

The SPORT-NMR Software: A Tool for Determining Relaxation Times in Unresolved NMR Spectra

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A software package which allows the correct determination of individual relaxation times for all the nonequivalent nuclei in poorly resolved NMR spectra is described. The procedure used, based on the fitting of each spectrum in the series recorded in the relaxation experiment, should improve the analysis of relaxation data in terms of quantitative dynamic information, especially in anisotropic phases. Tests on simulated data and experimental examples concerning ¹H and ¹³C *T*_{1ρ} measurement in a solid copolymer and ²H *T*_{1Z} and *T*_{1Q} measurement in a liquid crystal are shown and discussed.

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INTRODUCTION

The partial superposition of peaks in NMR spectra, which is often the case in anisotropic phases, does not allow quantitative information to be obtained in a straightforward manner. In fact, the error on the individual peak integrals due to the overlap not only prevents a quantitative analysis of the spectrum, but is also particularly critical in the measurement of relaxation times, where the trend of peak integrals as a function of an experimental parameter is fitted with a suitable curve. A correct determination of relaxation times for nonequivalent nuclei is important in order to obtain detailed dynamic information, giving, for example, the capability to distinguish between inherent multiexponential decays, often encountered in the solid state, and the superposition of peaks with single-exponential decays but different relaxation times.

Several methods have been proposed to cope with the problem of the scarce resolution in NMR spectra, and in particular two different approaches can be distinguished: deconvolution techniques, which directly apply to time-domain data, and curve fitting of the spectrum. Where reliable quantitative analyses are required, as for example in the determination of relaxation times, the latter method is to be preferred; moreover, the spectrum fitting appears to be more suitable for the analysis of spectra in anisotropic phases, where different lineshapes and

linewidths are often encountered because of the presence of structural and dynamic heterogeneities.

Whereas several programs for the fitting of NMR spectra are available, to the best of our knowledge no software package exists which yields relaxation times using a fitting procedure for the analysis of the spectra. In the present paper we describe the program “SPORT-NMR,” an acronym for “Separating Peaks for Obtaining Relaxation Times in Nuclear Magnetic Resonance,” which applies a least-squares fitting procedure for the separation of different contributions in the NMR spectrum to the determination of relaxation times in a wide range of experiments.

The program is freely available at the Internet site www.icqem.pi.cnr.it or via anonymous ftp to [indigo.icqem.pi.cnr.it](ftp://indigo.icqem.pi.cnr.it).

TECHNICAL DETAILS OF THE SOFTWARE PACKAGE

“SPORT-NMR” is a package of Mathematica (1) which adds new functions that can be used within the Mathematica environment. This allows the exploitation of the functions already present in the Mathematica main program and in the related available packages; the environment chosen guarantees ease and flexibility in the use of the program, from the input of the data to the graphical representation of the results, as well as wide future improvements. SPORT-NMR adds more than 40 functions to Mathematica; the subroutines which execute the heaviest numerical calculations, required for the fitting, are written in Fortran 77 and are based on the “normal equations” method (2) and on the minimization of the least-square deviations as a goodness-of-fit criterion. The user can vary the default values for the maximum number of iterations, the convergence criterion, and the single-step variation percentage of the parameters in order to exert a partial control on the fitting procedure.

SPORT-NMR works on experimental preprocessed data, i.e., data which have previously undergone apodization, Fourier transformation, and phase and baseline correction. At present the program supports the Bruker “JCAMP-DX” ASCII format for the input data files, containing the spectral data and the acquisition and processing parameters.

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TABLE 1
Pulse Sequences Supported by SPORT-NMR, Relaxation Times Measured by Them, and Corresponding Fitting Functions^a

Pulse sequence	Relaxation times	Fitting functions
Inversion–recovery (9)	$T_1(\text{X})$ and $T_1(^1\text{H})$	$a[1 - \sum_i b_i e^{-x/T_i^1}]$
Saturation–recovery	$T_1(\text{X})$ and $T_1(^1\text{H})$	$\sum_i a_i e^{-x/T_i^1}$
Torchia (10)	$T_1(\text{X})$ in solids	$\sum_i a_i e^{-x/T_{1X}}$
Variable contact pulse and Variable spin-lock time (11)	$T_{1\rho}(^1\text{H})$ in solids	$\sum_i a_i e^{-x/T_{1\rho}^1}$
Variable heteronuclear spin-lock time (12)	$T_{1\rho}(\text{X})$ in solids	$\sum_i a_i e^{-x/T_{1\rho X}^1}$
Delayed CP (13)	$T_2(^1\text{H})$ in solids	Different functions ^b
IRCP (14)	T_{XH} in solids	$a[1 - 2e^{-\alpha x/T_{\text{XH}}} + e^{\alpha\tau/T_{\text{XH}}}]e^{-\alpha/T_{1\rho}^1}$
		$\alpha = 1 - \frac{T_{\text{XH}}}{T_{1\rho}^1}; \tau = \tau_1 + x$
Wimperis	$T_{1Z}(^2\text{H})$ and $T_{1Q}(^2\text{H})$ in liquid crystals	$a[1 - \sum_i b_i e^{-x/T_{1Z}^i}]^c$ $a + \sum_i b_i e^{-x/T_{1Q}^i}$

^a In the fitting functions, a and b are parameters determined by the fitting procedure, x is the variable delay, and the sum runs over the i index between 1 and the number of functions considered.

^b The functions commonly used for describing the proton FID are available.

^c The two equations refer to sum and difference of the intensities of the two peaks of the doublet, respectively.

The NMR pulse sequences supported at the moment by the program are reported in Table 1.

The workstations used to run the program were a Silicon Graphics “Indigo” (33 MHz IP12 processor) for the Mathematica frontend (version 2.2) and Fortran routines and an IBM R-6000/590 for the Mathematica kernel (version 2.2).

SPECTRAL FITTING

A spectrum can be analytically reproduced if each peak can be expressed by means of a mathematical function. In NMR a peak usually has a lineshape that can be described by a Lorentzian or a Gaussian function. It is well known, however, that intermediate cases are sometimes encountered, due, for instance, to the simultaneous presence of homogeneous and inhomogeneous line broadening mechanisms. This has been empirically taken into account in the fitting procedure allowing for a linear combination of a Lorentzian and a Gaussian function. A peak is therefore in general fully described by means of four parameters: amplitude, linewidth, chemical shift, and the Gaussian/Lorentzian relative percentage. Initial estimates of these parameters for each peak and the fixing *a priori* of the number of peaks are required in the fitting procedure. All parameters can be fitted simultaneously, although in some cases it can be useful or necessary to keep some of them fixed. This may be true, for example, when some parameters are known from the theory or from other measurements, or when the strong correlation between the parameters prevents obtaining a good fit.

THE PROGRAM

The program is structured to guarantee the maximum flexibility to the user: a set of commands is available and the order

of execution is not strictly defined. However, a first indispensable step is the reading of the experimental spectra and acquisition parameters of interest, as for example the type of pulse sequence, the values of the variable delay, if any, and the spectral window amplitude. All the data points are stored in a two-dimensional matrix, the (i, j) th element of which corresponds to the i th point of the j th spectrum in the series, associated with a particular value of the variable delay in the case of relaxation time measurements. When only a smaller spectral region needs to be investigated, the data in excess can be discarded in order to simplify the subsequent calculations and reduce the computing time.

Once the experimental data have been read, the best way to proceed usually consists in fitting the first spectrum of the series, preferably the completely relaxed one, which has the best signal-to-noise ratio, obtaining the optimized peak parameters' values. To this end a unique command allows the initial parameters to be interactively set; calls the Fortran subroutine which performs the fitting and, at the same time, shows the partial results in a dedicated window; then calculates the integrals for each peak; saves the result of the fitting in a text file; displays the parameters determined with the corresponding errors, as well as the fitting variance; and finally comes back to the Mathematica environment. The calculation of the integrals is performed by Mathematica through the application of symbolic integration routines. The results of the fittings for each spectrum are automatically stored in suitable files, so that they can be recalled in subsequent sessions by means of a proper command.

The goodness of the fit can normally be assessed by the user from the value of the variance and visually by plotting together experimental and fitted spectra or their difference (see Fig. 1). In spectra where strong peak overlapping is present, the anal-

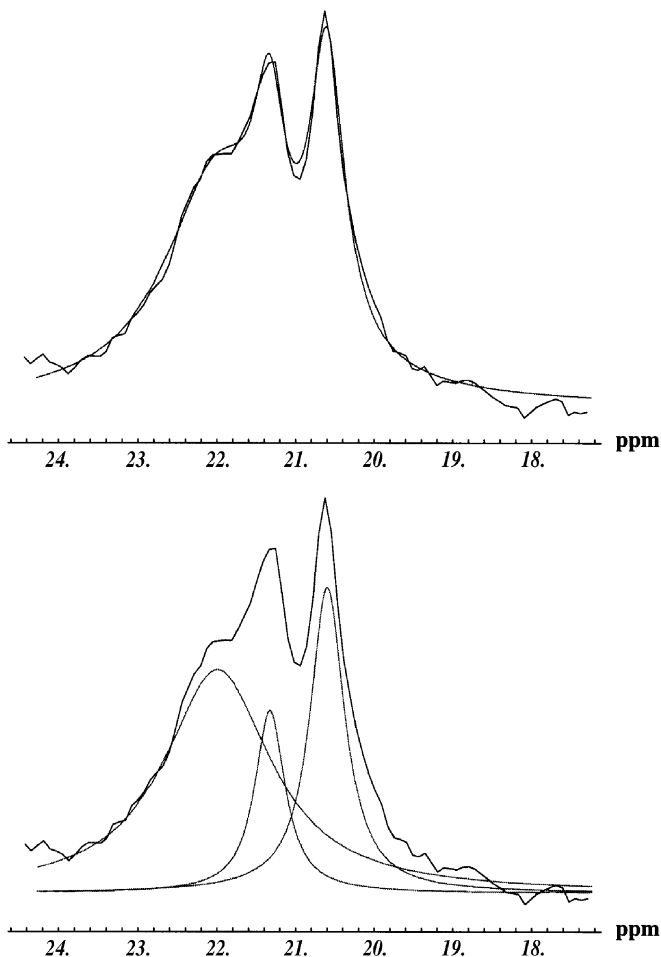


FIG. 1. Portion of the ^{13}C CP-MAS spectrum of EPR-Ti and global (top) or single peak (bottom) fitting curves obtained with SPORT-NMR.

ysis of the correlation between the variable parameters is recommended: if values of correlation coefficients close to 1 are present, the fitting results may be intrinsically biased by the choice of the parameters to fit and of the initial parameter values.

Once a satisfactory reproduction of the first spectrum has been obtained, a fitting of all the other spectra of the series can be performed manually, i.e., by giving the initial values of the parameters spectrum by spectrum, or by means of a command which proceeds automatically, fixing lineshape, linewidth, and chemical shift parameters to the values found for the first spectrum, and taking the amplitudes as the only variable parameters (see Fig. 2).

At this point it is possible to determine the relaxation time of interest for each peak by fitting the trend of the peak areas with the experimental variable delay by means of suitable functions (see Fig. 3). The functions employed, corresponding to the different pulse sequences supported by the program, are reported in Table 1. Besides the relaxation times, the parameters calculated by the fitting are initial amplitudes and, in some cases, other parameters

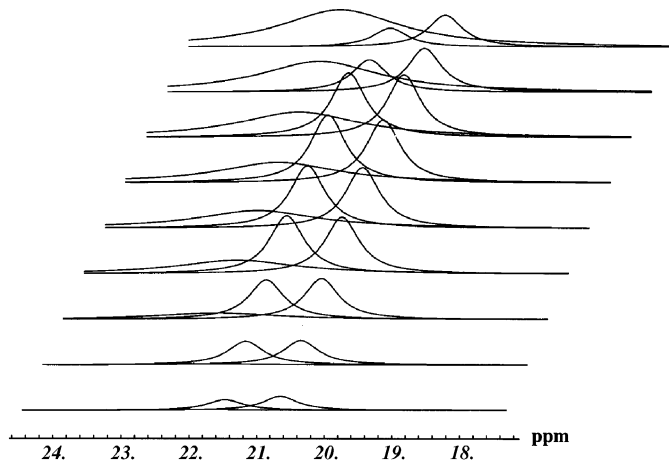


FIG. 2. Trend of calculated peaks of EPR-Ti in a variable cross-polarization time experiment for the measurement of ^1H $T_{1\rho}$. The cross-polarization time used in the different spectra ranges from 1.5 to 80 ms from top to bottom.

which take into account experimental imperfections. For instance, in the case of an inversion–recovery pulse sequence, the parameters b_i correct the theoretical trend in the case of a nonperfect inversion after the 180° pulse (3).

The fitting procedure can be completely automatic, being the type of function chosen by the program on the basis of the pulse sequence employed; to this end, the initial parameter values in the fitting do not necessarily have to be set manually, but are calculated according to the integrals determined in the case of the amplitude parameters, or set to default values for the remaining parameters. However, since the program allows for multiexponential behavior, the number of relaxation time components needs to be set by the user. This may be done following a trial-and-error procedure with increasing number of components until a good fit is obtained; the validity of the fit can be assessed using the same criteria described for the fitting of the spectra.

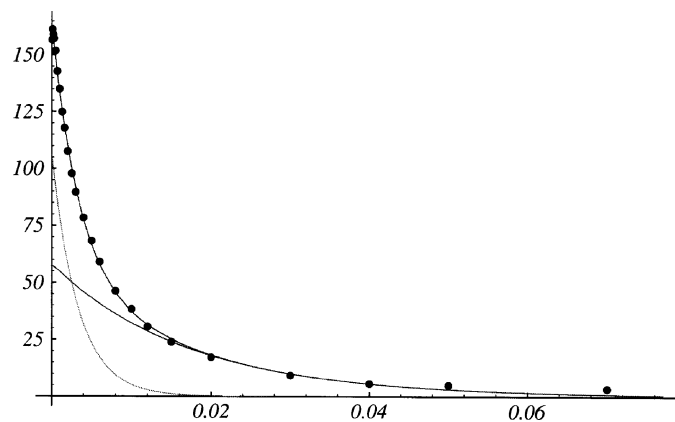


FIG. 3. Trend of the integrals of a peak, global biexponential fitting curve, and single exponentials in a variable spin-lock experiment for the measurement of ^{13}C $T_{1\rho}$.

In the case of the determination of ${}^2\text{H } T_{1Z}$ and T_{1Q} in partially ordered phases by means of the Wimperis pulse sequence (4), a preliminary procedure is provided by the program: these relaxation times are determined from the trend of the sum and the difference of the areas of the two components of the doublet generated by the quadrupolar interaction, rather than from the trend of the areas of a single peak (5); the sums and differences of the different doublets are calculated automatically before the fitting routine is called.

Several graphical functions allow the visualization of experimental and fitted data with many options, thus rendering the control over the whole procedure easy and flexible, from the reading of experimental spectra to the determination of relaxation times. Experimental and fitted spectra can be shown individually, together for comparison, or as stacked plots in order to see the trend. In all cases the spectra can be displayed either entirely or expanding a region of interest. Moreover, the fitted spectra can be visualized as the overlap of the different peaks or extracting the single peaks contributing to the whole spectrum from the context and displaying them individually. The peak areas can be graphically displayed against the variable delay, and the curve fitting which describes this trend can be shown together with the areas, also separating the single contributions in the case of multiexponential decays. All the graphical functions can be adapted to personal demands by using the many options already provided by the standard Mathematica functions.

Further details on the results of the spectral fitting, such as the partial and total correlation coefficients (2) between all the pairs of parameters determined by the least-squares method, are not displayed in the default output, but can be recalled. Commands which show the list of the integrals of all peaks in a spectrum or of the integrals of one peak along the series of spectra, as well as a summary of all the relaxation times determined, are provided. Other facilities, such as an on-line help manual showing the meaning and the usage of the commands, are available.

TESTS ON SIMULATED DATA

The program has been tested on simulated data. To this end a specific routine has been implemented in the program for the synthesis of a series of spectra of a relaxation experiment given a set of spectral and relaxation parameters, as well as the noise level required.

The tests performed on the program aimed at the assessment of the stability and sensitivity of the method. The results of two tests are reported in Fig. 4 and Table 2 and in Fig. 5 and Table 3, respectively. In the first test, particularly indicative of the

sensitivity of the method, the influence of increasing degree of peak overlap on the relaxation time determined is examined; in the different simulated experiments the case of two peaks was considered, keeping the intensity and linewidth constant, while varying the relative distance. Lorentzian peaks were used, this type of lineshape being more critical in the case of overlap. In all cases, the simulation and subsequent data analysis were repeated three times (see Table 2); the results obtained allowed the presence of systematic errors to be ruled out. It is evident from the data that significant errors are present only in the case of very strong overlap, these errors arising from nonoptimal spectral fitting results due to an increasing correlation between parameters with increasing overlap. This can be noticed in Fig. 4, where the global and partial fitting curves of the relaxed spectra in the different simulated experiments are reported. Although in all cases a good global fitting is obtained, in the last two cases, where very strong overlap occurs, the two individual peaks have different relative intensities. However, it must be pointed out that errors in the spectral fitting are heavily influenced by the noise level, particularly in the case of strong peak superposition, as highlighted by the second test, where the case of maximum overlap examined in the previous test has been investigated as a function of noise level (see Table 3 and Fig. 5). The experiment simulated with zero noise yields spectral fittings with zero variance and, consequently, precise relaxation times. With increasing noise level the scatter of the relaxation times determined remarkably increases, and, moreover, the spectral fitting becomes strongly dependent on the initial choice of parameter values. However, even in the most critical case of maximum superposition and noise level, the relaxation times determined differ by less than 20% from the true values.

The tests on simulated experiments clearly indicate that the errors in the determination of relaxation times result from a combined effect of peak superposition and noise; however, only when both these factors are particularly critical do the errors become significant. It can be thus positively stated that the method used is sufficiently sensitive, stable, and free from systematic errors.

APPLICATION TO EXPERIMENTAL DATA

SPORT-NMR has been extensively used on experimental data in many fields (6), and here two meaningful examples concerning solid polymers and liquid crystals are reported. In both cases the NMR experiments were carried out on a Bruker AMX-300 spectrometer.

FIG. 4. Simulated spectra and global (left) or single peak (right) fitting curves obtained with SPORT-NMR. The spectra reported are those relative to the longest delay in a Torchia experiment, and were simulated with the parameters reported in Table 2; the distance between the two peaks is, from top to bottom, 10, 6, 4, 3, 2, and 1 ppm.

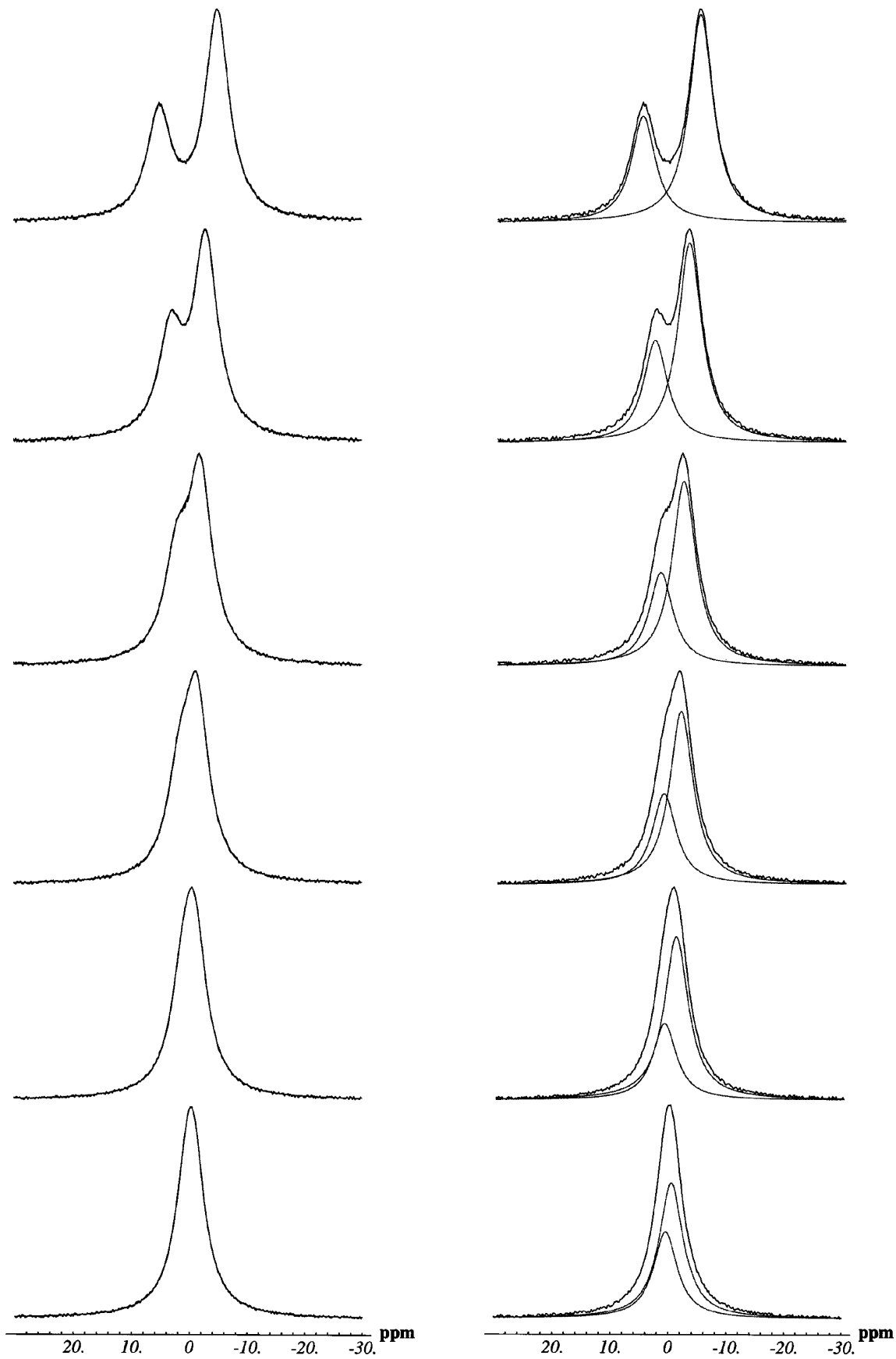


TABLE 2
Spin-Lattice Relaxation Times Obtained by Applying the Program to a Simulated Torchia Experiment^a

Distance between peaks (ppm)	T_1 (A)	T_1 (B)
10	10.00	3.00
	9.98	3.00
	10.02	3.00
6	10.03	3.00
	10.02	2.98
	9.98	3.00
4	10.11	3.00
	10.04	2.99
	10.06	3.02
3	9.94	2.96
	10.05	3.00
	10.01	3.00
2	10.37	3.06
	10.74	3.18
	9.80	2.98
1	9.14	2.90
	8.93	2.79
	11.10	3.14

^a Thirty spectra were synthesized with suitably chosen delays ranging from 0.1 to 102.4 s considering two Lorentzian peaks of 5 ppm linewidth, 50 and 100 a.u. amplitude, and 10 and 3 s relaxation time, respectively, and separated by a variable distance. A random noise of 1 a.u. (in the same scale of the amplitudes) was added to the spectra. The results obtained repeating the experiment simulation and subsequent fitting procedure three times are reported.

¹H $T_{1\rho}$ of EPR-Ti by Means of Variable Contact Time Pulse Sequence

The SPORT-NMR software has been heavily employed for the study of the dynamics and morphology of three polyolefinic elastomers (two ethylene/propylene random copolymers and an ethylene/propylene/ethylidene norbornene random terpolymer) by means of ¹H and ¹³C solid-state NMR (7). Because of the presence of numerous overlapping peaks in the ¹³C MAS spectra of these elastomers, the software was used to determine all relaxation times (¹H and ¹³C T_1 and $T_{1\rho}$). In fact, a correct measurement of the relaxation times for individual peaks was important for each sample, and especially for the ethylene/propylene random copolymer obtained with a heterogeneous catalyst system based on MgCl₂-supported TiCl₄ and electron donors (EPR-Ti) (7), where rubbery and crystalline phases coexist: this heterophasicity, giving rise to more complex spec-

tra, renders indispensable the separation of peaks in order to distinguish between relaxation times of nuclei belonging to different phases. For instance, in the methyl resonances region of the ¹³C spectrum (19–24 ppm) three heavily superimposed resonances can be identified, two belonging to different monomeric sequences of the rubbery phase and another to the crystalline polypropylenic phase. The measurement of the integrals and, therefore, of the relaxation times, without a previous separation of overlapping peaks, could be performed only for the three peaks globally, whereas using SPORT-NMR the spectrum could be well reproduced as a sum of three peaks, all with a Lorentzian shape (Fig. 1). In the measurement of proton spin-lattice relaxation times in the rotating frame, the former procedure did not allow any multiexponential trend for the curve integrals vs variable delay to be found and led to an average value of 23 ± 1 ms for ¹H $T_{1\rho}$. In contrast, individual relaxation times for the three peaks could be obtained by means of SPORT-NMR and the results are reported in Table 4 together with the peak assignment. It must be pointed out that the relaxation time of the methyl protons belonging to the crystalline phase is about half the relaxation times of the elastomeric methyl protons. This result highlights relevant differences between the individual relaxation times, and it is perfectly consistent with the average result obtained with the fitting of the overall integral decay, which is inherently unable to reveal decay constants differing by a factor of less than three.

Striking differences were found for the carbon spin-lattice relaxation times in the rotating frame measured from the overall peak area and using “SPORT-NMR”: the former procedure yielded a two-exponential decay with time constants 14 ± 2 ms and 94 ± 16 ms, whereas the latter gave a monoexponential trend for the two methyl carbons of the amorphous phase and a two-exponential one for the methyl carbon of the crystalline phase, as indicated in Table 4. In this case the global analysis reveals its limits in the interpretation of the two-exponential relaxation behavior attributable, in principle, either to the superposition of two peaks with different single-exponential behavior or to a similar two-exponential behavior of all the contributing peaks. On the other hand, the application of the software reveals a more complex situation, allowing determination not only of the number of relaxation time components for each peak, but also of their correct values.

²H T_{1z} and T_{1Q} of FAB-OC6 by Means of the Wimperis Pulse Sequence

Each deuterium nucleus in a partially oriented phase, such as a liquid crystalline phase, gives rise to a symmetrical doublet centered on the isotropic resonance frequency, originated from

FIG. 5. Simulated spectra and global (left) or single peak (right) fitting curves obtained with SPORT-NMR. The spectra reported are those relative to the longest delay in a Torchia experiment and were simulated with the parameters reported in Table 3; the noise level is, from top to bottom, 0, 0.2, 0.5, 1, 2, and 5 a.u.

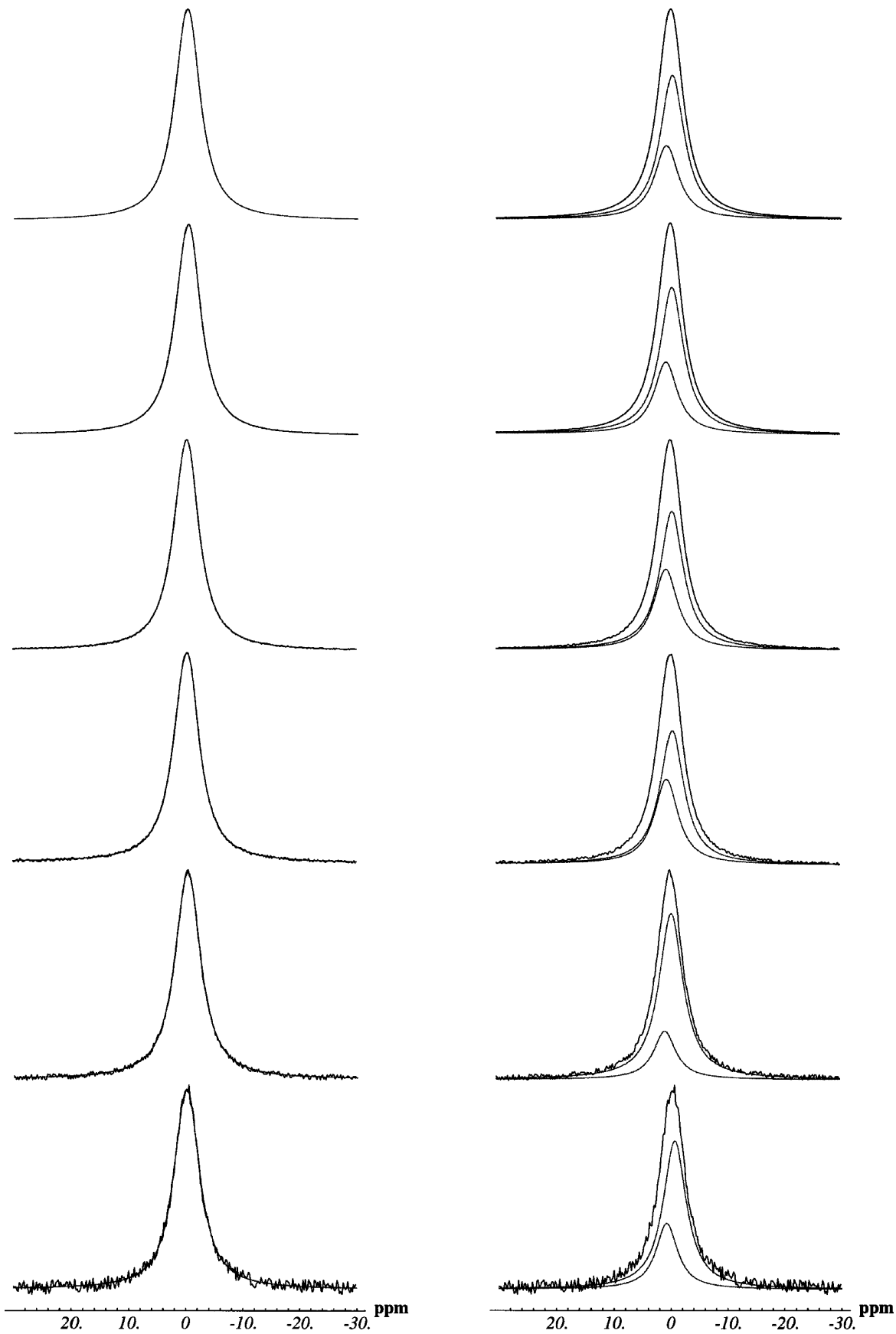


TABLE 3
Spin-Lattice Relaxation Times Obtained by Applying the Program to a Simulated Torchia Experiment^a

Noise	T_1 (A)	T_1 (B)
0	10.00	3.00
	10.01	3.04
	10.36	3.09
0.2	10.18	3.05
	10.03	2.98
	9.09	3.02
0.5	10.37	3.01
	9.14	2.90
	8.93	2.79
1	11.10	3.14
	12.19	3.34
	12.34	3.44
2	8.92	2.65
	8.26	3.50
	9.22	2.36
5	8.26	2.95

^a Thirty spectra were synthesized with suitably chosen delays ranging from 0.1 to 102.4 s considering two Lorentzian peaks of 5 ppm linewidth, 50 and 100 a.u. amplitude, and 10 and 3 s relaxation time, respectively, and separated by 1 ppm. A variable random noise ranging from 0 to 5 a.u. (in the same scale of the amplitudes) was added to the spectra. Except for the case of 0 noise, the test was repeated three times and the three sets of results are reported.

the quadrupolar Hamiltonian, which is the predominant internal interaction. The Wimperis pulse sequence allows the deuterium spin-lattice Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) relaxation times for all nuclei to be simultaneously determined from the trend of the sum and difference of the integrals of the two components of each doublet, respectively, against the variable delay of the sequence. This technique was applied to a sample of *p*'-hexyloxybenzyliden-*p*-fluoroaniline (FAB-OC6), partially deuterated on the aniline ring and on the alkoxy chain (see Fig. 6) (8). A portion of the corresponding ²H NMR

TABLE 4
Proton and Carbon Spin-Lattice Relaxation Times in the Rotating Frame, Measured for the Methyl Resonances of EPR-Ti by Means of SPORT-NMR, and Attribution of the Three Signals^a

¹³ C chemical shift	¹ H $T_{1\rho}$ (ms)	¹³ C $T_{1\rho}$ (ms)	Monomer sequence
22.1	12.6 ± 0.6	11 ± 2	PPP (crystalline)
		210 ± 70	
21.4	28 ± 1	31 ± 3	PPP (amorphous)
20.7	30.2 ± 0.8	37 ± 3	PPE and EPE (amorphous)

^a P, propylene; E, ethylene.

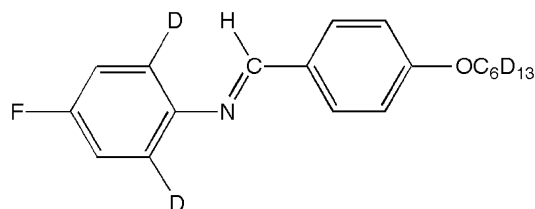


FIG. 6. The molecular structure of FAB-OC6-*d*₁₅.

spectrum together with the fitted spectrum is shown in Fig. 7. The internal doublet is assigned to methyl deuterons and the external doublet to deuterons belonging to the adjoining methylene group, whereas the remaining resonances arise from the aromatic deuterons, which show a relevant dipolar coupling with neighboring aromatic protons, giving rise to further splitting into doublets. As can be seen from the spectrum, the correct determination of the relaxation times is disturbed by the overlap of methyl and aromatic peaks, which is more remarkable on the right side of the spectrum because of the differences in the isotropic chemical shift between aromatic and methyl deuterons. The use of SPORT-NMR overcomes this problem and, moreover, renders completely automatic the time-consuming procedure of calculating the integrals for every peak,

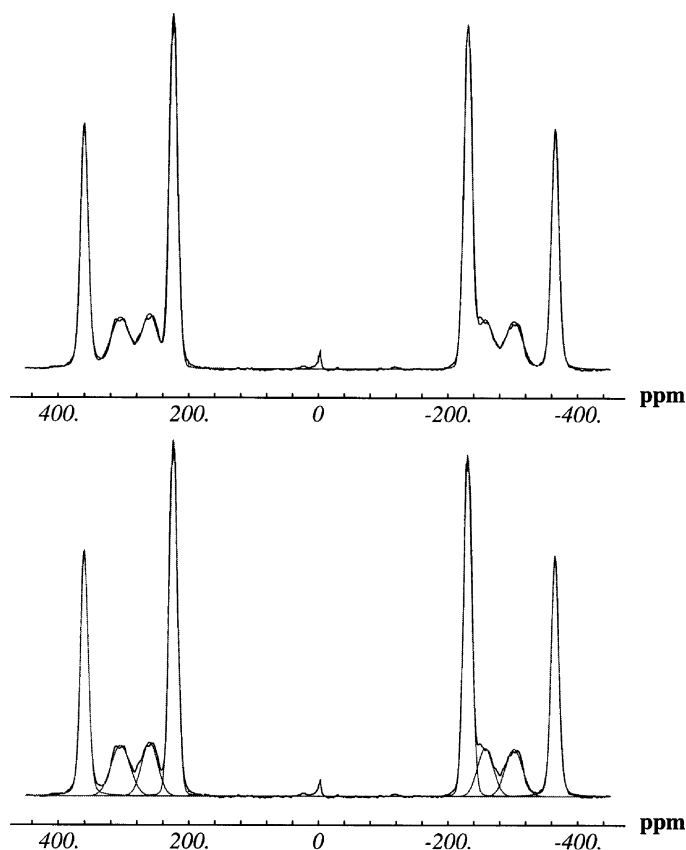


FIG. 7. Portion of the ²H spectrum of FAB-OC6-*d*₁₅ and global (top) or single peak (bottom) fitting curves obtained with SPORT-NMR.

TABLE 5
**Zeeman (T_{1z}) and Quadrupolar (T_{1Q}) Spin-Lattice Relaxation Times of Selected Deuterons of FAB-OC6- d_{15} ,
 Measured Both with the Traditional Method and Using SPORT-NMR**

Type of deuteron	Lineshape parameter (Gaussian %)	T_{1z} traditional method (ms)	T_{1z} SPORT-NMR (ms)	T_{1Q} traditional method (ms)	T_{1Q} SPORT-NMR (ms)
CD ₃	92	480 ± 35	518 ± 9	460 ± 30	511 ± 8
CD ₂	73	206 ± 2	206 ± 1	248 ± 8	243 ± 4
Aromatic	100	10 ± 2	11.5 ± 0.3	10 ± 2	13.8 ± 0.8

transferring the resulting data into a suitable spreadsheet program, calculating the necessary sums and differences, and, finally, performing their fitting.

A comparison between the relaxation times obtained with the traditional method and by application of SPORT-NMR is reported in Table 5. Note that the two sets of data are practically identical in the case of the methylene deuterons, whose peaks do not suffer from significant superposition; in contrast, both methyl and aromatic deuterons show differences between the two sets of results. In all cases the traditional method yields larger errors in relaxation times, mainly due to the error in the measurement of peak integrals; in the case of the aromatic deuterons, moreover, it must be pointed out that with the traditional method the relaxation times have been obtained only from the external peak of the dipolar doublet, thus reducing the problem of the superposition, but halving the signal-to-noise ratio and thus contributing to increase the error. As far as the methyl deuterons are concerned, the overlap with the remarkably peaks of aromatic deuterons, which have remarkably lower relaxation times, is responsible for the underestimated values found with the standard procedure.

CONCLUSIONS

The results obtained on both simulated and experimental data, here reported, were used to test the software package SPORT-NMR and to verify that it worked properly. They demonstrated its reliability and flexibility in calculating relaxation times in the case of poor spectral resolution. Therefore, SPORT-NMR can be a useful tool in NMR in general and, in particular, in relaxation studies of anisotropic

materials (solid and liquid crystals), where peak overlapping very often occurs.

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