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NQR DETECTION OF SODIUM NITRITE RECRYSTALLIZED IN WOOD

Jérémy Jover^{(1),(3)}, Sarra Aissani^{(1),(2)}, Laouès Guendouz⁽²⁾, André Thomas⁽³⁾, Daniel Canet⁽¹⁾ *

⁽¹⁾ Méthodologie RMN (CRM²; UMR 7036, UL-CNRS), Université de Lorraine, Campus Aiguillettes, B.P. 70239, 54506 Vandœuvre-lès-Nancy (cedex), France

⁽²⁾ Lien, Université de Lorraine, Campus Aiguillettes, B.P. 70239, 54506 Vandœuvre-lès-Nancy (cedex), France

⁽³⁾ Cran, Université de Lorraine, Campus Aiguillettes, B.P. 70239, 54506 Vandœuvre-lès-Nancy (cedex), France

e-mail : daniel.canet@univ-lorraine.fr

Abstract

Cylindrical pieces of wood which can be placed in 10mm o.d. NMR sample tubes have been impregnated by an aqueous solution of sodium nitrite (NaNO_2). They were subsequently dried and examined by ^{14}N quadrupole resonance. To our surprise, we were able to observe a signal at the right frequency (4.64 MHz, the highest frequency NaNO_2 line). This implies that the material has been properly embedded but also that sodium nitrite was properly recrystallized. This latter point was more than speculative. Anyway, we could observe that it works for spruce, beech, ash, maritime pine, but not for oak (which is known to be difficult to impregnate). Instrumental parameters have been optimized for reducing the duration of the experiment. If the first measurements required around four hours, we obtain at the present time acceptable results in about four minutes or less.

In addition, we have designed a simple NLLS (Non Linear Least Squares) algorithm by which the spectral parameters of the NQR signal can be retrieved even if the peak is hardly visible in the frequency domain.

Extensive measurements have been performed on NaNO_2 recrystallized in spruce. They show, among other things, that the totality of NaNO_2 which has penetrated the material has actually recrystallized and seemingly for ever. Various assays have been carried out as a function of impregnation and drying conditions. The evolution of the width of the NaNO_2 line reflects defects in the crystal lattice of NaNO_2 due probably to alteration of the wood structure.

Introduction

This work represents an attempt for detecting by NQR a molecule which has been imbedded in wood, the far-off objective being material labelling. In fact, our objective is rather to demonstrate the feasibility of this approach. Moreover, because we are familiar with ^{14}N quadrupole resonance, we have focused on this quadrupolar nucleus in spite of its low sensitivity. Indeed, we are facing several challenges: how to insert a substance within the material? If wood is impregnated, what is the amount of the substance which has recrystallized (if any)? Will it be possible to use NQR as a sensor? This paper is devoted to these questions. For simplicity, we have chosen a molecule often used as a model in Nitrogen-14 Quadrupole Resonance, namely sodium nitrite NaNO_2 . It has the further advantage of being soluble in water and can be considered as bio-compatible in certain circumstances (food preservation).

Experimental

Impregnation

Small cylindrical pieces of wood of 70 mm height and 8 mm diameter were machined so that they could fit into 10 mm o.d. tubes (employed for NMR measurements). They were impregnated with a saturated aqueous solution of sodium nitrite with the help of a specially constructed device (figure 1). Impregnation can be possibly performed under high pressure (up to 15 bar)¹, but also under partial vacuum. We mean by “partial vacuum” soft pumping of the vessel containing the wood rod immersed in the aqueous solution of sodium nitrite. This has the virtue of removing air thus facilitating the impregnation process. In the case of impregnation “under high pressure”, pumping is first applied to the wood rod (again for removing air) and then the rod is immersed in the pressurised aqueous solution. Only raw material (without any preparation prior to impregnation) led to significant results (see below).

Wood samples were impregnated for 48 hours. They were subsequently dried either out in the open (ambient temperature and moisture) or in a dry kiln at 103°C (highest limit before wood degradation²) for a stabilization period (controlled by weighing at regular intervals) which generally did not exceed 48 hours.

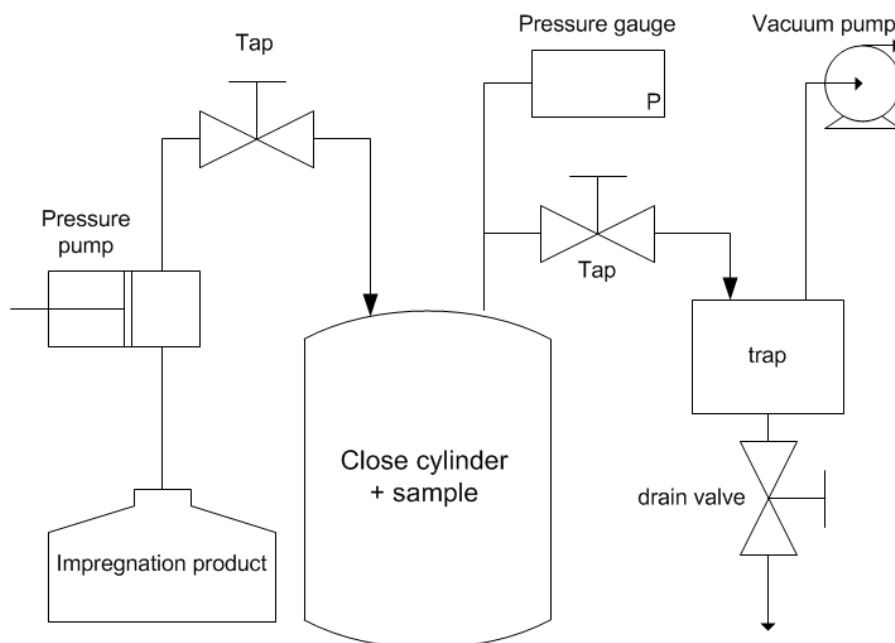


Figure 1. Block diagram of the impregnation device.

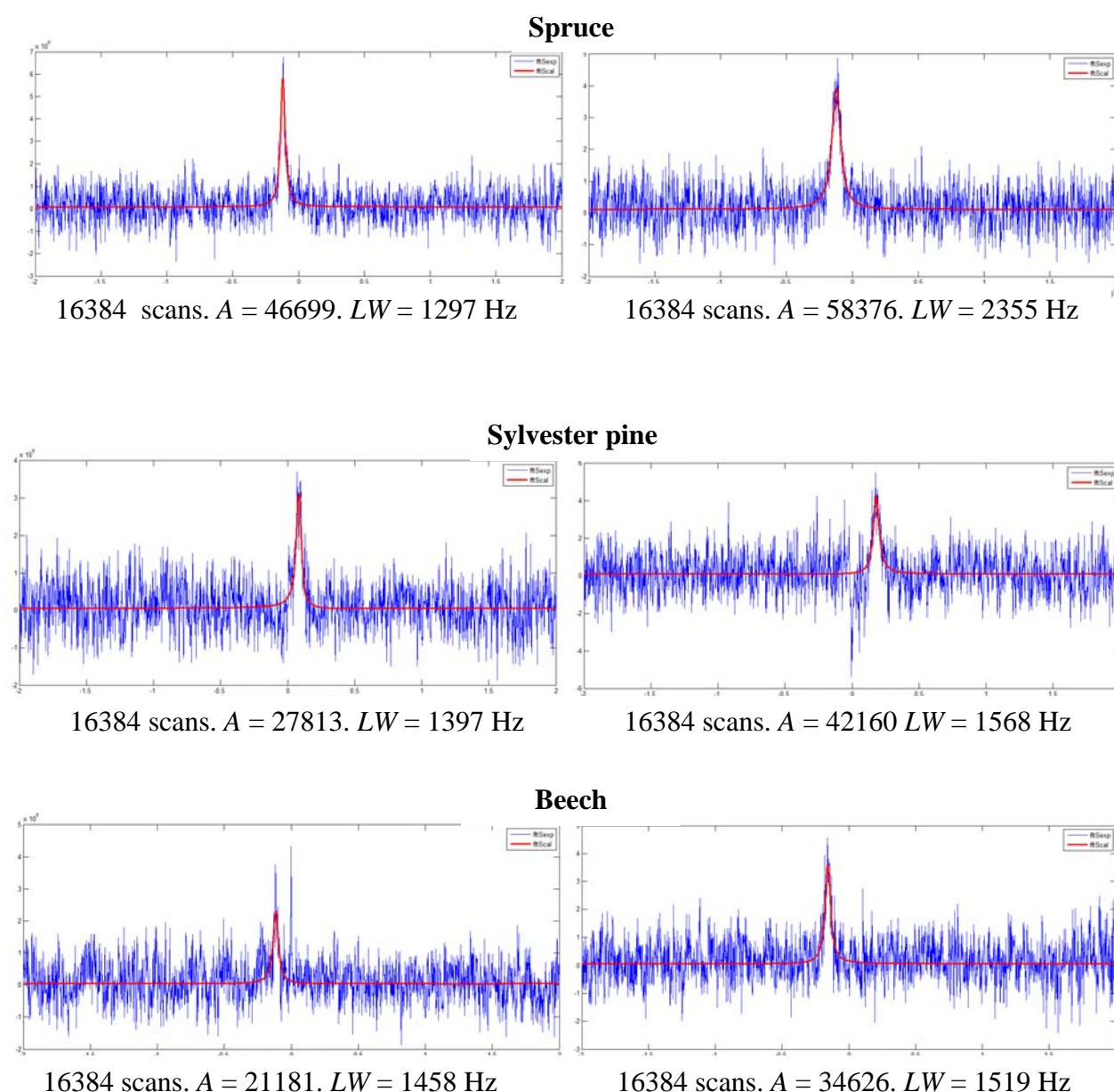
Nitrogen-14 Quadrupole Resonance

NQR experiments were carried out at 4.64 MHz (the highest resonance frequency of NaNO_2) and at ambient temperature with a home-made spectrometer described previously³. For the most recent measurements, a new probe was constructed: still with a solenoidal coil surrounding the sample but with a cylindrical shield at a distance of 8 cm from the solenoid center. This prevents electromagnetic reflections thus parasitic capacitors which exist in the previous probes. Also, tuning and matching of this probe involve equilibrated circuits. All measurements reported here have been performed with a simple low power pulse of 100 μs duration (corresponding to the first maximum of the nutation curve). A dead time (between

the end of the pulse and the beginning of acquisition) of 300 μ s along with low power pulses avoids baseline distortions. A repetition delay of 0.5 s was allowed between two consecutive acquisitions. Typically, with this new probe, 4096 transients were accumulated but, as shown later, much less accumulation can be envisioned.

Results

It was almost a surprise to observe a NQR signal in most impregnated wood samples. This implies that, within this material, sodium nitrite has recrystallized upon drying. Moreover, relatively sharp lines indicate few (if any) defects in the lattice. Such experiments proved to be successful for almost all species that we have tried. Spectra are reported in figure 2.



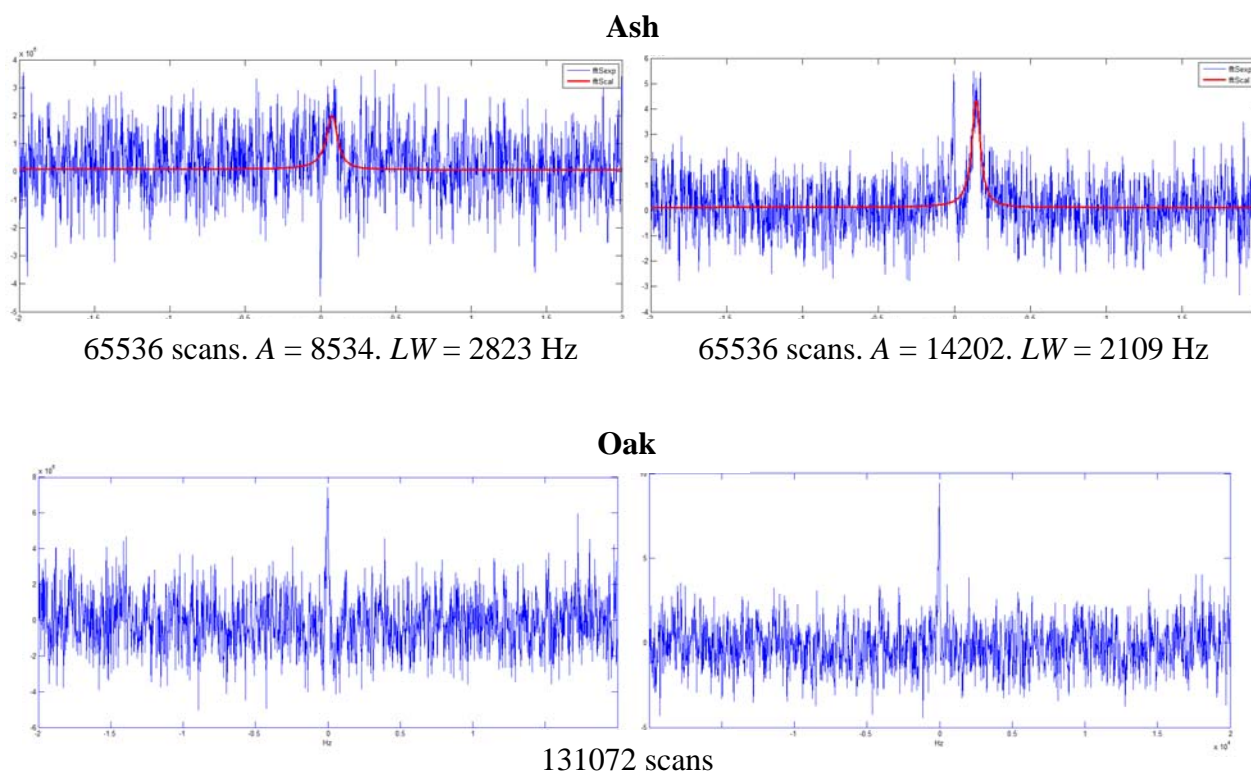


Figure 2. 4.64 MHz spectra of recrystallized NaNO_2 in different wood species (impregnation under partial vacuum) with the two drying modes described in the text. Left column: out in the open; right column: dry kiln. Continuous curves (in red) correspond to recalculated spectra (see below). A stands for the peak area normalized to 4096 scans whereas LW is the line-width at half-height.

The first obvious observation concerns the ability of the different species to be impregnated by aqueous solutions of sodium nitrite. This can be quantified by the peak area in either of the two series, thus by the amount of recrystallized NaNO_2 . This impregnation ability is in the order spruce>Sylvester pine>beech>ash>oak (for the latter, we just observe the spike at zero frequency and it is indeed well known that oak is difficult to impregnate⁴). Two other properties concern the drying mode: less NaNO_2 is recrystallized in the case “out in the open” while line-widths are smaller than in the case “dry kiln”. The interpretation of the first feature is immediate: upon heating at a higher temperature, more water is eliminated. The second feature can be explained by the fact that taking the material at a relatively elevated temperature modifies its structure entailing some defects in the crystal lattice of NaNO_2 ⁵ (due to possible interactions of NaNO_2 with the material). Notice that these early experiments have

been performed with the old probe. In fact, the above trends have been confirmed by accurate measurements carried out with the new probe on spruce samples. Relevant spectra are shown in figure 3.

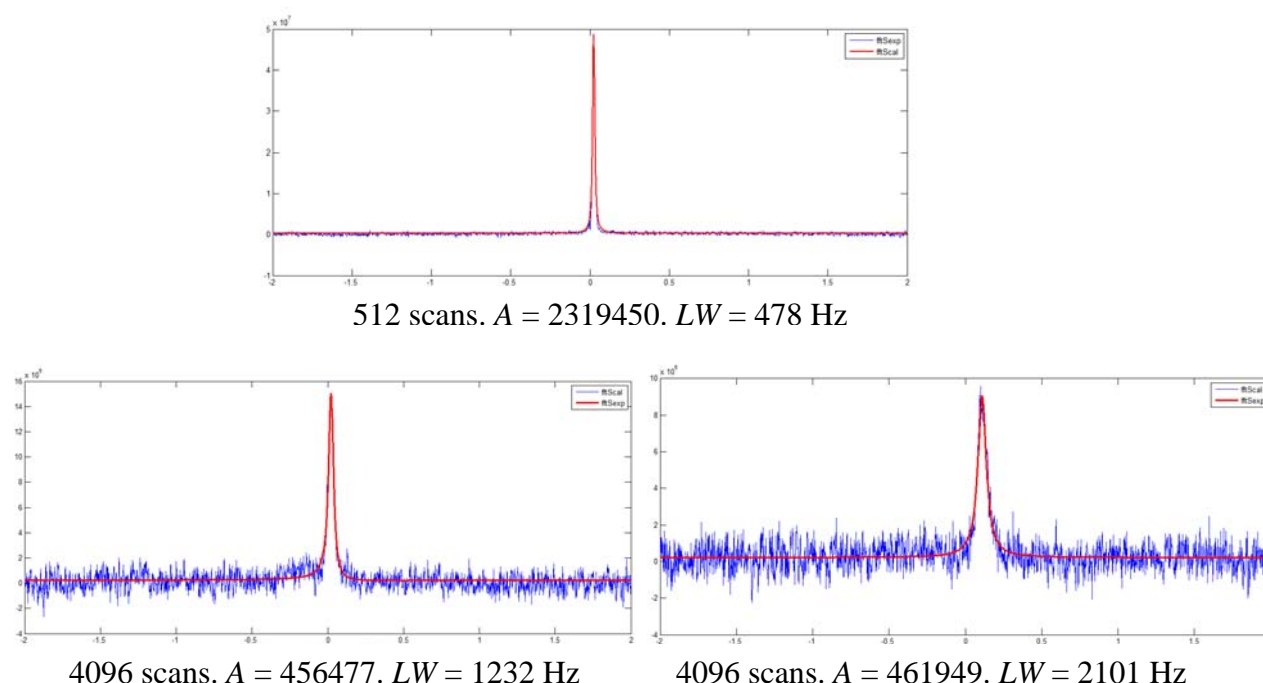


Figure 3. 4.64 MHz spectra of NaNO_2 obtained with the new probe. Top: reference spectrum of a NaNO_2 powder sample of the same size as the spruce samples (bottom). Impregnation was carried out under partial vacuum. Left: out in the open; right: dry kiln. Continuous curves (in red) correspond to recalculated spectra (see below). A stands for the peak area normalized to 4096 scans whereas LW is the line-width at half height.

It can be seen that the amount of recrystallized NaNO_2 is hardly larger when the sample has been subjected to the dry kiln. This was already recognized in figure 2 but seems to be specific of spruce (for other species, less NaNO_2 is recrystallised out in the open). This amount, as determined by peak areas (the quantities A), is five times larger in the powder than in wood. From the weight of NaNO_2 in the powder sample, we arrive at the absolute weight of NaNO_2 in the spruce sample (650 mg). It turns out that this value coincides almost perfectly with weighing data (before impregnation and after drying). The next issue is evidently the line-width of the recrystallized NaNO_2 NQR signal. In the case of spruce, there is an order of magnitude when going from crystallized powder to NaNO_2 recrystallized in wood (with

drying “out in the open”). As already mentioned, this can be reasonably attributed to defects in the crystalline lattice which arise from interactions with the material. These defects are still more important (line-width increases by a factor of two) when drying is carried out in a kiln. As assumed above, this is very likely due to structural modifications within the material and thus to modifications of the interactions with NaNO_2 .

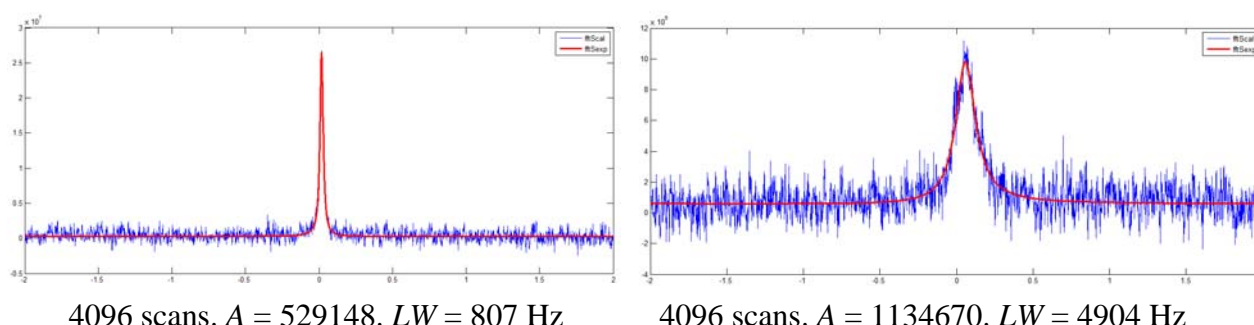


Figure 4. 4.64 MHz spectra of NaNO_2 in spruce. Impregnation was carried out under a pressure of 15 bars. Left: drying out in the open; right: drying in the kiln. Continuous curves (in red) correspond to recalculated spectra (see below). A stands for the peak area normalized to 4096 scans whereas LW is the line-width at half height.

In order to increase the amount of NaNO_2 in wood, impregnation was achieved under a pressure of 15 bars⁶ (see figure 1). The spectra obtained subsequently to drying are displayed in figure 4. They are quite different from those corresponding to impregnation under partial vacuum. In the case of drying “out in the open”, we observe a sharper line and roughly the same amount of recrystallized NaNO_2 . Conversely, when the sample has been dried in the kiln, the line-width increases considerably and the amount of recrystallized NaNO_2 is roughly twice that of the sample impregnated under partial vacuum. On the other hand, weighing the sample before impregnation and after drying in the kiln indicates that the quasi totality of sodium nitrite corresponds to the A value of the right spectrum of figure 4. Again, these observations can be interpreted by invoking interactions between NaNO_2 and wood. When the sample has dried “out in the open”, only a part of water is taken off (probably the part near the surface as for samples which have been impregnated under partial vacuum), leaving a limited

quantity of recrystallized NaNO_2 (about half the total amount of sodium nitrite). It is observed that the line-width is even weaker than in the case of impregnation under partial vacuum. This means that the interactions of recrystallized NaNO_2 with the material are weakened due to the impregnation mode. Conversely, as all water has been eliminated by the drying process in the kiln (see above), and owing to the large line-width (right spectrum of figure 4), we can infer that the spruce sample was impregnated to the core and that high pressure has contributed to alter the material and, as a consequence, to enhance the interactions undergone by sodium nitrite. Indeed, alteration of the material is especially deleterious when, prior to impregnation, the piece of wood is dried in the kiln. This procedure was attempted, again with the hope to increase the amount of recrystallized sodium nitrite⁷. It turns out that, in these conditions, we totally failed to observe any NQR signal (with impregnation under partial vacuum or under high pressure). This could mean that water, which is naturally present in wood, is necessary for keeping a structure prone to recrystallization of embedded sodium nitrite. Finally, we have checked that, when sodium nitrite recrystallizes in wood, its NQR spectrum remains the same for months and probably longer.

Data analysis

All results, in terms of peak area (A) or line-width at half-height (LW), which have been given until now have been obtained through the procedure described below.

As seen above, obtaining a spectrum with a suitable signal-to-noise ratio (S/N) requires the accumulation of a large number of transients. Let us recall that the spectrum (frequency domain) results from the Fourier transform of accumulated free induction decays (fids; time domain). As a consequence, when the NQR line is relatively broad, the S/N is evidently lowered. Hence, a better strategy is to look at the time domain data since the parameter of interest is the amplitude A of the fid (which is also the peak area in the frequency domain)

while the fid damping factor is related to the line-width (LW) in the frequency domain. It is also important to realize that, in our case, the spectrum involves a single line, this point facilitating any fitting procedure.

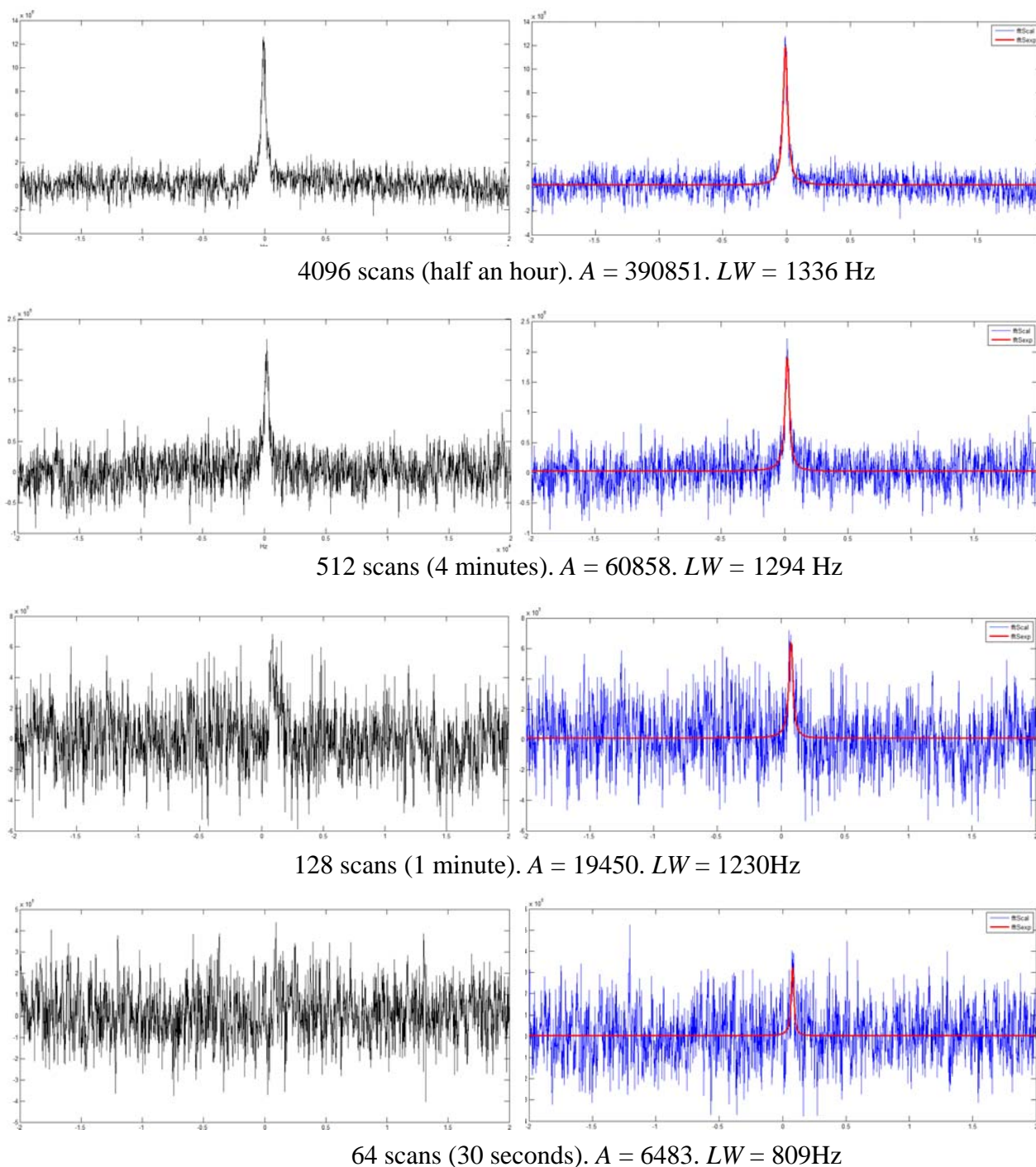


Figure 5. 4.64 MHz spectra of NaNO_2 in spruce (impregnation under partial vacuum; drying out in the open. Left column: raw spectra. Right column; the same raw spectra with the reconstructed spectra (continuous curves in red) with parameters derived from time domain data fitting.

In figure 5 are gathered a series of spectra (frequency domain) as a function of the number of scans (or, equivalently, as a function of the measuring time). Of course, with 4096 scans (half an hour of measuring time) the peak is perfectly defined with an excellent S/N. 512 scans (4 minutes of measuring time) appear convenient for properly observing the NaNO_2 peak. However, for future applications, this measuring time might still be too long. With one minute measuring time, we can guess the presence of a peak but this is no longer true for a measuring time of 30 seconds.

Now, we are going to show that a simple non linear least squares (NLLS) fitting procedure applied to the time domain data (fid) is able not only to reveal the presence of a peak but also to provide reliably the parameters of interest, namely A and LW . Such least-squares procedures are relatively common in multiline NMR spectra^{8,9} and make use of the following mathematical model for the fid (in the case of a single line and assuming that the fid is devoid of any dc component)

$$S(t) = A \exp(2i\pi\nu_0 t) \exp(i\varphi) \exp[-\pi(LW)t] \quad (1)$$

The parameters A and LW have been defined earlier; ν_0 is the resonance frequency with respect to the carrier frequency and φ the phase factor. Alternatively the damping function $\exp[-\pi(LW)t]$ can be replaced by a Gaussian function. A dedicated software has been developed under MATLAB. It requires starting values for these four parameters and provides refined values along with reconstructed spectrum in the frequency domain. The starting values can be derived from the experimental spectrum if it is sufficiently legible. Otherwise, as the spectral parameters of the considered NQR signal can be relatively easily guessed, they can be used manually as input parameters. As shown in the right column of figure 5, reconstructed spectra are perfectly consistent with spectra obtained from Fourier transform of the experimental fids. It was even possible to detect, thanks to the fitting of time domain data, a signal which is invisible in the frequency domain (bottom spectra of figure 5). The A values

are, as expected, approximately proportional to the number of scans while *LW* values remain of the same order of magnitude.

Conclusion

When this project started, it was considered as very challenging and rather utopian. The first result was looked at with some mistrust because it required extensive time averaging (several hours) and involved some artefacts. In fact, with some tenacity, several instrumental improvements and with appropriate data processing, we were able to obtain very consistent and reproducible results in a very reasonable measuring time (lower limit: 30 seconds). Extensive studies of spruce impregnated by sodium nitrite as a function of impregnation and drying conditions have shown that heating always modify the wood structure, as reflected by the NaNO_2 signal line-width. This latter property is indicative of interactions between the NaNO_2 crystal lattice and the material. In particular, it was noticed that drying wood at elevated temperature prior to impregnation totally precludes the formation of NaNO_2 crystals. Otherwise, it was shown that in soft conditions (without going to elevated temperatures), a large amount of NaNO_2 could be recrystallized in spruce wood. This opens the way of material labelling by nitrogen containing compounds and its further detection by nitrogen-14 Quadrupole Resonance.

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