Application of Maximum Entropy Method (MEM) for Precise Determination of NQR Frequencies

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The maximum entropy method (MEM) is applied to the analysis of the closely spaced nuclear quadrupole resonance spectra of ^{35}Cl in hexachlorobenzene and ^{14}N in *trans*-azobenzene. The superiority of the MEM to usual FFT spectra is discussed with respect to the precision of frequency measurements and the noise characteristics in broad and noisy NQR spectra.

Key words: Maximum Entropy Method; Nuclear Quadrupole Resonance; Phase Transition; Spectral Analysis

The Maximum Entropy Method (MEM) has successfully been applied to high-resolution 1D and 2D NMR [1–6]; its characteristic is the extreme accuracy with which the position of resonance peaks can be determined even for complex multiple lines embedded in vast noise, though only poor information can be obtained about the lineshapes and the line intensities.

In the case of nuclear quadrupole resonance (NQR) the resonance lines are usually well-separated from each other so that individual excitation of each resonance and/or the usual Fourier transform method can be used for the frequency measurement with sufficient accuracy. However, one often encounters very poor NQR signals embedded in vast noise, and sometimes multiple NQR lines exist in a narrow frequency range, or, due to a complicated temperature dependence of the individual resonance frequencies, accidental merging of resonance lines can happen, or, associated with phase transitions, intrinsic coalescence of the lines occurs. In such cases a precise measurement of the NQR is very difficult even with pulse Fourier transform technique. Then the MEM for the analysis of complex NQR spectra seems to be promising, as experienced in NMR spectral analyses.

We selected as our first example the ^{35}Cl NQR spectrum of hexachlorobenzene. This substance gives three ^{35}Cl NQR lines [7, 8], the separation of which decreases on heating from low temperature and merges into almost a single line near room temperature. We collected the time-domain free induction decay (FID) signals of ^{35}Cl in C_6Cl_6 under conditions where the excitation frequency of the resonance is shifted from the average resonance frequency by about 30 kHz and the power of the rf-pulse is about 700 W. The FID data were sampled using a transient recorder with a sampling interval of 2 μs and 1024 sampling points. Several spectral data were collected by changing the temperature between 276 and 291 K.

We analyzed the FID data by usual FFT and MEM: In FFT we used all the sampling points of the FID data whereas in MEM we took up only 256 data points in order to reduce the calculation time. A MEM program [9] based on the Burg algorithm [10] was used. We simulated for the optimum condition in MEM by adjusting the order of prediction filter error, m, and found that the most reliable spectra are reproduced by putting $m = {}^1/_5$ (number of data points).

Typical results by FFT and MEM are compared in Fig. 1; the very noisy FID signal taken with only four times signal averaging leads to a low-quality FFT spectrum in which one cannot see any discernible structure, whereas in the MEM spectrum one can distinguish clearly three resonance lines. Figure 2 shows the temperature dependence of the ^{35}Cl resonance. Between 276 and 283 K, where the three lines are well-separated, we do not see any significant differ-

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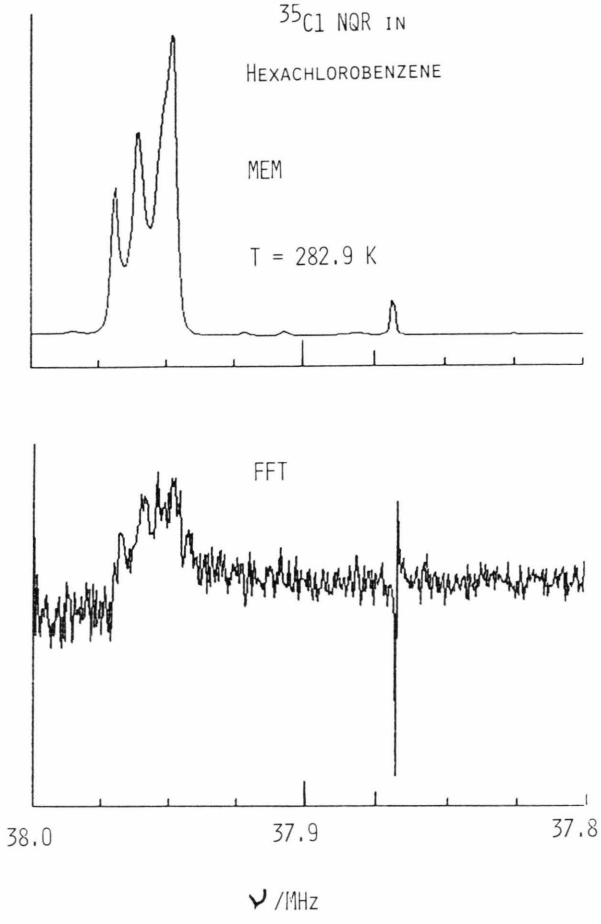

Fig. 1. Comparison between MEM and FFT spectra of ^{35}Cl NQR in hexachlorobenzene at 282.9 K. The number of data points used for the analyses are 256 and 1024 for MEM and FFT, respectively. The number of signal averaging is 4.

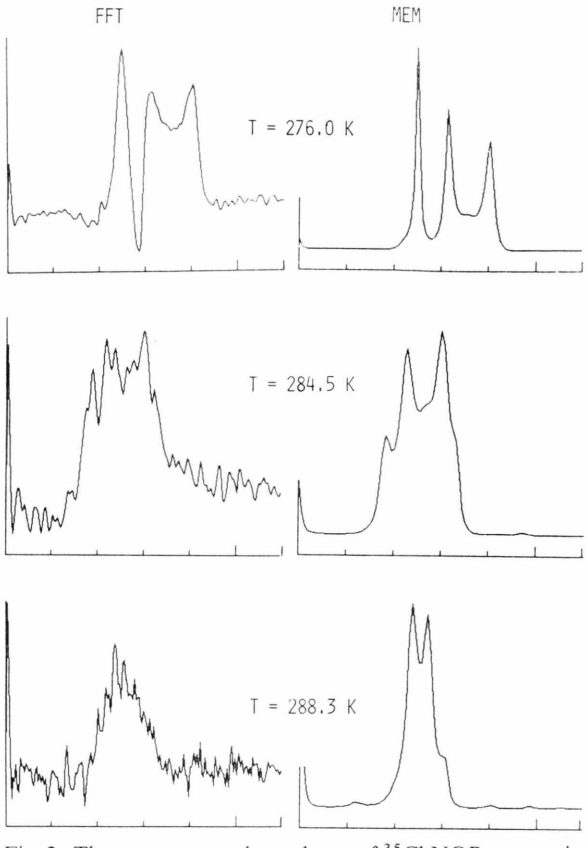

Fig. 2. The temperature dependence of ^{35}Cl NQR spectra in hexachlorobenzene obtained by MEM and FFT. The number of data points used for the analyses are 256 and 1024 for MEM and FFT, respectively.

ence between the Fourier transformed spectra and MEM spectra except that the overall noise is much more efficiently filtered in the MEM than in the FFT method. However, above 284 K it becomes difficult to determine the peak positions of the higher two lines, ν_1 and ν_2, by FFT because they almost overlap, and at last we can hardly distinguish between ν_1 and ν_2 by FFT at 285 K even after 1024 times signal averaging. In the MEM spectra, however, the position of all three lines can clearly be determined in this temperature region. Thus we could determine the closely located three resonance frequencies very accurately, as shown in Figure 3.

The second example to which we applied the MEM is the complex behaviour of the ^{14}N NQR spectrum

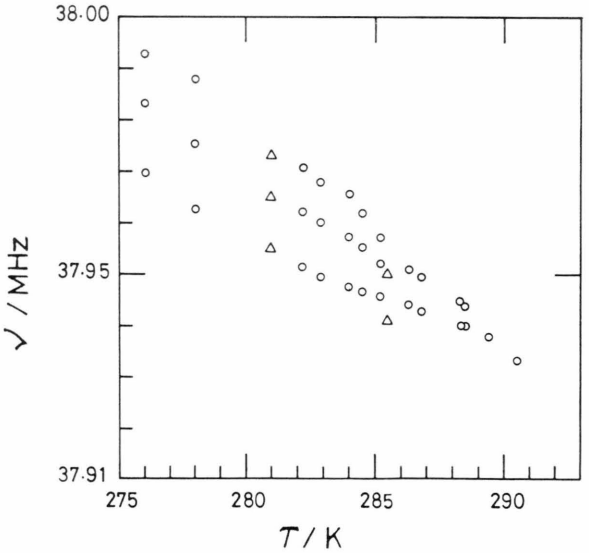

Fig. 3. Temperature dependence of ^{35}Cl NQR frequencies in hexachlorobenzene. ○: this work; △: Ref. [8].

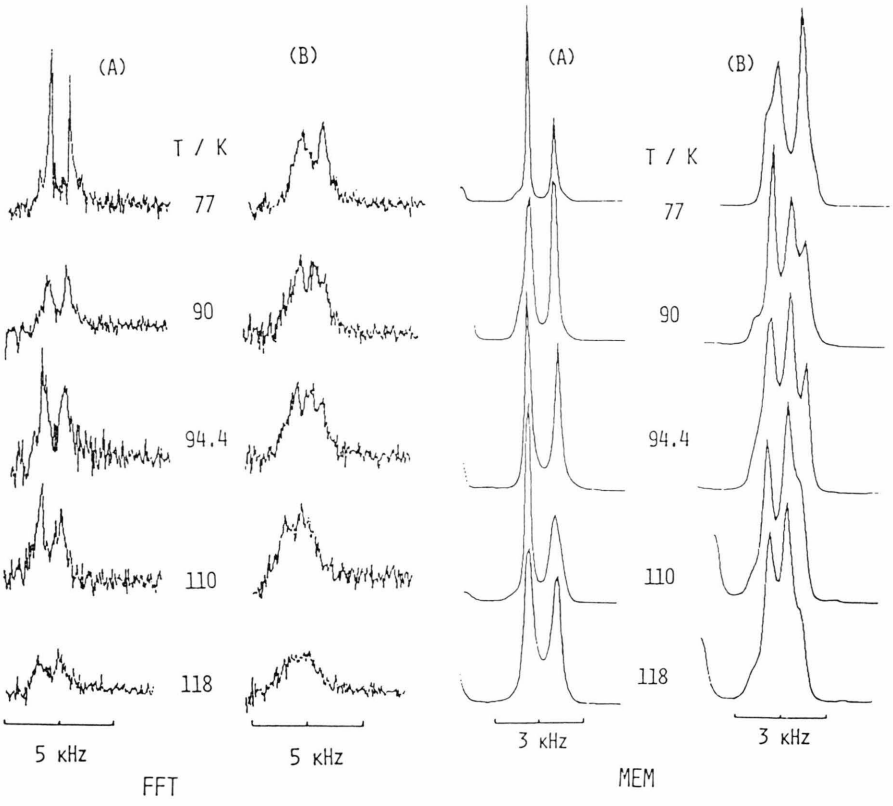

Fig. 4. Temperature dependence of the fine structures in ^{14}N NQR lines (ν_+) in *trans*-azobenzene. A and B denote two inequivalent nitrogen sites in the crystal. All the FFT spectra were taken after 1024 times signal averaging with a sampling interval of 20 μs and the 1024 datapoints. The number of datapoints used for MEM spectra is 256.

near a novel phase transition in *trans*-azobenzene crystal. In this material we found a phase transition at about 90 K by a proton relaxation time measurement [11] and examined it closely by ^{14}N NQR [12]; two pairs of resonance lines were observed, corresponding to two inequivalent nitrogen sites, A and B, among which the ν_+ lines of both A and B are doublets with a peak separation of about 1.6 kHz between 77 K and the phase transition point T_C, as shown in Figure 4. The FFT spectrum showed barely that ν_+ of B changes into a triplet above T_C, and the fine structure in the spectrum became undiscernible on heating up to 110 K due to rapid decrease in the s/n ratio. The MEM spectrum, on the other hand, distinguishes clearly the variation in the ν_+ line from doublet to triplet on heating through T_C and again to doublet on further heating. Thus Fig. 4 indicates that the MEM is superior to the usual FFT for examing subtle changes in the noisy NQR spectrum caused by a phase transition.

It should be noted that the general means of finding the optimum conditions for the MEM are still not established. Since the use of an improper value of m may lead to unwarranted spectra, it seems to be practical to use the MEM in combination with the FFT method. The latter can be used to examine the reliability of the MEM spectra.

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