

October, 1972

APPLICATIONS NOTE #3Rapid Scan Nmr Spectroscopy

It has recently been reported by Dadok, et al.,¹ that the information present in a cw nmr spectrum scanned at rates faster than those compatible with slow passage conditions,² can be deconvoluted and is of use in the laboratory. These workers found that the scanning of spectra at relatively rapid rates produces the expected summation of a large number of decaying frequency elements, one from each spectral line. Such a spectrum is shown in Figure I.

However, it is possible to extract a standard cw slow passage nmr spectrum from these data by cross correlating this spectral response with that of a reference sample containing only a single nmr line. Thus, the ringing of a single line is correlated with the much more complex ringing of a number of lines to produce a correlogram which corresponds to the standard slow passage nmr spectrum.

This technique has at least two significant advantages. The first, and most obvious, is that it facilitates the examination of any spectral width of interest, regardless of the placement of other strong lines. By contrast, in FT-Nmr, the examination of a spectral region smaller than the entire spectral width will produce a large amount of confusing frequency "fold-back," or aliasing. In most cases, this fold-back will obscure the information in the smaller region.

In the rapid scan experiment, however, the scanning of a smaller region does not perturb the lines outside this frequency range significantly, and the region can be examined in detail. While the rapid scan technique does not have quite the Fellgett's³ advantage present in the FT-Nmr experiment, where all frequencies are examined simultaneously, it does allow much more rapid data collection than conventional cw-nmr spectroscopy. This speed of acquisition is clearly the second significant advantage of this technique, in that it allows more data to be examined per unit time. This can be advantageous for those who wish to perform Fourier but are, for some reason, lacking some of the components for a given spectrometer, and for those who wish to do kinetic studies on some older spectrometer.

In our experiments, we obtained a rapid scan spectrum of the quartet of acetaldehyde in the standard reference sample provided with the HA-100. The sweep width used was 500 hz and was generated using an external voltage-controlled oscillator swept by the 1080 sweep ramp. This spectral width was chosen so that only the quartet was within the 500 hz region. Data were accumulated at several sweep rates and

stored on the NIC-294 disk for later analysis and program development. The reference spectrum was the chloroform line of the standard TMS-CHCl₃ sample scanned over 500 hz at similar scan rates. The resulting spectra were correlated using a special correlation program, which has been submitted to the NUS library (NUS-80/U-7234).

The results showed that a spectrum could indeed be obtained and correlated using the 1080 data system and software and that significant information could be obtained in this manner. It was empirically established that a sampling frequency of approximately twice the sweep width produced spectra that were usable, but more information in this point is needed. Figure I shows the rapid scan spectrum of acetaldehyde, taken as described above, at a sampling frequency of 1000 hz, Figure II shows the reference chloroform spectrum taken under the same conditions, and Figure III shows the spectrum resulting from the correlation of the first two spectra.

In his original paper, Dadok also suggested that it should be possible to generate a reference spectrum theoretically, rather than having to measure one each time. We pursued this matter slightly and developed the rather simplified approximation of

$$e^{a\omega} \sin b\omega^2$$

to describe the reference spectrum. A theoretical spectrum produced in this fashion is shown in Figure IV. In this spectrum, a was chosen to represent a Time Constant of -3 and b was chosen to represent a spectral width of 500 hz.

The result of correlating this reference spectrum and the acetaldehyde spectrum is shown in Figure V. We will be glad to discuss our findings with anyone interested. The program for correlation can be obtained from the NUS library at no charge by all 1080 owners.

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References:

1. J. Dadok, R. F. Spiecher, A. A. Bothner-By, Correlation Nmr Spectroscopy - A Bridge Between FT and Cw Nmr Techniques, Paper 15.4, 13th Experimental Nmr Conference, Asilomar, California, 1972.
2. J. A. Pople, W. G. Schneider, H. J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, New York (1959).
3. P. Fellget, Thesis, Cambridge University (1951).

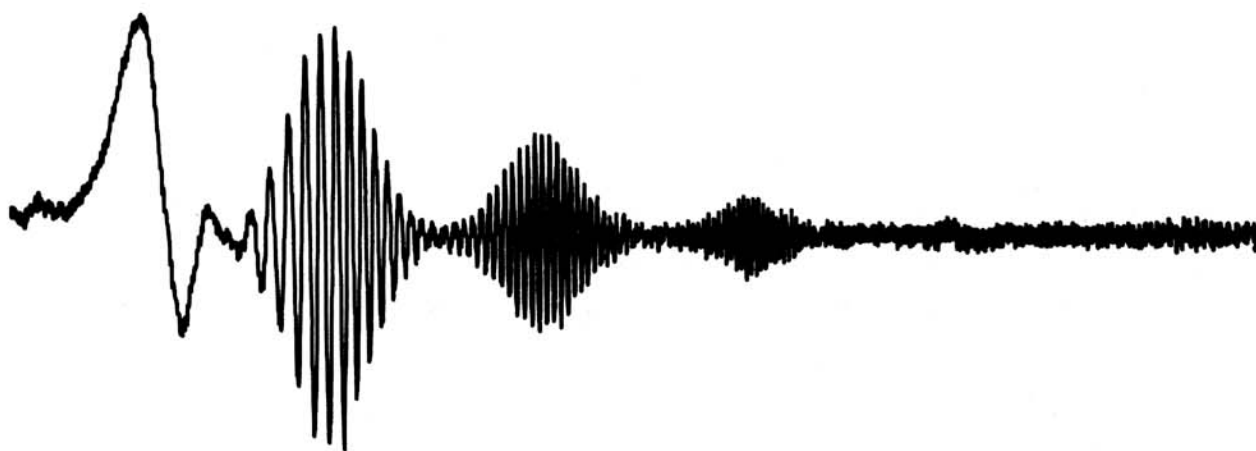


Figure I.



Figure II.



Figure III.

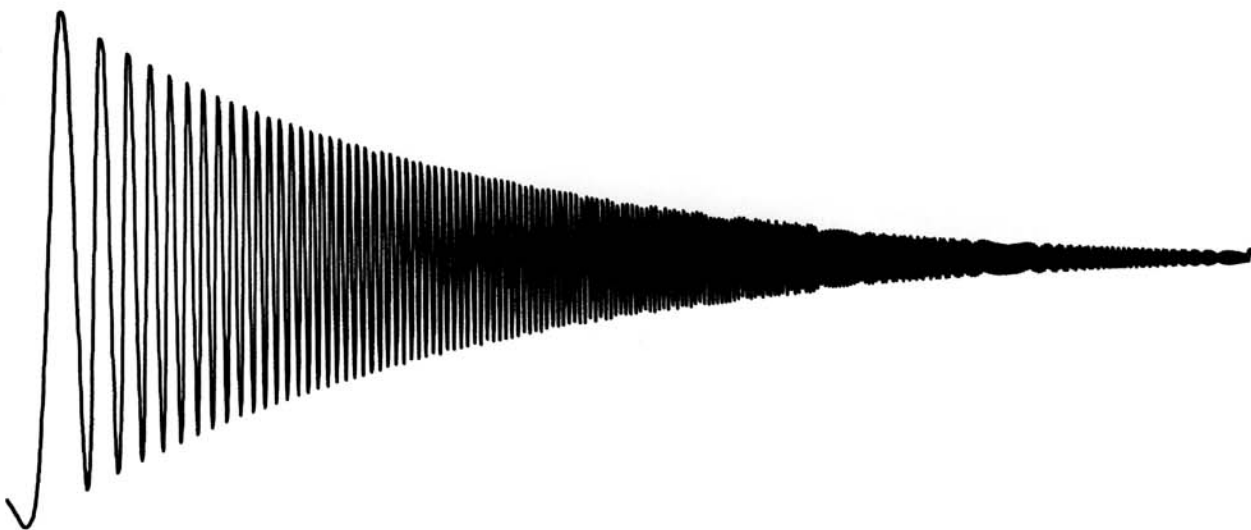


Figure IV.

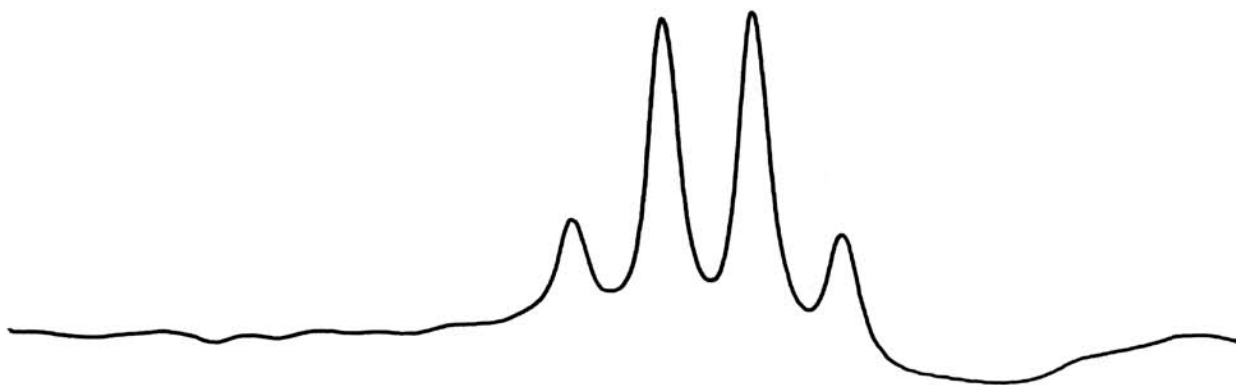


Figure V.