

A Thermometer for Nonspinning Solid-State NMR Spectroscopy

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Received June 1, 2000; revised July 20, 2000

We discuss a method to determine temperature in a static NMR experiment from the temperature variation of the lead nitrate peak shift. © 2000 Academic Press

Key Words: temperature; lead nitrate; chemical shift; calibration; ²⁰⁷Pb.

Accurate temperature measurement in variable-temperature solid-state nuclear magnetic resonance (NMR) spectroscopy and relaxometry can be quite difficult. The observation of changes in ¹³C spectra at solid-state phase transitions (1, 2) has been used to calibrate temperature in magic-angle-spinning (MAS) probes, as has the measurement of ¹³C resonance isotropic shifts due to Curie–Law behavior. (3) The observation of temperature-dependent isotropic shifts of the ²⁰⁷Pb resonance of lead nitrate (4, 5) has provided a convenient thermometer for MAS spectroscopy. In this Communication we describe a straightforward thermometric measurement for a nonspinning solid-state NMR experiment in a standard spectrometer with a multinuclear probe. It is based on our extensions of the work of Bielecki and Burum (4) and Neue *et al.* (5). To carry out the measurement one must be able to change samples, frequency, and appropriate spectrometer hardware while the probe, which is not changed, is at temperature.

The measurement of temperature in the probe is based on the variation of the ²⁰⁷Pb spectrum of a sample of lead nitrate and is calibrated relative to literature data on its isotropic shift. The temperature variation of the isotropic chemical shift of Pb(NO₃)₂ has been calibrated using the melting points of acetone, benzene, and citric acid by Bielecki and Burum in a magic-angle-spinning experiment (4), with a temperature coefficient of the isotropic chemical shift of 0.753 ± 0.002 ppm/K. Neue and Dybowski (6) provide an absolute reference by the definition of the isotropic shift at 295 K as –3490.4 ppm, which is more convenient than the reference of 273 K used by Bielecki and Burum.

The isotropic-shift variation with temperature is quite useful for the measurement of temperature in MAS spectroscopy, but locating the isotropic point of a powder spectrum quickly and efficiently for temperature measurement is not a trivial exercise. We have developed a method that relies on identifying the chemical shift of the prominent

highest point of the spectrum of a static lead nitrate sample that is handy for measurement of temperature in systems where the sample is not spinning. In the course of carrying out these experiments, we have reconfirmed the temperature coefficients of the isotropic point (4, 6) by careful thermocouple measurement of the temperature in the sample between room temperature and 370 K and at a point a few millimeters away in the probe. The absolute temperature, as determined by the thermocouple, is known to at least ±0.5 K. The powder spectra (processed with no line broadening) of high signal-to-noise ratio were analyzed to determine δ_⊥ and δ_{||}, from which δ_{iso} was calculated and a temperature assigned. δ_{peak} (which is close to δ_⊥) was determined directly from the spectrum.

The important result is the variation of the shift of this peak with temperature. We find the simple linear expression

$$\delta_{\text{peak}}(T) = -\{3670.6 \pm 1.0 \text{ ppm}\} + \{0.666 \pm 0.003 \text{ ppm/K}\}T. \quad [1]$$

This variation is due to the change of isotropic and anisotropic components of the chemical shift. We note for completeness that our experiment gives the following temperature variation of the isotropic chemical shift:

$$\delta_{\text{iso}}(T) = -\{3713.9 \pm 1.0 \text{ ppm}\} + \{0.758 \pm 0.002 \text{ ppm/K}\}T. \quad [2]$$

The small uncertainties in these equations result from a Simplex linear fit of the data and reflect the high signal-to-noise ratio of the spectra.

Equation [1] provides the basis for measuring temperature in a static probe because the peak can easily be determined accurately in a limited number of scans without recourse to fitting or calculation. Table 1 contains a compilation of results for temperature determination. The maximum deviation of the values of the temperature coefficient of the isotropic shift in these measurements amounts to 0.9% of the average.

TABLE 1
Parameters for Variation of Lead Nitrate Chemical Shifts

| | Ref. (1) | Ref. (3) | This work |
|--------------------------------|-----------------------------|---------------------------|-----------------------------|
| δ_{iso} (295 K) | — | -3490.4 ppm | -3490.4 ppm |
| $d\delta_{\text{iso}}/dT$ | 0.753 (± 0.002) ppm/K | 0.76 (± 0.01) ppm/K | 0.758 (± 0.002) ppm/K |
| δ_{peak} (295 K) | — | — | -3474 (± 1) ppm |
| $d\delta_{\text{peak}}/dT$ | — | — | 0.666 (± 0.003) ppm/K |

Care must be taken when inverting these relationships since the arbitrary parameter, B , in $\delta = AT + B$ is numerically large. Its uncertainty will lead to a large and meaningless uncertainty in the intercept D for $T = C\delta + D$. Generally it is preferable to calibrate the spectrometer temperature near room temperature, at a temperature T^* , using Eq. [1] to specify the shift δ_{peak}^* at this temperature. One determines other temperatures relative to that temperature by Eq. [3],

$$T - T^* = \{1.50 \pm 0.01 \text{ K/ppm}\} \{\delta_{\text{peak}} - \delta_{\text{peak}}^*\}. \quad [3]$$

For an experiment in which one accumulates 16 scans on a sample in a typical 7-mm rotor, the peak position can easily be determined to within 0.5 ppm, which leads to an uncertainty in the calculated temperature (relative to the calibration temperature) of less than ± 1 K.

If lead nitrate is incorporated into the sample, then one need only begin the experiment after temperature measurement. However, if necessary, one can remove the lead nitrate and insert the sample of interest, giving time for the sample to equilibrate. Equilibration times may be estimated by observing the peak shift of a lead nitrate sample as a function of time after a change of temperature.

ACKNOWLEDGMENT

We acknowledge the support of the Petroleum Research Fund of the American Chemical Society under Grant 33633-AC5.

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