JOURNAL OF MAGNETIC RESONANCE **79**, 352–356 (1988)

COMMUNICATIONS

Baseline Distortion in Real-Fourier-Transform NMR Spectra

DOMINIQUE MARION* AND AD BAX

Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases,
National Institutes of Health, Bethesda, Maryland 20892

Received April 18, 1988

In many types of two-dimensional NMR experiments, the sensitivity limitation is not the thermal noise, but the presence of baseline distortions, t_1 ridges, t_1 noise, or other artifacts (*1–5*). As demonstrated by Otting *et al.* (*1*), one serious source of baseline problems originates from incorrect use of the discrete Fourier transform algorithm. This so-called "first data point problem" applies both to real and to complex data and can largely be circumvented by appropriate scaling of the first data point of the FID. A second source of baseline distortion arises from delayed sampling of the free induction decay, requiring linear frequency-dependent phase correction in the frequency domain (*6, 7*).

Here we address a different problem that causes similar effects on the baseline of 2D NMR spectra. This problem only applies to real data, or to "complex" data where the real and imaginary components are sampled in a sequential manner. It is shown below that if the detected signal is a decaying sinusoid,

$$s(t) = \sin(2\pi f t + \phi)\exp(-t/T_2), \qquad [1]$$

the baseline in the final spectrum will be distorted after suitable phase correction unless the phase error, ϕ, is an integral multiple of 90°.

To consider the effects of folding, which are the source of the baseline problems discussed here, it is necessary to consider the digitized signal. First, a complex signal and its Fourier transform are analyzed. The decaying digitized signal is described by

$$s_n = \exp\{i(\pi n f/f_N + \phi)\}\exp\{-n/(2f_N T_2)\}, \qquad [2]$$

where f_N is the Nyquist frequency, $f_N = 1/(2\Delta)$, and Δ is the dwell time. The discrete complex Fourier transform of s_n is given by

$$S_k = \sum_{n=0}^{N-1} s_n \exp\{i(2\pi nk/N)\}. \qquad [3]$$

This expression can be rewritten as a sum of absorptive (A_k) and dispersive (D_k) Lorentzian components,

---

* On leave from the Centre de Biophysique Moléculaire CNRS, 1A Av. de la Recherche Scientifique, 45071 Orleans Cedex 2, France.

0022-2364/88 $3.00

$$\mathrm{Real}(S_k) = \cos\phi A_k - \sin\phi D_k \quad [4a]$$

$$\mathrm{Imag}(S_k) = \cos\phi D_k + \sin\phi A_k, \quad [4b]$$

with

$$A_k = \sum_{j=-\infty}^{\infty} T_2/\{1 + 4\pi^2 T_2^2(kf_N/N + jf_N - f)^2\} \quad [5a]$$

$$D_k = \sum_{j=-\infty}^{\infty} 2\pi T_2(kf_N/N + jf_N - f)/\{1 + 4\pi^2 T_2^2(kf_N/N + jf_N - f)^2\}, \quad [5b]$$

where the index j accounts for the periodicity of the Fourier transform. The absorption-mode component, A_k, can be retrieved from the Fourier transform, S_k, by phase correction:

$$A_k = \cos\phi\ \mathrm{Real}\{S_k\} + \sin\phi\ \mathrm{Imag}\{S_k\}. \quad [6]$$

Next, a real signal will be considered:

$$\begin{aligned} s'(t) &= 2\cos(2\pi ft + \phi)\exp(-t/T_2) \\ &= [\exp\{i(2\pi ft + \phi)\} + \exp\{-i(2\pi ft + \phi)\}]\exp(-t/T_2). \end{aligned} \quad [7]$$

Note that the phase, ϕ, has opposite sign for the two opposite frequencies.

The discrete Fourier transform of [7] yields

$$\mathrm{Real}(S'_k) = \cos\phi A_k - \sin\phi D_k + \cos\phi A_{-k} + \sin\phi D_{-k} \quad [8a]$$

$$\mathrm{Imag}(S'_k) = \cos\phi D_k + \sin\phi A_k + \cos\phi D_{-k} - \sin\phi A_{-k}. \quad [8b]$$

Phase correction, analogous to Eq. [6], yields

$$\mathrm{Real}(S'_k) = A_k + \cos(2\phi)A_{-k} + \sin(2\phi)D_{-k}. \quad [9]$$

This demonstrates that it is impossible to phase the spectrum to the absorption mode using a frequency-independent phase correction. This effect is graphically shown in Fig. 1, before and after phase correction. The solid line in this figure corresponds to positive frequencies obtained after a real Fourier transformation. The broken line is its mirror image with respect to zero frequency. Although the negative frequencies usually are not displayed after a real Fourier transformation, it should be noted that the tails of the resonances with negative frequencies extend into the positive frequency region. In particular, the long tails of the dispersive part of the component with negative frequency can cause serious baseline distortions in the positive frequency region.

Figure 2 shows a set of phase-corrected real-Fourier-transform spectra, obtained from a signal of which the initial phase (at $t = 0$) was incremented in multiples of 15°. As can be seen from the vertical expansions, only for $\phi = 0°$ or $\phi = 90°$ is a flat baseline obtained. The spectra for $\phi = 0°$ and $\phi = 90°$ are different because the first one corresponds to $A_k + A_{-k}$ and the second one corresponds to $A_k - A_{-k}$. Thus, for the 0° case, the tails of the absorption-mode resonances add, and for the second case they subtract. This is a relatively small effect unless resonances are very close to the

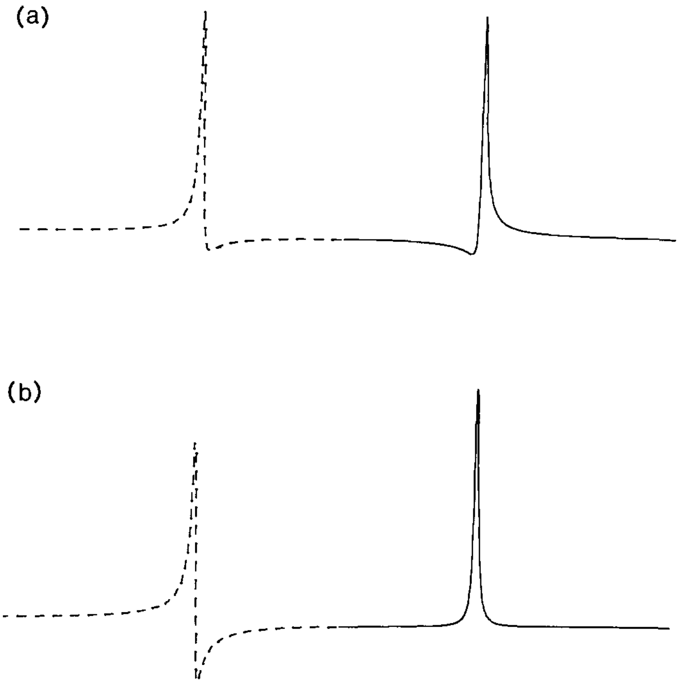

FIG. 1. (a) Fourier transform of the signal, $s(t) = \cos(ft + \pi/6)$. The real Fourier transform does not distinguish between positive frequencies (solid line) and negative frequencies (broken line), and only one-half of these data is usually displayed. (b) After phase correction, the resonance with the positive frequency is phased to the absorption mode, but the tails of the dispersion of the resonance at opposite frequency cause baseline distortion in the positive frequency region.

edge of the spectrum. The extent to which the baseline distortion is visible depends also on the minimum distance between resonances and the edges of the spectrum. If large margins are chosen at either side of the spectrum, the baseline distortion approaches a near-linear tilt of the spectral region of interest. For two-dimensional experiments, such an oversampling procedure requires large amounts of data storage space and it generally is preferable to avoid the distortion by adjusting the signal phase relative to the receiver phase or by using acquisition of complex data points, with the real and imaginary components sampled simultaneously.

The baseline distortion discussed above can lead to serious ridges in phase-sensitive 2D spectra. These effects can be seen most clearly for spectra that have in-phase resonances, such as NOESY (*8*), ROESY (*9*), or HOHAHA (*10, 11*). Experiments in which there is no net intensity of the diagonal or cross multiplet (for example, multiple-quantum-filtered COSY) do not exhibit this type of baseline distortion. In the F_1 dimension of 2D spectra, the folding baseline distortion is only present when the TPPI procedure is used to separate positive and negative frequencies (*12*), or when the transmitter is positioned at one side of the spectrum and a real Fourier transformation is used. When the hypercomplex data acquisition procedure is followed (*13*), the folding baseline distortion is also absent. In contrast to the baseline distortion that

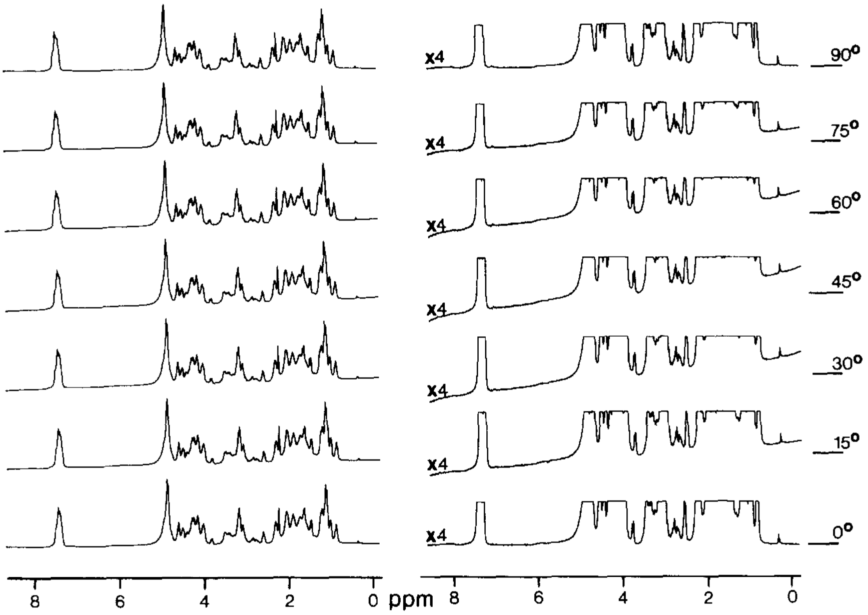

FIG. 2. The 270 MHz real Fourier transform spectra of a sample of the 23-amino-acid peptide magainin-2, in 2:1 (v/v) D_2O/trifluoroethanol-d_3. The spectra are shown for phase increments of 15° of the acquired signal, keeping the receiver phase constant. The delay between the pulse and the first data point was adjusted similarly for all spectra, such that no frequency-dependent phase correction was needed.

is obtained if the scaling of the first data point of the FID is misset (*1*), the baseline distortion introduced by the nonzero zero-order phase correction cannot be removed completely by *linear* baseline correction routines. The zero-order phase of the acquired signal depends on a number of experimental parameters, such as probe tuning and receiver gain setting. This may account for the experimental observation made by us and others that the severity of the baseline problem in 2D spectra varies from day to day. If sequential sampling is used in the t_2 dimension of 2D experiments, it is therefore important to adjust the signal phase to either 0° or 90° prior to the start of the experiment.

As is well known, linearly frequency-dependent phase corrections are another origin of baseline distortion in 1D and 2D spectra (*6, 7*). This applies to the cases of both simultaneous and sequential acquisition of complex data. In the F_2 dimension of 2D spectra, this error can be minimized by adjustment of the delay between the pulse and the time the first data point is taken (*14*); in the F_1 dimension the error can be minimized by using short pulses or offset-compensated pulses.

ACKNOWLEDGMENTS

We thank Drs. D. Rubin and D. I. Hoult for stimulating discussions during the preparation of this manuscript. D.M. acknowledges financial support from the Centre National de la Recherche Scientifique and from the CNRS-NIH exchange agreement.

REFERENCES

1. G. Otting, H. Widmer, G. Wagner, and K. Wüthrich, *J. Magn. Reson.* **66,** 187 (1986).
2. R. A. Klevit, *J. Magn. Reson.* **62,** 551 (1985).
3. W. Denk, G. Wagner, M. Rance, and K. Wüthrich, *J. Magn. Reson.* **62,** 350 (1985).
4. A. F. Mehlkopf, D. Korbee, T. A. Tiggelman, and R. Freeman, *J. Magn. Reson.* **58,** 315 (1984).
5. S. Glaser and H. R. Kalbitzer, *J. Magn. Reson.* **68,** 350 (1986); R. W. Dykstra and A. J. Wand, *J. Magn. Reson.* **75,** 158 (1987).
6. E. O. Stejskal and J. Schaefer, *J. Magn. Reson.* **14,** 160 (1974).
7. P. Plateau, C. Dumas, and M. Guéron, *J. Magn. Reson.* **54,** 46 (1983).
8. J. Jeener, B. H. Meier, P. Bachmann, and R. R. Ernst, *J. Chem. Phys.* **71,** 4546 (1979).
9. A. A. Bothner-By, R. L. Stephens, J. Lee, C. D. Warren, and R. W. Jeanloz, *J. Am. Chem. Soc.* **106,** 811 (1984).
10. L. Braunschweiler and R. R. Ernst, *J. Magn. Reson.* **53,** 521 (1983).
11. A. Bax and D. G. Davis, *J. Magn. Reson.* **65,** 355 (1985).
12. D. Marion and K. Wüthrich, *Biochem. Biophys. Res. Commun.* **113,** 967 (1983).
13. D. J. States, R. A. Haberkorn, and D. J. Ruben, *J. Magn. Reson.* **48,** 286 (1982).
14. D. I. Hoult, C.-N. Chen, H. Eden, and M. Eden, *J. Magn. Reson.* **51,** 110 (1983).