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Algorithm of Data Processing in Correlation NMR Spectroscopy

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The algorithm for data processing in correlation NMR spectroscopy has been closely checked. Procedures have been proposed by which one can obtain the spectrum free from artifacts and can carry out phase correction of the spectrum easily.

In correlation NMR spectroscopy developed by Dadok and Sprecher,[1] the steady-state spectrum is derived from the response to a linear rapid frequency scan. In previous papers,[2–8] we have described a system where a variety of capabilities were incorporated to allow additional freedom in the correlation technique. So far we have written several programs which are based on different algorithms for dealing with the rapid scan response. It has been noticed that in some cases, even when the baseline of the rapid scan response is sufficiently flat, the finally obtained spectrum is accompanied by an oscillation which is spread over the entire range of frequency. In view of this, the algorithm for data processing in correlation NMR has been closely checked. It will be shown how improper ways of data processing result in artifacts in the final steady-state spectrum. Procedures will be described by which one can obtain the spectrum free from artifacts and can make phase correction of the spectrum easily.

Data Processing of Correlation NMR Spectroscopy

It has been shown[9] that the steady-state NMR spectrum $H(f)$ can be obtained by Fourier transforming the free induction decay $h(t)$ which is given by

$$h(t) = g(t)\exp(-ibt^2/2), \tag{1}$$

where $b/2\pi$ is the sweep rate of the linear rapid frequency scan in Hz/s, and $g(t)$ is the inverse Fourier transform of the rapid scan response $G(f)$ which is observed after the phase sensitive detection of the radio frequency. It will hereafter be assumed that the rapid scan response $G(f)$ is sampled using N data points at a time interval of Δt s or at every $\Delta f = b\Delta t/2\pi$ Hz of the spectrum. The values of $G(f)$ at $s\Delta t$ s and at frequency positions of $s\Delta f$ Hz where $s=0,1,\cdots,N-1$ will be denoted by $G[s]$.

Quadrature Phase Detection. The quadrature phase detection of the rapid scan response would provide $G[s]$ expressed in complex numbers as

$$G[s] = X[s] + iY[s], \quad s=0,\ 1,\cdots,\ N-1, \tag{2}$$

where $X[s]$ and $Y[s]$ are the response in quadrature. Inverse Fourier transformation of $G[s]$ gives $g[k]$,

$$\begin{aligned} g[k] &\equiv A[k] - iB[k] \\ &= (1/N)\sum_{s=0}^{N-1}(X[s] + iY[s])\exp(2\pi iks/N), \\ &\qquad k=0,\ 1,\cdots,\ N-1, \end{aligned} \tag{3}$$

where

$$A[k] = 0, \quad k = N/2+1,\ N/2+2,\cdots,\ N-1, \tag{4a}$$

$$B[0] = 0, \tag{4b}$$

$$B[k] = 0, \quad k = N/2,\ N/2+1,\cdots,\ N-1. \tag{4c}$$

The $N/2+1$ values of $A[k]$ and $B[k]$ ($k=0,1,\cdots,\ N/2$) are used to calculate the discrete values $h[k]$ ($k=0,1,\cdots,\ N/2$) of the free induction decay $h(t)$ at $k\delta t$ s where

$$\begin{aligned} \delta t &= 1/N\Delta f \\ &= 2\pi/Nb\Delta t, \end{aligned} \tag{5a}$$

which is given by

$$\begin{aligned} h[k] &\equiv D[k] - iE[k] \\ &= (A[k] - iB[k])(\cos(b(k\delta t)^2/2) \\ &\quad - i\sin(b(k\delta t)^2/2)), \\ &\qquad k=0,\ 1,\cdots,\ N/2, \end{aligned} \tag{6a}$$

with

$$E[0] = 0. \tag{6b}$$

The N values $H[s]$ ($s=0,1,\cdots,N-1$) which represent the steady-state spectrum $H(f)$ at $s\delta f$ Hz where

$$\begin{aligned} \delta f &= 1/N\delta t \\ &= b\Delta t/2\pi \\ &= \Delta f \end{aligned} \tag{5b}$$

can be derived by putting

$$\begin{aligned} &D[k] - iE[k] = 0, \\ &\qquad k = N/2+1,\ N/2+2,\cdots,\ N-1, \end{aligned} \tag{7}$$

and Fourier transforming $h[k]$ ($k=0,1,\cdots,N-1$) according to the following equation:

$$\begin{aligned} H[s] &\equiv U[s] + iV[s] \\ &= \sum_{k=0}^{N-1}(D[k] - iE[k])\exp(-2\pi isk/N), \\ &\qquad s = 0,\ 1,\cdots,\ N-1. \end{aligned} \tag{8}$$

The phase correction of the spectrum is performed by mixing $U[s]$ and $V[s]$,

$$\begin{aligned} &U[s]' = U[s]\cos\theta + V[s]\sin\theta, \\ &\qquad s = 0,\ 1,\cdots,\ N-1, \end{aligned} \tag{9a}$$

$$\begin{aligned} &V[s]' = -U[s]\sin\theta + V[s]\cos\theta, \\ &\qquad s = 0,\ 1,\cdots,\ N-1. \end{aligned} \tag{9b}$$

Single Phase Detection. In the case of single phase detection which is generally used, inverse Fourier analysis of the rapid scan response $X[s]$ ($s=0,\ 1,\cdots,\ N-1$) in Eq. 2 gives

$$\begin{aligned} &A[k]' = (1/N)\sum_{s=0}^{N-1}X[s]\cos(2\pi ks/N), \\ &\qquad k = 0,\ 1,\cdots,\ N/2, \end{aligned} \tag{10a}$$

$$B[k]' = -(1/N)\sum_{s=0}^{N-1} X[s]\sin(2\pi ks/N),$$
$$k = 1, 2, \cdots, N/2-1, \qquad (10b)$$
$$B[0]' = B[N/2]' = 0. \qquad (10c)$$

It should be noted that $A[k]'$ and $B[k]'$ in Eq. 10 are related to $A[k]$ and $B[k]$ obtained by Eq. 3 as in the following:

$$A[0] = A[0]', \qquad (11a)$$
$$A[k] = 2A[k]', \qquad k = 1, 2, \cdots, N/2-1, \qquad (11b)$$
$$A[N/2] = A[N/2]', \qquad (11c)$$
$$B[0] = B[0]' = 0, \qquad (11d)$$
$$B[k] = 2B[k]', \qquad k = 1, 2, \cdots, N/2-1, \qquad (11e)$$
$$B[N/2] = B[N/2]' = 0. \qquad (11f)$$

In order to calculate the steady-state spectrum with a phase correction angle of θ, the free induction decay $h[k]$ ($k=0,1,\cdots,N/2$) is obtained by Eq. 6 after Eq. 11 is applied to $A[k]'$ and $B[k]'$ ($k=0,1,\cdots,N/2$), which is modified to $D[k]'$ ($k=0,1,\cdots,N/2$) and $E[k]'$ ($k=1,2,\cdots,N/2-1$) by the following relation:

$$D[0]' = D[0]\cos\theta, \qquad (12a)$$
$$D[k]' = (1/2)(D[k]\cos\theta + E[k]\sin\theta),$$
$$k = 1, 2, \cdots, N/2-1, \qquad (12b)$$
$$D[N/2]' = D[N/2]\cos\theta, \qquad (12c)$$
$$E[k]' = -(1/2)(D[k]\sin\theta - E[k]\cos\theta),$$
$$k = 1, 2, \cdots, N/2-1. \qquad (12d)$$

Inverse Fourier synthesis of $D[k]'$ and $E[k]'$ is then performed to give N values of the phase-corrected steady-state spectrum $U[s]'$,

$$U[s]' = D[0]' + 2\sum_{k=1}^{N/2-1}(D[k]'\cos(2\pi sk/N)$$
$$- E[k]'\sin(2\pi sk/N)) + D[N/2]'\cos(\pi s),$$
$$s = 0, 1, \cdots, N-1. \qquad (13)$$

Discussion

For the convenience of the following discussion, a schematic diagram of the algorithms of correlation NMR is illustrated in Fig. 1, where Procudure A and Procedure B correspond to the cases of quadrature phase and single phase detections described in the previous section, respectively.

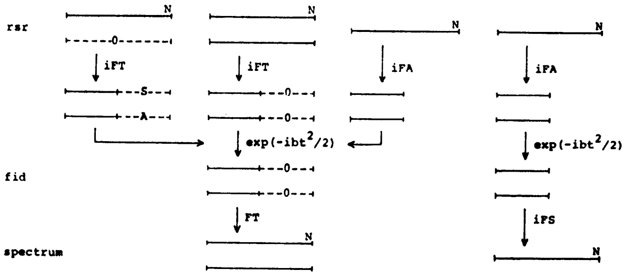

Fig. 1. Schematic diagram of the algorithms of correlation NMR spectroscopy. The symbols iFT, FT, iFA, and iFS stand for inverse Fourier transformation, Fourier transformation, inverse Fourier analysis, and inverse Fourier synthesis, respectively.

It is necessary for correct data processing in the correlation technique that the in-phase component $U[s]'$ of the spectrum becomes identical to the rapid scan response $X[s]$ when the phase correction angle θ is zero and the sweep rate b is extrapolated to zero. Procedures A and B satisfy this condition. What is important in obtaining the correct result is that $N/2+1$ points rather than $N/2$ points of the free induction decay have to be calculated by Eq. 6 before Eq. 8 or Eq. 13 is used to obtain the spectrum. Unless the $N/2+1$st point of the free induction decay is used in the calculation, an oscillation appears which is equally spread over the entire range of the spectrum. This point will also be discussed later.

In the case of single phase detection which is generally used, a most natural way in mathematical sense to obtain the spectrum is to use a combination of inverse Fourier analysis (Eq. 10) and inverse Fourier synthesis (Eq. 13) as shown in Procedure B. This procedure is equivalent to what has been given by Patt.[10] A disadvantage of Procedure B to Procedure A is that whenever one wants to change the phase of the spectrum, one has to go back to the free induction decay $D[k]'$ and $E[k]'$ by performing inverse Fourier analysis of the phase-corrected spectrum $U[s]'$, and inverse Fourier synthesize it again using the appropriate value of θ (Eqs. 12—13). When one wants to change the phase of the spectrum by mixing its in-phase and out-of-phase components (Eq. 9), Procedure A should be followed starting with the rapid scan response observed by quadrature phase detection. In this case, a combination of inverse Fourier transform (Eq. 3) and Fourier transform (Eq. 8) of complex numbers is employed to obtain the spectrum.

It should be noticed that, even when single phase detection is employed, the in-phase and out-of-phase components of the spectrum can be calculated and the phase correction of the spectrum can easily be made by mixing these components if one uses a combination of Eqs. 10—11 and Eqs. 6—9 as shown in Procedure C of Fig. 1. In this case, the free induction decay is calculated by Eq. 6 after $A[k]'$ and $B[k]'$ are modified to $A[k]$ and $B[k]$ using Eq. 11; Eps. 7—9 involving Fourier transformation of complex numbers are then used to obtain the phase-corrected spectrum.

Another way of dealing with the single phase detected rapid scan response $X[s]$ ($s=0,1,\cdots,N-1$) is to inverse Fourier transform it assuming that its imaginary part $Y[s]$ ($s=0,1,\cdots,N-1$) is all zero as shown in Procedure D of Fig. 1. This procedure is similar to the one outlined by Gupta, Ferretti, and Becker[9] without detailed discussion on the algorithm and the values of the calculated data. It can be shown that the values $A[k]'$ and $B[k]'$ obtained by the inverse Fourier transformation of $X[s]$,

$$g[k]' \equiv A[k]' - iB[k]'$$
$$= (1/N)\sum_{s=0}^{N-1} X[s]\exp(2\pi iks/N),$$
$$k = 0, 1, \cdots, N-1, \qquad (14)$$

are identical to those given by Eq. 10 for $k=0,1,\cdots,N/2$

and that

$$A[k]' = A[N-k]', \quad k = N/2+1,\ N/2+2, \cdots, N-1, \tag{15a}$$

$$B[k]' = -B[N-k]', \quad k = N/2+1,\ N/2+2, \cdots, N-1. \tag{15b}$$

Therefore, after $A[k]$ and $B[k]$ ($k=0,1,\cdots,N/2$) are obtained using Eq. 11, the phase-corrected spectrum can be calculated by Eqs. 6—9 just as in the case of quadrature phase detection.

In Procedures B, C, and D, it must always be remembered that $A[k]'$ and $B[k]'$ where $k=1,2,\cdots,N/2-1$ are to be multiplied by a factor of two to obtain $A[k]$ and $B[k]$ ($k=0,1,\cdots,N/2$) according to the relation in Eq. 11 before Eq. 6 is used to calculate the free induction decay. This is closely related to the fact that the first and $N/2+1$st points of $A[k]'$ are different from others in a sense that these two points are equal in magnitude to $A[0]$ and $A[N/2]$ which would be observed when quadrature detection is employed with two detectors each of which has kept its gain exactly the same as in the case of single phase detection; as far as other points ($k=1,2,\cdots,N/2-1$) are concerned, the coefficients $A[k]$ and $B[k]$ are twice as large as $A[k]'$ and $B[k]'$. If $A[k]'$ and $B[k]'$ where $k=0,1,\cdots,N/2$ are substituted into Eq. 6 to obtain the free induction decay, an oscillation appears in the final spectrum in addition to that the magnitude of the spectrum is half as large as it should be. This oscillation is exactly the same in origin as the one observed when the $N/2+1$st point of the free induction decay is eliminated in Eq. 8 or Eq. 13. What actually happens is that the baseline level for the even-numbered points of the obtained spectrum is different from that for the odd-numbered points. Another kind of artifact which is observed when one fails to modify $A[k]'$ and $B[k]'$ is that the average value of the spectrum depends on the value of first point of the free induction decay which is calculated from the rapid scan response and on the number of sampling points. In this case, it would become impossible to compare the intensities of signals from two or more spectra simply by reading their values.

A different type of oscillation which is inherent in correlation NMR appears when the baseline of the rapid scan response is tilted. This can effectively be removed by *wing processing* which has been previously described.6,8)

One can obtain a smoothed spectrum $U[s]'$ at $s\delta f/m = sb\Delta t/2m\pi$ Hz where $s=0,1,\cdots,mN-1$ when *zero supplement*6,11) of the free induction decay is carried out to make it m times in length; equation 7 is replaced by

$$D[k] - iE[k] = 0, \quad k = N/2+1,\ N/2+2, \cdots, mN-1, \tag{16}$$

to get $h[k]$ ($k=0,1,\cdots,mN-1$), or Eq. 12c is replaced by

$$D[N/2]' = (1/2)D[N/2]\cos\theta \tag{17a}$$

and Eqs. 12a—b, 17a, and 12d are supplemented by

$$D[k]' = 0, \quad k = N/2+1,\ N/2+2, \cdots, mN/2, \tag{17b}$$

$$E[N/2]' = -(1/2)D[N/2]\sin\theta, \tag{17c}$$

$$E[k]' = 0, \quad k = N/2+1,\ N/2+2, \cdots, mN/2-1, \tag{17d}$$

to get $D[k]'$ ($k=0,1,\cdots,mN/2$) and $E[k]'$ ($k=1,2,\cdots,mN/2-1$) before Fourier transformation or inverse Fourier synthesis to obtain mN data points is made, respectively. Although the values $U[s]'$, $s=0,m,2m,\cdots,(N-1)m$, obtained by these procedures are equal to $U[s]'$, $s=0,1,2,\cdots,N-1$, which are obtained without *zero supplement*, the values of the interpolated points $U[s]'$, $s\neq 0,m,2m,\cdots,(N-1)m$, which lie near either end of the spectrum become different from what they should be even when the sweep rate b is extrapolated to zero. In this case, the method of *wing processing*6) has also been proved useful in order to decrease the error of the interpolated values.

In the case of conventional pulse Fourier transform NMR, Fourier analysis of the free induction decay is performed to obtain the spectrum; N' points of the free induction decay is Fourier analyzed to give the in-phase and out-of-phase spectra each of which is made of $N'/2+1$ data points. On the other hand, in the case of quadrature phase detection pulse Fourier transform NMR, a set of $N'/2$ points of the free induction decay observed in quadrature is used to obtain $N'/2$ points of the in-phase and $N'/2$ points of the out-of-phase components of the spectrum. A similar procedure can be used in the case of correlation NMR. The free induction decay in Eq. 6 is modified to

$$h[k]'' \equiv D[k]'' - iE[k]'', \quad k = 0, 1, \cdots, N/2-1, \tag{18}$$

using the relation

$$D[0]'' - iE[0]'' = (D[0] + D[N/2]) - i(E[0] + E[N/2]), \tag{19a}$$

$$D[k]'' - iE[k]'' = D[k] - iE[k], \quad k = 1, 2, \cdots, N/2-1, \tag{19b}$$

and the spectrum $H[s]''$ which consists of $N/2$ data points is obtained by Fourier transforming $N/2$ data points of $h[k]''$. The values $H[s]''$, $s=0,1,2,\cdots,N/2-1$, obtained by this procedure are equal to $H[s]$, $s=0,2,4,\cdots,N-2$, obtained by Eq. 8. The phase correction of the spectrum can then be done by mixing the in-phase and out-of-phase components of $H[s]''$.

It should be noted that in quadrature phase detection pulse Fourier transform NMR, N' points of the in-phase and N' points of the out-of-phase components of the spectrum can be calculated from a set of $N'/2+1$ points of the free induction decay if one follows the procedure in Eqs. 7—9. In this case, one has to have a size of computer memory which is twice as large as what is needed to store the free induction decay. If one follows the procedure in Eqs. 12—13 involving inverse Fourier synthesis, one obtains N' points of the phase-corrected spectrum without having an additional size of memory at a sacrifice of convenience of the phase correction.

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