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APPLICATIONS OF ADIABATIC RAPID PASSAGE TO CORRELATION NMR SPECTROSCOPY. I. SOLVENT LINE SUPPRESSION

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An adiabatic rapid passage method has been proposed for eliminating unwanted lines in correlation NMR spectroscopy. As illustrative examples, correlation NMR spectra of bovine pancreatic ribonuclease A and HEW lysozyme are given where the HDO line is suppressed by the present technique.

It has been shown[1,2] that correlation NMR is generally comparable in sensitivity with pulse FT NMR. Since only a necessary portion of the spectrum can be scanned in the correlation NMR method, the problem of dynamic range is much less serious than in the case of pulse FT method. In order to make the correlation NMR spectroscopy more versatile, various attempts are now being made in this laboratory. In this note, we report an adiabatic rapid passage method which can be used to suppress unwanted lines in correlation NMR spectra. This technique is analogous to the WEFT method[3] in the pulse FT NMR.

A JEOL 100 MHz PS-100 spectrometer with a few modifications is employed at a modulation frequency of about 8 kHz. A sequence of two frequency sweeps is used as shown in Fig. 1. In Sweep 1 is used an RF power which is chosen sufficiently high to meet the condition of adiabatic rapid passage for a given sweep rate. After a delay time of $T_{int} - T_s$, Sweep 2 is initiated at a weak RF level, and the transient response is collected on a JEOL JEC-6 computer (16 bits/word, 12K words of memory) through an 8-bit A/D converter. If necessary this sequence is repeated and the

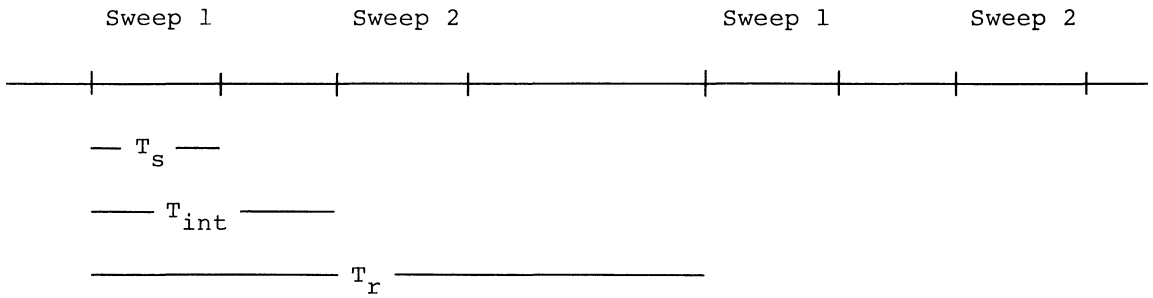

Fig. 1. A sequence of two frequency sweeps for an adiabatic rapid passage correlation NMR; Sweep 1 at a high RF level is for adiabatic rapid passage and Sweep 2 at a low RF level for sampling the transient response. T_s is the sweep time, T_{int} the sweep interval, and T_r the repetition time.

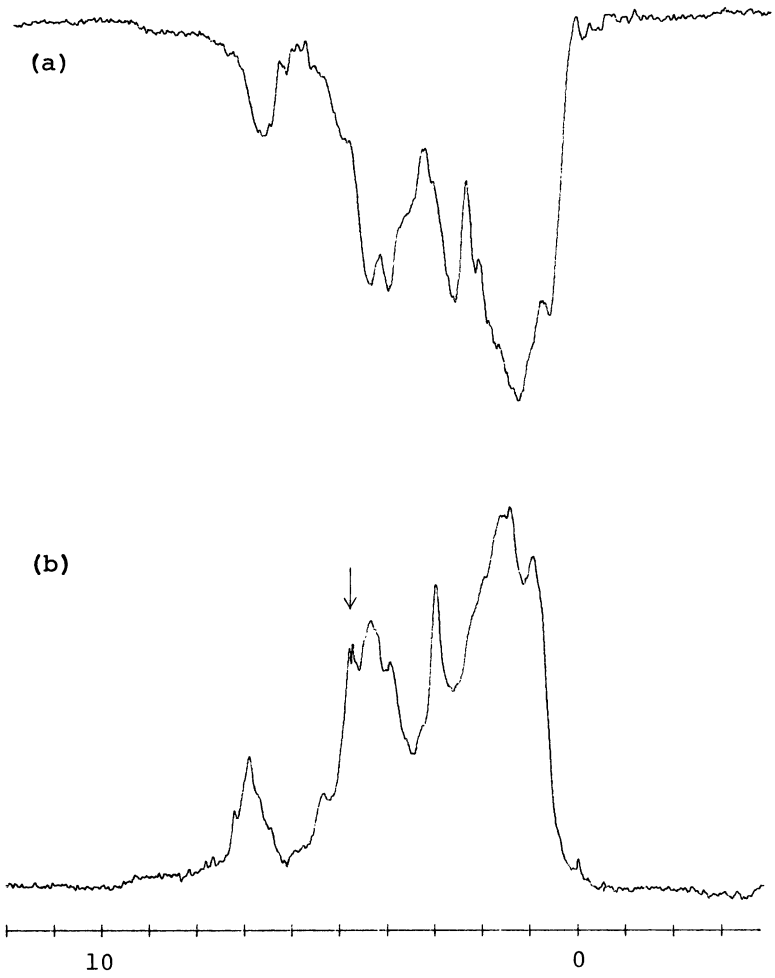

Fig. 2. The transient response (a) and correlation NMR spectrum (b) at 100 MHz of bovine pancreatic ribonuclease A (10%(w/v) in 99.8% D_2O, pH = 6.70). The HDO line has been suppressed by an adiabatic rapid passage at the sweep rate of 1942 Hz/s with T_s = 0.819 s, T_{int} = 0.97 s, T_r = 5.0 s; the number of sampling points is 4096 and the number of scans 256. Chemical shifts in ppm are from external TMS. The residual HDO line is shown by an arrow.

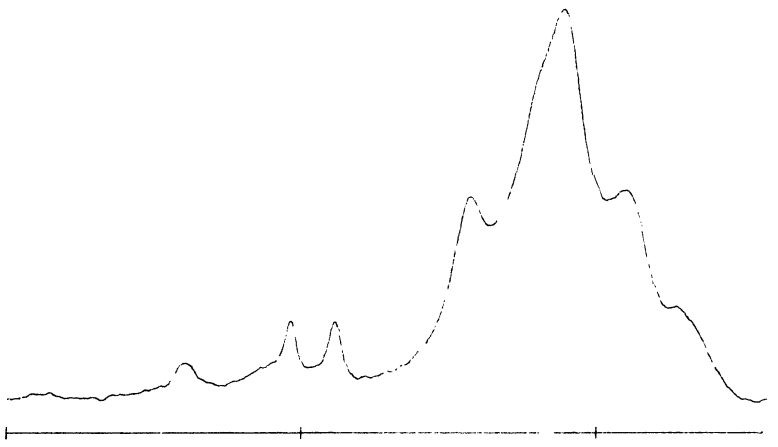

Fig. 3. The aromatic region of the NMR spectrum at 100 MHz of bovine pancreatic ribonuclease A (10%(w/v) in 99.8% D_2O, pH = 6.70), obtained by the straight correlation NMR method. One division is equal to 100 Hz. The sweep rate is 530 Hz/s, the sweep time 0.486 s, the number of sampling points 1024, and the number of scans 1024.

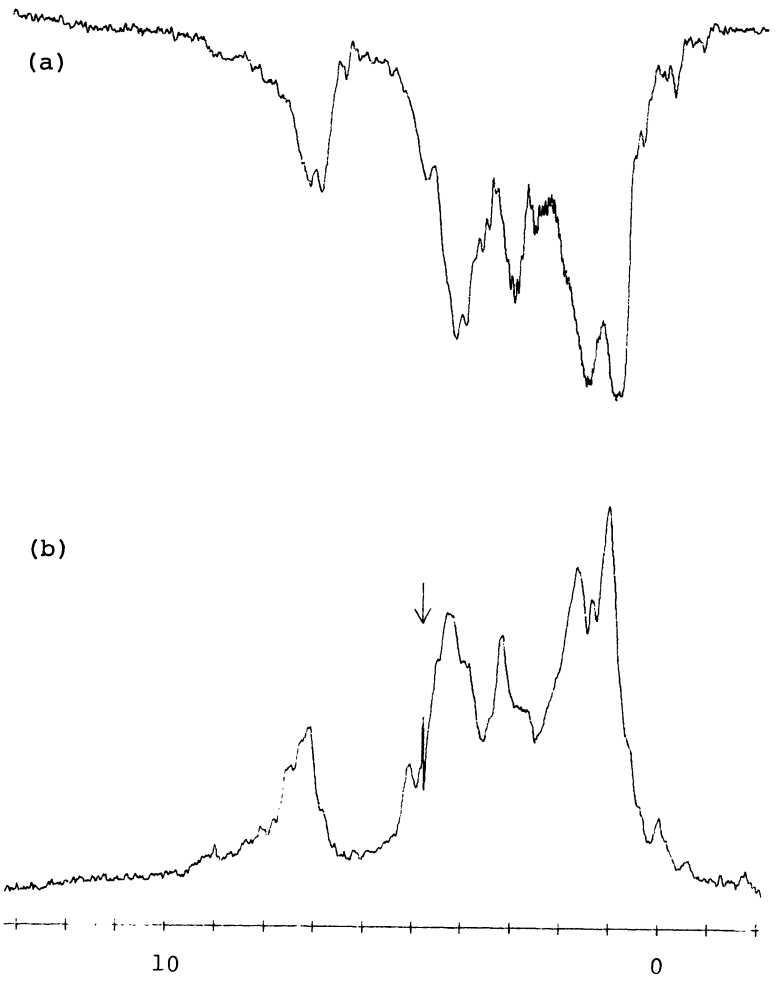

Fig. 4. The transient response (a) and correlation NMR spectrum (b) at 100 MHz of HEW lysozyme (10%(w/v) in 99.8% D_2O, pH = 1.73). The HDO line has been suppressed by an adiabatic rapid passage at the sweep rate of 1499.5 Hz/s with T_s = 1.024 s, T_{int} = 1.7 s, T_r = 6.0 s; the number of sampling points is 4096 and the number of scans 128. Chemical shifts in ppm are from external TMS. The residual HDO line is shown by an arrow.

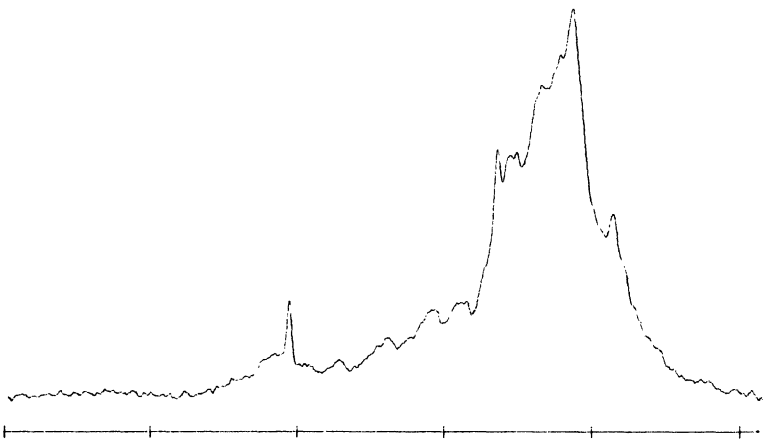

Fig. 5. The aromatic region of the NMR spectrum at 100 MHz of HEW lysozyme (10%(w/v) in 99.8% D_2O, pH = 1.73), obtained by the straight correlation NMR method. One division is equal to 100 Hz. The sweep rate is 530 Hz/s, the sweep time 0.973 s, the number of sampling points 2048, and the number of scans 256.

transients accumulated to improve the signal-to-noise ratio. Data processing which follows is performed on a HITAC 8800/8700 computer system at the Computer Center, the University of Tokyo with the aid of an interactive graphic system HITAC 8811. Details of the experiments will be described elsewhere.

Some of the experimental results are given in Figs. 2 - 5. In all of these experiments, transients were collected at 35°C, and no window function was used to obtain the correlation NMR spectra. Figure 2 shows a transient response and its correlation NMR spectrum of bovine pancreatic ribonuclease A (lyophilized three times from 99.8% D_2O, 30 mg/0.3 ml D_2O(99.8%), pH = 6.70), where the HDO line has been suppressed by an adiabatic rapid passage at the sweep rate of 1942 Hz/s with T_s = 0.819 s, T_{int} = 0.97 s, T_r = 5.0 s. The transient response was sampled using 4096 data points and accumulated 256 times. The same sample was used to obtain by the straight correlation NMR method the aromatic region of the spectrum (Fig. 3) where the sweep rate is 530 Hz/s, the sweep time 0.486 s, the number of sampling points 1024, and the number of scans 1024.

Figure 4 shows the results for HEW lysozyme (not lyophilized from D_2O, 30 mg/0.3 ml D_2O(99.8%), pH = 1.73); the sweep rate is 1499.5 Hz/s, T_s = 1.024 s, T_{int} = 1.7 s, T_r = 6.0 s, the number of sampling points is 4096, and the number of scans 128. The aromatic region of the spectrum of the same sample obtained by the straight correlation NMR method is shown in Fig. 5; the sweep rate is 530 Hz/s, the sweep time 0.973 s, the number of sampling points 2048, and the number of scans 256.

The present technique of adiabatic rapid passage should allow additional freedom in using the correlation NMR spectroscopy. The method described in this note can also be used to measure spin-lattice relaxation times, and the result will be reported in a later publication.[4]

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