

A New Pulsed Nuclear Quadrupole Resonance Spectrometer

G. L. Petersen

RITEC, Inc., 60 Alhambra Rd. Suite 5, Warwick, Rhode Island 02886

P. J. Bray

Department of Physics, Brown University, Providence, Rhode Island 02912

R. A. Marino

Department of Physics and Astronomy, Hunter College of C.U.N.Y., New York, New York 10021

Z. Naturforsch. **49a**, 65–70 (1994); received November 18, 1993

A new pulsed nuclear quadrupole resonance spectrometer is described and a number of Nitrogen-14 spectra are shown and discussed. The spectrometer is computer interfaced and both data acquisition and all adjustments other than the matching network tuning are automatic. Spectra may be produced using fast Fourier transforms or by the Clark Method. The latter is particularly valuable when very wide line widths are encountered.

Key words: Nuclear quadrupole resonance; Spectrometer; Instrumentation; Fourier transform.

Introduction

In the past few years there have been significant improvements in nuclear magnetic resonance instrumentation. In many cases these instruments have been used for both NMR and NQR studies. However, the best spectrometers that are commercially available are expensive, not usually capable of operating at low frequencies, and were not specifically designed for NQR. This paper reports on the beginning of an effort to apply modern circuitry and signal processing techniques toward the production of a pulsed spectrometer specifically for low frequency NMR and NQR applications.

The spectrometer consists of a personal computer containing a data acquisition card, a Ritec Advanced Measurement system (RAM), a low frequency NQR impedance matching network [1], a shielded sample coil, and an oscilloscope. A simple block diagram is given in Figure 1.

Digital information passes via the data acquisition card from the computer to the RAM for control of all spectrometer parameters other than matching network tuning. Analog information produced by a nu-

clear resonance is digitized by the data acquisition card and processed by the computer to produce a Fourier transform of the resonance. Averaging and other digital signal processing techniques may be performed by the computer. The oscilloscope is needed to monitor the operation of the spectrometer and to aid in tuning the impedance matching network.

Signal Processing Technique

The signal processing scheme of the spectrometer uses superheterodyne techniques not only in the receiver section but also in the production of the transmitter frequency. The basic ideas are illustrated in Figure 2.

The direct digital synthesizer is operated at the intermediate frequency plus the operating frequency ($IF + F$). When this frequency is multiplied (mixed) by the IF oscillator the difference frequency F is produced along with the sum frequency which is rejected by a low-pass filter. This signal is used by the gated amplifier to produce a high power burst or bursts at frequency F .

The received signal, either an echo or FID, is amplified and multiplied by the synthesizer output. The difference frequency (IF) is selected and amplified by the IF amplifier. Two more multipliers are used to multiply the output of the IF amplifier by 0° and 90° phase reference signals at the intermediate frequency.

* Presented at the XIIth International Symposium on Nuclear Quadrupole Resonance, Zürich, July 19–23, 1993.

Reprint requests to Gary Petersen, Ritec Inc. 60 Alhambra Rd. Suite 5, Warwick, RI 02886, USA.

0932-0784 / 94 / 0100-0065 \$ 01.30/0. – Please order a reprint rather than making your own copy.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

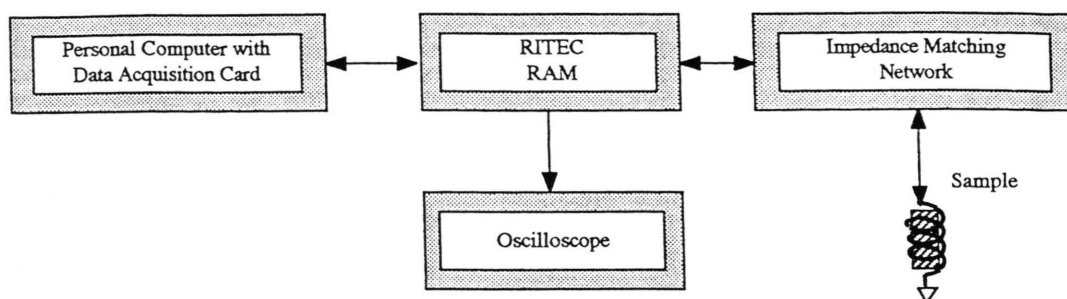


Fig. 1. Basic Elements of NQR spectrometer.

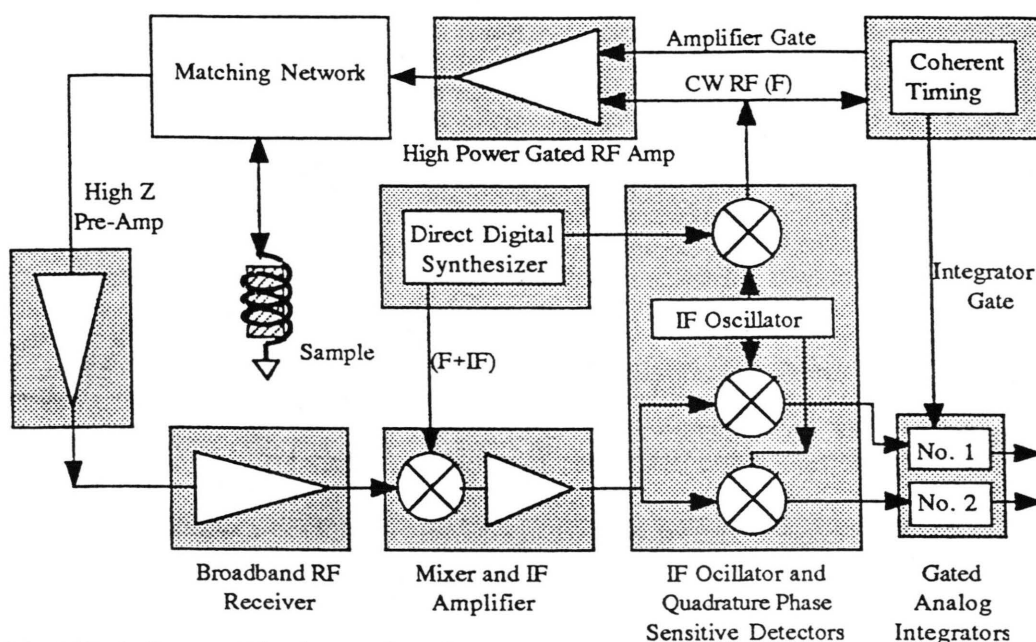


Fig. 2. Block diagram of signal processing scheme.

In this case the difference frequency is zero and a detected output is produced. The sum frequency component is either filtered out or removed by the integrators.

Advantages of Mixing Process

There are several advantages of the frequency mixing process used in Superheterodyne receivers:

- 1) The difficult tuning process required to match the receiver's frequency response to that of the signal is eliminated because the only narrow band amplification process is at the intermediate frequency (IF).

- 2) The phases of the quadrature phase detector references can be finely adjusted to insure accurate operation over the complete range of frequencies because detection occurs at the fixed IF frequency.
- 3) In our implementation of this process the frequency of operation and the receiver tuning are accomplished simultaneously by setting the frequency of the synthesizer. The result is an automatically tracking receiver.

Quadrature Phase Detection and Analog Integration

Although the mixing process shifts the frequency of the received signal to the intermediate frequency (IF),

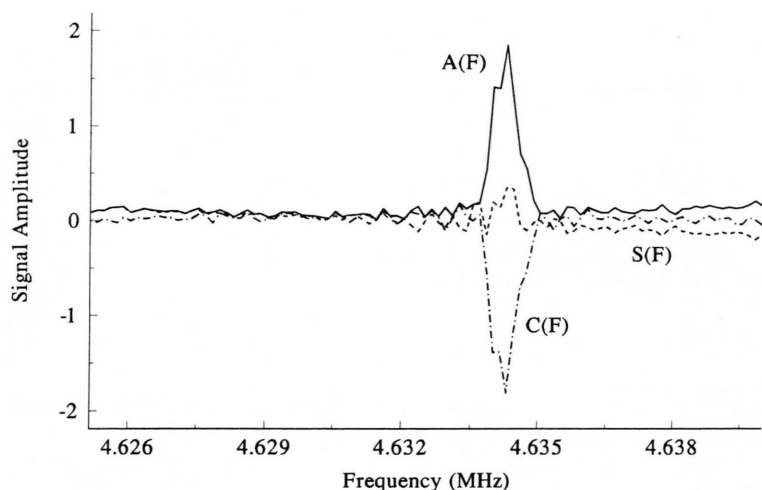


Fig. 3. Room temperature ^{14}N spectrum of sodium nitrite (from Echo).

the multiplier circuit outputs (phase sensitive detectors) produce the same output as would occur if the unshifted NQR signal were multiplied by the transmitted frequency. All phase information is preserved during the frequency shifting (mixing) process. The outputs of the Integrators can be expressed by

$$\text{Integrator No. 1} = C(F) = \int_{t_1}^{t_2} F(t) \cos(\omega t) dt,$$

$$\text{Integrator No. 2} = S(F) = \int_{t_1}^{t_2} F(t) \sin(\omega t) dt,$$

where t_1 marks the beginning of the integrator gate and t_2 the end. $F(t)$ is the time dependent amplified NQR signal, and $C(F)$ and $S(F)$ refer to the cosine and sine transforms. If the examined signal is a FID, t_1 starts as soon as the receiver has recovered from the high power RF burst and t_2 extends out to encompass all of the observable signal. If the signal is an echo, the gate is set to include all of the echo but reject the FID. Note that the expressions shown above are similar to the real and imaginary parts of the Fourier transform given by

$$G(F) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(t) [\cos(\omega t) + j \sin(\omega t)] dt.$$

However, the actual Fourier transform integrates from minus infinity to infinity, whereas the analog circuits integrate only during the gate which selects the signal. This problem, which distorts the line shapes obtained from free induction decays, is also present when digital Fast-Fourier-Transforms (FFTs) are employed.

Clark Method

The use of analog integrators to produce the line-shape was developed by Clark [2] and is known as the Clark Method. A good analysis of the method is given by Avogadro *et al.* [3]. The procedure is as follows:

1. The transmitter is stepped through the frequency of interest and the outputs of the two integrators are recorded at each frequency.
2. The line-shape may be displayed either as an amplitude spectrum

$$A(F) = [C(F)^2 + S(F)^2]^{1/2}$$

or as a cosine spectrum ($C(F)$) after phase corrections have been made.

Experimental Results

The spectrum shown in Fig. 3 was recorded by integrating the echo formed by a $90^\circ/180^\circ$ pulse pair, with no averaging. Note that the $S(F)$ transform is nearly at phase quadrature (nulled). When working with echoes, the ideal integration limits can nearly be satisfied because the gate opens before the signal appears and ends after it is complete. The phase compensation is accomplished by considering $S(F)$ and $C(F)$ as orthogonal vector components and rotating the coordinate axes until $C(F)$ is maximized and $S(F)$ is nulled.

The spectrum of Fig. 4 was recorded by integrating the free induction decay following a 90° RF pulse using the same sample as for Figure 3. The dead time

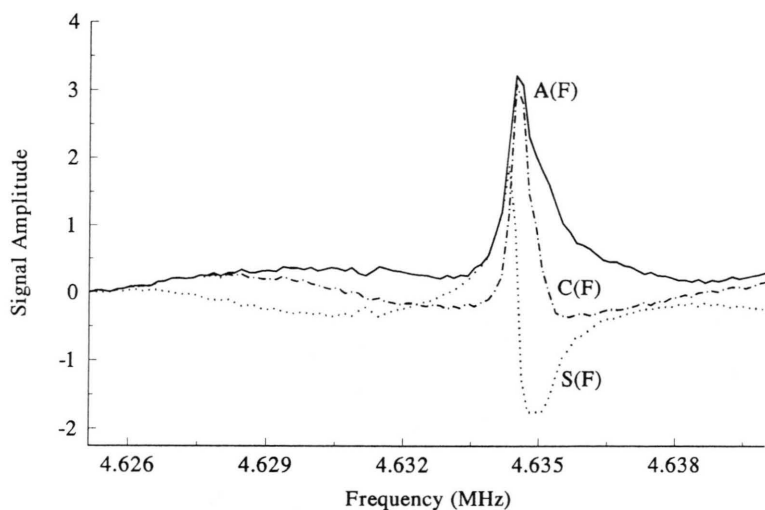


Fig. 4. Room temperature ^{14}N spectrum of sodium nitrite (from FID).

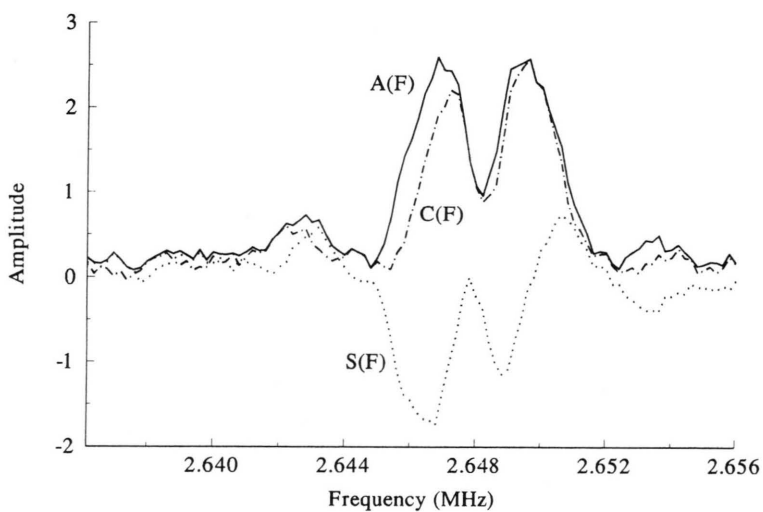


Fig. 5. 77° K ^{14}N spectrum of 9 vinyl carbazole (from Echo).

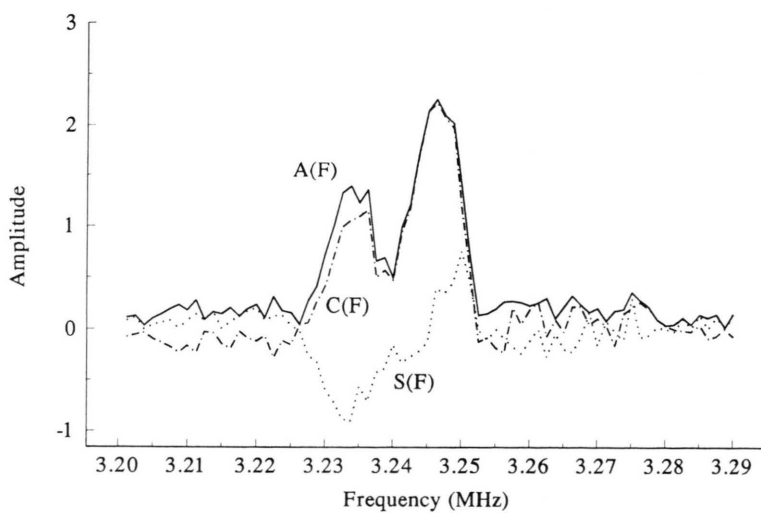


Fig. 6. 77° K ^{14}N spectrum of HMT hexahydrate (from Echo).

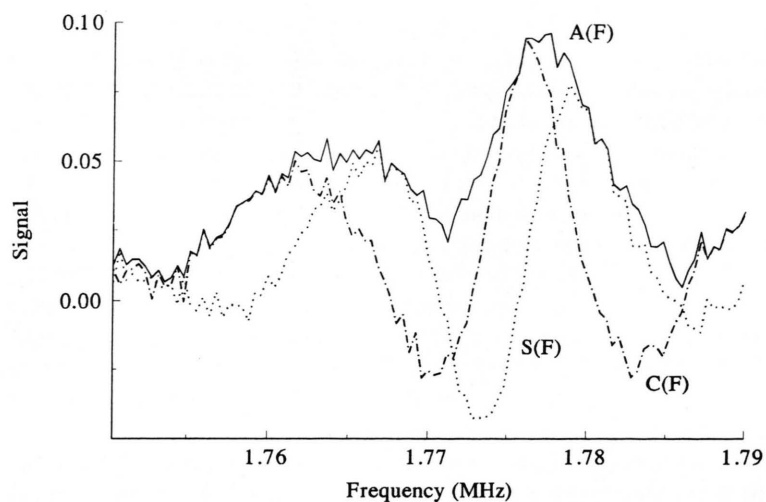


Fig. 7. Room temperature ^{23}Na spectrum of sodium hydroxide (from FID).

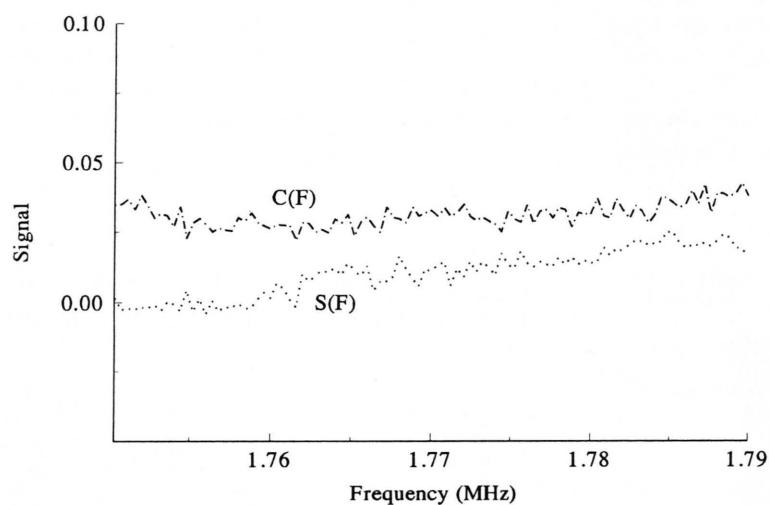


Fig. 8. Spectrum obtained after removing sodium hydroxide sample.

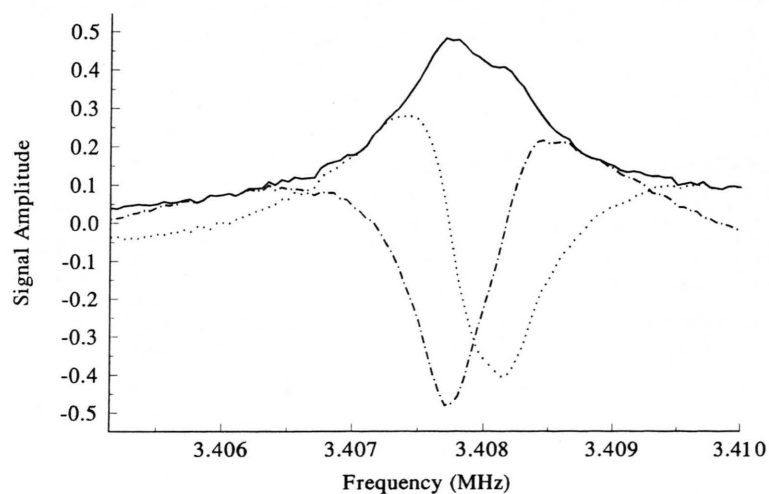


Fig. 9. 77° K ^{14}N spectrum of HMT (from FID).

of the system was approximately 150 μ sec. Because the FID contains only half of the Fourier Spectrum, the amplitude spectrum (A(F)) is artificially broadened and C(F) after phase compensation is a better representation of the line shape, even though the dead time causes the C(F) curve to go negative on either side of the resonant peak.

The line shape shown in Fig. 5 was obtained by integrating the echo and was expected to be a single frequency line. However, the RF pulses were too close together in time, and some of the FID from the second pulse was included in the gate resulting in the apparent double line structure.

One of the advantages of the Clark method is that wide lines may be studied without the requirement that the spectrum of the driving pulses be very wide. The hexamethylene tetramine hexahydrate spectrum shown in Fig. 6 is a good example of a rather wide line width. In this case the double line shape is real and confirmed by earlier unpublished work.

The resonance shown in Fig. 7 is interesting because it points out some of the difficulties of working

with FIDs. The line width is rather wide (>10 kHz), therefore, the FID will decay quickly and the dead time becomes very important. In this experiment the receiving coil was damped to reduce the recovery time to about 50 μ sec. However, even this dead time causes the artificial broadening and oscillations that appear on either side of the central portion (1.778 MHz [4]) of the spectrum. The dead line problems exhibited here should be eliminated by working with echoes. In fact, the proper investigation of any wide-line resonance using a pulsed spectrometer requires examining echoes rather than the FID. Unfortunately, the single attempt to produce a Sodium Hydroxide spectrum using echoes was unsuccessful.

Figure 8 was recorded to show the response of the system with the sample removed. All settings are the same as those of Figure 7.

Figure 9 shows the asymmetric shape of the hexamethylene tetramine spectrum [5] as well as illustrating the control the Clark Method gives in establishing the desired number of points within the line shape.

- [1] G. L. Petersen, Low Frequency NQR Matching Network, *The NQR Newsletter*, edited by R. A. Marino, 1, 2 (1993), p. 20.
- [2] W. G. Clark, Pulsed Nuclear Resonance Apparatus, *Rev. Sci. Instrum.* **35**, 316 (1964).
- [3] A. Avogadro, G. Bonera, and M. Villa, *J. Magn. Res.* **35**, 387 (1979).
- [4] D. T. Amm, S. L. Segal, T. J. Bastow, and K. R. Jeffrey, *Z. Naturforsch.* **41a**, 305 (1986).
- [5] A. Colligiani and R. Ambrosetti, *J. Chem. Phys.* **60**, 1871 (1974).