Computer Enhanced SRO NQR-Spectrometer *

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An automatic computer supported SRO NQR spectrometer system was constructed for the measurement of time dependent NQR signal intensities. The system has several functions: fast scanning (500 kHz/25 s), averaging, smoothing, automatic noise level estimation, automatic peak detection, etc. The process of the $\beta \rightarrow \alpha$ phase transition of p-dichlorobenzene is illustrated by the 3-dimensional spectrum.

Introduction

We have investigated the phase transitions and polymorphisms of organic chlorocarbons by using mainly NQR and DSC (Differential Scanning Calorimetry) techniques. In these studies it was found that several of the compounds show very slow phase transitions. It has been reported that measurements of the time-dependence of NQR signals at various temperatures provide useful information about nucleation and growth-processes in phase transitions [1–3].

In the present work, a fully automatized NQR spectrometer was developed for the purpose of such measurements.

Experimental

Hardware

The hardware (Fig. 1 a) consists of an analog and a digital system. The power sources for the two systems are independent from each other. The digital system (a microcomputer and the peripheral equipments) is sealed with aluminium plates. The analog system was constructed from commercial electronic devices and a home-made LC-push-pull type superregenerative spectrometer which is externally quenched (frequency 50 kHz) and frequency modulated (80 Hz) [4].

The spectrometer is swept by means of a variable capacitor diode, biased by a saw-tooth voltage function transferred from the computer via a D/A-converter (D/A-0 ch). The output voltage of a lock-in amplifier is fed to the computer via an A/D-converter (A/D-0 ch). During data acquisition, the peripheral equipments are automatically turned off because they sometimes generate noise. The on/off switching is set by a TTL level condition (D/A-2 ch).

A small Zeeman coil is set around a sealed brass tube in which a thermo-couple (chromel-alumel), the RF-coil, and the sample tube are mounted. The TTL signal from the D/A-converter turns on or off the Zeeman coil current to compensate the background (see below).

Software and Functions

The software system is described by HP BASIC 3.0. Figure 1 b shows the outline of the system which comprises 5 sets of function groups. In Fig. 1 b, each block forms a so-called "menu". The items in the menu are displaced on the softkey label positions on the screen, each position corresponding to one of the ten softkeys on the keyboard. One can easily select the menu or the item (function) wanted by pressing the corresponding softkey. In this paper only several important functions will be explained. The details of all the functions and their algorithm will shortly be reported.

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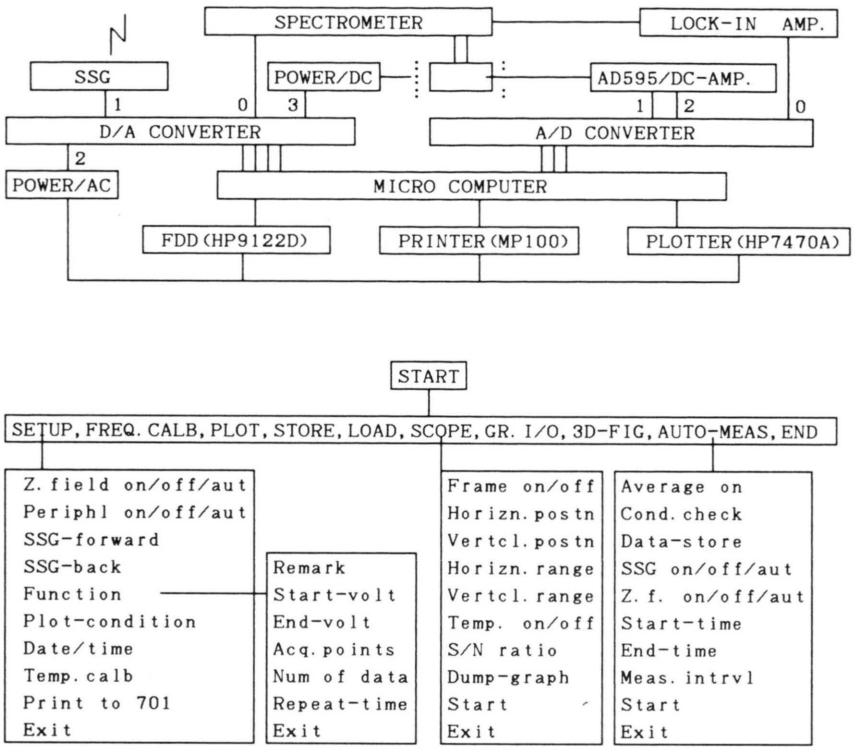

Fig. 1. Block diagrams of the systems. a) Hardware system. The numbers attached to A/D and D/A converters (0, 1, 2, 3) mean their channel numbers. "SSG" is a standard signal generator controlled via a D/A-1 ch. "POWER/DC" is the source of Zeeman field. "AD 595" is an IC-thermometer. "FDD" is a floppy disk driver. MICRO COMPUTER is HP9816s (768 kB). – b) Construction of the software system (70 kB, 1700 steps). "Acq. points" is the number of raw data points acquired into a buffer by "fast handshake mode". The average value of the raw data thus obtained is stored as one data point.

1. SETUP: This is an option to set up the condition of measurement.

⟨Z. field on/off/aut⟩ is a toggle switch that turns on and off the current of the Zeeman coil (ca. 30 Gauss at 2.2 A). The "aut" mode emulates Zeeman modulation. ⟨Periphl on/off/aut⟩ is a toggle switch of the AC-power for the peripheral equipments. When the switch is "aut", the AC-power turns off only during data-acquisition. The above two functions are very effective for noise-reduction.

2. FREQ. CALB.: This option converts a voltage-linear abscissa to a frequency-linear one. By using the signals (including sidebands) from the SSG (Standard Signal Generator), several frequency pairs and the corresponding bias voltage are picked up with a pointing device (rotary knob). The frequency vs. voltage function is determined by a least-squares method using the data thus obtained. After the conversion, the NQR spectrum is plotted on a frequency-linear scale.

3. SCOPE: This function works as a digital oscilloscope.

⟨S/N ratio⟩ is a function to convert the digit scale of the intensity to a signal-to-noise ratio scale. ⟨Start⟩ is the switch to scan the spectrometer. The CRT plots the spectrum in real time. The scanning speed is about 20 points/s under a standard condition (num. of data = 1000, acq. points = 2, scanning range = 1 to 10 volts (ca. 500 kHz)).

4. 3D-FIG: This option is a tool to draw a three-dimensional spectrum.

5. AUTO-MEAS: This is a function to measure repeatedly NQR spectra under a condition programmed beforehand.

6. OPTIONAL FUNCTIONS: The system has also the following functions: ⟨Noise-level⟩: a routine to estimate automatically the noise level of an NQR spectrum; ⟨Peak-check⟩: a function to detect automatically the slope positions and the center of the derivative curve; ⟨Smooth⟩: a routine to smooth a noisy spectrum by using a moving average method [5].

Results

Figure 2 demonstrates an example of the background compensation using a Zeeman field. Figures 2a, 2b, and 2c are NQR spectra of p-dichlorobenzene (pDCB) measured under the condition "SSG-on". As shown in Fig. 2, this method is effective to compensate a noisy and/or drifting background.

Figure 3 demonstrates the effect of combined smoothing and averaging in weak signals.

Figure 3a shows a single scan spectrum of pDCB (90 mg).

Figure 3b is the 49 scans spectrum whose S/N ratio should be enhanced by a factor of ca. 7.

Figure 3c is the 9-points smoothing spectrum of Figure 3b. The spectrum is comparable to the 100 scans spectrum of 3a. In this way, the combination of averaging and smoothing methods can considerably reduce the running time required and the sample size. In this case, the 3b-spectrum was obtained within 40 minutes. It is possible to shorten the running time by 20 minutes if the measurement is made in the mode: Zeeman field off.

Mcdonald and Hacobian reported on the time dependence of T_2^* in the $\alpha \rightarrow \beta$ phase transition of pDCB [3]. We measured with our system the time dependence of the NQR signal intensity during this transition.

The specimen set in the sample container was maintained at 314 K by circulating water from an electronically thermo-controlled bath. The NQR

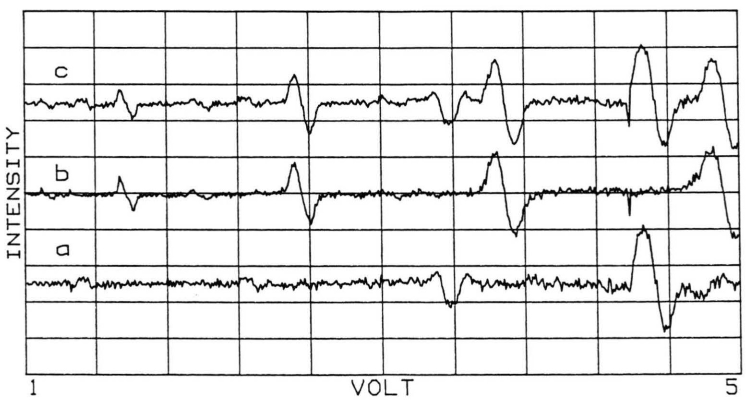

Fig. 2. Background compensation using Zeeman field. – a) Zeeman field off-spectrum. b) Zeeman field on-spectrum. c) Difference spectrum, a) – b).

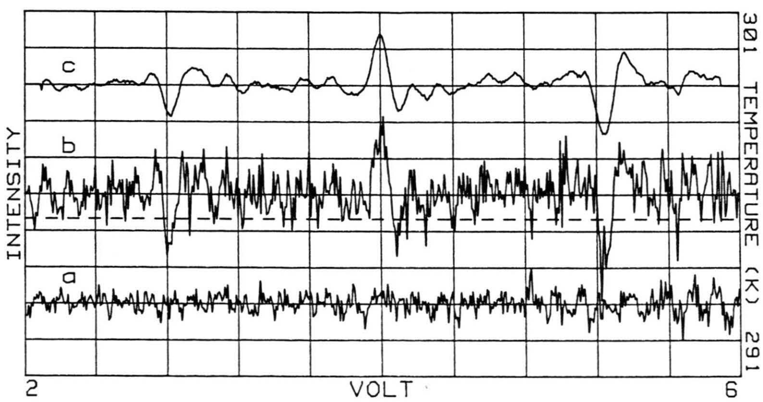

Fig. 3. Averaging and smoothing effects in a weak signal. Sample: p-dichlorobenzene (90 mg), condition: Number of data = 500, acq. points = 2, time const = 10 msec, T = 293.2 K. a) Single scan spectrum, b) 49 scans spectrum, and c) the 9-points smoothing spectrum of b).

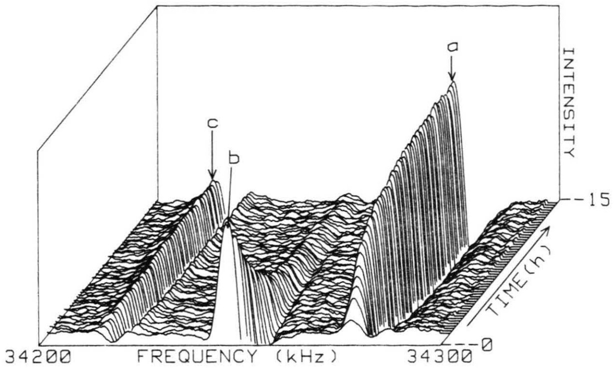

Fig. 4. Three-dimensional NQR spectrum of p-dichlorobenzene during $\beta \rightarrow \alpha$ transition at 293.2 K. a)–c): NQR signals of α-phase, β-phase and sideband of a), respectively.

spectra were repeatedly measured at intervals of 15 minutes by the ⟨AUTO-MEAS⟩ routine. After 6 hours, the spectrum indicated that the $\alpha \rightarrow \beta$ phase transition was almost completed. At this point, the bath temperature was reset to 293 K.

Figure 4 shows the 3-dimensional spectrum of the time dependence of the α and β signal intensities in β-pDCB thus obtained. In the figure, the $\beta \rightarrow \alpha$ phase transition is clearly demonstrated by the decrease of the β signal and the increase of the α signal. However, one can not quantitatively determine the line intensity by using SRO. To overcome the disadvantage, a system equipped with a regenerative oscillator will be developed.

Acknowledgement

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[1] M. Hashimoto and A. Weiss, J. Mol. Struct. **58,** 243 (1980).
[2] A. Weiss, J. Mol. Struct. **83,** 181 (1982).
[3] A. D. Mcdonald and S. Hacobian, J. Mol. Struct. **111,** 209 (1983).
[4] A. Hirai, H. Abe, and H. Yasuoka, BUSSEI **1967,** 697 (1967).
[5] A. Savitzky and M. J. E. Golay, Anal. Chem. **36,** 1627 (1964).