

Measurement of Longitudinal and Rotating Frame Relaxation Times through Fully J -Decoupled Homonuclear Spectra

F. Guenneau, P. Mutzenhardt, D. Grandclaude, and D. Canet

Laboratoire de Méthodologie RMN, (UPRESA CNRS 7042; FR CNRS 1742-INCM), Université Henri Poincaré,
B.P. 239, 54506 Vandoeuvre-les-Nancy Cedex, France

Received April 21, 1999; revised June 2, 1999

It is shown that fully J -decoupled homonuclear spectra involving Lorentzian lines can be readily obtained by straightforward processing of the 2D data arising from a conventional spin echo sequence ($\pi/2-t_1/2-\pi-t_1/2$ -Acq(t_2)) used in the so-called J -resolved experiment. The method simply rests on power spectra with the drawback of lines having meaningless relative intensities. In principle, the experiment should also yield transverse relaxation times. Several tests demonstrate that this is not so, due to pulse imperfections and nonresolved long-range J couplings. Conversely, longitudinal and rotating frame relaxation times can be easily determined by means of an appropriate preparation period (for instance, a saturation-recovery period in the case of longitudinal relaxation) inserted before the 2D spin echo sequence. Since one is dealing with a single line per nucleus, relaxation measurements become reliable and accurate. © 1999 Academic Press

illusory. Nevertheless, the quality of the decoupled spectra obtained in this way and the simplicity of the procedure suggests that the two-dimensional spin echo sequence can be employed as a sort of “black-box” for probing any evolution which may occur prior to its application. This feature will be invoked here for determining longitudinal and rotating frame relaxation times in proton systems whose normal spectra are so overcrowded that standard measurements prove to be untractable.

THEORY

At the onset, let us consider a single line represented in the time domain by

$$f(t) = ae^{-t/T_2} e^{i\varphi} e^{2i\pi\nu_0 t}, \quad [1]$$

a being its intensity, T_2 the transverse relaxation time, φ the phase factor, and ν_0 the resonance frequency. The Fourier transform of $f(t)$ yields

$$\begin{aligned} F(\nu) &= FT[f(t)] \\ &= [\cos \varphi A(\nu - \nu_0) - \sin \varphi D(\nu - \nu_0)] \\ &\quad + i[\cos \varphi D(\nu - \nu_0) + \sin \varphi A(\nu - \nu_0)] \\ &= \text{Re} + i \text{Im}. \end{aligned} \quad [2]$$

A and D being the absorption and dispersion spectra, respectively,

$$\begin{aligned} A(\nu - \nu_0) &= a \frac{T_2}{1 + 4\pi^2 T_2^2 (\nu - \nu_0)^2} \\ D(\nu - \nu_0) &= a \frac{2\pi T_2^2 (\nu - \nu_0)}{1 + 4\pi^2 T_2^2 (\nu - \nu_0)^2}. \end{aligned} \quad [3]$$

The power spectrum ($\text{Re}^2 + \text{Im}^2$) is readily calculated:

INTRODUCTION

“Decoupled” proton NMR spectra, based on two-dimensional J -spectroscopy (1), require invariably heavy data processing (2, 3), a satisfactory outcome not always being warranted. This is due to the inherent hypercomplex nature of the data which precludes directly obtaining pure absorption spectra, leading to lines affected by the so-called phase-twist problem. Magnitude spectra are of little help because their peaks involve important wings which result in a degraded resolution; moreover, as explained below, such spectra are not quantitative. To circumvent this problem, one possibility lies in the construction of whole echoes either in the t_1 (4) or the t_2 (5) dimension. However, the success of such a strategy is strongly dependent on the algorithm used for analyzing the experimentally available half-echo and anyway involves a large amount of calculations. In the present study, it is shown that *power spectra* remove the phase-twist problem in a rather straightforward manner while leading, at the same time, to high-resolution Lorentzian lines, however, at the expense of meaningless relative intensities in the fully decoupled spectrum. Because such spectra arise from spin echo experiments, it was hoped that transverse relaxation times would be attainable as well. Unfortunately, various experimental factors render this hope

$$P(\nu) = a^2 \frac{T_2^2}{1 + 4\pi^2 T_2^2 (\nu - \nu_0)^2}. \quad [4]$$

It is just a *Lorentzian line* of the same linewidth as the absorption spectrum, of intensity equal to $a^2 T_2$. This feature is in fact the key to the method presented here because it affords a high-resolution spectrum irrespective of the phase factor affecting the considered signals.

Now, we must consider the standard “ J -resolved” spin echo sequence $[(\pi/2)-t_1/2-(\pi)-t_1/2-\text{Acq}(t_2)]$ applied to a doublet of splitting J . In the time domain, the two lines are represented by

$$f_+(t_1, t_2) = (a/2)\exp(-t_1/T_2)\exp(i\pi J t_1) \\ \times \exp(-t_2/T_2^*)\exp[2i\pi(\nu_a + J/2)t_2], \quad [5]$$

and

$$f_-(t_1, t_2) = (a/2)\exp(-t_1/T_2)\exp(-i\pi J t_1) \\ \times \exp(-t_2/T_2^*)\exp[2i\pi(\nu_a - J/2)t_2], \quad [6]$$

T_2 and T_2^* being the effective transverse relaxation times in the time domains t_1 and t_2 , respectively. We first deal with the signal f_+ , recognizing that conclusions regarding f_- can be drawn by changing J into $-J$. The corresponding power spectrum, in the frequency domain, can be expressed as

$$p_+(\nu_1, \nu_2) = (a^2/4) \frac{T_2^2}{1 + 4\pi^2 T_2^2 (J/2 - \nu_1)^2} \\ \times \frac{T_2^{*2}}{1 + 4\pi^2 T_2^{*2} (\nu_a + J/2 - \nu_2)^2}. \quad [7]$$

It is well-known that a decoupled spectrum can be obtained (I) (i) by a 45° tilt which amounts to change ν_2 into $\nu'_2 = \nu_2 - \nu_1$ and (ii) by a projection upon the ν'_2 axis, which corresponds to an integral with respect to ν_1 . This yields

$$p_+(\nu'_2) = (a^2/4) T_2 T_2^* \int_{-\infty}^{+\infty} \frac{T_2}{1 + 4\pi^2 T_2^2 (J/2 - \nu_1)^2} \\ \times \frac{T_2^*}{1 + 4\pi^2 T_2^{*2} (\nu_a + J/2 - \nu'_2 - \nu_1)^2} d\nu_1, \quad [8]$$

which can be recast in terms of inverse Fourier transforms,

$$p_+(\nu'_2) = (a^2/16) T_2 T_2^* \int_{-\infty}^{+\infty} \\ \times \{[FT(\exp(i\pi J t_1)\exp(-|t_1|/T_2))]$$

$$\times [FT(\exp[2i\pi(\nu_a + J/2 - \nu_1)t_2]\exp(-|t_2|/T_2^*))]\} d\nu_1. \quad [9]$$

Consistent with [8], the first Fourier transform in [9] is assumed to yield a ν_1 frequency function and the second one a ν'_2 frequency function. Thus, making explicit the Fourier transforms, we can write [9] as

$$p_+(\nu'_2) = (a^2/16) T_2 T_2^* \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \\ \times \exp\left(-\frac{|t_1|}{T_2} - \frac{|t_2|}{T_2^*}\right) \exp[2\pi(J/2 - \nu_1)t_1] \\ \times \exp[2\pi(\nu_a + J/2 - \nu'_2 - \nu_1)t_2] dt_1 dt_2 d\nu_1. \quad [10]$$

Eq. [10] can be written as

$$p_+(\nu'_2) = (a^2/16) T_2 T_2^* \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp\left(-\frac{|t_1|}{T_2} - \frac{|t_2|}{T_2^*}\right) \exp(\pi J t_1) \exp[2\pi(\nu_a + J/2 - \nu'_2)t_2] \\ \times \left[\int_{-\infty}^{+\infty} \exp[-2\pi\nu_1(t_1 + t_2)] d\nu_1 \right] dt_1 dt_2. \quad [11]$$

The ν_1 integral is just twice the Dirac function $\delta(t_1 + t_2)$. Using one of the properties of Dirac functions (i.e., $\int_{-\infty}^{+\infty} f(t)\delta(t)dt = f(0)$), we can transform [11] as

$$p_+(\nu'_2) = \left(\frac{a^2}{8}\right) T_2 T_2^* \int_{-\infty}^{+\infty} \exp\left(-\frac{|t_2|}{T_2} - \frac{|t_2|}{T_2^*}\right) \\ \times \exp[2\pi(\nu_a - \nu'_2)t_2] dt_2. \quad [12]$$

It appears now clearly that $p_+(\nu'_2)$ is a *Lorentzian function* associated with a signal at the frequency $\nu'_2 = \nu_a$ and of transverse relaxation time $(T_2 T_2^*)/(T_2 + T_2^*)$. It can be noticed that [12] is, as expected, independent of J ; consequently the same result is obtained for $p_-(\nu'_2)$ and the final spectrum is devoid of any J -splitting. The analytical function for the line-shape in the decoupled (power) spectrum arising from a doublet is obtained by calculating the integral in [12]:

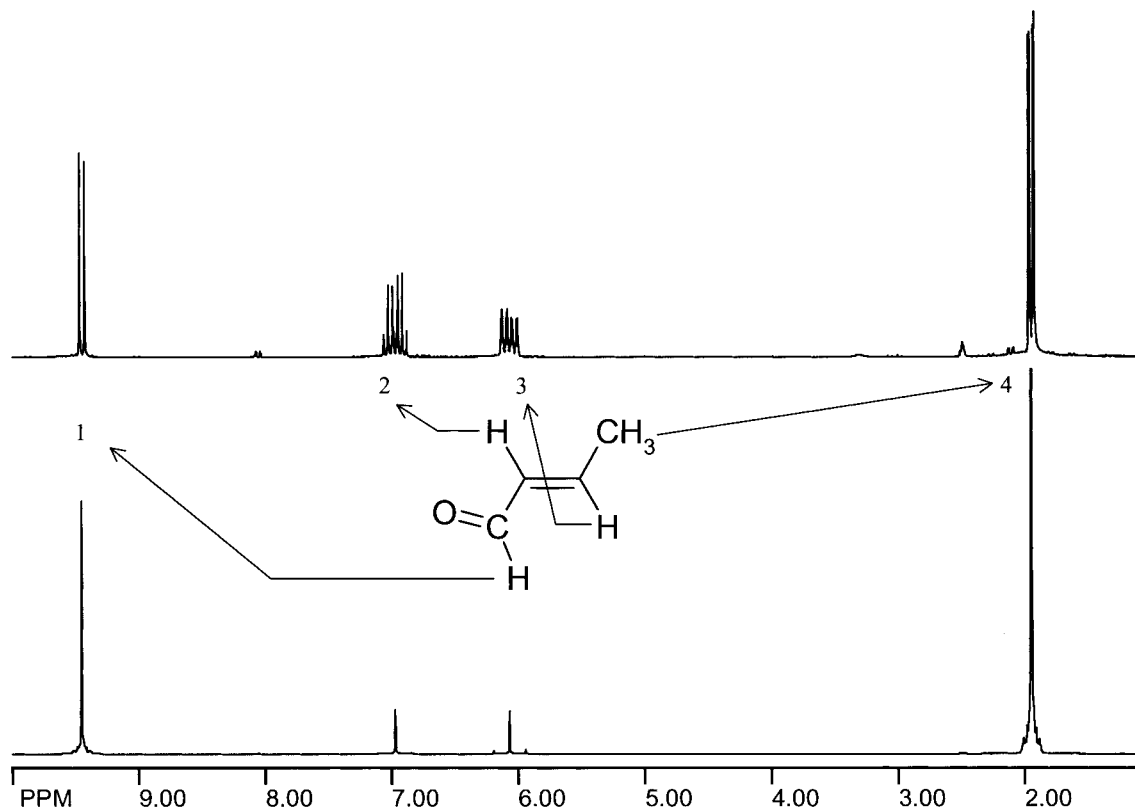


FIG. 1. Top: the conventional (200 MHz) ^1H spectrum of *trans*-crotonaldehyde. Bottom: the corresponding fully decoupled spectrum (in the power mode) exhibiting sharp lines, devoid, however, of any quantitative meaning. There were 512 t_1 increments of 40 ms (one scan for each increment with the sequence $(\pi/2)_x-t_1/2-(\pi)_y-t_1/2-\text{Acq}(t_2)$). Recycle time: 100 s; 8 K in the t_2 dimension for a spectral width of 3000 Hz.

$$p_a(\nu'_2) = 2 \left(\frac{a}{2} \right)^2 \frac{(T_2 T_2^*)^2}{T_2 + T_2^*} \frac{1}{1 + 4\pi^2 \left(\frac{T_2 T_2^*}{T_2 + T_2^*} \right)^2 (\nu_a - \nu'_2)^2} \quad [13]$$

The lack of quantitivity is evident from [13] and is simply due to the fact that the square of a sum is not equal to the sum of the squares (it can be noted that, for the same reason, this drawback would also affect magnitude spectra). Nevertheless, high-resolution spectra are very easily (without any special data processing) obtained as exemplified by Figs. 1 and 2. From the above treatment, it can be seen that the linewidth at half height is slightly increased with respect to a conventional spectrum; instead of $1/(\pi T_2^*)$, we have $1/(\pi T_2) + 1/(\pi T_2^*)$ for the actual "fully decoupled" spectra, which represents a minor penalty largely compensated for by the ease of obtaining such spectra. This feature is especially visible in the spectrum of 4-androstene 3,17-dione (Fig. 2; abbreviated below as androstene) where, starting from an overcrowded spectrum, we finally end up with a series of well-resolved singlets which, in spite of the lack of quantitivity, should greatly facilitate the assignment of the numerous protons in this molecule (2).

AN ATTEMPT TO DETERMINE THE TRANSVERSE RELAXATION TIME FROM FULLY DECOUPLED SPECTRA

Owing to the fact that one is dealing with a spin-echo sequence and that J -modulation is ultimately suppressed through fully decoupled spectra, one may hope to determine transverse relaxation times. Indeed, Eq. [13] contains in principle the relevant information, the problem being to extract the true T_2 (the effective relaxation time acting during the t_1 time interval), although this goal cannot be reached directly due to the complicated dependence of [13] upon T_2 and T_2^* . A first approach would be to perform a series of exponential multiplications in the t_1 domain and to monitor the changes in a given line of the decoupled spectrum. Let us denote by A its effective amplitude (the area in the frequency domain ν'_2), by H its height, and by Lw its linewidth at half height. First, it can be seen that the sum of the inverses of relaxation times can be deduced from Lw or, alternatively, from the ratio A/H :

$$\frac{1}{T_2} + \frac{1}{T_2^*} = \frac{A}{H} = \pi Lw. \quad [14]$$

Suppose now that we treat the raw data set with different

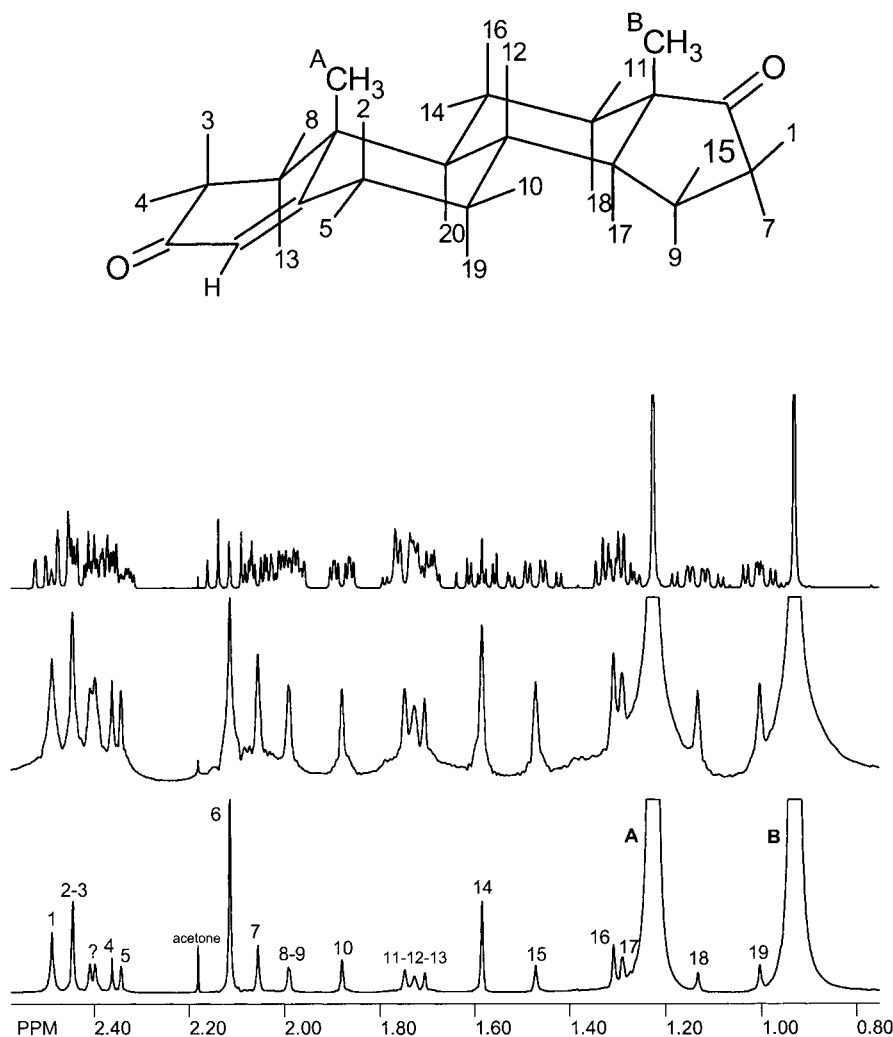


FIG. 2. Top: the conventional spectrum (600 MHz) of 4-androstene 3,17-dione (androstene). Middle: the fully decoupled spectrum in the magnitude mode. Bottom: the fully decoupled spectrum in the power mode (note the improved resolution and the overall quality). The experiments were carried out with a Bruker AMX spectrometer. There were 512 t_1 increments of 12.5 ms (eight scans for each increment with the EXORCYCLE (6) phase cycle). Repetition time: 10 s; 2 K in the t_2 dimension for a spectral width of 1500 Hz.

exponential multiplications in the t_1 domain. Let x_i equal the relevant line broadening and y_i equal the inverse of the amplitude under these conditions of exponential multiplication. From [13] we can write

$$y_i = \frac{2}{a^2 T_2 T_2^*} + \frac{2\pi}{a^2 T_2^*} x_i \quad [15]$$

and easily extract the slope and intercept of this linear representation. Their ratio leads to the T_2 value

$$\frac{\text{slope}}{\text{intercept}} = \pi T_2. \quad [16]$$

As illustrated in Fig. 3, the method proved to be efficient

with small line-broadenings (not exceeding 10% of the expected natural linewidth). However, the T_2 value determined that way is seen to be strongly dependent on experimental conditions: the experiments from which data of Fig. 3 are extracted are of the type CPMG (7) with autocompensated 180° pulses. These results clearly indicate that increasing the number of 180° pulses would presumably lead to the true T_2 value (which, because extreme narrowing conditions prevail, should be of the order of T_1 , equal to 16 s). This suggests replacing the single 180° pulse of the echo sequence by a CPMG pulse train. Unfortunately, this method fails probably due to a distribution of flip angles over the whole sample (having its origin in the radiofrequency field inhomogeneity). This distribution entails an incomplete coherence transfer, thus an imperfect J modulation leading to poorly decoupled spectra.

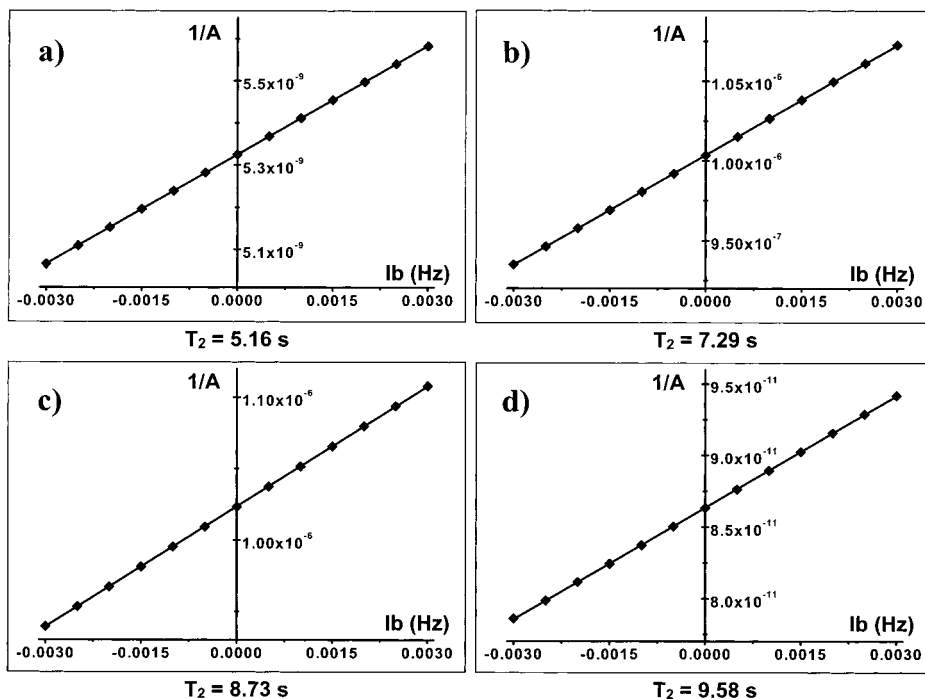


FIG. 3. An attempt to determine T_2 from the evolution of fully decoupled spectra with line broadening (lb) applied in the t_1 dimension. The linear evolution of $1/A$ (A , amplitude) obtained for the aldehydic proton of *trans*-crotonaldehyde yields an effective T_2 (see Eq. [16]). Experiments performed with the sequence (pseudo CPMG): $(\pi/2)_x - [t_1/(2n) - (\pi)_y - t_1/(2n)]_n - \text{Acq}(t_2)$. (a) $n = 1$, (b) $n = 2$, (c) $n = 4$, (d) $n = 8$. There were 512 t_1 increments of 40 ms (one scan for each increment). Recycle time: 100 s; 8 K in the t_2 dimension for a spectral width of 3000 Hz.

The deleterious effect of 180° pulse imperfections (partly corrected by a train of pulses in the CPMG manner) on T_2 determination has been confirmed by a second approach which makes use of a series of data sets, each involving a different shift of the origin in the t_1 time domain (denoted below by Δ). This amounts to delay the sampling by Δ , meaning that the various data sets should differ only by damping factors of the form $\exp(-\Delta/T_2)$. Because we are dealing with power spectra, each line in the decoupled spectrum should decrease according to $\exp[-\Delta/(T_2/2)]$ and thus afford a straightforward determination of T_2 . However, most evolution curves exhibit oscillations superimposed to the expected exponential decay as exemplified in Fig. 4. This feature can be explained by the existence of small J -couplings whose values are comparable to the resolution in any of the two dimensions. In order to understand this modulation, we have carried out some tedious calculations which are summarized below. The line height in the power spectrum for an unresolved (or poorly resolved) doublet of splitting J is given by

$$P_0 = \left(\frac{aT_2}{1 + \pi^2 T_2^2 J^2} \right)^2, \quad [17]$$

where $a/2$ is the amplitude of each line in the doublet and the height is assumed to be measured at the resonance frequency

(in the middle of the doublet). When the origin in the time domain is shifted by a quantity Δ , we obtain

$$P_\Delta = A \exp[-\Delta/(T_2/2)][1 + \cos(2\pi J\Delta - u)] \quad [18]$$

with $A = (a^2 T_2^2)/(2(1 + \pi^2 T_2^2 J^2))$ and $\tan u = (2\pi T_2 J)/(1 - \pi^2 T_2^2 J^2)$.

It can be seen that P_Δ tends to P_0 when Δ goes to zero. It must be emphasized that the above results concern a doublet and are therefore oversimplified with respect to actual situations. For instance, the decay curve of Fig. 4 corresponds presumably to a quartet resulting from a long-range coupling between the aldehydic proton and the methyl protons of *trans*-crotonaldehyde (TCA). Moreover, only one dimension is considered in these calculations. Indeed, a simulation (Fig. 5) corresponding to the totality of the two-dimensional data treatment employed here exhibits qualitatively the same behavior as in Fig. 4, confirming the modulation appearing in Eq. [18]. It is interesting to note that the analysis of the oscillatory decay leads to (i) an apparent T_2 consistent with the one deduced from the first approach (see Figs. 3 and 4) and (ii) a reasonable J -coupling value.

Finally, we must admit that it is difficult, if not impossible, to extract a proper T_2 value from fully decoupled spectra even though such spectra arise from spin echo experiments. The

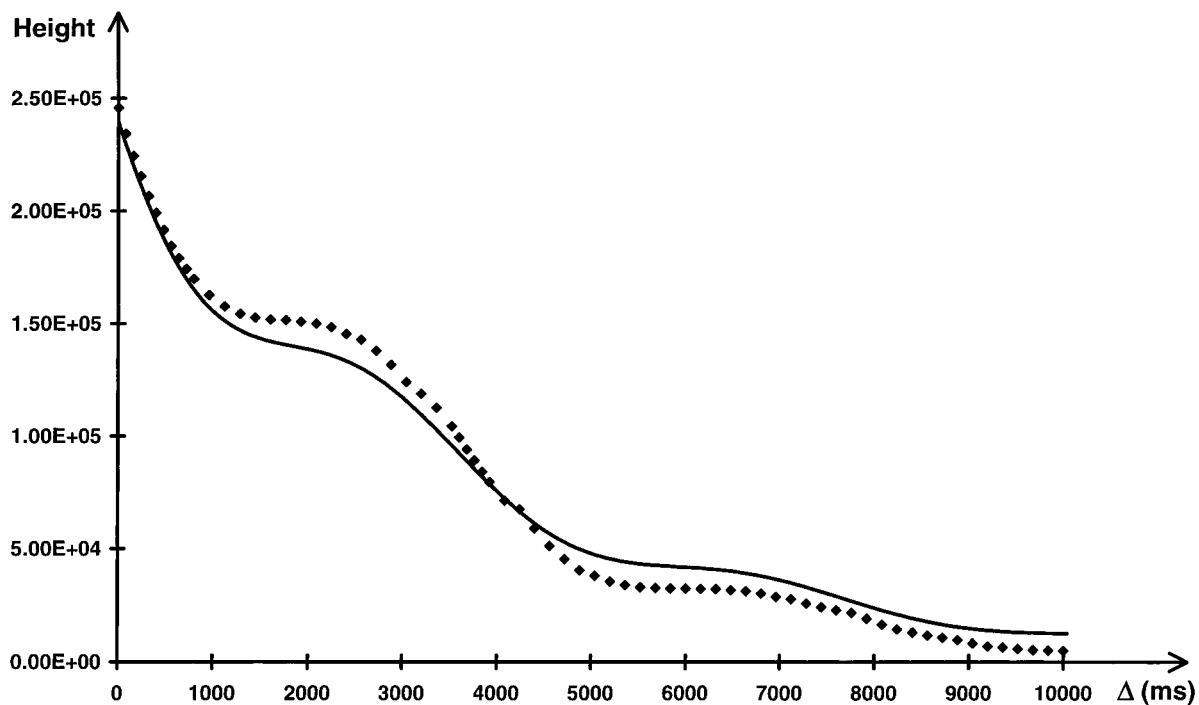


FIG. 4. The decay of the aldehyde proton line in the decoupled spectrum of *trans*-crotonaldehyde (power mode). Filled diamonds are considered experimental data as they have been obtained by shifting by a quantity Δ the origin in the time domain t_1 . The continuous curve is calculated from the fitted values of A , T_2 , B , J , and φ in $A \exp(-\Delta/T_2)[1 + B \cos(2\pi J\Delta + \varphi)]$: $T_2 = 6.8$ s; $B = 0.15$; $J = 0.24$ Hz; $\varphi = 1.74$ rad. The data arise from the experiment of Fig. 3b.

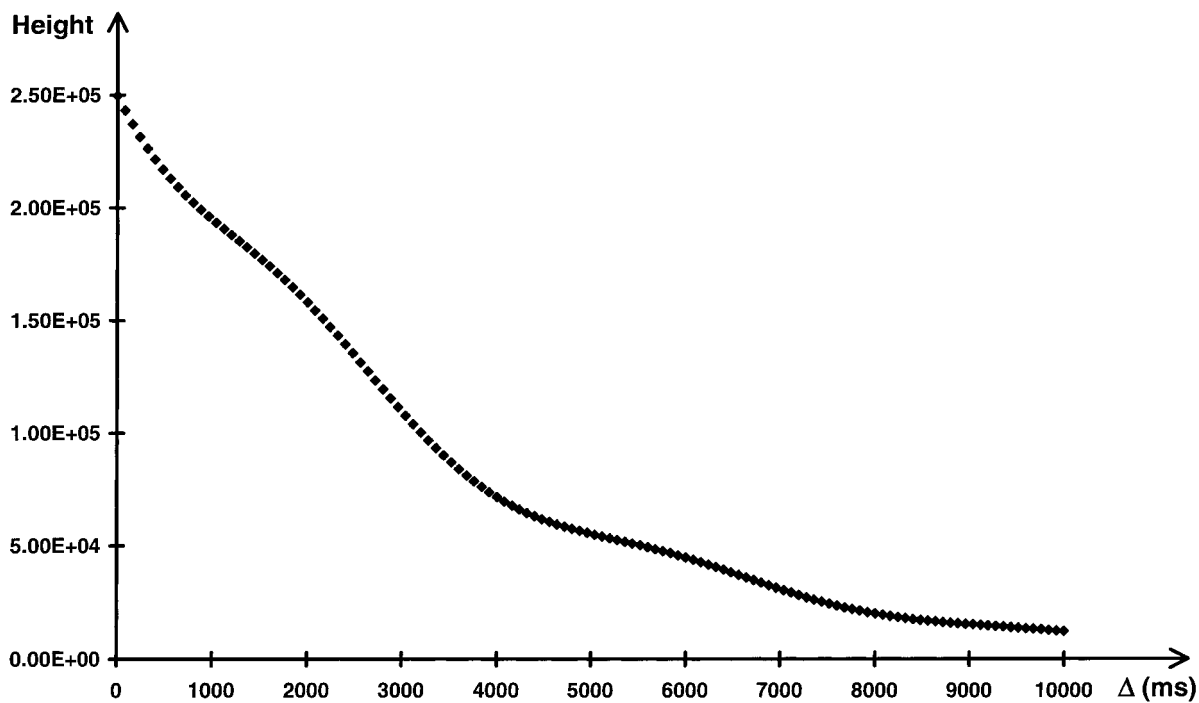


FIG. 5. The decay obtained from two-dimensional synthetic data treated in the same way as in Fig. 4. The data are based on a doublet of splitting $J = 0.25$ Hz with $T_2 = 6.4$ s and $T_2^* = 1.1$ s.

TABLE 1
¹H Relaxation Parameters (in s) of TCA

Proton number	1	2	3	4
T_1 , inversion-recovery ^a	14.9	13.2	19.4	7.9
T_1 , saturation-recovery ^a	15.4	12.9	19.4	8.2
T_1 , saturation-recovery, fully decoupled spectrum ^a	16.3	13.8	18.5	8.1
T_1 , saturation-recovery ^b	16.2	13.4	20.6	8.7
T_1 , selective ^b	22.7	18.9	27.1	9.1
($3 < T_1 >/2$) ^c	(23.6)	(20.0)	(29.2)	(12.3)
T_1 , semiselective ^{b,d}		17.5	25.7	
$T_{1\rho}$ ^{b,e}	19.3	17.2	18.0	7.1
$T_{1\rho}$, fully decoupled spectrum ^{b,e}		16.9	18.5	

Note. In DMSO-*d*₆ 50% v/v; carefully degassed; measurements performed at 25°C. For proton numbering, see Fig. 1.

^a 9.4 T; Bruker Avance DRX.

^b 4.7 T; homemade spectrometer.

^c Calculated with the average of all available nonselective T_1 's.

^d Protons 2 and 3 inverted simultaneously.

^e Selective (protons 1 and 4 individually excited) or semiselective experiments (protons 2 and 3 excited simultaneously).

major obstacle comes from 180° pulse imperfections, with further complications arising from long range J -couplings if the method involving a shift of the time domain t_1 is retained. These observations suggest using decoupled spectra solely as a tool for probing spin dynamics. This is further discussed in the next section.

FULLY DECOUPLED SPECTRA AS A TOOL FOR MEASURING T_1 AND $T_{1\rho}$ RELAXATION TIMES IN COUPLED SPIN SYSTEMS

The validity of our experimental approach (to be described below) was checked with longitudinal and rotating frame relaxation in *trans*-crotonaldehyde. The proton NMR spectrum of this molecule extends over a wide chemical shift range (2 to 9.5 ppm) and exhibits well-separated multiplets with a wealth of splittings. Indeed, the separation between the different multiplets is sufficient for performing relaxation measurements by conventional methods. Furthermore, this small spin system lends itself to a relatively simple interpretation of the experimental results. All results concerning TCA are gathered in Table 1. Standard nonselective T_1 measurements have been performed according to the fast inversion-recovery technique (8) (waiting time: 60 s) or to the saturation-recovery technique (9) with, in this case, two long (2 and 4 ms, respectively) saturating pulses of the form $(\alpha)_x(2\alpha)_y$ applied prior to the evolution period and practically no waiting time. Selective T_1 relaxation times were obtained by selectively inverting the multiplet of interest with a DANTE pulse train (10, 11). It can be seen from Table 1 that all nonselective T_1 determinations are consistent within experimental error. However, selective T_1 show a marked increase with respect to the corresponding

nonselective T_1 , except in the case of methyl protons. For protons 1, 2, and 3, this is easily explained by the absence of cross-relaxation contribution in the selective relaxation measurement, a well-known property usually dubbed “ $\frac{3}{2}$ effect” (12) and roughly verified here. Of course, for methyl protons, the essential relaxation contribution arises from dipolar interaction within the methyl group, making almost identical selective and nonselective T_1 values.

Due to large relaxation times, $T_{1\rho}$ measurements require very long spin-locking periods (several tens of seconds). To prevent any damage to the probe, low-power radiofrequency fields must be employed making it impossible to spin-lock simultaneously the magnetization of all protons. Results reported in Table 1 must therefore be considered as selective for the aldehydic proton as well as for the methyl protons. It can be observed that $T_{1\rho}$ is slightly smaller than the corresponding selective T_1 , which is not surprising due to expected additional contributions to transverse relaxation (exchange for instance). The case of ethylenic protons is not so easily interpreted. The relevant magnetizations are simultaneously spin-locked and the $T_{1\rho}$ are seen to be almost identical and close to the mean value of the corresponding nonselective T_1 . This amazing feature may be attributable to a sort of equilibration by Hartmann–Hahn transfers (13) and not to cross-relaxation as indicated by the results of a homologous T_1 experiment (see Table 1; semiselective inversion of ethylenic protons).

We turn to the determination of T_1 or $T_{1\rho}$ from fully decoupled spectra. The relevant experiments just imply a perturbation prior to the two-dimensional spin echo sequence; this perturbation must fulfill the two following conditions (i) being, of course, sensitive to the considered relaxation parameter and (ii) not involving a sign change for the signals which are thereafter subjected to the decoupling procedure because the relaxation parameter is extracted from power spectra. With these requirements in mind, we have used the following sequences for T_1 (saturation-recovery) and $T_{1\rho}$ (spin-lock; SL) measurements, respectively:

$$(\alpha)_x(2\alpha)_y-\tau-(\pi/2)-t_1/2-(\pi)-t_1/2-\text{Acq}(t_2)$$

$$(\pi/2)_x-\tau_{(\text{SL})_y}-t_1/2-(\pi)-t_1/2-\text{Acq}(t_2).$$

It can be recalled that a two-dimensional measurement is actually associated with each τ value.

Generally, the EXORCYCLE phase cycle (6) was used for the echo sequence. In the case of TCA, the $T_{1\rho}$ experiment was again performed in a semiselective way in order to limit the power deposition during the spin-lock period. Owing to the important duration of each experiment, the verification was limited to the spectral region corresponding to protons 2 and 3. The experimental data are exploited by following, as a function of τ , the intensity of a given line in the fully decoupled spectrum. It can be recalled that power spectra are employed. As a consequence the evolutions must be accounted for by

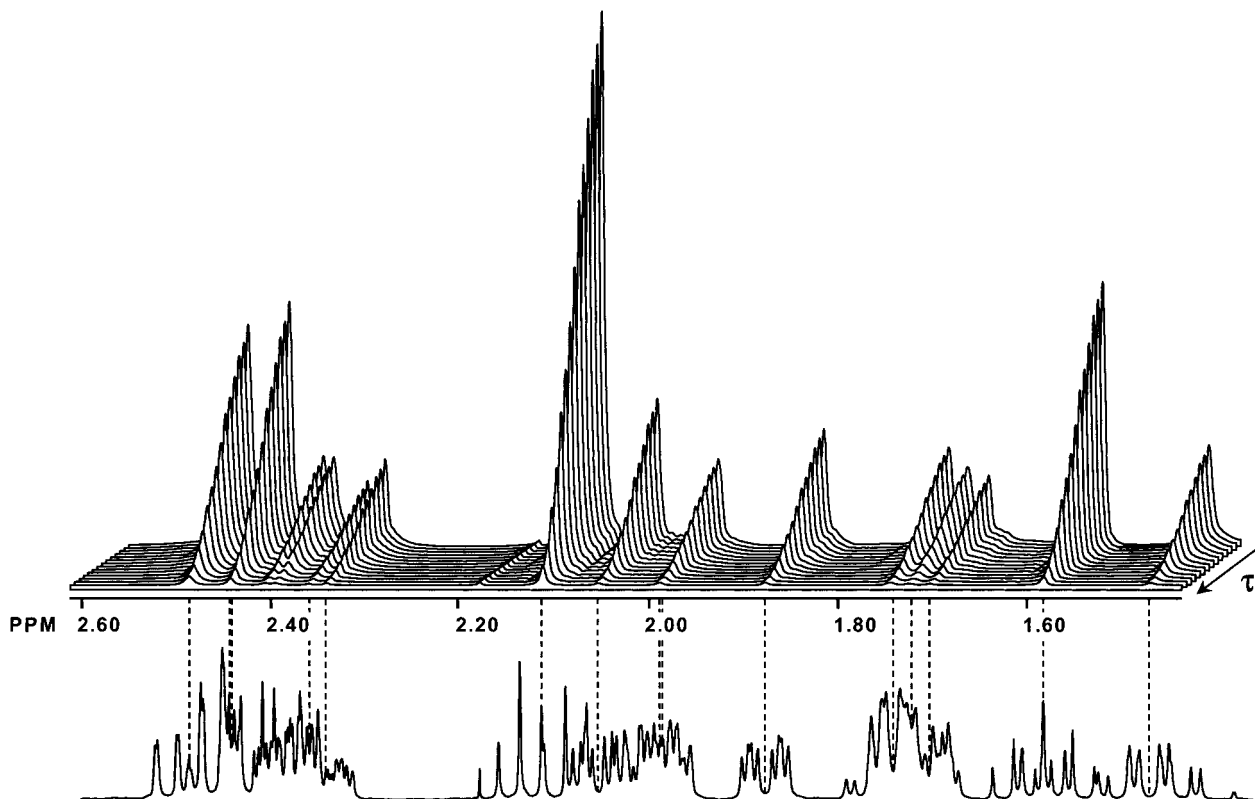


FIG. 6. An example of $T_{1\rho}$ determination by means of fully decoupled spectra of androstene. Only one part of the spectrum is displayed. Top: the conventional spectrum. The successive traces correspond to the following τ values: 0, 25, 50, 100, 150, 200, 300, 400, 500, 600, 800, 1000, 1300, and 1600 ms. The experiment was carried out with a Bruker Avance DRX spectrometer operating at 9.4 T. There were 128 t_1 increments of 12.5 ms (eight scans for each increment). Repetition time: 10 s; 2 K in the t_2 dimension for a spectral width of 900 Hz.

$[K(1 - e^{-\tau/T_1})]^2$ and $[Ke^{-\tau/T_{1\rho}}]^2$, K being a scaling factor specific to each line. The method is seen to be valid as indicated by the data given in Table 1 which are identical (within

experimental accuracy) to those obtained by standard measurements. Once validated, the method can be applied to a more demonstrative case. The complexity of the conventional spec-

TABLE 2
 ^1H Relaxation Parameters (in s) of Androstene

Proton number	1	2–3	4	5	6	7	8–9	10	11	12
T_1 , inversion-recovery	n/a	n/a	n/a	n/a	1.22	n/a	n/a	1.01	n/a	n/a
T_1 , saturation-recovery, fully decoupled spectrum	1.19	1.06	1.12	0.96	1.22	0.73	0.85	1.00	1.39	0.93
$T_{1\rho}$	n/a	n/a	n/a	n/a	1.01	n/a	n/a	0.85	n/a	n/a
$T_{1\rho}$, fully decoupled spectrum	1.02	0.89	0.85	0.85	1.01	0.73	0.90	0.84	0.91	0.82
Proton number	13	14	15	16	17	18	19	A	B	
T_1 , inversion-recovery	n/a	0.96	0.75	n/a	n/a	0.95	1.32	1.16	1.41	
T_1 , saturation-recovery, fully decoupled spectrum	0.68	0.96	0.76	1.36	1.05	0.94	1.29	1.18	1.40	
$T_{1\rho}$	n/a	0.94	0.85	n/a	n/a	0.90	0.91	1.03	1.30	
$T_{1\rho}$, fully decoupled spectrum	0.80	0.94	0.83	0.97	0.94	0.87	0.98	1.02	1.28	

Note. 2% in weight in CDCl_3 ; carefully degassed; measurements performed at 25°C with a Bruker Avance DRX spectrometer operating at 9.4 T. For proton numbering, see Fig. 2. Amplitude of the spin-lock radiofrequency field: $\gamma B_1/2\pi = 2$ kHz. Overlapping multiplets are responsible for missing values (n/a) in the standard measurement rows.

trum of androstene obviously precludes relaxation measurements of most protons. Conversely, such a measurement is straightforward when mediated by fully decoupled spectra. This is exemplified in Fig. 6, the results being provided in Table 2. In fact standard $T_{1\rho}$ or T_1 measurements could be performed on some well-separated multiplets; they yield the same result as those obtained with fully decoupled spectra (see Table 2). Moreover, all data are nonselective even for $T_{1\rho}$ as normal spin-lock experiments could be run thanks to a relatively small spectral width and short relaxation times. Most of the time, $T_{1\rho}$ is slightly smaller than T_1 , presumably, as for TCA, because of other contributions. Exceptionally $T_{1\rho}$ is found unexpectedly to be larger than T_1 . Again, we can invoke Hartmann–Hahn transfers which are prone to affect the $T_{1\rho}$ decay (13). Indeed, this effect would be more pronounced for pairs of protons, close to the carrier frequency and consequently for which the Hartmann–Hahn condition (equality of the effective radiofrequency amplitudes) is better satisfied.

CONCLUSION

In this paper, we have taken advantage of a seemingly unused property, namely that power spectra exhibit high-resolution Lorentzian lines. First, this allows one to obtain, from spin echo experiments, fully decoupled spectra in a straightforward although nonquantitative manner. Second, those spectra are able to reflect quantitatively any evolution occurring prior to the spin echo sequence. In that way, the method is ideally suited for the determination of relaxation parameters in those homonuclear coupled spin systems, which lead to overcrowded standard spectra.

ACKNOWLEDGMENT

We are grateful to Dr. Christian Roumestand (University of Montpellier) for the 600-MHz experiment.

REFERENCES

1. W. P. Aue, J. Karhan, and R. R. Ernst, Homonuclear broad-band decoupling and two-dimensional J -resolved NMR spectroscopy, *J. Chem. Phys.* **64**, 4226–4227 (1976).
2. M. Woodley and R. Freeman, "Decoupled" proton NMR spectra, *J. Magn. Reson. A* **109**, 103–112 (1994) and references therein.
3. M. Woodley and R. Freeman, Elimination of spin–spin splittings from high-resolution proton NMR spectra, *J. Magn. Reson. A* **111**, 225–228 (1994).
4. J. M. Nuzillard, Time-reversal of NMR signals by linear prediction. Application to phase-sensitive homonuclear J -resolved spectroscopy, *J. Magn. Reson. A* **118**, 132–135 (1996).
5. F. Guenneau, P. Mutzenhardt, and D. Canet, A procedure for obtaining pure absorption 2D J -spectra. Application to quantitative fully J -decoupled homonuclear NMR spectra. to appear.
6. G. Bodenhausen, R. Freeman, and D. L. Turner, Suppression of artifacts in two-dimensional J -spectroscopy, *J. Magn. Reson.* **27**, 511–514 (1977).
7. S. Meiboom and D. Gill, Modified spin-echo method for measuring nuclear relaxation times, *Rev. Sci. Instrum.* **29**, 688–691 (1958).
8. D. Canet, G. C. Levy, and I. R. Peat, Time saving in ^{13}C spin–lattice relaxation measurements by inversion-recovery, *J. Magn. Reson.* **18**, 199–204 (1975).
9. J. L. Markley, W. L. Horsley, and M. P. Klein, Spin–lattice relaxation measurements in slowly relaxing complex spectra, *J. Chem. Phys.* **55**, 3604–3605 (1971).
10. G. A. Morris and R. Freeman, Selective excitation in Fourier transform nuclear magnetic resonance, *J. Magn. Reson.* **29**, 433–462 (1978).
11. D. Boudot, D. Canet, J. Brondeau, and J. C. Boubel, DANTE-Z. A new approach for accurate frequency selectivity using hard pulses, *J. Magn. Reson.* **83**, 428–439 (1989).
12. A. Abragam, "The Principles of Nuclear Magnetism," pp. 294–297, Oxford Univ. Press, Oxford (1961).
13. See, for instance, K. Elbayed and D. Canet, Behaviour of a coupled two-spin- $\frac{1}{2}$ system in the presence of a spin-locking radio-frequency field. Relaxation and Hartmann–Hahn transfers, *Mol. Phys.* **71**, 979–993 (1990).