

HIGH AND VERY HIGH TEMPERATURE NMR

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The knowledge of behavior laws of materials need, at high and very high temperature, the development of macroscopic and microscopic measurements which are able to work under severe conditions. It appears that NMR spectroscopy is one of the most powerful technique to investigate the environment and the motion of a wide variety of atoms ^1H , ^2D , ^7Li , ^9Be , ^{11}B , ^{14}N , ^{17}O , ^{19}F , ^{23}Na , ^{27}Al , ^{29}Si , ^{31}P , ^{35}Cl , ^{39}K ... in solid and liquid materials. Up to now, its use at high or very high temperature was limited by challenging technical performances^[1]. We have realized an instrument which overcomes most of these problems.

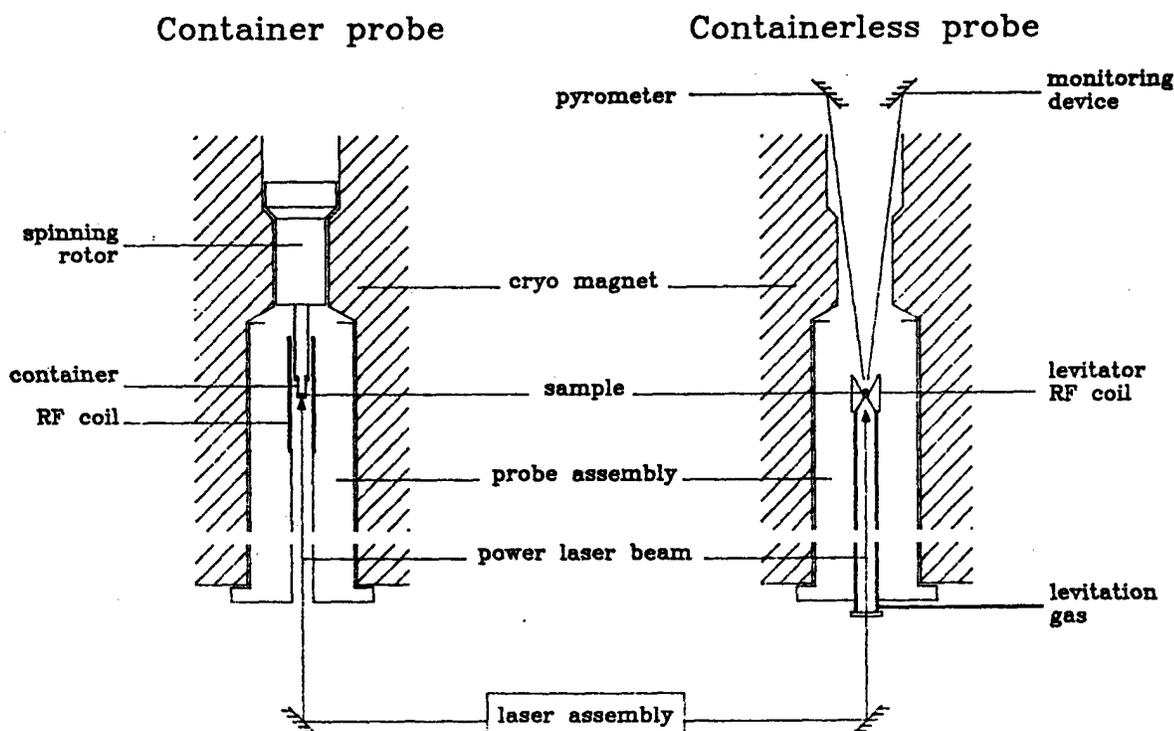


Figure 1: Schematic of high temperature probe

1/ Heating mode

One of the challenge was, firstly, to insure the appropriate heating of the sample in the NMR probe (with a maximized filling factor) at the wished temperature with a minimum thermal power and, secondly, to thermally separate the sample and the RF coil. These goals could be only achieved by using a CW laser radiation: YAG/Nd³⁺ laser for metallic sample or CO₂ laser (10.6 μm) for

oxide materials. Through an appropriate optical head the heating could be precisely localized and carefully controlled, therefore in order to insure an excellent signal to noise ratio the RF coil can be cooled with a flux of evaporated liquid nitrogen. Nevertheless the required power for a temperature of 1000°C is about 25 W which can be compared to the 300 W required for heating the whole probe at 150 to 200°C with a hot gas design.

Together with an accurate and reproducible temperature measurement an important point in all the high temperature spectroscopy is to avoid any chemical interaction between the sample and its holder. It is well known that these interactions increase with the temperature and, according to the specificity of the working conditions under very high magnetic fields, two ranges of temperature could be roughly defined: below and over 1000°C, that means in container or containerless conditions.

2/ Container probe

The sample holder must have excellent dielectric properties and also totally absorb 10.6 μ m radiation ensuring the heating of the sample by heat transfer. Various materials could be used: glassy quartz or hexagonal boron nitride and in this case, a flow of neutral gas can be used to prevent the oxidation of BN in B₂O₃ which vaporize and could also react with the material under examination. A classical BRUKER probe with minor modifications has been used with silica tubes of 5 to 10 mm of diameter rotating at a frequency of a few hertz (7-10 Hz) figure 1. In order to obtain the better thermal homogeneity, double tube containers with different heat exchanger materials are currently under test.

3/ Containerless probe

If the requirements are: firstly no interaction between the sample and its holder, secondly working conditions in either reducing, neutral or oxidizing atmospheres, thirdly, very large range of temperature in the solid or liquid state, they are only met by a levitation technique. Such a device is mainly based on the use of a convergent/divergent nozzle and a flowing gas which sustains a solid or a liquid particle in the divergent part of the nozzle without any contact with its walls: "aerodynamic levitation". A stable levitation regime could be maintained for long periods of time for low vaporizing liquids having an appropriate surface tension^[2]. The sample weight ranges between 20 to 120 mg. The best working conditions are obtained with nozzles having the following dimensions: hole diameter 2 to 3.5 mm, both convergent and divergent parts angle 60°/h = 10 mm, and a gas flow rate, controlled by an electronic flow

meter, ranging between 1.3 to 1.5 l.mn⁻¹. The control of the levitation regime i.e. the position of the liquid particle in the nozzle is carried out through a high resolution video system. The complete setup of containerless probe equipment is shown figure 1.

4/ Temperature measurement

Traditional temperature measurements by thermocouples or platinum probes cannot be used in a RF coil during the NMR experience. Usually such a measure is realized with the same geometry and heating conditions without running the NMR. For temperature above 1000°C, the sample temperature is measured by optical pyrometers working at different wavelength to avoid the measurement of the emission factor. Those measurements are exactly calibrated against known phase transitions in the sample or the heat exchanger material (i.e. solid liquid transition), easily detected by NMR experiments.

5/ Optimization of RF coil

The performance demands of the RF coil are the following: it has to exhibit an axial geometry to allow laser heating; it has to be able to excite solids as well as liquid sample requiring high H₁, without a too high quality factor; this latter requirement allows for a short dead time, an important parameter in the case of solid state broad line.

Another demand is to be able to make a resonator out of a levitator geometry, keeping on with the previous RF demands. We faced these problems on developing a computerized analysis of the probehead radio-frequency circuitry. It leads us to an automatic determination of the tuning and matching components for a given geometry of the resonator. The resonator analysis has been resolved numerically as a solution of the Laplace equation for the specified geometry. Such an analysis allows an agreement between calculated and measured H₁ values of about 5%.

6/ results

This high temperature technique has proved its efficiency in studying the high temperature phase transitions in LiNaSO₄ system^[3] in which it has been possible to

describe the mechanism leading to superionic (518°C) and solid/liquid (620°C) transitions through ^7Li and ^{23}Na NMR studies, including

relaxation measurements and 2D nutation experiment at 518°C.

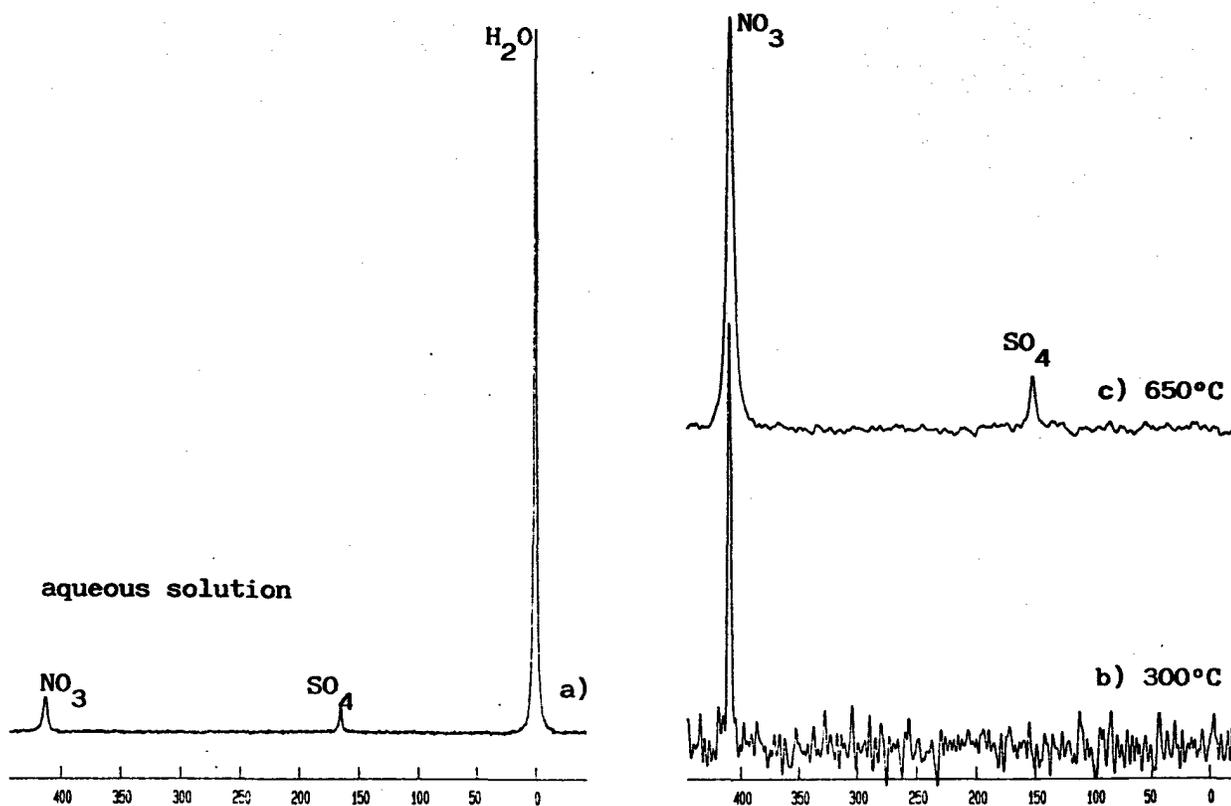


Figure 2: ^{17}O spectra of $\text{NaNO}_3(60\%)/\text{K}_2\text{SO}_4(40\%)$ system at high temperature

A wide variety of nuclei is now proved to be visible at *natural abundance* and high temperature in the liquid phase: ^{23}Na , ^{39}K , ^{14}N and even ^{17}O (figure 2) in $\text{NaNO}_3/\text{K}_2\text{SO}_4$ mixtures, ^{23}Na , ^7Li and ^{17}O in LiNASO_4 , ^{23}Na , $^{35,37}\text{Cl}$ in liquid NaCl etc.. Figure 2 shows a set of 3 spectra obtained for $\text{NaNO}_3(60\%)/\text{K}_2\text{SO}_4(40\%)$ a) for aqueous solution showing 3 peaks at 0 ppm (H_2O), 166 ppm (SO_4) and 414 ppm (NO_3), b) at 300°C showing clearly the NO_3 (410 ppm)

main component of the liquid phase and c) at 650°C showing the two components: NO_3 (410 ppm) and SO_4 (153 ppm). One important point is that those spectra are *quantitatively* representative of the liquid phase composition and could thus be used for phase diagram studies of that kind of systems. In addition, chemical shift evolution is observed for most of the nuclei of the tested systems and should thus provide a mean of directly measurement of temperature through NMR experiment.

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