Observation of a High Resolution Proton NMR with a 920 MHz Superconducting Magnet

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We have performed the proton NMR measurements of H_2O and ethylbenzene (C_6H_5–CH_2–CH_3) using the superconducting magnet operating at 21.6 T (920 MHz for proton) in the persistent mode. It is found that both homogeneity and stability of the magnet have a specification sufficient for a high resolution NMR.

An NMR system for high magnetic field is required for chemistry and biochemistry, because NMR sensitivity and resolution increase with the external magnetic field. In particular, NMR measurement of proton around the NMR frequency of 1 GHz is desired, because the NMR line width becomes narrow around 1 GHz using the TROSY pulse sequence.[1] Recently, a superconducting (SC) magnet operating at 21.6 T (920 MHz for proton) in the persistent mode was developed by the National Institute for Materials Science (NIMS).[2] In this letter, we have performed the proton NMR measurements of H_2O and ethylbenzene (C_6H_5–CH_2–CH_3) at 920 MHz and report the FT-NMR spectra.

The superconducting magnet consists of Nb_3Sn and NbTi coils. The magnet is operated at 1.6 K. The magnetic field is 21.6 T which is the highest field produced by a SC NMR magnet. The room temperature (RT) bore is 54 mm in diameter. The field distribution is corrected with the 9 channel SC shim resulting in the field homogeneity smaller than ±0.1 ppm in a volume of 10 mm in diameter and 20 mm in height.

Although the final goal of our development is a solution NMR system, we have developed a preliminary spectrometer, RT shim and probe which implement only a solid-state specification yet. The NMR power amplifier and spectrometer up to 1 GHz are custom-made by Thamway Ltd. The power amplifier is 50 W. The spectrometer is designed for a phase coherent pulsed method and is stabilized in the accuracy of ±0.1 ppm/°C. The resolution of an AD converter is up to 1.2 Hz. No NMR-lock is used. The prototype of probe was built with an LC resonator composed of transmission lines as inductor (L) and of capacitors (C) for a frequency range between 900 MHz and 1 GHz. The probe was installed in the 19 channel RT matrix shim. The total resolution of the probe with the RT shim may be almost comparable to or better than 0.01 ppm in 10 mm DSV (Diameter Spherical Volume). The sensitivity of the probe may be worse than that of a commercial probe for a lower field, because the probe is still a prototype.

The samples of $CDCl_3$ diluted ethylbenzene (20%) and 100% H_2O were sealed in glass tubes of 5 mm in diameter. The NMR measurements were performed at 920.2208 MHz without averaging signal nor spinning sample. The FT spectra were obtained by Fourier transforming a free induction decay (FID) signal.

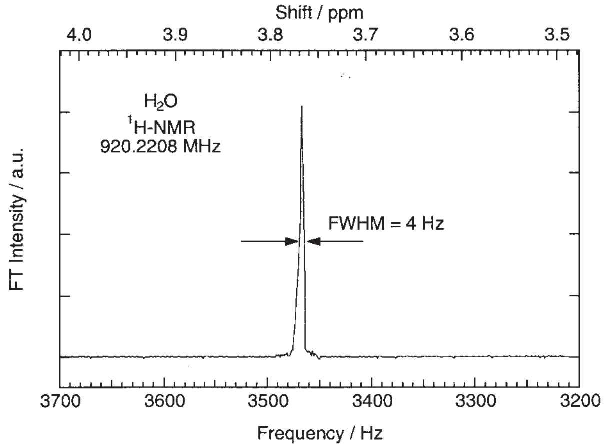

Figure 1. The proton FT-NMR spectrum of H_2O measured at 920.2208 MHz.

Figure 1 shows the proton FT-NMR spectrum of H_2O. The FID signal obtained by a single 90° pulse of 8 μs width was digitized with a sampling rate of 2.5 kHz for 4096 points. The full line-width at half maximum (FWHM) of the spectrum reaches about 4 Hz. Usually a FWHM for ^{1}H in H_2O is less than 1 Hz. The FWHM of 4 Hz is caused (1) by lack of performance of the present RT shim, (2) by magnetization of the probe materials especially the LC resonator,[3,4] and (3) by no use of sample spinning technique. We have measured the stability of the SC magnet from the proton frequency. The proton frequency varied linearly by −220 Hz in 90 hours, yielding a rate of −2.4 Hz/h.

Figure 2 shows the proton FT-NMR spectrum of ethylben-

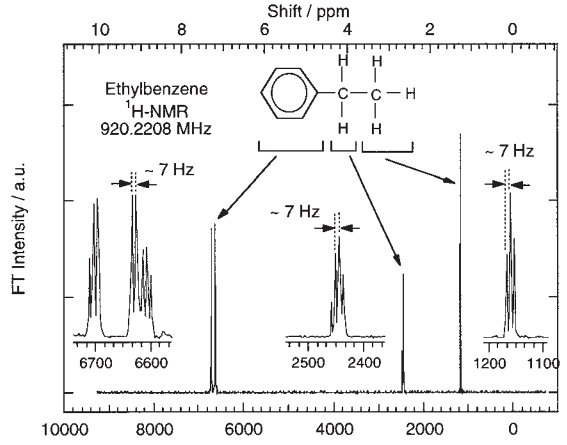

Figure 2. The proton FT-NMR spectrum of ethylbenzene measured at 920.2208 MHz. Insets show the spectra expanding the each peak.

zene measured at 920.2208 MHz. The FID signal obtained by a single 90 ° pulse of 50 μs width was digitized with a sampling rate of 5 kHz for 4096 points. Three peaks were observed corresponding to phenyl (C_6H_5-), methylene (-CH_2-) and methyl (-CH_3) groups. The peaks corresponding to methylene and methyl groups have quartet and triplet fine structures due to the J couplings, respectively. The value of J (7 ± 2 Hz) is consistent with the reported value. The spectrum of the phenyl group has a relatively complicated fine structure, at least 8 peaks, due to the existences of the chemically nonequivalent sites therein.

In summary, we have performed high field proton NMR measurements of H_2O and ethylbenzene. The resolution of 4 Hz for H_2O is achieved with SC shim, RT shim and no sample spinning. We also have measured the stability of the SC magnet for a week from the proton NMR, which shows -2.4 Hz/h. These results indicate that the SC magnet and SC shim may have the specifications sufficient for high resolution NMR measurements of liquid. An NMR probe and RT Lagrange shim for the solution NMR are desired to be developed. The probe materials are required to have magnetic susceptibility lower than $\pm 0.1 \times 10^{-6}$ cgs/cm^3.[4]

References

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