Spectral Smoothing in Correlation NMR Spectroscopy

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(Received February 26, 1976)

A method has been proposed to eliminate a baseline oscillation which appears in a correlation NMR spectrum when one wants to observe peaks on the tilted baseline. An interpolation process in correlation NMR spectroscopy is also discussed which minimizes the number of sampling points.

In correlation NMR,[1,2] only a necessary portion of the spectrum can be scanned, and therefore, dynamic range problems which are frequently encountered in pulse FT NMR is much less serious. We have described in previous papers[3-6] a system for correlation NMR and some of its applications. In the present system, the theoretical function method[2] has been used to compensate the effect of the linear sweep; a rapid scan response is Fourier transformed, and then multiplied by $\exp(-ibt^2/2)$ where b is the sweep rate in radians per second to obtain the free induction decay, which is Fourier transformed again to give the correlation NMR spectrum. In the Fourier transform of a discrete, finite sequence of values, the sequence is assumed to be periodic; the last point of a sequence is assumed to be followed by the first point of the next sequence. As a result of this, when the baseline of the rapid scan response is tilted to a great extent and the first and the last points of a data sequence are quite different in magnitude, the correlation NMR spectrum obtained by the process involving multiplication by $\exp(-ibt^2/2)$ may show an oscillation of the baseline. This situation is actually encountered when one wants to observe small peaks which lie on the shoulder of large one.

One possible way to circumvent the above difficulty is application of an exponential window to the free induction decay which is derived from the rapid scan response. However, this could improve the situation only at the expense of additional line broadening. Another possibility is to apply an apodization window to the rapid scan response. This procedure may cause distortion near either end of the spectrum. In the present paper, we will report a method involving a *wing processing* which was found to be quite useful in observing peaks on the tilted baseline.

Experimental

A JEOL PS-100 NMR spectrometer operating at 100 MHz was modified for correlation spectroscopy as previously described.[3,5] A general program CORNMR was written to process the rapid scan response with the theoretical function method described by Gupta, Ferretti, and Becker.[2]

Results and Discussion

Figure 1a shows a rapid scan response for 2 mM ethanol in H_2O where ethanol peaks are on the shoulder of the large water signal. The conventional correlation NMR procedure leads to a spectrum as reproduced in Fig. 1b. In the present method, the rapid scan response with N data points is provided on its both ends with *wings*; the first point is provided with a *wing* with $N/2$ identical values which is equal to that of the first point, and the last point with a *wing* with $N/2$ identical values equal to that of the last point. The *winged* rapid scan response with $2N$ data points thus obtained is processed by the theoretical function method, and the spectrum is cut out of the relevant part of the final result. The rapid scan response given in Fig. 1a is treated with the above method, and the *winged* rapid scan response (Fig. 2a) was used to obtain the final spectrum shown in Fig. 2b.

Although the oscillation of the baseline is considerably decreased, there is still some residual fine oscillation in Fig. 2b. As discussed above, this comes from the fact that there is a difference in magnitude between the first and the $2N$-th points of the *winged* rapid scan response. A quarter of each *wing* is then replaced by a quarter cycle of the sine function to smoothly connect the *wings*, giving rise to a repetition of smoothly connected rapid scan response. The *winged* rapid scan response obtained by this procedure (Fig. 3a) gave the spectrum which is reproduced in Fig. 3b,

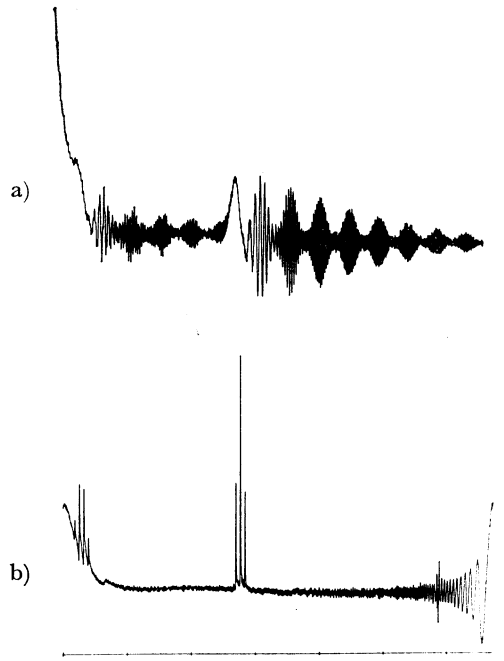

Fig. 1. (a) A rapid single scan response and (b) the correlation NMR spectrum at 100 MHz of 2 mM ethanol in H_2O. Sweep rate, 328.2 Hz/s; sampling time, 2.048 s; number of sampling points, 4096. One division is equal to 100 Hz.

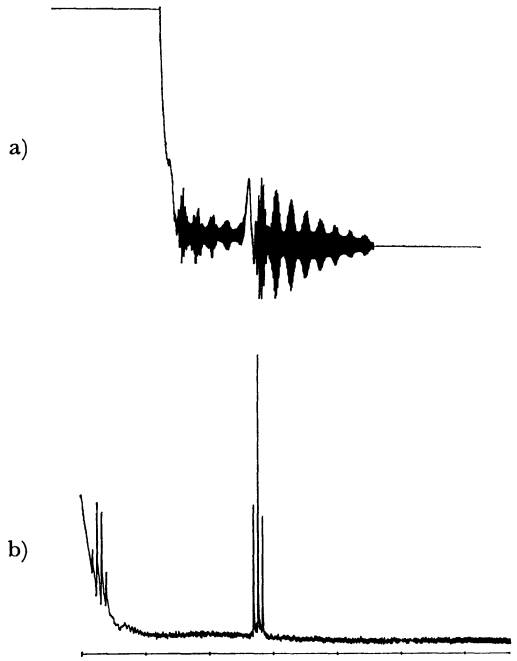

Fig. 2. (a) A rapid scan response in Fig. 1a supplemented with *wings* with 2048 points on its both ends, and (b) the correlation NMR spectrum obtained from it.

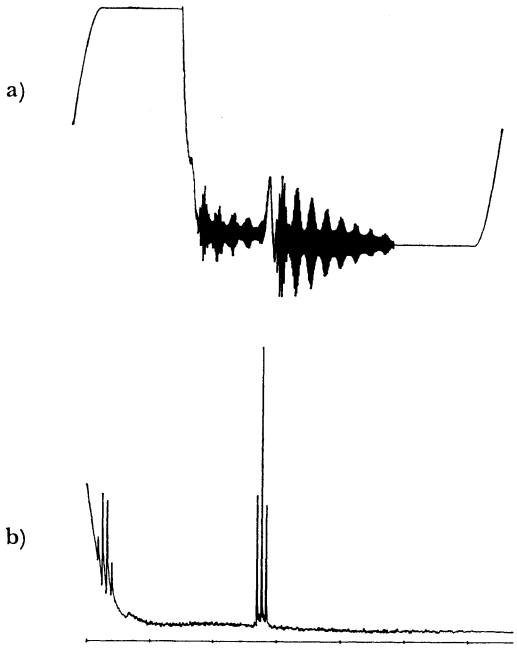

Fig. 3. (a) A rapid scan response in Fig. 2a with *wings* modified by replacing a quarter of each of them by the sine function, and (b) the correlation NMR spectrum obtained from it.

where the undesirable oscillation of the baseline is clearly eliminated. It should be noted that the procedure described here does not give rise to any distortion of the spectrum such as line broadening.

The resonance conditions are met sequentially in correlation NMR spectroscopy. Therefore, if only a necessary portion of the spectrum is scanned, the number of sampling points can be made very small without violating the sampling theorem. Sometimes, the final spectrum obtained using the minimum number of sampling points may not be smooth enough, so that it is quite difficult to find the peak maxima. However, interpolation can easily be done by supplementing a sufficient number of zeroes at the end of the free induction decay which is derived from the rapid scan response. Bartholdi and Ernst[7] have discussed the effect of supplementing zeroes at the end of the free induction decay obtained in the case of pulse FT NMR. In correlation NMR, this feature should especially be important when one wants to observe, for example, carbon-13 spectra where signals scatter over a wide range of frequency.

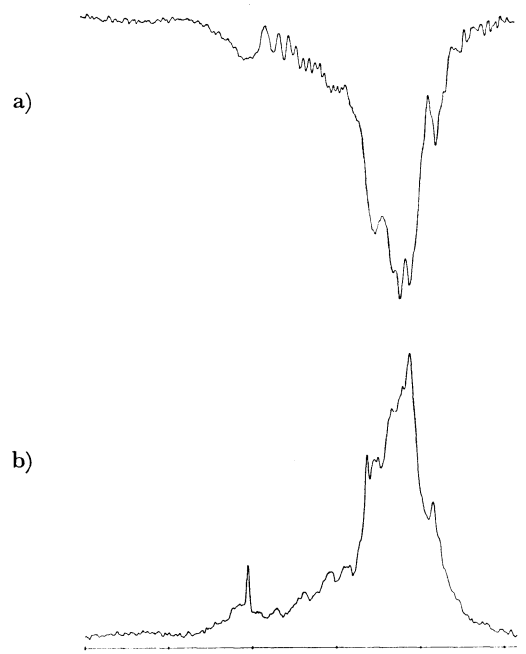

Fig. 4. (a) Rapid scan response and (b) the correlation NMR spectrum at 100 MHz of the aromatic region of hen egg white lysozyme in D_2O (10% (w/v) in 99.8% D_2O, pH=1.73, 35 °C). Sweep rate, 530.0 Hz/s; sampling time, 0.9728 s; number of sampling points, 2048; number of accumulations, 256; phase correction angle to obtain the spectrum, 180°. One division is equal to 100 Hz.

Figure 4a shows a rapid scan response for the aromatic region of hen egg white lysozyme in D_2O, where the sweep rate, sampling time, and number of sampling points are 530.0 Hz/s, 0.9728 s, and 2048, respectively. The spectrum obtained from this rapid scan response is given in Fig. 4b. Since the narrowest signal has a width of approximately 5 Hz, 256 data points should have been sufficient under the experimental condition to acquire all necessary information. The total of 256 data points which have been picked out of every eight points of the rapid scan response was used to obtain the free induction decay, from which the correlation NMR spectrum was derived; the histidine C-2 proton part of the spectrum is reproduced

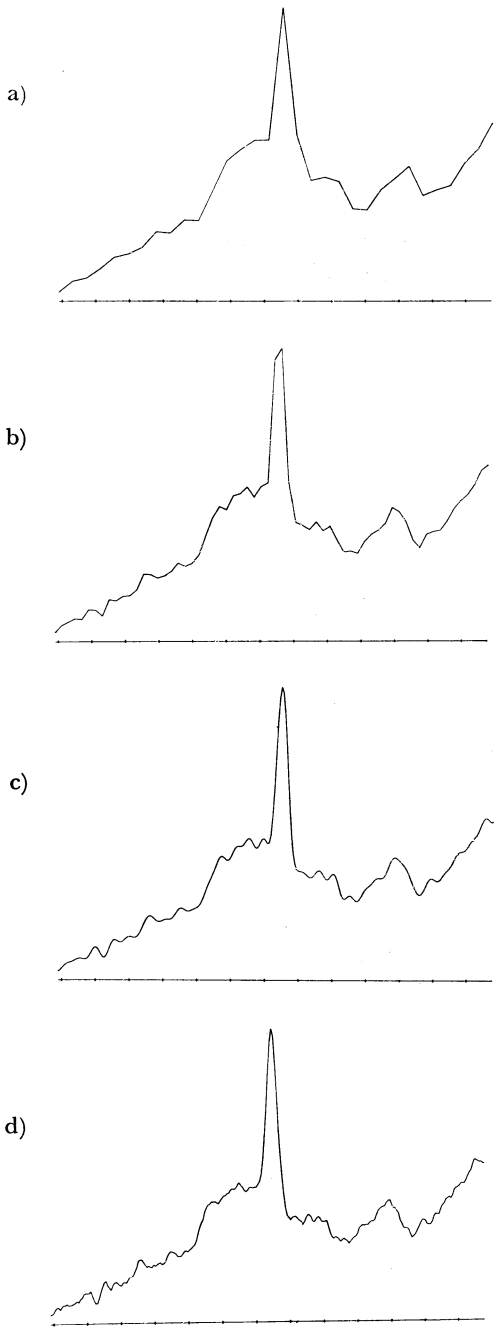

Fig. 5. Correlation NMR spectra of the histidine C-2 proton of hen egg white lysozyme in D_2O. Spectrum (a) was obtained by using 256 data points which are picked out of every eight points of the rapid scan response in Fig. 4a. The free induction decay used to obtain the spectrum (a) was made twice and eight times in length by supplementing zeroes at its end, from which spectra (b) and (c) were derived, respectively. The corresponding part of the spectrum shown in Fig. 4b is reproduced in (d). One division is equal to 10 Hz.

in Fig. 5a. The spectra in Figs. 5b and 5c are obtained when the number of data points of the free induction decay is made twice and eight times respectively in length by supplementing zeroes at its end. Figure 5c is quite similar with the exception of high-frequency noise to Fig. 5d which is a part of the spectrum in Fig. 4b derived using 2048 data points.

In conclusion, the present techniques to achieve spectral smoothing should allow additional freedom in using correlation NMR spectroscopy.

The authors wish to thank Professor S. Fujiwara for his continual encouragement.

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