

Some Experimental Data on the Fundamental performance of JNM-3H-60 Type High-resolution NMR Apparatus.I.

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Some Experimental Data on the Fundamental Performance of JNM-3H-60 type High-resolution NMR Apparatus. I.

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The electronic investigation is now in progress on molecular structures in gas and liquid states by means of high-resolution nuclear magnetic resonance (NMR), under the support of the Institutional Research Grant of the Ministry of Education (1965-1966).

In 1965, high-resolution NMR spectrometer, 3H-60 type of the Japan Electron Optics Laboratory Co. Ltd., was equipped as the first step in a series of the investigation. The main features of the spectrometer are as follows :

1. The electromagnet provides a homogeneous magnetic field that can be varied from near zero to 15,000 gauss.
2. The frequencies of the oscillator supplying rf energy to the sample under study are 50 and 60 Mc.
3. NMR signals are detected by the bridge circuit of Anderson's type.
4. Other various components such as a superstabilizer, an NMR-control and a base-line stabilizer are attached to the spectrometer.
5. As accessories, a spin-decoupler and a variable temperature unit are attached.
6. The JRA-1 type spectrum-accumulator was kindly contributed by the Japan Electron Optics Laboratory Co. Ltd., to whom the authors express their deep gratitude for their kindness.

When NMR technique is used for the electronic study on molecular structures and chemical phenomena in liquid or gas states, parameters of chemical shift and spin-coupling constant play an important role in the study. Therefore, high-resolution, high-stability and high-sensitivity are required for the apparatus.

In this sense, examinations of the NMR apparatus were made on the fundamental performance and some experimental data are reported in the present paper.

1. Resolution and Reproducibility

High-resolution proton spectra at 60 Mc of methyl group in pure ethylbenzene are shown in Fig. 1. The central part in the spectra is theoretically predicted as complicated lines and it is said that to split these lines into fine components is not so easy. In Fig. 1, this central part is roughly splitted into two main lines separated by 0.64 cps. Therefore, two lines separated by about 0.3 cps seem to be distinguishable, that

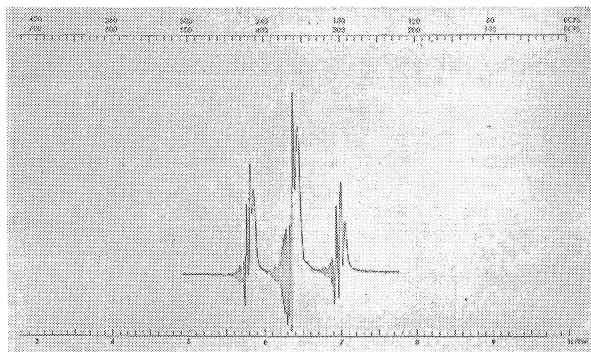


Fig. 1. High-resolution proton spectra of methyl group in pure ethylbenzene.

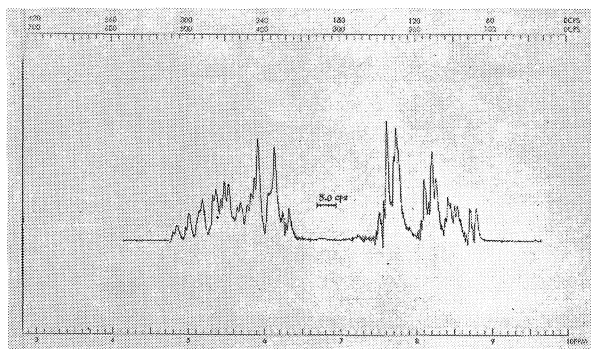


Fig. 2. High-resolution proton spectra of ring-protons in pure salicylaldehyde.

is, the resolution of 5×10^{-9} is expected for the apparatus. In Fig. 2, fine separation of about 0.3 cps can be certainly observed. Moreover, to be obtained stable resolution is required for the NMR study. So, examinations on the reproducibility of the high-resolution were carried out on the methyl-spectra in ethylbenzene. Then, the reproducibility for about 10 minutes spent by recording four spectra continuously, is likely to be sufficient for ordinary NMR studies.

A check on the reproducibility of the whole spectra was done for the cases of the sweep of 9 ppm/10 minutes and 9 ppm/5 minutes. Fig. 3 shows the results of the check of the reproducibility for 40 minutes. In the figure, a full sweeping time was 10 minutes and continuously repeated to record the same spectra four times. The sample is ethylbenzene contained a trace of tetramethylsilane (TMS) as an internal standard. From high-field side,

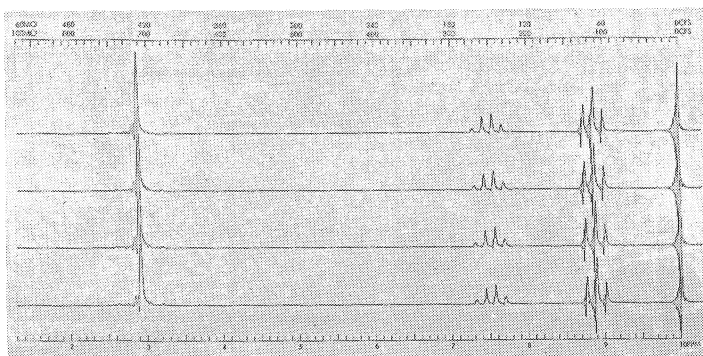


Fig. 3. Reproducibility of spectra for 40 minutes (sample is pure ethylbenzene contained a trace of TMS as an internal standard.)

or right-hand side in the figure, signals of TMS, methyl (triplet), methylene (quadruplet) and phenyl groups are appeared. The figure shows that the maximum drift of positions of corresponding spectral lines for each sweep is less than 0.2 cps.

2. Sensitivity and Other Data

For samples of low solubility such as natural compounds and for high-resolution NMR studies, high-sensitivity is severely required. For this purpose, various techniques are employed and lately CAT (computer of averaging transients) method is widely used.

The spectra shown in Fig. 4 are proton signals of 1% solution of ethylbenzene in carbon tetrachloride, in which three-four patterns of ethyl radical are clearly recorded. This corresponds to the detectability of proton signal of the proton concentration of about 0.016 mol/liter.

To improve signal-to-noise ratio of spectra, proton spectra shown in Fig. 4 were accumulated eight times by JRA-1 accumulator. Accumulated spectra are shown in Fig. 5, where signal-to-noise ratio became clearly large. But spectral line of phenyl radical became broader than original one, this is probably caused by the drift of the magnetic field for about 90 minutes, times for measurements.

Detailed NMR information is obtained by using a variable temperature unit. This unit permits sample temperature from -160°C to $+200^{\circ}\text{C}$. Spectra of 1,3-propane-diol at $+10^{\circ}\text{C}$ and $+200^{\circ}\text{C}$ are shown in Figs. 6 and 7, And also, spectra of ethanol at $+10^{\circ}\text{C}$ and -70°C are shown in Figs. 8 and

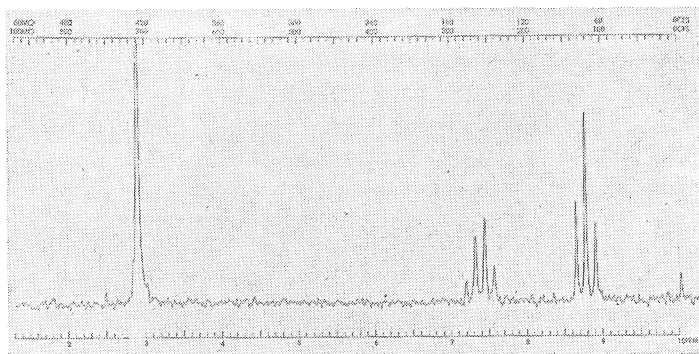


Fig. 4. Proton resonance spectra of 1% ethylbenzene solution in CCl_4 , contained a trace of TMS as an internal standard.

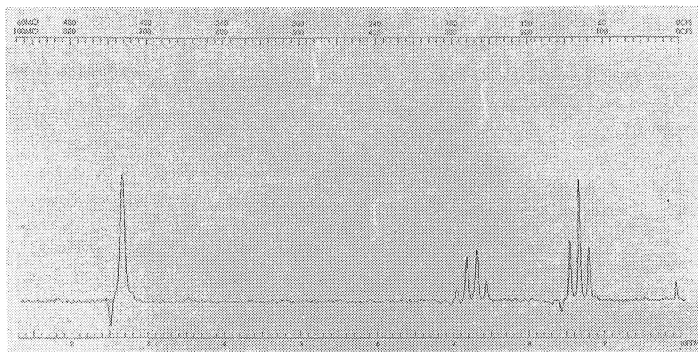


Fig. 5. Accumulated proton spectra of 1% ethylbenzene solution (eight times accumulations).

9. In these spectra, well-known dependence on temperature of hydroxyl proton signal was observed.

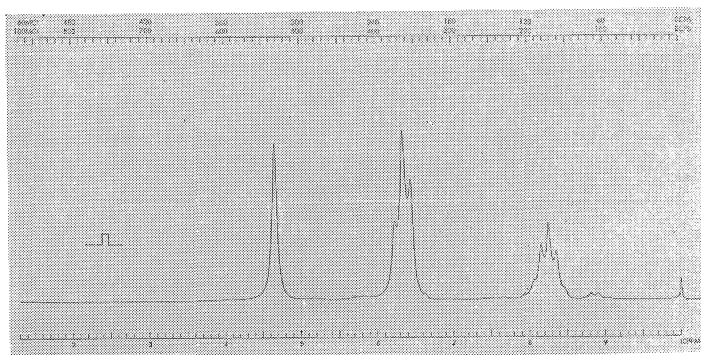


Fig. 6.

Proton resonance spectra of 1,3-propane-diol at +10°C. (Internal standard : TMS)

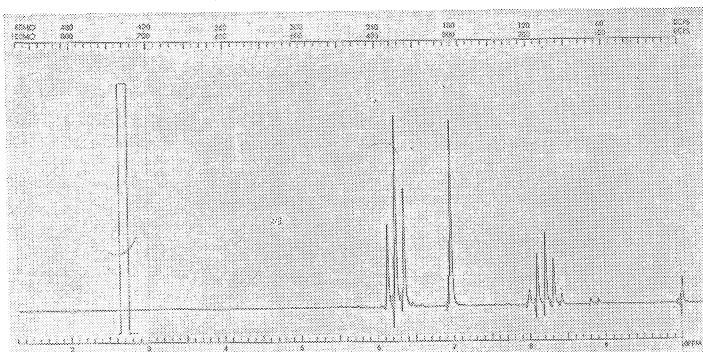


Fig. 7.

Proton resonance spectra of 1,3-propane-diol at +200°C. (Internal standard : TMS)

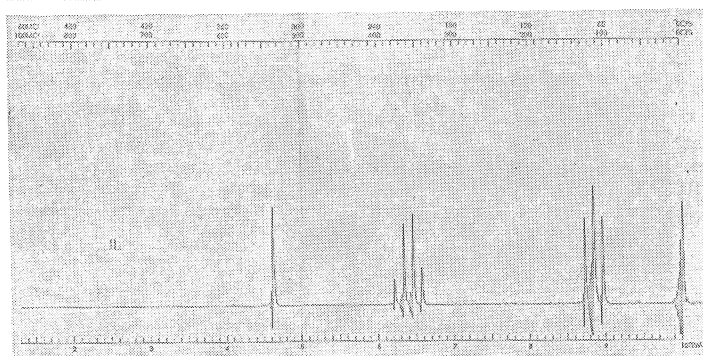


Fig. 8.

Proton resonance spectra of ethanol at +10°C. (Internal standard : TMS)

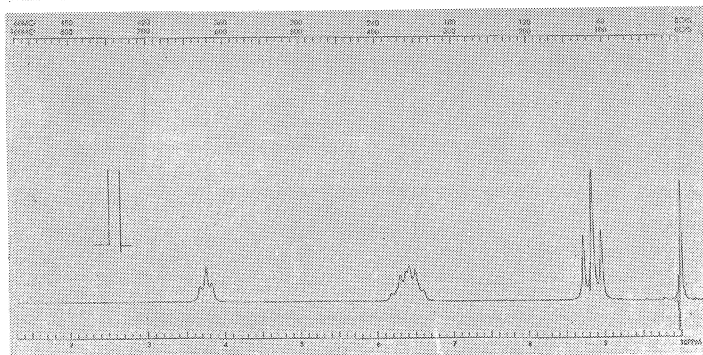


Fig. 9.

Low-temperature spectra of ethanol at -70°C. (Internal standard: TMS)