

Quartz Crystal Temperature Sensor for MAS NMR

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Quartz crystal temperature sensors (QCTS) were tested for the first time as wireless thermometers in NMR MAS rotors utilizing the NMR RF technique itself for exciting and receiving electro-mechanical quartz resonances. This new tool in MAS NMR has a high sensitivity, linearity, and precision. When compared to the frequently used calibration of the variable temperature in the NMR system by a solid state NMR chemical shift thermometer (CST), such as lead nitrate, QCTS shows a number of advantages. It is an inert thermometer in close contact with solid samples operating parallel to the NMR experiment. QCTS can be manufactured for any frequency to be near a NMR frequency of interest (typically 1 to 2 MHz below or above). Due to the strong response of the crystal, signal detection is possible without changing the tuning of the MAS probe. The NMR signal is not influenced due to the relative sharp crystal resonance, restricted excitation by finite pulses, high probe Q values, and commonly used audio filters. The quadratic dependence of the temperature increase on spinning speed is the same for the QCTS and for the CST lead nitrate and is discussed in terms of frictional heat in accordance with the literature about lead nitrate and with the results of a simple rotor speed jump experiment with differently radial located lead nitrate in the rotor. © 1997 Academic Press

interference with electromagnetic fields (e.g., eddy currents).

Temperature measurements in operating MAS rotors have been a challenge since the invention of magic angle spinning in NMR. This is due to a typically used separate temperature calibration of the NMR system and moreover to a dependence of any output (e.g., from CST or solid phase transition) on spinning speed (8, 9), rotor material (8), and sample structure. This paper shows the first known test results of QCTS under MAS conditions. Some comparisons are made to lead nitrate, one of the most sensitive solid chemical shift thermometers (8, 9). As can be seen from the literature, calibrations for lead nitrate and also for other CST have been made at spinning speeds above 1500 Hz, in order to derive high enough intensity for the isotropic line. According to (8, 9) and to experimental results shown here, spinning affects temperature and creates gradients along the rotor in several ways and differently at different temperatures. Static or nearly static measurements would be best and precise for calibration purposes. A QCTS gives a sharp, intense line with and without spinning and enables an accurate temperature calibration at the location of the small crystal plate. Since no commercial specification of the temperature coefficient was available for the raw crystals, which are needed for MAS purposes, a calibration was necessary.

Advantages of QCTS under MAS which will become obvious are temperature determination in close contact to the rotating sample, and available frequencies near any NMR frequency of interest. At the same time it is a low cost sensor.

Disadvantages are size restrictions (only diameters of 5 or 6 mm are available commercially) and some side resonance effects with raw crystals which must be used here so far. The latter will be discussed below.

Pressure influences (radial forces under MAS) on the resonance of lead nitrate could be excluded in (8). Assuming that extreme centrifugal forces at high MAS speeds distort the geometry of the lattice similar to grinding after which the lattice reverts slowly to the normal arrangement (shown by neutron diffraction studies (10)), a change of linewidth or even a line splitting would be expected after rapid speed jumps. This could not be observed. A rotor speed jump experiment of differently radial located lead nitrate could

INTRODUCTION

Temperature measurements with piezoelectric crystals are very common and widely used (1–4). Piezoelectric ringing phenomena produced by RF pulses in NMR were investigated and published already in the beginning of the 1980s (5). A direct study of quartz crystals confirmed the capability of the NMR transmitter–receiver system to detect the quartz oscillations easily utilizing the electrical field interaction between crystal and coil (6).

The idea of using a quartz crystal temperature sensor (QCTS) as a wireless thermometer in NMR was first published by Wang and Leigh (7) who showed an application with biological tissues in NMR imaging. A commercially obtained quartz plate was positioned in the center of a helium-filled glass cylinder (for good thermal contact) which had been attached to the samples in the NMR scanner. The reported advantages were high sensitivity and resolution, short detection time, long term stability, and immunity to

confirm that the frequency shift is clearly independent of centrifugal forces (11). Results are briefly reported here below. For QCTS this could be excluded in this paper by a combined comparison with lead nitrate. Consequently, for QCTS the resonance dependence on spinning speed is discussed also only in terms of frictional heat.

EXPERIMENTAL

First tests were performed on a Varian UNITY *plus* 400 and later ^{UNITY} INOVA 400 utilizing a Varian variable temperature (VT) CP/MAS probe with a 7-mm rotor. A temperature setting was possible via bearing gas while the drive gas, which had only contact with the cap of the rotor, was kept at ambient temperature.

The QCTS, comprising thin concentric plates of 5 mm diameter, fit exactly in the 7-mm o.d. rotor. In order to let the quartz oscillate freely, the sample should have no contact with the center part. Since powder samples develop a concave surface after a short spin up, this is fulfilled automatically.

Calibration of the QCTS and of lead nitrate was performed in a quasi static state. This was done using the liquid chemical shift thermometer, ethylene glycol, in a glass bulb which was put into a rotor near to the QCTS and surrounded with a thin layer of lead nitrate. Some KBr powder was positioned below the bulb as a filler and for balance. A quasi static state implies spinning at 500 Hz using only bearing gas. This relative slow rotation was the starting point for all further investigations of temperature inside the rotor under MAS conditions. According to a supplier's information (see Acknowledgement for name and address), the QCTS had to be calibrated because of a slight dependence of the temperature coefficient α (see below) on the operating conditions. Commercial QCTS plates of a specified coefficient are placed in a metal housing and have thin metal contacts which had to be avoided here due to eddy current problems while using cross polarization. The lack of such contacts affects α .

VARIABLE TEMPERATURE MAS WITH QCTS

QCTS are produced as thin concentric quartz plates which have been cut under a certain angle out of a single crystal (a so called QuaT-cut, which is a slightly tilted Y-cut) to have a maximum temperature coefficient (12). The mechanical resonance frequency f of the thickness-shear oscillation follows the equation

$$f = f_0[1 + \alpha(T - T_0) + \beta(T - T_0)^2 + \gamma(T - T_0)^3] \quad [1]$$

with typical values for $\alpha = 9 \times 10^{-5} \text{ K}^{-1}$, $\beta = 5 \times 10^{-8} \text{ K}^{-2}$ and $\gamma = 3 \times 10^{-11} \text{ K}^{-3}$, which implies a linear behavior over a reasonable range of temperature. f_0 is a frequency

measured at a reference temperature T_0 . Typical values of basic resonances range from 1 to 35 MHz and are linear dependent on the plate thickness, which is on the order of 0.1 mm for 20 MHz. Only odd harmonics exist which can be exploited, as well as the intrinsic (basic) resonance.

Mechanical oscillations are excited by an alternating external electrical field near the resonance (7). In a NMR coil this is the electrical component of the RF field. Some microseconds of irradiation lead to a large signal response, an "electrical" FID. Commercial sensors are designed to produce a crisp signal to be free of unwanted spurious frequencies. Raw crystals as they have been used here for MAS tend to have broader side resonances above the sharp main resonance. Some crystals even show a reversible jump of the main resonance to a side resonance during the course of temperature changes. This is a well-known behavior (supplier information). Commercially available QCTS are optimized to have the lowest possible side resonances (see (7)). This is achieved by an additional cut along a secant of the circular plate and mechanical plate holders, fixing the plate at the edges. Such treatments are not possible for our application under MAS. However, out of a few raw quartz plates one can be found with low side resonances. Another way recommended by the supplier is placing small spots of glue at the nodes on the plate surface in order to damp unwanted resonances. This technique is still to be investigated. Side resonances show the same temperature dependence as the main resonance and have no impact on the accuracy of the method (Fig. 1a).

Since the main (sharp) resonance survives much longer in the free oscillating plate than broad side resonances, backward linear prediction can be used in each case to filter them out (Fig. 1b). It is recommended to use QCTS of lower basic resonance because they show a purer resonance which seems to be due to higher robustness. Since the spectral amplitude and phase are not constant during temperature or spinning speed changes and frequency is the only key parameter, a normalization and absolute value mode is used in the spectra presentation. For most of the following tests, a crystal resonating around 93.5 MHz (5th harmonic) was exploited. In order to come closer to a NMR frequency (100 MHz for ¹³C, for example) another quartz with a 3rd harmonics at 99 MHz was also tested. In this case the NMR sample in the rotor, together with the QCTS, was hexamethylbenzene, a standard solid sample for ¹³C NMR.

Figure 2 gives step-by-step results after at least 15-min waiting for thermal equilibrium and shows a good linearity of the resonance. The spin rate was kept at a rather low level (500 Hz with bearing air only) in order to prevent disturbances by cool drive air and air friction. The slope is 6.97 kHz/°C. This corresponds to an α coefficient of $7.45 \times 10^{-5} \text{ K}^{-1}$. The linewidth is on the same order which makes it possible to measure temperatures with an accuracy of about 0.1 K. However, this accuracy is restricted to the crystal position only and

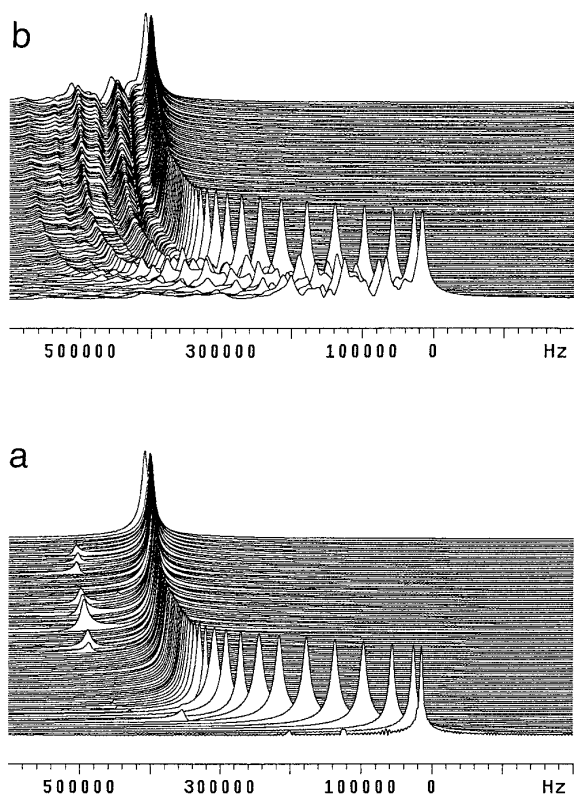


FIG. 1. QCTS resonances (5th harmonic near 93.5 MHz) during a temperature jump from 30°C (referenced to 0 Hz) to 90°C, demonstrating the method. The first scan follows 5.5 s after start. Time between each of the 100 single scans is 5 s. The last two spectra are taken with time steps of 60 and 600 s, respectively. Spectra in (a) are backward linear predicted in order to get rid of broader side resonances of low intensity, shown in (b). Absolute value and normalized amplitude mode are used in order to get rid of phase and amplitude differences between scans, which are inherent in the rotating mechanical system.

is an illusion for the whole sample volume of a rotor, taking into account temperature gradients up to a few degrees within a rotor (8) and probably also spinning speed dependence of the temperature gradients inside the sample. For the highest possible accuracy, a small sample disk as near as possible to the quartz disk should be used.

The broader linewidth of resonance lines in comparison to (7) seems to be caused by a nonoptimal resonance circuit for the QCTS signal. In (7) a separate detection circuit was used for this purpose. Applying QCTS with metallic contacts as in (7) did not improve the linewidth and is not recommended as such contacts survive using short pulses but explode when applying a cross polarization RF field due to heat by high eddy currents.

SPINNING SPEED DEPENDENCE OF TEMPERATURE— QCTS AND LEAD NITRATE

From the physical point of view, fast spinning of a rotor produces frictional heat. At the same time this should be

slightly compensated by cooling caused by the Joule–Thompson effect at the drive and bearing jets. Moreover the temperature under MAS is influenced by the probe design due to different friction with different designs.

The general behavior of the temperature inside a rotor under MAS conditions was shown in (8, 9) for the CST lead nitrate and in (13) for a ^{15}N CTS. In order to test the pressure independence of the chemical shift of lead nitrate, which was reported as a result of a rather complicated experiment in (8) and which was described briefly in the Introduction of this paper, a much simpler and striking experiment was performed in the frame of this paper, published partially in (11). A small amount of lead nitrate was filled into the axial hole (1.5 mm in diameter) of a cylindrical rotor insert (Kelf) of 5 mm o.d. and 4 mm length. A second larger part was positioned at the rotor wall above the insert which formed a layer of about 1 mm thickness with spinning. After a speed jump from 500 to 6000 Hz within 5 s, the shift of the lines of both samples could be monitored as a function of time. Assuming a frequency shift by radial forces the two lines were expected at different final positions due to about three times larger forces at the rotor wall. The smaller signal of the inner lead nitrate was moving slower to higher frequencies than the larger signal due to a thermal isolation by the plastic insert, but reached the same final position of the larger signal at thermal equilibrium. Consequently, a pressure influence could be excluded at least for a 7-mm rotor spinning below 6000 Hz.

With this in mind, a comparison of lead nitrate and a QCTS could give an answer to the question as to whether the resonance of the QCTS shows a radial force influence.

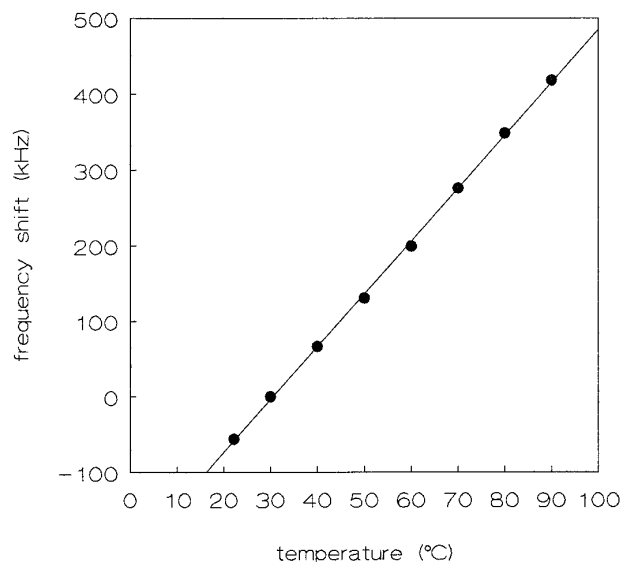


FIG. 2. Calibration curve for the same QCTS as described in the legend to Fig. 1. Low spinning (500 Hz) is used. The temperature coefficient α is 6.97 kHz/°C.

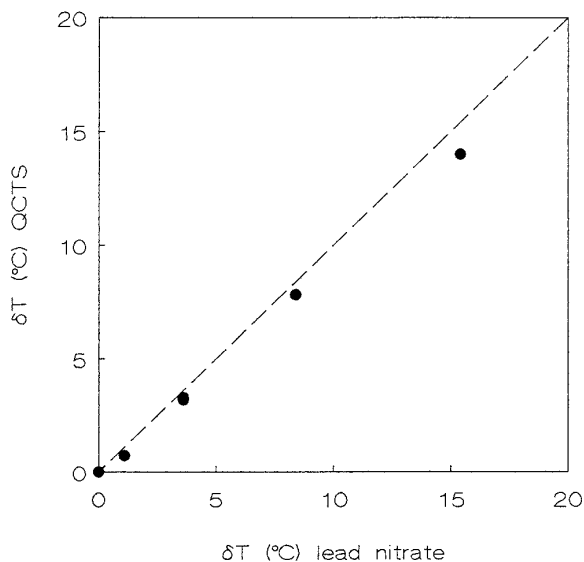


FIG. 3. Temperature increase with sample spinning—a comparison of results from a QCTS and a small lead nitrate sample disk which are positioned close together in a rotor. δT is set to 0°C at a spinning speed of 500 Hz. Spinning speeds are 1500, 3000, 4500, and 6000 Hz. The increase in temperature δT is proportional to the square of the spinning speed. A temperature coefficient of 0.61 ppm/°C is used for lead nitrate (see text).

A speed step experiment with lead nitrate and a QCTS (93.5 MHz) was performed at ambient temperature and results are shown in Fig. 3 in a direct comparison. In this experiment the QCTS was positioned on top of a small disk of lead nitrate in order to exclude any influence of a temperature gradient. The frequency shift is proportional to the square of the spinning speed for lead nitrate as well as for the QCTS. At all speeds between 500 and 6000 Hz the QCTS shows nearly the same temperature increase as the CST. Differences are within the mean square error limit of 1°C of the method at ambient temperature. This indicates that radial forces could be excluded also for the QCTS up to 6000 Hz in a 7-mm rotor. For lead nitrate a temperature coefficient of 0.61 ppm/°C was used which was determined parallel to the temperature coefficient of the QCTS (6.97 kHz/°C) in comparison to ethylene glycol (see Experimental). Reference (8) reports 0.70 ppm/°C and Ref. (9) 0.75 ppm/°C. Such a difference is surprising and the reason is not clear. However, this is not a subject of the current paper. We believe that our calibration approach, combining the standard NMR thermometer ethylene glycol with lead nitrate and the QCTS in one rotor and operating at 500 Hz spinning speed (only with bearing VT gas), is the most reliable.

Figure 4 shows in more detail that spinning is influencing the sample temperature in a complex way especially at temperatures different to ambient temperature. Here the spinning is increased step by step from 500 up to 6000 Hz. The starting temperature of the QCTS is 90°C at 500 Hz spinning (only bearing air). Adding drive air (ambient temperature),

the QCTS indicates a temperature decrease which is overlaid by the known temperature increase with spinning due to friction. Figure 4 demonstrates that a non-quasi static calibration would not take into account changes in operating conditions in reality (such as temperature of drive gas, and changes of flow ratio bearing/drive gas, changes in rotor or cap material) which can easily lead to a couple of degrees deviation.

NMR RESULTS IN PRESENCE OF QCTS

Running C13-MAS and CP/MAS spectra together with the QCTS resonating around 93.5 MHz (5th harmonic) did not influence the spectra quality. In this case the probe had to be tuned down in order to acquire the QCTS signal. The spectrum in Fig. 5 was taken at a spectral width of 5 MHz, a pulse length of 0.6 μ s (excitation profile of about ± 1.7 MHz) and a repetition time of one second together with a QCTS resonating at 99 MHz (3rd harmonics), just about 1.5 MHz below ^{13}C . Here no probe retuning was necessary in order to excite and observe the piezo-electrical resonance. The QCTS signal which is at least 30 dB higher after retuning the probe to 99 MHz is damped due to the high Q value of the CP/MAS probe but is still quite easily observed. The number of scans was set to 256 in order to have a good overall signal to noise. To observe the QCTS resonance with one scan and with a much higher signal-to-noise ratio, one must go “QCTS-on-resonance” but without probe retuning. Using a regular ^{13}C 90° pulse (5 μ s) or cross polarization, the QCTS signal disappears because of the reduced excitation range.

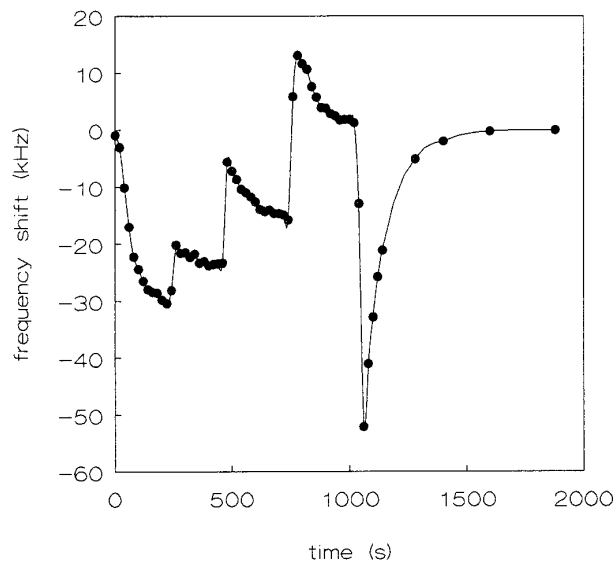


FIG. 4. QCTS resonance as a function of time and spinning speed at a bearing air temperature of 90°C. Spinning speeds undergo the same steps as described in the legend to Fig. 3: 500, 1500, 3000, 4500, 6000, and again 500 Hz.

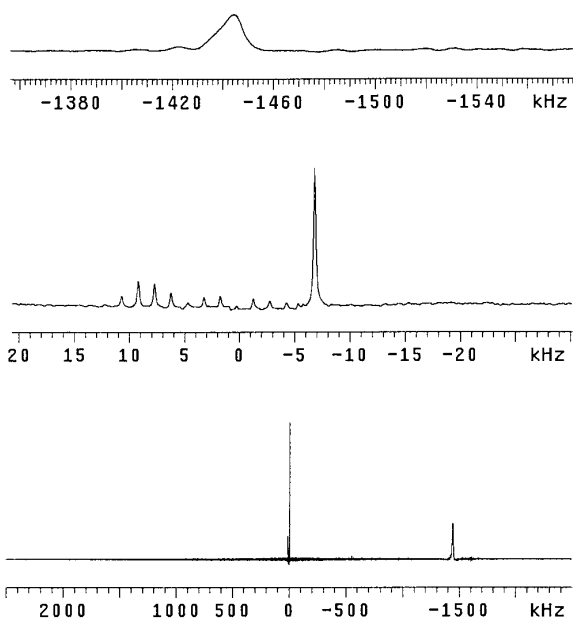


FIG. 5. ^{13}C MAS spectrum (256 scans, pulse-acquire) of hexamethylbenzene (100.5 MHz) rotating at 1500 Hz together with a QCTS (99 MHz). The spectral window is 5 MHz and an excitation pulse of $0.6\ \mu\text{s}$ has been used.

CONCLUSIONS

It has been shown that QCTS could be used in operating MAS NMR rotors utilizing the NMR technique and exploiting the electrical interaction.

The new tool has a good linearity and a high sensitivity. The resonance frequency can be adjusted near to any NMR frequency of interest by selecting the thickness of the quartz plate and using the existing odd harmonics with equivalent

temperature behavior and similar intensity. Consequently, temperature can be measured parallel to the NMR signal simply by shifting the carrier frequency to the QCTS resonance region without retuning the probe.

In order to check for any stress influence (radial force) on the temperature output of the QCTS, the spinning speed dependence was monitored together with lead nitrate in the same rotor. For lead nitrate any stress influence was already clearly excluded (8, 11). Since no significant difference between the temperature outputs of both materials could be detected, a stress influence on the QCTS has been excluded.

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