JOURNAL OF MAGNETIC RESONANCE 35, 167–169 (1979)

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-

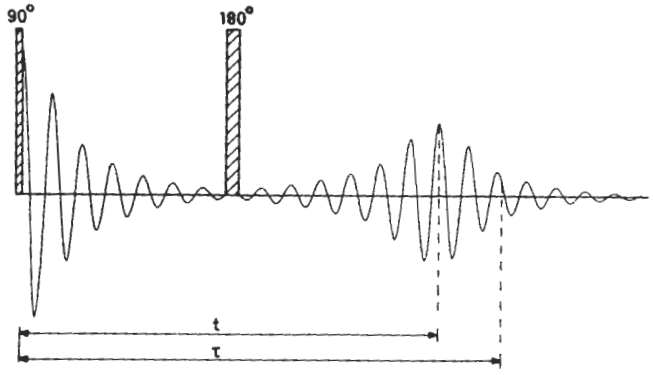

FIG. 1. Scheme of the method for obtaining homonuclear broadband-decoupled absorption spectra. Sampling points are taken at a fixed time after the initial 90° pulse, for various values of $t \le \tau$.

0022-2364/79/070167-03$02.00/0

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*).

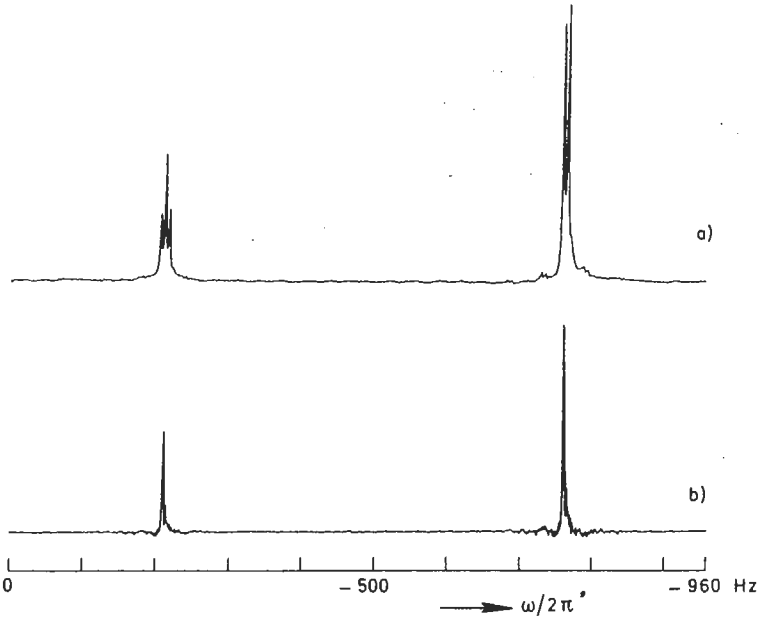

FIG. 2. ^{1}H spectra of 1,1,2-trichloroethane (a) obtained with a FID experiment, and (b) the homonuclear broadband-decoupled absorption spectrum.

The sensitivity of this meth
and the amplitude dependen
using the concept of 2D Fo
approach, in connection with

This research was made possible

1. W. P. AUE, J. KARHAN, AND R
2. W. BREMSER, H. D. W. HILL,
3. K. NAGAYAMA, P. BACHMAN
(1978).
4. A. F. MEHLKOPF, D. Phil Thesi
5. W. P. AUE, E. BARTHOLDI, AN

Department of Applied Physi
Delft University of Technolog
P. O. Box 5046
2600 GA Delft
The Netherlands

Received February 22, 1979

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.

ACKNOWLEDGMENT

This research was made possible by a scholarship from the Delft University Fund (A.B.).

REFERENCES

1. W. P. AUE, J. KARHAN, AND R. R. ERNST, *J. Chem. Phys.* **64,** 4226 (1976).
2. W. BREMSER, H. D. W. HILL, AND R. FREEMAN, *Messtechnik* **79,** 14 (1971).
3. K. NAGAYAMA, P. BACHMANN, K. WÜHTRICH, AND R. R. ERNST, *J. Magn. Reson.* **31,** 133 (1978).
4. A. F. MEHLKOPF, D. Phil Thesis, Delft University of Technology, 1978.
5. W. P. AUE, E. BARTHOLDI, AND R. R. ERNST, *J. Chem. Phys.* **64,** 2229 (1976).

A. BAX
A. F. MEHLKOPF
J. SMIDT

Department of Applied Physics
Delft University of Technology
P. O. Box 5046
2600 GA Delft
The Netherlands

Received February 22, 1979