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Homonuclear Broadband-Decoupled Absorption Spectra, with Linewidths Which Are Independent of the Transverse Relaxation Rate

Recently Aue *et al.* (*1*) presented a method for obtaining a homonuclear broadband-decoupled high-resolution NMR spectrum by means of diagonal projection of a 2D *J*-resolved absolute-value spectrum. Resolution in such a projection is severely limited by the fact that resonance lines have absolute-value lineshapes (*2*). As has been shown by Nagayama *et al.* (*3*) it is impossible to obtain a homonuclear broadband-decoupled spectrum via projection of a phase-sensitive spectrum which is obtained by using the method of Aue *et al.* (*1*). Until now it was impossible to eliminate the absolute-value character in the decoupled spectrum.

A new method is introduced here by which it is possible to obtain a decoupled absorption spectrum with linewidths which are independent of the transverse relaxation rate. The basic schemes of the method described by Aue *et al.* (*1*) and our new method are the same: spin echoes are created by means of 90–180° pulse sequences, for different intervals $t/2$ between the 90 and 180° pulses (Fig. 1). In our method the magnetization is measured at a fixed time τ after the initial 90° pulse, as a function of time t. Following the arguments of Aue *et al.* the observed magnetization, corresponding to a resonance line k of a set j of magnetically equivalent nuclei, is given in the case of weak coupling by

$$M_{jk}(t) = M^0_{jk} \exp(-\tau/T_{2jk}) \exp((t-\tau)/T_2^{\dagger}) \cos(\Omega_j(\tau - t) + \nu_{jk}\tau), \qquad 0 \le t \le \tau, \tag{1}$$

where M^0_{jk} is the amplitude of the magnetization just after the initial 90° pulse, Ω_j is given by $\Omega_j = \gamma H_0(1-\sigma_j)$, and γ, H_0 and σ_j have their usual meanings. The multiplet splitting is denoted by $\nu_{jk} = \Sigma_l J_{jl} m_{lk}$ with coupling constants J_{jl} and magnetic quan-

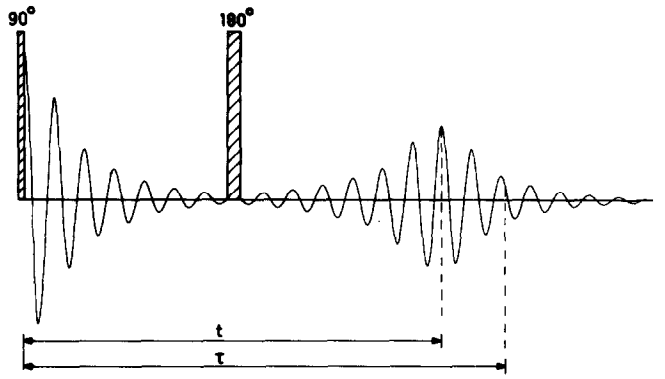

FIG. 1. Scheme of the method for obtaining homonuclear broadband-decoupled absorption spectra. Sampling points are taken at a fixed time after the initial 90° pulse, for various values of $t \le \tau$.

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tum numbers m_{lk} of nucleus l. The quantity T_{2jk} is the transverse relaxation time of resonance line jk, and $T_2^{\dagger}$ describes the influence of magnetic field inhomogeneity. Because of the symmetry in a multiplet of a weakly coupled spin system, if $\nu_{jk} \neq 0$ there will always be a component jk' with $\nu_{jk} = -\nu_{jk'}$. The observed magnetization corresponding to the sum of both components will therefore be proportional to $\cos(\Omega_j(\tau - t))\cos(\nu_{jk}\tau)$, while a component with $\nu_{jk} = 0$ will be proportional to $\cos(\Omega_j(\tau - t))$. So we can write the observed sum of the magnetization components k of multiplet j at time τ after the 90° pulse similar to Eq. [1] as

$$\sum_k M_{jk}(t) = \sum_k M_{jk}^0 \exp(-\tau/T_{2jk}) \exp((t-\tau)/T_2^{\dagger}) \cos(\nu_{jk}\tau) \cos(\Omega_j(\tau - t)),$$
$$0 \leq t \leq \tau. \qquad [2]$$

The cosine Fourier transform of Eq. [2] as a function of $(\tau - t)$ gives for $\omega > 0$ a pure absorption signal at frequency Ω_j:

$$S^c(\omega) = (\Sigma_k M_{jk}^0 \exp(-\tau/T_{2jk}) \cos(\nu_{jk}\tau)) \frac{T_2^{\dagger}}{2(1 + T_2^{\dagger 2}(\omega - \Omega_j)^2)}. \qquad [3]$$

Equation [3] represents a homonuclear broadband-decoupled absorption spectrum. Linewidths are determined by $T_2^{\dagger}$ and are independent of the transverse relaxation time T_{2jk}. However, intensities in the resulting spectrum do depend on T_{2jk} and on $\cos(\nu_{jk}\tau)$. An example of a decoupled absorption spectrum of 1,1,2-trichloroethane is given in Fig. 2. The spectrum was recorded on our home-built 7T HR NMR spectrometer (*4*).

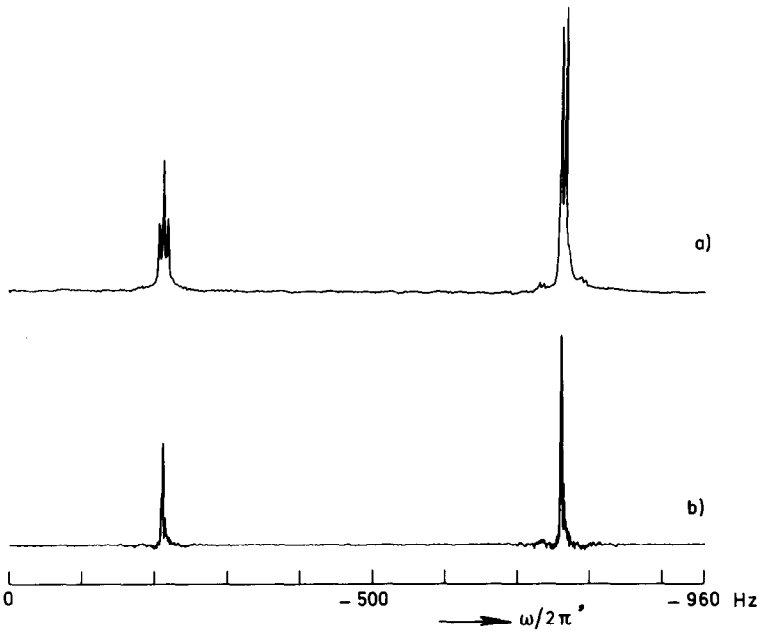

FIG. 2. ^{1}H spectra of 1,1,2-trichloroethane (a) obtained with a FID experiment, and (b) the homonuclear broadband-decoupled absorption spectrum.

The sensitivity of this method can be improved, measuring time can be shortened, and the amplitude dependence of $\cos(\nu_{jk}\tau)$ can be eliminated by varying time τ and using the concept of 2D Fourier transformation (*5*). Details concerning this 2D approach, in connection with optimal data processing, will be given later.

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