

Absorption Spectra From Phase-Modulated Spin Echoes

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Received December 14, 1978

A method is presented by which pure absorption spectra can be derived from spin echoes with a symmetric envelope amplitude, but with arbitrary phases ϕ in the centers of the echoes. It is shown that without any phase correction, absorption spectra can be obtained in which the amplitudes of the spectral lines are either proportional to $\cos \phi$ or $\sin \phi$, or independent of ϕ . As an example a T_2 measurement of 1,1,2-trichloroethane is given.

In many NMR techniques, for instance in the DEFT (1) and SEFT (2) experiments, in T_2 measurements, and in most kinds of 2D J spectroscopy (3), one is confronted with the fact that the phases of the signals at the center of the echo are modulated because of the spin-spin coupling in the molecule (4, 5). In many cases of one-dimensional spectroscopy one can eliminate this phase disturbance only by making an absolute-value calculation (5); this introduces line broadening. In most kinds of 2D J spectroscopy the phase modulation is used as the spreading parameter in the second time dimension (3, 6, 7). After 2D Fourier transformation, lineshapes are obtained with a so-called "phase-twist" (6). From this it is impossible to obtain absorption spectra in both dimensions, so the obtainable resolution is decreased. It will be shown that these problems can be solved if one uses the whole echo.

GENERAL CONSIDERATIONS

The time signal of one of the spectral lines in one of the spin echoes in a Carr-Purcell experiment (Fig. 1) can be described as

$$s_i(t) = M_{0i} \exp(-\tau/T_{2i}) \exp(-t/T_{2i}) \cos(\omega_s t + \phi_i) h(t), \quad [1]$$

where M_{0i} is the amplitude of the observed signal immediately after the 90° pulse, ω_s is the frequency of the signal, ϕ_i is an arbitrary phase angle, $h(t)$ describes the influence of the magnetic field inhomogeneity, and τ is the time between the first 90° pulse and the center of the echo considered. For $h(t)$ the relation

$$h(t) = h(-t) \quad [2]$$

holds. If we neglect the influence of transverse relaxation during the echo, the time

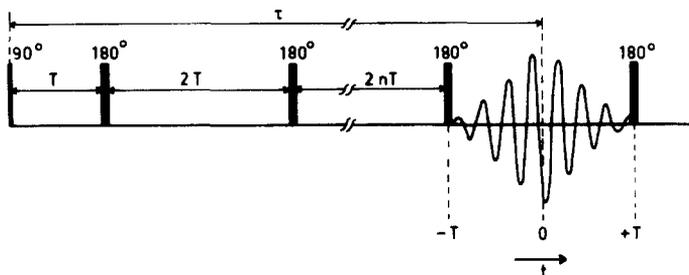


FIG. 1. Example of a spin echo in a Carr-Purcell experiment.

signal of Eq. [1] can be written as

$$s_i(t) = M_{0i} e^{-\tau/T_{2i}} [h(t) \cos(\omega_s t) \cos \phi_1 - h(t) \sin(\omega_s t) \sin \phi_i]. \quad [3]$$

This means that $s_i(t)$ is the sum of an odd sine and an even cosine function. By cosine Fourier transformation of Eq. [3] from $-T$ to $+T$ the sine function cancels, and by sine transformation the cosine function cancels. This gives for the cosine transform of Eq. [3] at frequency ω_c

$$S_i^c(\omega_c) = \int_{-T}^T s_i(t) \cos(\omega_c t) dt = 2M_{0i} e^{-\tau/T_{2i}} \cos \phi_1 \int_0^T \cos(\omega_s t) h(t) \cos(\omega_c t) dt, \quad [4a]$$

and for the sine transform

$$S_i^s(\omega_c) = \int_{-T}^T s_i(t) \sin(\omega_c t) dt = 2M_{0i} e^{-\tau/T_{2i}} \sin \phi_i \int_0^T \sin(\omega_s t) h(t) \sin(\omega_c t) dt. \quad [4b]$$

Assuming that ω_{si} is much larger than the decay rate of $h(t)$, ω_{si} and $\omega_c > 0$ and $h(T) \approx 0$, Eqs. [4] both represent pure absorption lines, with amplitudes proportional to $\cos \phi_i$ and $\sin \phi_i$, respectively. The absolute spectrum defined by

$$|S_i(\omega_c)| = [S_i^c(\omega_c)^2 + S_i^s(\omega_c)^2]^{1/2} \quad [5]$$

represents a spectrum with a pure absorption line and an amplitude independent of ϕ_i . Supposing that the magnetic field homogeneity has a Lorentzian shape, one may write the function $h(t)$ as

$$h(t) = \exp(-|t|/T_2^\dagger). \quad [6]$$

The absolute spectrum becomes

$$|S_i(\omega_c)| = M_{0i} e^{-\tau/T_{2i}} \frac{T_2^\dagger}{1 + T_2^{\dagger 2} (\omega_s - \omega_i)^2}, \quad [7]$$

which is a pure Lorentzian lineshape. As is clear from Eqs. [4] Fourier transformation of the whole echo gives a spectral line with the same lineshape and linewidth as would have been obtained from Fourier transformation of half of the

echo for the case $\phi_i = 0$. The derivations have been given only for one signal frequency ω_{s_i} and one phase angle ϕ_i ; they are obviously also applicable if we are dealing with a signal of the form $s(t) = \sum_i M_{0_i} \cos(\omega_{s_i} t + \phi_i) h(t)$. This implies that we can obtain pure absorption lines over the whole spectrum without any phase correction, if the amplitudes of the signals are symmetric around $t = 0$. The asymmetry of the spin echo caused by T_{2i} , Eq. [1], gives a distortion of the absorption spectrum, which will be small if $(T_{2i})^{-1}$ is much smaller than the decay rate of $h(t)$.

In practice the effect will also be partly eliminated by digital-filtering the signal around $t = 0$ with the optimum S/N filter. In fact the method described is not only limited to spin echoes, but can be applied on all kinds of time signals which are transformed in such a way that they have a symmetric envelope amplitude around a certain time T .

COMPUTATIONAL REALIZATION

In practice the signal is digitized. In the usual discrete Fourier transformation program available it is supposed that the first data point corresponds to $t = 0$. In our case the first data point corresponds to $t = -T$, which means that the time axis has to be shifted over a distance T . The relation between the two Fourier transforms is given by

$$S(\omega_c) = \int_0^{2T} s(t+T) e^{i\omega_c t} dt = e^{-i\omega_c T} \int_{-T}^T s(t') e^{i\omega_c t'} dt'. \quad [8]$$

The terms $S^c(\omega_c)$ and $S^s(\omega_c)$ are the real and the imaginary parts of $S(\omega_c)$, respectively. If the signal consists of $2N$ data points, then ω_c has the values $2\pi n(1/2T)$, so

$$\exp(-i\omega_c T) = (-1)^{n-1}, \quad n = 1, 2, \dots, N, \quad [9]$$

for the n th point in the frequency spectrum. Changing the signs of all even points in the frequency spectrum gives us absorption spectra similar to Eqs. [4], in amplitude proportional to $\cos \phi$ and $\sin \phi$. An absolute-value calculation according to Eq. [5] gives a ϕ -independent spectrum with absorption lineshapes.

EXPERIMENTAL RESULTS

As an example of the Fourier transform of a whole spin echo, a T_2 measurement of the protons of 1,1,2-trichloroethane is shown. A pulse sequence according to Fig. 1 has been used. The distance between the eleven 180° pulses was 1.76 sec; the sampling time was 1.60 sec per echo. The echoes have been weighted with $\exp(-t/0.4)$ around their centers. Figure 2a gives the absolute-value display obtained from the right halves of the echoes. In Fig. 2b, $S^c(\omega_c)$, Eq. [4a], for the whole echoes is given. The amplitude modulation of the lines outside the centers of the multiplets is clearly visible. Figure 2c shows the absolute-value display obtained after Fourier transformation of the whole spin echoes. The lines have absorption lineshapes and

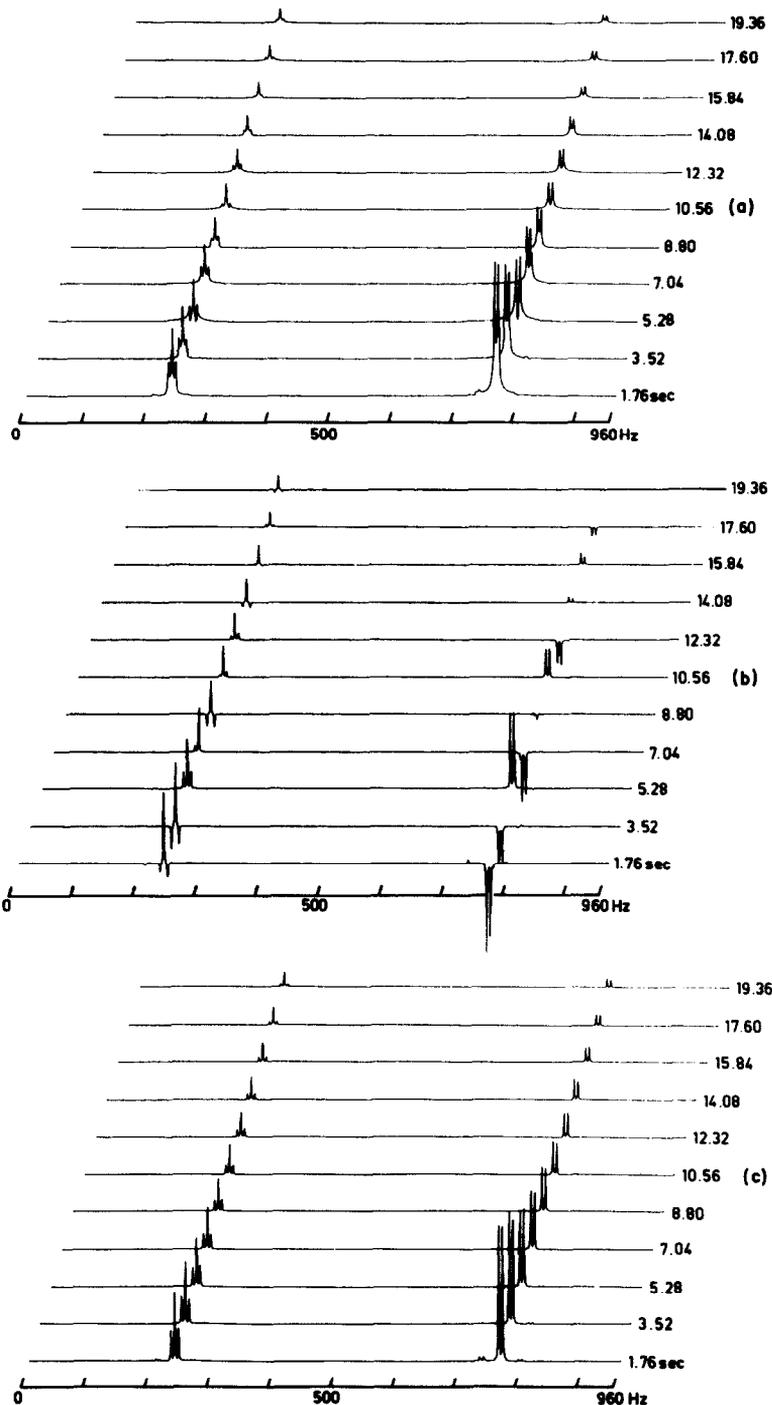


FIG. 2. Proton spectra of 1,1,2-trichloroethane obtained from 11 spin echoes in a Carr-Purcell experiment. (a) Absolute-value display obtained from the right halves of the echoes; (b) cosine Fourier transforms of the whole spin echoes; (c) absolute-value display obtained from the whole spin echoes.

are clearly narrower than those in Fig. 2a. The T_2 values of the doublet are 5.7 sec, the center line of the triplet has a T_2 value of 10.8 sec, and both the outer lines have T_2 values of 6.3 sec.

ACKNOWLEDGMENTS

We acknowledge the help of H. Emonts, P. de Jong, and T. Tiggelman with the software development, and we wish to thank Dr. S. Emid and Dr. W. Bovée for critically going through the article and making valuable suggestions.

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