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Reduction of the temperature gradients in laser assisted high temperature MAS NMR

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ABSTRACT

Laser assisted magic angle spinning (MAS) solid state NMR experiments enable studying physicochemical properties at very high temperatures with high resolution. Large temperature gradients however, can degrade resolution and precision of this technique. Due to the strong temperature dependence of the ²⁰⁷Pb chemical-shift in lead nitrate, a temperature difference along the sample leads to a broadening of the signal. A second moment analysis of the NMR spectra serves as an analytical method to quantify the temperature gradient. We show how an arbitrary line-shape can be decomposed into a set of Gaussian functions from which the 2nd moment is calculated in an analytical fashion which improves the numerical stability of the analysis. It was found that measuring the FID in a non-steady temperature state can reduce the temperature gradient inside the rotor, caused by the single-sided heating.

1. Introduction

High temperature nuclear magnetic resonance (HT NMR) is a useful analytical method for investigating properties of materials from microscopic parameters *in situ*, while they are manifesting properties of interest, such as phase transitions and high temperature phases [1–5]. Further, dynamics can be analyzed in terms of activation energies by analysis of longitudinal relaxation of nuclear magnetization and of exchange rates [1,5–10].

The use of a laser beam as heating source in high temperature magic angle spinning (MAS) NMR was first proposed by Taulelle et al. [11] in 1989 and has been gaining increased attention ever since [2,4,6,12–14]. With this method temperatures up to 1200 K in MAS NMR measurements have been reported [12]. Heating through laser irradiation ensures that essentially only the sample and the rotor are heated up, in contrast to heating through the bearing gas [12]. This brings two main advantages, first, a probe with temperature resistant materials is not required, only the MAS rotor needs to be modified, second, heating of the solenoid (detection) coil can be avoided, which would otherwise cause a decrease in the signal to noise ratio and require retuning of the probe at different temperatures. On the other hand, laser irradiation has the disadvantage of introducing a large temperature gradient along the sample [13], because the sample container is heated only from a single side. The

temperature gradient over the sample further reduces the achievable temperature and eventually also broadens the NMR spectra.

Measuring the temperature of the sample inside the spinning rotor constitutes one of the major difficulties in HT MAS NMR. Conventionally, temperatures are calibrated with NMR measurements of samples which present strong temperature dependent features [15], such as sharp temperature transitions [16], relaxation [12,17], quartz oscillators [18] or, more commonly, a well defined dependence of the chemical-shift with the temperature. Such samples are termed chemical-shift thermometers. Various substances suitable for this purpose have been proposed differing in the temperature range over which they can be applied, the precision of temperature determination and the availability of the materials. For instance, known chemical-shift thermometers are ¹¹⁹Sn of the paramagnetic stannates Sm₂Sn₂O₇, Nd₂Sn₂O₇, Y_{1.8}Sm_{0.2}Sn₂O₇ and Pr₂Sn₂O₇ [19,20], ⁷⁹Br of KBr [17] and ²⁰⁷Pb of Pb(NO₃)₂ [21,22] and of CH₃NH₃PbCl₃ [15].

In this paper we study the temperature gradient build-up in laser assisted HT MAS NMR by looking at the second moment of ²⁰⁷Pb NMR spectra of Pb(NO₃)₂ in a temperature range from 20 to 220 °C. We exploit our understanding of the heat transport mechanism inside the NMR rotor to design a pulse sequence and test the idea of reducing the temperature gradient during the measurement by acquiring the FID in a non-steady temperature state.

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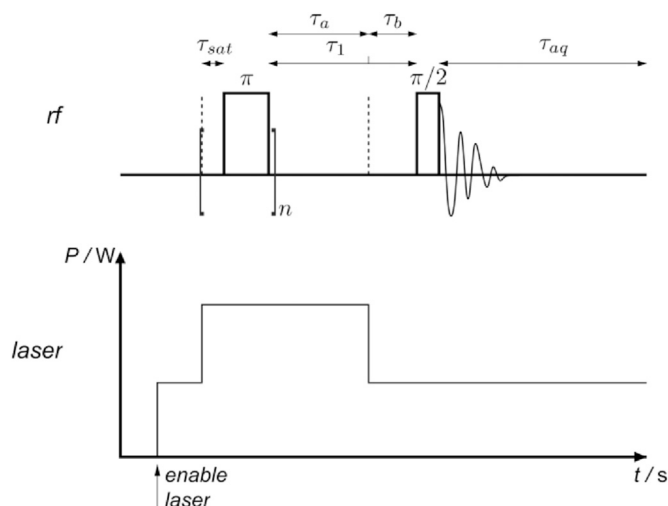


Fig. 1. Pulse sequence designed to find the time τ_b in which the temperature gradient in the sample reaches its minimum. The laser is switched between two different powers P_{pulse} and P_{bias} . The variable time τ_b defines the delay between switching down the irradiation power and the $\pi/2$ NMR pulse. A saturation sequence is used to obtain reproducible results. τ_1 is constant and defines the time between the saturation sequence and the $\pi/2$ pulse. After a single $\pi/2$ pulse the FID is measured.

2. Methods

2.1. NMR measurements

All NMR experiments were conducted at a magnetic field of 11.7 T on a Bruker Avance III spectrometer with a Bruker Biospin laser MAS probe for 7 mm rotors. A LIMO 200-F400-DL980, class 4 laser (980 nm), operated with a diode controller CS400 from AMTRON, was used. The laser is directed to the MAS probe through a fiber, a Bragg-mirror reflects the laser beam onto the bottom of the rotor, which consequently is heated up. A thermocouple measures the temperature of the Bragg-mirror which was kept below 333 K with an independent nitrogen source, to ensure reflection efficiency of the mirror. All measurements were performed at a spinning speed of $\nu_r = 3$ kHz. The bearing and drive pressures are important, since they have an influence on the sample temperature, therefore they were kept constant at 1500 mBar and 500 to 540 mBar, respectively. ^{207}Pb chemical shift values are reported by using the δ scale and are referenced to $(\text{CH}_3)_4\text{Pb}$, used as an external reference [23], last delays of 17 s were used for single excitation measurements. 98.6% pure $\text{Pb}(\text{NO}_3)_2$ from VWR-prolabo was used. Takahasi et al. [22] found that the temperature dependence of the isotropic chemical shift of lead nitrate follows the quadratic relation:

$$T = -5.2 \times 10^{-4} \frac{\text{K}}{\text{ppm}^2} \cdot \delta_{\text{iso}}^2 + 1.3 \frac{\text{K}}{\text{ppm}} \cdot \delta_{\text{iso}} + 303.3 \text{K} \quad (1)$$

Note that the shifts are given relative to the isotropic chemical shift at 303.3 K.

Fig. 1 shows the pulse sequence designed to reduce the temperature gradient. Further details on the pulse sequence as well as on the interface between spectrometer and laser unit are given in the *Supporting Information*. This pulse sequence permits acquiring the signal in a non-stationary temperature state. The laser irradiation intensity is switched between two values. During a time τ_a the laser intensity is set at its high value for a sufficiently long time to ensure thermal equilibrium. Subsequently, the laser is switched to a lower value and after a variable time τ_b , a $\pi/2$ NMR pulse is applied and the signal acquired. Note that τ_1 is constant ($\tau_1 = \tau_a + \tau_b$). The recycle delay used with this pulse sequence was 16 s.

The design of the insert of the rotors used in the 7 mm laser MAS

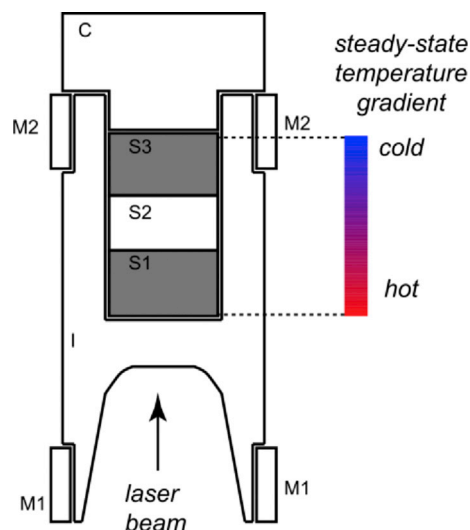


Fig. 2. Schematic sketch of a cylindrical insert for 7 mm MAS rotors used in the commercial probe head. The laser beam strikes the rotor insert (I) at the bottom. C is the corresponding insert cap, M1 and M2 are the MACOR rings. While heating, a temperature gradient builds up inside the rotor, at a steady state temperature the axial gradient is linear and is represented by the colored bar. The $\text{Pb}(\text{NO}_3)_2$ sample is arranged into two layers (grey areas, S1 and S3) separated by a SiO_2 layer (white area, S2). This setup was used to experimentally determine the temperature gradient inside the insert.

probe is shown in Fig. 2. The AlN inserts and insert caps are held by two MACOR rings to an external ZrO_2 spinner, a further zirconia cap (rotor cap) is placed on top of the spinner. This design was conceived to insulate the rotor inserts from the stator. Thereby, cooling of the sample through air flow and a consequent heating of the stator are reduced. The thermal conductivities of the insert materials differ approximately by two orders of magnitude (from 2 to $2 \cdot 10^2 \text{ W m}^{-1} \text{ K}^{-1}$ in ZrO_2 and AlN, respectively [24]). The rotor was packed with two different lead nitrate layers separated by a SiO_2 layer, similar to the packing proposed by Bielecki and Burum [21]. For differentiation, the lower layer had a slightly larger amount of lead nitrate.

2.2. Moment analysis

As the resonance frequency of the measured lead nitrate sample is temperature dependent, the broadening of the signal can be used to determine the temperature gradient along the sample. The temperature gradient is likely to cause an asymmetry in the line shape of the NMR signal. In that case, the variance of a single Gaussian/Lorentzian cannot be used as indicator of the line broadening, as it is not possible to accurately fit the spectrum. To overcome this problem, the spectra can be analyzed in terms of the second moment. However, it should be noted that a direct analysis of the second moment from the spectra is not numerically stable. Instead, a stable result can be obtained if the NMR spectrum is deconvoluted into Gaussian functions.

The second moment M_2 about the first moment M_1 is defined as [25]:

$$M_2 = \frac{\int_{-\infty}^{\infty} (x - M_1)^2 f(x) dx}{\int_{-\infty}^{\infty} f(x) dx} \quad (2)$$

with:

$$M_1 = \frac{\int_{-\infty}^{\infty} x f(x) dx}{\int_{-\infty}^{\infty} f(x) dx} \quad (3)$$

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