

A Spectrometer System for Determination of Line Shape in NQR Spectrum

Masahiko SUHARA

Department of Chemistry, Faculty of Science, Kanazawa University

(Received May 25, 1972)

Abstract A sensitive spectrometer system capable of reproducing faithfully the line shape in NQR has been shown. Several types of regenerative oscillator have been examined and it was found that the Kushida type oscillator is very superior. Magnetic field modulation of on-off current or antisymmetric half-sine one was utilized in order to obtain the absorption line shape. We developed a frequency marker circuit, which produces pips on a pen recorder at predetermined frequency increments. This circuit can also trigger a digital voltmeter and a printer in order to record the spectrogram with a suitable frequency interval. Using the spectrometer system, a very good S/N ratio has been obtained for ^{35}Cl NQR lines in $\text{Cu}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$ and *p*-dichlorobenzene. From these results it has been found that this spectrometer system is useful to investigate the line shape of NQR line.

Introduction

In NQR spectroscopy, as well as in NMR, it is interesting to investigate the origin of the spectral line shape, although the analysis of the line shape has much difficulty because of a various mechanisms of line broadening such as magnetic dipole-dipole interaction, lattice defect, crystal strain, lattice vibration, hindered rotation, etc. Most of the works on the NQR line shape have been done with respect to line width rather than actual line shape, because of the lack of the reliable spectrometer.

In the present study, a sensitive spectrometer system capable of reproducing faithfully the line shape of NQR has been demonstrated.

General Consideration

Requirements for a good spectrometer include wide frequency coverage, high

sensitivity and low distortion. The radio-frequency or VHF oscillator of the spectrometer should be capable of tuning over a wide frequency range in order to cover the frequency of NQR. To detect the very weak signal of NQR, a spectrometer of high sensitivity is required. The spectrometer system also requires the good reproducibility of the shape of resonance line.

In general, the nuclear quadrupole interaction is characterized by a shorter relaxation time than nuclear magnetic interaction: hence a greater rf field is needed to produce an observable resonance.

Two types of radio-frequency oscillators are in general used for NQR studies; the super-regenerative oscillator and the regenerative one. Each type of circuit has characteristic advantages and disadvantages. Although the former has much higher sensitivity and also it has been used in most of the NQR experiment, because it is very suitable to detect the NQR when it is operated in high level of rf field, it gives in general a very distorted representation of the spectral line depending upon the frequency and the amplitude of the quenching voltage. In addition to this, the side band spectrum prevents to distinguish the main resonance peak especially when the original spectrum is multiplet with a frequency interval smaller than quenching frequency. The regenerative oscillator in principle is a simpler device and has a good response to NQR. It is, however, less sensitive and suffers seriously from microphonics. In order to obtain the true resonance line shape, the super-regenerative oscillator is abandoned in favor of a regenerative one, although it has been shown that, by adjusting the quenching voltage, quenching frequency or plate voltage of the rf oscillator¹⁾ or by adjusting the frequency difference between the locked signal and the rf pulses²⁾ in the super-regenerative oscillator, a pure absorption or dispersion line shape can be obtainable.

Regenerative Oscillators

The autodyne operates in three distinct regenerative modes; low level grid detection, anode detection and high level grid detection.

The modes may be demonstrated by a strong NQR line or by NMR in paramagnetically doped water. No ambiguity exists except when there is unusually heavy loading of the sample coil. As a rule, one of the modes serves the operator's purpose and the others should be avoided.

The low level grid detection mode³⁻⁵⁾ is characterized by an rf level from 0.07 up to 0.3 V. This mode is useful in the case of resonance saturation. The output noise, which rises rapidly with increasing rf level, restricts the rf amplitude.

Anode detection was first utilized by Bruin⁶⁾ in a grid-biased autodyne. No advantage in this mode of operation exists, as adjustments are critical and sensitivity is inferior to that of the high level detection mode.

The high level oscillator detection described by Wang⁷⁾ is noted for its good

response to NQR when operating in the regenerative mode. It is also known as a circuit which demands special care in construction and operation. Its main handicaps are excessive sensitivity to stray capacitances and high hum pick up. One may add the difficulty in manipulating the audio signal feed-back circuit.

Recently, an NQR spectrometer using low noise field effect transistor has also been developed ^{8,9)}.

In the present work, the four types of the regenerative oscillator were examined. The Kushida type oscillator was very superior than others at all points.

*Pound-Watkins-Knight type oscillator*³⁾ ---- This is a very familiar oscillator detector in NMR and sometimes in NQR. The operational condition is good in lower rf level. Although it is not so suitable for the chlorine NQR experiment, it may be useful for the detection of the intense line. The circuit used had a good sensitivity but less stability in the frequency region less than 22 MHz depending on the characteristics of the rf amplifier in it. The signal of ³⁵Cl NQR in SbCl₃ was ~20 dB above noise on the recording chart ¹⁰⁾. However, this circuit could not be used because of our purpose of Cl NQR studies, most of which has much higher frequency region than 22 MHz.

*Knight type oscillator*¹¹⁾ ---- This circuit is a quite simple but more important high-level oscillating limiter. It is suitable for application to the problems in nuclear resonance which require rf levels between 1~20 V rms. The NMR signal in Cu²⁺ doped water was detected on the oscilloscope screen with the signal-to-noise ratio of ~10 at 10 MHz. Although this circuit is suitable for NQR because of the high level rf oscillator, it could not be utilized in our work since the maximum workable frequency was ~12 MHz.

*Wang type oscillator*⁷⁾ ---- A regenerative autodyne wired as a cathode biased grid-dip-meter, which is equal to Wang's spectrometer, was developed by D. Gill et al ¹²⁾. We could not succeed to detect the NQR signal by means of this type circuit examined, probably due to the constructive problems.

Kushida type oscillator^{4,5,13)} ---- This circuit possesses high sensitivity and good frequency stability and can reproduce faithfully the line shape of the nuclear resonance in the different frequency region. The spectrometer is a single tube (2C51 or 5670) ¹⁴⁾ push-pull marginal oscillator detector. The oscillation frequency is determined by the resonant circuit consisting of the grid butterfly condenser, the sample coil, and transmission line. A several turns sample coil may be resonated at ~50 MHz with the grid butterfly condenser. The operating frequency is between 10~100 MHz by changing the turn of coil, the length of the transmission line and the butterfly condenser. The oscillation level of the spectrometer may be monitored with a grid current micro-ammeter and can be altered by adjusting the capacity of the grid-plate coupling capacitors. Magnetic shielding of the spectrometer is important in order to prevent pick up from the magnetic modulation coils. Therefore, with the exception of the sample coil, the spectrometer was completely enclosed in a soft iron

box with wall thickness of 10 mm. The circuit diagram of the spectrometer is shown in Fig.1.

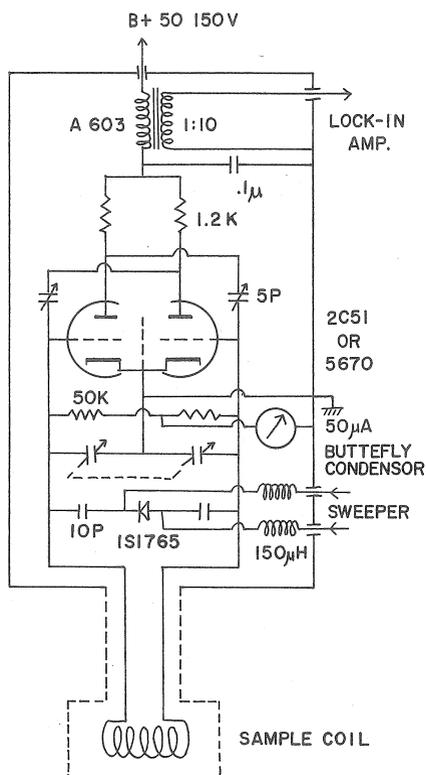


Fig. 1. Kushida type oscillator circuit

Modulation

In magnetic resonance experiment, the nuclear signal can be detected through modulations; one is frequency modulation and other magnetic field modulation (or Zeeman modulation). In principle, the use of frequency modulation of the source oscillator of a radio-frequency spectrometer offers an attractive mode of operation. As the frequency of the spectrometer oscillator moves back and forth in the region of an absorption line of the sample, the latter produces amplitude modulation, which can be observed by means of an amplitude detector, followed by narrow-band amplification and phase-sensitive detection at the modulation frequency. In practice, however, a very serious difficulty arises, namely, that the incidental amplitude modulation which results from practical efforts to modulate the oscillator frequency produces a large back ground signal at the modulation frequency which at best causes bad drift in the base line, and at worst may swamp the amplifier-detector system. In order to keep the frequency deviation low enough to avoid this complication, one is

usually forced to use weak modulation (peak deviation \ll line-width). The trouble with weak modulation is that the strength of the signal produced by the line is less than the maximum available, and also that the line shape obtained corresponds to the derivative of the absorption line. Additional trouble by using the frequency modulation is the modulation broadening in the observed line, depending on the modulation amplitude. On the other hand, advantages of magnetic field modulation are that (i) only nuclear quadrupole resonances are modulated, so that piezoelectric resonances and rf interference have negligible effect, (ii) the absorption line shape, not its derivative, is recorded, (iii) no connection or adjustments to the rf circuits of the spectrometer are necessary and (iv) the modulation has no effect on methods of frequency measurement. The only important requirements are that for half the modulation cycle the magnetic field should be zero and that for most of the remaining part of the cycle it should be large enough effectively to erase the resonance. There is a problem of the poor mark-to-space ratio since large current should be generated across the low-resistance coil. This can be solved by utilizing thyristor.

Magnetic Field Modulation

An on-off magnetic field modulation was used in this experiment. A very large in-input signal of 200 Hz to a 200 watts audio power amplifier gives a square out-put power, which is fed to the modulation coil after rectified by power diode. Reduction of modulation pick-up was achieved by carefully adjusting the relative position of a coil connected with the modulation coil in series. In this case, a conventional lock-in-amplifier was operated at 200 Hz. An antisymmetric half-sine current

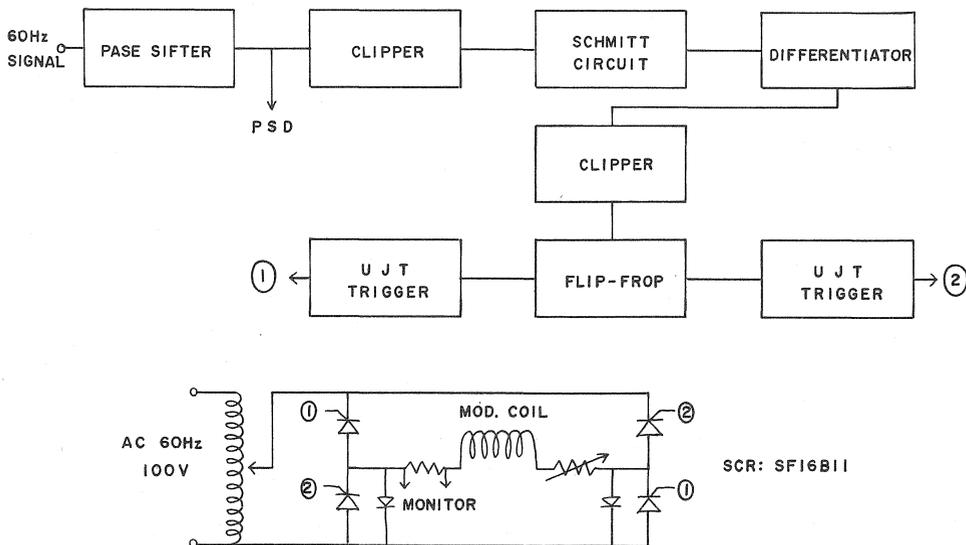


Fig. 2. Block diagram of magnetic field modulator by antisymmetric half-sine waveform

waveform^{14,15)} was also used for magnetic field modulation. This waveform can be generated by appropriately delaying the trigger pulses, since a thyristor (or SCR) remains an effectively open circuit until triggered. A 30 Hz antisymmetric current is obtained by synchronizing the firing of the SCR's at a 30 Hz repetition rate from the 60 Hz power line. A block diagram of a suitable circuit is shown in Fig.2. In this case, a synchronous second harmonic detection by the reference signal generated from a doubler should be carried out. The magnetic field strength was measured by a Gaussmeter (Kangyo Denki Kiki, KG-300). Several modulation coils examined have a dimension of a length of 40~70 cm on the outside of a 12 cm diameter Dewar vessel.

Frequency Sweep and Frequency Modulation

In order to set the center of the band in which the resonance occurs, the main tuning butterfly condenser in the spectrometer is used. The frequency sweep width was adjusted by the bias voltage on a voltage-sensitive silicon diode capacitor (NEC 1S1756, $Q=1000$ at $V_R=2.5V$, $f=20$ MHz). In order to sweep the oscillator frequency, the Green Pot continuous-rotation potentiometer (Midori Sokuki, Model CPP-45, linearity = 0.4%), which varies the bias voltage on 1S1765, is driven manually or by a 1 rpm synchronous motor through a 8 speed gearbox (step function speed reductor 1/1 to 1/20). Sometimes, it is useful to get the first derivative of the resonance line. We can obtain the derivative by the frequency modulation which is achieved by applying the modulation in-put of an audio frequency to the voltage-sensitive diode from an external audio oscillator through an internal attenuator. Modulation amplitude can be measured according to the method described by Koi¹⁷⁾, which is illustrated in Fig. 3.

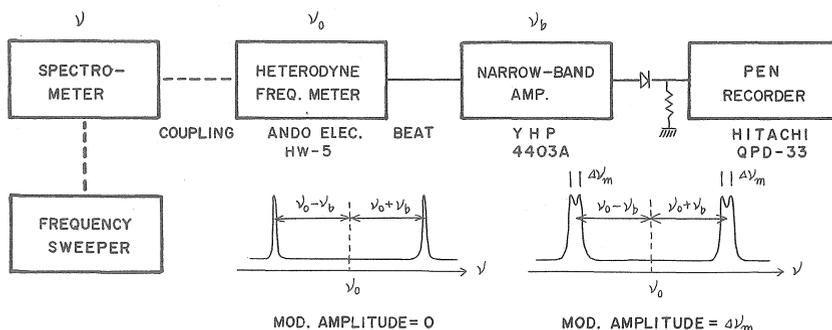


Fig. 3. Modulation amplitude measuring system and recorded beats

Frequency Marker

In radio-frequency spectroscopy one must conveniently use a electronic counter

for measuring the frequency of the rf source. Because visual monitoring of long graphically recorded experiments is tedious we developed an automatic pip marker which uses the convenient digital information displayed by a counter to emit pips at predetermined frequency increments, i. e., 0.1, 1, and 10 kHz. A switching transistor derived by a or-circuit, which follows the collector voltage of the particular flip-flop circuit that displays the decimal digital representation wanted, produces pips on the pen recorder. A diagram of the circuit is shown in Fig. 4. The similar marker circuit¹⁸⁾ has been developed using a relay followed by a cathode follower. A commercial model frequency counter utilized for this marker was Matsushita Communication Ind. Co., Model VP-433 with VP-0428.

Using the same circuit described above a digital voltmeter with a digital printer can be triggered in order to record the spectrogram with a suitable frequency interval automatically.

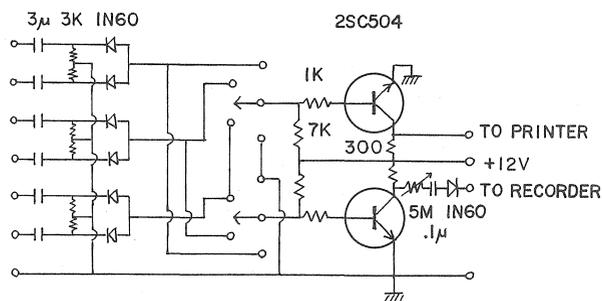


Fig. 4. Frequency marker circuit

Over-All Operation

The block diagram of the whole measuring system is shown in Fig. 5. The absorption line was recorded by means of conventional narrow-band and phase-sensitive detection technique, using a lock-in-amplifier Model LI-572A of NF Circuit Design Block Co. The resonance output was displayed on an analog pen-recorder Hitachi Model QPD-33 or on a digital printer through a digital voltmeter Takeda Riken TR 6515.

The level of oscillation in the regenerative oscillator was kept sufficiently weak by monitoring the grid current, in order to have no tendency for the line to saturate. Since the resonance frequency has a temperature dependence of the order of few kHz/°C in ³⁵Cl NQR, even a temperature inhomogeneity of the order of 0.1°C in the sample may cause a considerable broadening of the line width. Therefore, for the precise measurement of the line shape, it is essential to keep the sample at a constant temperature. The sample was immersed in a fluid paraffin, petroleum ether, *n*-pentane or *iso*-pentane, whose temperature was kept at any temperature. For the

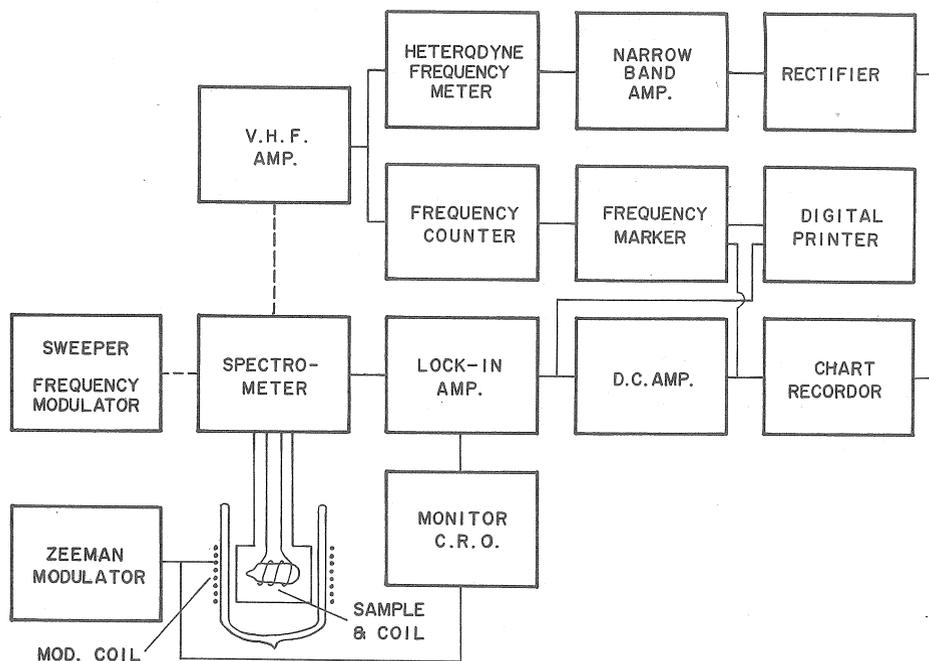


Fig. 5. Block diagram of NQR spectrometer system

observations at liquid nitrogen temperature, the sample holder was immersed directly in liquid nitrogen. Adjusting the current through a small heater immersed in liquid nitrogen, the desired temperature can be attained by inletting the cold nitrogen gas flow into a Dewar vessel. The alternative control can be performed by the different walls between liquid nitrogen and coolant in which the sample is immersed. During the observation the temperature can be maintained within 0.01 °C. The temperature was measured by using a copper-constantan thermocouple affixed to the sample tube, which was calibrated by the boiling temperatures of liquid nitrogen, benzene and water, the sublimation temperature of dry ice, and ice temperature. The error in the measurement was 0.5 K.

Examples of Observation

The NQR absorption line due to ^{35}Cl nucleus in $\text{Cu}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$ at liquid nitrogen temperature was obtained by magnetic field modulation. The display on chart of the spectrum together with the frequency marks of 1 kHz interval is shown in Fig. 6-a. By means of frequency modulation, Fig. 6-b shows the derivative of the absorption line of ^{35}Cl NQR in *p*-dichlorobenzene at room temperature. A very good S/N ratio obtained in these examples has verified that the spectrometer system developed is useful to investigate the line shape of NQR spectrum.

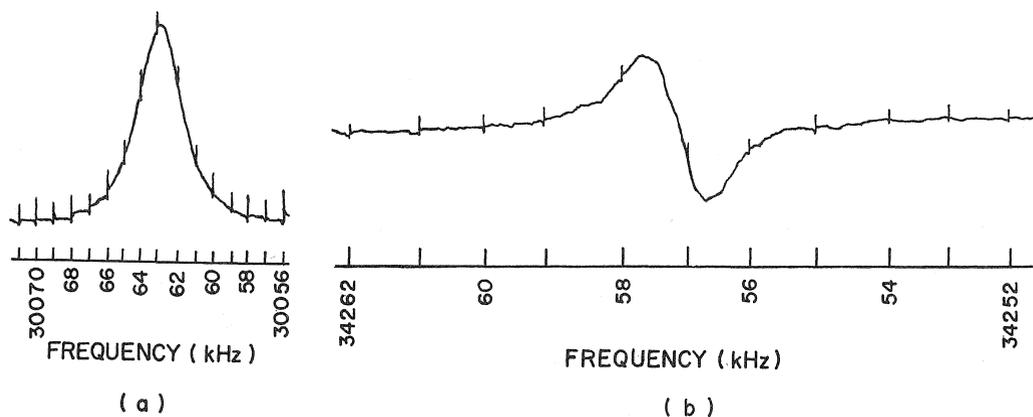


Fig. 6. ^{35}Cl NQR spectrum in powder samples of
 (a) $\text{Cu}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 77K (Absorption curve)
 (b) *p*-dichlorobenzene at room temperature (Derivative curve)

Acknowledgments

The author wishes to thank Professor S. Aono for his encouragement. Thanks are also due to Dr. Y. Yamagata, Department of Physics, for valuable suggestions on instrumentation. Technical assistances by Mr. K. Endo, Mr. K. Shimizu and Mr. T. Yoshii are appreciated.

References

- 1) K. Tsukada, *J. Phys. Soc. Japan*, **11**, 956 (1956).
- 2) D. A. Tong, *J. Phys.*, E, **1**, 1153 (1968).
- 3) R. V. Pound and W. D. Knight, *Rev. Sci. Instr.*, **21**, 219 (1950).
- 4) G. B. Benedek and T. Kushida, *Phys. Rev.*, **118**, 46 (1960).
- 5) T. Cole, T. Kushida and H. C. Heller, *J. Chem. Phys.*, **38**, 2915 (1963).
- 6) H. Bluin, *Rev. Sci. Instr.*, **37**, 1412 (1966).
- 7) T. C. Wang, *Phys. Rev.*, **99**, 566 (1955).
- 8) T. L. Viswanathan, T. R. Viswanathan and K. V. Sane, *Rev. Sci. Instr.*, **39**, 472 (1968).
- 9) T. L. Viswanathan and T. R. Viswanathan, *Rev. Sci. Instr.*, **40**, 477 (1969).
- 10) K. Endo, M. Suhara and S. Aono, Presented at the 22nd. Annual Meeting of the Chemical Soc. of Japan, Tokyo, April (1969).
- 11) W. D. Knight, *Rev. Sci. Instr.*, **32**, 95 (1961).
- 12) D. Gill, M. Hayek, Y. Alon and A. Simievic, *Rev. Sci. Instr.*, **38**, 1588 (1967).
- 13) Y. Imaeda, *J. Sci. Hiroshima Univ.*, Ser. A, **23**, 239 (1960).
- 14) It was found that, when several tubes of Toshiba (Japan) 5670 were inserted in the tube-base instead of the tubes of 5670 or 2C51 of RCA, Western or G.E., the oscillation level decreased by one-order in magnitude. Hence in the same working condition the use of Toshiba 5670 gives much decrease in sensitivity.

- 15) D. A. Tong, *J. Phys. E*, **1**, 1162 (1968).
- 16) G. M. Muha, *Rev. Sci. Instr.*, **41**, 1238 (1970).
- 17) Y. Koi, *J. Phys. Soc. Japan*, **12**, 49 (1957).
- 18) L. Wharton and D. Cleaves, *Rev. Sci. Instr.*, **33**, 562 (1962).