromagnet used in that study. Below 100 K $\frac{1}{2}(d\delta_c/dT)$ is very small and no line broadening due to a temperature gradient can, therefore, be detected. As temperature is increased we observe, however, a substantial increase of W_0. The linewidth reaches a maximum of about 80 Hz at 205 K and then decreases slightly to a value of 73 Hz at 288 K. We attribute the increase ΔW_0 in the linewidth to a temperature gradient ΔT in the sample. ΔT can be estimated according to

$$\Delta T = \Delta W_0 2/(d\delta_{dc}/dT). \qquad [1]$$

From the data in Table 1 and Eq. [1] we obtain roughly a temperature gradient of ~2 K at sample temperatures between 130 and 300 K. This gradient is tolerable if one considers the ease of high speed spinning when room temperature gas can be employed for driving the rotor. Note, however, that the temperature gradients may be different under other conditions, especially if rotors of different sizes are employed.

In the course of our experiments we observed that the sample temperatures T depended not only on T_{bi} but also on the rotation frequency ν_r. This effect is demonstrated in Fig. 2, where ^{15}N CPMAS NMR spectra of TTAA are shown at different values of ν_r, and two different inlet bearing gas temperatures of $T_{\mathrm{bi}} \approx 170$ K (Fig. 2a) and 294 K (Fig. 2b). It is easily seen that in both spectral series the four lines move inward due to an increase of the sample temperature T as ν_r is increased. As indicated in Table 2, there is also an increase ΔW_0 in the linewidth of the order of 10 to 20 Hz; again, this effect can be interpreted in terms of a temperature gradient of the order of 1 to 2 K. As before, the actual sample temperatures T were calculated from the separations of the inner lines δ_{dc} according to Ref. (*16*). All data are assembled in Table 2. Increasing the rotation frequency from 5 to 10 kHz leads to an increase of the sample temperature T of 16 K at $T_{\mathrm{bi}} \approx 294$ K and of 31 K at $T_{\mathrm{bi}} \approx 170$ K. The total temperature increase is 33 K at $T_{\mathrm{bi}} \approx 294$ K when ν_r increases from 2

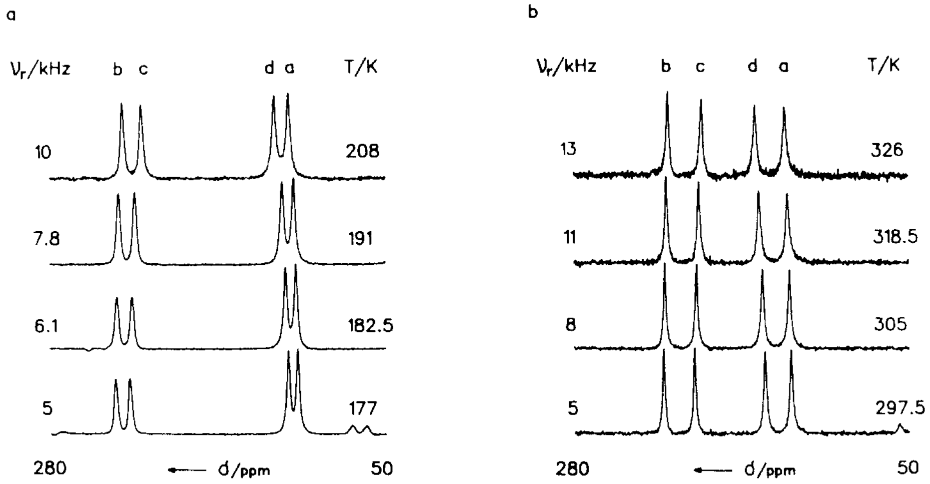

FIG. 2. The 30.41 MHz ^{15}N CPMAS NMR spectra of 95% ^{15}N-enriched TTAA (50 mg in a 5 mm silicon nitride rotor) as a function of the rotation frequency ν_r at two different inlet bearing gas temperatures (a) $T_{bi} \simeq 170$ K at (b) $T_{bi} \approx 294$ K. The driving gas temperature was $T_d \approx 294$ K in both cases. In the spectra with $\nu_r = 5$ kHz rotational sidebands of lines *b* and *c* appear at high field. No line broadening or zero filling was employed. Twenty scans each spectrum, 7 ms CP time, 5 s repetition time, 5 μs 90° pulses. ν_r is the rotation frequency, and *T* is the sample temperature (Table 2) in K calculated from δ_{dc} according to Ref. (*16*).

to 13 kHz! We were not able to detect this large temperature increase in the outlet gas stream. By contrast, this temperature increase could be independently verified by placing a Pt resistance thermometer outside the gas stream close to the midpoint of the stator.

TABLE 2

Line Separation δ_{dc}, Sample Temperature *T*, Linewidths W_0 of Signal *c*, and Temperature-Induced Shift Changes $\frac{1}{2}(d\delta_{dc}/dT)$ (*16*) as a Function of the Rotation Frequency ν_r at Two Temperatures T_{bi}

T_{bi} [K]	ν_r [kHz]	δ_{dc} [ppm]	T [K]	W_0 [Hz]	$\frac{1}{2}(d\delta_{dc}/dT)$ [Hz/K]
294	2	49.3	293	—	6.3
	3	48.8	294	68	6.3
	4	48.5	295.5	68	6.3
	5	47.5	297.5	68	6.3
	6	46.8	299	68	6.2
	7	45.8	301.5	73	6.1
	8	44.5	305	73	6.0
	9	42.7	309.5	78	5.9
	10	41.3	313	78	5.8
	11	39.3	318.5	78	5.6
	12	37.5	323.5	78	5.5
	13	36.7	326	83	5.4
≈170	5	108.2	177	95	
	6.1	104.5	182.5	95	
	7.8	100.5	191	95	
	10	91	208	95	

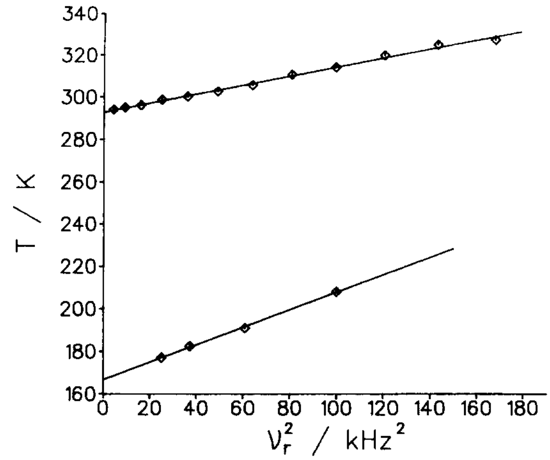

FIG. 3. Plot of the sample temperatures T versus the square of the rotation frequency ν_r for two different inlet bearing gas temperatures $T_{bi} = 294$ K (upper curve) and $T_{bi} \approx 170$ K (lower curve).

Plotting the sample temperatures T vs ν_r gave a quadratic dependence of the type

$$T = a\nu_r^2 + T(\nu_r = 0). \qquad [2]$$

Equation [2] was verified by plotting T vs ν_r^2 as shown in Fig. 3. Straight lines are observed. By linear regression analysis we obtain

$$T = 0.21\nu_r^2 + 293 \text{ K} \quad \text{at} \quad T_{bi} \approx 294 \text{ K} \qquad [3]$$

and

$$T = 0.41\nu_r^2 + 167 \text{ K} \quad \text{at} \quad T_{bi} \approx 170 \text{ K}. \qquad [4]$$

The a values depend on a number of different factors which are difficult to assess at present. Equations [3] and [4] show that a increases when T_{bi} is lowered. It was found that a also depends on the type of rotor used. Thus, a is slightly smaller for sapphire rotors than for the silicon nitride rotor employed in the experiments of Figs. 1 and 2. Whether this is due to the properties of the surface or of the material itself could not be decided. Also, one can anticipate that a will also depend on the type of gas used.

The observed temperature increase ΔT is probably due to the friction between the rotor and the bearing gas. Thus, in stable sample spinning, part of the kinetic energy $E_k \sim \nu_r^2$ of sample rotation is converted into heat, i.e., into a temperature increase of the bearing gas. Before the latter leaves the stator it leads to an increase of the temperature of the stator and the rotor and to temperature gradients in the probe. This could explain the observation that ΔT is proportional to ν_r^2. The observation that ΔT decreases with increasing temperature can then be explained with the increase of the heat capacities of the sample and the bearing gas. Sample heating in high speed MAS should then be minimized if the bearing gas flux could be substantially increased.

In conclusion, VT high speed MAS experiments are possible if a small temperature gradient over the sample is tolerable. Each experimental setup must be calibrated with a given sample temperature measuring device using a chemical-shift thermometer such as TTAA. A more precise temperature measurement would result from the addition of small amount of a chemical-shift thermometer to the sample that is going to be measured.

After submission of this manuscript Bjorholm and Jacobsen published a paper (*19*) in which a similar temperature increase induced by high speed MAS was described.

ACKNOWLEDGMENTS

This work was supported by the Commission of the European Communities, Brussels; the Bundesministerium für Forschung und Technologie, Bonn; and the Fonds der Chemischen Industrie, Frankfurt.

REFERENCES

1. V. Langer, P. Daugaard, and H. J. Jakobsen, *J. Magn. Reson.* **70,** 472 (1986).
2. S. F. Dec, R. A. Wind, G. E. Maciel, and F. E. Anthonio, *J. Magn. Reson.* **70,** 335 (1986).
3. H. J. Jakobsen, P. Daugaard, and V. Langer, *J. Magn. Reson.* **76,** 162 (1988).
4. N. C. Nielsen, H. Bildsoe, and H. J. Jakobsen, *J. Magn. Reson.* **80,** 149 (1988).
5. S. F. Dec, C. E. Bronniman, R. A. Wind, and G. E. Maciel, *J. Magn. Reson.* **82,** 454 (1989).
6. R. A. Wind, S. F. Dec, H. Lock, and G. E. Maciel, *J. Magn. Reson.* **79,** 136 (1988).
7. W. T. Dixon, *J. Magn. Reson.* **44,** 220 (1981).
8. A. Schmidt, S. O. Smith, D. P. Raleigh, J. E. Roberts, R. G. Griffin, and S. Vega, *J. Chem. Phys.* **85,** 4248 (1986).
9. A. Schmidt and S. Vega, *J. Chem. Phys.* **87,** 6895 (1987).
10. C. A. Fyfe, "Solid State NMR for Chemists," C. F. C. Press, Guelph, Ontario, 1983.
11. J. R. Lyerla, C. S. Yannoni, and C. A. Fyfe, *Acc. Chem. Res.* **15,** 208 (1982).
12. A. D. English, *J. Magn. Reson.* **57,** 491 (1984).
13. J. F. Haw, R. A. Crook, and R. C. Crosby, *J. Magn. Reson.* **66,** 551 (1986).
14. G. C. Campbell, R. C. Crosby, and J. F. Haw, *J. Magn. Reson.* **69,** 191 (1986).
15. J. F. Haw, G. C. Campbell, and R. C. Crosby, *Anal. Chem.* **58,** 3172 (1986).
16. B. Wehrle, F. Aguilar-Parrilla, and H. H. Limbach, *J. Magn. Reson.* **87,** 584 (1990).
17. F. D. Doty and P. D. Ellis, *Rev. Sci. Instrum.* **52,** 1868 (1981).
18. R. D. Kendrick, S. Friedrich, B. Wehrle, H. H. Limbach, and C. S. Yannoni, *J. Magn. Reson.* **65,** 159 (1985).
19. T. Bjorholm and H. J. Jakobsen, *J. Magn. Reson.* **84,** 204 (1989).